

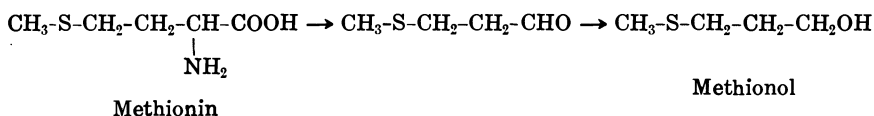
# BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

## Über die Synthese von Methionol.

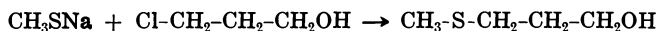
Von Shiro AKABORI und Takeo KANEKO.

(Eingegangen am 14. Dezember 1938.)

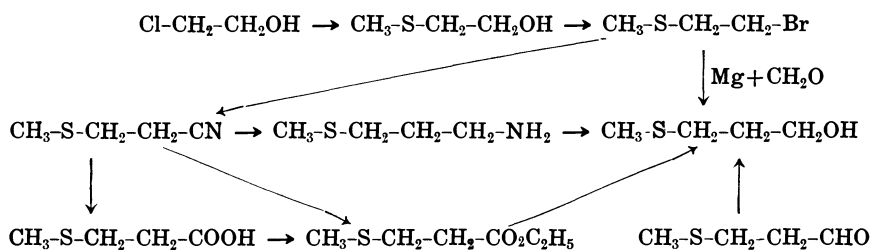
Vor zwei Jahren haben die Verfasser<sup>(1)</sup> von dem Vorkommen des  $\gamma$ -Methylmercapto-propylalkohols im „Shoyu“ (der japanischen Suppenwürze) als Hauptprinzip des Aromas berichtet und für den schwefelhaltigen Alkohol den Namen „Methionol“ vorgeschlagen, weil es kaum zu bezweifeln ist, dass der Alkohol im „Shoyu“ aus Methionin folgenderweise entsteht.



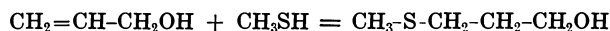
Die Synthese des Methionols ist von uns nach W. R. Kirner<sup>(2)</sup> durch Umsetzung von Trimethylenchlorhydrin mit Natrium-methylmercaptid durchgeführt worden.



Es sind aber noch verschiedene andere, vom Äthylenchlorhydrin ausgehende Wege zur Synthese von Methionol möglich, z.B. wie folgt.



Wir haben alle die oben angegebenen Wege geprüft, konnten aber in keinem Fall befriedigende Ausbeuten erhalten. Nun ist es uns auffallenderweise geglückt, eine neue sehr einfache Synthese aufzufinden. Diese beruht darauf, dass sich Methylmercaptan an die Doppelbindung des Allylalkohols nach folgender Gleichung anlagert.



Ohne Katalysator geht die Reaktion äusserst langsam vor sich, lässt sich aber durch Zusatz von geeigneten Katalysatoren (z.B. Quecksilber-

(1) *Proc. Imp. Acad. (Tokyo)*, **12** (1936), 131.

(2) *J. Am. Chem. Soc.*, **50** (1928), 2446.

salz) erheblich beschleunigen. Interessanterweise ist Sauerstoff als Katalysator stark wirksam ebenso wie bei der Anlagerung von Bromwasserstoff an die Doppelbindung des Allylbromids.<sup>(3)</sup> Der Einfluss des Lichtes auf die Reaktion ist auch merklich, wie aus der folgenden Tabelle ersichtlich ist. Die Tabelle zeigt die Resultate unserer Experimente, die folgenderweise ausgeführt worden sind.

Eine Mischung von 10 g. Allylkohol und 10 g. Methylmercaptan wurde unter Zusatz (oder ohne) Katalysator in einer geschlossener Röhre, jeweils verschiedene Zeitenlang bei wechselnden Temperaturen gehalten. Die Reaktionsflüssigkeit wurde unter vermindertem Druck der fraktionierenden Destillation unterworfen. Die bei 99–101°/23 mm. übergehende Fraktion erwies sich als Methionol. Es wurde in Form seines Doppelsalzes mit Quecksilberchlorid ( $C_4H_{10}OS \cdot 2\frac{1}{2}HgCl_2$ , Schmp. 128–128.5°) identifiziert.

| Nr. der Experimente | Katalysator     |        | Atmosphäre über der Reaktionsflüssigkeit | Reaktionstemperatur | Reaktionsdauer | Ausbeute an Methionol in g. | Ausbeute in % |
|---------------------|-----------------|--------|------------------------------------------|---------------------|----------------|-----------------------------|---------------|
| 1                   | $(CH_3S)_2Hg$   | 0.5 g. | Luft                                     | 110°                | 24 Stunden     | 7.5                         | 41            |
| 2                   | —               | —      | „                                        | „                   | „              | 1.5                         | 8             |
| 3                   | $(CH_3S)_2Hg$   | 0.5 g. | „                                        | 140–150°            | 5 Stunden      | 11                          | 61            |
| 4                   | $(CH_3COO)_2Hg$ | 0.6 g. | „                                        | 140–160°            | 22 Stunden     | 11                          | 61            |
| 5                   | $(CH_3S)_2Hg$   | 0.5 g. | O <sub>2</sub>                           | Zimmertemp.         | 1 Monat        | 17                          | 93            |
| 6*                  | $(CH_3S)_2Hg$   | 0.5 g. | H <sub>2</sub>                           | „                   | 17 Tage        | 4                           | 22            |
| 7*                  | —               | —      | O <sub>2</sub>                           | „                   | 1 Monat        | 4                           | 22            |
| 8                   | —               | —      | H <sub>2</sub>                           | „                   | „              | 0                           | 0             |
| 9*                  | $(CH_3S)_2Hg$   | 0.5 g. | Luft                                     | „                   | 17 Tage        | 10                          | 55            |
| 10                  | $(CH_3S)_2Hg$   | 0.5 g. | H <sub>2</sub>                           | „                   | 1 Monat        | 6                           | 33            |
| 11                  | —               | —      | O <sub>2</sub>                           | „                   | „              | 11                          | 61            |

Mit \* versehene Experimente wurden in der Dunkelkammer, die übriger bei diffusum Licht ausgeführt.

Die Katalytische Wirkung des Sauerstoffs wird durch Beleuchtung sehr verstärkt. Licht allein ohne Sauerstoff übt aber keinen Einfluss auf die obige Anlagerungsreaktion aus.

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zu Osaka.*

(3) Y. Urushibara und M. Takebayashi, dies Bulletin, **11** (1936), 798; **12** (1937), 138, 173.

## On the Nature of Foam. III. The Foam Formation of Ternary System, Acetic Acid—Benzene—Water.

By Tunetaka SASAKI.

(Received December 14, 1938.)

The foam formation of the ternary system of acetic acid—ethyl ether—water (AEW) was reported and some explanations were given in the preceding paper.<sup>(1)</sup> It was further confirmed that the ternary system of acetic acid—benzene—water (ABW) shows a similar behaviour in the foam formation to the system of AEW. The present paper describes the investigation of the foam formation of the ternary liquid system of ABW.

**Experimental Procedure.** In the ternary system or ABW, benzene is insoluble in water, while acetic acid is soluble in all proportions both

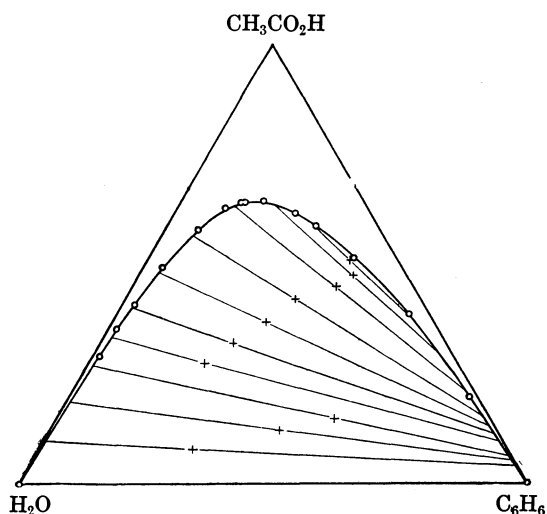


Fig. 1.

in water and in benzene. The mutual solubility curve and tie-lines of this system are obtained by the same methods as were described in the preceding paper,<sup>(1)</sup> and the data of which are given in Tables 1 and 2, respectively. These data are depicted in Fig. 1. To draw tie-lines, we take one point corresponding to the composition given in Table 2, which is situated in the heterogeneous region of Fig. 1, and draw a straight line so as its section made by the mutual solubility curve is divided at that point in two portions, the ratio of which being equal to that of

corresponding volumes of upper and lower layers shown in Table 2.

Measurements of the foam formation were then undertaken by means of the shaking apparatus in the same manner as was described in the preceding paper.<sup>(1)</sup> Thus the foam height  $H$  and the stability  $S$  have been measured after ten seconds' shaking of a solution with the frequency of 300 vibrations per minute at about 20°C.

**Experimental Results.** The results of measurements are shown in Table 3.<sup>(2)</sup> Here, the product of  $S$  and  $H$  is considered to be the measure of the foam formation. Fig. 2 shows the diagram which represents the relation between composition and foam formation of ABW-system.

(1) Sasaki, this Bulletin, **13** (1938), 669.

(2) Only a part of the data are shown for the economy of spaces.

Table 1.

| Volume ratio of limiting turbid mixture (about 20°) |         |       |
|-----------------------------------------------------|---------|-------|
| Acetic acid                                         | Benzene | Water |
| 0                                                   | 0       | 10.00 |
| 1.98                                                | 7.90    | 0.12  |
| 2.92                                                | 0.14    | 6.94  |
| 3.53                                                | 0.17    | 6.30  |
| 3.85                                                | 5.77    | 0.38  |
| 4.10                                                | 0.23    | 5.67  |
| 4.93                                                | 0.38    | 4.69  |
| 5.15                                                | 4.04    | 0.81  |
| 5.80                                                | 0.65    | 3.55  |
| 5.89                                                | 2.93    | 1.18  |
| 6.17                                                | 2.39    | 1.44  |
| 6.28                                                | 0.93    | 2.77  |
| 6.40                                                | 1.20    | 2.40  |
| 6.41                                                | 2.05    | 1.64  |
| 6.42                                                | 1.63    | 1.95  |
| 0                                                   | 10.00   | 0     |

Table 2.

| Composition in volume ratio |         |       | Volume ratio |             |
|-----------------------------|---------|-------|--------------|-------------|
| Acetic acid                 | Benzene | Water | upper layer  | lower layer |
| 5.10                        | 4.00    | 0.90  | 0.625        | 1.000       |
| 4.74                        | 4.21    | 1.05  | 0.920        | 1.000       |
| 4.50                        | 4.00    | 1.50  | 0.785        | 1.000       |
| 4.21                        | 3.44    | 2.35  | 0.578        | 1.000       |
| 3.71                        | 3.05    | 3.24  | 0.486        | 1.000       |
| 3.21                        | 2.62    | 4.17  | 0.385        | 1.000       |
| 2.80                        | 2.30    | 4.90  | 0.322        | 1.000       |
| 1.50                        | 5.50    | 3.00  | 1.381        | 1.000       |
| 1.23                        | 4.53    | 4.24  | 0.907        | 1.000       |
| 0.82                        | 3.02    | 6.16  | 0.452        | 1.000       |

Table 3.

| Composition in volume ratio |         |       | Height of foam, $H(\text{cm.})$ | Stability of foam, $S(\text{second})$ | Degree of foam formation, $S \cdot H$ |
|-----------------------------|---------|-------|---------------------------------|---------------------------------------|---------------------------------------|
| Acetic acid                 | Benzene | Water |                                 |                                       |                                       |
| 0                           | 1.50    | 8.50  | 0                               | 0                                     | 0                                     |
| 0                           | 2.63    | 7.37  | 0                               | 0                                     | 0                                     |
| 0.04                        | 4.98    | 4.98  | 0                               | 0                                     | 0                                     |
| 0.33                        | 5.92    | 3.75  | 0                               | 0                                     | 0                                     |
| 0.50                        | 0       | 9.50  | 2.2                             | 12.5                                  | 27.5                                  |
| 0.50                        | 0.80    | 8.70  | 3.1                             | 7.0                                   | 21.7                                  |
| 0.50                        | 2.00    | 7.50  | 2.6                             | 5.9                                   | 15.3                                  |
| 0.50                        | 5.00    | 4.50  | 1.1                             | 5.1                                   | 5.6                                   |
| 0.80                        | 0       | 9.20  | 2.2                             | 13.5                                  | 29.7                                  |
| 0.80                        | 3.40    | 5.80  | 1.4                             | 4.6                                   | 64.4                                  |
| 1.00                        | 0       | 9.00  | 2.3                             | 15.0                                  | 34.5                                  |
| 1.00                        | 1.30    | 7.70  | 1.6                             | 7.1                                   | 11.4                                  |
| 1.00                        | 2.50    | 6.50  | 1.4                             | 4.9                                   | 6.9                                   |
| 1.00                        | 4.50    | 4.50  | 0.7                             | 2.6                                   | 1.8                                   |
| 1.10                        | 4.90    | 4.00  | 0                               | 0                                     | 0                                     |
| 1.20                        | 0       | 8.80  | 2.2                             | 12.6                                  | 27.7                                  |
| 1.48                        | 0.10    | 8.42  | 1.7                             | 5.8                                   | 9.9                                   |
| 1.50                        | 0       | 8.50  | 2.5                             | 12.6                                  | 31.5                                  |
| 1.50                        | 3.20    | 5.30  | 0.6                             | 1.8                                   | 1.1                                   |
| 1.60                        | 0.70    | 7.70  | 1.4                             | 4.8                                   | 6.7                                   |
| 1.95                        | 3.42    | 4.63  | 0                               | 0                                     | 0                                     |
| 1.98                        | 7.90    | 0.11  | 0                               | 0                                     | 0                                     |
| 2.00                        | 0       | 8.00  | 1.9                             | 9.7                                   | 18.4                                  |
| 2.00                        | 1.30    | 6.70  | 0.8                             | 3.1                                   | 2.5                                   |
| 2.50                        | 1.25    | 6.25  | 0                               | 0                                     | 0                                     |
| 3.00                        | 0.47    | 6.53  | 0                               | 0                                     | 0                                     |
| 3.49                        | 1.78    | 4.73  | 0                               | 0                                     | 0                                     |
| 3.50                        | 0       | 6.50  | 1.9                             | 3.0                                   | 5.7                                   |
| 3.80                        | 5.90    | 0.30  | 0                               | 0                                     | 0                                     |
| 4.50                        | 5.00    | 0.50  | 1.2                             | 1.5                                   | 1.8                                   |
| 4.82                        | 0.38    | 4.80  | 0                               | 0                                     | 0                                     |
| 4.90                        | 2.50    | 2.60  | 0                               | 0                                     | 0                                     |
| 4.90                        | 4.32    | 0.78  | 1.9                             | 8.4                                   | 16.0                                  |



Table 3.—(Concluded)

| Composition in volume ratio |         |       | Height of foam,<br>$H(\text{cm.})$ | Stability of foam,<br>$S(\text{second})$ | Degree of foam<br>formation, $S \cdot H$ |
|-----------------------------|---------|-------|------------------------------------|------------------------------------------|------------------------------------------|
| Acetic<br>acid              | Benzene | Water |                                    |                                          |                                          |
| 5.00                        | 4.40    | 0.60  | 1.1                                | 1.4                                      | 1.5                                      |
| 5.17                        | 3.90    | 0.95  | 0                                  | 0                                        | 0                                        |
| 5.22                        | 3.94    | 0.84  | 1.6                                | 4.9                                      | 7.8                                      |
| 5.30                        | 4.00    | 0.70  | 1.2                                | 1.8                                      | 2.2                                      |
| 5.32                        | 4.68    | 0     | 0                                  | 0                                        | 0                                        |
| 5.90                        | 3.00    | 1.10  | 2.0                                | 6.9                                      | 13.8                                     |
| 6.00                        | 3.00    | 1.00  | 1.6                                | 2.3                                      | 3.7                                      |
| 6.15                        | 0.87    | 2.98  | 0                                  | 0                                        | 0                                        |
| 6.32                        | 1.96    | 1.72  | 0                                  | 0                                        | 0                                        |
| 6.48                        | 1.33    | 2.19  | 1.6                                | 1.9                                      | 3.0                                      |
| 6.50                        | 2.00    | 1.50  | 0.8                                | 2.1                                      | 1.7                                      |
| 7.00                        | 0       | 3.00  | 1.0                                | 1.3                                      | 1.3                                      |
| 7.00                        | 1.50    | 1.50  | 1.0                                | 1.3                                      | 1.3                                      |

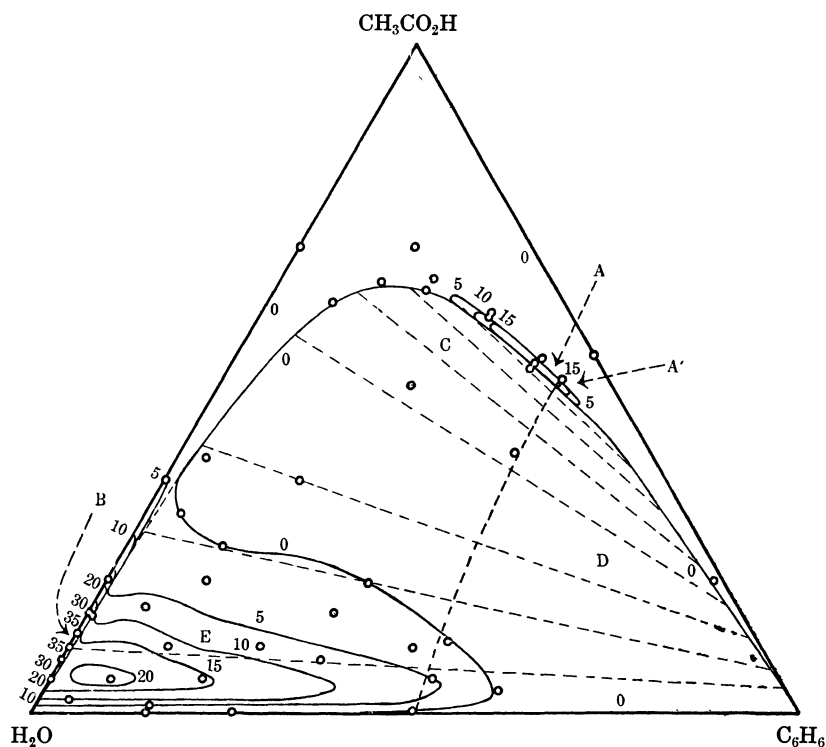


Fig. 2.

**Discussion.** The diagram of the foam formation of ABW-system, like that of AEW-system, is separated into two regions by the mutual solubility curve, that is homogeneous and heterogeneous regions.

(1) *Homogeneous region.* The surface of the diagram has two maxima of foam formation along the mutual solubility curve at the vicinity of the points A and B in Fig. 2, respectively. The other portions of the

homogeneous region can froth more or less. In this region, the shape of surface of the diagram, as a whole, is analogous to that of AEW-system, and the maximum near the point B is explained from its position being close to the composition of maximum foam formation in the binary system of acetic acid–water, as in the case of AEW-system. In the case of ABW-system, however, homogeneous region near the point B is so narrow that the diagram of this part is composed of two steep surfaces forming a sharp edge as shown in Fig. 2.

The foam formation also shows its maximum near the point A in Fig. 2, but it is less exaggerated in this system than in AEW-system and the height of maximum near the point A is even smaller than that near the point B in ABW-system. The explanation was made in the preceding paper<sup>(1)</sup> upon the foam formation of the system near the point A, referring to the analogous phenomena of opalescence and anomalous viscosity exhibited by the ternary system of benzene–ethyl alcohol–water, as due to its liability to form emulsion.

In the present case, the conditions are more favourable for this explanation, because the opalescent zone of benzene–ethyl alcohol–water system and the region A in Fig. 2 coincide each other and they are both situated in the vicinity of the point of intersection made by the mutual solubility curve and the locus of middle points of tie-lines (A' in Fig. 2.). We can explain, therefore, the maximum of foam formation, the critical opalescence and the anomalous viscosity from the colloidal behaviour of corresponding systems.

(2) *Heterogeneous region.* Heterogeneous region may be divided into three parts, namely, region C, D and E in Fig. 2.

(a) *Region C.* In the system of this region, an upper layer consisting of water, acetic acid and excessive benzene is smaller in volume compared with a lower one consisting of acetic acid, benzene and excessive water, while the surface tension of the former is smaller than that of the latter but not so markedly as in the system of E region. These relations are shown in the sixth column of Table 4.

Table 4.

| Composition in volume ratio |         |       | Surface tension (relative) |             | Foam formation                                             |                                |
|-----------------------------|---------|-------|----------------------------|-------------|------------------------------------------------------------|--------------------------------|
| Acetic acid                 | Benzene | Water | upper layer                | lower layer | $V^* < V_1$                                                | $V_u > V_1$                    |
| 4.83                        | 3.92    | 1.25  | 0.402                      | 0.421       | C region in Fig 2, non foamy.                              | D region in Fig. 2, non foamy. |
| 4.31                        | 3.54    | 2.15  | 0.416                      | 0.465       |                                                            |                                |
| 2.42                        | 4.35    | 3.23  | 0.421                      | 0.553       |                                                            |                                |
| 1.26                        | 5.04    | 3.70  | 0.416                      | 0.651       | E region in Fig. 2, remarkably foamy. (three layered film) |                                |
| 0.74                        | 2.72    | 6.53  | 0.407                      | 0.740       |                                                            |                                |
| 0                           | 5.00    | 5.00  | 0.419                      | 0.999       |                                                            |                                |

\*  $V_u$  and  $V_l$  denote volumes of upper and lower liquids respectively, coexisting in the corresponding heterogeneous system.

When we shake a system of this region, the film of air bubble produced in the liquid becomes heterogeneous and the foam cannot be produced<sup>(3)</sup> as in the corresponding case of AEW-system.

(b) Region D. This corresponds to the heterogeneous region, the lower layer of which, consisting of acetic acid, benzene and excessive water and having a smaller volume, is dispersed in an upper one consisting of acetic acid, water and excessive benzene. The last column of Table 4 corresponds to this region.

In such system, certain degree of foam formation can be expected on shaking, because emulsion droplets of larger surface tension than the dispersing medium do not interfere with the foam produced in this system as was observed in AEW-system. But in the mixture corresponding to this region of ABW-system, practically no foam can be produced on shaking. It is perhaps because the upper layer of this system does not foam while that of AEW-system foams a little.

(c) Region E. In the heterogeneous system belonging to this region, the upper layer consisting of acetic acid, water and excessive benzene is smaller in volume and markedly smaller in surface tension than the lower one consisting of acetic acid, benzene and excessive water, as shown in the sixth column of Table 4.

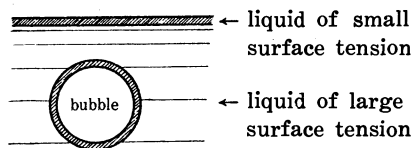


Fig. 3a.

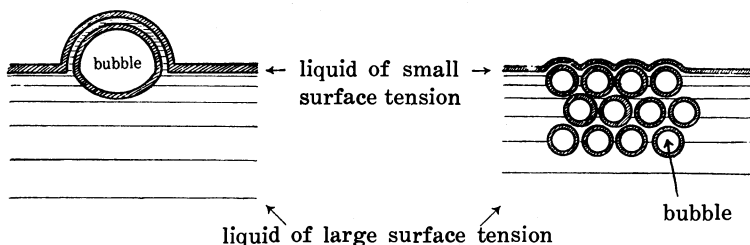


Fig. 3b.

In ABW-system of this region, the upper layer is dispersed in the lower one on shaking. At the same time, air bubbles are also produced both in emulsion droplets and in the dispersing medium, but bubbles in the dispersing medium readily and entirely go into the interior of the emulsion droplets on account of the large difference in surface tension between both layers. Thus, air bubbles are covered with homogeneous films made of emulsion droplets which are again surrounded by the dispersing medium. These circumstances are readily understood from Fig. 3a, as in the case of the corresponding system of AEW.<sup>(1)</sup>

Such air bubbles go up to and accumulate at the interface of benzene-water, and produce the foam as shown in Fig. 3b. Now, the foam is

(3) Sasaki, this Bulletin, **11** (1936), 797.

covered at least by three layers of homogeneous films, of which middle layer is an aqueous mixture of larger surface tension than the outer ones. Therefore, air in bubbles cannot escape towards outside on account of the difficulty in breaking the innermost films (i.e. exposing itself to the middle layer). In other words, the foam is stabilised in such systems.

Although mere emulsion drops containing air bubbles were observed in AEW-system of this region, fairly stable foam is produced in the case of ABW-system. In Fig. 2, relatively larger zone of remarkable foam formation can be seen in the region E. It will be emphasized that these foams, consisting of triple layered films, are entirely different in its nature from the ordinary foams covered with single homogeneous film.

In region E of ABW-system, surface constituting the diagram is steep along the straight line connecting the vertices of benzene and water. This means that a heterogeneous mixture of water and benzene foams considerably by the addition of small quantity of acetic acid. Such phenomenon can also be observed when we substitute benzene for liquid aliphatic hydrocarbon such as hexane. This suggests an interesting practical application of detecting trace of surface active substances usually existing as impurities in hexane or its homologues. Namely, when we shake water with a relatively small volume of hexane which was obtained by the usual method of repeated distillation from commercial products, foam formation may be observed. No foam can be produced, however, in the mixture of water and hexane from which traces of impurities are carefully removed by shaking it for a long time with fuming sulphuric acid and distilling.<sup>(4)</sup> This is explained from the fact that the impurities mainly consist of surface active substances and behave just like acetic acid in the case of ABW-system.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed by a grant given to Prof. Sameshima from Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

### Summary.

(1) The foam formation of liquid ternary system of acetic acid-benzene-water (ABW) has been measured by means of a shaking apparatus, and a diagram has been drawn between the degree of foam formation and the composition.

(2) The foam formation of homogeneous system of ABW is analogous to that of acetic acid-ethyl ether-water (AEW), showing two maxima of foam formation. In the heterogeneous system of ABW, however, remarkable foam formation can be observed, instead of mere emulsion droplets containing bubbles in the case of AEW-system.

(3) The explanation of foam formation in heterogeneous ABW-system has been attempted.

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(4) A. Weissberger and E. Proskauer, "Organic Solvents," 99, (1935).

## Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. IV. Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche der Oxyde von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel.<sup>(1)</sup>

Von Noriyoshi MORITA, Haruo TANAKA und Toshizo TITANI.

(Eingegangen am 26. Dezember 1938.)

**Inhaltsübersicht.** Unter Verwendung der Oxyde der zur vierten Hauptreihe des periodischen Systems gehörigen Elemente, nämlich der Oxyde von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel als Katalysator wird die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und an schwerem Sauerstoff angereichertem Wasserdampf untersucht. Misst man die katalytische Wirksamkeit eines bestimmten Oxyds durch die Temperatur, wo die Austauschreaktion an seiner Oberfläche erst bemerkbar wird, so findet man, dass sie sich mit zunehmender Gruppennummer periodisch verändert. Am stärksten wirksam ist das Manganoxyd, am schwächsten dagegen das Titanoxyd, und die Oxyde der anderen Elemente ordnen sich betreffend ihrer katalytischen Wirksamkeit zwischen diesen beiden Extremen.

**Einleitung und Versuchsanordnung.** Seit letztem Jahr beschäftigen wir uns mit dem Versuch über die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und sauerstoffhaltigen Verbindungen, hauptsächlich Wasserdampf, an der Oberfläche der Oxyde der verschiedenen Arten der Elemente. Während dieses Versuches fanden wir, dass es eine gewisse Regelmässigkeit zwischen der katalytischen Wirksamkeit des Oxyds eines bestimmten Elements und dem Platz gibt, den das betreffende Element im periodischen System einnimmt. Als ein schönes Beispiel dafür teilen wir hier die Versuche mit, die wir mit den Oxyden der zur vierten Hauptreihe gehörigen Elemente, nämlich mit den Oxyden von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel, ausgeführt haben. Die Versuchsmethode und -anordnung, die wir dabei benutzt haben, ist im grossen und ganzen dieselbe wie die in I. Mitteil. beschrieben wurde. Deshalb wird jede Einzelheit auf dort verwiesen und hier sollen nur die Darstellungsmethode der zum Versuch verwendeten Oxyde und die damit gewonnenen Versuchsergebnisse mitgeteilt werden.

**Darstellung der Oxyde.** Calciumoxyd  $\text{CaO}$ —Käufliches reines Calciumoxyd wird zunächst sorgfältig zerkleinert und dann im Porzellantiegel bis auf ca.  $900^{\circ}\text{C}$ . etwa vier Stunden lang erhitzt.

Titanoxyd  $\text{TiO}_2$ —Pulveriges reines Titanoxyd aus dem Handel wird in verdünnter Salzsäure einige Stunden lang erwärmt und dann mit destilliertem Wasser so lange gewaschen, bis keine Chlorionen im Filtrat mehr nachgewiesen werden können. Das so gereinigte Oxyd wird im Luftbad gut getrocknet und zum Schluss im Porzellantiegel bis auf etwa  $800^{\circ}\text{C}$ . einige Stunden lang erhitzt.

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(1) I. Mitteil.: Dies Bulletin, **13** (1938), 357; II. Mitteil.: *ibid.*, **13** (1938), 601; III Mitteil.: *ibid.*, **13** (1938), 656.

Vanadinoxid  $V_2O_5$ —Reines Ammoniumvanadat aus dem Handel wird im Porzellantiegel sorgfältig erhitzt. Das dadurch gewonnene Vanadin-pentoxid wird aber durch die weitere Erhitzung bis auf einige Grade über seinen Schmelzpunkt ( $658^\circ\text{C.}$ ) vollkommen geschmolzen und nach der Abkühlung wird das Geschmolzene zu kleinen Körnchen zerkleinert.

Chromoxyd  $\text{Cr}_2\text{O}_3$ —Der Niederschlag von Chromhydroxyd, der sich beim Versetzen der wässrigen Lösung von reinem Chrom(III)-nitrat mit verdünnter Ammoniaklösung abgeschieden hat, wird zunächst mit destilliertem Wasser gründlich gewaschen, dann im Luftbad getrocknet und zum Schluss durch die Erhitzung im Porzellantiegel bis auf etwa  $600^\circ\text{C.}$  restlos bis zum Oxyd entwässert. Das so gewonnene Oxyd wird aber vor dem Gebrauch wieder bis auf  $700^\circ\text{C.}$  im Sauerstoffstrom einige Stunden lang erhitzt.

Manganoxyd  $\text{Mn}_3\text{O}_4$ —Die wässrige Lösung von reinem Mangan(II)-chlorid wird mit Natriumcarbonat versetzt und das dabei abgeschiedene Mangancarbonat, nachdem es mit destilliertem Wasser gründlich gewaschen worden ist, im Luftbad gut getrocknet. Das so gewonnene Carbonat wird dann im Sauerstoffstrom über Nacht lang sorgfältig erhitzt, bis es sich vollkommen in Oxyd verwandelt hat. Deshalb dürfte es die Zusammensetzung von  $\text{Mn}_3\text{O}_4$  besitzen.

Eisenoxyd  $\text{Fe}_2\text{O}_3$ —Der Niederschlag von Eisenoxydhydrat, der sich bei der Versetzung der wässrigen Lösung von „Eisennitrat, krist.“ aus Kahlbaum mit Ammoniakwasser abgeschieden hat, wird mit heissem Wasser mehrmals gewaschen und im Luftbad getrocknet. Dann wird er durch die etwa einstündige Erhitzung im Porzellantiegel bis auf ca.  $800^\circ\text{C.}$  vollkommen bis zum Oxyd zersetzt.

Nickeloxyd  $\text{NiO}$ —Der Niederschlag von Nickeloxydhydrat, der durch die Versetzung der wässrigen Lösung des reinen Nickelsulfats mit Ätznatron hergestellt worden ist, wird mit destilliertem Wasser so lange gewaschen, bis keine Sulfationen im Filtrat mehr nachgewiesen werden können. Dann wird er im Luftbad getrocknet und zum Schluss im Porzellantiegel bis auf ca.  $800^\circ\text{C.}$  eine Stunde lang erhitzt.

**Versuchsergebnisse.** Die Ergebnisse der Austauschversuche, die unter Benutzung der oben beschriebenen Arten der Oxyde ausgeführt wurden, sind in folgenden Tabellen 1 bis 7 zusammengestellt. In diesen Tabellen besitzen die einzelnen Buchstaben bzw. Abkürzungen folgende Bedeutungen:

$\Delta s_a$  und  $\Delta s_e$ : der gewöhnlichem Wasser gegenüber gemessene Dichteüberschuss des zum Versuch benutzten an schwerem Sauerstoff angereicherten schweren Wassers und zwar  $\Delta s_a$  der Dichteüberschuss vor dem Versuch, dagegen  $\Delta s_e$  der nach dem Versuch.

$\Delta s_a(\text{O})$ : solch ein Anteil des gesamten und anfänglichen Dichteüberschusses ( $\Delta s_a$ ) des schweren Wassers, der lediglich auf die Anreicherung der schweren Sauerstoffisotope zurückgeführt werden kann.

%A: diese Quantität, die weiter unten das „prozentuale Austauschmass“ benannt werden soll, stellt das prozentuale Verhältnis der wirklich gefundenen Abnahme der Dichte des schweren Wassers, nämlich  $\Delta s_a - \Delta s_e$ , gegen den theoretischen Wert dar, der sich beim vollständigen Austausch ergeben würde. Dieser letztere Wert kann aber mit Hilfe des

Mengenverhältnisses des zum Versuch verwendeten gasförmigen Sauerstoffs und des Wasserdampfes sowie von  $\Delta s_a$  und  $\Delta s_a(O)$  leicht errechnet werden (vgl. I. Mitteil.).

$M$ : Menge des zum Versuch verwendeten Oxyds in g.

Das bei jedem Versuch in der vorliegenden Arbeit verwendete Reaktionsgasgemisch aus Sauerstoff und Wasserdampf besitzt, ebenso wie bei den Versuchen in I. Mitteil., die Zusammensetzung von  $O_2:H_2O = 2:1$ , und die in der ersten Spalte der Tabellen angegebene Versuchsnr. zeigt die zeitliche Reihenfolge der einzelnen Versuche.

Tabelle 1. Calciumoxyd.  $\Delta s_a = 41.6 \gamma$ ,  $\Delta s_a(O) = 26.1 \gamma$ ,  $M = 8 \text{ g.}$

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 5           | 350               | 40.0                     | 1.6                                   | 7                    |
| 6           | 420               | 38.6                     | 3.0                                   | 14                   |
| 2           | 510               | 31.1                     | 10.5                                  | 47                   |
| 4           | 560               | 20.6                     | 21.0                                  | 95                   |
| 1           | 610               | 18.4                     | 23.2                                  | 104                  |
| 3           | 690               | 19.4                     | 22.2                                  | 100                  |

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

Tabelle 2. Titanoxyd.  $\Delta s_a = 41.6 \gamma$ ,  $\Delta s_a(O) = 26.1 \gamma$ ,  $M = 9 \text{ g.}$

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 2           | 510               | 40.5                     | 1.1                                   | 5                    |
| 5           | 530               | 40.3                     | 1.3                                   | 6                    |
| 1           | 600               | 38.5                     | 3.1                                   | 14                   |
| 4           | 650               | 37.9                     | 3.7                                   | 17                   |
| 3           | 690               | 31.3                     | 10.3                                  | 46                   |
| 6           | 790               | 20.5                     | 21.1                                  | 95                   |

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

Tabelle 3. Vanadinoxid.  $\Delta s_a = 31.3 \gamma$ ,  $\Delta s_a(O) = 19.5 \gamma$ ,  $M = 10 \text{ g.}$

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 2           | 380               | 30.5                     | 0.8                                   | 5                    |
| 3           | 460               | 30.2                     | 1.1                                   | 7                    |
| 1           | 540               | 29.2                     | 2.1                                   | 12                   |
| 4           | 600               | 26.3                     | 5.0                                   | 30                   |
| —           | 658 (Schmp.)      | —                        | —                                     | —                    |

$$\% A = \frac{\Delta s_a - \Delta s_e}{16.9} \times 100$$

Tabelle 4. Chromoxyd.  $\Delta s_a = 36.8 \gamma$ ,  $\Delta s_a(O) = 22.8 \gamma$ ,  $M = 7 \text{ g}$ .

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 5           | 380               | 34.8                     | 2.0                                   | 10                   |
| 4           | 410               | 33.9                     | 2.9                                   | 15                   |
| 2           | 460               | 24.6                     | 12.2                                  | 62                   |
| 3           | 510               | 16.2                     | 20.6                                  | 106                  |
| 1           | 540               | 16.6                     | 20.2                                  | 104                  |

$$\% A = \frac{\Delta s_a - \Delta s_e}{19.5} \times 100$$

Tabelle 5. Manganoxyd.<sup>(2)</sup>  $\Delta s_a = 33.5 \gamma$ ,  $\Delta s_a(O) = 23.1 \gamma$ ,  $M = 11 \text{ g}$ .

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 7           | 210               | 35.5                     | 0.0                                   | 0                    |
| 8           | 250               | 35.5                     | 0.0                                   | 0                    |
| 6           | 300               | 26.5                     | 9.0                                   | 45                   |
| 4           | 350               | 20.0                     | 15.5                                  | 78                   |
| 3           | 400               | 17.1                     | 18.4                                  | 93                   |
| 2           | 450               | 17.2                     | 18.3                                  | 92                   |
| 5           | 500               | 16.7                     | 18.8                                  | 95                   |
| 1           | 550               | 15.1                     | 20.4                                  | 103                  |

$$\% A = \frac{\Delta s_a - \Delta s_e}{19.8} \times 100$$

Tabelle 6. Eisenoxyd.  $\Delta s_a = 41.6 \gamma$ ,  $\Delta s_a(O) = 26.1 \gamma$ ,  $M = 15 \text{ g}$ .

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 7           | 400               | 40.6                     | 1.0                                   | 4                    |
| 5           | 450               | 37.4                     | 4.2                                   | 19                   |
| 2           | 500               | 34.6                     | 7.0                                   | 32                   |
| 6           | 550               | 31.1                     | 10.5                                  | 47                   |
| 4           | 600               | 24.8                     | 16.8                                  | 76                   |
| 1           | 680               | 18.1                     | 23.5                                  | 106                  |
| 3           | 760               | 17.8                     | 23.8                                  | 107                  |

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

(2) Dieser Versuch wurde von Tanaka durchgeführt.



Tabelle 7. Nickeloxyd.  $\Delta s_a = 41.6 \gamma$ ,  $\Delta s_a(O) = 26.1 \gamma$ ,  $M = 8 \text{ g.}$ 

| Versuchsnr. | Temperatur<br>°C. | $\Delta s_e$ in $\gamma$ | $\Delta s_a - \Delta s_e$ in $\gamma$ | Austauschmass<br>% A |
|-------------|-------------------|--------------------------|---------------------------------------|----------------------|
| 3           | 400               | 40.6                     | 1.0                                   | 4                    |
| 5           | 470               | 37.8                     | 3.8                                   | 17                   |
| 1           | 550               | 23.3                     | 18.3                                  | 82                   |
| 4           | 630               | 19.6                     | 22.0                                  | 99                   |
| 2           | 700               | 18.4                     | 23.2                                  | 104                  |
| 6           | 740               | 19.4                     | 22.2                                  | 100                  |

$$\% A = \frac{\Delta s_a - \Delta s_e}{22.2} \times 100$$

**Diskussion.** Wenn man die in den oberen Tabellen 1 bis 7 angegebenen Werte von Austauschmass %A gegen die Versuchstemperatur einzeichnet, ergibt sich die Kurvengruppe, die in Abb. 1 wiedergegeben ist. Aus dieser Abb. ersieht man aber ohne weiteres, dass die katalytische Austauschreaktion der O-Atome zwischen gasförmigen Sauerstoff und Wasserdampf am leichtesten an der Oberfläche des Manganoxys dagegen am schwersten an Titanoxyd stattfindet, während die anderen Oxyde betreffend ihrer katalytischen Wirksamkeit sich zwischen diesen beiden

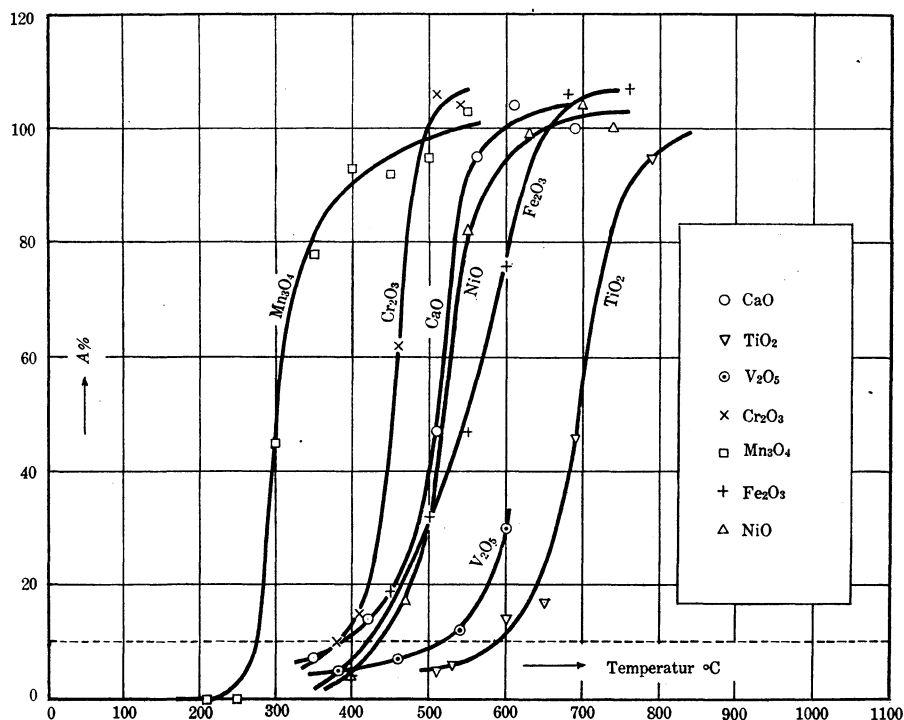


Abb. 1. Die Abhängigkeit des Austauschmasses % A von der Versuchstemperatur.

Extremen anordnen. Die Form u. a. die Neigung dieser Kurve hängt offenbar von manchen Faktoren ab, wie z.B. von der Menge, Beschaffenheit sowie der Korngrösse des benutzten Katalysators und weiter von der Strömungsgeschwindigkeit des reagierenden Gasgemisches. Aber erstens weil die Strömungsgeschwindigkeit des Gasgemisches immer genau dieselbe war und die Menge sowie die Korngrösse der einzelnen Katalysatoren auch nicht viel von einander abwich und zweitens weil die Form der Kurven in Abb. 1 an ihrem unteren Ende durch diese Faktoren am wenigstens beeinflusst wird, darf man die katalytische Wirksamkeit jedes Katalysators in der ersten Annäherung durch die Temperatur vergleichen, wo die Austauschreaktion an der Oberfläche des betreffenden Katalysators erst bemerkbar wird. Aus diesem Grunde wird aus der Kurvengruppe in Abb. 1 solch eine Temperatur  $t(10\%)$  entnommen, wo das gefundene Austauschmass  $\%A$  erst 10% beträgt. Wenn man nun die so gefundenen Werte von  $t(10\%)$ , die in der letzten Spalte der Tabelle 8 wiedergegeben sind, gegen die Nummer der Gruppe, zu der das Element jedes betreffenden Oxyds im periodischen System gehört, einzeichnet, dann erhält man die Kurve, die in der nebenstehenden Abb. 2 gezeigt wird. Bei dieser Einzeichnung tragen wir aber die Temperatur  $t(10\%)$  in der Ordinate absichtlich von oben nach unten ein, um dadurch die Punkte der einzelnen Oxyde nach der Reihenfolge ihrer katalytischen Wirksamkeit von oben nach unten sich anordnen zu lassen. Diese Kurve zeigt, dass die katalytische Wirksamkeit des Oxyds sich mit der Gruppennummer im periodischen System ziemlich regelmässig und zwar periodisch verändert; am stärksten wirksam ist das zur siebenten Gruppe gehörige Manganoxyd, dagegen am schwächsten das zur vierten Gruppe gehörige Titanoxyd, während die zu den anderen Gruppen gehörigen Oxyde in Bezug auf die katalytische Wirksamkeit zwischen diesen beiden Extremen ziemlich regelmässig angeordnet sind. Diesähnliche Regelmässigkeit können wir auch bei den zu anderen Reihen des periodischen Systems gehörigen Elemente finden, obwohl bei diesen anderen Reihen das Versuchsmaterial nicht so lückenlos wie bei der hier untersuchten vierten Reihe erhältlich ist und weiter der Unterschied der katalytischen Wirksamkeit zwischen einzelnen Oxyden mit zunehmender Gruppennummer immer weniger ausgeprägt zu werden scheint. Wenn wir aber z.B. statt des fehlenden Punktes für Scandiumoxyd in Abb. 2 den für Aluminiumoxyd, das zur dritten Reihe gehört, in derselben Abb. einzeichnen, so liegt er doch ziemlich gut auf der dort angegebenen Kurve, wie der viereckige Punkt zeigt.

Über den Mechanismus der katalytischen Austauschreaktion an der Oberfläche der hier untersuchten Oxyde lässt sich nicht ohne weiteres etwas Sicheres aussagen, bis weitere ausführliche Versuche mit jedem Oxyd durchgeführt werden. Aber wenigstens aus den bisher untersuchten Versuchsergebnissen mit Platin (vgl. I. Mitteil.) und Kupferoxyd (vgl. III. Mitteil.) zu urteilen, liegt die Vermutung nahe, dass beim Oxyd, das zur niedrigeren Gruppe gehört wie z.B. Calciumoxyd, die aktivierte Adsorption des Wasserdampfes bzw. die Bildung der Zwischenverbindung zwischen Wasser und dem in Rede stehenden Oxyd der massgebende Prozess ist, während beim Oxyd, das zur höheren Gruppe gehört, wie z.B. Manganoxyd, die aktivierte Adsorption des Sauerstoffgases an dem betreffenden Oxyd die massgebende Rolle spielt.

Tabelle 8. Vergleich der katalytischen Wirksamkeit der verschiedenen Oxyde.

| Oxyde                          | Die zum Versuch benutzte Menge in g. | $t(10\%)$<br>°C. |
|--------------------------------|--------------------------------------|------------------|
| CaO                            | 8                                    | 390              |
| TiO <sub>2</sub>               | 9                                    | 590              |
| V <sub>2</sub> O <sub>5</sub>  | 10                                   | 520              |
| Cr <sub>2</sub> O <sub>3</sub> | 7                                    | 380              |
| Mn <sub>2</sub> O <sub>4</sub> | 11                                   | 280              |
| Fe <sub>2</sub> O <sub>3</sub> | 15                                   | 420              |
| NiO                            | 8                                    | 430              |

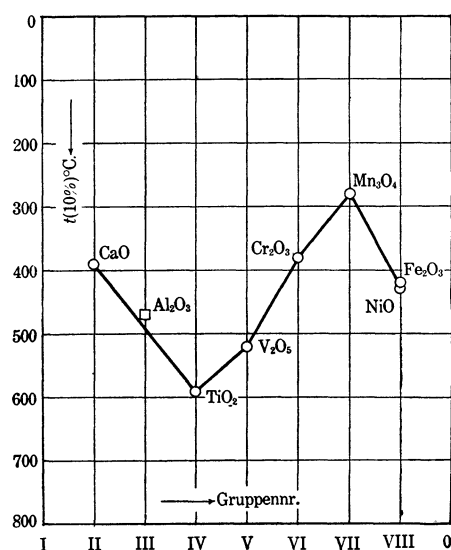


Abb. 2. Abhängigkeit der katalytischen Wirksamkeit der verschiedenen Oxyde von der Gruppennummer im periodischen System.

Zum Schluss möchten wir der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung zur Ausführung dieser Arbeit unseren wärmsten Dank aussprechen.

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## The OH-Vibration Spectrum in the Photographic Infrared. II.

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In our previous work<sup>(1)</sup> we studied the near infrared absorption bands of monovalent alcohols and ortho-substituted phenols in the liquid state as well as in carbon tetrachloride solutions. The present paper deals with the investigation extended to the vapours of these substances. The experimental apparatus was essentially the same as that described in our

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(1) Mizushima, Uehara, and Morino, this Bulletin, **12** (1937), 132.

previous paper, except that a three-meter absorption tube of glass was used.

The observed wave lengths of absorption maxima corresponding to the second and third overtones are shown, respectively, in the second and fourth columns of Table 1. Our values for the second overtone are in

Table 1. Wave length ( $\text{\AA}$ ) of absorption maxima of OH vibration bands.

| Substance                                    | $\nu_2$              |              | $\nu_3$              |              |
|----------------------------------------------|----------------------|--------------|----------------------|--------------|
|                                              | Vapour               | Solution     | Vapour               | Solution     |
| CH <sub>3</sub> OH                           | 9473<br>9514         | 9593         | 7282<br>7311         | 7376         |
| C <sub>2</sub> H <sub>5</sub> OH             | 9533                 | 9621         | 7323                 | 7411         |
| <i>n</i> -C <sub>3</sub> H <sub>7</sub> OH   | 9510<br>9557         | 9626         | 7304<br>7353         | 7411         |
| <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH   | 9511<br>9557         | 9610         | 7308<br>7356         | 7430         |
| HCOOH                                        | 9773<br>9815         | —<br>—       | 7513<br>7534         | —<br>—       |
| CH <sub>3</sub> COOH                         | 9760                 | —            | 7501                 | —            |
| C <sub>2</sub> H <sub>5</sub> COOH           | 9761                 | —            | 7502                 | —            |
| C <sub>6</sub> H <sub>5</sub> OH             | 9564                 | 9679         | 7345                 | 7446         |
| <i>o</i> -C <sub>6</sub> H <sub>4</sub> ClOH | 9568<br>9812         | 9687<br>9907 | 7346<br>7569         | 7446<br>7621 |
| <i>o</i> -C <sub>6</sub> H <sub>4</sub> BrOH | 9564<br>9884         | 9682<br>9995 | 7346<br>—            | 7462<br>7710 |
| C <sub>2</sub> H <sub>4</sub> ClOH           | 9486<br>9538<br>9646 | 9595<br>9726 | 7287<br>7334<br>7429 | —<br>—<br>—  |

general in good agreement with those of Badger and Bauer,<sup>(2)</sup> Herzberg and Verleger,<sup>(3)</sup> and Naherniac,<sup>(4)</sup> so far as the comparison can be made. For methyl alcohol Badger and Bauer<sup>(5)</sup> carried out also high dispersion measurement in the region of the third overtone.

The two absorption maxima observed for some alcohols and acids probably belong to different branches of the same vibration band, while those for ortho-halogenated phenols which have much larger wave length differences correspond to different bands of the two molecular species

(2) Badger and Bauer, *J. Chem. Phys.*, **4** (1936), 711.

(3) Herzberg und Verleger, *Physik. Z.*, **37** (1936), 444.

(4) Naherniac, *Ann. phys.*, **7** (1937), 528.

(5) Badger and Bauer, *J. Chem. Phys.*, **4** (1936), 469.

given by the quantum mechanical resonance<sup>(1) (6) (7)</sup> (see Fig. 1). Of the two absorption maxima observed for the latter substances, that having the wave-length nearly equal to that of phenol is assigned to configuration II of Fig. 1 in which the interaction between OH and Cl is much smaller than that expected in the alternative configuration. The relative number of molecules in configuration II is, however, much smaller than that expected from the intensity ratio of the said two absorption maxima, as was shown by our previous dipole measurement.<sup>(8)</sup> This is due to the interaction between the chlorine and the hydroxyl hydrogen which reduces the absorption intensity of OH vibration considerably. The wave lengths of absorption maxima found for acids are much longer than those for alcohols, which indicates that practically all the molecules of acids assume configuration I of Fig. 2. This results is in conformity with the conclusion from the dipole measurement.<sup>(9) (10)</sup>

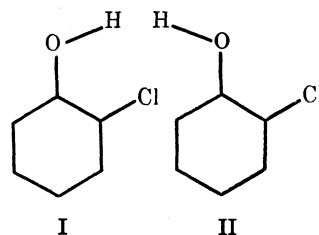


Fig. 1.

The absorption maxima observed for vapours have longer wave lengths by ca. 100 Å than those for the dilute carbon tetrachloride solutions<sup>(11)</sup> (third and fifth columns of Table 1). This fact is interesting when compared with the observation of Errera and Mollet<sup>(12)</sup> that for the fundamental tone the absorption maximum of the vapour of  $C_2H_5OH$  has practically the same wave length as that of the carbon tetrachloride solution. The effect of solvent molecule is, therefore, much larger for a higher quantum state than that for a lower one.

For ethylene chlorhydrin we observed three absorption maxima ( $\nu_2^a = 9486$  Å,  $\nu_2^b = 9538$  Å,  $\nu_2^c = 9646$  Å) in the vapour state and two ( $\nu_2^d = 9595$  Å,  $\nu_2^e = 9726$  Å) in dilute carbon tetrachloride solutions. From the experimental results obtained for the other substances shown in Table 1, it may be considered that  $\nu_2^a$  and  $\nu_2^b$  correspond to  $\nu_2^d$  and  $\nu_2^e$  to  $\nu_2^c$ . It is possible that these two absorption regions of ethylene chlorhydrin may have an explanation similar to that applied to the ortho-halogenated phenols. From the observed values of dipole moment<sup>(13)</sup> it

(6) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464; Wulf, Liddel, and Hendricks, *ibid.*, **58** (1936), 2287.

(7) Pauling, *J. Am. Chem. Soc.*, **58** (1936), 94.

(8) Kozima and Mizushima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **31** (1937), 296.

(9) Zahn, *Phys. Rev.*, **37** (1931), 1516; *Trans. Faraday Soc.*, **30** (1934), 804.

(10) Mizushima, *J. Chem. Soc. Japan*, **57** (1936), 936.

(11) In our previous communication we calculated the frequency of infinitesimal vibration  $\omega$  and the anharmonicity factor  $x$  from our experimental values for the second and third overtones, putting the vibrational level of the quantum number  $v$  as

$$G(v) = \omega \left( v + \frac{1}{2} \right) - x\omega \left( v + \frac{1}{2} \right)^2$$

Using  $\omega$  and  $x$  thus obtained we can calculate the frequencies of the fundamental tone and first overtone for  $C_2H_5OH$  as 3648  $cm^{-1}$  and 7114  $cm^{-1}$  respectively, both of which are in good agreement with the experimental values of Errera and Mollet (3640  $cm^{-1}$ ) and Wulf and Liddel (7090  $cm^{-1}$ ).

(12) Errera and Mollet, *Nature*, **138** (1936), 882; *Compt. rend.*, **204** (1937), 259.

(13) Zahn, *Physik. Z.*, **33** (1932), 525.

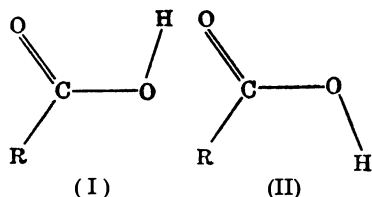


Fig. 2. The two molecular configurations of carboxylic acids expected from the quantum mechanical resonance.

Table 2. Wave length variation of absorption maximum of ethylene chlorhydrin with concentration.

| 1 : x*      | Wave length (Å) of absorption maximum. |            |
|-------------|----------------------------------------|------------|
| pure liquid | 9760                                   | —          |
| 1 : 1       | 9755                                   | —          |
| 1 : 4       | 9731                                   | —          |
| 1 : 8       | 9724                                   | 9621       |
| 1 : 16      | 9724                                   | 9616       |
| 1 : 80      | 9725                                   | 9609       |
| 1 : 300     | 9726                                   | 9595       |
| vapour      | 9646                                   | 9538, 9486 |

\* The solution consists of one part by volume of ethylene chlorhydrin and x parts of carbon tetrachloride.

is concluded that the molecular configuration of ethylene chlorhydrin corresponds either to the trans form  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{OH}$  or to the cis form  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{OH}$ , but it is not unreasonable to assume the coexistence of these two forms, since the change in abundance ratio does not affect the apparent value of dipole moment. Then  $\nu_2^a$  and  $\nu_2^b$  ( $\nu_2^d$  in solution) can be assigned to the trans form and  $\nu_2^c$  ( $\nu_2^e$  in solution) to the cis form, as the former will have wave lengths not much different from those of alcohols owing to the smaller interaction between Cl and OH. This assignment is in conformity with the behaviours of these bands in carbon tetrachloride solutions as stated in the following (see Table 2). In the liquid state and in concentrated solutions we observed a broad band around  $\lambda = 9760 \text{ Å}$ , which on dilution becomes sharper and is shifted towards higher frequency region until the absorption maximum attains the wave length of  $9726 \text{ Å}$ , i.e.  $\nu_2^c$  of the cis form. From a certain dilution on there appears in the shorter wave length region another band, which we have assigned to the trans form ( $\nu_2^d$ ). In other words the OH vibration of the cis form can be observed in all the conditions mentioned above, while that of the trans form only in the dilute solutions and in the vapour. This fact is just what we would expect from the configurations of these two molecular species, since the trans form will easily form *intermolecular* hydrogen bond (such as in the case of alcohols)<sup>(14)</sup> and therefore the OH vibration of a single molecule can hardly be observed in concentrated solutions, while there is much less probability for such bonding for the cis form whose hydroxyl hydrogen is coupled with the chlorine in the same molecule.

We are indebted to Hattori-Hôkôkai and Ôji-Seishi-Kaisha for grants in aid of this research.

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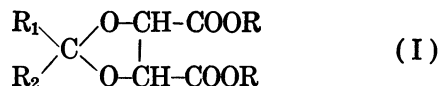
(14) According to Errera and Mollet<sup>(12)</sup> the OH band due to the isolated molecule of ethyl alcohol can be observed only in dilute solutions.

## Synthesis of Cyclic Derivatives of Tartaric Acid by Condensing Alkyl *d*-Tartrates with Aliphatic Ketones. (Optical Activity and Chemical Structure in Tartaric Acid. V.\*)

By Yojiro TSUZUKI.

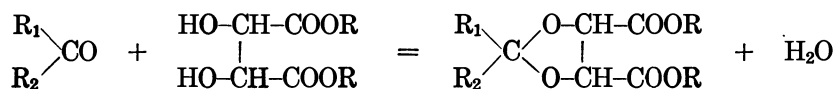
(Received December 27, 1938.)

It was reported in the previous communications<sup>(1)</sup> that various cyclic derivatives of tartaric acid having the constitution



were synthesized by condensing alkyl *d*-tartrates with some aliphatic aldehydes and ketones as well as with alicyclic ketones. These compounds are suitable materials for the study of the relation between optical activity and chemical structure of tartaric acid, since they are all liquid compounds showing high lævo-rotation and exhibiting simple rotatory dispersion. And, indeed, the author has shown that the groups  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}$  exert a certain definite effect on the optical rotatory power of the condensation products, in good agreement with the requirement of the molecular theories of de Malleman<sup>(2)</sup> as well as of Boys.<sup>(3)</sup>

The purpose of the present work is to amplify the materials by condensing alkyl *d*-tartrates with a series of aliphatic ketones, in order to observe how the substituents  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}$  influence the optical activity of the resulting compounds.



The following condensations were carried out: ethyl *d*-tartrate with methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl amyl ketone, dipropyl ketone and with methyl nonyl ketone, and in addition to these, methyl ethyl ketone with methyl *d*-tartrate, propyl *d*-tartrate and with isopropyl *d*-tartrate. The method of condensation was almost the same as in the cases of alicyclic ketones with ethyl *d*-tartrate<sup>(4)</sup> using also in this case phosphorus pentoxide as the condensation reagent. It is, however, to be noted that in the cases of symmetrical ketones, the temperature of the reaction must be lower and the duration of the reaction must accordingly be longer than in the cases of unsymmetrical ketones.

\* Paper IV, this Bulletin, **12** (1937), 487.

(1) Y. Tsuzuki, this Bulletin, **10** (1935), 255; **11** (1936), 362; **11** (1936), 586; **12** (1937), 487.

(2) R. de Malleman, *Trans. Faraday Soc.*, **26** (1930), 281.

(3) F. S. Boys, *Proc. Roy. Soc. (London)*, A, **144** (1934), 655.

(4) Y. Tsuzuki, this Bulletin, **12** (1937), 487.



The condensation proceeds very smoothly in every case. The yield is fairly good, being 30–50% of the theoretical amount. The purification of the product is carried out in the same way as before, i.e. by evaporating off unchanged ketone and by dissolving out unchanged alkyl tartrate with aqueous borax. In the cases of propyl and isopropyl tartrates the purification is somewhat difficult, since these tartrates are not so easily soluble in borate; in these cases the above process of purification must be repeatedly performed, whereby the yield was somewhat impoverished.

The condensation products thus obtained and purified are transparent colourless liquids, showing strong lævo-rotation. Optical rotatory powers have also been measured in ethyl alcohol, in benzene and in cyclohexane. The optical activity and its solvent effect will be discussed in the following paper.

#### Ethyl methylethylmethylene-*d*-tartrate.

$C_{12}H_{20}O_6$  (260.16). (I)  $R_1 = CH_3$ ,  $R_2 = C_2H_5$ ,  $R = C_2H_5$

To a mixture of 15 g. ethyl *d*-tartrate and 15 g. methyl ethyl ketone (Takeda's product, fractionated, b.p. 78.3–79°) was added 8 g. phosphorus pentoxide in portions at 70° during a period of 30 minutes. The liquid coloured pale yellow and the phosphorus pentoxide deeply brownish red. After the whole of phosphorus pentoxide was added, the mixture was maintained at this temperature for 30 minutes, and after cooling, the reaction product was extracted with ether. The ethereal solution was washed several times with a saturated solution of borax to remove unchanged ethyl *d*-tartrate and was finally dried over anhydrous sodium sulphate. After evaporating off the ether, the product was purified by fractional distillation in vacuo. Colourless liquid. Yield 8.5 g. Boiling point 158° (17 mm.),  $n_D^{20}$  1.4361,  $d_4^{20}$  1.0973,  $M_D$  61.99 (62.01),  $[\alpha]_D^{20}$  –35.02°,  $[M]_D^{20}$  –91.10°.  $[\alpha]_B^{20}$  –36.0° (in ethyl alcohol, 4.45%),  $[M]_B^{20}$  –91.5° (in ethyl alcohol).  $[\alpha]_B^{20}$  –40.2° (in benzene, 5.232%),  $[M]_B^{20}$  –104.6° (in benzene).  $[\alpha]_B^{20}$  –31.62° (in cyclohexane, 3.265%),  $[M]_B^{20}$  –82.25° (in cyclohexane).

#### Ethyl methylpropylmethylene-*d*-tartrate.

$C_{13}H_{22}O_6$  (274.18). (I)  $R_1 = CH_3$ ,  $R_2 = C_3H_7$ ,  $R = C_2H_5$

Ethyl *d*-tartrate (21 g.) and 13 g. methyl propyl ketone (Takeda's product, fractionated, b.p. 100–102°) gave 9 g. pure product. Colourless liquid boiling at 167.5° (20 mm.).  $n_D^{20}$  1.4370,  $d_4^{20}$  1.0770,  $M_D$  66.69 (66.62),  $[\alpha]_D^{20}$  –32.05°,  $[M]_D^{20}$  –87.88°.  $[\alpha]_B^{20}$  –31.8° (in ethyl alcohol, 5.400%),  $[M]_B^{20}$  –87.2° (in ethyl alcohol).  $[\alpha]_B^{20}$  –36.4° (in benzene, 5.534%),  $[M]_B^{20}$  –99.8° (in benzene).  $[\alpha]_B^{20}$  –28.86° (in cyclohexane, 3.611%),  $[M]_B^{20}$  –79.14° (in cyclohexane).

#### Ethyl diethylmethylene-*d*-tartrate.

$C_{13}H_{22}O_6$  (274.18). (I)  $R_1 = R_2 = C_2H_5$ ,  $R = C_2H_5$

Ethyl *d*-tartrate (21 g.) and 13 g. diethyl ketone (Takeda's product, fractionated, b.p. 100–102°) gave 10.5 g. pure condensation product, when 20 g.  $P_2O_5$  was added to the mixture at 60–70° during 50 minutes. Almost colourless liquid boiling at 169° (22 mm.).  $n_D^{20}$  1.4390,  $d_4^{20}$  1.0850,  $M_D$  66.45 (66.62),  $[\alpha]_D^{20}$  –23.06°,  $[M]_D^{20}$  –63.23°.  $[\alpha]_B^{20}$  –25.3° (in ethyl alcohol, 4.854%),

$[M]_D^{20}$   $-69.4^\circ$  (in ethyl alcohol).  $[\alpha]_D^{20}$   $-33.0^\circ$  (in benzene, 5.108%),  $[M]_D^{20}$   $-90.5^\circ$  (in benzene).  $[\alpha]_D^{20}$   $-20.89^\circ$  (in cyclohexane, 3.631%),  $[M]_D^{20}$   $-57.27^\circ$  (in cyclohexane).

#### Ethyl methylamylmethylene-*d*-tartrate.

$C_{15}H_{26}O_6$  (302.21). (I)  $R_1 = CH_3$ ,  $R_2 = C_5H_{11}$ ,  $R = C_2H_5$

To a mixture of 12.6 g. ethyl *d*-tartrate and 7 g. methyl amyl ketone (Takeda's product, fractionated, b.p.  $148^\circ$ ) was added 13 g. phosphorus pentoxide at  $80-90^\circ$ , during a period of 50 minutes, and heating was continued for one hour to maintain this temperature. Yield 8 g. Colourless liquid boiling at  $180^\circ$  (15 mm.),  $n_D^{20}$  1.4399,  $d_4^{20}$  1.0478,  $M_D$  76.00 (75.87),  $[\alpha]_D^{20}$   $-26.59^\circ$ ,  $[M]_D^{20}$   $-80.36^\circ$ .  $[\alpha]_D^{20}$   $-27.33^\circ$  (in ethyl alcohol, 6.917%),  $[M]_D^{20}$   $-82.6^\circ$  (in ethyl alcohol).  $[\alpha]_D^{20}$   $-31.13^\circ$  (in benzene, 4.7656%),  $[M]_D^{20}$   $-94.1^\circ$  (in benzene).  $[\alpha]_D^{20}$   $-24.19^\circ$  (in cyclohexane, 4.2583%),  $[M]_D^{20}$   $-73.10^\circ$  (in cyclohexane).

#### Ethyl dipropylmethylene-*d*-tartrate.

$C_{15}H_{26}O_6$  (302.21). (I)  $R_1 = R_2 = C_3H_7$ ,  $R = C_2H_5$

To a mixture of 15 g. ethyl *d*-tartrate and 8.3 g. di-*n*-propyl ketone (prepared from *n*-butyric acid by passing it over  $ThO_2$  at  $380-480^\circ$ , b.p.  $142-144^\circ$ ) was added 15 g.  $P_2O_5$  at  $80-90^\circ$ . Yield 6 g. Pure colourless liquid boiling at  $175^\circ$  (16 mm.),  $n_D^{20}$  1.4424,  $d_4^{20}$  1.0521,  $M_D$  76.07 (75.87),  $[\alpha]_D^{20}$   $-19.77^\circ$ ,  $[M]_D^{20}$   $-59.74^\circ$ .  $[\alpha]_D^{20}$   $-22.45^\circ$  (in ethyl alcohol, 6.000%),  $[M]_D^{20}$   $-67.86^\circ$  (in ethyl alcohol).  $[\alpha]_D^{20}$   $-28.47^\circ$  (in benzene, 5.126%),  $[M]_D^{20}$   $-86.03^\circ$  (in benzene).  $[\alpha]_D^{20}$   $-18.17^\circ$  (in cyclohexane, 5.952%),  $[M]_D^{20}$   $-54.91^\circ$  (in cyclohexane).

#### Ethyl methylnonylmethylene-*d*-tartrate.

$C_{19}H_{34}O_6$  (358.27). (I)  $R_1 = CH_3$ ,  $R_2 = C_9H_{19}$ ,  $R = C_2H_5$

To a mixture of 10 g. ethyl *d*-tartrate and 8.5 g. methyl nonyl ketone (Th. Schuchardt) was added 10 g.  $P_2O_5$  in portions at  $90^\circ$  during one hour, and the reaction mixture was further heated at  $80^\circ$  for one hour. Yield 6 g. Colourless liquid boiling at  $218^\circ$  (15 mm.),  $n_D^{20}$  1.4465,  $d_4^{20}$  1.0086,  $M_D$  94.82 (94.34),  $[\alpha]_D^{20}$   $-21.33^\circ$ ,  $[M]_D^{20}$   $-76.41^\circ$ .  $[\alpha]_D^{20}$   $-21.38^\circ$  (in ethyl alcohol, 7.5645%),  $[M]_D^{20}$   $-76.59^\circ$  (in ethyl alcohol).  $[\alpha]_D^{20}$   $-26.03^\circ$  (in benzene, 5.9822%),  $[M]_D^{20}$   $-93.44^\circ$  (in benzene).  $[\alpha]_D^{20}$   $-18.93^\circ$  (in cyclohexane, 5.4008%),  $[M]_D^{20}$   $-67.82^\circ$  (in cyclohexane).

#### Methyl methylethylmethylene-*d*-tartrate.

$C_{10}H_{16}O_6$  (232.16). (I)  $R_1 = CH_3$ ,  $R_2 = C_2H_5$ ,  $R = CH_3$

Methyl *d*-tartrate (15 g.), b.p.  $163^\circ$  (20 mm.), and 15 g. methyl ethyl ketone gave 9 g. pure colourless liquid boiling at  $141^\circ$  (15 mm.).  $n_D^{20}$  1.4420,  $d_4^{20}$  1.1607,  $M_D$  52.92 (52.87),  $[\alpha]_D^{20}$   $-35.79^\circ$ ,  $[M]_D^{20}$   $-83.08^\circ$ .

#### Propyl methylethylmethylene-*d*-tartrate.

$C_{14}H_{24}O_6$  (288.19). (I)  $R_1 = CH_3$ ,  $R_2 = C_2H_5$ ,  $R = C_3H_7$

Propyl *d*-tartrate (15 g.), b.p.  $171^\circ$  (15 mm.), and 15 g. methyl ethyl ketone gave 9 g. pure product. To remove the unreacted propyl *d*-tartrate,

the ethereal extract of the mixture must be repeatedly washed with borax solution, since the ester is not so easily soluble in this solution as ethyl *d*-tartrate. Pale yellow liquid. Boiling point 167° (15 mm.).  $n_D^{20}$  1.4399,  $d_4^{20}$  1.0603,  $M_D$  71.62 (71.25),  $[\alpha]_D^{20}$  -30.07°,  $[M]_D^{20}$  -86.65°.

**Isopropyl methylethylmethylened-tartrate.**

$C_{14}H_{24}O_6$  (288.19). (I)  $R_1 = CH_3$ ,  $R_2 = C_2H_5$ ,  $R = (CH_3)_2CH$

To a mixture of 15 g. isopropyl *d*-tartrate, b.p. 155° (17 mm.), and 15 g. methyl ethyl ketone was added 15 g. phosphorus pentoxide at 70° in portions during one hour. The phosphorus oxide coloured deep brown but the liquid not so strongly. The liquid was decanted from the dehydrating reagent, and the unchanged ketone was evaporated off. The ethereal extract of the residual liquid was washed with  $N/2$   $KBO_2$ ,<sup>(5)</sup> in order to remove the unreacted isopropyl tartrate, dried over sodium sulphate, and fractionated in vacuo. This process of purification was repeated once. Yield 8 g. Colourless liquid. Boiling point 115–117° (0.5 mm.).  $n_D^{20}$  1.43321,  $d_4^{20}$  1.0460,  $M_D$  71.63 (71.25),  $[\alpha]_D^{20}$  -30.32°,  $[M]_D^{20}$  -87.36°.

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(5) The high efficiency of the use of  $KBO_2$  in the separation has been clearly shown by quantitative studies, Y. Tsuzuki, this Bulletin, **13** (1938), 337.

## The Isomerization of Dimethyl Maleate by Hydrogen Bromide and by Hydrogen Chloride.

By Osamu SIMAMURA.

(Received December 28, 1938.)

**Introduction.** In the previous papers<sup>(1)(2)</sup> it was reported that hydrogen bromide, in presence of oxygen, caused the isomerization of isostilbene to stilbene in the dark at room temperature either in absence of solvents or in benzene solution, while neither hydrogen bromide nor oxygen was active when present alone. Reduced nickel, which is in itself inactive to the isomerization of isostilbene to stilbene, was found also to co-operate with hydrogen bromide to accelerate the isomerization in absence of solvents, and another ferromagnetic metal, reduced iron, was shown to be capable of promoting the isomerization with hydrogen bromide, although the effect was smaller than that of reduced nickel.

It may be added here that subsequent experiments have shown that no isomerization of isostilbene to stilbene takes place with hydrogen

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(1) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507.

(2) Y. Urushibara and O. Simamura, *ibid.*, **13** (1938), 566.

chloride either alone or in presence of any of oxygen, reduced nickel, and benzoyl peroxide under essentially the same experimental conditions as described in the cited reports.<sup>(1) (2)</sup>

The investigation has now been extended to the catalyzed isomerization of dimethyl maleate to dimethyl fumarate with the view of ascertaining whether oxygen co-operates with hydrogen bromide in accelerating the rearrangement just as that of isostilbene to stilbene, and it is the more interesting in view of the well-known conversion of maleic into fumaric acid by aqueous hydrogen halides,<sup>(3)</sup> which was investigated without taking account of the then unrevealed influence of oxygen. N. W. Hanson and D. M. Williams<sup>(4)</sup> showed that dimethyl fumarate was a by-product in the bromination catalyzed by hydrogen bromide of dimethyl maleate in carbon tetrachloride in the dark. It is, however, not clear whether dimethyl fumarate was produced by the sole action of hydrogen bromide or oxygen had any influence on it. In the present investigation it has been established that dimethyl maleate is isomerized to the fumarate by the catalytic action of hydrogen bromide and of hydrogen chloride and the presence of oxygen is indifferent to this catalyzed transformation under the present experimental conditions. The effect of reduced nickel, which is much weaker than that of oxygen in the case of isostilbene, has not been examined.

**Materials.** *Dimethyl Maleate.* 90 Grammes of maleic acid was dissolved in 1200 c.c. of methanol containing 75 g. of concentrated sulphuric acid and the solution was boiled on a water bath for ten hours. Then 450 c.c. of methanol was distilled off, the cooled reaction mixture poured into ice water and extracted repeatedly with carbon tetrachloride. The carbon tetrachloride layer was shaken with aqueous sodium carbonate solution, washed with water, and then dried with anhydrous sodium sulphate. After carbon tetrachloride was distilled off under the ordinary pressure the remaining oil was fractionated through a Widmer column and the middle fraction boiling at 88–88.5° under 6 mm. was collected ( $n_D^{20}$  1.4429).

*Hydrogen Bromide.* Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a wash bottle containing tetralin and then through U-tubes filled with anhydrous calcium bromide and with anthracene respectively. For further purification, after bubbled through a bubble counter in which a part of the gas was liquefied by cooling with solid carbon dioxide and ether, the hydrogen bromide was collected in a receiver surrounded by liquid air. Then traces of incondensable gases were eliminated by repeated melting and solidification of the hydrogen bromide and evacuation of the vessel. Finally the gas was fractionated, a middle portion being collected in a gas burette. In some experiments hydrogen bromide was purified by passing through cold tetralin and over moist red phosphorus, anhydrous calcium bromide, and phosphorus pentoxide. It made no difference in the experimental results which of the methods was used in preparing hydrogen bromide.

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(3) Skraup, *Monatsh.*, **12** (1891), 118.

(4) *J. Chem. Soc.*, **1930**, 1059.

*Hydrogen Chloride.* Hydrogen chloride was prepared from concentrated hydrochloric and sulphuric acids, dried by passing through concentrated sulphuric acid, condensed in a receiver cooled with liquid air, and then fractionated as in the case of hydrogen bromide.

*Carbon Tetrachloride.* A purest commercial product was boiled with alkaline potassium permanganate solution for six hours, washed with water, dried with calcium chloride, and then distilled over phosphorus pentoxide.

**Experimental Procedures and Results.** All the experiments were conducted in the dark at room temperature and the extent of reaction was examined under a photographic lamp.

(1) *Isomerization by Hydrogen Bromide.* In a glass tube with a capacity of 7–8 c.c. 0.2 c.c. of dimethyl maleate was taken, the air in the tube was evacuated, hydrogen introduced and again thoroughly evacuated; after the admission of 5 c.c. of hydrogen bromide (the volume of gas refers to the ordinary pressure) the tube was sealed off. In the course of one minute or two dimethyl maleate changed with an evolution of heat into a solid crystalline mass, which was then taken out of the tube by breaking it and crystallized from methanol, melting point 102–103°. In admixture with an authentic specimen of dimethyl fumarate the melting point showed no depression. In some experiments dimethyl maleate contained in a side tube attached to the reaction tube was vacuum-distilled into the latter under the complete exclusion of air, and the side tube having been severed by sealing off, the above-mentioned procedure was pursued; the results were the same. Catechol (5 mg.) added beforehand to dimethyl maleate had no influence on the isomerization by hydrogen bromide, whereas it is quite active in preventing that of isostilbene to stilbene caused by the joint action of hydrogen bromide and oxygen.

(2) *Isomerization by Hydrogen Bromide in Carbon Tetrachloride.* One c.c. of dimethyl maleate and 10 c.c. of carbon tetrachloride (with or without addition of catechol) were pipetted into a glass tube of 65 c.c. capacity, which was evacuated with simultaneous cooling with solid carbon dioxide and ether; the solidified mixture was then melted under evacuation and about 10 per cent of carbon tetrachloride was distilled off, thus traces of air being eliminated from the solution. Then 5–10 c.c. of hydrogen bromide was introduced, the tube sealed off and left to stand in the dark for a certain period. By a capillary seal attached to it the tube was connected to the vacuum line with a piece of rubber tubing, inside which the seal was broken by crushing from without. Introduction of hydrogen and subsequent evacuation enabled the complete removal of hydrogen bromide avoiding the complicating access of air. The carbon tetrachloride solution was washed with aqueous sodium carbonate solution and then with water, and dried over anhydrous sodium sulphate. On distilling off carbon tetrachloride and cooling the remaining mixture, of which Beilstein's test indicated the presence of bromine, dimethyl fumarate crystallized out. Though the experiments were of the qualitative nature the extent of isomerization was approximately estimated by noting the temperature at which the last crystals disappeared when the sample was heated very gradually in a water bath, and determining the composi-

tion from the composition-fusing point curve drawn by R. Schmidt.<sup>(5)</sup> Some of the results are tabulated in Table 1.

Table 1.

| Exp. No. | Hydrogen bromide admitted (c.c.) | Catechol added (mg.) | Reaction time (hours) | Fumarate produced (per cent) |
|----------|----------------------------------|----------------------|-----------------------|------------------------------|
| 27       | 10                               | 0                    | 20.5                  | 18                           |
| 28       | 10                               | 20                   | 20.5                  | 20                           |
| 29       | 5                                | 0                    | 2.5                   | 11                           |
| 30       | 5                                | 40                   | 2.5                   | 14                           |

Table 2.

| Exp. No. | Hydrogen bromide admitted (c.c.) | Oxygen added (c.c.) | Reaction time (hours) | Fumarate produced (per cent) |
|----------|----------------------------------|---------------------|-----------------------|------------------------------|
| 47       | 5                                | 0                   | 5                     | 15                           |
| 48       | 5                                | 5                   | 5                     | 13                           |
| 49       | 5                                | 0                   | 24.5                  | 20                           |
| 50       | 5                                | 5                   | 24.5                  | 19                           |

As the reaction in carbon tetrachloride was much slower than in absence of solvents the effect of oxygen on the reaction could be conveniently examined. In the experiments with added oxygen the reaction mixture, after removal of hydrogen bromide, was immediately evaporated and the composition estimated (Table 2). The increase of the amount of oxygen added up to 50 c.c. had no perceptible influence on the results. In every pair of conjugate runs a difference of one or two per cent in the amount of fumarate produced was observed; in all likelihood this might not be a real difference in view of the experimental accuracy and the conclusion is that oxygen and catechol have no influence on the isomerization caused by hydrogen bromide of dimethyl maleate to the fumarate.

(3) *Isomerization by Hydrogen Chloride.* The experimental details were quite the same as described in (1). It was about one hour before the precipitation of dimethyl fumarate set in and the reaction was slowly brought to completion in the course of more than ten hours. The addition of catechol caused no alteration of the progress of the reaction. In presence of a larger amount of hydrogen chloride the isomerization was of course rapid: in a vessel with a capacity of 65 c.c. 0.2 c.c. of dimethyl maleate and 50 c.c. of hydrogen chloride were sealed; the isomeric ester began to deposit in five minutes, and the conversion was nearly completed in 40–45 minutes.

(4) *Isomerization by Hydrogen Chloride in Carbon Tetrachloride.* The procedure described in (2) was closely followed substituting hydrogen chloride for the bromide. The results are summarized in Table 3.

(5) *Z. physik. Chem.*, B, **1** (1928), 209.

Table 3.

| Exp. No. | Hydrogen chloride admitted (c.c.) | Oxygen added (c.c.) | Reaction time (hours) | Fumarate produced (per cent) |
|----------|-----------------------------------|---------------------|-----------------------|------------------------------|
| 7        | 5                                 | 0                   | 21                    | 4                            |
| 8        | 25                                | 0                   | 42                    | 18                           |
| 9        | 25                                | 20                  | 42                    | 17                           |

**Discussion.** Numerous investigations on the isomerization of the maleinoid to the fumaroid compounds are available and the action of halogens which are effective in the light in causing the transformation is attributed to halogen atoms formed by the absorption of light quantum. The inversion is supposed to occur in a molecule formed by the addition of the halogen atom thus produced to the ethenoid linkage, the subsequent elimination of the halogen atom regenerating the isomeric ethenoid form.

M. S. Kharasch, J. V. Mansfield, and F. R. Mayo<sup>(6)</sup> have observed, that isostilbene is isomerized to stilbene by hydrogen bromide either in the light or in the presence of a peroxidic substance and not by hydrogen bromide alone, that the catalyzed transformation is prevented by anti-oxidants (e.g. hydroquinone, catechol), and that hydrogen chloride is ineffective in causing the isomerization under any of the conditions. Thus they have been led to the belief, that in this reaction the active catalysts are bromine atoms which are produced by the action of a peroxide or light on hydrogen bromide. Further, Y. Urushibara and O. Simamura<sup>(1) (2)</sup> have reported that oxygen, too, is effective in activating hydrogen bromide to isomerize isostilbene to stilbene.

As detailed in the experimental part of the present communication dimethyl maleate is converted into the fumarate by hydrogen bromide and by hydrogen chloride and the influence of oxygen is not perceptible. However, the possibility of the influence of oxygen cannot totally be excluded. The effect of oxygen, if any, must be negligibly small compared with that of hydrogen bromide alone; but the possibility of the effectiveness of oxygen in the case of hydrogen chloride can readily be ruled out on the basis of the stability of the latter toward oxygen and by the experimental fact that hydrogen chloride and oxygen do not cause the isomerisation of isostilbene. Thus the conversion of dimethyl maleate into the fumarate by hydrogen halides belongs to another type of catalyzed cis-trans isomerization apparently distinct from that of isostilbene by hydrogen bromide and oxygen.

Concerning the mechanism of the conversion of maleic into fumaric acid caused by aqueous hydrogen halides several speculations are available. From a kinetic study of the reaction E. M. Terry and L. Eichelberger<sup>(7)</sup> have proposed a hypothesis, that the catalyst goes into interaction with carboxyl groups and "saturates" them, and that this removes the stabilizing influence of the carboxyl group upon the double bond, facilitating the

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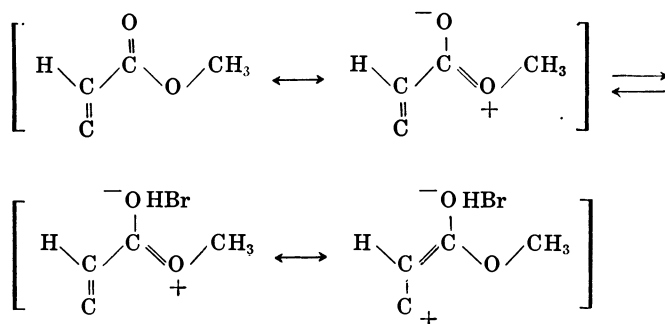
(6) *J. Am. Chem. Soc.*, **59** (1937), 1155.

(7) *J. Am. Chem. Soc.*, **47** (1925), 1402.



activation of the latter to the isomeric change. This idea of the interaction of the group adjacent to double bond with the catalyst may be applicable to account for the mechanism of the isomerization of dimethyl maleate under consideration, because hydrogen halides do not isomerize isostilbene but dimethyl maleate, and it seems highly probable that the carbomethoxyl group plays an important role. Moreover, as the experiments have been made either without solvents or in non-hydroxylic one, the hypothesis can be stated in a more concrete form: the association of the ester group with hydrogen halides by means of, for example, hydrogen bond formation deforms more or less the electronic configuration of the molecule, and thus destroys the rigidity of the double bond. In support of the idea that the addition of the acids to ester group takes place, a work of O. Maass and D. McIntosh<sup>(8)</sup> may be cited, who confirmed the existence of an addition compound  $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 \cdot \text{HBr}$ , and further W. Gordy and P. C. Martin<sup>(9)</sup> concluded the formation of hydrogen bond between hydrogen chloride and ethyl acetate from a study of the infrared absorption spectra.

It seems to be hardly possible, that the addition should take place at the oxidic oxygen as W. A. Waters<sup>(10)</sup> seems to believe, because then this oxygen atom would have to gain in positive charge against the opposing influence of the carbonyl group. On the other hand, if in the carboxylic ester molecule the resonance effect is considerable as contended by S. Mizushima and M. Kubo,<sup>(11)</sup> more negative charge will concentrate on the carbonyl oxygen atom than otherwise; thus the association with hydrogen halides may take place through the carbonyl oxygen, and the subsequent activation of the double bond as formulated below:



The formation of co-ordination link through hydrogen atom and carbonyl group prior to the isomerization has already been postulated by G. R. Clemons and S. B. Graham<sup>(12)</sup> who have noticed the catalytic action of primary and secondary amines, especially of piperidine, on the isomerization of dimethyl maleate. Their assumption seems to be appropriate in view of the analogy between the catalytic actions of piperidine

(8) *J. Am. Chem. Soc.*, **34** (1912), 1272.

(9) *Phys. Rev.*, **52** (1937), 1075.

(10) W. A. Waters, "Physical Aspects of Organic Chemistry," 2nd Ed., 266, London (1937).

(11) This Bulletin, **13** (1938), 174.

(12) *J. Chem. Soc.*, **1930**, 213.

and hydrogen halides, the former, too, being ineffective in causing the transformation of isostilbene to stilbene as confirmed by the present author.

### Summary.

(1) No isomerization of isostilbene to stilbene occurs with hydrogen chloride in the presence of either reduced nickel or oxygen.

(2) Hydrogen bromide and hydrogen chloride cause the isomerization of dimethyl maleate to the fumarate either in absence of solvents or in carbon tetrachloride solution.

(3) Oxygen has no effect on the isomerization of dimethyl maleate by hydrogen halides.

(4) The isomerization of dimethyl maleate by hydrogen halides belongs to another type of catalyzed cis-trans isomerization apparently distinct from that of isostilbene by hydrogen bromide and oxygen.

(5) A hypothesis has been proposed concerning the mechanism of the isomerization of dimethyl maleate caused by hydrogen halides.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragements throughout the work and to Prof. S. Mizushima for valuable advices. Thanks are also due to the Japan Society for the Promotion of Scientific Research (Nippon Gakujutsu Shinko-Kwai) and to Ozi Seisi Company for grants.

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# Chemical Studies of the Western Pacific Ocean. I. The Chemical Composition of the Oceanic Salt. Part 1.

By Yasuo MIYAKE.

(Received December 28, 1938.)

Under the guidance of Prof. Okada, Director of the Central Meteorological Observatory of Japan, a thorough investigation of the Western Pacific Ocean is now being contemplated. The present author, being charged with the chemical survey in this project, intends to determine first the chemical composition of the sea salt, precision in analyses being esteemed above all. The present paper records the results of the chemical analyses of the sea salt.

Today, we have a large number of reliable determinations<sup>(1)</sup> of the chemical composition of oceanic salt, among which W. Dittmar's seventy-seven analyses of samples of water collected from various localities and depths in the memorial "Challenger"-Expedition, are still highly regarded for their exactness. We can easily see in these numerous analyses that there is an astonishing close agreement among them. However, contemporary geochemistry is not satisfied with such mere agreement, and requires the delicate differences between them to the accuracy of the second order. In such minute differences, we have a possibility of perceiving the true sources and cycles of the elements occurring in the sea which are quite obscure even at the present time. In spite of numerous active chemical investigations in oceanography, these being mainly in the domains of fishery and chemical industry, accurate chemical analysis of waters from the Pacific Ocean near Japan has not yet been made from the stand point of exact analytical chemistry.

**Samples of Sea Water.** The dates and positions of collection are shown in Table 1.

Table 1.

| No. | Date           | Position |         | No. | Date         | Position |         |
|-----|----------------|----------|---------|-----|--------------|----------|---------|
|     |                | Lat. N   | Long. E |     |              | Lat. N   | Long. E |
| 31  | Oct. 10, 1937. | 24°53'   | 125°53' | 61  | Dec. 1, 1937 | 27°23'   | 136°48' |
| 32  | " 10, "        | 25°25'   | 126°48' | 62  | " 2, "       | 25°46'   | 137°17' |
| 36  | " 11, "        | 27°25'   | 129°45' | 64  | " " "        | 24°42'   | 137°50' |
| 38  | " 12, "        | 29°12'   | 131°53' | 67  | " " "        | 24°36'   | 139°27' |
| 40  | " " "          | 30°28'   | 133°32' | 70  | " 4, "       | 25°02'   | 141°30' |
| 42  | " " "          | 31°13'   | 134°29' | 73  | " 8, "       | 27°32'   | 141°58' |
| 45  | " 13, "        | 33°05'   | 137°01' | 75  | " 9, "       | 29°38'   | 140°56' |
| 56  | Nov. 30, "     | 32°40'   | 137°50' | 76  | " " "        | 30°09'   | 140°40' |
| 57  | Dec. 1, "      | 30°04'   | 136°40' | 81  | " 10, "      | 23°08'   | 139°49' |

(1) F.W. Clarke, "The Data of Geochemistry," 126, Washington (1924).

**Methods of Analysis.** The analytical procedures adopted will be briefly described in the following paragraphs.

(1) *Chlorinity.* The chloride determination of sea water is one of the most important problems in oceanographical research. The analytical method which is now internationally accepted, is M. Knudsen's system, in which Mohr's argentometry is adopted as a chemical procedure. We can determine the chloride content of sea water very easily, by Knudsen's volumetrical apparatus, the normal sea water supplied from his laboratory, and his hydrographical tables. However, this system has a very serious weakness in its analytical procedure. Mohr's argentometry needs much improvement from the stand point of today's analytical chemistry.<sup>(2)</sup>

There are two large sources of errors in this method of titration, one is due to the strong colloidal nature of the silver chloride precipitate, and the sign of this error tends to be minus while the other is a plus one which comes from the sensibility of the indicator. The latter is always about 0.15%, if the titration is done under a careful control, although it has no effect on the determination of chloride of sea water. On the other hand, the former is always larger and more serious, because its magnitude varies with the analytical conditions, i.e. the concentration of the solution, the rate of stirring, the velocity of the titration, etc. To obtain good results, one must stir the solution just enough during the titration, and one must not cease stirring before ascertaining that the red colour indicating the end point will not disappear again.

Fluorescein or its sodium salt uranin, for which we are indebted to K. Fajans and his collaborator, is a superior adsorption indicator for the chloride determination. Kolthoff<sup>(3)</sup> and Böttiger<sup>(4)</sup> stated that the argentometric titration with this indicator is very accurate when compared with the potentiometric titration. The present author has also verified the superiority of this indicator. He has contrived to use this dyestuff for the chloride determination of sea water, and obtained very satisfactory results. The indicator used is a mixture of 5 c.c. of 0.1% uranin solution and 100 c.c. of 1% starch solution, the starch serving as a protective colloid; and 2 c.c. of this indicator is added to each 15 c.c. of sea water.

Although the new indicator is used instead of potassium chromate, it is not at all necessary to change any other procedure of Knudsen's system. At any rate it is important that this improvement makes the best use of his hydrographical tables and his volumetric apparatus. The mean error of the titration with this new indicator is always under 0.015%, and the time needed for each titration is shorter than one half of that required for Mohr's method. Since the colour change at the end point is quite clear, and owing to the protective colloid, there is no danger of under titration caused by the too early appearance of the end point.

Burettes and pipettes, made according to Knudsen's type by Fujiwara Brothers and Co., were accurately calibrated.

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(2) Lottermoser and Lorenz, *Kolloid-Z.*, **68** (1934), 201.

(3) I.M. Kolthoff and L.H. van Berk, *Z. anal. Chem.*, **70** (1927), 369.

(4) W. Böttiger and K.O. Schmidt, *Z. anorg. allgem. Chem.*, **137** (1924), 246.

(2) *Sodium and potassium.* A 30 c.c. sample of sea water was taken with a pipette; the sulphate ion was removed in the presence of acid with a solution of barium chloride; and the excess of barium chloride with calcium and magnesium was completely precipitated as carbonates and filtered off. After weighing the total chlorides of alkalies as usual, potassium was determined in the form of potassium chloroplatinate.

(3) *Calcium and magnesium.* A 100 c.c. portion of sea water was taken. First, after adding ammonium chloride containing a little ammonia, calcium oxalate was precipitated by boiling with ammonium oxalate. The precipitation was repeated two or three times in order to remove the occluded magnesium as much as possible. Calcium oxalate was filtered off; the precipitation was repeated. Finally it was ignited to calcium oxide. Weighing was done with due care of its hygroscopic nature.

Magnesium was determined with the filtrate from the calcium determination by the magnesium ammonium phosphate method: the precipitation was repeated and then ignited to magnesium pyrophosphate.

(4) *Sulphate.* A 30 c.c. sample was taken; a little hydrochloric acid was added; and the sulphate ion was precipitated by boiling with barium chloride. The precipitate of barium sulphate was allowed to settle down by standing for several hours and was then filtered through the finest filter (Swedish filtering paper No. 00). It was thoroughly washed with hot water until no chloride ion was detectable in the filtrate and then ignited to a constant weight.

(5) *Carbonate.* Although we could obtain undoubtedly a more accurate result by the back titration method for the determination of total carbonate ion in sea water than by direct titration, the latter method was used. A 100 c.c. portion of sea water was titrated with a standard hydrochloric acid solution with methyl orange as the indicator.

(6) *Bromine.* The determinations of this element with several gravimetric methods were tried many times without success owing to the small amount of free chlorine usually produced together with bromine, the values being apt to be too high. The colorimetric method (the method of W. J. Dibdin and L. H. Cooper<sup>(5)</sup>) was finally successful, which, however, is not so accurate as the gravimetric method.

(7) *Strontium and boron.* Strontium and boron in sea water were also determined. The details of the results will be published in the following paper.

**The Results of the Analyses.** Table 2 shows the results of the analyses, in which each element is expressed in number of grams per kilogram of sea water. Strontium is included in the weight of calcium. Likewise, only the chlorinity is mentioned here instead of chlorine and bromine.

**The Composition of the Sea Salt from the Western Pacific.** The percentage composition of oceanic salt, which has been computed from the data of total analysis mentioned above, is shown in Table 3. We can see

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(5) F.D. Snell and C.T. Snell. "Colorimetric Methods of Analysis," 544, New York (1936).

that a very similar result has been obtained in each analysis, regardless of the position of securing the sample. This agreement seems to indicate a homogeneity in the composition of the sea salt of the Western Pacific Ocean.

Table 2.

| No.     | Chlorinity         | SO <sub>4</sub>     | CO <sub>3</sub>     | Ca                  | Mg                  | Na                   | K                   |
|---------|--------------------|---------------------|---------------------|---------------------|---------------------|----------------------|---------------------|
| 31      | 19.29              | 2.6973              | 0.0710              | 0.4276              | 1.3023              | 10.5795              | 0.3787              |
| 32      | 19.27              | 2.6893              | 0.0698              | 0.4295              | 1.2967              | 10.6457              | 0.3693              |
| 36      | 19.22              | 2.6734              | 0.0710              | 0.4253              | 1.2978              | 10.5937              | 0.3663              |
| 38      | 19.17              | 2.6790              | 0.0701              | 0.4234              | 1.2989              | 10.5018              | 0.3875              |
| 40      | 19.13              | 2.6657              | 0.0681              | 0.4225              | 1.2931              | 10.5308              | 0.3682              |
| 42      | 19.10              | 2.6658              | 0.0698              | 0.4263              | 1.2989              | 10.4320              | 0.3706              |
| 45      | 18.91              | 2.6531              | 0.0701              | 0.4218              | 1.2853              | 10.4038              | 0.3232              |
| 56      | 19.15              | 2.6925              | 0.0698              | 0.4264              | 1.2993              | 10.4439              | 0.3752              |
| 57      | 19.23              | —                   | 0.0701              | 0.4249              | 1.2971              | —                    | —                   |
| 61      | 19.19              | —                   | 0.0700              | 0.4266              | 1.2935              | 10.6183              | 0.3605              |
| 62      | 19.17              | 2.6820              | —                   | —                   | —                   | —                    | —                   |
| 64      | 19.15              | 2.6710              | 0.0671              | 0.4271              | 1.2908              | 10.6118              | 0.3272              |
| 67      | 19.22              | 2.6708              | —                   | —                   | —                   | —                    | —                   |
| 70      | 19.22              | 2.6975              | 0.0701              | 0.4235              | 1.2958              | 10.5477              | 0.3826              |
| 73      | 19.28              | —                   | 0.0701              | 0.4228              | 1.3052              | 10.5715              | 0.3760              |
| 75      | 19.18              | 2.6656              | —                   | —                   | —                   | —                    | —                   |
| 76      | 19.13              | —                   | 0.0710              | 0.4272              | 1.2962              | 10.5109              | 0.3731              |
| 81      | 19.23              | 2.6902              | 0.0701              | 0.4269              | 1.3038              | 10.5809              | 0.3682              |
| Average | 19.17 <sub>7</sub> | 2.6780 <sub>5</sub> | 0.0698 <sub>8</sub> | 0.4254 <sub>5</sub> | 1.2969 <sub>8</sub> | 10.5521 <sub>7</sub> | 0.3661 <sub>6</sub> |

Table 3.

| No.     | Cl                                        | Br   | CO <sub>3</sub> | SO <sub>4</sub>                          | Ca                                       | Mg                                       | Na                                        | K                                        |
|---------|-------------------------------------------|------|-----------------|------------------------------------------|------------------------------------------|------------------------------------------|-------------------------------------------|------------------------------------------|
| 31      | 55.38                                     | 0.19 | 0.20            | 7.76                                     | 1.23                                     | 3.74                                     | 30.42                                     | 1.09                                     |
| 32      | 55.28                                     | 0.19 | 0.20            | 7.73                                     | 1.23                                     | 3.73                                     | 30.59                                     | 1.06                                     |
| 36      | 55.33                                     | 0.19 | 0.20            | 7.71                                     | 1.23                                     | 3.74                                     | 30.54                                     | 1.06                                     |
| 38      | 55.38                                     | 0.19 | 0.20            | 7.75                                     | 1.23                                     | 3.76                                     | 30.38                                     | 1.12                                     |
| 40      | 55.36                                     | 0.19 | 0.20            | 7.72                                     | 1.22                                     | 3.75                                     | 30.50                                     | 1.07                                     |
| 42      | 55.44                                     | 0.19 | 0.20            | 7.75                                     | 1.24                                     | 3.78                                     | 30.33                                     | 1.08                                     |
| 45      | 55.37                                     | 0.19 | 0.20            | 7.78                                     | 1.24                                     | 3.77                                     | 30.51                                     | 0.95                                     |
| 56      | 55.44                                     | 0.19 | 0.20            | 7.81                                     | 1.24                                     | 3.77                                     | 30.28                                     | 1.09                                     |
| 64      | 55.29                                     | 0.19 | 0.20            | 7.73                                     | 1.23                                     | 3.73                                     | 30.69                                     | 0.95                                     |
| 70      | 55.35                                     | 0.19 | 0.20            | 7.78                                     | 1.22                                     | 3.74                                     | 30.42                                     | 1.10                                     |
| 81      | 55.33                                     | 0.19 | 0.20            | 7.75                                     | 1.23                                     | 3.76                                     | 30.49                                     | 1.06                                     |
| Average | 55.35 <sub>9</sub><br>± 0.03 <sub>3</sub> | 0.19 | 0.20            | 7.75 <sub>2</sub><br>± 0.02 <sub>2</sub> | 1.23 <sub>1</sub><br>± 0.00 <sub>5</sub> | 3.75 <sub>2</sub><br>± 0.01 <sub>5</sub> | 30.46 <sub>8</sub><br>± 0.09 <sub>3</sub> | 1.05 <sub>7</sub><br>± 0.03 <sub>7</sub> |

**The Comparison of Compositions between the World's Average and the Western Pacific Ocean.** From these results, we can obtain the average composition of the salt of the Western Pacific, taking into consideration the content of bromine, strontium and boric acid. In Table 4, the total salt composition of the Western Pacific is compared with those of the world's mean. For the average composition of the world, the values

calculated by T. G. Thompson<sup>(6)</sup> and by H. Wattenberg<sup>(7)</sup> have been adopted, and also the analyses of W. Dittmar<sup>(8)</sup> have been used as a reference. As seen from this table, the differences in the compositions between the world's average and the Western Pacific are very small, except that the values of sodium and potassium are a little lower, while on the contrary those of chloride and magnesium are but slightly higher, than the world's average. This tendency will become much clearer, when the amount of each component is represented as the number of mols per kilo-gram of water, assuming that the chlorinities are the same. In Table 5 the number of each element has been calculated when the chlorinity is  $\text{Cl} = 19.374\%$

Table 4. The Percentage Compositions of the Oceanic Salt.

|                    | Thompson | Wattenberg | Dittmar | Average | The Western Pacific |
|--------------------|----------|------------|---------|---------|---------------------|
| Na                 | 30.60    | 30.43      | 30.59   | 30.52   | 30.47               |
| Mg                 | 3.70     | 3.72       | 3.73    | 3.73    | 3.74                |
| Ca                 | 1.19     | 1.19       | 1.20    | 1.19    | 1.19                |
| Sr                 | 0.04     | 0.04       | —       | 0.04    | 0.04                |
| K                  | 1.09     | 1.11       | 1.11    | 1.10    | 1.06                |
| Cl                 | 55.18    | 55.14      | 55.29   | 55.17   | 55.31               |
| SO <sub>4</sub>    | 7.72     | 7.70       | 7.69    | 7.70    | 7.73                |
| CO <sub>3</sub>    | 0.30     | 0.40       | 0.21    | 0.30    | 0.20                |
| Br                 | 0.19     | 0.19       | 0.19    | 0.19    | 0.19                |
| B(OH) <sub>3</sub> | —        | 0.08       | —       | 0.08    | 0.08                |

Table 5. The Number of Mols per kilo-gram Water.  $\text{Cl} = 19.374\%$ .

|                    | Thompson | Wattenberg | Dittmar | Average | The Western Pacific |
|--------------------|----------|------------|---------|---------|---------------------|
| Na                 | 0.4662   | 0.4638     | 0.4652  | 0.4651  | 0.4634              |
| K                  | 0.0098   | 0.0099     | 0.0093  | 0.0097  | 0.0095              |
| Mg                 | 0.0533   | 0.0535     | 0.0534  | 0.0534  | 0.0539              |
| Ca                 | 0.0104   | 0.0104     | 0.0105  | 0.0104  | 0.0104              |
| Sr                 | —        | 0.00015    | —       | 0.00015 | 0.00017             |
| Cl                 | 0.5454   | 0.5454     | 0.5454  | 0.5454  | 0.5454              |
| Br                 | 0.0008   | 0.00083    | 0.00083 | 0.0008  | 0.0008              |
| SO <sub>4</sub>    | 0.0281   | 0.0281     | 0.0280  | 0.0281  | 0.0282              |
| CO <sub>3</sub>    | 0.0017   | 0.0023     | 0.0012  | 0.0017  | 0.0012              |
| B(OH) <sub>3</sub> | 0.00045  | 0.00045    | —       | 0.00045 | 0.00043             |

In according with the custom of oceanography, the ratio of the number of the promilles of each element to the chlorinity has been calculated and compared in a like manner with the world's average (Table 6). Since the ratio of the chlorinity to the salinity is almost constant, the result of the comparison is naturally the same as that of Table 5.

(6) T.G. Thompson, "Bulletin of the National Research Council, No. 85, Physics of the Earth. V. Oceanography," 69, New York (1932).

(7) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

(8) H.W. Harvey, "The Chemistry and Physics of Sea Water," 36, Cambridge (1928).

Table 6.

|                 | Thompson | Wattenberg | Dittmar | Average | The Western Pacific    |
|-----------------|----------|------------|---------|---------|------------------------|
| Na              | 0.55342  | 0.55105    | 0.55326 | 0.55258 | $0.54974 \pm 0.001975$ |
| K               | 0.01971  | 0.02000    | 0.02007 | 0.01993 | $0.01909 \pm 0.000620$ |
| Mg              | 0.06697  | 0.06746    | 0.06728 | 0.06719 | $0.06736 \pm 0.000192$ |
| Ca              | 0.02152  | 0.02157    | 0.02170 | 0.02159 | $0.02155 \pm 0.000067$ |
| SO <sub>4</sub> | 0.13962  | 0.13947    | 0.13908 | 0.13939 | $0.13967 \pm 0.000375$ |

**A Comparison between the Western Pacific and the Northeastern Pacific.** It is interesting to compare the salt compositions of the western and the northeastern parts of the Pacific Ocean. T. G. Thompson and his collaborators<sup>(9)</sup> have determined very precisely the salt compositions of the opposite side of the Pacific Ocean. The comparison of the chlorinity ratios on both sides of the ocean is shown in Table 7. It is quite noteworthy that there is an astonishing agreement between the analytical results of the west and the northeast. This agreement is by no means accidental, because the mean deviation of the analytical results are very small as shown in Table 3.

In spite of this good unity, however, we have to acknowledge the small, but significant discrepancy in the ratios of magnesium to the chlorinity. It will be investigated in the near future whether this discrepancy is substantial or not.

Table 7. A Comparison of Chlorinity Ratios of Elements in the Northeastern and the Western Pacific Ocean.

|                 | Northeast | West    |
|-----------------|-----------|---------|
| Na              | 0.5495    | 0.5497  |
| K               | 0.0191    | 0.0191  |
| Mg              | 0.0669    | 0.0676  |
| Ca              | 0.02150   | 0.02155 |
| SO <sub>4</sub> | 0.1396    | 0.1397  |

### Summary.

(1) The major constituents of sea water from the Western Pacific Ocean near Japan have been quantitatively determined. The analytical results are as follows: the difference in the compositions between the world's average and the Western Pacific is very small, except that the values of sodium and potassium are a little lower, while those of chloride and magnesium are but slightly higher, in the latter than in the former.

(2) It is quite noteworthy that there is an astonishing agreement between the analytical results of the west and the northeast side of the Pacific Ocean.

(9) *Loc. cit.*, p. 94-203.



(3) A new indicator has been used for the determination of chlorinity; that is a mixed solution of fluorescein and starch. The superiority of this indicator has been briefly discussed.

In conclusion, the author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

*The Central Meteorological Observatory  
of Japan, Tokyo,*

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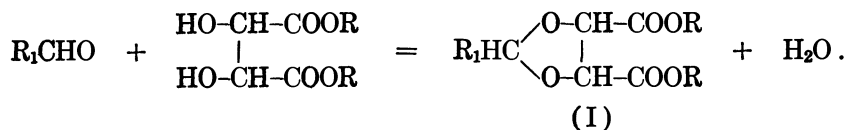
## Synthesis of Cyclic Derivatives of Tartaric Acid by Condensing Alkyl *d*-Tartrates with Aromatic Aldehydes. (Optical Activity and Chemical Structure in Tartaric Acid. VI.\*)

By Yojiro TSUZUKI.

(Received January 10, 1939.)

In a paper of a series of synthetic studies on the cyclic derivatives of tartaric acid, the author has noticed that a substituent exerts a certain remarkable effect due to the position on the optical activity of the compound, and has pointed out that this effect is closely related with the phenomena of light-absorption, so that it must be considered as a definitely electronic effect.<sup>(1)</sup>

The purpose of the present work is to prepare cyclic compounds of similar structure by condensing alkyl *d*-tartrates with various aromatic aldehydes, in order to investigate the electronic effect of a substituent on optical activity by observing how the position and the chemical nature of a substituent in the aromatic nucleus of the resulting compounds affect the optical activity.

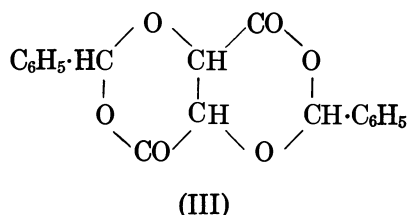
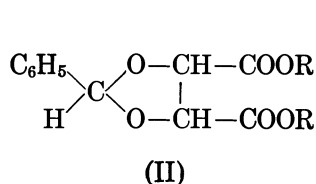


The condensation of tartaric acid and its esters with benzaldehyde has already been reported by several authors, and the products were used for the study of the optical activity of tartaric acid, since they are strongly

\* Paper V: this Bulletin, **14** (1939), 19.

(1) Y. Tsuzuki, this Bulletin, **12** (1937), 487.

lævo-rotatory and their behaviours with respect to the optical activity are simple. Thus B. Jones<sup>(2)</sup> obtained methyl and ethyl benzylidene-tartrates (II, R = CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>) by condensing respective tartaric esters with benzaldehyde by means of phosphorus pentoxide as dehydrating agent, and showed that their rotatory dispersions are simple. Dibenzylidene-tartrate (III) was obtained by van Ekenstein and Blanksma<sup>(3)</sup> and its rotatory dispersion was shown by Austin<sup>(4)</sup> to be also simple. Various derivatives of this compound were prepared by J. W. Pette<sup>(5)</sup> from tartaric acid and aldehydes by the action of phosphorus pentoxide.



The author has carried out the condensations of ethyl *d*-tartrate with *o*-, *m*- and *p*-nitrobenzaldehydes, *o*- and *m*-hydroxybenzaldehydes, *p*-methoxybenzaldehyde, *o*-, *m*- and *p*-chlorobenzaldehydes, piperonal, and with cinnamic aldehyde, and further the condensation of benzaldehyde with propyl, butyl and benzyl *d*-tartrates. Phosphorus pentoxide was always used as the condensing agent with great advantage.

The general method of preparation is analogous to that of the former cases, but the temperature of the reaction must be suitably regulated according to the stability of the aldehyde. In the cases of chlorobenzaldehydes, the temperature is the highest, while in the cases of hydroxybenzaldehydes it is far lower and in the case of cinnamic aldehyde it is the lowest.

Many of the condensation products are solids of low melting points. The optical rotatory power was observed in ethyl alcohol, benzene, and cyclohexane. The magnitudes of their optical activities are found various. Some of them are strongly negative, while some others less negative, and even positive. Discussion will be made on this subject in the next paper.

**Ethyl *o*-Nitrobenzylidene-*d*-tartrate** (I, R<sub>1</sub> = *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>, R = C<sub>2</sub>H<sub>5</sub>). To a solution of 7 g. *o*-nitrobenzaldehyde (Kahlbaum) and 10 g. ethyl *d*-tartrate was added 7 g. phosphorus pentoxide in portions at 80–100° in the course of 40 minutes, and the mixture was kept at this temperature for further 15 minutes. The reaction mixture was poured into 50 c.c. water, when the condensation product appeared as a yellow oil, which was solidified on repeatedly rubbing it in fresh water. It was purified by recrystallisation from 80% ethyl alcohol. Pale yellow needles. Yield

(2) B. Jones, *J. Chem. Soc.*, **1933**, 788. H. O. L. Fischer and H. Appel used zinc chloride as the dehydrating agent in preparing the methyl ester, *Helv. Chim. Acta*, **17** (1934), 1581.

(3) *Rec. trav. chim.*, **25** (1906), 162.

(4) T. M. Lowry, "Optical Rotatory Power," 290, London (1935).

(5) J. W. Pette, *Rec. trav. chim.*, **53** (1934), 967.

2.3 g. Melting point  $60^{\circ}$ .  $[\alpha]_D^{20} +40.3^{\circ}$ ,  $[M]_D^{20} +136.7^{\circ}$  (in ethyl alcohol, 3.618%).  $[\alpha]_D^{20} +34.3^{\circ}$ ,  $[M]_D^{20} +116.3^{\circ}$  (in benzene, 4.864%).  $[\alpha]_D^{20} +6.9^{\circ}$ ,  $[M]_D^{20} +23.4^{\circ}$  (in cyclohexane, 0.6726%). Found: N, 4.21. Calc. for  $C_{15}H_{17}NO_8$  (339.14): N, 4.13%.

**Ethyl *m*-Nitrobenzylidene-*d*-tartrate.** To a mixture of 5 g. *m*-nitrobenzaldehyde (Kahlbaum) and 7 g. ethyl *d*-tartrate was added 8 g. phosphorus pentoxide in portions at  $115$ – $125^{\circ}$  in the course of 40 minutes and the heating of the mixture was continued at that temperature for 30 minutes. The brown liquid was poured into cold water. The separating brown oil was solidified by repeatedly rubbing in cold water. It was purified by recrystallising four times from absolute alcohol. Pale yellow needles. Melting point  $43.5$ – $44^{\circ}$ . Yield 3 g.  $[\alpha]_D^{20} -35.65^{\circ}$ ,  $[M]_D^{20} -120.9^{\circ}$  (in alcohol, 3.295%).  $[\alpha]_D^{20} -37.35^{\circ}$ ,  $[M]_D^{20} -126.7^{\circ}$  (in benzene, 7.638%).  $[\alpha]_D^{20} -26.1^{\circ}$ ,  $[M]_D^{20} -88.3^{\circ}$  (in cyclohexane, 1%). Found: N, 4.37. Calc. for  $C_{15}H_{17}NO_8$  (339.14): N, 4.13%.

**Ethyl *p*-Nitrobenzylidene-*d*-tartrate.** Phosphorus pentoxide (8 g.) was added in portions to a mixture of 6 g. *p*-nitrobenzaldehyde (Kahlbaum) and 8.5 g. ethyl *d*-tartrate at  $100$ – $108^{\circ}$  in the course of 25 minutes, and heating was continued for 15 minutes. Yield 4 g. Pale yellow needles (from absolute alcohol) melting at  $59$ – $59.5^{\circ}$ .  $[\alpha]_D^{20} -22.2^{\circ}$ ,  $[M]_D^{20} -75.2^{\circ}$  (in alcohol, 2.113%).  $[\alpha]_D^{20} -25.5^{\circ}$ ,  $[M]_D^{20} -86.5^{\circ}$  (in benzene, 6.136%).  $[\alpha]_D^{20} -15.4^{\circ}$ ,  $[M]_D^{20} -52.3^{\circ}$  (in cyclohexane, 0.77%). Found: N, 4.27. Calc. for  $C_{15}H_{17}NO_8$  (339.14): N, 4.13%.

**Ethyl *o*-Hydroxybenzylidene-*d*-tartrate** (I,  $R_1 = o\text{-OH}\cdot C_6H_4$ ,  $R = C_2H_5$ ). To a mixture of 5 g. salicylaldehyde (Takeda) and 8.5 g. ethyl *d*-tartrate was added 7 g. phosphorus pentoxide in portions at  $40$ – $50^{\circ}$  in the course of 30 minutes. The reaction mixture was poured into cold water. The separating oil resisted solidification. Purification was done by precipitating four times from ethyl alcoholic solution with water, and washing with petroleum ether. Colourless crystals. Yield 2 g. Melting point  $59^{\circ}$  after sintering.  $[\alpha]_D^{20} -35.8^{\circ}$ ,  $[M]_D^{20} -111.3^{\circ}$  (in alcohol, 1.6%).  $[\alpha]_D^{20} -55.1^{\circ}$ ,  $[M]_D^{20} -170.8^{\circ}$  (in benzene, 3%).  $[\alpha]_D^{20} -53.7^{\circ}$ ,  $[M]_D^{20} -166^{\circ}$  (in cyclohexane, 0.4%). Saponification equivalent: 154.4. Calc. for  $C_{15}H_{18}O_7$ : 155.07.

**Ethyl *m*-Hydroxybenzylidene-*d*-tartrate.** To a mixture of 4.7 g. *m*-hydroxybenzaldehyde (Th. Schuchardt) and 8 g. ethyl *d*-tartrate was added 8 g. phosphorus pentoxide in portions at  $70$ – $80^{\circ}$  in the course of 30 minutes. The reaction product was poured into water, when a brown oil separated out. The oil was purified by precipitating from water-alcohol three times and finally by distilling in vacuum. Colourless crystals. Melting point  $37$ – $38.5^{\circ}$ . Boiling point  $207^{\circ}$  (0.5 mm.). Difficultly soluble in cyclohexane.  $[\alpha]_D^{20} -32.5^{\circ}$ ,  $[M]_D^{20} -101^{\circ}$  (in alcohol, 5.5%).  $[\alpha]_D^{20} -26.1^{\circ}$ ,  $[M]_D^{20} -80.9^{\circ}$  (in benzene, 1.138%). Saponification equivalent: 155.1. Calc. for  $C_{15}H_{18}O_7$ : 155.07.

**Ethyl *p*-Methoxybenzylidene-*d*-tartrate** (I,  $R_1 = p\text{-CH}_3O\cdot C_6H_4$ ,  $R = C_2H_5$ ). To a mixture of 7 g. aubepine (Merck) and 10 g. ethyl *d*-tartrate

was added 10 g. phosphorus pentoxide at 50–60° in the course of 30 minutes and the reaction mixture was heated at 65° for one hour. The ethereal extract of the reaction product, washed repeatedly with a concentrated solution of  $\text{KBO}_2$ , dried over anhydrous sodium sulphate, and fractionated in vacuum, gave 5 g. pale yellow viscous liquid boiling at 183° (0.3 mm.).  $[\alpha]_D^{20} -27.86^\circ$ ,  $[\text{M}]_D^{20} -90.3^\circ$  (in alcohol, 3.604%).  $[\alpha]_D^{20} -26.87^\circ$ ,  $[\text{M}]_D^{20} -87.09^\circ$  (in benzene, 6.570%).  $[\alpha]_D^{20} -18.3^\circ$ ,  $[\text{M}]_D^{20} -59.4^\circ$  (in cyclohexane, 1.364%). Saponification equivalent: 161.0. Calc. for  $\text{C}_{16}\text{H}_{20}\text{O}_7$ : 162.08.

**Ethyl *o*-Chlorobenzylidene-*d*-tartrate** (I,  $\text{R}_1 = o\text{-Cl-C}_6\text{H}_4$ ,  $\text{R} = \text{C}_2\text{H}_5$ ). To a solution of 5.5 g. *o*-chlorobenzaldehyde (Takeda) and 8 g. ethyl *d*-tartrate was added 8 g. phosphorus pentoxide at 100–120° in the course of 40 minutes. The reaction product was poured into cold water. The separating oil, reprecipitated twice from ethyl alcohol with water, suddenly solidified to colourless crystals. Melting point 36–36.5°. Yield 6 g.  $[\alpha]_D^{20} -15.9^\circ$ ,  $[\text{M}]_D^{20} -52.2^\circ$  (in alcohol, 4.164%).  $[\alpha]_D^{20} -28.6^\circ$ ,  $[\text{M}]_D^{20} -94.0^\circ$  (in benzene, 8.158%).  $[\alpha]_D^{20} -22.1^\circ$ ,  $[\text{M}]_D^{20} -72.6^\circ$  (in cyclohexane, 1.358%). Found: Cl, 10.41 (Piria-Schiff). Calc. for  $\text{C}_{15}\text{H}_{17}\text{O}_6\text{Cl}$  (328.60): Cl, 10.79%.

**Ethyl *m*-Chlorobenzylidene-*d*-tartrate.** To a mixture of 3.05 g. *m*-chlorobenzaldehyde<sup>(6)</sup> and 4.50 g. ethyl *d*-tartrate was added 5 g. phosphorus pentoxide at 100° in the course of 40 minutes and the heating was continued for 20 minutes. The liquid was more easily coloured than in the case of the *o*-compound. The reaction product, poured into water, reprecipitated twice from water-alcohol, and finally fractionated in vacuum, gave 3 g. colourless crystals. Boiling point 153° (1 mm.). Melting point 29–30°.  $[\alpha]_D^{20} -31.44^\circ$ ,  $[\text{M}]_D^{20} -103.3^\circ$  (in alcohol, 3.455%).  $[\alpha]_D^{20} -30.16^\circ$ ,  $[\text{M}]_D^{20} -99.10^\circ$  (in benzene, 2.171%).  $[\alpha]_D^{20} -18.47^\circ$ ,  $[\text{M}]_D^{20} -60.7^\circ$  (in cyclohexane, 1.3205%). Found: Cl, 10.64 (Piria-Schiff). Calc. for  $\text{C}_{15}\text{H}_{17}\text{O}_6\text{Cl}$  (328.60): Cl, 10.79%.

**Ethyl *p*-Chlorobenzylidene-*d*-tartrate.** To a mixture of 3 g. *p*-chlorobenzaldehyde<sup>(7)</sup> and 6 g. ethyl *d*-tartrate was added 5 g. phosphorus pentoxide at 110–120° in the course of 40 minutes. The phosphoric acid was coloured reddish, but the liquid only faintly yellow, and the heating was continued for further 30 minutes. The reaction product was extracted with ether. The ethereal solution, shaken thrice with concentrated  $\text{KBO}_2$ , dried over sodium sulphate, and fractionated in vacuum, gave a viscous pale yellowish liquid (4 g.) boiling at 180° (0.5 mm.).  $[\alpha]_D^{20} -28.1^\circ$ ,  $[\text{M}]_D^{20} -92.3^\circ$  (in alcohol, 1.496%).  $[\alpha]_D^{20} -26.8^\circ$ ,  $[\text{M}]_D^{20} -88.2^\circ$  (in benzene, 3.955%).  $[\alpha]_D^{20} -14.7^\circ$ ,  $[\text{M}]_D^{20} -48.3^\circ$  (in cyclohexane, 1.302%). Found: Cl, 10.42 (Piria-Schiff). Calc. for  $\text{C}_{15}\text{H}_{17}\text{O}_6\text{Cl}$  (328.60): Cl, 10.79%.

**Ethyl Cinnamylidene-*d*-tartrate** (I,  $\text{R}_1 = \text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}$ ,  $\text{R} = \text{C}_2\text{H}_5$ ). To a solution of 5.12 g. cinnamic aldehyde (Shuzui) and 8 g. ethyl *d*-

(6) Prepared from *m*-nitrobenzaldehyde (Kahlbaum), b.p. 105° (25 mm.), "Organic Syntheses," **13**, 28.

(7) Prepared from *p*-chlorotoluene, b.p. 98° (18 mm.), m.p. 47°, "Organic Syntheses," **12**, 12.

tartrate was added 8 g. phosphorus pentoxide in portions with gentle warming. The brownish-coloured liquid was poured into water. The separating oil was reprecipitated twice from dilute alcohol, solidified, and recrystallised from petroleum ether. Colourless crystals melting at  $54.4^\circ$ . Yield 1.5 g.  $[\alpha]_D^{20} -3.70^\circ$ ,  $[M]_D^{20} -11.9^\circ$  (in alcohol, 4.046%).  $[\alpha]_D^{20} -21.0^\circ$ ,  $[M]_D^{20} -67.3^\circ$  (in benzene, 4.348%).  $[\alpha]_D^{20} +12.5^\circ$ ,  $[M]_D^{20} +40^\circ$  (in cyclohexane, 0.697%). Saponification equivalent: 161.8. Calc. for  $C_{17}H_{20}O_6$ : 160.08.

**Ethyl 3,4-Methylenedioxybenzylidene-*d*-tartrate** (I,  $R_1 = \text{O}-\text{CH}_2-\text{O}-$ ,  $R = C_2H_5$ ). To a mixture of 5.1 g. piperonal (Merck) and 7 g. ethyl *d*-tartrate was added 6 g. phosphorus pentoxide in portions at  $60^\circ$  in the course of 30 minutes. The deeply coloured liquid was poured into water and repeatedly rubbed in water. The solidified product was recrystallised from ethyl alcohol four times. Colourless silky needles. Yield 1 g. Melting point  $40.5-41.5^\circ$ .  $[\alpha]_D^{20} -32.6^\circ$ ,  $[M]_D^{20} -110^\circ$  (in alcohol, 2.715%).  $[\alpha]_D^{20} -31.0^\circ$ ,  $[M]_D^{20} -105^\circ$  (in benzene, 4.010%).  $[\alpha]_D^{20} -18.9^\circ$ ,  $[M]_D^{20} -63.8^\circ$  (in cyclohexane, 0.958%). Saponification equivalent: 169.6. Calc. for  $C_{16}H_{18}O_8$ : 169.07.

**Propyl Benzylidene-*d*-tartrate** (I,  $R_1 = C_6H_5$ ,  $R = C_3H_7$ ). To a solution of dipropyl *d*-tartrate (16 g.) and freshly distilled benzaldehyde (15 g.) was added 15 g. phosphorus pentoxide in portions at  $60-70^\circ$ . The liquid was coloured deeply brown. The product was extracted with ether. The ethereal solution was washed by shaking with  $KBO_2$  solution five times. After evaporating off ether and benzaldehyde, the residue was fractionated in vacuum. This process of purification was once repeated. Colourless liquid boiling at  $169^\circ$  (0.3 mm.). Yield 9 g.  $d_4^{20}$  1.1333.  $n_D^{20}$  1.4882,  $M_D$  81.93 (81.50).  $[\alpha]_D^{20} -35.87^\circ$ ,  $[M]_D^{20} -115.6^\circ$  (homog.). Found: C, 63.50; H, 6.96. Calc. for  $C_{17}H_{22}O_6$  (322.18): C, 63.32; H, 6.88%.

**Butyl Benzylidene-*d*-tartrate** (I,  $R_1 = C_6H_5$ ,  $R = C_4H_9$ ). To a solution of dibutyl *d*-tartrate (15 g.) and freshly distilled benzaldehyde (8 g.) was added 10 g. phosphorus pentoxide in portions at  $60^\circ$  in the course of 30 minutes, and thereafter heated at  $60-70^\circ$  further for 30 minutes. The liquid mixture was deeply coloured. The ethereal extract was shaken with  $N/2 KBO_2$  four times and once with water, and dried over sodium sulphate. After evaporating off ether, the residue was fractionally distilled. Almost colourless liquid. Yield 9 g. Purification is effected by shaking the ethereal solution with  $N/2 KBO_2$  several times, drying over sodium sulphate, and by fractional distillation in vacuum. This process was once repeated. Colourless liquid. Boiling point  $189-190^\circ$  (0.2 mm.).  $d_4^{20}$  1.1004,  $d_4^{25}$  1.0974.  $n_D^{20}$  1.4830,  $M_D$  91.14 (90.74).  $[\alpha]_D^{20} -31.22^\circ$ ,  $[M]_D^{20} -109.3^\circ$  (homog.). Found: C, 65.08; H, 7.24. Calc. for  $C_{19}H_{26}O_6$  (350.21): C, 65.10; H, 7.48%.

**Benzyl Benzylidene-*d*-tartrate** (I,  $R_1 = C_6H_5$ ,  $R = C_6H_5 \cdot CH_2$ ). To a mixture of benzyl *d*-tartrate (10 g.) and freshly distilled benzaldehyde

(3.22 g.) was added 7 g. phosphorus pentoxide in portions at 70° in the course of 60 minutes. The resulted fatty mass was poured into water, and the separating solid was recrystallised from absolute alcohol three times. White crystals. Yield 4 g. Melting point 86°.  $[\alpha]_D^{20} -39.7^\circ$ ,  $[M]_D^{20} -166^\circ$  (in alcohol, 1.356%).  $[\alpha]_D^{20} -39.38^\circ$ ,  $[M]_D^{20} -164.8^\circ$  (in benzene, 12.18%). Found: C, 71.64; H, 5.30. Calc. for  $C_{25}H_{22}O_6$  (418.18): C, 71.74; H, 5.30%.

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## Austauschreaktion der Wasserstoffatome zwischen Nitrophenol und Wasser. III. Aktivierungsenergie.<sup>(1)</sup>

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(Eingegangen am 27. Januar 1939.)

**Inhaltsübersicht.** Die Austauschreaktion der Kernwasserstoffatome des *m*- und *p*-Nitrophenols in alkalischer Lösung wird bei verschiedenen Temperaturen zwischen 100° und 139°C. untersucht. Die dabei gefundenen Werte der (scheinbaren) mittleren Geschwindigkeitskonstante  $\bar{k}$  in 1 N KOH-Lösung kann durch die Ausdrücke wiedergegeben werden:

$$\log \bar{k}(\text{meta}) = (9.3 \pm 0.7) - \frac{29,000 \pm 1,200}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1},$$

$$\log \bar{k}(\text{para}) = (9.0 \pm 0.6) - \frac{28,400 \pm 1,000}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1}.$$

Für *p*-Nitrophenol gilt fast dieselbe Aktivierungsenergie wie in 1 N KOH-Lösung auch in 3 N KOH-Lösung. Rechnet man die oben angegebene direkt experimentell gefundene (scheinbare) Geschwindigkeitskonstante  $\bar{k}$  in die (wahre) Geschwindigkeitskonstante  $\bar{k}_0$  für die grundlegende Reaktion zwischen Phenolationen und neutralen Phenolmolekülen um, dann wird sie durch die Ausdrücke wiedergegeben:

$$\bar{k}_0(\text{meta}) = 10^{11.3} e^{-\frac{29,000}{RT}} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1},$$

$$\bar{k}_0(\text{para}) = 10^{11.0} e^{-\frac{28,400}{RT}} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1}.$$

Die so gefundenen Werte der Aktivierungsenergie für die Nitrophenole werden mit dem früher gefundenen Wert (24,800 cal.) für das unsubstituierte Phenol verglichen und der Einfluss der Nitrogruppe auf die Austauschreaktion der Kernwasserstoffatome wird diskutiert.

**Einleitung.** Wir kamen beim letzten Versuch (vgl. II. Mittl.) zu dem Schluss, dass die Austauschreaktion der Kernwasserstoffatome des Nitrophenols in alkalischer Lösung hauptsächlich zwischen Phenolationen

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(1) I. Mittl.: dies Bulletin, **13** (1938), 318; II. Mittl.: *ibid.*, **13** (1938), 595 und 631.



und neutralen Phenolmolekülen stattfindet, wie das folgende Schema zeigt:



Daranschliessend untersuchten wir mit Hilfe derselben Versuchsmethode wie beim Nitrophenol die Austauschreaktion des unsubstituierten Phenols in alkalischer Lösung und kamen zu dem Ergebnis, dass die mittlere Geschwindigkeitskonstante  $\bar{k}_0$  für die der Reaktion (1) entsprechende grundlegende Reaktion zwischen unsubstituierten Phenolationen und neutralen Phenolmolekülen durch den Ausdruck (2) richtig wiedergegeben werden kann:<sup>(2)</sup>

$$\bar{k}_0(\text{Phenol}) = 10^{10.8} e^{-\frac{24,800}{RT}} (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1} \quad (2).$$

Es liegt deshalb nahe, die Aktivierungsenergie der Reaktion (1) für die isomerischen Arten der Nitrophenole zu bestimmen und diese mit dem früher bestimmten Wert für das unsubstituierte Phenol zu vergleichen.

**Versuch.** Aus dem oben erwähnten Grund wird zunächst das Austauschäquivalent  $na$  des *m*- und *p*-Nitrophenols<sup>(3)</sup> in der mit KOH versetzten Lösung mit Hilfe genau derselben Versuchsmethode, wie die in II. Mittl. beschrieben wurde, bei verschiedenen Temperaturen und verschiedenen Versuchsdauern bestimmt. Die dabei benutzte Versuchstemperatur ist 100°. 110° (bzw. 111°), 131° und 139°C. und die (analytische) Konzentration von KOH beträgt beim *m*-Nitrophenol 1 N. Dagegen werden beim *p*-Nitrophenol zwei verschiedene Stärkegrade der Lösung benutzt, nämlich 1 N und 3 N. Unter Verwendung der auf diese Weise bei verschiedenen Versuchsdauern bestimmten Werte des Austauschäquivalents  $na$  wird die Quantität  $(-X \log Y)$  mit Hilfe der Gl. (3) berechnet (vgl. Gl. (16) in I. Mittl.) :

$$X = \frac{V}{(n_2 M_{\text{ph}} + \frac{a_1}{a_2} M_{\text{ph}} + \frac{2}{a_2} M_{\text{w}})},$$

$$Y = \frac{1 - \frac{na - n_1 a_1}{n_2 a_2}}{1 + \frac{na - n_1 a_1}{\frac{2M_{\text{w}}}{M_{\text{ph}}} + n_1 a_1}} \quad (3).$$

In diesen Gl. bedeutet  $V$  das Volumen der Lösung,  $M_{\text{ph}}$  und  $M_{\text{w}}$  resp. die Molzahl des zum Versuch benutzten Nitrophenols und des schweren Wassers,  $a_1$  den Verteilungsquotient des Hydroxylwasserstoffs,  $a_2$  den des Kernwasserstoffs,  $n_1$  die Anzahl der Hydroxylwasserstoffatome und  $n_2$  die der (in der „zweiten“ Stufe der Reaktion) austauschbaren Kern-

(2) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 631.

(3) *o*-Nitrophenol wurde nicht untersucht, weil es bei allen untersuchten Temperaturen im Wasser nicht genügend leicht löslich ist.

wasserstoffatome in einem Nitrophenolmolekül. Deshalb wird bei der praktischen Durchführung der Berechnung  $\alpha_1 = 1.08$ ,  $\alpha_2 = 0.90$ ,  $n_1 = 1$ ,  $n_2 = 2$  für *p*- und 3 für *m*-Nitrophenol gesetzt und  $V$  mit Hilfe des in Tabelle 1 in II. Mittl. angegebenen spezifischen Volumens der Lösung rechnerisch ermittelt. Die mittlere Geschwindigkeitskonstante  $\bar{k}$  der Austauschreaktion der Kernwasserstoffatome bei der betreffenden Temperatur wird dann gemäss der folgenden Beziehung (4) zwischen der Quantität ( $-X \log Y$ ) und der Versuchsdauer  $t$  graphisch bestimmt (vgl. Gl. (15) in I. Mittl.):

$$-X \log Y = \frac{\bar{k}}{2.303} t \quad (4).$$

Die so gewonnenen Versuchsergebnisse sind in Tabellen 1 bis 3 zusammengestellt.

Tabelle 1. *m*-Nitrophenol in 1 N KOH-Lösung.

| Versuchstemp. °C. | Versuchsdauer in Stdn. | $M_{ph}$ | $M_w$  | $nx$ | $-X \log Y$ | $\bar{k}/2.303$       |
|-------------------|------------------------|----------|--------|------|-------------|-----------------------|
| 100               | 50                     | 0.0219   | 0.0617 | 1.45 | 0.00139     | 0.0000323             |
|                   | 150                    | 0.0217   | 0.0550 | 2.34 | 0.00562     |                       |
|                   | 260                    | 0.0208   | 0.0549 | 2.66 | 0.00748     |                       |
| 110               | 3                      | 0.0216   | 0.0556 | 1.93 | 0.00035     | 0.000066<br>~0.000080 |
|                   | 80                     | 0.0218   | 0.0557 | 2.47 | 0.00636     |                       |
|                   | 150                    | 0.0217   | 0.0556 | 2.95 | 0.00982     |                       |
| 131               | 3                      | 0.0218   | 0.0552 | 1.68 | 0.00242     | 0.00063<br>~0.00068   |
|                   | 5                      | 0.0215   | 0.0561 | 1.90 | 0.00347     |                       |
|                   | 8                      | 0.0221   | 0.0554 | 2.22 | 0.00511     |                       |
| 139               | 2                      | 0.0220   | 0.0540 | 1.89 | 0.00352     | 0.00095<br>~0.00105   |
|                   | 5                      | 0.0216   | 0.0559 | 2.30 | 0.00558     |                       |
|                   | 9                      | 0.0218   | 0.0548 | 2.70 | 0.00820     |                       |

Tabelle 2. *p*-Nitrophenol in 1 N KOH-Lösung.

| Versuchstemp. °C. | Versuchsdauer in Stdn. | $M_{ph}$ | $M_w$  | $nx$ | $-X \log Y$ | $\bar{k}/2.303$       |
|-------------------|------------------------|----------|--------|------|-------------|-----------------------|
| 100               | 2                      | 0.0411   | 0.114  | 1.16 | 0.00046     | 0.000030<br>~0.000037 |
|                   | 50                     | 0.0216   | 0.0555 | 1.31 | 0.00138     |                       |
|                   | 150                    | 0.0222   | 0.0553 | 1.96 | 0.00617     |                       |
|                   | 260                    | 0.0188   | 0.0850 | 2.52 | 0.00763     |                       |
| 110               | 30                     | 0.0219   | 0.0557 | 1.52 | 0.00276     | 0.000087              |
|                   | 80                     | 0.0222   | 0.0559 | 2.06 | 0.00723     |                       |
|                   | 147                    | 0.0219   | 0.0540 | 2.46 | 0.0127      |                       |
| 131               | 3                      | 0.0220   | 0.0551 | 1.43 | 0.00213     | 0.00051<br>~0.00055   |
|                   | 5                      | 0.0216   | 0.0559 | 1.49 | 0.00251     |                       |
|                   | 8                      | 0.0218   | 0.0551 | 1.74 | 0.00440     |                       |
|                   | 9.5                    | 0.0215   | 0.0551 | 1.80 | 0.00486     |                       |
| 139               | 2                      | 0.0216   | 0.0548 | 1.64 | 0.00363     | 0.00117<br>~0.00130   |
|                   | 4                      | 0.0216   | 0.0558 | 1.78 | 0.00467     |                       |
|                   | 7                      | 0.0216   | 0.0558 | 2.15 | 0.00828     |                       |

Tabelle 3. *p*-Nitrophenol in 2.93 N KOH-Lösung.

| Versuchs-<br>temp. °C. | Versuchs-<br>dauer in<br>Std. | $M_{ph}$ | $M_w$  | $n\alpha$ | $-X \log Y$ | $\bar{k}/2.303$       |
|------------------------|-------------------------------|----------|--------|-----------|-------------|-----------------------|
| 100                    | 2                             | 0.0216   | 0.0532 | 1.28      | 0.00114     | 0.000095<br>~0.000110 |
|                        | 50                            | 0.0216   | 0.0549 | 1.83      | 0.00497     |                       |
|                        | 100                           | 0.0216   | 0.0555 | 2.36      | 0.0109      |                       |
| 111                    | 10                            | 0.0216   | 0.0553 | 1.41      | 0.00194     | 0.00024<br>~0.00026   |
|                        | 20                            | 0.0216   | 0.0553 | 1.86      | 0.00524     |                       |
|                        | 43                            | 0.0216   | 0.0552 | 2.32      | 0.0112      |                       |
| 130                    | 3                             | 0.0216   | 0.0552 | 1.77      | 0.00458     | 0.00128<br>~0.00140   |
|                        | 5                             | 0.0216   | 0.0553 | 2.08      | 0.0746      |                       |
|                        | 8                             | 0.0216   | 0.0554 | 2.27      | 0.098       |                       |
| 139                    | 1                             | 0.0216   | 0.0551 | 1.71      | 0.0415      | 0.0030<br>~0.0033     |
|                        | 3                             | 0.0216   | 0.0552 | 2.18      | 0.0894      |                       |

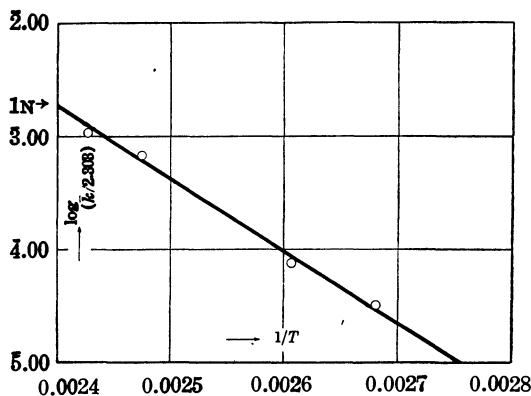
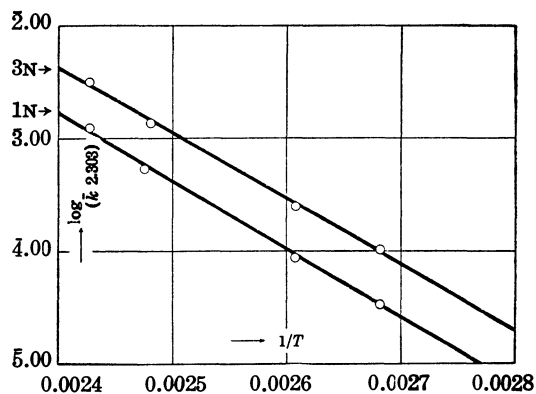
Unter Benutzung der in diesen Tabellen 1 bis 3 angegebenen Daten können wir nun die Aktivierungsenergie der Reaktion auf die übliche Weise ohne weiteres bestimmen, indem wir  $\log(\bar{k}/2.303)$  gegen das Reziproke der absoluten Temperatur  $1/T$  einzeichnen. Die dadurch gewonnenen geraden Linien in Abb. 1 und 2 können wir aber durch die Ausdrücke gut wiedergeben:

$$\log(\bar{k}/2.303) (\text{meta, 1 N}) = (12.5 \pm 0.7) - \frac{29,000 \pm 1,200}{4.574 T} (\text{Mol/Liter})^{-1} (\text{Stunde})^{-1},$$

$$\log(\bar{k}/2.303) (\text{para, 1 N}) = (12.2 \pm 0.6) - \frac{28,400 \pm 1,000}{4.574 T} \quad , \quad ,$$

$$\log(\bar{k}/2.303) (\text{para, 3 N}) = (12.4 \pm 0.6) - \frac{28,000 \pm 1,000}{4.574 T} \quad , \quad , \quad (5).$$

Diese Konstante  $\bar{k}$  entspricht aber, wie aus der Ableitung der Gl.(3) und (4) ohne weiteres klar ist (vgl. dazu II. Mittl.), der stöchiometrischen Gl.(6):

Abb. 1. *m*-Nitrophenol.Abb. 2. *p*-Nitrophenol.

Dagegen verläuft die wirkliche Reaktion, wie darauf schon in II. Mittl. hingewiesen wurde, hauptsächlich zwischen Phenolationen und neutralen Phenolmolekülen gemäss der schon oben angegebenen Gl.(1). Wenn wir deshalb unter passenden Voraussetzungen die oben angegebene stöchiometrische Geschwindigkeitskonstante  $\bar{k}$  (5) für die Reaktion (6) in die wahre Geschwindigkeitskonstante  $\bar{k}_0$  für die Reaktion (1) umrechnen, dann ergeben sich die Gln. ( $\bar{k}_0 = k_6$  in Gl. (18), II. Mittl.):

$$\bar{k}_0(\text{meta}, 1 \text{ N}) = 10^{11.3 \pm 0.7} \exp\left(-\frac{29,000 \pm 1,200}{RT}\right) (\text{Mol/Liter})^{-1}(\text{Sekunde})^{-1},$$

$$\bar{k}_0(\text{para}, 1 \text{ N}) = 10^{11.0 \pm 0.6} \exp\left(-\frac{28,400 \pm 1,000}{RT}\right) (\text{Mol/Liter})^{-1}(\text{Sekunde})^{-1},$$

$$\bar{k}_0(\text{para}, 3 \text{ N}) = 10^{10.8 \pm 0.6} \exp\left(-\frac{28,000 \pm 1,000}{RT}\right) (\text{Mol/Liter})^{-1}(\text{Sekunde})^{-1} \quad (7).$$

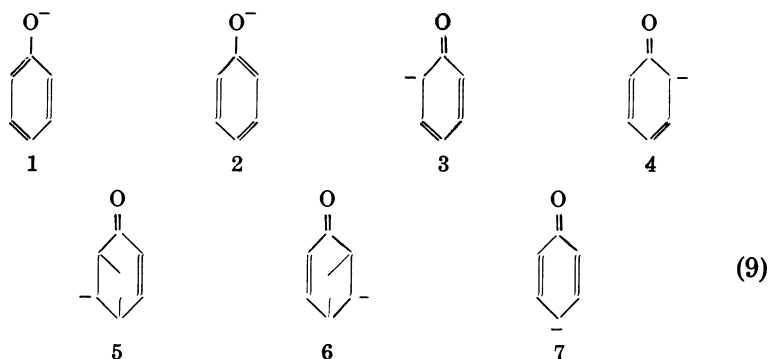
**Diskussion.** Aus diesen letzten Gl.(7) ersehen wir, dass der Stossfaktor sowie die Aktivierungsenergie der Reaktion für die beiden isomerenischen Arten des Nitrophenols innerhalb des Messfehlerbereichs ganz übereinstimmt und weiter die grundlegende Reaktion (1) ebenso wie beim unsubstituierten Phenol als die normal verlaufende bimolekulare Reaktion aufgefasst werden kann. Für das unsubstituierte Phenol erhielten wir beim letzten Versuch<sup>(2)</sup> den Ausdruck für seine (wahre) Geschwindigkeitskonstante:

$$\bar{k}_0(\text{Phenol}) = 10^{10.8} \exp\left(-\frac{24,800}{RT}\right) \quad (8).$$

Die Aktivierungsenergie für *m*- und *p*-Nitrophenol ist deshalb um etwa 4 Kcal. grösser als die für das unsubstituierte Phenol. Den Grund für diesen ziemlich beträchtlichen Unterschied der Aktivierungsenergie hat man offenbar im Einfluss der im Benzolkern eingeführten Nitrogruppe zu suchen. Nach der gewöhnlichen elektrophilen Substitutionsregel wirkt die Hydroxylgruppe fördernd, dagegen die Nitrogruppe störend auf die Substitutionsreaktion der Kernwasserstoffatome, die sich der Hydroxyl- bzw. Nitrogruppe gegenüber in *o*- und *p*-Stellung befinden. Wenn wir deshalb einfacherweise annehmen, dass diese beiden entgegengesetzten Effekte der Hydroxyl- und Nitrogruppe in einem Nitrophenolmolekül bloss additiv wirken, dann müsste das *m*-Nitrophenol viel schwieriger als das *p*-Nitrophenol reagieren, ohne dass der störende Effekt der Nitrogruppe unvergleichbar geringer als der fördernde Effekt der Hydroxylgruppe sein sollte, wie darauf schon in I. Mittl. hingewiesen wurde (vgl. dazu Formel (3) in I. Mittl.). Aber diese letzte Voraussetzung entspricht der Wirklichkeit nicht, weil die Aktivierungsenergie für Nitrophenole sich in der vorliegenden Arbeit deutlich grösser als die für das unsubstituierte Phenol erwies.

Die Experimentalresultate weisen aber ohne weiteres darauf hin, dass man das Problem am zweckmässigsten auf folgende Weise zu behandeln hat. Wir ziehen nämlich zunächst nur den dirigierenden Effekt der Hydroxylgruppe auf die Kernaustauschreaktion in Betracht und dann

den Effekt der Nitrogruppe als die (kleine) Störung auf diesen massgebenden Effekt der Hydroxylgruppe in Rechnung. Nun wird als die Hauptsache für den dirigierenden Effekt der Hydroxylgruppe im allgemeinen die Mesomerie des Phenolmoleküls bzw. -ions angenommen.<sup>(4)</sup> Gemäss dieser Annahme kommen bei der Austauschreaktion der Kernwasserstoffatome des Phenols die folgenden sieben mesomerischen Formen in Betracht:<sup>(5)</sup>



Unter diesen sieben Formen müssen beim gewöhnlichen unsubstituierten Phenol die *o*- und *p*-Chinoidformen, nämlich die Formen 3, 4 und 7, den *m*-Chinoidformen 5 und 6 gegenüber überwiegend grösseres statistisches Gewicht besitzen,<sup>(6)</sup> weil der wirkliche Austausch hauptsächlich an der *o*- und *p*-Stellung stattfindet. Diese Sachlage erfährt aber beim Nitrophenol durch die Einführung der Nitrogruppe eine gewisse Störung.

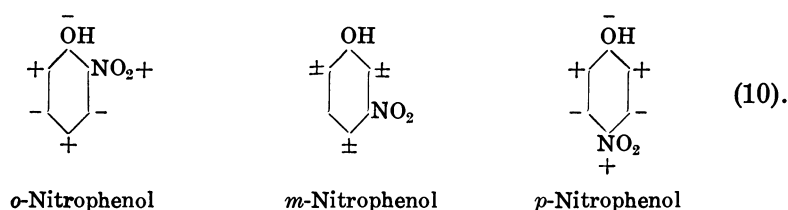
Wird nämlich irgendein Kernwasserstoffatom, das sich der Hydroxylgruppe gegenüber in *o*-, *m*- bzw. *p*-Stellung befindet, durch die Nitrogruppe substituiert, dann werden die Elektronen (bzw. Elektronenwolke) im ganzen Molekül durch den „induktiven Effekt“ dieser Gruppe nach ihrer Stellung mehr oder weniger angezogen bzw. angehäuft. Durch diese Elektronenverschiebung wird aber die Elektronendichte an den anderen Stellen im Phenolmolekül und folglich auch die Austauschwahrscheinlichkeit an diesen betreffenden Stellen vermindert. Wenn z.B. das eine in *m*-Stellung befindliche H-Atom durch die Nitrogruppe substituiert wird, dann werden die Elektronen, die bisher hauptsächlich (bis auf die an der Hydroxylgruppe) an der *o*- und *p*-Stellung angehäuft waren, mehr oder weniger nach der *m*-Stellung angezogen und dadurch die Austauschreak-

(4) Vgl. dazu K.H. Gieb, *Z. physik. Chem.*, A, **180** (1937), 211.

(5) Bei dieser Bezeichnung haben wir statt des neutralen Phenolmoleküls das Phenolation in Rechnung gezogen, weil die wirkliche Austauschreaktion zwischen Phenolationen und neutralen (schweren) Phenolmolekülen stattfindet. Wir haben weiter die mesomerischen Formeln nach dem Prinzip des „ersten“ Nährungsverfahrens aufgezeichnet. Deshalb sehen die *m*-Chinoidformen im Vergleich mit den anderen Formen etwas eigentümlich aus. Diese Eigentümlichkeit können wir aber umgehen, wenn wir uns des „zweiten“ Nährungsverfahrens bedienen (vgl. dazu W. Hückel, *Z. Elektrochem.*, **43** (1937), 752 und 827).

(6) In jedem Fall besitzen natürlich die Benzenoidformen 1 und 2 im Vergleich mit den anderen Formen immer unvergleichbar grösseres statistisches Gewicht. Bei der vorliegenden Diskussion soll der Vergleich nur zwischen den verschiedenen Chinoidformen ausgeführt werden.

tion an der *o*- und *p*-Stellung erschwert. Auf ähnliche Weise können wir auch die Schwierigkeit, mit der die Austauschreaktion des *p*-Nitrophenols stattfindet, erklären. Doch weil in diesem Fall die Elektronen schon von vorn herein, d.h. beim unsubstituierten Phenol, an der *p*-Stellung ziemlich deutlich angehäuft sind (vgl. oben), haben wir den störenden Effekt der Nitrogruppe lieber auf dem folgenden Wege mittelbar in Rechnung zu ziehen. Wird nämlich die Nitrogruppe in *p*-Stellung des Phenolmoleküls eingeführt, dann wird das statistische Gewicht der *p*-Chinoidform in höherem Masse als bisher vergrößert, und zwar dadurch, dass die Elektronen hauptsächlich von der Hydroxylgruppe nach der in *p*-Stellung befindlichen Nitrogruppe angezogen werden. Dadurch wird aber das statistische Gewicht der Benzenoidformen 1 und 2 und folglich weiter das der sich mit diesen im Gleichgewicht befindlichen *o*-Chinoidformen 3 und 4 verringert. Den störenden Effekt der in *p*-Stellung eingeführten Nitrogruppe können wir deshalb dem oben angegebenen unmittelbar störenden Effekt der in *m*-Stellung eingeführten Nitrogruppe gegenüber mehr als einen mittelbaren Effekt auffassen. Alle diese Verhältnisse lassen sich zusammen mit dem *o*-Nitrophenol durch die folgenden Formeln schematisch zum Ausdruck bringen:



In dieser Bezeichnung bedeutet das Pluszeichen die durch die Hydroxylgruppe bewirkte Anreicherung, dagegen das Minuszeichen die durch die Nitrogruppe bewirkte Verarmung an Elektronendichte in einer bestimmten Stelle des Benzolkerns. Beim *m*-Nitrophenol fallen nun diese beiden entgegengesetzten Effekte der Hydroxyl- und Nitrogruppe überall ganz zusammen. Deshalb wird die Leichtigkeit, mit der die Kernaustauschreaktion beim unsubstituierten Phenol stattfindet, beim *m*-Nitrophenol durch den störenden Effekt der Nitrogruppe sozusagen unmittelbar herabgesetzt. Dagegen wird beim *p*-Nitrophenol die der Hydroxylgruppe gegenüber in *o*-Stellung stattfindende Anreicherung an Elektronen durch den störenden Effekt der Nitrogruppe nicht direkt beeinflusst, weil die von dieser letzteren Gruppe herbeigeführte Verarmung an Elektronen der Hydroxylgruppe gegenüber in *m*-Stellung stattfindet. Da aber in diesem Fall, wie das Minuszeichen an der Hydroxylgruppe zeigt, die Hydroxylgruppe selbst den störenden Effekt der Nitrogruppe erleidet und dadurch die Elektronendichte an dieser Gruppe verringert wird, wird die von dieser Gruppe herrührende Anreicherung an Elektronen in *o*-Stellung auch auf mittelbarem Wege beeinflusst und zwar so, dass die Austauschreaktion an dieser Stelle erschwert wird.

Die vorliegenden Versuchsergebnisse, dass die Aktivierungsenergie für das *p*-Nitrophenol ebenso hoch wie die für *m*-Nitrophenol ist, zeigt aber, dass die Verarmung an Elektronen in den betreffenden Stellen, die

beim *p*-Nitrophenol auf mittelbarem dagegen beim *m*-Nitrophenol auf unmittelbarem Wege durch die Nitrogruppe herbeigeführt wird, in den beiden Fällen fast von derselben Grössenordnung ist. Dies ist aber nicht der Fall beim *o*-Nitrophenol, weil die Kernaustauschreaktion bei dieser Verbindung, wie beim letzten Versuch (I. Mittl.) gefunden wurde, deutlich schwieriger als bei den anderen beiden Isomeren stattfindet. Diesen Unterschied können wir jedoch mit Hilfe der schon damals hingewiesenen plausiblen Annahme ohne besondere Schwierigkeit so erklären, dass beim *o*-Nitrophenol die Wasserstoffbindung (Chelation) zwischen der benachbarten Hydroxyl- und Nitrogruppe gebildet wird. Durch diese Wechselwirkung zwischen der Hydroxyl- und Nitrogruppe werden die Elektronen ähnlich wie beim *p*-Nitrophenol von der ersteren Gruppe nach der letzteren angezogen. Aber weil diese Verschiebung der Elektronen von der Hydroxylgruppe nach der Nitrogruppe beim *o*-Nitrophenol wegen der Wasserstoffbindung in viel höherem Masse als beim *p*-Nitrophenol herbeigeführt wird, geht die Austauschreaktion der Kernwasserstoffatome im ersteren Fall viel schwieriger vor sich als im letzteren. Auf diese Weise können wir den Unterschied der Reaktionsfähigkeit der Kernwasserstoffatome zwischen dem gewöhnlichen unsubstituierten Phenol und dem Nitrophenol einerseits und zwischen den drei isomerischen Arten des Nitrophenols anderseits mindestens qualitativ befriedigend erklären.

Zum Schluss möchten wir der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Ausführung der vorliegenden Arbeit unseren wärmsten Dank aussprechen.

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## The Sorption of Gases on Reduced Nickel. I: Hydrogen, Oxygen, and Hydrogen Bromide.

By Matsuji TAKEBAYASHI.

(Received January 26, 1939.)

Y. Urushibara and the present author have found that reduced nickel and reduced iron reverse the direction of the addition of hydrogen bromide to ethenoid compounds, such as allyl bromide and undecenoic acid, in the same way as oxygen.<sup>(1)</sup> As for the catalytic activity of reduced nickel

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(1) This Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173; **13** (1938), 331, 400, 404, 574.



in these reactions it has been observed that reduced nickel that has never been in contact with air after reduction shows a much greater effect than that that has been exposed to air,<sup>(2)</sup> that the metal reduced at a temperature higher than specified for the hydrogenating catalyst is even more active than that prepared as usually,<sup>(3)</sup> and that nickel filings exhibit an activity comparable to that of reduced nickel.<sup>(4)</sup> Further, Urushibara and O. Simamura have found that isostilbene is transformed into stilbene by hydrogen bromide in the presence of either oxygen or reduced nickel.<sup>(5)</sup>

Thus some reactions other than hydrogenation have been found to be catalyzed by reduced nickel. In all these cases, however, reduced nickel is always with hydrogen bromide, reduced nickel and oxygen can take place of each other, and antioxidants, such as catechol and hydroquinone, eliminate to a greater or smaller extent the effect of reduced nickel as well as of oxygen.<sup>(6)</sup>

Further, Urushibara and Simamura,<sup>(7)</sup> studying the reaction of reduced nickel and hydrogen bromide with and without the addition of oxygen, observed that, while practically no reaction took place in the absence of oxygen, hydrogen and nickel dibromide were produced in the presence of oxygen. A balance experiment revealed that the amount of hydrogen generated was short of the equivalent to that of nickel dibromide produced, thus suggesting the formation of water; and comparative experiments with traces of water but without oxygen led to the very probable assumption that the catalyst accelerating the reaction of reduced nickel and hydrogen bromide to give hydrogen and nickel dibromide was not oxygen but the traces of water produced by the action of hydrogen bromide on nickel oxide formed from reduced nickel and oxygen. In fact, reduced nickel which had been exposed to air reacted with hydrogen bromide without added oxygen in the same way as freshly reduced nickel in the presence of oxygen. However, to exclude the possibility of the catalytic action of molecular oxygen on the reaction of hydrogen bromide and nickel, it seemed desirable to investigate the nature of the sorption of oxygen on reduced nickel.

Thus the present author has been induced to study the sorption of gases, especially hydrogen, oxygen, and hydrogen bromide, on reduced nickel. The experiments described below, however, are by no means intended for an exact investigation of the sorption itself, but have been carried out with a view to knowing the behaviours of reduced nickel toward these gaseous substances.

**Apparatus, Materials, and Methods.** The main part of the apparatus, as shown in Fig. 1, consists of a burette (B) for measuring the quantity of the gas sorbed, a Töpler pump (T) for pumping out the gas sorbed when

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(2) Compare Exp. 7 and 8 of this Bulletin, **11** (1936), 693 with Exp. 3 of *ibid.*, **13** (1938), 401.

(3) Compare Exp. 1 and 2 of this Bulletin, **12** (1937), 53 with Exp. 3 of *ibid.*, **13** (1938), 401.

(4) This Bulletin **13** (1938), 400.

(5) *Ibid.*, **12** (1937), 507; **13** (1938), 566.

(6) *Ibid.*, **13** (1938), 400, 404, 566.

(7) *Ibid.*, **13** (1938), 407, 570.

the desorbed amount is to be measured, and a sorption tube (S) made of Terex glass and connected by means of a mercury seal.

Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. Hydrogen was generated by the action of dilute sulphuric acid on zinc, and purified according to the directions of A. Klemenc.<sup>(8)</sup> Oxygen, a commercial material, was dried by passing over phosphorus pentoxide. Hydrogen bromide was prepared by the action of bromine on hot tetralin and purified according to the directions of A. Klemenc.<sup>(9)</sup>

In every experiment, 1.00 g. of reduced nickel, prepared as mentioned above, was taken in the sorption tube, heated at 350°C. in the atmosphere of hydrogen for two hours to refresh the surfaces and then in vacuum for an hour to remove hydrogen, and cooled to room temperature in vacuum. Then the sorption tube containing the nickel was immersed in a thermostat; and the gas of 1 atmospheric pressure was introduced into the tube. The volume of the gas sorbed was determined by subtracting the volume of the sorption tube and the connecting tubing from the decrease of the gas in the burette. All the volumes recorded in this paper have been calculated to the normal temperature and pressure. Other particulars of the experiments are given below for respective cases.

Throughout the experiments described in this paper vacuum or evacuation was effected by a rotary pump, and pressures not exceeding 1 mm. Hg were regarded as good for the purpose.

**The Sorption of Hydrogen.** The sorption of hydrogen on reduced nickel has already been studied by several investigators and the activated adsorption of hydrogen on the metal has been ascertained by them.<sup>(10)</sup> The present experiments on the sorption of hydrogen were carried out

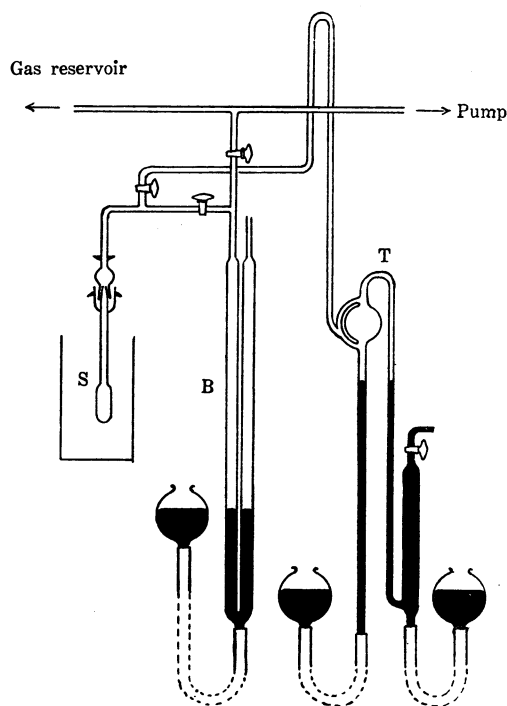


Fig. 1.

(8) A. Klemenc, "Die Behandlung und Reindarstellung von Gasen", 97, Leipzig (1938).

(9) *Loc. cit.*, (8), 196.

(10) H. Taylor and R. Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273; W. Russel and H. Taylor, *J. Phys. Chem.*, **29** (1925), 1325; N. Nikitin, *Z. anorg. allgem. Chem.*, **154** (1926), 130; A. Benton and T. White, *J. Am. Chem. Soc.*, **52** (1930), 2325; S. Iijima, *Rev. Phys. Chem. Japan*, **7** (1932), 3, 24, 36; **8** (1933), 44; **12** (1938), 1.

for the purpose of comparison with those of oxygen and hydrogen bromide. The relation between time and the amount of hydrogen sorbed on 1.00 g. of reduced nickel at 20°C. was observed as shown in Tables 1 and 2. Curves I and II of Fig. 2 correspond to Tables 1 and 2 respectively.

Table 1.  
The Sorption of  
Hydrogen at 20°C.

| Time<br>(min.) | Hydrogen<br>sorbed (c.c.) |
|----------------|---------------------------|
| 3/4            | 0.93                      |
| 3              | 1.12                      |
| 6              | 1.21                      |
| 10             | 1.26                      |
| 20             | 1.32                      |
| 30             | 1.36                      |
| 55             | 1.38                      |
| 70             | 1.39                      |
| 85             | 1.42                      |
| 100            | 1.42                      |
| 130            | 1.44                      |
| 190            | 1.45                      |
| 1225           | 1.49                      |

Table 2.  
The Sorption of  
Hydrogen at 20°C.

| Time<br>(min.) | Hydrogen<br>sorbed (c.c.) |
|----------------|---------------------------|
| 1/2            | 0.68                      |
| 2              | 0.84                      |
| 4              | 0.91                      |
| 9              | 1.00                      |
| 14             | 1.04                      |
| 24             | 1.10                      |
| 45             | 1.17                      |
| 75             | 1.20                      |
| 105            | 1.21                      |

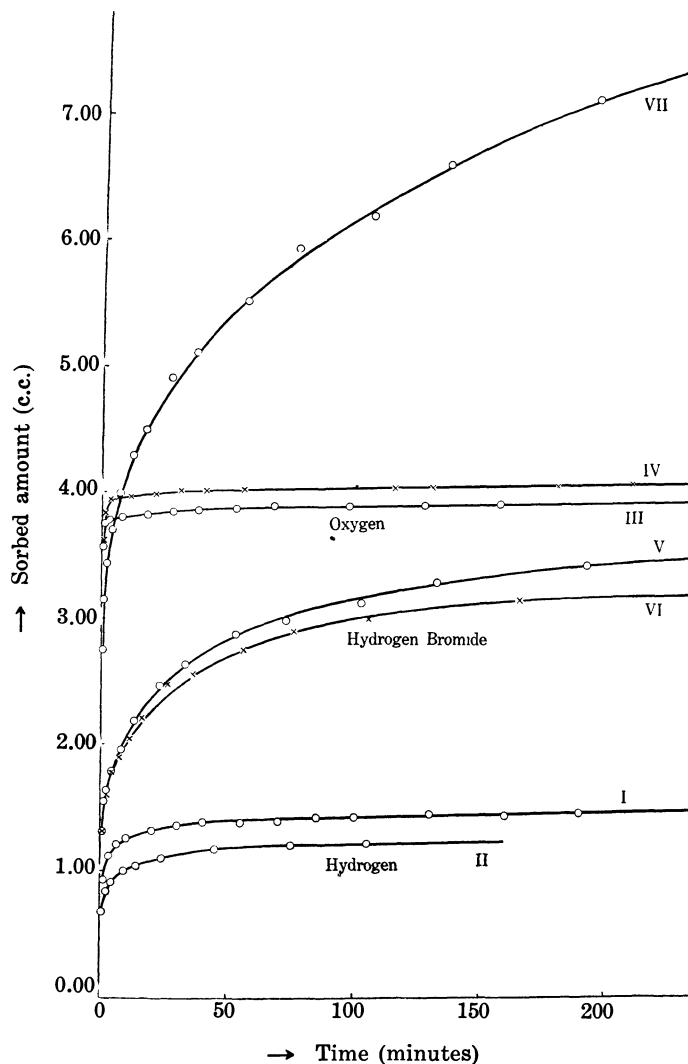


Fig. 2.

In an experiment, reduced nickel (1.00 g.) was nearly saturated with hydrogen at 20°C., when 2.21 c.c. was sorbed in 1220 minutes; then the hydrogen was evacuated for three hours; and hydrogen was again introduced at 20°C., when 0.8 c.c. was sorbed in 1245 minutes. The partial recovery of the capacity for sorption showed that at least a part of hydrogen sorbed on reduced nickel could be desorbed in three hours' evacuation.

**The Sorption of Oxygen.** It has been observed that reduced nickel is easily oxidized in air, and evolves heat and sometimes takes fire when it comes into contact with air.

The sorption of oxygen on freshly reduced nickel was measured at 20°C. The results are given in Tables 3 and 4 and graphically represented by Curves III and IV in Fig. 2. If compared with hydrogen, oxygen is much more rapidly and abundantly sorbed on reduced nickel. The characteristic shapes of the curves indicate that the sorption is nearly accomplished within one minute or two.

Reduced nickel (1.00 g.) was saturated with oxygen at 20°C., when 3.06 c.c. was sorbed in 1541 minutes, and then stood in vacuum for four hours at the same temperature; oxygen was again introduced at 20°C., when no more oxygen was sorbed in 1406 minutes. Thus it was shown that oxygen, once sorbed on reduced nickel, can never be desorbed in vacuum. It is very probable that the whole oxygen sorbed is bound

Table 3. The Sorption of  
Oxygen at 20°C.

| Time (min.) | Oxygen sorbed<br>(c c.) |
|-------------|-------------------------|
| 3/4         | 3.56                    |
| 1           | 3.75                    |
| 3           | 3.78                    |
| 8           | 3.80                    |
| 18          | 3.82                    |
| 28          | 3.84                    |
| 38          | 3.85                    |
| 58          | 3.87                    |
| 68          | 3.89                    |
| 98          | 3.89                    |
| 128         | 3.90                    |
| 158         | 3.91                    |
| 1440        | 3.94                    |

Table 4. The Sorption of  
Oxygen at 20°C.

| Time (min.) | Oxygen sorbed<br>(c.c.) |
|-------------|-------------------------|
| 3/4         | 3.62                    |
| 1           | 3.84                    |
| 3           | 3.94                    |
| 6           | 3.95                    |
| 11          | 3.96                    |
| 21          | 3.98                    |
| 31          | 4.01                    |
| 41          | 4.01                    |
| 56          | 4.02                    |
| 116         | 4.02                    |
| 131         | 4.04                    |
| 181         | 4.05                    |
| 211         | 4.07                    |
| 1440        | 4.08                    |
| 1566        | 4.09                    |
| 1601        | 4.08                    |
| 1996        | 4.09                    |

chemically on nickel. Further the sorption curves (III and IV) indicate that reduced nickel is covered very quickly with a film of the oxide and hereafter oxygen can reach the metal only very slowly through the film. The rapid and abrupt sorption of oxygen on reduced nickel may be attributed partly to a transient rise of the temperature due to the evolution of heat which may favour the very quick formation of the oxide film.

An approximate calculation from the heat of formation of nickel oxide (58.08 Cal.) indicates that, when 4 c.c. of oxygen is combined with 1 g. of reduced nickel with no loss of heat, the temperature of the metal may be raised from 20°C. to above 200°C. Since it can be supposed that the higher the temperature the more oxygen would be sorbed, the oxidation of reduced nickel and the evolution of heat might be promoted reciprocally under somewhat adiabatic conditions. Thus the phenomenon observed when reduced nickel comes into contact with air is explicable.

It was then examined if the oxygen-stained surface of reduced nickel could be cleaned with hydrogen at comparatively low temperatures. Reduced nickel (1.00 g.), which had sorbed 3.75 c.c. of oxygen to saturation at 20°C. in 1370 minutes and then stood in vacuum for three hours, sorbed 2.48 c.c. of hydrogen at 20°C. in 1187 minutes. After hydrogen was evacuated at 20°C. for three hours, the reduced nickel sorbed 1.14 c.c. of oxygen at 20°C. in 1308 minutes. In a similar way, reduced nickel, which had sorbed 3.43 c.c. of oxygen to saturation at 20°C. in 2570 minutes and stood in vacuum for three hours, sorbed 8.14 c.c. of hydrogen at 96–98°C. in 330 minutes. Then the metal, after evacuation of hydrogen, sorbed 2.52 c.c. of oxygen at 20°C. in 1320 minutes. Thus the oxygen-stained nickel sorbed more hydrogen than freshly reduced nickel, and in view of the amounts of hydrogen sorbed it may be supposed that the reduction of the oxide film with hydrogen of 1 atmospheric pressure can be effected partly even at the ordinary temperature and more profoundly at 100°C. Then the consumption of oxygen by the hydrogen-treated nickel may be attributed to the partial recovery of the capacity for the sorption of oxygen rather than to the oxidation of hydrogen remaining unremoved after three hours' evacuation. In this connection it may be added that reduced nickel, which had sorbed fully hydrogen and stood in vacuum for three hours, sorbed apparently rather a smaller amount (3.10 c.c.) of oxygen than fresh nickel.

**The Sorption of Hydrogen Bromide.** The sorption of hydrogen bromide on freshly reduced nickel was measured at 20°C. in the dark. The results are given in Tables 5 and 6 and represented by Curves V and VI in Fig. 2. The gradual and extensive sorption suggests an activated adsorption.

Table 5. The Sorption of Hydrogen Bromide at 20°C.

| Time (min.) | Hydrogen Bromide sorbed (c.c.) |
|-------------|--------------------------------|
| 1/2         | 1.32                           |
| 1           | 1.55                           |
| 2           | 1.64                           |
| 4           | 1.79                           |
| 8           | 1.96                           |
| 13          | 2.19                           |
| 23          | 2.46                           |
| 33          | 2.63                           |
| 53          | 2.87                           |
| 73          | 2.97                           |
| 103         | 3.13                           |
| 133         | 3.28                           |
| 193         | 3.42                           |
| 253         | 3.57                           |
| 1493        | 4.99                           |

Table 6. The Sorption of Hydrogen Bromide at 20°C.

| Time (min.) | Hydrogen Bromide sorbed (c.c.) |
|-------------|--------------------------------|
| 1/2         | 1.32                           |
| 1           | 1.53                           |
| 2           | 1.60                           |
| 4           | 1.78                           |
| 7           | 1.89                           |
| 11          | 2.04                           |
| 16          | 2.21                           |
| 26          | 2.47                           |
| 36          | 2.55                           |
| 56          | 2.74                           |
| 76          | 2.89                           |
| 106         | 2.99                           |
| 166         | 3.15                           |
| 1386        | 4.87                           |

Table 7. The Sorption of Hydrogen Bromide on Oxygen-stained Reduced Nickel at 20°C.

| Time (min.) | Hydrogen Bromide sorbed (c.c.) |
|-------------|--------------------------------|
| 1/2         | 2.75                           |
| 1           | 3.15                           |
| 2           | 3.43                           |
| 4           | 3.70                           |
| 7           | 3.99                           |
| 12          | 4.29                           |
| 17          | 4.49                           |
| 27          | 4.91                           |
| 37          | 5.11                           |
| 57          | 5.52                           |
| 77          | 5.94                           |
| 107         | 6.20                           |
| 137         | 6.62                           |
| 197         | 7.15                           |
| 257         | 7.63                           |
| 317         | 7.98                           |
| 1442        | 12.38                          |
| 1737        | 22.39                          |

Reduced nickel (1.00 g.), which had sorbed 3.45 c.c. of oxygen to saturation, consumed much more hydrogen bromide. The results are given in Table 7 and represented by Curve VII in Fig. 2. Here the possibility of the action of molecular oxygen can be readily excluded in view of the clarified nature of the sorption of oxygen on reduced nickel. As already discussed by Urushibara and Simamura<sup>(7)</sup> it is supposed that traces of water formed by the action of hydrogen bromide on nickel oxide accelerate the reaction of metallic nickel and hydrogen bromide to give hydrogen and nickel dibromide. Hence, the real amounts of hydrogen bromide withdrawn from the gaseous phase must be far greater than the values of the apparent sorption given in Table 7.

The author expresses his hearty thanks to Prof. Urushibara for his kind guidance and to Dr. I. Sano for valuable advices. Thanks are also due to Nippon Gakujutsu Shinko Kwai (Japan Society for the Promotion of Scientific Research) and to Oji Seishi Co. for grants.

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## Chemical Studies of the Western Pacific Ocean. II. The Chemical Composition of the Oceanic Salt. Part 2.\*

By Yasuo MIYAKE.

(Received January 9, 1939.)

**Methods of Analysis (Continued).** *Strontium.* It is but lately that strontium was found to be the fifth in abundance among the metallic elements in sea water. Desgrez and Meunier<sup>(1)</sup> determined strontium in the waters of the English Channel by the spectroscopic method, in which the intensity of strontium line 4607 Å was compared with the reference line 4427 Å of iron. They obtained the result that the channel water contains 13.5 mg. of strontium per litre. T. G. Thompson and B. D. Thomas,<sup>(2)</sup> who recently repeated the spectroscopic analysis, ascertained the value of Desgrez and Meunier for this element.

It is interesting that the ratio of strontium to calcium in sea water is 0.033, which is considerably higher than the ratio 0.0059, calculated from the Clarke number. As has been discussed by H. Wattenberg,<sup>(3)</sup> this discrepancy is probably due to the difference in the solubilities of calcium carbonate and strontium carbonate. Since these determinations were both made spectroscopically, the present author attempted a gravimetric analysis of the element. The separation of this small amount of strontium from calcium is, of course, a rather difficult task. R. Fresenius' method<sup>(4)</sup> of separation, in which the nitrate of both elements are swirled in a mixture of alcohol and ether, was adopted. Since calcium nitrate is about 160 times more soluble than strontium nitrate in a mixture of equal volumes of absolute alcohol and absolute ether, strontium nitrate remains insoluble. 1000 c.c. of sea water, to which ammonium chloride containing little ammonia had been added, was heated to boiling and a sufficient quantity of ammonium oxalate was poured to precipitate calcium and strontium completely. The filtrate was examined if any calcium was present. The precipitation was repeated several times in order to remove magnesium as completely as possible. The oxalates of calcium and strontium were converted by ignition into oxides, and then dissolved in dilute nitric acid, evaporated to dryness on a water bath and finally dried completely in an air bath at above 130°C. The procedure of separation, hereafter, was carried on with alcohol and ether according to the direction of Hillebrand and Lundell. The separation was repeated twice and a very small quantity of undissolved strontium nitrate was filtered off on a small filter paper and ignited to a constant weight.

From this gravimetrical result, the content of strontium in the sea water of the Pacific Ocean near Japan has been found to be 14.4 mg. per

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\* Part 1: this volume, 29.

(1) A. Desgrez and J. Meunier, *Compt. rend.*, **183** (1926), 689.

(2) *Bull. Nat. Research Council*, **85** (1932), 95.

(3) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

(4) Hillebrand and Lundell, "Applied Inorganic Analysis," 490, New York (1929).

litre, which is almost of the same order in amount in values as the results from the spectroscopic method. The slight difference between the two methods is unavoidable because of the inherent difficulties of the analytical processes.

*Boron.* After the geochemical studies of boron had been published by V. M. Goldschmidt and Cl. Peters,<sup>(5)</sup> the boric acid content in sea water became one of the most interesting subject in oceanographical chemistry. V. M. Goldschmidt and his collaborator determined precisely the boron content in various earth crust forming materials by the spectroscopic method. Thereby, they obtained the result that sea water contains 30 mg. of  $B_2O_3$  per litre, a value considerably larger than L. Dieulafait's<sup>(6)</sup> old data. According to L. Dieulafait's determination, which is frequently referred to in text-books of oceanography, the quantity of boron in sea water has been estimated to be at least 0.2 mg. per litre. As H. Wattenberg<sup>(3)</sup> stated in his recent paper, this is one of the few cases, where the older analyses gave a value too low for the rarer elements in the sea water.

Immediately after the investigation of Goldschmidt and Peters, H. Wattenberg<sup>(7)</sup> tried to ascertain the boric acid content in sea water by the direct titration method, using mannitol and a sodium hydroxide solution. He obtained by this method quite easily 15.6 mg. and 16.1 mg. of  $B_2O_3$  per litre, which are in good agreement in the order of the magnitude with Goldschmidt's value. At the same time, independently of H. Wattenberg, E. G. Moberg and M. W. Harding<sup>(8)</sup> of the Scripps Institute obtained almost the same result. If these higher values are correct, then besides carbonic acid, boric acid must be taken into consideration in the acid-base equilibrium in sea water. So K. Buch,<sup>(9)</sup> using the data of the above mentioned authors and the one obtained by himself, calculated theoretically the influence of the boric acid upon the *pH* value of sea water; at the same time, he gave the chlorinity ratio of boron in sea water, which seemed to be almost constant and expressible by the following formula:

$$B\% = 0.00023 \sim 0.00025 \times Cl\%$$

Now, an attempt was made to determine the boric acid content in waters of the Pacific Ocean near Japan by the gravimetric methods inasmuch as all of the former values had been obtained either spectrographically or volumetrically.

At first Gooch and Jones' method has been tried. It determines boron gravimetrically as calcium borate, after the extraction of the borate with ethyl alcohol and expelling it as a methyl ester. A 1000 c.c. portion of sea water, was evaporated to dryness, and then methyl alcohol was added, followed by an extraction overnight.

(5) V.M. Goldschmidt and Cl. Peters, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1932**, 402, 528.

(6) L. Dieulafait, *Compt. rend.*, **85** (1877), 1352.

(7) H. Wattenberg, "Wiss. Ergeb. Meteor-Exp.," VIII, 132, Berlin (1933).

(8) E.G. Moberg and M.W. Harding, *Science*, **77** (1933), 510.

(9) K. Buch, *J. conseil intern. exploration mer*, **8** (1933), 309.



With all the scrupulous care, the results obtained were always too low, when compared with the former values. By this method, there could not be obtained a value higher than 1.2 mg. of  $\text{H}_3\text{BO}_3$  per litre. The second method adopted was Chapin's procedure, in which boric acid in sea salt is expelled directly with the vapour of methyl alcohol, thus forming a methyl ester of boric acid, which is converted to calcium borate. As by Jones and Gooch's method, values so high as the titrimetric ones could not be obtained by this method. The maximum value was 7.3 mg. of  $\text{H}_3\text{BO}_3$  per litre.

In both of these cases, the chief sources of failure lay probably in the difficulty in extracting or expelling the small amount of boric acid from so large a bulk of other salts. After several trials had been in vain, the original plan of gravimetric determination was given up and the method of direct titration of sea water was adopted by modifying H. Wattenberg's procedure at a few points.

To a 100 c.c. portion of sea water, a slight excess of hydrochloric acid solution was added and after heating under suction to remove carbon dioxide completely, the excess of hydrochloric acid was cautiously titrated with a solution of sodium hydroxide using *p*-nitrophenol as the indicator. Then a small quantity of mannitol was added to produce free acid which was titrated with a 0.1 or 0.05 N solution of sodium hydroxide (the indicator, phenolphthalein).

Also invert sugar was used in place of mannitol, as recommended by I. M. Kolthoff.<sup>(10)</sup> The values of both procedures were in good agreement with those of Wattenberg and others. The results are given in Table 1.

Table 1.

| Position |         | Chlorinity | B (mg. / l.) | B (‰) / Cl (‰) |
|----------|---------|------------|--------------|----------------|
| Lat. N   | Long. E |            |              |                |
| 36°14'   | 141°26' | 19.24      | 4.73         | 0.000246       |
| 38°22'   | 142°35' | 18.76      | 4.73         | 0.000252       |

The chlorinity ratios of boron here obtained were almost the same as the upper limit of the values calculated by K. Buch. To eliminate the influences of other salts, known quantities of boric acid were added to the sea water and titrated as usual, the results were completely additive. Recently I. Igelsrud, T. G. Thompson, and B. M. G. Zwicker<sup>(11)</sup> determined the boron content in sea water on 377 samples from the coastal waters of the Northeastern Pacific. They obtained the result that the average boron-chlorinity ratio is 0.0223 (this is not the ratio of the number of promille boron to the chlorinity as described above, but the value milligram atom boron divided by the chlorinity). When compared with this average, the boron-chlorinity ratio obtained by the author seems to be

(10) I.M. Kolthoff, "Die Massanalyse," 119, Berlin (1928).

(11) I. Igelsrud, T.G. Thompson, and B.M.G. Zwicker, *Am. J. Sci.*, [5], **35** (1938), 47.

slightly larger (0.0228, 0.0234). A further quantitative discussion will be done in future.

### Summary.

(1) Strontium in sea water from the Western Pacific Ocean has been determined gravimetrically; the analytical result: 14.4 mg. Sr per litre.

(2) Boron in sea water has been determined volumetrically; the analytical result: 4.73 mg. B per litre.

The author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his assistance in the analytical work.

*The Central Meteorological  
Observatory of Japan.*

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### Chemical Studies of the Western Pacific Ocean. III. Freezing Point, Osmotic Pressure, Boiling Point and Vapour Pressure of Sea Water.

By Yasuo MIYAKE.

(Received January 9, 1939.)

**Freezing Point.** The freezing point of sea water was measured by Knudsen and Hansen<sup>(1)</sup> in 1903, and it is expressed by the following empirical formula:

$$\tau = -0.0086 - 0.064633 \sigma_0 - 0.0001055 \sigma_0^2$$

where  $\tau$  is the freezing point, and  $\sigma_0 = (S_0 - 1) \times 1000$ , in which  $S_0$  represents the specific gravity of sea water at 0°C. with reference to distilled water at 4°C. The relation between the freezing point and chlorinity,

$$\tau = -0.0966 Cl - 0.00000520 Cl^3$$

was derived by B. D. Thomas<sup>(2)</sup> from Knudsen-Hansen's formula. The present author has repeated the measurement of the freezing point of sea water and obtained a new empirical formula which seems to be more adequate than the former equations.

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(1) O. Krümmel, "Handbuch der Ozeanographie," Band 1, 240, Stuttgart (1907).

(2) *Bull. Nat. Research Council*, **85** (1932), 84.

**Experimental.** Sea water of known chlorinity was diluted with water into six samples. The chlorinity, the position, the depth and the date of collection of the original sea water are as follows: Cl, 18.54‰; N 39°46', E 143°16'; 145 m.; March 17th, 1938. The measurements were made by the ordinary method. Into a beaker containing about 100 c.c. of sample water, a Beckmann's thermometer and a certified stem thermometer ( $-20^{\circ} \sim 50^{\circ}\text{C}.$ ) were inserted and the content was cooled indirectly with a cooling mixture under incessant stirring. The temperature of the water, taken at intervals of thirty seconds, was plotted giving the cooling curve. The freezing point was determined from the tangent of the curve after the state of supercooling was broken. At first, the freezing point of distilled water was carefully measured and the reading was used as a reference standard. The difference between the reading of a sample and that of the standard directly gives the depression  $\Delta T$  of the freezing point of sea water.

**Results of the Measurements.** The results of the measurements are given in Table 1.

Table 1.

| Cl (‰) | Salinity (‰) | Depression of the Freezing Point, $\Delta T$ |
|--------|--------------|----------------------------------------------|
| 18.54  | 33.49        | 1.895                                        |
| 13.07  | 23.62        | 1.350                                        |
| 9.37   | 16.94        | 0.970                                        |
| 7.53   | 13.62        | 0.770                                        |
| 4.75   | 8.60         | 0.495                                        |
| 1.90   | 3.46         | 0.195                                        |

As shown in Fig. 1, the relation between the chlorinity and the freezing point depression is almost linear and may be represented by the following simple formula:

$$\Delta T = 0.102710 \text{ Cl.}$$

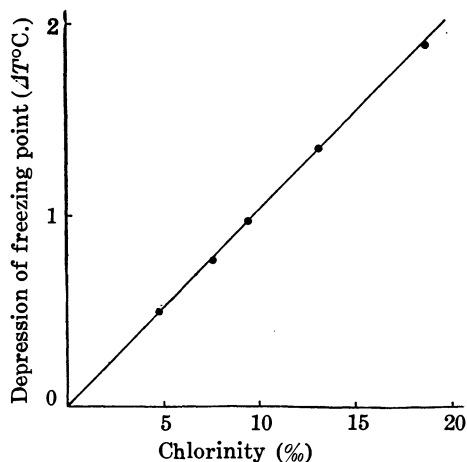


Fig. 1. The relation between freezing point depression and chlorinity.

**A Comparison of Author's Formula with Knudsen-Hansen's Equation.** The freezing point of sea water of various chlorinities was next measured. The results have been compared with the values calculated from the equation of Knudsen-Hansen and from the new formula. From the experimental results shown in Table 2, we can see that the values obtained by the present formula are in good agreement with the measurements, the average deviation between them being only  $\pm 0.005^{\circ}\text{C}.$ ; on the other hand, the values calculated from Knudsen-Hansen's formula constantly show a deviation of about  $0.08^{\circ}\text{C}.$ , giving values that are too high. The comparison shows clearly that the new formula is superior to Knudsen-Hansen's formula.

Table 2.

| Chlorinity | $\Delta T$ , observed | $\Delta T$ , calculated by the new formula | $\Delta T$ , calculated by Knudsen's formula |
|------------|-----------------------|--------------------------------------------|----------------------------------------------|
| 18.22      | 1.875                 | 1.872                                      | 1.792                                        |
| 18.28      | 1.875                 | 1.878                                      | 1.798                                        |
| 18.42      | 1.900                 | 1.892                                      | 1.812                                        |
| 18.48      | 1.890                 | 1.898                                      | 1.819                                        |
| 18.57      | 1.915                 | 1.907                                      | 1.828                                        |
| 18.59      | 1.915                 | 1.909                                      | 1.830                                        |
| 18.60      | 1.915                 | 1.910                                      | 1.831                                        |
| 18.75      | 1.935                 | 1.926                                      | 1.846                                        |
| 19.38*     | 1.985                 | 1.991                                      | 1.911                                        |
| 19.39**    | 1.990                 | 1.992                                      | 1.912                                        |

\* The standard water supplied by the Imperial Fisheries Experimental Station, Japan.

\*\* The standard water supplied by Prof. Knudsen.

**The Calculation of the Osmotic Pressure of Sea Water:** When the depression of the freezing point of a solution is known, its osmotic pressure can readily be estimated. The theoretical relation between osmotic pressure and freezing point depression is given by the next formula:

$$P_0 = \frac{41.35 r \delta}{T_0} \Delta T(\text{atm.})$$

where  $P_0$  is the osmotic pressure at  $0^\circ\text{C}.$ ;  $r$ , the heat of fusion of water, 79.65 cal.;  $\delta$ , the density of water at  $0^\circ\text{C}.$ ;  $\Delta T$ , the freezing point depression. Substituting numerical values in the formula, we obtain the simple equation:

$$P_0 = 12.06 \times \Delta T.$$

In Table 3, the osmotic pressure corresponding to various chlorinity values, calculated by the above formula with additional correction for the heat of solution, are given. The empirical relation between osmotic pressure, chlorinity and temperature is represented by the following equation:

$$P_t = 1.240 \text{ Cl} + 0.00454 \text{ Cl} \cdot t.$$

Table 3.

| Cl (‰) | $\Delta T$ | $P_0$ (atm.) | Cl (‰) | $\Delta T$ | $P_0$ (atm.) |
|--------|------------|--------------|--------|------------|--------------|
| 1      | 0.103      | 1.24         | 12     | 1.233      | 14.88        |
| 2      | 0.205      | 2.47         | 13     | 1.335      | 16.12        |
| 3      | 0.308      | 3.71         | 14     | 1.438      | 17.36        |
| 4      | 0.411      | 4.96         | 15     | 1.541      | 18.60        |
| 5      | 0.514      | 6.20         | 16     | 1.643      | 19.83        |
| 6      | 0.616      | 7.43         | 17     | 1.746      | 21.09        |
| 7      | 0.719      | 8.67         | 18     | 1.849      | 22.34        |
| 8      | 0.822      | 9.91         | 19     | 1.951      | 23.58        |
| 9      | 0.924      | 11.15        | 20     | 2.054      | 24.82        |
| 10     | 1.027      | 12.40        | 21     | 2.157      | 26.07        |
| 11     | 1.130      | 13.64        | 22     | 2.260      | 27.31        |

When the temperature is constant, the osmotic pressure increases by 1.24 atm. per unit increase in chlorinity. In Table 4 and Fig. 2, the osmotic pressures at 0°C. calculated by author's formula are compared with those by Krümmel and Stenius.<sup>(1)</sup> Here the concentration of sea salt is expressed in terms of salinity instead of chlorinity. As seen in this table and Fig. 2, author's values for the osmotic pressure are slightly larger than those of Krümmel and Stenius.

Table 4. Osmotic pressure of sea water at 0°C. (atm.)

| Salinity (‰) | Krümmel-Stenius | Miyake |
|--------------|-----------------|--------|
| 5            | 3.23            | 3.41   |
| 10           | 6.44            | 6.84   |
| 15           | 9.69            | 10.28  |
| 20           | 12.98           | 13.72  |
| 25           | 16.32           | 17.16  |
| 30           | 19.67           | 20.59  |
| 35           | 23.12           | 24.05  |
| 40           | 26.59           | 27.49  |

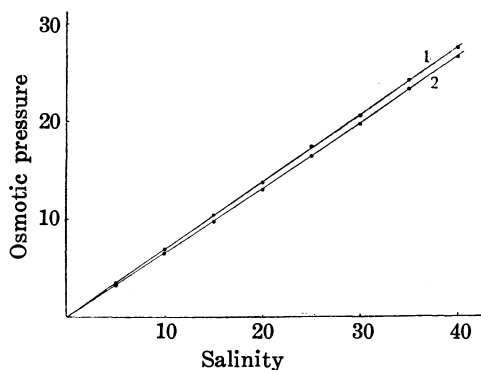


Fig. 2. The relation between osmotic pressure and salinity.

1: Miyake. 2: Krümmel-Stenius.

**The Calculation of the Boiling Point Elevation.** If we know the osmotic pressure of sea water, then we can estimate the boiling point elevation by the following equation:

$$P = \frac{41.35 \, l \, \delta}{T} \Delta T,$$

where  $l$  is the heat of evaporation of water, i.e. 536.6 cal.

But,

$$P = P_0(1 - 0.00366(T - T_0))$$

Therefore,

$$\Delta T = 0.02397 P_0.$$

The numerical values calculated by this equation are shown in Table 5, where the results are compared with Krümmel's data.<sup>(1)</sup>

Table 5. Boiling point elevation of sea water.  $\Delta T^\circ\text{C}$ .

| Salinity (‰) | 5    | 10   | 15   | 20   | 25   | 30   | 35   | 40   |
|--------------|------|------|------|------|------|------|------|------|
| Miyake       | 0.08 | 0.16 | 0.25 | 0.33 | 0.41 | 0.49 | 0.58 | 0.66 |
| Krümmel      | 0.08 | 0.16 | 0.23 | 0.31 | 0.39 | 0.47 | 0.56 | 0.64 |

The experimental formula between the salinity and the boiling point elevation may be expressed as follows:

$$\Delta T = 0.01645 S. \quad S: \text{the salinity.}$$

**The Depression of the Vapour Pressure.** We can easily calculate the vapour pressure depression for sea water at its boiling point when the boiling point elevation is known. There are two means of calculating the depression of the vapour pressure, i.e., one is from the pressure of saturated water vapour near 100°C. under the pressure of 760 mm. Hg (1); and the other is from the boiling point data of water at pressures slightly lower than 760 mm. Hg (2). These data have been quoted from Landolt-Börnstein's Tables, and the results of the calculation are as follows:

Table 6. The depression of the vapour pressure. (mm. Hg)

| Salinity (‰) | 5    | 10                | 15                | 20   | 25    | 30                 | 35    | 40    |
|--------------|------|-------------------|-------------------|------|-------|--------------------|-------|-------|
| From (1)     | 2.17 | 4.34              | 6.76              | 8.91 | 11.07 | 13.21              | 15.60 | 17.75 |
| From (2)     | 2.17 | 4.33              | 6.77              | 8.93 | 11.07 | 13.20              | 15.62 | 17.75 |
| Average      | 2.17 | 4.33 <sub>5</sub> | 6.76 <sub>5</sub> | 8.92 | 11.07 | 13.20 <sub>5</sub> | 15.61 | 17.75 |
| Krümmel      | 2.13 | 4.23              | 6.45              | 8.47 | 10.73 | 12.97              | 15.23 | 17.55 |

### Summary.

(1) The freezing point of sea water from the Western Pacific Ocean has been measured and a new empirical formula for the relation between freezing point and chlorinity has been obtained, which seems to be more adequate than Knudsen-Hansen's equation.

(2) The osmotic pressure, the boiling point elevation and the depression of the vapour pressure of sea water have been calculated.

The author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

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## On the Nature of Foam. IV. Phase Inversion and Foaming of Emulsion Consisting of Acetic Acid, Ethyl Ether and Water.

By Tunetaka SASAKI.

(Received February 10, 1939.)

It was reported in the preceding paper,<sup>(1)</sup> that the heterogeneous region of the system consisting of acetic acid, ethyl ether and water (AEW-system) is divided into two parts, namely, foamy and non foamy region. It was discovered, by a more detailed observation, that between these foamy and non foamy regions, there exist some system in which foam is produced by a certain mode of shaking, while it is not produced by another mode of shaking. Moreover, the type of emulsion is different in each of the above two cases. Present paper describes such phase inversion of AEW-emulsion produced by shakings and its influence upon the foam formation.

### Experiments.

**I. Foam-Nonfoam System.**<sup>(2)</sup> We take a certain composition of AEW-system, for example, the system consisting of 2.33 c.c. of acetic acid, 3.79 c.c. of ethyl ether and 3.88 c.c. of water which corresponds to the point (a) in the mutual solubility diagram of AEW-system as shown in Fig. 1, and shake in a test tube. Then, the following two cases are observed according to two different modes of shaking.

(1) The test tube is held vertically by hand, shaken up and down several times strongly in the usual manner, and then left at rest. In this case the formation of emulsion was observed without any indication of the foam formation.

(2) At first, the upper portion of the test tube is held and the lower portion is made to swing forwards and backwards until considerable amounts of upper and lower liquids are mixed together, then, the usual up-and-down shaking as in (1) is made and emulsification is completed. Observation after shaking shows the foam formation in the resulting emulsion.

**II. Mode of Shaking and Emulsion Type.** The results of section (I) show, that a certain system of AEW foams or does not foam according to the different modes of shaking. Such phenomena have not been observed up to the present. To investigate these phenomena more precisely, we have made close observations to the two emulsions obtained in (1) and (2) of section (I).

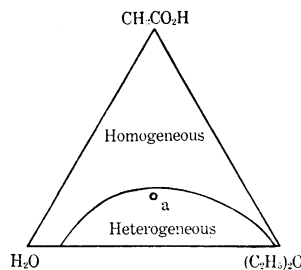


Fig. 1.

(1) Sasaki, this Bulletin, 13 (1938), 669.

(2) The term is used for such a system as shown in this section.



These emulsions are both unstable, their disperse phases consisting of comparatively large liquid drops. It may be called mechanical suspension rather than true emulsion. When we trace, however, the process of breaking up these two emulsions, following differences are observed between them.

(1) In emulsion which is described in (1) of section (I), it can clearly be observed with naked eyes, that emulsion droplets move upwards in the dispersing medium increasing their size as they go up, and at the top of emulsion, in the course of time, they are separated from the dispersing medium as a transparent liquid layer upon the bulk. Thus, emulsion finally breaks up perfectly into two transparent liquid layers. Fig. 2 shows these behaviours.

(2) In emulsion which is described in (2) of section (I), the appearance is just reverse. Emulsion droplets sink in the dispersing medium, they grow in their size as they go down, and in the course of time they are separated, at the bottom, from the dispersing medium into transparent layer. The emulsion finally breaks up into two layers. These relations are also shown in Fig. 3.

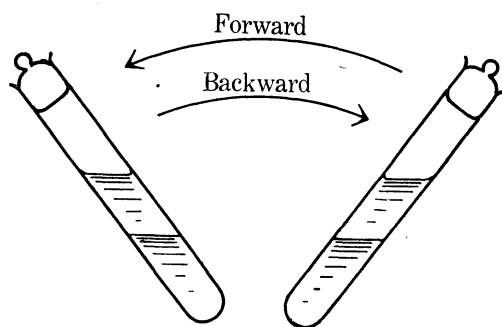
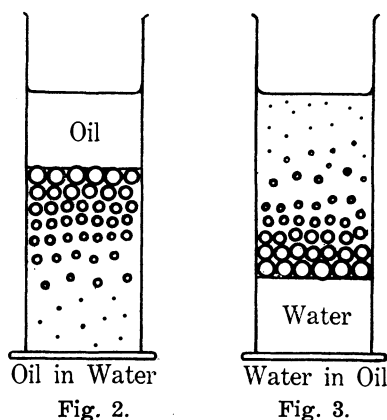


Fig. 4.

It is concluded from the above observations, that in the case of emulsion (1) or Fig. 2, the upper layer of original heterogeneous system is dispersed in the lower one. It may be called oil-in-water (O-in-W) emulsion, as the upper layer mainly consists of ethyl ether which is insoluble in the lower layer of aqueous mixture. In the case of emulsion (2) or Fig. 3, on the contrary, the lower layer of original system is dispersed in the upper one, or it may be called water-in-oil (W-in-O) emulsion. Thus, it is evident that in a certain composition of AEW-system, the mode of shaking described in (1) of section (I) favours the emulsification of oil in water which does not foam, while another mode of shaking as described in (2) of section (I) favours the emulsification of water in oil which foams. The foam formation of this system will be discussed later.

Further experiments show that the formation of O-in-W emulsion is still more facilitated by shaking a test tube in the following manner. The lower part of the test tube is held by hand and the upper portion is shaken with forward and backward motion, which is better described as a jerk. It is illustrated in Fig. 4,



**IV. Zone of Phase Inversion.** In order to investigate this zone of phase inversion more precisely, we carried out, further, the following experiments.

We take systems belonging to this zone, namely, in the vicinity of the line PQ, and applied to them the following modes of shaking.

(1) The mode of shaking as shown in (1) of section (III) or the following method is employed which gives the same effect. The test tube is supported vertically, pulled upwards quickly and then brought down slowly. After repeating these motions several times, it is shaken up and down as in the usual manner.

(2) The mode of shaking as shown in (2) of section (III) is also adopted here.

(3) The test tube is simply shaken up and down as in the usual manner, from the beginning.

Up-and-down shaking involved in the above three modes of shaking is performed by the same shaking apparatus and in the same condition as described in the preceding paper<sup>(1)</sup> (50 vibrations for 10 seconds with amplitude of 12 cm.). Various quantities are measured for emulsion thus produced which are shown in Table 2. In this table, stability of

Table 2.

| System | Composition in volume (c.c.) |             |       | Mode of shaking                              |                                                  |                             | Volume ratio |             |
|--------|------------------------------|-------------|-------|----------------------------------------------|--------------------------------------------------|-----------------------------|--------------|-------------|
|        | Acetic acid                  | Ethyl ether | Water | (1)                                          | (2)                                              | (3)                         | Upper layer  | Lower layer |
| (a)    | 2.33                         | 3.79        | 3.88  | O-in-W<br>$S_e = 24$<br>$S_f = 0$<br>$H = 0$ | W-in-O<br>$S_e = 41$<br>$S_f = 1.5$<br>$H = 0.6$ | O-in-W<br>same<br>as<br>(1) | 0.66         | 1.00        |
| (b)    | 2.40                         | 3.90        | 3.70  | O-in-W<br>$S_e = 28$<br>$S_f = 0$<br>$H = 0$ | W-in-O<br>$S_e = 44$<br>$S_f = 1.7$<br>$H = 0.5$ | W-in-O<br>same<br>as<br>(2) | 0.72         | 1.00        |
| (c)    | 0.38                         | 3.66        | 5.96  | O-in-W<br>$S_e = 10$<br>$S_f = 0$<br>$H = 0$ | W-in-O<br>$S_e = 12.5$<br>$S_f = 0$<br>$H = 0$   | O-in-W<br>or<br>W-in-O      | 0.45         | 1.00        |

$S_e$  and  $S_f$  denote stabilities of emulsion and foam in second respectively;  $H$ , height of foam zone in cm.

emulsion or foam is expressed by time required from immediately after shaking to the complete collapse of emulsion droplets or foam zone, respectively. Height of foam zone is also measured soon after shaking.

**V. Discussion.** First of all, the experiments of section (I) show, that there exists a system of certain composition which can behave both foamy and non foamy, according to the modes of shaking. It is expected, that such difference in the foam formation is necessarily ascribed to the difference in the nature of emulsions in which these phenomena are

taking place. In fact, it is confirmed, as described in section (II), that the foamy emulsion is W-in-O type (Fig. 3), while the non foamy emulsion is O-in-W one (Fig. 2). Thus, the phenomena of foam formation of such systems are closely related to the type of emulsion or the possibility of phase inversion which is caused especially by the mode of shaking.

Now, it is worth while to give a glance to the theories of type determination or phase inversion of emulsion.

The type of emulsion is generally considered to be determined by the nature of emulsifying agent. Bancroft<sup>(3)</sup> considered, that the interfacial tension between emulsifying agent and water or oil plays an important rôle and liquid which constitutes an interface of smaller interfacial tension forms a dispersing medium. Langmuir,<sup>(4)</sup> Harkins<sup>(4)</sup> and Hildebrand<sup>(4)</sup> indicated the relation between the type of emulsion and the molecular shape of emulsifying agent, which enables the explanation of the facts, that Na-soap favours the emulsification of O-in-W type, while Mg- or Al-soap favours that of W-in-O type. The phenomena of phase inversion are also influenced by above conditions. Clowes<sup>(5)</sup> succeeded to invert O-in-W emulsion stabilized by Na-oleate into W-in-O emulsion by adding Ca-salt to it. Bhatnagar<sup>(6)</sup> studied the effect of added electrolyte to the type or phase inversion of emulsion. Parsons and Wilson<sup>(7)</sup> also made the systematic investigation upon these lines.

Now, all these explanations assume the existence of the emulsifying agent of definite kind and its selective determination of type of emulsion. The emulsifying agent stabilizes one type of emulsion selectively to the opposite one. Above explanation, however, cannot be applied in the case where it is difficult to determine which of the liquid components is an emulsifying agent. It may be emphasized, that in these systems which belong to mechanical suspension rather than true emulsion, the readiness or tendency with which certain type of emulsion is produced, is the different matter from the stability of emulsion thus produced, as can be seen in the later part of this paper. Both of these factors are generally involved in all above theories and it is interesting to find the analogy between these relations and the suggestion made by Foulk<sup>(8)</sup> upon the mechanism of foam formation. The tendency of establishing either type of emulsion is sometimes confused with the stability. We, further, consider the cases where the effects of the other factors than the stability are predominant.

Briggs<sup>(9)</sup> noted, that a certain type of emulsion are quickly produced by the method of intermittent shaking. It is frequently experienced, that the emulsification is facilitated by adding the disperse phase little by little and not all at once. Wa. Ostwald<sup>(10)</sup> discussed the influence of volume ratio of two liquid components upon the type of emulsion and

(3) Bancroft, *J. Phys. Chem.*, **17** (1913), 501.

(4) Langmuir, *J. Am. Chem. Soc.*, **39** (1917), 1848; Harkins and co-workers, *ibid.*, **39** (1917), 354, 541; Finkle, Draper, and Hildebrand, *ibid.*, **45** (1923), 2780.

(5) Clowes, *J. Phys. Chem.*, **20** (1916), 407.

(6) Bhatnagar, *J. Chem. Soc.*, **117** (1920), 542; **119** (1921), 61, 1760.

(7) Parsons and Wilson, *Ind. Eng. Chem.*, **13** (1921), 1116.

(8) Foulk, *Ind. Eng. Chem.*, **21** (1929), 815.

(9) Briggs, *J. Phys. Chem.*, **24** (1920), 120.

(10) Wa. Ostwald, *Kolloid-Z.*, **6** (1910), 103.

indicated the critical volume ratio at which the system undergoes phase inversion. Robertson<sup>(11)</sup> and Bhatnagar<sup>(6)</sup> also observed the same effect. Ostwald<sup>(10)</sup> further pointed out another possibility, that the emulsion type is determined by the influence depending upon whether the glass surface of the vessel is wetted with oil or water previous to making emulsion and said, that in certain system of two liquids, the poorer wetting liquid will be emulsified in the better one. Although these factors are overshadowed in its determining effect by the nature of the emulsifying agent, as discussed by Briggs and Schmidt,<sup>(12)</sup> they have considerable effects in the case of unstable and coarser mechanical suspensions with no emulsifying agent specified.<sup>(6)</sup> These factors rather affect the process of establishment of emulsion type, and not the stability of emulsion produced. The mode of shaking discussed in this paper is also considered to be one of these factors where the emulsifying agent has little significance.

It is described in section (III), that the heterogeneous region of AEW-system is divided into three parts, referring to the type of emulsion, as shown in Fig. 5. The region A of this diagram mainly consists of systems having fairly larger volume of an upper layer ( $V_u$ ) than that of a lower one ( $V_l$ ). Such a system shows the tendency of the lower layer being dispersed in the upper one, namely, W-in-O emulsion, no matter what the mode of shaking. This tendency seems to be determined mainly by the ratio  $V_u:V_l$  as suggested by Bhatnagar<sup>(6)</sup> and Robertson,<sup>(11)</sup> namely, in case where there is marked difference in volume between two layers, liquid of larger volume shows the tendency of becoming a dispersing medium, and this tendency is more remarkable as the difference in volume grows larger. In the region B, the relation is reverse. Here  $V_l$  is markedly larger than  $V_u$ , and the system of this region shows the tendency of the upper layer being dispersed in the lower one, namely, O-in-W emulsion results, independent of the mode of shaking.

It is interesting to note, that the region A contains a system in which  $V_u$  is smaller than  $V_l$  and yet the upper layer becomes a dispersing medium on shaking. This suggests that some other factors, in addition to volume ratio, influence the tendency in establishing an emulsion type. Specific action of interface, for example, can be considered.

Phase inversion zone, namely, the region in which a system shows the tendency of producing both types of emulsions according to the mode of shaking, is situated along PQ line in Fig. 5. Such possibility of forming two types of emulsions from one and the same system was once pointed out by Ostwald.<sup>(10)</sup> Woodman<sup>(13)</sup> studied the system of cresylic acid-gelatine-water, and observed that, in certain case, both types of emulsions are possible, depending mainly upon the mode of shaking. The fact was confirmed distinctly in the present experiments.

When we trace the locus of middle points of tie-lines (i.e. points corresponding to the system in which  $V_u = V_l$ ), dotted line MN is obtained in Fig. 5. Now, if the emulsion type is determined by the volume ratio

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(11) Robertson, *Kolloid-Z.*, **7** (1910), 7.

(12) Briggs and Schmidt, *J. Phys. Chem.*, **19** (1915), 478.

(13) Woodman, *J. Phys. Chem.*, **30** (1926), 658.

of two liquids alone, phase inversion zone is reduced to the line PQ which must coincide to the line MN. In practice, phase inversion zone has a narrow area instead of a line, and does not coincide to the line MN which is situated in the region A, as shown in Fig. 5. This means, that the position of the phase inversion zone cannot be determined by volume ratio alone, and also indicates the influences of some other factors. The specific action, at the interface, of acetic acid is quoted for example. It is clear, that in regions A and B, the influence of relative volume ratio is remarkable, while in phase inversion zone, the effect of the mode of shaking is predominant in determination of emulsion type.

Now, we are confronted to the explanation of the mechanisms of shaking. Woodman,<sup>(13)</sup> in his experiments, attempted the explanation which, however, is complicated because adsorption, aging and partition between two phases of an emulsifying agent (gelatine) must be taken into account. In the present case, however, such disturbing factors due to the emulsifying agent are absent and mechanisms seem to be more simple.

In the case of shaking described in (1) of section (III), the lower part of a test tube is fixed and the upper portion of it is swung. Accordingly, the upper layer in the tube is first thrown against the upper end of the tube by the action of centrifugal force, and then follows the lower layer. Thus, the upper layer is crushed into droplets by compression between wall and the lower layer in which it is dispersed. Repeated shaking in this manner, therefore, establishes O-in-W emulsion and subsequent ordinary shaking of up-and-down motion also favours to increase the degree of dispersion of above emulsion type. The mode of shaking described in later part of (1) of section (IV) can be considered to give the same effect as the above case.

In the case of shaking mentioned in (2) of section (III), the upper portion of the tube is fixed and the lower portion is made to swing. In this case, the lower layer is not stirred, as it is confined between the upper layer and wall of the tube, while the upper layer is agitated, especially strong at the free surface. The agitation is extended down to the interface of two layers, where the lower liquid is stirred up and is gradually dispersed into the upper one. W-in-O emulsion is, therefore, established as the shaking goes on, and subsequent ordinary up-and-down shaking also increases the degree of dispersion of this emulsion type.

The question arises as to what type would the ordinary up-and-down shaking favour to produce when it is applied from the beginning. It will be discussed upon this point.

In Table 2, three systems, (a), (b) and (c) are all taken in the phase inversion zone, and so the mode of shaking described in (1) or (2) of section (IV) favours to produce O-in-W or W-in-O emulsion respectively, in these systems. In the case, however, where usual up-and-down shaking is applied from the beginning as described in (3) of section (IV), system (a) produces O-in-W emulsion, system (b) that of W-in-O type, and system (c) occasionally produces both types of them. Each of these emulsion types is considered to be more favourable, respectively, than the other possible type. In phase inversion zone, those systems which are situated near the region A, generally show the tendency

to produce emulsion of the similar type to that in the region A (W-in-O emulsion as in (b) ), and those near the region B show the tendency of producing emulsion of the same type as that in the region B (O-in-W emulsion as in (a) ), by up-and-down shaking. Between these systems of (a) and (b), it is possible to consider the existence of such a system as (c), namely, the system which occasionally shows the tendency to produce both types of emulsions by up-and-down shaking.

It can also be seen from this table, that the type of emulsion once determined by a certain mode of shaking, is hard to be inverted by another mode of shaking. For example, system (b) produces W-in-O emulsion by usual up-and-down shaking, but when O-in-W emulsion is once established by the mode of shaking described in (1) of section (IV), subsequent up-and-down shaking only favours to increase the degree of dispersion of O-in-W type.

It is suggested in the earlier part of this section, that the distinction must be made between the tendency in establishment of emulsion type and the stability. Now, confirmations are made upon this point in Table 2. In the system (a), O-in-W emulsion is favourable to be produced in preference to W-in-O emulsion by usual mode of shaking, although emulsion of the latter type once produced is far more stable than that of the former, as shown in Table 2.

The general differences in behaviour or appearance between O-in-W and W-in-O emulsions are summarised in Table 3. It is said,<sup>(14)</sup> that

Table 3.

| O-in-W emulsion                                                                                                        | W-in-O emulsion                                                                                                 |
|------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|
| Produced by shaking of the mode (1)                                                                                    | Produced by shaking of the mode (2)                                                                             |
| Emulsion drop moves upwards.<br>Oily layer is separated upon the bulk (Fig. 2).<br>Emulsion is comparatively unstable. | Emulsion drop sinks.<br>Aqueous layer is separated at the bottom (Fig. 3).<br>Emulsion is comparatively stable. |
| System does not foam.<br>Bubble-in-drop system occurs frequently.                                                      | Foamy system occurs frequently.                                                                                 |

there exists difference in stability between two possible types of drops formed at the interface separating two liquids. The present experiment shows it quantitatively.

Last of all, the explanation must be made upon the foam formation of the system shown in section (I). It is called for convenience sake foam-nonfoam system. Existence of such system is restricted in the region which forms a portion of phase inversion zone and at the same time forms a portion of foamy region of heterogeneous system of AEW.

(14) Rehinder and Wenström, *Kolloid-Z.*, **53** (1930), 145.

In Fig. 6, A' surrounded by dotted line, shows the foamy region<sup>(1)</sup> and hatching indicates the region of foam-nonfoam system.

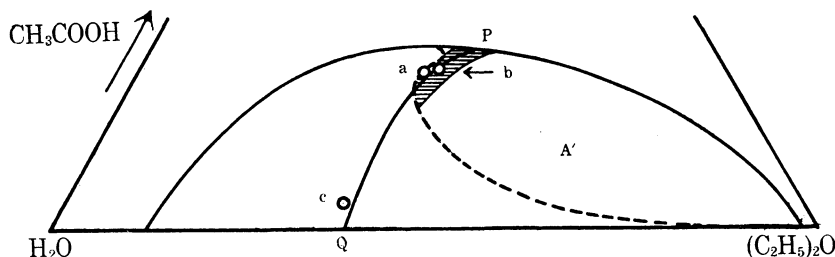


Fig. 6.

When we shake a system belonging to this region (system (a) or (b)), both types of emulsions are occasionally produced. In the case of O-in-W emulsion, bubbles which are produced at the same time in aqueous medium by shaking, are destroyed by emulsion droplets having smaller surface tension than that of dispersing medium, and no foam can be produced. In the case of W-in-O emulsion, on the other hand, emulsion droplets having larger surface tension than that of dispersing medium neither break bubbles, nor interfere with the foam formation of the system. These behaviours were schematically explained in the preceding report.<sup>(1)</sup> Accordingly, the above systems do not foam by shaking of the mode (1), while they can foam by shaking of the mode (2) of section (IV).

In the case of the system (c), the conditions are different. This system also belongs to phase inversion zone, but it is distant from the foamy region A'. So the system does not foam even when it forms W-in-O emulsion by shaking of the mode (2), while it produces emulsion droplets containing air bubbles, when it forms O-in-W emulsion by shaking of the mode (1) of section (IV), owing to the marked difference in surface tension between two phases.<sup>(1)</sup>

In foam-nonfoam system, therefore, the emulsion type is most readily confirmed by the presence or absence of the foam formation immediately after shaking. If the type of emulsion is inverted by some accident during the shaking, sharp change in foam formation can be observed. Thus, in a foam-nonfoam system which shows strong tendency to establish non foamy emulsion, foam formation can be seen so far as it is carefully shaken by the mode (2). It, however, turns suddenly into non foamy system, when it is shaken too strongly.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

### Summary.

(1) It has been discovered, that there is certain heterogeneous system consisting of acetic acid, ethyl ether and water, which behaves



both foamy and non foamy, according to the different modes of shaking. This behaviour in foam formation is due to the difference in the type of emulsions produced.

(2) Three modes of shaking were noted and their influences upon the type of emulsion have been discussed.

(3) The heterogeneous region of this system is divided into three parts, according to the type of emulsion produced by shaking, namely, oil-in-water region, water-in-oil region and phase inversion zone. In phase inversion zone, both types of emulsions are possible to be produced by different modes of shaking. Observations and discussions were made upon these emulsions.

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## The Electrolytic Formation of Persulphate. Part V. With Alternating Current Superimposed on Direct Current.

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(Received February 21, 1939.)

The previous parts<sup>(1)</sup> of the present investigation dealt with the mechanism of persulphate formation and various influences of experimental conditions, when sulphate solutions were electrolysed with D.C. It was shown that the current efficiency, which will be denoted as C.E. hereafter, of electrolyses of sulphate solutions without diaphragm did not seem inferior to those of electrolyses with the same, so it could be assumed therefrom that cathodic reduction did not take place to any considerable extent in those cases. If it is the case, it cannot be expected that the C.E. will be improved by such a means as suppressing the cathodic reduction, but it is possible that the anodic oxidation will be influenced, favourably or unfavourably, when A.C. is superimposed upon D.C.

Various treatments of the Pt-anode prior to electrolysis caused more or less change in the C.E.,<sup>(2)</sup> and the best result was obtained when the anode had been heated by passing A.C. through it. In the present case A.C. takes part in the electrolysis itself, so that the circumstances are evidently much more complicated.

**Experimental.** The anode consists of a spiral of Pt-wire which is 0.1 cm. in diameter and 30.5 cm. long. It is thoroughly ignited im-

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(1) Parts I–IV, this Bulletin, **11** (1936), 1; **11** (1936), 650; **12** (1937), 331; **12** (1937), 425 respectively.

(2) Part III, *ibid.*, **12** (1937), 331.

mediately before use and is kept rotating during electrolysis. The cathode consists of a Pt-plate, 5 cm.  $\times$  2.5 cm. The volume of electrolyte, unless specified, is 130 c.c. and it is electrolysed at 15°C. with the same amount of electricity by D.C., 3397 coulombs. A.C. which is of 60 cycles and 100 volts is superimposed upon it. The connection is as shown by Dr. Tanaka.<sup>(3)</sup> The analysis of the electrolysed solution is made by the same methods as those described in Part I. The C.E. is calculated with regard to D.C. only.

*Experiment 1.* 10 N sulphuric acid is electrolysed and the volume of the electrolyte is varied from 130 to 490 c.c. The C.E. are shown in Table 1 and Fig. 1 which are all referred to the total C.E. Those regarding to Caro's acid are always found less than 1% in these cases and are not shown here. The current density which is abbreviated as C.D. is referred to D. C. only.

Table 1. The C.E. of electrolysis of  
10 N  $\text{H}_2\text{SO}_4$ . With 0.1 amp. A.C.  
superimposed on D.C.

| C.D.<br>(amp./dm <sup>2</sup> .) | 10   | 20   | 40   | 60   | 80   |
|----------------------------------|------|------|------|------|------|
| Volume of<br>electrolyte (c.c.)  |      |      |      |      |      |
| 130                              | 0.2% | 0.3  | 6.2  | 14.1 | 24.5 |
| 195                              | 14.9 | 15.7 | 19.9 | —    | 27.9 |
| 260                              | 8.3  | 13.3 | 23.0 | —    | 47.4 |
| 325                              | 0.9  | 3.0  | 13.0 | —    | 28.7 |
| 490                              | 0.7  | 1.3  | 5.5  | —    | 19.8 |

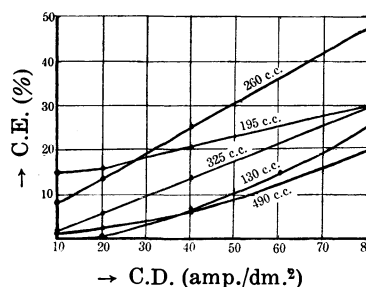


Fig. 1.

*Experiment 2.* 10 N sulphuric acid is electrolysed with diaphragm. Two different porcelain cylinders are used as diaphragm, one 38 mm. and the other 55 mm. in diameter. The anode is kept rotating at the center of the cylinder, and the solution inside it becomes the anolyte. With the smaller diaphragm, the anolyte is 45 c.c. and the catholyte 85 c.c.; with the bigger one, the anolyte 100 c.c. and the catholyte 30 c.c.

The catholyte is found not to contain peroxidic products. Therefore the C.E. shown in Table 2 and Fig. 2 are the results obtained by analysis of the anolyte. The C.E. of the electrolysis without diaphragm described in Experiment 1 is also shown in the figure for comparison. It is interesting to observe that when diaphragm is used the anodic oxidation takes place even with smaller C.D., while without diaphragm no, or very little, C.E. is obtained and also that the C.E. fluctuates little as the C.D. changes, when diaphragm is employed.

As stated already in the previous parts, the C.E. was not influenced much by the use of diaphragm when electrolysis was performed with D.C. only. It is observed in this case that the dimensions of diaphragm

(3) *J. Electrochem. Assoc. Japan*, 4 (1936), 4.

do not influence the C.E. considerably, although the greater cylinder is rather more favourable.

Table 2. The C.E. of electrolysis of 10 N  $\text{H}_2\text{SO}_4$ . With 0.1 amp. A.C. superimposed on D.C.

|                     | C.D. (amp./dm <sup>2</sup> .) | 10    | 20   | 40   | 80    |
|---------------------|-------------------------------|-------|------|------|-------|
| Diaphr. dia. 38 mm. | The total C.E.                | 16.3% | 18.1 | 18.8 | 15.9  |
|                     | The Caro's acid C.E.          | 0.3   | 0.2  | 0.1  | trace |
| Diaphr. dia. 55 mm. | The total C.E.                | 13.8  | 16.6 | 19.2 | 16.6  |
|                     | The Caro's acid C.E.          | 2.8   | 1.6  | 0.4  | 0.4   |

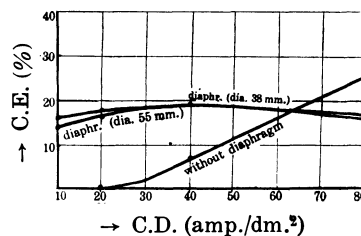


Fig. 2.

*Experiment 3.* Sulphuric acid containing a small quantity of potassium sulphate is electrolysed. The results are shown in Table 3 and Fig. 3. It can be seen that the C.E. is somewhat improved by replacing part of sulphuric acid with the sulphate when the present case and Experiments 1 and 2 are compared. In the electrolysis with diaphragm, the catholyte is found, in this case also, to contain no peroxidic products. The presence of diaphragm improves the C.E. at smaller C.D., and the bigger diaphragm is more favourable to the C.E., as in Experiment 2.

Table 3. The C.E. of electrolysis of  $\text{H}_2\text{SO}_4$  containing  $\text{K}_2\text{SO}_4$ . With 0.1 amp. A.C. superimposed on D.C.

|                                                                | C.D. (amp./dm <sup>2</sup> .) | 10   | 20   | 40   | 80   |
|----------------------------------------------------------------|-------------------------------|------|------|------|------|
| 0.65N $\text{K}_2\text{SO}_4$<br>9N $\text{H}_2\text{SO}_4$    | Without diaphragm             | 3.4% | 8.3  | 21.8 | 39.5 |
| 0.64N $\text{K}_2\text{SO}_4$<br>9.36N $\text{H}_2\text{SO}_4$ | With diaphragm (dia. 38 mm.)  | 18.1 | 13.5 | 19.0 | 49.3 |
| 0.64N $\text{K}_2\text{SO}_4$<br>9.36N $\text{H}_2\text{SO}_4$ | With diaphragm (dia. 55 mm.)  | 20.3 | 27.4 | 32.7 | 40.5 |

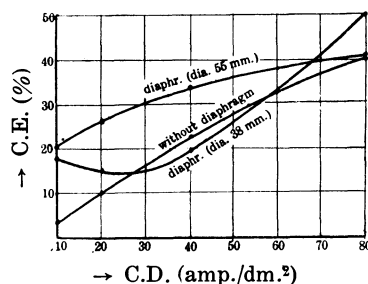


Fig. 3.

*Experiment 4.* A solution which is 0.64 N and 9.36 N respectively as regard to sodium sulphate and sulphuric acid is electrolysed. As in Experiment 3, the bigger diaphragm is more favourable to the C.E. than the smaller, but the difference is small. It is seen from the present case in comparison with the previous case in which the potassium salt is employed that potassium sulphate is more favourable in increasing the C.E. of persulphate formation than sodium sulphate. Such a difference between two sulphates is attributed to that Na-ions<sup>(4)</sup> are more effective catalysor to decompose persulphate than K-ions, as stated in Part I.

(4) A. Kailan and E. Leisek, *Monatsh.*, **50** (1928), 403.

Caro's acid is found less than 1% in C.E. in each electrolysis. The results are shown in Table 4 and Fig. 4.

Table 4. The C.E. of a solution which is 0.64 N  $\text{Na}_2\text{SO}_4$  and 9.36 N  $\text{H}_2\text{SO}_4$ . With 0.1 amp. A.C. superimposed on D.C.

| C.D. (amp./dm <sup>2</sup> .) | 10   | 20  | 40   | 80   |
|-------------------------------|------|-----|------|------|
| Without diaphragm             | 3.4% | 6.8 | 14.9 | 23.6 |
| With diaphragm (dia. 38 mm.)  | 3.4  | 7.8 | 14.9 | 20.4 |
| With diaphragm (dia. 55 mm.)  | 4.2  | 7.8 | 15.2 | 24.2 |

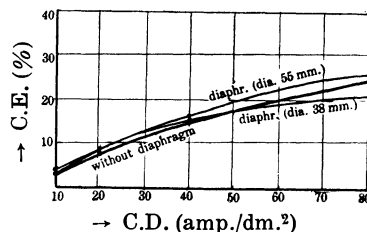


Fig. 4.

*Experiment 5.* The electrolyte is 0.64 N and 9.36 N with regard to ammonium sulphate and sulphuric acid respectively. The C.E. which is shown in Table 5 and Fig. 5 is nearly similar to that of Experiment 3 in which potassium sulphate is used, but is better than that of Experiment 4 in which the sodium salt is employed.

Table 5. The C.E. of a solution which is 0.64 N  $(\text{NH}_4)_2\text{SO}_4$  and 9.36 N  $\text{H}_2\text{SO}_4$ . With 0.1 amp. A.C. superimposed on D.C.

| C.D. (amp./dm <sup>2</sup> .) | 10    | 20   | 40   | 80   |
|-------------------------------|-------|------|------|------|
| Without diaphragm             | 13.3% | 17.6 | 25.9 | 40.1 |
| With diaphragm (dia. 38 mm.)  | 11.3  | 18.9 | 23.2 | 33.1 |
| With diaphragm (dia. 55 mm.)  | 16.7  | 22.5 | 32.0 | 48.3 |

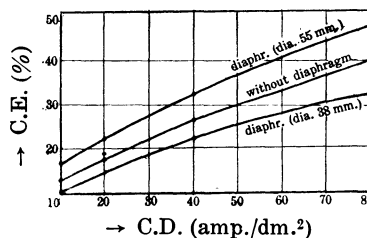


Fig. 5.

*Experiments 6, 7, and 8.* Three solutions which are 2 N and 8 N, 4 N and 6 N, and 6 N and 4 N as to ammonium sulphate and sulphuric acid respectively are electrolysed in these experiments. The more concentrated as to the sulphate the solution is, the greater is the C.E. But the present C.E. are inferior to those of corresponding cases described in Part I in which D.C. only took part. Therefore A.C. is not favourable to increase the C.E. of persulphate formation. The formation of Caro's acid in these cases is less than 1% in C.E. The results are shown in Table 6 and Fig. 6, 7, and 8.

*Experiments 9 and 10.* A solution which is 2 N ammonium sulphate and 8 N sulphuric acid, the same one as in Experiment 5, is electrolysed, but in the present case the quantity of A.C. is varied, the other conditions remaining the same. The influence of the amount of A.C. on the C.E. in these cases is not considerable. The results are shown in Table 7 and Fig. 9 and 10.

Table 6. The C.E. of electrolyses of solutions which contain  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ . With 0.1 amp. A.C. superimposed on D.C.

|                                                               | C.D. (amp./dm <sup>2</sup> .) | 10    | 20   | 40   | 80   |
|---------------------------------------------------------------|-------------------------------|-------|------|------|------|
| 2N $(\text{NH}_4)_2\text{SO}_4$<br>8N $\text{H}_2\text{SO}_4$ | Without diaphragm             | 21.9% | 26.7 | 42.3 | 50.3 |
|                                                               | With diaphragm (dia. 38 mm.)  | 18.1  | 20.3 | 29.0 | 43.8 |
|                                                               | With diaphragm (dia. 55 mm.)  | 18.5  | 26.4 | 39.7 | 48.1 |
| 4N $(\text{NH}_4)_2\text{SO}_4$<br>6N $\text{H}_2\text{SO}_4$ | Without diaphragm             | 26.8  | 37.4 | 52.1 | 54.5 |
|                                                               | With diaphragm (dia. 38 mm.)  | 25.4  | 31.6 | 44.0 | 49.0 |
|                                                               | With diaphragm (dia. 55 mm.)  | 29.6  | 40.3 | 53.5 | 61.8 |
| 6N $(\text{NH}_4)_2\text{SO}_4$<br>4N $\text{H}_2\text{SO}_4$ | Without diaphragm             | 37.9  | 46.4 | 60.0 | 64.0 |
|                                                               | With diaphragm (dia. 38 mm.)  | 36.5  | 50.5 | 57.8 | 63.6 |
|                                                               | With diaphragm (dia. 55 mm.)  | 37.3  | 50.8 | 62.5 | 65.5 |

Table 7. The C.E. of electrolyses of a solution which is 2 and 8 N as to  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  respectively. A.C. is superimposed upon D.C.

|                      | C.D. (amp./dm <sup>2</sup> .) | 10    | 20   | 40   | 80   |
|----------------------|-------------------------------|-------|------|------|------|
| A.C.<br>0.01<br>amp. | Without diaphragm             | 15.6% | 22.5 | 39.3 | 46.8 |
|                      | With diaphragm (dia. 38 mm.)  | 15.1  | 21.8 | 39.4 | 44.9 |
|                      | With diaphragm (dia. 55 mm.)  | 20.2  | 27.8 | 38.0 | 41.2 |
| A.C.<br>0.2<br>amp.  | Without diaphragm             | 10.5  | 32.0 | 41.2 | 44.6 |
|                      | With diaphragm (dia. 38 mm.)  | 22.2  | 34.5 | 42.3 | 45.0 |
|                      | With diaphragm (dia. 55 mm.)  | 27.8  | 36.7 | 43.3 | 45.8 |

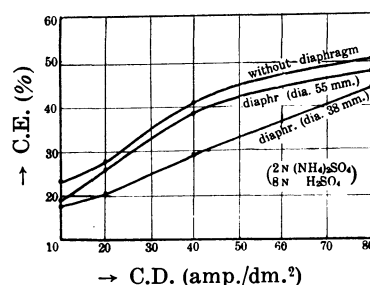


Fig. 6.

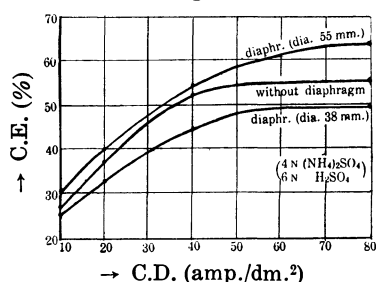


Fig. 7.

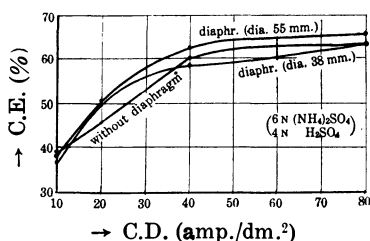


Fig. 8.

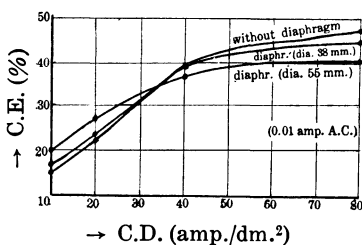


Fig. 9.

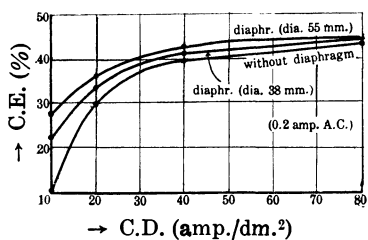


Fig. 10.

*Experiment 11.* 15 N sulphuric acid is electrolysed at 15°C. without diaphragm for 5 hours. The C.D. is 30 amp./dm.<sup>2</sup> as to D.C., and A.C. is 0.1 amp. The same solution was electrolysed, with D.C. only, in Experiment 5 of Part II. In the latter case the Caro's acid C.E. fell off as the time went on, but in the present case it is kept nearly constant during the course of electrolysis. The total C.E. is almost the same in these two cases, falling off gradually with time. The results are shown in Table 8 and Fig. 11.

Table 8. The C.E. of electrolysis of 15 N H<sub>2</sub>SO<sub>4</sub> without diaphragm. C.D. is 30 amp./dm.<sup>2</sup> by D.C., and A.C. is superimposed on D.C.

| Time (hour)          | 1     | 2    | 3    | 5    |
|----------------------|-------|------|------|------|
| The total C.E.       | 60.7% | 57.1 | 49.6 | 28.6 |
| The Caro's acid C.E. | 15.3  | 18.5 | 17.8 | 17.7 |

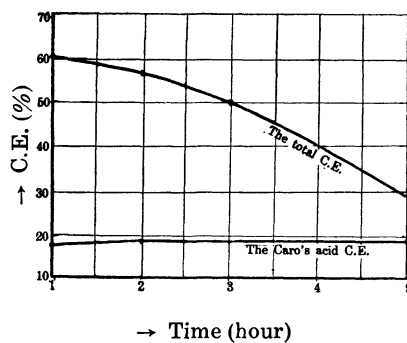


Fig. 11.

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## Austauschreaktion der Sauerstoffatome zwischen einigen anorganischen Anionen und Wasser.<sup>(1)</sup>

Von Toshizo TITANI und Kokiti GOTO.

(Eingegangen am 27. Februar 1939.)

**Inhaltsübersicht.** Die Austauschreaktion der O-Atome zwischen einigen anorganischen Anionen, d.h.  $K_2SO_4$ ,  $KNO_3$ ,  $NaClO_3$ ,  $K_2CO_3$ ,  $KH_2AsO_4$ ,  $KH_2PO_4$  und  $KHSO_4$ , und Wasser in neutraler, alkalischer sowie saurer Lösung wird untersucht. Daraufhin kommen wir zu dem Schluss, dass die Reaktion nicht nur durch  $OH^-$ -Ionen sondern auch durch  $H^+$ -Ionen katalysiert wird. Als Mechanismus der Reaktion scheint uns in erster Linie der der Verseifung des organischen Esters am naheliegendsten in Betracht zu kommen. Aber für die Reaktion in saurer Lösung und besonders bei erhöhten Temperaturen können wir auch nicht ausser Acht lassen, dass die Austauschreaktion durch die Zwischenbildung der Anhydridmoleküle der betreffenden Säuren herbeigeführt wird.

**Einleitung.** Die Untersuchung der Austauschreaktion der O-Atome zwischen verschiedenen Arten der Anionen und Wasser ist insofern von

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(1) Vorläufig mitgeteilt in diesem Bulletin, **13** (1938), 667.



Interesse als sie über das Verhalten der in Rede stehenden Anionen in wässrigen Lösungen einiges Licht werfen kann. Aus diesem Grunde haben wir die vorliegenden Versuche ausgeführt. Aber während dieser Zeit wurde dieselbe Aufgabe auch von anderer Seite aufgenommen, von der bereits einige interessante Ergebnisse vorliegen. Blumenthal und Herbert<sup>(2)</sup> fanden z.B., dass Kaliumphosphat  $K_3PO_4$  seine ganzen vier O-Atome leicht gegen die des Wassers austauscht. Nach dem Versuch von Ingold und seinen Mitarbeitern<sup>(3)</sup> wurde ferner gefunden, dass die sämtlichen O-Atome des Natriumsulfats  $Na_2SO_4$  in der mit Alkali versetzten Lösung gegen die des Wassers schnell ausgetauscht wird. Da aber die von Blumenthal und Herbert untersuchte Lösung von Kaliumphosphat in Wasser wegen der hydrolytischen Spaltung des Salzes ohne jeden Zusatz schon von selbst alkalisch reagiert, können wir die von allen diesen Autoren gewonnenen Ergebnisse kurz so zusammenfassen, dass die Austauschreaktion der O-Atome der anorganischen Anionen durch  $OH^-$ -Ionen katalysiert wird. Nach unserem eigenen Versuch ergibt sich aber, dass diese Reaktion nicht nur durch  $OH^-$ -Ionen sondern auch durch  $H^+$ -Ionen katalysiert wird. Wir kamen zu dieser Annahme durch die Versuche, die mit den Lösungen von (i)  $K_2SO_4$ ,  $KNO_3$ ,  $NaClO_3$ ; (ii)  $K_2CO_3$ ; und (iii)  $KH_2AsO_4$ ,  $KH_2PO_4$ ,  $KHSO_4$  sowie mit dem Gemisch von  $K_2SO_4 + KHSO_4$ ,  $KNO_3 + KHSO_4$ ,  $NaClO_3 + KHSO_4$ ,  $K_2SO_4 + HCl$  und  $NaClO_3 + HCl$  ausgeführt wurden. Die Lösung der ersten dieser Gruppen reagiert offensichtlich neutral, die der zweiten alkalisch und die der letzten dritten sauer. Die messbar schnell verlaufende Austauschreaktion wird aber nur bei diesen beiden letzten Gruppen gefunden. Dagegen bei der ersten Gruppe, d.h. in neutraler Lösung, ist die Reaktion sogar bei ziemlich erhöhten Temperaturen kaum zu bemerken.

**Versuchsanordnung.** Eine abgewogene Menge des betreffenden Salzes wird in eine ebenfalls gut abgewogene Menge des an schwerem Sauerstoff angereicherten Wassers aufgelöst und die so hergestellte homogene Lösung wird in einem zugeschmolzenen Glasrohr bei einer bestimmten Temperatur, d.h. bei Zimmertemperatur, bei 100°C. bzw. bei 180°C., während einer gemessenen Zeitdauer stehen gelassen. Als Thermostat benutzten wir bei 100°C. das siedende Wasserbad, und bei 180°C. das elektrisch geheizte Luftbad. Nach der Erwärmung wird das Wasser durch die Destillation im Vakuum vom Salz abgeschieden und nötigenfalls wieder mit einer abgewogenen Menge des Salzes versetzt und erwärmt. Diese letzte Massnahmsregel ist oft nötig, wenn die Löslichkeit des betreffenden Salzes in Wasser bei der in Rede stehenden Temperatur nicht genügend gross ist. Nötigenfalls wiederholen wir deshalb denselben Prozess unter Verwendung immer desselben schweren Wassers einige Mal nacheinander, um die benötigte Menge des Salzes mit der angegebenen Menge des schweren Wassers restlos reagieren zu lassen. Eine einfache Rechnung zeigt,<sup>(4)</sup> dass die Veränderung der Dichte des schweren Wassers, die bei dieser Arbeitsweise durch die nacheinander folgend durch-

(2) E. Blumenthal und J.B.M. Herbert, *Trans. Faraday Soc.*, **33** (1937), 849.

(3) S.C. Datta, J.N.E. Day und C.K. Ingold, *J. Chem. Soc.*, **1937**, 1968.

(4) Vgl. dazu T. Titani und N. Morita, dies Bulletin, **13** (1938), 409.

geführte Destillation eventuell hervorgerufen wird, wohl ausser Acht gelassen werden darf. Wenn auf diese Weise der ganze Austauschversuch beendet worden ist, wird das vom Salz abgeschiedene Wasser wie üblich sorgfältig gereinigt und dessen Dichteüberschuss dem gewöhnlichen Wasser gegenüber mittels eines Quarzschwimmers genau gemessen. Andererseits berechnen wir mit Hilfe der verwendeten Menge des Salzes und schweren Wassers sowie dessen Gehaltes an schwerem Sauerstoff vor dem Versuch den theoretisch erwartenden Wert der Dichteabnahme des benutzten schweren Wassers, die sich beim vollständigen Austausch ergeben würde. Wir können deshalb durch den Vergleich des so berechneten Wertes der Dichteabnahme des schweren Wassers mit dem experimentell gefundenen über den Austausch der O-Atome der in Rede stehenden Anionen zu einem Schluss kommen.

Die Ergebnisse der so ausgeführten Versuche sind in den weiter unten angegebenen Tabellen zusammengestellt. Aber bevor wir auf diese eingehen, möchten wir noch einige Worte über die Bereitung bzw. Vorbehandlung der zum Versuch verwendeten Salze sowie des schweren Wassers sagen. Die zu vorliegenden Versuchen benutzten Salze alle enthalten kein Kristallisationswasser. Aber sicherheitshalber werden sie immer direkt vor dem Versuch sorgfältig getrocknet, indem wir sie im Vakuum bei einer geeigneten Temperatur genügend lang erwärmen. Dabei geben wir für die wasserstoffhaltigen primären Salze wie z.B.  $\text{KH}_2\text{PO}_4$  und  $\text{KH}_2\text{AsO}_4$  besonders darauf Acht, dass keine wirkliche Entwässerung stattfindet. Die wirklich benutzte Trocknungstemperatur sowie die Trocknungsdauer geben wir oberhalb jeder Tabelle in den Klammern nach der chemischen Formel des betreffenden Salzes an. Das Kaliumsulfat wird z.B. durch die fünfstündige Erwärmung im Vakuum bei ca.  $200^\circ\text{C}$ . getrocknet. Das zum Versuch benutzte, an schwerem Sauerstoff angereicherte schwere Wasser wird durch die fraktionierte Destillation des gewöhnlichen Wassers bereitet. Deshalb ist es nicht nur an schwerem Sauerstoff sondern auch an schwerem Wasserstoff bis zu einem gewissen Grad angereichert. Die oberhalb jeder Tabelle angegebene Anzahl  $\Delta s_a$  zeigt den gesamten Dichteüberschuss des benutzten schweren Wassers vor dem Versuch. Von diesem gesamten anfänglichen Dichteüberschuss  $\Delta s_a$  ist aber der Betrag  $\Delta s_a(\text{O})$ , ebenfalls oberhalb jeder Tabelle angegeben, auf die Anreicherung der schweren Sauerstoffisotope zurückzuführen. Da aber  $\Delta s_a$  durchschnittlich 35 bis 40  $\gamma$  und  $\Delta s_a(\text{O})$  23 bis 26  $\gamma$  beträgt, ist der Gehalt des von uns benutzten schweren Wassers an schwerem Sauerstoff im Vergleich mit den von anderen Autoren benutzten verhältnismässig klein. Jedoch weil wir erstens mit diesem Wasser bei jedem Versuch ziemlich reichlich verfahren und zweitens der Dichteüberschuss des schweren Wassers mittels Quarzschwimmers bis unter  $\pm 0.5 \gamma$  genau gemessen werden konnte, dürfen die damit gewonnenen Ergebnisse wohl als genügend genau angesehen werden.

**Versuche in neutraler Lösung.** Die Austauschreaktion in neutraler Lösung kann nur äusserst schwer stattfinden, wie die folgenden drei Versuche mit  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$  und  $\text{NaClO}_3$  zeigen.

## Versuch 1. Kaliumsulfat.

$K_2SO_4$ (200°C., 5 Stdn.),  $\Delta s_a = 35.5 \gamma$  und  $\Delta s_a(O) = 23.1 \gamma$  bei Zimmertemp.,  
dagegen  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$  bei 100° und 180°C.

| Versuchs-<br>temp. °C. | Versuchs-<br>dauer in Stdn. | $K_2SO_4$<br>in g. | $H_2O$<br>in g. | Dichteabnahme in $\gamma$ |      | Anzahl der<br>Teilversuche |
|------------------------|-----------------------------|--------------------|-----------------|---------------------------|------|----------------------------|
|                        |                             |                    |                 | gef.                      | ber. |                            |
| Zimmertemp.            | 72                          | 28.0               | 20.0            | 1.2                       | 9.5  | 14                         |
| 100                    | 20                          | 25.0               | 20.0            | 0.8                       | 8.8  | 6                          |
| 180                    | 100                         | 21.0               | 20.0            | 2.1                       | 7.9  | 4                          |

## Versuch 2. Kaliumnitrat.

$KNO_3$ (240°C., 6 Stdn.),  $\Delta s_a = 35.5 \gamma$  und  $\Delta s_a(O) = 23.1 \gamma$  bei Zimmertemp.,  
80° und 100°C., dagegen  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$  bei 180°C.

| Versuchs-<br>temp. °C. | Versuchs-<br>dauer in Stdn. | $KNO_3$<br>in g. | $H_2O$<br>in g. | Dichteabnahme in $\gamma$ |      | Anzahl der<br>Teilversuche |
|------------------------|-----------------------------|------------------|-----------------|---------------------------|------|----------------------------|
|                        |                             |                  |                 | gef.                      | ber. |                            |
| Zimmertemp.            | 72                          | 36.0             | 20.0            | 1.7                       | 11.4 | 5                          |
| 80                     | 72                          | 25.2             | 20.0            | 1.1                       | 9.3  | 2                          |
| 100                    | 72                          | 25.0             | 20.0            | 1.0                       | 9.3  | 1                          |
| 180                    | 100                         | 38.0             | 20.0            | 1.3                       | 13.2 | 1                          |

## Versuch 3. Natriumchlorat.

$NaClO_3$ (200°C., 8 Stdn.),  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$ .

| Versuchs-<br>temp. °C. | Versuchs-<br>dauer in Stdn. | $NaClO_3$<br>in g. | $H_2O$<br>in g. | Dichteabnahme in $\gamma$ |      | Anzahl der<br>Teilversuche |
|------------------------|-----------------------------|--------------------|-----------------|---------------------------|------|----------------------------|
|                        |                             |                    |                 | gef.                      | ber. |                            |
| 100                    | 10                          | 40.0               | 20.0            | 1.3                       | 13.2 | 1                          |

**Versuche in alkalischer Lösung.** Dieser Versuch wird in der vorliegenden Arbeit nur mit der Lösung des Kaliumcarbonats durchgeführt, weil die katalytische Wirkung der  $OH^-$ -Ionen schon durch die Versuche von den anderen Autoren als einwandfrei nachgewiesen wurde.<sup>(2) (3)</sup>

## Versuch 4. Kaliumcarbonat.

$K_2CO_3$ (200°C., 5 Stdn.),  $\Delta s_a = 35.5 \gamma$  und  $\Delta s_a(O) = 22.6 \gamma$  bei Zimmertemp.,  
dagegen  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$  bei 100° und 180°C.

| Versuchs-<br>temp. °C.     | Versuchs-<br>dauer in Stdn. | $K_2CO_3$<br>in g. | $H_2O$<br>in g. | Dichteabnahme in $\gamma$ |      | Anzahl der<br>Teilversuche |
|----------------------------|-----------------------------|--------------------|-----------------|---------------------------|------|----------------------------|
|                            |                             |                    |                 | gef.                      | ber. |                            |
| Zimmertemp. <sup>(5)</sup> | 72                          | 45.0               | 20.0            | 0.2                       | 9.3  | 3                          |
| 100                        | 30                          | 40.0               | 20.0            | 11.1                      | 11.5 | 1                          |
| 180                        | 5                           | 40.0               | 20.0            | 10.7                      | 11.5 | 1                          |

(5) Vgl. auch T. Titani, N. Morita und K. Goto, dies Bulletin, **13** (1938), 329.

**Versuche in saurer Lösung.** Diese Versuche werden zunächst mit den Lösungen einiger saurer Salze und dann mit den der neutralen Salze, die aber durch den Zusatz des Kaliumbisulfats  $\text{KHSO}_4$  bzw. konzentrierter Salzsäure  $\text{HCl}$  angesäuert ist, ausgeführt. In den beiden Fällen geht die Austauschreaktion, besonders bei erhöhten Temperaturen, ziemlich schnell vor sich.

**Versuch 5. Primäres Kaliumarsenat.**

$\text{KH}_2\text{AsO}_4(100^\circ\text{C.}, 10 \text{ Stdn.}), \Delta s_a = 41.6 \gamma$  und  $\Delta s_a(\text{O}) = 26.1 \gamma$ .

| Versuchstemp. | Versuchsdauer in Stdn. | $\text{KH}_2\text{AsO}_4$ in g. | $\text{H}_2\text{O}$ in g. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|---------------|------------------------|---------------------------------|----------------------------|---------------------------|------|-------------------------|
|               |                        |                                 |                            | gef.                      | ber. |                         |
| Zimmertemp.   | 70                     | 27.0                            | 10.0                       | 17.0                      | 16.9 | 1                       |
| „             | 70                     | 27.0                            | 10.0                       | 16.2                      | 16.9 | 1                       |

**Versuch 6. Primäres Kaliumphosphat.**

$\text{KH}_2\text{PO}_4(150^\circ\text{C.}, 6 \text{ Stdn.}), \Delta s_a = 41.6 \gamma$  und  $\Delta s_a(\text{O}) = 26.1 \gamma$ .

| Versuchstemp. $^\circ\text{C.}$ | Versuchsdauer in Stdn. | $\text{KH}_2\text{PO}_4$ in g. | $\text{H}_2\text{O}$ in g. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|---------------------------------|------------------------|--------------------------------|----------------------------|---------------------------|------|-------------------------|
|                                 |                        |                                |                            | gef.                      | ber. |                         |
| Zimmertemp.                     | 20                     | 28.5                           | 20.0                       | 4.6                       | 13.7 | 3                       |
| 100                             | 100                    | 30.0                           | 20.0                       | 13.0                      | 14.1 | 1                       |

**Versuch 7. Kaliumbisulfat.**

$\text{KHSO}_4(150^\circ\text{C.}, 8 \text{ Stdn.}), \Delta s_a = 41.6 \gamma$  und  $\Delta s_a(\text{O}) = 26.1 \gamma$ .

| Versuchstemp. $^\circ\text{C.}$ | Versuchsdauer in Stdn. | $\text{KHSO}_4$ in g. | $\text{H}_2\text{O}$ in g. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|---------------------------------|------------------------|-----------------------|----------------------------|---------------------------|------|-------------------------|
|                                 |                        |                       |                            | gef.                      | ber. |                         |
| Zimmertemp.                     | 20                     | 30.0                  | 20.0                       | 6.0                       | 12.9 | 3                       |
| 100                             | 20                     | 24.0                  | 20.0                       | 10.8                      | 11.5 | 1                       |
| 180                             | 100                    | 30.0                  | 20.0                       | 12.6                      | 12.9 | 1                       |

**Versuch 8. Kaliumsulfat+Kaliumbisulfat.**

Die beiden Salze werden genau so wie beim Versuch 1 bzw. 7 vorbehandelt.  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(\text{O}) = 26.1 \gamma$ .

| Versuchstemp. $^\circ\text{C.}$ | Versuchsdauer in Stdn. | $\text{K}_2\text{SO}_4$ in g. | $\text{KHSO}_4$ in g. | $\text{H}_2\text{O}$ in g. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|---------------------------------|------------------------|-------------------------------|-----------------------|----------------------------|---------------------------|------|-------------------------|
|                                 |                        |                               |                       |                            | gef.                      | ber. |                         |
| 100                             | 20                     | 20.0                          | 4.0                   | 20.0                       | 2.0                       | 9.3  | 4                       |
| 100                             | 20                     | 30.0                          | 2.4                   | 20.0                       | 2.7                       | 10.8 | 6                       |
| 180                             | 20                     | 23.5                          | 6.75                  | 20.0                       | 9.5                       | 11.0 | 5                       |
| 180                             | 20                     | 22.0                          | 2.4                   | 20.0                       | 8.5                       | 9.3  | 4                       |

## Versuch 9. Kaliumnitrat + Kaliumbisulfat.

Die beiden Salze werden genau so wie beim Versuch 2 bzw. 7 vorbehandelt.  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$ .

| Versuchstemp. °C. | Versuchsdauer in Stdn. | KNO <sub>3</sub> in g. | KHSO <sub>4</sub> in g. | H <sub>2</sub> O in g. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|-------------------|------------------------|------------------------|-------------------------|------------------------|---------------------------|------|-------------------------|
|                   |                        |                        |                         |                        | gef.                      | ber. |                         |
| 180               | 20                     | 15.0                   | 3.0                     | 20.0                   | —                         | 8.4  | 1                       |

Bei diesem Versuch bemerkten wir, dass die Lösung sich während der Erwärmung allmählich schwach bräunlich gelb färbte und zugleich ein rotbrauner Dampf entwickelt wurde, der aber nicht entweichen konnte, da die Lösung wie üblich in einem zugeschmolzenen Glasrohr erwärmt wurde. Diese Färbung der Lösung sowie der Dampfphase blieb aber sogar noch nach der Erkaltung der Röhre zurück, obwohl in viel geringerem Masse als während der Erwärmung, und die so verunreinigte Lösung erwies sich sehr schwer zu reinigen. Deshalb haben wir diesen Versuch unterbrochen.

## Versuch 10. Natriumchlorat + Kaliumbisulfat.

Die beiden Salze werden genau so wie beim Versuch 3 bzw. 7 vorbehandelt.  $\Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$ .

| Versuchstemp. °C. | Versuchsdauer in Stdn. | NaClO <sub>3</sub> in g. | KHSO <sub>4</sub> in g. | H <sub>2</sub> O in g. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|-------------------|------------------------|--------------------------|-------------------------|------------------------|---------------------------|------|-------------------------|
|                   |                        |                          |                         |                        | gef.                      | ber. |                         |
| 100               | 10                     | 33.0                     | 6.0                     | 20.0                   | 12.9                      | 13.4 | 1                       |

Bei diesem Versuch bemerkten wir ähnlich wie beim vorhergehenden Versuch 9, dass die Lösung allmählich schwach gelb und die Dampfphase schwach gelblich braun während der Erwärmung gefärbt wurde und diese Färbung sogar nach der Erkaltung der Röhre, wenn auch in viel geringerem Masse als während der Erwärmung, zurückblieb. Aber weil das von dieser Lösung durch die Destillationen im Vakuum abgetrennte Wasser im Gegenteil zu dem vorhergehenden Versuch 9 mit KNO<sub>3</sub> ziemlich leicht gereinigt werden konnte, haben wir seinen Dichteüberschuss wie üblich bestimmt und fanden, dass die so gemessene Dichteabnahme des Wassers hinreichend gut mit dem berechneten Wert übereinstimmt, wie die obige Tabelle zeigt.

## Versuch 11. Kaliumsulfat + Salzsäure.

Man lässt 5.0 g. gut getrocknetes Kaliumsulfat zusammen mit 0.15 c.c. 37 prozentiger Salzsäure in 20.0 g. schweres Wasser sich auflösen und die so hergestellte Lösung in einem zugeschmolzenen Glasrohr 20 bzw. 100 Stdn. lang bei 180°C. stehen. Dann wird das Wasser durch die Destillation im Vakuum vom zugesetzten Kaliumsulfat abgetrennt und die dabei

zusammen mit dem Wasser abdestillierte Salzsäure unter Zusatz einer minimalen Menge festen Ätzkalis neutralisiert. Das auf diese Weise vom Kaliumsulfat sowie von der Salzsäure abgeschiedene Wasser wird wieder mit 5.0 g. Kaliumsulfat und 0.15 c.c. Salzsäure versetzt und 20 bzw. 100 Stdn. lang bei 180°C. stehen gelassen. Nach viermaliger Behandlung ein und desselben schweren Wassers immer mit erneutem Salz und Säure wird es davon abgeschieden, richtig gereinigt und sein Dichteüberschuss genau gemessen.

$K_2SO_4(200^\circ C., 5 \text{ Stdn.}), HCl(37\%), \Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$ .

| Versuchstemp. °C. | Versuchsdauer in Stdn. | $K_2SO_4$ in g. | $HCl(37\%)$ in c.c. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|-------------------|------------------------|-----------------|---------------------|---------------------------|------|-------------------------|
|                   |                        |                 |                     | gef.                      | ber. |                         |
| 180               | 20                     | 20.0            | 0.6                 | 5.6                       | 7.6  | 4                       |
| 180               | 100                    | 20.0            | 0.6                 | 5.0                       | 7.6  | 4                       |

#### Versuch 12. Natriumchlorat + Salzsäure.

Der Versuch wird auf ähnliche Weise wie beim vorerwähnten Versuch 11 ausgeführt.

$NaClO_3(200^\circ C., 8 \text{ Stdn.}), HCl(37\%), \Delta s_a = 41.6 \gamma$  und  $\Delta s_a(O) = 26.1 \gamma$ .

| Versuchstemp. °C. | Versuchsdauer in Stdn. | $NaClO_3$ in g. | $HCl(37\%)$ in c.c. | Dichteabnahme in $\gamma$ |      | Anzahl der Teilversuche |
|-------------------|------------------------|-----------------|---------------------|---------------------------|------|-------------------------|
|                   |                        |                 |                     | gef.                      | ber. |                         |
| 100               | 10                     | 25.0            | 0.15                | 5.2                       | 10.0 | 1                       |

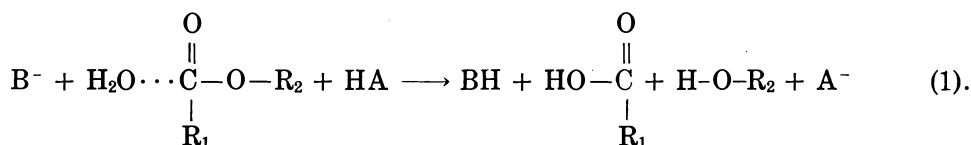
Bei diesem Versuch fanden wir ebenso wie beim Versuch 10 mit Natriumchlorat und Kaliumbisulfat aber in viel geringerem Masse als dabei, dass die Lösung sowie die Dampfphase während der Erwärmung schwach gelb gefärbt wurde.

**Diskussion.** Aus den oben angegebenen Versuchsergebnissen darf wohl geschlossen werden, dass die Austauschreaktion der O-Atome der anorganischen Anionen in wässriger Lösung nicht nur durch  $OH'$ -Ionen sondern auch durch  $H'$ -Ionen katalysiert wird.<sup>(6)</sup> Die naheliegendste Annahme für den Mechanismus dieser Austauschreaktion ist deshalb, wie darauf schon von Herbert und Lauder<sup>(7)</sup> hingewiesen wurde, dass sie nach dem ähnlichen Mechanismus wie bei der Verseifung des organischen Esters in wässriger Lösung verläuft. Betreffend des Mechanismus der Verseifung des Esters, oder im allgemeinen solch einer Reaktion, die nicht nur durch  $H'$ -Ionen sondern auch durch  $OH'$ -Ionen katalysiert wird, wird

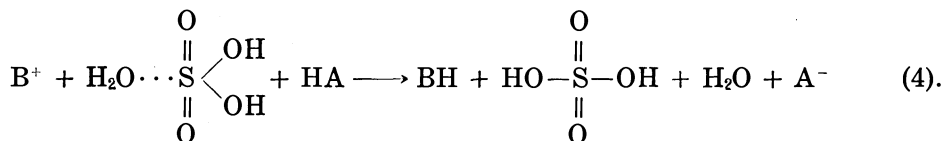
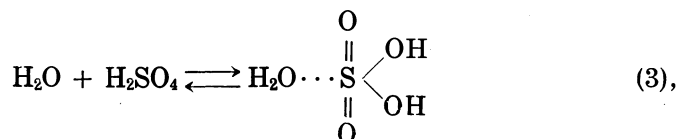
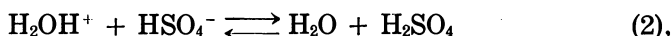
(6) Die katalytische Wirkung der  $H'$ - und  $OH'$ -Ionen auf die Austauschreaktion der O-Atome des Acetons in wässriger Lösung wurde schon von M. Cohn und H.C. Urey (*J. Am. Chem. Soc.*, **60** (1938), 679 und *J. Chem. Phys.*, **6** (1938), 175) gefunden.

(7) J.B.M. Herbert und I. Lauder, *Trans. Faraday Soc.*, **34** (1938), 1219; *Nature*, **142** (1938), 954.

neuerdings eine Theorie von Horiuti und Sakamoto<sup>(8)</sup> aufgestellt. Danach muss der geschwindigkeitsbestimmende Prozess bei dieser Art der säurebasen-katalytischen Reaktion derart sein, dass ein Proton von einer Brönstedtschen Säure zu einem Brückensauerstoffatom des Zwischenkomplexes bzw. Quasimoleküls angehängt wird, das sich zwischen dem betreffenden Estermolekül und Wasser bildet, und zugleich ein Proton von diesem Zwischenkomplex zu einer Brönstedtschen Base abgegeben wird. Das Estermolekül wird dabei durch die quantenmechanische Resonanz zwischen diesen beiden Prozessen in seine Bestandteile abgespalten. Das Reaktionsschema kann nämlich folgendermassen ausgedrückt werden:



In dieser Formel bedeutet HA und B<sup>-</sup> resp. die Brönstedtsche Säure und Base und R<sub>1</sub> und R<sub>2</sub> ein organisches Radikal. Aber weil die in der vorliegenden Arbeit untersuchte Austauschreaktion der anorganischen Anionen ebenfalls durch H<sup>+</sup>- und OH<sup>-</sup>-Ionen katalysiert wird, liegt die Annahme nahe, dass diese Reaktion auch nach dem ähnlichen Mechanismus verläuft. Wir können z.B. die Austauschreaktion des Bisulfations etwa wie folgend formulieren:



Dem durch Reaktion (2) gebildete neutralen undissoziierten Säuremolekül wird bei der darauffolgenden Reaktion (3) ein Wassermolekül angelagert und ein Zwischenkomplex bzw. Quasimolekül gebildet. Diese beiden Reaktionen müssen aber sehr schnell verlaufen und folglich sich immer im Gleichgewicht halten. Beim letzten geschwindigkeitsbestimmenden Prozess (4) wird aber, ähnlich wie bei der Verseifung des Esters, ein Proton von einer Brönstedtschen Säure HA an einem Hydroxylsauerstoffatom dieses Zwischenkomplexes angehängt, zugleich ein Proton von diesem letzteren zu einer Brönstedtschen Base B<sup>-</sup> abgegeben und der Zwischenkomplex wieder im Säuremolekül und Wasser abgespalten. Es ist ohne weiteres klar, dass die sämtlichen O-Atome des Säuremoleküls und folglich des betreffenden Anions durch die nacheinander folgende Zirkulation

(8) J. Horiuti und Y. Sakamoto, noch nicht veröffentlicht.

dieser drei Teilreaktionen (2) bis (4) allmählich gegen die des Wassers ausgetauscht werden.

Falls nun die Austauschreaktion der O-Atome der anorganischen Anionen wirklich nach dem oben angegebenen der Verseifung des organischen Esters ähnlichen Mechanismus stattfindet, dann kann es sehr aussichtsreich sein, die säurekatalysierte Austauschreaktion der O-Atome nicht nur in einem an schwerem Sauerstoff angereicherten Wasser, d.h. nicht nur in  $\text{H}_2\text{O}^{18}$ , sondern auch in einem an beigen Arten der schweren Isotope angereicherten Wasser, nämlich in  $\text{D}_2\text{O}^{18}$ , auszuführen und die Austauschgeschwindigkeit in beiden Fällen zu vergleichen. Aber bevor wir auf diese Frage eingehen, müssen wir noch eine andere Möglichkeit für den Mechanismus der Austauschreaktion in Erwägung ziehen. Nämlich, dass das durch die oben angegebene Reaktion (2) gebildete undissoziierte Säuremolekül reversibel in Anhydridmolekül und Wasser gespalten wird, wie z.B.:



Wenn solch eine reversible Dissoziation des Säuremoleküls wirklich in der Lösung stattfindet, dann kann die Austauschreaktion offensichtlich auch dadurch herbeigeführt werden und diese letztere Möglichkeit können wir besonders bei den Versuchen in saurer Lösung und bei erhöhten Temperaturen nicht ausser Acht lassen. Wir haben tatsächlich bei den Versuchen in saurer Lösung mit solchen Anionen, die flüchtige Anhydridmoleküle bilden können, wie z.B. beim Versuch 9 mit Kaliumnitrat + Kaliumbisulfat, beim Versuch 10 mit Natriumchlorat + Kaliumbisulfat sowie beim Versuch 12 mit Natriumchlorat + Salzsäure, ein deutliches Anzeichen für die Bildung der Anhydridmoleküle der betreffenden Säuren und zugleich die ziemlich glatt verlaufende Austauschreaktion beobachten können. Aber augenblicklich ist es uns nicht möglich, zwischen diesen beiden Möglichkeiten so ohne weiteres einen Entscheid zu treffen, bis die Reaktion noch eingehender wie z.B. kinetisch untersucht wird. Jedoch allem Anschein nach möchten wir lieber annehmen, dass im allgemeinen die beiden Mechanismen gleichzeitig bzw. nebeneinander eine Rolle spielen. Diese Annahme liegt natürlich um so näher, wenn die Reaktion in saurer Lösung stattfindet. Aber auch wenn die Reaktion in alkalischer Lösung ausgeführt wird, lässt sich die Möglichkeit der Austauschreaktion durch die Anhydridbildung nicht ohne weiteres von der Hand weisen, falls die Alkalinität von der hydrolytischen Spaltung des in Rede stehenden Salzes selbst herbeigeführt wird, wie z.B. dies beim vorliegenden Versuch 4 mit Kaliumcarbonat der Fall ist.

Zum Schluss möchten wir der Nippon-Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Ausführung der vorliegenden Arbeit unseren wärmsten Dank aussprechen.

*Physikalisch-chemisches Laboratorium  
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*und*

*Siomi Institut für physikalische  
und chemische Forschung.*



# The Molecular Configuration of Diphenyl Ether as Revealed by Dipole Moment Data.

By Keniti HIGASI and Shojiro UYEO.

(Received February 18, 1939.)

The dipole moments of 2,2'-dinitro-, 2,2'-diiodo- and 2,2'-dimethyl-diphenyl ethers were measured in benzene and hexane solutions at 27° and 50°. Four isomers of dimethyl-diphenyl ethers were also studied in benzene solution at 30°. The results obtained for them lead to the conclusion that each benzene ring is perpendicular to the other ring in the molecules considered.

It is not long ago that diphenyl ether, quite a familiar substance to chemists, was found to be playing an important role in the natural world, its skeleton being often found in extracts from plants etc. For instance the work of H. Kondo and his pupils<sup>(1)</sup> might be mentioned, who discovered the skeleton of this molecule in many alkaloids extracted from plants proper to Japan. In connection with this, Y. Asahina and his co-workers<sup>(2)</sup> showed that diphenyl ether is also the mother structure of some acids which are found in lichens. Moreover, certain alkaloids, derivatives of diphenyl ether, have recently been found to be of special interest from the chemotherapeutical point of view.<sup>(3)</sup> Thus, it has become necessary for pharmacutists as well as for chemists to make a research into the molecular configuration of diphenyl ether.

Many investigations of this substance are known from the side of pure physics and chemistry and many heated discussions have taken place about the valency angle of its oxygen atom. The paper of Hare and Mack<sup>(4)</sup> is probably the first one relating to this angle. It was based on the collision area method, and gave the angle as 107°, but this value is not certain. We must mention next, the investigation by the dipole moment method, by which an abnormally large angle was deduced at first.<sup>(5)</sup> But the interpretations of the results were severely criticized by Bennett,<sup>(6)</sup> who concluded the angle of 109.5° as the more trustworthy. Afterwards, the problem of the valency angle was reexamined by Sutton and Hampson<sup>(7)</sup> and the angle of diphenyl ether was determined as  $128^\circ \pm 4^\circ$ .<sup>(8)</sup>

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(1) Kondo and Tomita, *Arch. Pharm.*, **274** (1936), 65.

(2) Asahina and co-workers, *Ber.*, **66** (1933), 689, 893, 1031, 1215, etc.; see also Richter-Anschutz, "Chemie der Kohlenstoffverbindungen," Vol. II, 1, 394-398.

(3) Unpublished.

(4) Hare and Mack, *J. Am. Chem. Soc.*, **54** (1932), 4272.

(5) Hampson, Farmer, and Sutton, *Proc. Roy. Soc. (London)*, A, **143** (1933), 147; Bergmann and Tschudnowsky, *Z. physik. Chem.*, B, **17** (1932), 107; Smyth and Walls, *J. Am. Chem. Soc.*, **54** (1932), 3230.

(6) Bennett, *Trans. Faraday Soc.*, **30** (1934), 853.

(7) Sutton and Hampson, *ibid.*, **31** (1935), 945.

(8) Quite recently a revision of this angle was carried out by Coop and Sutton, by making a new determination of dipole moment in the vapour phase, *J. Chem. Soc.*, **1938**, 1869. The corrected value is  $124^\circ \pm 5^\circ$  which shows a better agreement with the value of Maxwell than their earlier one.

On the other hand, using the electron diffraction method, Maxwell and his co-workers<sup>(9)</sup> obtained the value of  $118^\circ \pm 3^\circ$ , which lies between  $128^\circ$  and  $109^\circ$  (Fig. 1).

Contrary to the valency angle of oxygen, little attention has been paid to the problem of the structure of the molecule as a whole, i.e. about

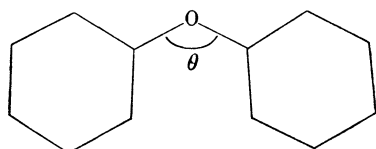


Fig. 1.

the orientation of each benzene nucleus in it. This is in sharp contrast to the development of study on the stereo-chemistry of diphenyl derivatives. Pauling,<sup>(10)</sup> however, suggested in conversation with Sutton that the two benzene rings might be fixed in the same plane—a result which is expected if there be strong resonance

among the following structures A and B (Fig. 2). But there seemed no further support for it than the apparent widening of the angle of oxygen.<sup>(7)</sup> The other structure which the organic chemists imagine instinctively to

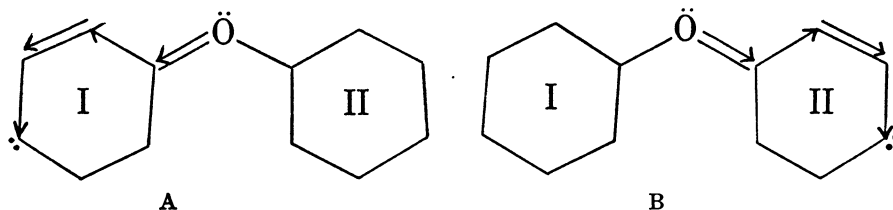


Fig. 2.

be stable is that the two benzene rings are perpendicular to the plane of the valency of oxygen. For instance, Smyth<sup>(11)</sup> seemed to hold this opinion when he spoke of the rotational vibration around this position.

Morino<sup>(12)</sup> has recently made calculations on the interaction force between the H atoms of the neighbouring rings. One of the results is that the plane structure corresponds to a big increase in the potential energy and is unstable unless a pronounced resonance does occur. The second result is that Smyth's structure does not correspond to the lowest position of this potential energy, and that this condition is attained when one benzene ring is approximately perpendicular to the other (Fig. 3). The present investigation was undertaken in order to examine the suggestions of Pauling and Smyth in view of the recent research of Morino.

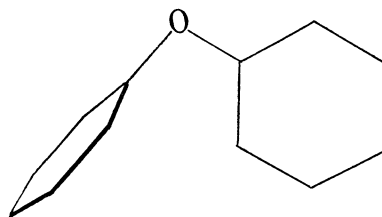


Fig. 3.

### Experimental.

In order to realise the aim thus outlined, it was decided to measure dipole moments in solution and to do this over a wide range of temperature

(9) Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, **3** (1935), 699.

(10) Cited in the paper of Sutton and Hampson, *Trans. Faraday Soc.*, **31** (1935), 945.

(11) Smyth and Walls, *J. Am. Chem. Soc.*, **54** (1932), 3230.

(12) Private communication; the details of his calculation will appear shortly.

with the use of as many solvents as possible. Attention had also to be given to the choice of the solute substances; and 2,2'-dinitro- and 2,2'-diiodo-diphenyl ethers (m.p. 115° and 66° respectively) were prepared<sup>(13)</sup> in the present research, the reason being that these substances can be obtained in the form of pure crystals and also because they have many advantages over their position isomers in the discussion of molecular structure. Five isomers of dimethyl-diphenyl ethers, the pure samples of which had been prepared by Dr. Tomita<sup>(14)</sup> and were kindly given to us, were also studied for comparison.

Full details of the present research, i.e. the apparatus, the data of dielectric constants and densities, preparations of materials and their purity etc. will not be described here, because they may be found in other places.<sup>(15)</sup> In the following tables the results are summarized in six columns: (1) The sample employed as solute, (2) the temperature in °C., (3) the solvent employed, (4) the polarisation, (5) the dipole moment calculated from  $P - MR_D$ , (6) the dipole moment calculated after Groves-Sugden,<sup>(16)</sup> viz.  $P - 1.05 MR_D$ .

The results of these tables present many features. One is the small solvent effect as seen from the difference between the apparent moments in solution. This gives a clear proof that the observed moments are fairly trustworthy and moreover, that benzene does not exert such an anomalous solvent action to the solute as it does on ethylene chloride.<sup>(17)</sup> From this, one can safely expect that the small temperature coefficient of moment in benzene is reliable. Moreover, one may notice that the difference between  $\mu$  and  $\mu'$  is quite small in the case of dinitro- and diiodo-compounds. There-

Table 1.

| Substance                    | $t^{\circ}\text{C.}$ | Solvent                | $P(\text{c c})$ | $\mu(\text{D})$ | $\mu'(\text{D})$ |
|------------------------------|----------------------|------------------------|-----------------|-----------------|------------------|
| 2,2'-Dimethyl-diphenyl ether | 27                   | Benzene                | 75.2            | 0.83            | 0.73             |
|                              | 50                   | „                      | 74.4            | 0.84            | 0.73             |
|                              | 27                   | Hexane                 | 74.7            | 0.82            | 0.72             |
| 2,2'-Dinitro-diphenyl ether  | 27                   | Benzene                | 970             | 6.64            | 6.62             |
|                              | 50                   | „                      | 890             | 6.57            | 6.56             |
|                              | 27                   | Dioxan <sup>(18)</sup> | 992             | 6.72            | 6.70             |
| 2,2'-Diiodo-diphenyl ether   | 27                   | Benzene                | 230             | 2.72            | 2.69             |
|                              | 50                   | „                      | 225             | 2.78            | 2.74             |
|                              | 27                   | Hexane                 | 228             | 2.70            | 2.67             |

(13) Higasi and Uyeo, *J. Chem. Soc. Japan*, **60** (1939), 204.

(14) Tomita, *J. Pharm. Soc. Japan*, **57** (1937), 76.

(15) Apparatus, Higasi, this Bulletin, **13** (1938), 158. The data of dielectric constants and densities, Uyeo and Higasi, *J. Chem. Soc. Japan*, **60** (1939), 199, 204. Preparation of Materials, Higasi and Uyeo<sup>(13)</sup>, Tomita<sup>(14)</sup>.

(16) Groves and Sugden, *J. Chem. Soc.*, **1935**, 971.

(17) Mizushima, Morino, and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159.

(18) 2,2'-Dinitro-diphenyl ether is hardly soluble in hexane, so dioxan was employed as solvent instead of hexane. As this solvent may not be so neutral as hexane, allowance must be made of its specific action on the moment.

Table 2.

| Substance                                    | $t^{\circ}\text{C.}$ | Solvent | $P(\text{c.c.})$ | $\mu(\text{D})$ | $\mu'(\text{D})$ |
|----------------------------------------------|----------------------|---------|------------------|-----------------|------------------|
| 3,3'-Dimethyl-diphenyl ether                 | 30                   | Benzene | 101.0            | 1.40            | 1.35             |
| 4,4'-Dimethyl-diphenyl ether <sup>(19)</sup> | "                    | "       | 104.6            | 1.46            | 1.41             |
| 3,4'-Dimethyl-diphenyl ether                 | "                    | "       | 102.0            | 1.42            | 1.36             |
| 3,4-Dimethyl-diphenyl ether                  | "                    | "       | 109.0            | 1.53            | 1.49             |

fore, it is evident that the error arising from atomic polarisation is insignificant in these molecules. For dimethyl-diphenyl ethers, however, this error becomes rather serious on account of their small moments.

It may be concluded, therefore, that the moments of the above molecules are not much affected by solvent,<sup>(20)</sup> temperature, and also by the choice of atomic polarisation, and if dimethyl-diphenyl ethers should be regarded as an exception, these are affected only by the last.

### Discussion.

For convenience' sake we shall first discuss the results of Table 1. And then, using the conclusions drawn from them, we shall discuss the dipole moments of isomeric dimethyl-diphenyl ethers (Table 2).

**Free Rotation and Contour Map of Moment.** The molecule of 2,2'-disubstituted diphenyl ether has four polar linkages, i.e. two C—O bonds and two C—X bonds (X being the substituent), but we may represent the two C—O bond moments by its resultant ( $\mu_1$ ) which bisects the valency angle of the oxygen atom (Fig. 4). According to the classical view of organic chemistry, this molecule has two axes of rotation, so that for describing the intramolecular configuration, two parameters,  $\theta_1$  and  $\theta_2$  are necessary which will be defined as follows.

Consider a Cartesian co-ordinate system (Fig. 5) and let the Z axis coincide with the direction of  $\mu_1$  and choose the YZ plane on the C—O—C plane. Now, each substituent is capable of rotation around the corresponding C—O line, the azimuths of rotation  $\theta_1$  and  $\theta_2$  for  $\mu_2$ , right and left respectively, will be defined as follows:  $\theta_1$  and  $\theta_2$  are zero, when they lie on the YZ plane on the right side of the corresponding C—O line, and the positive sense is taken as in the left hand screw (see Fig. 5).

(19) The result for 4,4'-dimethyl-diphenyl ether may be compared with that of Hampson, Farmer, and Sutton, *Proc. Roy. Soc. (London)*, A, **143** (1933), 147. They gave it  $P = 104.5$  c.c. at  $25^{\circ}\text{C.}$  which corresponds to  $P = 103.8$  c.c. at  $30^{\circ}\text{C.}$  The dipole moment of this substance was newly determined in the vapour phase by Coop and Sutton, *J. Chem. Soc.*, **1938**, 1869. The result was  $\mu = 1.44$  D, and  $P_2$  at  $30^{\circ}$  estimated from it is 108.0 c.c.

(20) It may be too bold to say so without any corresponding data in the vapour phase. But according to the theory of solvent effect, this error would not be serious—not so serious at least as 4,4'-disubstituted diphenyl ether.

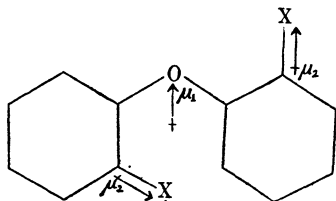


Fig. 4.

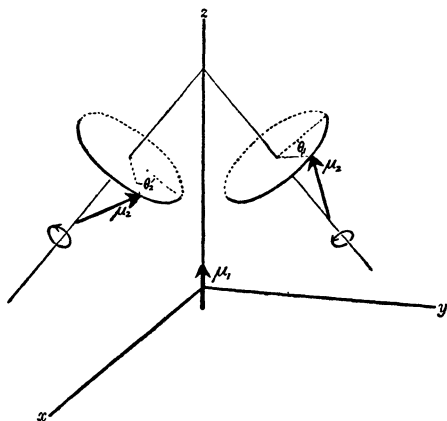


Fig. 5.

And the moment of a molecule as a whole,  $\mu$  can be expressed by the following relation.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (1)$$

where

$$\left. \begin{aligned} \mu_x &= \mu_2(\sin \theta_1 + \sin \theta_2) \sin 60^\circ \\ \mu_y &= \mu_2(\cos \theta_1 + \cos \theta_2) \sin 60^\circ \cos \varphi \\ \mu_z &= \mu_1 + 2\mu_2 \cos \varphi \cos 60^\circ + \mu_2 \sin \varphi (\cos \theta_1 - \cos \theta_2) \sin 60^\circ \end{aligned} \right\} \quad (2)$$

where  $\varphi$  denotes half of the valency angle of oxygen.

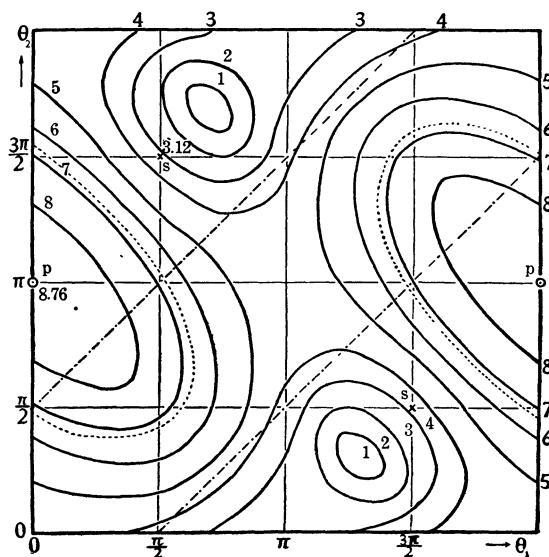


Fig. 6. 2,2'-Dinitro-diphenyl ether :  $\mu_1 = 1.14D$ ,  $\mu_2 = 3.80D$ .

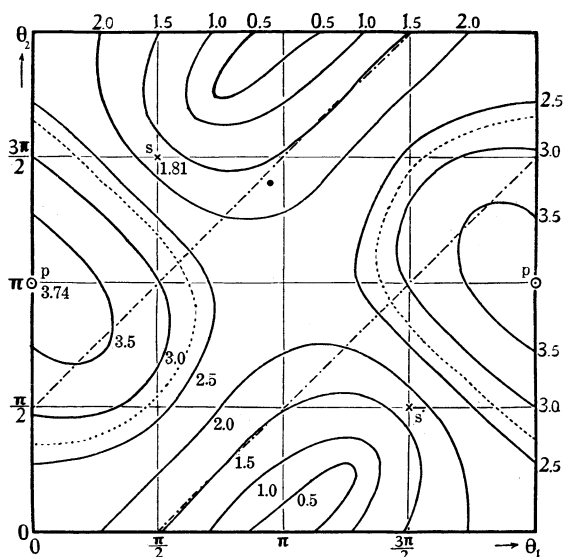


Fig. 7. 2,2'-Diiodo-diphenyl ether :  $\mu_1 = 1.14\text{D}$ ,  $\mu_2 = 1.30\text{D}$ .

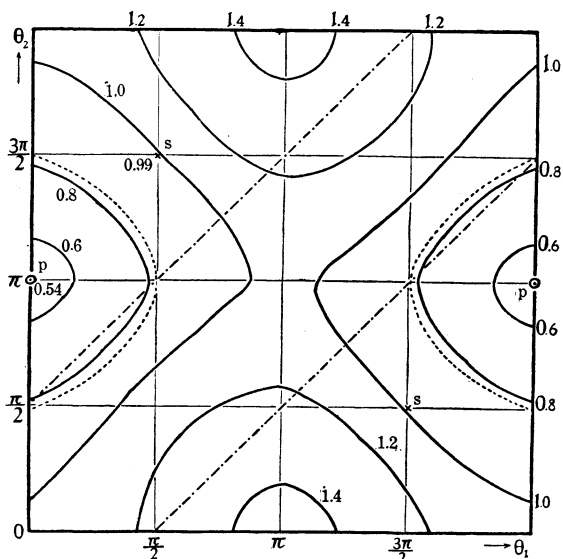


Fig. 8. 2,2'-Dimethyl-diphenyl ether :  $\mu_1 = 1.14\text{D}$ ,  $\mu_2 = -0.30\text{D}$ .

As  $\mu_1$ ,  $\mu_2$  and  $\varphi$  can be estimated, we can easily calculate the total moment  $\mu$  as a function of  $\theta_1$  and  $\theta_2$ . The results of the calculation by this way are shown in the three contour maps of dipole moment (see Fig. 6, 7, and 8). The assumptions which were made in this calculation are as follows. (1) Half of the oxygen valency angle,  $\varphi = 118^\circ/2$ ; (2) the resultant moment of two C—O bond moments,  $\mu_1 = 1.14\text{D}$ ; <sup>(21)</sup> (3) the C—X bond moment,  $\mu_2 = 3.80\text{D}$  (X = NO<sub>2</sub>),  $1.30\text{D}$  (X = I),  $-0.30\text{D}$  (X = CH<sub>3</sub>).

(21) According to the new determination by Coop and Sutton, *J. Chem. Soc.*, **1938**, 1869, the moment of diphenyl ether in the vapour phase is  $1.14\text{D}$ .

It is clear that the reliability of the contour maps (Fig. 6, 7, and 8) is dependent upon the validity of these assumptions as well as that of the above equations. Therefore, we shall discuss these more carefully afterwards. But in the following, we shall assume that the contour maps are fairly correct, and using them we shall discuss the molecular configuration of diphenyl ether.

**The Plane Formula of Pauling.** There are three plane formulae for disubstituted diphenyl ether, i.e., A, B, and C (Fig. 9). In the case of 2,2'-disubstituted compounds, however, the structures B and C should be excluded on account of big repulsion.

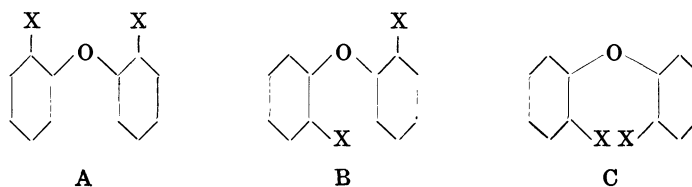


Fig. 9.

No explanation will be needed for the structure C. On constructing a model<sup>(22)</sup> of a 2,2'-disubstituted molecule, it will be also understood why the structure B is untenable. For instance, at a model of 2,2'-diiododiphenyl ether, one would find the distance between I and H atoms (of the neighbouring ring), if they are in the structure B, much smaller than the H-I distance of the chemically combined atoms. For dinitrodiphenyl ether the N-H distance for B would be estimated as 0.3 Å in contrast to the N-H distance of 1.0 Å of the combined atoms. Therefore, it is quite evident that a considerable repulsion occurs at this structure.<sup>(23)</sup>

Thus the only possible structure is A which corresponds to a point,  $\theta_1 = 0$ ,  $\theta_2 = \pi$  in the contour maps (marked by  $\odot$  in Fig. 6, 7, 8). And the moments at this position are calculated as 8.76D, 3.74D, 0.54D for dinitro-, diiodo-, and dimethyl-diphenyl ethers, respectively, while the observed moments are 6.64D, 2.72D, and 0.83D, respectively. The differences are certainly too large to be explained as experimental errors.

**The Configuration according to Smyth.** If we neglect the mutual interaction between the substituent groups, according to Smyth, there should be two probable configurations of disubstituted diphenyl ether; i.e. trans (D) and cis (E) forms (see Fig. 10) and the molecule might be supposed to be vibrating near both positions. In the 2,2'-disubstituted compounds, however, the substituents X approach each other and a big repulsion results at the cis position. For example, in 2,2'-diiodo-diphenyl ether the

(22) A molecular model can be easily constructed with the use of data found in books like Stuart, "Molekülstruktur," Sidgwick, "Covalent Links in Chemistry." See also Pauling and Huggins, *Z. Krist.*, **84** (1933), 205.

(23) In order to make this structure stable, the valency angle of oxygen should be widened to a great extent, more than ca. 160°.

I—I distance becomes  $2\text{\AA}$  for the E structure, while that of the combined atoms is  $2.7\text{\AA}$ . In the molecule of 2,2'-dinitro-diphenyl ether, the O—O

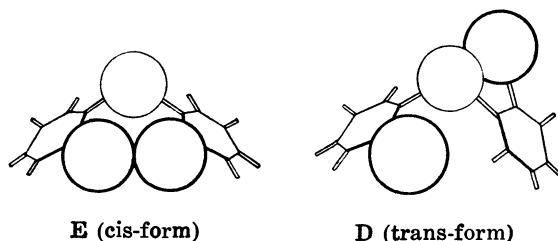


Fig. 10. Molecular model according to Smyth of 2,2'-disubstituted diphenyl ether.  
○ Oxygen atom.    ○ Substituent.

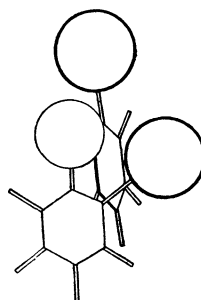


Fig. 11. Molecular model according to Morino of 2,2'-disubstituted diphenyl ether.

distance for E becomes less than  $1.9\text{\AA}$ , which is certainly larger than that of the combined atoms  $1.2\text{\AA}$ , but smaller than that of closest packing  $2.72\text{\AA}$ . Therefore this position seems to be also improbable.

As a conclusion from the above, we may say that the trans form D has a much lower potential energy than cis form E and it will be sufficient to consider vibrations near this position which corresponds to the points  $\theta_1 = \frac{\pi}{2}$ ,  $\theta_2 = \frac{3\pi}{2}$  and  $\theta_1 = \frac{3\pi}{2}$ ,  $\theta_2 = \frac{\pi}{2}$  (marked with  $\times$  in the contour diagrams).

If the vibration has a small amplitude, we may expect at inspection of the map that the moment will not differ very much from that for the structure D. Therefore, for 2,2'-dinitro-, diiodo-, and dimethyl-diphenyl ether, the moments of 3.1D, 1.8D and 1.0D are estimated respectively. The difference between these and the observed moments are much more pronounced.

**The Molecular Configuration according to Morino.** The potential due to the repulsion between H atoms of the neighbouring rings was carefully traced by Morino of the Chemical Institute and it was found that the lowest valley in the potential diagram lies on two straight lines  $\theta_2 = \theta_1 \pm \frac{\pi}{2}$  in the contour map—approximately speaking, one benzene ring is situated perpendicular to the other.

If all the positions on these lines are equally probable, the mean moment  $\bar{\mu}$  is calculated as follows by putting  $\theta_2 = \theta_1 \pm \frac{\pi}{2}$  in equation (1).

$$\bar{\mu}^2 = \frac{\int_0^{2\pi} \mu^2 d\theta_1}{\int_0^{2\pi} d\theta_1} \quad (3)$$

This definite integral is easily evaluated, and the resultant equation is



$$\bar{\mu}^2 = (\mu_1 + \mu_2 \cos \varphi)^2 + 1.5\mu_2^2 \quad (4)$$

Putting  $\varphi = 59^\circ$ ,  $\mu_1 = 1.14\text{D}$ ,  $\mu_2 = 3.80\text{D}$ ,  $1.30\text{D}$ ,  $-0.30\text{D}$  for  $-\text{NO}_2$ ,  $-\text{I}$ ,  $-\text{CH}_3$  respectively, the following values shown in the third column of the table are obtained.

Table 3.

| Substance                                                 | Observed value | Calculated moment |         |       |
|-----------------------------------------------------------|----------------|-------------------|---------|-------|
|                                                           |                | Morino            | Pauling | Smyth |
| 2,2'-( $\text{NO}_2\text{C}_6\text{H}_4$ ) <sub>2</sub> O | 6.64D          | 5.59D             | 8.76D   | 3.1D  |
| 2,2'-( $\text{IC}_6\text{H}_4$ ) <sub>2</sub> O           | 2.72D          | 2.41D             | 3.74D   | 1.8D  |
| 2,2'-( $\text{CH}_3\text{C}_6\text{H}_4$ ) <sub>2</sub> O | 0.83D          | 1.05D             | 0.54D   | 1.0D  |

Although, the calculated moments do not show close agreement with the experimental values, the differences between them are not so marked as in the cases of the Pauling and Smyth structures.

In the above calculation we assumed that any position on the lines of  $\theta_2 = \theta_1 \pm \frac{\pi}{2}$  is equally probable.<sup>(24)</sup> But this assumption becomes certainly invalid when a big atom or group is introduced to the 2,2'-position. For instance, the structure F would be rather improbable on account of great repulsion (Fig. 12). The dipole moment at this position,  $\theta_1 = \pi$ ,  $\theta_2 = \frac{3\pi}{2}$  ( $\theta_2 = \theta_1 + \frac{\pi}{2}$ ),  $\theta_1 = \pi$ ,  $\theta_2 = \frac{\pi}{2}$  ( $\theta_2 = \theta_1 - \frac{\pi}{2}$ ) is much smaller than the average value, viz. 3.72D, 1.52D for dinitro- and diiodo-diphenyl ether, while it is larger than the average value in the case of dimethyl-diphenyl ether, i.e. 1.25D.

Therefore, if this structure is excluded in the above calculation the resulting moments would approach the observed values. Therefore, we may consider as follows: each benzene ring can rotate around the corresponding C-O axis on the two conditions: (1) one ring is almost perpendicular to the other and (2) the rotation near the position F is not allowed.

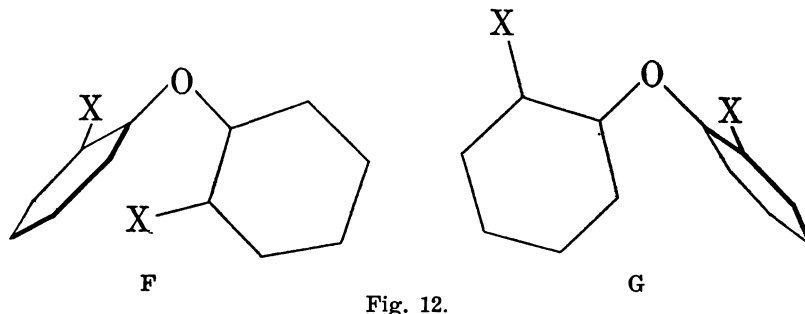


Fig. 12.

(24) This condition is satisfied in the case of diphenyl ether, but not necessarily so in the case of its derivatives.

In the contour map of dipole moment, we denoted the positions which correspond to the observed moment by the dotted lines (....) and the  $\theta_2 = \theta_1 \pm \frac{\pi}{2}$  relation by (---) lines. It should be noted that the crossing of two dotted lines is always found near the positions  $\theta_1 = \frac{\pi}{2}$ ,  $\theta_2 = \pi$  or  $\theta_1 = \frac{3\pi}{2}$ ,  $\theta_2 = \pi$  in each map for the three substances. This is an interesting fact which should not be overlooked as a mere coincidence. The simplest explanation for it is, of course, to suppose that the molecule considered has the solid structure G (Fig. 12) corresponding to the position  $\theta_1 = \pm \frac{\pi}{2}$ ,  $\theta_2 = \pi$ . (See also the model in Fig. 11.)

Alternatively, we may assume rotational vibration near this position. Because any vibration near it, (if its amplitude be small), would not much alter the value of average moment from that at G. Moreover, this vibrational structure explains the small temperature coefficient of dipole moment, because the increase in amplitude which should accompany the rise of temperature will not exert a very marked influence on the average dipole moment which is easily understood from the nature of the contour map.

**The Dipole Moments of Dimethyl-diphenyl Ethers.** So far, we have considered, 2,2'-disubstituted compounds only. Next, we shall discuss the results of the other derivatives of diphenyl ether in a few words. We can treat them just as we did before, and in the following table we show the comparison of the observed and calculated values (as the error due to the atomic polarisation is most serious in them, both  $\mu$  and  $\mu'$  are tabulated).

The observed moments show fairly good agreement with the mean moments calculated according to Morino. In this calculation, we assumed any position satisfying  $\theta_2 = \theta_1 \pm \frac{\pi}{2}$  is equally probable. This as-

Table 4.

|                              | Observed moment |        | Calculated moment |                         |
|------------------------------|-----------------|--------|-------------------|-------------------------|
|                              | $\mu$           | $\mu'$ | Morino            | Pauling <sup>(25)</sup> |
| 3,3'-Dimethyl-diphenyl ether | 1.40D           | 1.35D  | 1.35D             | 0.76D<br>1.33D<br>1.84D |
| 3,4'-Dimethyl-diphenyl ether | 1.42D           | 1.36D  | 1.40D             | 1.12D<br>1.68D          |
| 3,4-Dimethyl-diphenyl ether  | 1.53D           | 1.49D  | 1.46D             | 1.27D<br>1.48D          |
| 4,4'-Dimethyl-diphenyl ether | 1.46D           | 1.41D  | 1.45D             | 1.46D                   |

(25) The following values are assumed in this calculation :

$$\theta = 125^\circ, \mu_1 = 1.14\text{D}, \mu_2 = -0.35\text{D}$$

sumption can be justified in these cases because the substituents are separated far from the neighbouring benzene rings and also from each other, i.e. the repulsion force is expected to be small.

From the same reason, there are a few possible plane structures deduced from Pauling's theory which differ in dipole moment, and the observed moments lie between the corresponding maximum and minimum values.<sup>(25)</sup> But this is insignificant, because the Pauling structure was found to be rather contradicting in the above case of 2,2'-disubstituted diphenyl ether.

**Notes on Assumptions.** (1) *The valency angle of oxygen.* In the above discussion the valency angle of oxygen was assumed to be  $118^\circ$ .<sup>(9)</sup> What becomes if the angle be different from the assumed value, will be the next problem to be solved. If the widening of the angle did occur, Pauling's structure might be right after all? In order to answer this question, the following table may be found helpful in which the values of bond moments which are needed for Pauling's and Smyth's structure are given for different values of the valency angle.

Table 5.<sup>(26)</sup>

| Valency angle<br>of oxygen | $\mu(\text{C}-\text{NO}_2)$ |       | $\mu(\text{C}-\text{I})$ |       |
|----------------------------|-----------------------------|-------|--------------------------|-------|
|                            | Pauling                     | Smyth | Pauling                  | Smyth |
| $90^\circ$                 | 3.16                        | 7.79  | 0.90                     | 2.24  |
| $100^\circ$                | 2.92                        | 8.56  | 0.83                     | 2.46  |
| $110^\circ$                | 2.78                        | 9.58  | 0.79                     | 2.76  |
| $120^\circ$                | 2.74                        | 11.00 | 0.78                     | 3.16  |
| $130^\circ$                | 2.78                        | 13.00 | 0.79                     | 3.74  |
| $140^\circ$                | 2.92                        | 16.10 | 0.83                     | 4.62  |
| $150^\circ$                | 3.16                        | 21.22 | 0.90                     | 6.10  |

The bond moments assumed in the present paper are as follows:  $\mu(\text{C}-\text{NO}_2) = 3.80$ ,  $\mu(\text{C}-\text{I}) = 1.30$ ,  $\mu(\text{Ph}_2\text{O}) = 1.14$ . The same value for  $\mu(\text{Ph}_2\text{O})$  is employed in the calculation of Table 5.

At a glance at the above table it is evident that Smyth's structure can be ruled out, because it corresponds to a too big bond moment even when the angle decreases to  $90^\circ$ . On the other hand the bond moments for Pauling's structure are smaller than the value ordinarily proposed. With the widening of the angle, this difference gets smaller indeed, but even at  $\theta = 150^\circ$  it is still of a magnitude for which some explanation<sup>(27)</sup> is required.

(26) The moments are expressed in Debye units, i.e.  $10^{-18}$  e.s.u.

(27) The interaction moments which account for this will be

$$\delta\mu(\text{C}-\text{NO}_2) = 0.64\text{D} \quad \delta\mu(\text{C}-\text{I}) = 0.48\text{D}.$$

And if we take the moments of nitrobenzene and iodobenzene in the vapour phase, 4.23D and ca. 1.6D as the standard,  $\delta\mu(\text{C}-\text{NO}_2)$ ,  $\delta\mu(\text{C}-\text{I})$  will be 1.07D and 0.7D respectively. (Continued to the next page.)

(2) *Induction effect.* In the above discussion we neglected entirely the induction effect in the first approximation. But this effect on the bond moments of the molecule can be easily estimated<sup>(29)</sup> and in the following table the results of estimation are shown.

Table 6.<sup>(26)</sup> Induction effect on bond moment.

| Substance                                                             | Calculated moment without correction of induction | Calculated moment with correction of induction effect |
|-----------------------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------|
| 2,2'-(NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> O | 8.74                                              | 8.49                                                  |
| 2,2'-(I·C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> O                | 3.74                                              | 3.05                                                  |
| 2,2'-(CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> O | 0.54                                              | 0.54                                                  |

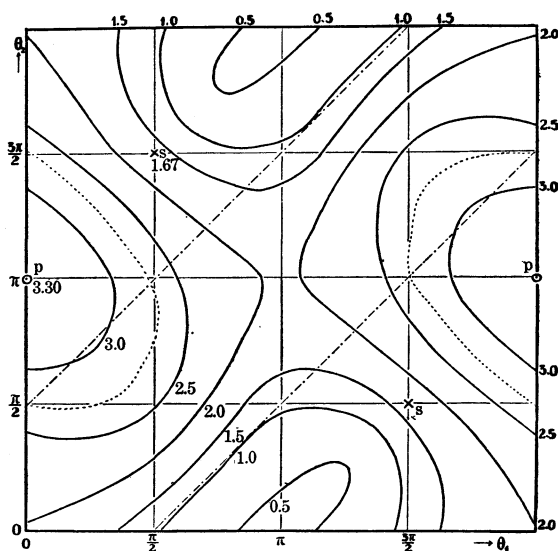


Fig. 13. 2,2'-Diiodo-diphenyl ether:  $\mu_1 = 1.10D$ ,  $\mu_2 = 1.10D$ .

It should be emphasized that the induction effect in 2,2'-dinitro-diphenyl ether is too small to be considered. Therefore if the change of bond moment be needed for this molecule it is clear that induction effect

On the other hand, we must recall that the group moment  $\mu(C-X)$  was assumed to lie on the C-X line in eq. (2). This assumption is certainly valid, when no interaction of moment occurs. But if such an interaction as considered by Sutton, *Trans. Faraday Soc.*, **31** (1935), 945, occurs, we must employ  $\sin(60^\circ + \delta)$ ,  $\cos(60^\circ + \delta)$  instead of  $\sin 60^\circ$ , etc. in the above equations. And if we confine our attention to the plane formula, the change in the angle of oxygen will bring about the same result as the introduction of  $\delta$ , viz., the widening of the angle can be interpreted as the finite value of  $\delta$ .

Therefore the writers do not regard this as a complete proof that the plane structure is improbable.

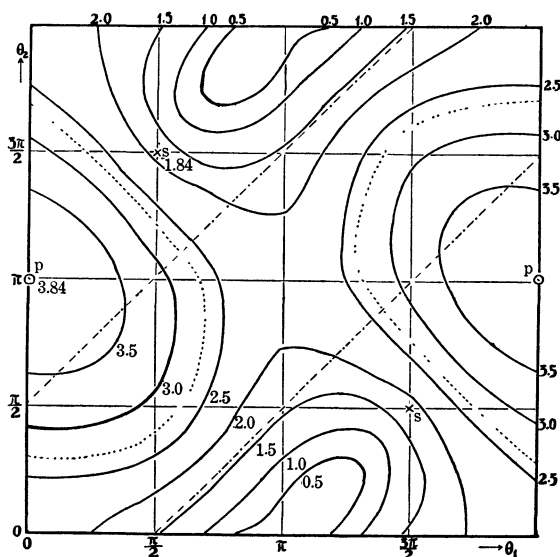
alone<sup>(28)</sup> cannot account for it. In the molecule of 2,2'-diiodo-diphenyl ether, however, a rather significant effect is expected from the big polarizability of iodine atom. Therefore a contour diagram of this molecule was constructed with the use of  $\varphi = 59^\circ$ ,  $\mu_1 = 1.10\text{D}$ ,  $\mu_2 = 1.10\text{D}$  instead of  $\mu_2 = 1.30\text{D}$  (Fig. 13). The comparison of it with Fig. 7 shows that almost the same conclusions can be drawn from here too.

(3) *Further test of bond moment.* In the following table the values of the bond moments assumed in the present paper are compared with those of Smallwood and Herzfeld<sup>(29)</sup> and also with the moments of  $\text{C}_6\text{H}_5\text{X}$ .<sup>(30)</sup>

Table 7.<sup>(26)</sup>

| Bond              | Bond moment assumed value $\mu_2$ | 4,4'-(X-C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> O |                                                 | Bond moment Smallwood <sup>(29)</sup> | $\mu(\text{C}_6\text{H}_5\text{X})^{(30)}$                   |
|-------------------|-----------------------------------|--------------------------------------------------------|-------------------------------------------------|---------------------------------------|--------------------------------------------------------------|
|                   |                                   | Calc. with $\mu_2$                                     | Observed                                        |                                       |                                                              |
| C-NO <sub>2</sub> | 3.80                              | 2.78                                                   | $\begin{cases} 2.79(10) \\ 2.62(7) \end{cases}$ | 3.75                                  | $\begin{cases} 3.98(\text{B}) \\ 4.23(\text{G}) \end{cases}$ |
| C-I               | 1.30                              | 0.55                                                   | —                                               | 1.25                                  | 1.38(B)                                                      |
| C-CH <sub>3</sub> | 0.30                              | 1.45                                                   | 1.46                                            | 0.43                                  | 0.37(G)                                                      |

Determinations in gas phase, and in benzene solution are indicated by G and B, respectively.

Fig. 14. 2,2'-Diiodo-diphenyl ether:  $\mu_1 = 1.14\text{D}$ ,  $\mu_2 = 1.35\text{D}$ .

(28) The interaction effect besides induction arises from "resonance" or "electromerism," and it seems fair not to disregard this. But it seems rather difficult to treat this effect quantitatively, except making some arbitrary allowance for it. This allowance was introduced to a certain extent, indeed, in the consideration of the various contour maps. (Fig. 13, 14, 15, and 16. See also foot-note 27.) The effect of "resonance" on the vector additivity of bond moment is often very important in aromatic compounds. "Other effect" of disubstituted benzene should be reexamined on this ground. We intend to treat this problem quantitatively in a near future, and there we shall discuss the topic of the present paper again.

(29) Smallwood and Herzfeld, *J. Am. Chem. Soc.*, **52** (1930), 1919.

(30) A Table of Dipole Moments, Appendix, *Trans. Faraday Soc.*, **30** (1934).

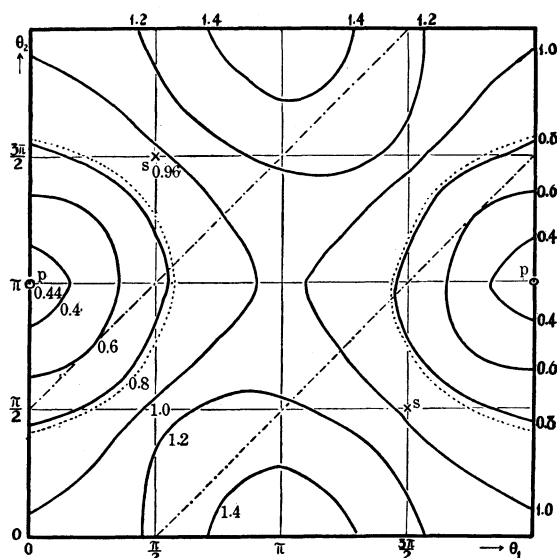


Fig. 15. 2,2'-Dimethyl-diphenyl ether :  $\nu_1 = 1.14D$ ,  $\nu_2 = -0.35D$ .

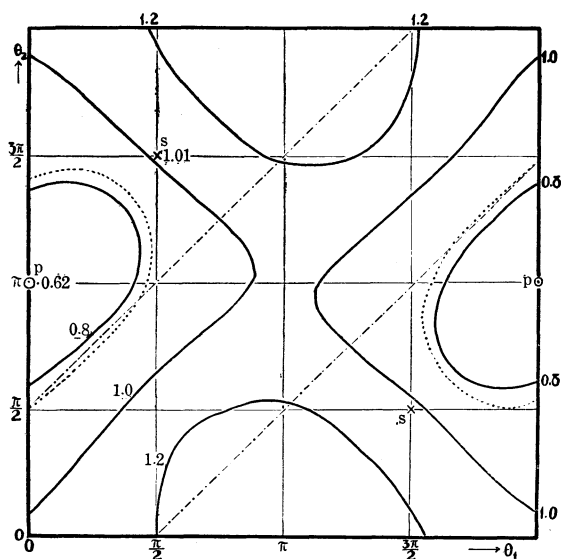


Fig. 16. 2,2'-Dimethyl-diphenyl ether :  $\nu_1 = 1.14D$ ,  $\nu_2 = -0.26D$ .

The values of the present paper are near those employed by Smallwood and Herzfeld. In the middle column of the same table the moments of 4,4'-(X·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O are shown. The calculated values were obtained with the use of the bond moments in the present paper. It should be noticed that they are in good agreement with the observed moments.

A further examination of this problem was made by drawing the contour maps with the choice of other bond moments (Fig. 14, 15, and

16). It is certain from this that the change in bond moment so far as it is small, does not alter the essential conclusions reached in the above discussion.

In conclusion the writers wish to thank Professor E. Ochiai and Professor S. Mizushima for many valuable suggestions in connection with the present investigation. They are also indebted to Dr. Tomita for the gift of materials, and to Dr. Morino for kind discussions.

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## Extended Co-ordination Theory. I. Configuration of Simple Compounds of Typical Elements.

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The present paper is to deal with an extension of Werner's co-ordination theory to simple compounds.

Chemical valences are usually classified into electrovalence, covalence and co-ordinate covalence, but it is impossible to draw sharp boundary-lines among them. It is a question of degree than of nature. We can easily understand this fact from the following examples of metallic halides. Whereas stannic chloride forms molecules of the formula  $\text{SnCl}_4$ , chromic chloride is a multinuclear complex<sup>(1)</sup> in which each chromic ion is surrounded by six chlorine ions octahedrally<sup>(2)</sup> and each chlorine ion is attached to three chromic ions by co-ordinate covalences. In solid cobaltous chloride, the covalent nature is less remarkable, though its crystal structure<sup>(3)</sup> shows that it is also a multinuclear complex. Even among bivalent cations we can find covalent compounds such as mercuric chloride which is one of the typical compounds having molecules. The colour of silver bromide is due to the second absorption band,<sup>(4)</sup> i.e., the co-ordination band, because neither silver nor bromine ion has the first absorption band.<sup>(5)</sup> The colour of silver iodide is also attributed to the co-ordination band from the same reason, and it is of interest to note that each silver ion is surrounded by four iodine ions tetrahedrally<sup>(6)</sup> just as in the yellow

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(1) R. Tsuchida, this Bulletin, **13** (1938), 436; *J. Chem. Soc. Japan*, **59** (1938), 586.

(2) N. Wooster, *Z. Krist.*, **74** (1930), 363.

(3) H. Grime and J. A. Santos, *Z. Krist.*, **88** (1934), 136.

(4) R. Tsuchida, this Bulletin, **13** (1938), 388; *J. Chem. Soc. Japan*, **59** (1938), 819.

(5) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 731.

(6) R. B. Wilsey, *Phil. Mag.*, **46** (1923), 487.



complex ion  $[\text{HgI}_4]^-$  which has only the second and the third band.<sup>(5)</sup> In short, solid silver bromide and iodide are not built up purely by electrovalence, but partly by co-ordinate covalence. Sodium chloride is usually regarded as one of the typical ionic compounds, but spectroscopic consideration reveals that it has tendency, though slight, of co-ordination.<sup>(1)</sup> As can be seen from these examples, it is impossible to distinguish the kinds of valences. For the purpose of the unitary treatment, therefore, every chemical valence may be regarded as a co-ordinate covalence or its extreme case. Thus by assuming that ions and molecules are built up by co-ordinating ions, molecules and electrons around cations, configuration of all the simple as well as complex compounds may be easily found.

The co-ordination is a mutual saturation of co-ordination numbers on both sides of the donor and the acceptor. For example, in  $[\text{Cu}(\text{NH}_3)_4]^{++}$ , both the co-ordination numbers of copper and nitrogen are satisfied by co-ordinating  $\text{NH}_3$  around  $\text{Cu}^{++}$ . Any ion in a compound may, therefore, be taken as the center of co-ordination in discussing the configuration of the compound. For the sake of convenience and consistency, however, cations as given by Kossel<sup>(7)</sup> are chosen as the co-ordination center. Thus in methane quadrivalent carbon cation is taken as the center and four hydrogen anions as ligands. In ammonia three hydrogen anions and a pair of electrons are assumed to co-ordinate around quinquevalent nitrogen cation. The valency of nitrogen, recovering two electrons, is now three. But in ammonium chloride, quinquevalent nitrogen cation is surrounded by four hydrogen anions and the resulting charge of the complex ion is plus one, the valency of nitrogen remaining unchanged.

The typical element, i.e., the element belonging to the subgroup A of the periodic table, is assumed to ionize forming the cation of the charge corresponding to the number of the group. Then the electronic configuration of the cations of the typical elements are as shown in Table 1.

Table 1.

| Group  | I   | II  | III | IV  | V   | VI  | VII | Electron distribution of the ion |          |            |              |              |          | The lowest co-ordination function |
|--------|-----|-----|-----|-----|-----|-----|-----|----------------------------------|----------|------------|--------------|--------------|----------|-----------------------------------|
| Charge | + 2 | + 3 | + 4 | + 5 | + 6 | + 7 | + 7 | 1<br>s                           | 2<br>s p | 3<br>s p d | 4<br>s p d f | 5<br>s p d f | 6<br>s p |                                   |
| Ions   | Li  | Be  | B   | C   | N   | O   | F   | 2                                |          |            |              |              |          | 2s                                |
|        | Na  | Mg  | Al  | Si  | P   | S   | Cl  | 2                                | 2 6      |            |              |              |          | 3s                                |
|        | K   | Ca  |     |     |     |     |     | 2                                | 2 6      | 2 6        |              |              |          | 4s                                |
|        |     |     | Ga  | Ge  | As  | Se  | Br  | 2                                | 2 6      | 2 6 10     |              |              |          | 4s                                |
|        | Rb  | Sr  |     |     |     |     |     | 2                                | 2 6      | 2 6 10     | 2 6          |              |          | 5s                                |
|        |     |     | In  | Sn  | Sb  | Te  | I   | 2                                | 2 6      | 2 6 10     | 2 6 10       |              |          | 5s                                |
|        | Cs  | Ba  |     |     |     |     |     | 2                                | 2 6      | 2 6 10     | 2 6 10       | 2 6          |          | 6s                                |
|        |     |     | Tl  | Pb  | Bi  | Po  | —   | 2                                | 2 6      | 2 6 10     | 2 6 10 14    | 2 6 10       |          | 6s                                |
|        | —   | Ra  |     |     |     |     |     | 2                                | 2 6      | 2 6 10     | 2 6 10 14    | 2 6 10       | 2 6      | 7s                                |

(7) W. Kossel, *Ann. Physik*, [4], **49** (1916), 229; *Z. Elektrochem.*, **26** (1920), 314.

These cations are co-ordinated with anions and pairs of electrons. Let us now consider the configuration of methane for example. In this compound four hydrogen anions are assumed to co-ordinate around the central quadrivalent carbon cation. All the ligands of a co-ordination compound are co-ordinated so that they may be equally distributed in space. Applying this rule in the present case, the four hydrogen anions should equally divide the space around the central carbon cation. There are two such ways, i.e., the tetragonal and the tetrahedral configuration. Now it is necessary to decide which configuration is more suitable. Let us imagine the electron distribution after co-ordination of the four hydrogen ions, by which four pairs of electrons are introduced. We may expect that these pairs of electrons should be distributed symmetrically by the above mentioned rule and at the same time should satisfy the wave-functions for the carbon ion. Now four functions,  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$ , are taken, and then we may expect to find that the symmetry of the resultant electron density distribution is either tetragonal or tetrahedral. The electron density distribution for  $2p$ 's together gives an octahedral symmetry, whereas that for  $2s$  a spherical symmetry. The resultant symmetry is, therefore, octahedral. Thus it is easily seen that the tetrahedral configuration completely fits the symmetry. Four hydrogen anions are, therefore, co-ordinated tetrahedrally around the carbon ion, the resulting molecule being similar to that derived by Pauling<sup>(8)</sup> by the ingenious method of hybridization. In ammonia three hydrogen anions and a pair of electrons are co-ordinated around a quinquivalent nitrogen cation. It is postulated that a pair of electrons has approximately the same share as other anions. Thus the co-ordination number is also four as in methane, and the configuration of ammonia is pyramidal, the angle  $\angle \text{HNH}$  being  $109^\circ$ . For water there are two such pairs of electrons, and from a similar reasoning as above, the configuration is V-shaped, the angle  $\angle \text{HOH}$  being  $109^\circ$ . In all these examples the co-ordination number was four and four eigenfunctions were taken for co-ordination. Let us define such eigenfunctions as co-ordination functions. The lowest co-ordination functions for cations of typical elements are shown in the last column of Table 1. It is postulated that the co-ordination functions could not be of different principal quantum numbers. Then for all the cations of typical elements, the co-ordination function begins with  $s$ , because the postulate forbids the participation of  $3d$  functions in co-ordination with  $4s$  and  $4p$  for  $\text{K}^+$  and  $\text{Ca}^{++}$  and so on. Now we can derive the configurations of the compounds of these ions for various co-ordination numbers.

The general rule for co-ordination stated above allows us only six kinds of co-ordination numbers, i.e., 1, 2, 3, 4, 6 and 8. As can be easily seen, the ions of the elements in the first horizontal series in the periodic table, i.e., Li, Be, B, C, N, O and F, could not co-ordinate more than four ligands, because the L-level contains only four eigenfunctions,  $2s$  and  $2p^3$ , and the above-stated postulate forbids the participation of  $3s$  and  $3p$  in co-ordination with  $2s$  and  $2p$ . The relation between the co-ordination number and the configuration is shown in Table 2 with examples.

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(8) L. Pauling, *J. Am. Chem. Soc.*, **53** (1931), 1367.

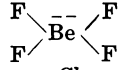
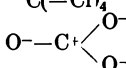
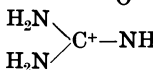
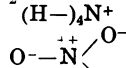
Table 2.

| Co-ordination number | Co-ordination functions | Resultant symmetry | Ions and molecules                                                                                                                                                         |
|----------------------|-------------------------|--------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 2                    | s p                     | Linear             | CO <sub>2</sub> , CH <sub>3</sub> MgI, BO <sub>2</sub> <sup>-</sup> , [FHF] <sup>-</sup> , etc.                                                                            |
| 3                    | p p p                   | Plane-triangular   | BCl <sub>3</sub> , SO <sub>3</sub> , [C(NH <sub>2</sub> ) <sub>3</sub> ] <sup>+</sup> , CO <sub>3</sub> <sup>-</sup> , etc.                                                |
| 4                    | s p p p                 | Tetrahedral        | CCl <sub>4</sub> , Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , SO <sub>4</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , [BeF <sub>4</sub> ] <sup>-</sup> , etc. |
| 6                    | s p p p d d             | Octahedral         | SF <sub>6</sub> , [AlF <sub>6</sub> ] <sup>3-</sup> , [SiF <sub>6</sub> ] <sup>=</sup> , etc.                                                                              |
| 8                    | p p p d d d d d         | Hexahedral         | [Ca(C <sub>2</sub> H <sub>5</sub> OH) <sub>8</sub> ] <sup>++</sup> , etc.                                                                                                  |

For the co-ordination numbers 3 and 8, the eigenfunction for s is not available as is shown in Table 2, because the participation of the function renders it impossible to find the trigonal and the hexahedral symmetry.

Making use of Table 2, we may easily find the configuration of various ions and molecules without any more consideration than the co-ordination number. Examples are given in Table 3 for the elements in the first horizontal series in the periodic table for which the co-ordination numbers, 1, 2, 3 and 4 only are allowed.

Table 3.

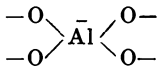
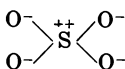
| Ion or molecule                                   | Central ion      | Ligands                       | Co-ordination number | Structure                                                                           | Configuration    |
|---------------------------------------------------|------------------|-------------------------------|----------------------|-------------------------------------------------------------------------------------|------------------|
| [FHF] <sup>-</sup>                                | H <sup>+</sup>   | 2F <sup>-</sup>               | 2                    | F—H—F                                                                               | Linear           |
| BeO <sub>2</sub> <sup>-</sup>                     | Be <sup>++</sup> | 2O <sup>-</sup>               | 2                    | O—Be—O                                                                              | „                |
| [BeF <sub>4</sub> ] <sup>-</sup>                  | „                | 4F <sup>-</sup>               | 4                    |  | Tetrahedral      |
| BCl <sub>3</sub>                                  | B <sup>3+</sup>  | 3Cl <sup>-</sup>              | 3                    |  | Plane-triangular |
| BO <sub>2</sub> <sup>-</sup>                      | „                | 2O <sup>-</sup>               | 2                    | O—B <sup>+</sup> —O                                                                 | Linear           |
| CCl <sub>4</sub>                                  | C <sup>4+</sup>  | 4Cl <sup>-</sup>              | 4                    | C—(Cl) <sub>4</sub>                                                                 | Tetrahedral      |
| CO <sub>3</sub> <sup>-</sup>                      | „                | 3O <sup>-</sup>               | 3                    |  | Plane-triangular |
| [C(NH <sub>2</sub> ) <sub>3</sub> ] <sup>+</sup>  | „                | 3NH <sub>2</sub> <sup>-</sup> | 3                    |  | Plane-triangular |
| NH <sub>4</sub> <sup>+</sup>                      | N <sup>5+</sup>  | 4H <sup>-</sup>               | 4                    | (H—) <sub>4</sub> N <sup>+</sup>                                                    | Tetrahedral      |
| NO <sub>3</sub> <sup>-</sup>                      | „                | 3O <sup>-</sup>               | 3                    |  | Plane-triangular |
| [Li(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup> | Li <sup>+</sup>  | 4NH <sub>3</sub>              | 4                    | (H <sub>3</sub> N) <sub>4</sub> Li <sup>+</sup>                                     | Tetrahedral      |

In Table 3 we find [FHF]<sup>-</sup>, an example of hydrogen bridge. From the present viewpoint, the hydrogen bridge is not so singular as has been usually believed, but one of the special cases of co-ordination. A co-

ordination band<sup>(9)</sup> due to a hydrogen bridge has been shown in the ultra-violet region. The trigonal configuration of carbonate, nitrate, and guanidonium<sup>(10)</sup> ions may be easily explained. The complex salts and the simple compounds can be discussed by the same method and their configurations may readily be derived by the same simple consideration. Thus the isomorphism between the sulphates and fluoroborates or ortho-silicates and fluoroberyllate may be clearly understood.

The elements of higher atomic number than neon can give ions and molecules of various co-ordination numbers, i.e., 1, 2, 3, 4, 6 and 8. Some of the examples are given in Table 4.

Table 4.

| Ion or molecule           | Central ion      | Ligands                        | Co-ordination number | Configuration                                                                                  |
|---------------------------|------------------|--------------------------------|----------------------|------------------------------------------------------------------------------------------------|
| $\text{CH}_3\text{MgI}$   | $\text{Mg}^{++}$ | $\text{CH}_3^-$ , $\text{I}^-$ | 2                    | Linear                                                                                         |
| $[\text{AlF}_6]^{3-}$     | $\text{Al}^{3+}$ | $6\text{F}^-$                  | 6                    | Octahedral                                                                                     |
| $[\text{AlO}_4]^{5-}$     | „                | $4\text{O}^-$                  | 4                    | Tetrahedral  |
| $[\text{SiO}_4]^{4-}$     | $\text{Si}^{++}$ | $4\text{O}^-$                  | 4                    | „                                                                                              |
| $\text{SO}_3$             | $\text{S}^{++}$  | $3\text{O}^-$                  | 3                    | Plane-trigonal                                                                                 |
| $\text{SF}_6$             | „                | $6\text{F}^-$                  | 6                    | Octahedral                                                                                     |
| $\text{SO}_4^{--}$        | „                | $4\text{O}^-$                  | 4                    | Tetrahedral  |
| $\text{PO}_4^{3-}$        | $\text{P}^{5+}$  | $4\text{O}^-$                  | 4                    | „                                                                                              |
| $\text{H}_2\text{PO}_2^-$ | „                | $2\text{H}^-$ , $2\text{O}^-$  | 4                    | „                                                                                              |
| $\text{ClO}_4^-$          | $\text{Cl}^{7+}$ | $4\text{O}^-$                  | 4                    | „                                                                                              |

In Table 4 we find sulphur hexafluoride, a compound of “expanded” shell. The octet theory<sup>(11)</sup> has failed to explain the dodecet structure. The groups  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  are the structural units of various silicate and alumino-silicate minerals.

Anomalies of valence-angles are seen among ions and molecules in which electrons are co-ordinated just as other ligands. For examples in the molecules of ammonia and water, there are pairs of electrons whose spins are neutralized. The present author has devised an automatic method of taking such electrons into consideration, by first removing the electrons from the atom and then co-ordinating them again together with other ligands. This consideration is applicable to all the ions and molecules in which the valencies of the elements of the central cations are lower than the maximum valencies shown by the group numbers in the periodic table. The configuration of such ions and molecules can easily be found automatically without any further consideration by a simple tabular method. Some examples are given in Table 5. In the first column

(9) R. Tsuchida and T. Tsumaki, this Bulletin, **13** (1938), 527.

(10) W. Theilacker, *Z. Krist.*, **76** (1931), 203.

(11) I. Langmuir, *J. Am. Chem. Soc.*, **41** (1919), 252.

is written the ion or molecule whose configuration is required. Then the ligands are tabulated, a pair of electrons and an odd electron being treated just as other ligands. The number of electrons to be co-ordinated can be readily found by balancing the valency of the central ion and the charges of the ligands with that of the entire ion or molecule. Then the co-ordination number is found, which in turn gives the configuration by Table 2.

Table 5.

| Ion or molecule               | Central ion      | Ligands                | Co-ordination number | Configuration | Angle       |           |            |
|-------------------------------|------------------|------------------------|----------------------|---------------|-------------|-----------|------------|
|                               |                  |                        |                      |               | Theoretical | Observed  | Literature |
| H <sub>2</sub> O              | O <sup>6+</sup>  | 2H <sup>-</sup> , :, : | 4                    | V-shaped      | 109°        | 105°      |            |
| NH <sub>3</sub>               | N <sup>5+</sup>  | 3H <sup>-</sup> , :    | 4                    | Pyramidal     | 109°        | 106°      |            |
| NO <sub>2</sub> <sup>-</sup>  | „                | 2O <sup>-</sup> , :    | 3                    | V-shaped      | 120°        | 132°      | (12)       |
| NO <sub>2</sub>               | „                | 2O <sup>-</sup> , .    | 3                    | „             | 120°        | 110°-120° | (13)       |
| CO <sub>2</sub>               | C <sup>4+</sup>  | 2O <sup>=</sup>        | 2                    | Linear        | 180°        | 180°      |            |
| SO <sub>2</sub>               | S <sup>6+</sup>  | 2O <sup>-</sup> , :    | 3                    | V-shaped      | 120°        | 122°      | (14)       |
| SO <sub>3</sub>               | „                | 3O <sup>=</sup>        | 3                    | Trigonal      | 120°        | 120°      | (15)       |
| SO <sub>3</sub> <sup>-</sup>  | „                | 3O <sup>=</sup> , :    | 4                    | Pyramidal     | 109°        | 111°      | (16)       |
| ClO <sub>2</sub> <sup>-</sup> | Cl <sup>7+</sup> | 2O <sup>-</sup> , :, : | 4                    | V-shaped      | 109°        | 114°      | (17)       |
| ClO <sub>3</sub> <sup>-</sup> | „                | 3O <sup>=</sup> , :    | 4                    | Pyramidal     | 109°        | 107°      | (18)       |

The angles derived by this method fairly coincide with the experimental data as can be seen from the table.

As is evident from Tables 2-5, the configuration of a molecule or an ion is determined only by the co-ordination number, if appropriate consideration is given to "non-bonding" electrons.

### Summary.

All the chemical linkages may be explained in terms of the co-ordinate covalence. By assuming that molecules and radical ions are built up by co-ordination of molecules, ions and electrons as ligands around central cations whose combining fields are given by sets of wave-functions, the configuration of all the simple as well as complex compounds could be readily found.

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Imperial University of Osaka.*

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- (12) W. H. Zachariasen, *J. Am. Chem. Soc.*, **53** (1931), 2123.  
 (13) G. Sutherland and W. G. Penny, *Nature*, **136** (1935), 146.  
 (14) P. C. Cross and L. D. Brockway, *J. Chem. Phys.*, **3** (1935), 821.  
 (15) H. Gerding and J. Lecomte, *Nature*, **142** (1938), 718.  
 (16) W. H. Zachariasen and N. E. Buckley, *Phys. Rev.*, **37** (1931), 1295.  
 (17) G. R. Levi and A. Scherillo, *Z. Krist.*, **76** (1930), 431.  
 (18) W. H. Zachariasen, *Z. Krist.*, **71** (1929), 517.

## On the Nature of Foam. V. Phase Inversion and Foam Formation of Emulsion Consisting of Acetic Acid, Benzene, and Water.

By Tunetaka SASAKI.

(Received March 10, 1939.)

It was reported in the preceding paper<sup>(1)</sup> that there exist two types of heterogeneous systems of acetic acid-ethyl ether-water (AEW), namely, the system which occasionally produces two types of emulsions (oil-in-water and water-in-oil) according to the two different modes of shaking, and the system which produces only one type of emulsion whatever the mode of shaking. Moreover, it was indicated the existence of a system which can behave both foamy and non foamy according to the two modes of shaking. Present paper describes the influence of the mode of shaking upon the type of emulsion and foam formation of the ternary heterogeneous system of acetic acid-benzene-water (ABW).

**Experiments.** In ABW-system, acetic acid is soluble in all proportions both in water and benzene, while benzene is insoluble in water. Mutual solubility diagram was obtained in the preceding paper<sup>(2)</sup> which is shown in Fig. 1. It covers a wide region of heterogeneous system.

A definite volume (10 c.c.) of this heterogeneous system is taken in a test tube and the following two modes of shaking are applied.

(1) The test tube is held by hand vertically, pulled upwards quickly and then brought down slowly. After repeating these motions several times, usual up-and-down shaking is applied.

(2) The upper portion of the test tube is held by hand and the lower portion of it is swung repeatedly. Usual up-and-down shaking is subsequently applied.

The determination of the type of emulsion which is produced by above two modes of shaking is made by observing the process of breaking up of resulting emulsion in the following manner.<sup>(1)</sup> The emulsion is determined to be O-in-W type<sup>(3)</sup> when the droplets of disperse phase increase their size as they go upwards and a liquid layer is gradually separated

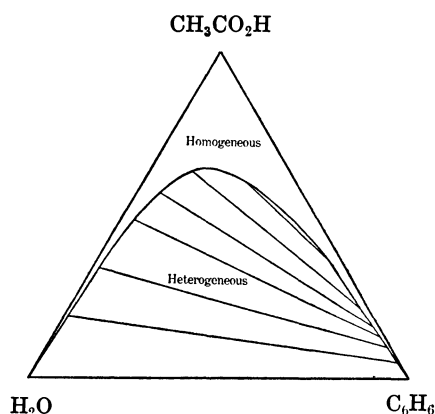


Fig. 1.

(1) Sasaki, this Bulletin, **14** (1939). 63.

(2) Sasaki, this Bulletin, **14** (1939), 3.

(3) O-in-Water represents emulsion in which the upper liquid layer of original heterogeneous system is dispersed in the lower one, and W-in-O represents the reverse type to O-in-W.

at the top from the bulk, while it is considered to be W-in-O type<sup>(3)</sup> when the droplets increase their size as they sink and a liquid layer is gradually separated at the bottom. Thus, in the various heterogeneous systems of ABW, the type of emulsion established by the above two modes of shaking were determined. Some of its data are shown in Table 1.

Table 1.

| Composition in volume (c.c.) |         |       | Mode of shaking |        | Composition in volume (c.c.) |         |       | Mode of shaking |        |
|------------------------------|---------|-------|-----------------|--------|------------------------------|---------|-------|-----------------|--------|
| Acetic acid                  | Benzene | Water | (1)             | (2)    | Acetic acid                  | Benzene | water | (1)             | (2)    |
| 50.0                         | 35.0    | 15.0  | O-in-W          | W-in-O | 22.1                         | 35.9    | 42.0  | O-in-W          | O-in-W |
| 45.5                         | 31.8    | 22.7  | O-in-W          | W-in-O | 21.0                         | 39.1    | 39.9  | O-in-W          | W-in-O |
| 41.6                         | 29.2    | 29.2  | O-in-W          | W-in-O | 20.2                         | 41.5    | 38.3  | O-in-W          | W-in-O |
| 38.5                         | 26.9    | 34.6  | O-in-W          | O-in-W | 19.4                         | 43.8    | 36.8  | W-in-O          | W-in-O |
| 36.2                         | 31.2    | 32.6  | O-in-W          | O-in-W | 18.0                         | 47.8    | 34.2  | W-in-O          | W-in-O |
| 33.8                         | 35.8    | 30.4  | O-in-W          | W-in-O | 16.8                         | 44.6    | 38.6  | W-in-O          | W-in-O |
| 32.0                         | 39.1    | 28.9  | O-in-W          | W-in-O | 15.7                         | 41.8    | 42.5  | O-in-W          | W-in-O |
| 30.1                         | 42.8    | 27.1  | W-in-O          | W-in-O | 15.1                         | 40.1    | 44.8  | O-in-W          | W-in-O |
| 28.4                         | 40.3    | 31.3  | W-in-O          | W-in-O | 14.6                         | 38.9    | 46.5  | O-in-W          | W-in-O |
| 26.9                         | 38.2    | 34.9  | O-in-W          | W-in-O | 14.2                         | 37.8    | 48.0  | O-in-W          | W-in-O |
| 25.5                         | 36.2    | 38.3  | O-in-W          | O-in-W | 13.8                         | 36.8    | 49.4  | O-in-W          | O-in-W |
| 23.2                         | 32.8    | 44.0  | O-in-W          | O-in-W |                              |         |       |                 |        |

It can be seen from this table that there exist two kinds of systems, that is, those systems which can produce only one type of emulsion independent of the modes of shaking, and those which occasionally produce both types of emulsion according to the different modes of shaking. In Fig. 2, A and B represent the region in which a system simply produces W-in-O or O-in-W emulsion respectively whatever the modes of shaking, and C represents the region in which a system shows the possibility of forming two types of emulsion, namely, it represents the phase inversion zone by shaking.

Precise investigations were further made upon the systems belonging to this phase inversion zone C. A definite volume (10 c.c.) of a system belonging to the phase inversion zone is taken and the following three modes of shaking are applied.

- (1) The test tube is shaken as described in (1).
- (2) The test tube is shaken as described in (2).
- (3) The usual up-and-down shaking alone is applied from the beginning.

The usual up-and-down shaking involved in the above three modes of shaking is performed by the same shaking apparatus and on the same conditions (50 vibrations for 10 seconds with amplitude of 12 cm.) as described in the preceding paper.<sup>(4)</sup> The type of resulting emulsion is determined by observing the behaviour of breaking up of emulsion, in the same manner as described before. Following quantities were measured

(4) Sasaki, this Bulletin, **13** (1938), 669.

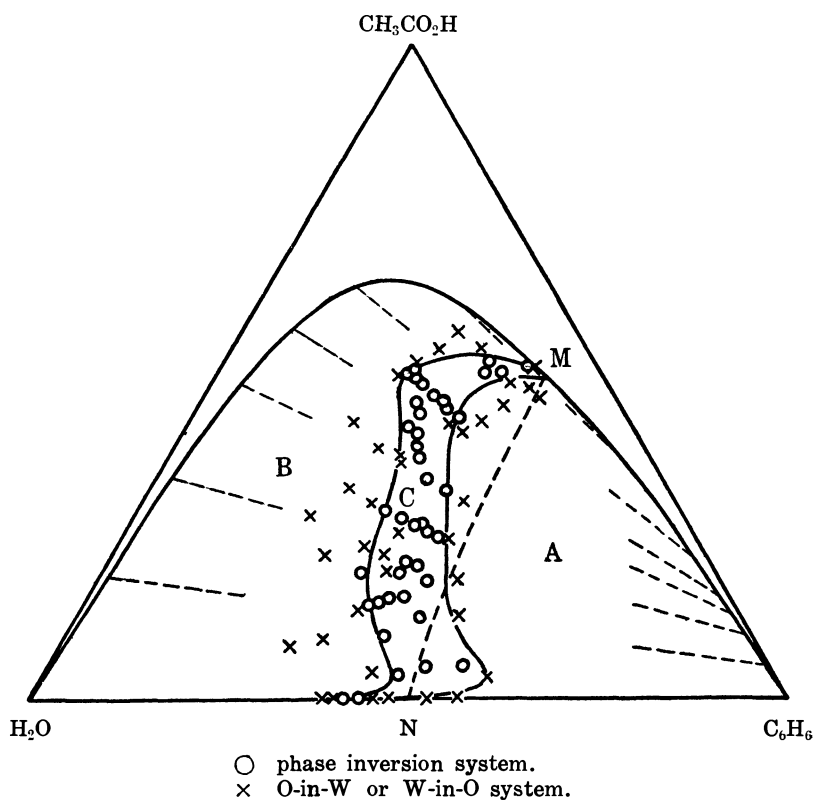


Fig. 2.

Table 2.

| System | Composition in volume (c.c.) |         |       | Mode of shaking                                 |                                              |                        | Volume ratio |             |
|--------|------------------------------|---------|-------|-------------------------------------------------|----------------------------------------------|------------------------|--------------|-------------|
|        | Acetic acid                  | Benzene | Water | (1)                                             | (2)                                          | (3)                    | Upper layer  | Lower layer |
| (a)    | 0.30                         | 5.70    | 4.00  | O-in-W<br>$S_e = 104$<br>$S_f = 5$<br>$H = 0.8$ | W-in-O<br>$S_e = 26$<br>$S_f = 0$<br>$H = 0$ | Same as in (2)         | 1.262        | 1.000       |
| (b)    | 0.48                         | 4.52    | 5.00  | O-in-W<br>$S_e = 112$<br>$S_f = 6$<br>$H = 0.8$ | W-in-O<br>$S_e = 25$<br>$S_f = 0$<br>$H = 0$ | Same as in (1)         | 0.905        | 1.000       |
| (c)    | 0.48                         | 5.19    | 4.33  | O-in-W<br>$S_e = 130$<br>$S_f = 6$<br>$H = 1.0$ | W-in-O<br>$S_e = 27$<br>$S_f = 0$<br>$H = 0$ | Same as in (1) and (2) | 1.174        | 1.000       |
| (d)    | 4.50                         | 3.00    | 2.50  | O-in-W<br>$S_e = 29$<br>$S_f = 0$<br>$H = 0$    | W-in-O<br>$S_e = 21$<br>$S_f = 0$<br>$H = 0$ | Same as in (1)         | 0.471        | 1.000       |

$S_e$  and  $S_f$  denote stabilities of emulsion and foam respectively in second, and  $H$  represents height of foam in cm.



at the same time, that is, the stabilities of emulsion and foam which are denoted by time required from immediately after shaking to the complete collapse of foam zone and emulsion droplets respectively, the height of foam zone directly after the shaking, and the phase volume ratio. The results are shown in Table 2.

**Discussion.** It is evident in Fig. 2, that the heterogeneous region of ABW-system is divided into three portions A, B, and C, as in the case of AEW-system.<sup>(1)</sup> The region A mainly consists of systems having a larger volume of an upper layer ( $V_u$ ) than that of a lower one ( $V_l$ ). In such region a system shows tendency of the lower layer being dispersed in the upper one and becomes W-in-O emulsion, whatever the mode of shaking.<sup>(1)</sup> This tendency increases with difference in volumes between two layers, i.e., the system becomes W-in-O emulsion more easily as it approaches the mutual solubility curve. In region B, the relation is reverse. In the system of this region,  $V_u$  is smaller than  $V_l$  and so the system shows the tendency of the upper layer being dispersed in the lower one, that is, O-in-W emulsion results whatever the mode of shaking. This tendency also becomes more remarkable as the system approaches the mutual solubility curve.

Region A also involves systems in which  $V_l$  is a little larger than  $V_u$ , as was observed in the case of AEW-system.<sup>(1)</sup> In such systems, the lower layer having larger volume is dispersed in the upper one which cannot simply be explained by the above phase volume effect alone. It is rather the case in general that a ternary system shows such anomalies as in this case and in AEW-system.<sup>(1)</sup> Some other factors must be introduced, in addition to the above volume effect, to explain these phenomena. Specific action of interface was quoted for instance, in the preceding paper.<sup>(1)</sup>

Phase inversion zone C, namely, the region in which a system shows the tendency of producing both types of emulsion according to the different modes of shaking is situated between two regions A and B as shown in Fig. 2. The mode of shaking described in (1) favours to produce O-in-W emulsion, while the shaking of the mode (2) favours to produce W-in-O emulsion. Recently, the relation between emulsion type and mode of shaking was also indicated by Andreas<sup>(5)</sup> in the case of a system of immiscible triple layered liquid which is in accordance with our explanations.

The existence of the phase inversion zone was pointed out already in the preceding paper,<sup>(1)</sup> but the sharp boundary of this zone was not obtained in the case of AEW-system. In the present case, however, this zone is determined distinctly as shown in Fig. 2. The zone C is not situated along the dotted line MN in Fig. 2 which represents the locus of points corresponding to systems of  $V_u$  being equal to  $V_l$ . This is the case just similar to that of AEW-system. The position of phase inversion zone, therefore, cannot be determined by the volume ratio alone. It is however possible to say that in regions A and B, the effect of relative volume ratio is remarkable, while in phase inversion zone, the effect of modes of shaking as described in (1) and (2) are predominant in de-

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(5) Andreas, *J. Chem. Education*, **15** (1938), 523.

termination of emulsion type. The influence of emulsifying agent is absent throughout in this system as in AEW-system.

In Table 2, three systems (a), (b) and (c) were all taken in the phase inversion zone C, so the shaking of the mode (1) or (2) favours to produce O-in-W or W-in-O emulsion respectively in these systems, on the same reason as was explained in the preceding paper.<sup>(1)</sup> In the present case, intermittent shaking described in (1) is especially effective<sup>(6)</sup> in producing O-in-W emulsion as it gives time to break relatively unstable W-in-O emulsion droplets produced simultaneously by shaking.

In the case of shaking of the mode (3) where the up-and-down shaking alone is applied from the beginning, these systems show difference in their behaviours. System (a) produces W-in-O emulsion, system (b) O-in-W emulsion and system (c) occasionally produces both types of them.

It was reported in the preceding paper<sup>(1)</sup> that in the phase inversion zone, those systems which are situated close to the region A show the tendency to produce emulsion of the similar type to that in region A (W-in-O) and those near the region B show the tendency of producing emulsion of the same type as that in region B (O-in-W). These facts were again confirmed in the present experiments. In Table 2, system (a) which is close to the region A, as shown in Fig. 3, has the tendency of producing emulsion of W-in-O type more easily than the other possible type of O-in-W emulsion on shaking. System (b), in the same manner, produces O-in-W emulsion more easily than that of W-in-O type. In the case of system (c), it is distant from both regions A and B, and it has equal tendency of producing both types of emulsions. All these three systems lie on a same tie-line, i.e., they consist of an upper and a lower layers of nearly one and the same composition respectively, and they merely differ in their volume ratio  $V_u:V_l$ . Above difference in behaviour of emulsion can therefore be ascribed mainly to the effect of volume ratio as shown in Table 2. It must be added that the system (c) which has equal tendencies of establishing both types of emulsions, is not always equally distant from two regions A and B, nor does it coincide with the middle point of a tie-line.

It happens frequently that the type of emulsion once established by a certain mode of shaking cannot be inverted by another mode of shaking, even in the phase inversion system. Thus in the system (b), O-in-W emulsion is relatively stable and simple up-and-down shaking produces emulsion of this type, but once W-in-O emulsion is established by the mode of shaking described in (1), subsequent up-and-down shaking merely favours to produce emulsion of the same type, instead of inverting it to another type. Sometimes, a certain mode of shaking which favours to produce one type of emulsion favours to accelerate the breaking-up of emulsion of another type which otherwise breaks up slowly. W-in-O emulsion of the system (c), for example, requires 130 seconds for the complete separation into two layers when it is left at rest after shaking. The time is reduced to about 84 seconds when it is shaken as described in (2). Such a phenomenon is similar to a demulsifying effect of one type of emulsify-

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(6) Briggs, *J. Phys. Chem.*, **24** (1920), 120.

ing agent to emulsion which is stabilized by the emulsifying agent of another type, as indicated by Clowes.<sup>(7)</sup>

It was suggested in the preceding paper<sup>(1)</sup> that distinction must be made between the tendency to establish a type of emulsion and its stability, showing the example of AEW-system. The confirmation is further made in the case of ABW-system. It can be seen in Table 2, that the system (a) shows the tendency of producing W-in-O emulsion by the usual up-and-down shaking, although it is far more unstable than O-in-W emulsion.

The general difference in behaviour or appearance between O-in-W and W-in-O emulsions of ABW-system is summarised in Table 3. The

Table 3.

| O-in-W emulsion                                                                                                         | W-in-O emulsion                                                                                                     |
|-------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Produced by shaking of the mode (1)                                                                                     | Produced by shaking of the mode (2)                                                                                 |
| Emulsion drops increase their size as they go upwards and a liquid layer is separated upon the bulk. Relatively stable. | Emulsion drops increase their size as they sink and a liquid layer is separated at the bottom. Relatively unstable. |
| Emulsion is brilliant in light.                                                                                         | Emulsion is frosted and white.                                                                                      |
| Foamy or non foamy, triple layered foam <sup>(2)</sup> occurs frequently. Foamy emulsion is nearly silent on shaking.   | Non foamy.<br>Emulsion is noisy when shaken.                                                                        |
| Air bubbles go upwards quickly with emulsion drops.                                                                     | Air bubbles go upwards slowly between emulsion props.                                                               |

nature of ABW-emulsion is somewhat different from that of AEW-emulsion. In ABW-system, O-in-W emulsion is more stable than W-in-O emulsion, while in AEW-system the latter is more stable than the former. It can be observed that heterogeneous system of ABW produces brilliant emulsion drops when O-in-W emulsion is formed on shaking. This is explained from the total refraction caused by emulsion drops which have smaller refractive index than that of dispersing medium. These behaviours can generally be observed in most other heterogeneous systems provided that there exists marked difference in refractive indices between two immiscible components. Emulsion is frosted and white in the case of W-in-O type. Emulsion usually makes noise on shaking, but it turns to be nearly silent when foam, acting as a cushion, is produced. Further, the motion of the air bubbles produced by shaking in the emulsion is also distinctive. In O-in-W emulsion the motion is quick, while in W-in-O emulsion it is slow as if the emulsion is fairly viscous.

Finally, it will be discussed upon the foam formation of ABW-emulsion. System (a), (b) and (c) foams when it is shaken by the mode (1), while it does not foam by shaking of the mode (2), as shown in Table 2. Existence of such a system has already been indicated in the preceding paper<sup>(1)</sup> for AEW-emulsion and was called foam-nonfoam system. The

(7) Clowes, *J. Phys. Chem.*, **20** (1916), 407.

effect of shaking upon foam-nonfoam system of ABW as described above is, however, just reverse to that of AEW in which foam is produced by shaking of the mode (2), while it is not produced by shaking of the mode (1).

It was concluded in the preceding paper<sup>(1)</sup> that the region of these foam-nonfoam systems is restricted in a portion of phase inversion zone which at the same time forms a part of foamy region of heterogeneous system. In Fig. 3, foamy region is expressed by B'<sup>(2)</sup> which is surrounded by a dotted line, and the phase inversion zone is also indicated by C. Hatched portion, therefore, corresponds to foam-nonfoam region of ABW-system. A system of this region foams when it produces O-in-W emulsion,

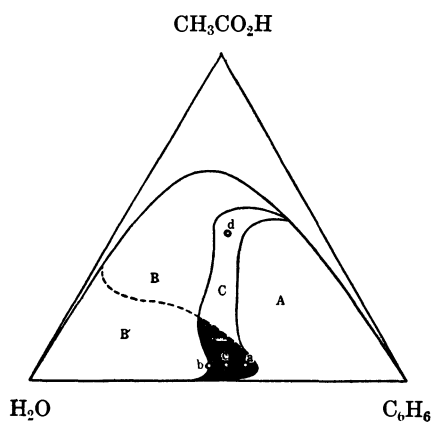


Fig. 3.

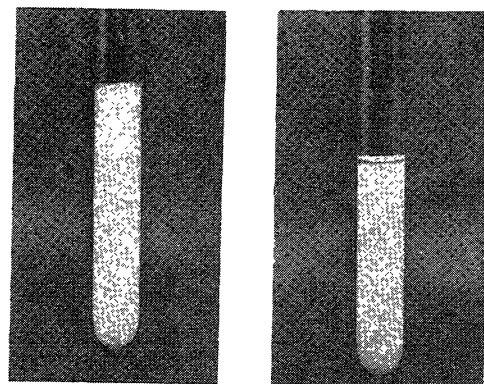
Foamy emulsion,  
produced by shaking  
of the mode (1).Non foamy emulsion,  
produced by shaking  
of the mode (2).

Fig. 4.

for emulsion droplets having fairly smaller surface tension than the dispersing medium favour to produce triple layered foam.<sup>(2)</sup> It does not foam when it produces W-in-O emulsion like as the system of A region. Fig. 4 shows an example of such foam-nonfoam system.

The reverse effect of two modes of shakings to the foam formation between ABW- and AEW- systems can be explained by the fact that the foamy region of heterogeneous system is situated in B region (O-in-W region) in the case of ABW-system, while it is situated in A region (W-in-O region) in the case of AEW-system, and so the mode of shaking to produce foamy emulsion is different between two systems.

In the system (d) which is situated in phase inversion zone but not in the foamy region, emulsions of both types can be produced by shaking, but foam is not produced in either of them.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

### Summary.

(1) The heterogeneous region of the system consisting of acetic acid, benzene and water (ABW) is divided into three regions A, B and C, referring to the type of emulsion produced by two different modes of shaking. Systems in region A or B produce water-in-oil or oil-in-water emulsion respectively, whatever the mode of shaking, and those in region C occasionally produce both types of emulsion according to the two modes of shaking. The region C is called the phase inversion zone by shaking.

(2) Some systems of this phase inversion zone behave both foamy and non foamy according to the two different modes of shaking. The existence of such foam-nonfoam system is restricted in a portion of the phase inversion zone which at the same time forms a portion of foamy region of heterogeneous system of ABW.

(3) The difference in nature or behaviour between two possible types of emulsions produced by one and the same system was compared in details, and its discussions were made.

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**Chemical Studies by Means of Molecular Beams. VII.\* A Method of Measuring the Intensity of Potassium Atomic Beams with an Incandescent Tungsten Surface. Part 1.**

By Kumasaburo KODERA.

(Received March 10, 1939.)

**Introduction.** An incandescent tungsten filament, when placed in alkali metal vapour, emits ions. This is because the atoms of alkali metal which strike the filament are ionized and evaporated. Generally, perfect ionization takes place when the ionization potential of the atoms is considerably smaller than the work function of tungsten.

This phenomenon was first discovered by Langmuir and Kingdon<sup>(1)</sup> with caesium; and later it was reported by Killian<sup>(2)</sup> with rubidium and potassium. In the case of sodium and lithium, the ionization can be effected with a tungsten filament whose surface is covered with a mono-atomic layer of oxygen.

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\* Preceding papers were published in Japanese in the *J. Chem. Soc. Japan*, **57** (1936), **58** (1937).

(1) I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc. (London)*, A, **107** (1925), 61.

(2) T. J. Killian, *Phys. Rev.*, **27** (1926), 578.

In 1929, Taylor<sup>(3)</sup> applied this phenomenon to the intensity measurement of an atomic beam of alkali metals. A fine tungsten filament surrounded by a cylindrical cathode is placed within the path of an atomic beam. The atoms which strike the filament are ionized and attracted towards the cathode. The ion current thus produced gives the intensity of that part of the atomic beam, provided the ionization is complete. This method of measurement with fine filaments has since been used to advantage but it has a drawback when it is desired to measure the total intensity or a large portion of the intensity of the current at one time. This is especially the case with a weak atomic beam of a large cross section.

This inconvenience may be avoided by using a ribbon of convenient width in place of a fine filament. The way of measurement is quite the same as with a fine filament, except that owing to a considerably larger evolution of heat a suitable additional device around the ribbon is necessary. However, this undesirable heat effect may be reduced to minimum, if we use the method of flashing. The whole cross section of a weak atomic beam is received by an unheated ribbon surface for a certain time, which is then electrically flashed for a short time and the ions thus formed are measured by a ballistic galvanometer.

The present investigation has been carried out with potassium atomic beams to learn the conditions of applicability of this method.

**Apparatus.** The apparatus used is shown in Fig. 1. F represents an oven for potassium made of nickel chrome steel, the construction being similar to that previously used by Nishibori<sup>(4)</sup> in our laboratory. The tungsten filaments for heating, which are inserted from the left hand, are not shown in the figure. Potassium atoms gush through the circular orifice O into a highly evacuated space and are caught by the surrounding cooled walls except for those which pass through the second circular orifice S1 and advance as a beam. S at the left side of S1 is a shutter for the atomic beam to which is attached a piece of iron to be operated from outside by a small electromagnet. The movement of the shutter is accurately controlled with a stop-watch electrically connected with it. A copper tube T<sub>1</sub> is cooled by liquid air contained in L<sub>1</sub> and serves to catch all atoms which have failed to pass through S1. The diameter of O is 0.1 mm. and that of S1 1.7 mm. The detector chamber is shown on the right

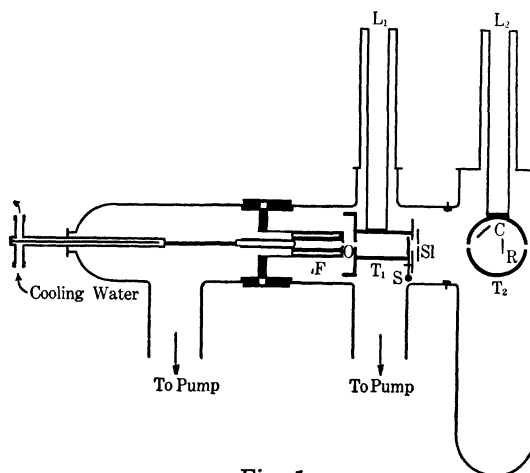


Fig. 1.

(3) J. B. Taylor, *Z. Physik*, **57** (1929), 242.

(4) E. Nishibori, *J. Chem. Soc. Japan*, **58** (1937), 22.

hand. R is a tungsten ribbon 5 cm. long, 5 mm. wide and 0.13 mm. thick and C is a nickel cathode for collecting ions.  $T_2$  is a copper tube cooled by liquid air in  $L_2$  and protects the tungsten ribbon from harmful vapours given off by such as sealing wax.

**Galvanometer circuit.** This is shown in Fig. 2. The cathode C is kept at 120 V. negative against the tungsten ribbon. G is a ballistic galvanometer made in the Institute of Physical and Chemical Research and has a sensitivity of  $3.77 \times 10^{-10}$  coulombs. The protecting copper tube  $T_2$  is kept at 6 V. positive against the ribbon to prevent ions from coming to it. The ribbon was heated with an alternating current of 10–42 A. taken from the sources of A. C. 100 V. and 200 V. through a step-down transformer. The temperature of the ribbon was measured with a Siemens optical pyrometer.

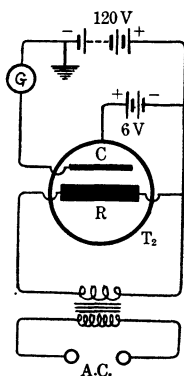


Fig. 2.

**The treatment of the tungsten ribbon.** As the surface of ordinary tungsten is always stained with alkali salts, it emits their ions when heated. The ribbon must therefore be freed from these by heating repeatedly for about 10 seconds in high vacuum at 1400–1500°C. until practically no ions could be detected by the galvanometer. It may be desirable to heat the tungsten

at much higher temperatures but in the present case, heat thus generated causes an undue heating of the apparatus. At any rate the above treatment proved quite satisfactory for the purpose.

**Purification of potassium.** Potassium used in this experiment was carefully distilled in high vacuum into a long glass tube of appropriate diameter and kept dry for occasional use. When wanted, a short piece of the tube is cut out and immediately introduced into the oven and then the whole apparatus is evacuated without delay.

**Method of measurement.** When the evacuation is complete a required constant temperature is applied to the oven to produce an atomic beam of a definite intensity. With the shutter kept closed, the ribbon is flashed to remove any freshly adsorbed alkali atoms, left to cool for some time, and then the shutter is opened for a definite time to fire potassium atoms upon the ribbon surface, which is then flashed and the deflection of the ballistic galvanometer is recorded. The time of exposure of the ribbon to the beam is accurately measured with the stop-watch mentioned above. In this measurement we must be sure that all colliding potassium atoms are completely adsorbed by the ribbon. This was ascertained by Taylor and Langmuir<sup>(5)</sup> in the case of caesium. They showed that as long as the temperature of tungsten is below about 800°K., the impinging atoms are entirely fixed on the tungsten, until a mono-atomic layer is formed. It may be, therefore considered that it is the same in the present case.

**Results. Uniformity of the ribbon surface.** The ionizing power of the hot ribbon surface may differ near the two ends because of unequal

(5) J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44** (1933), 423.



temperature distribution. Therefore, at least the uniform ionizing power of the portion which is uniform in temperature must be ascertained, if that part should be used for the intensity measurement. For this purpose the middle part of the ribbon which was to receive the atomic beam was shifted sideways by a special device not shown in the figure, exposing thereby different parts of the surface to the beam. The result obtained is shown in Fig. 3. The abscissa shows the displacement of the ribbon, while the ordinate represents the relative galvanometer deflections referred to position 2. All values agree with one another within a few per cent, showing that the uniformity is well rendered.

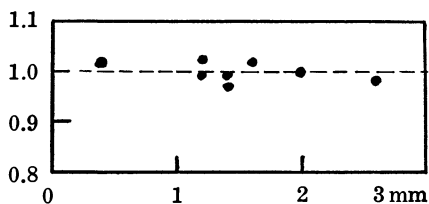


Fig. 3.

*Relation between the ribbon temperature and the ionization efficiency.*

Fig. 4 illustrates the results of our measurements made with the aim to obtain this important relation. The ribbon was exposed to the atomic beam in each case for a definite time. The deflections of the galvanometer resulted by the flashing at different temperatures are shown in the ordinate and the flashing temperature and the corresponding electric current used for the flashing, are indicated in the abscissa. Curve I was obtained with the oven temperature 136°C. and the time of exposure 40 sec., while curve II, with 232°C. and 30 sec. respectively. Obviously the surface concentration of adsorbed atoms is lower in the former case. In both cases the curves rise rapidly until about 800°C., which implies the rapid increase of the ionization efficiency with the rise of temperature. Above 800°C., curve I shows a constant value which suggests the

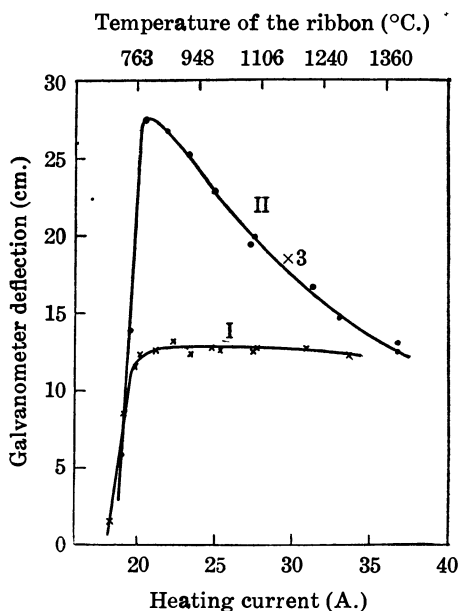


Fig. 4.

complete ionization of adsorbed atoms, while curve II has a maximum. This may be explained by the combined effect of the high surface concentration of adsorbed atoms and the surface migration which will be fully described in the next report.

*Relation between the surface concentration of adsorbed atoms and the ionization efficiency.* When applying this method of flashing to the intensity measurement of an atomic beam, it is of the utmost importance to know the influence of the surface concentration of adsorbed atoms upon the ionization efficiency. The following experiment will make this point clear.

An atomic beam of a constant intensity was produced and the time of exposure of the ribbon to it was varied. The surface concentration of adsorbed atoms thus obtained is proportional to the time of exposure, since the condensation coefficient may be assumed to be unity. The ribbon with adsorbed atoms was then flashed and the deflection of the galvanometer was noted. The results obtained are shown in Figs. 5 and

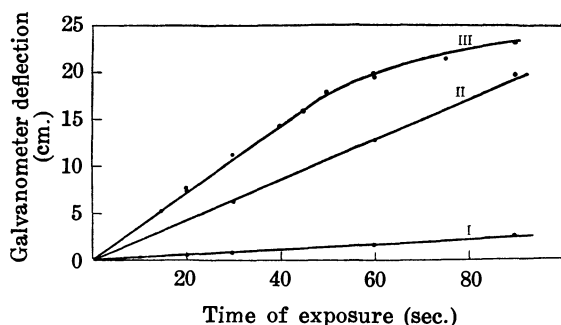


Fig. 5.

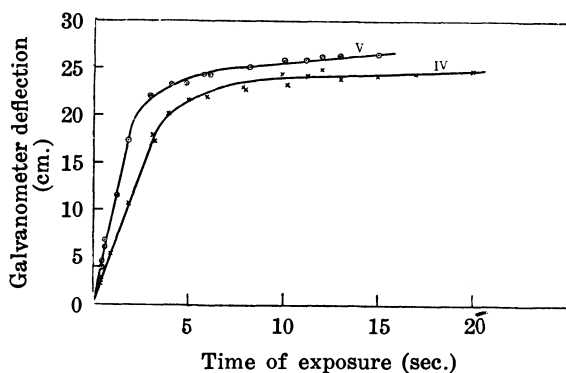


Fig. 6.

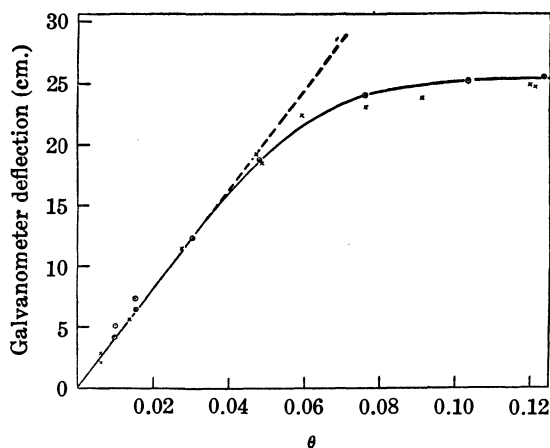


Fig. 7.

6, where the time of exposure is indicated in the abscissa and the galvanometer deflections in the ordinate. Curves I-V represent the results obtained with five different beam intensities, corresponding to respective oven temperatures. Each curve rises linearly until the galvanometer deflection becomes about 19 cm. This suggests that the ionization efficiency is 100 per cent in this range of surface concentration. (Curve III shows a slight deviation from a straight line, but this was found to be due to a small change in the oven temperature in the course of measurement.)

In reality, however, if the two curves in Fig. 6 is arranged to one with a smaller inclination (cf. Fig. 7), we see that the straight portion extends hardly to 15 cm. From this value, the highest surface concentration which still permits the perfect ionization of adsorbed atoms may be calculated. The results shown in Figs. 5 and 6 were obtained with deposits from a slightly divergent beam which has passed the last defining hole 3.45 mm. in diameter, perforated in the protector tube, so that the circular deposits formed on the ribbon is a little larger than the hole, namely 3.76 mm.

in diameter corresponding to the area of 0.111 cm.<sup>2</sup>. According to Taylor and Langmuir<sup>(5)</sup> the number of caesium atoms in the mono-atomic layer on tungsten is  $4.8 \times 10^{14}$  per cm.<sup>2</sup> of the apparent surface. This number is also applicable in the case of potassium. If we assume that the maximum surface concentration allowable for perfect ionization corresponds to 15 cm. of the galvanometer deflection, the number of ions which causes this deflection will be

$$\frac{150 \times 3 \times 3.77 \times 10^{-10} \times 2}{1.6 \times 10^{-19}} = 2.12 \times 10^{12},$$

where  $3.77 \times 10^{-10}$  is the sensitivity of the galvanometer which was used at 1/3 of its full sensitivity by means of an Ayrton shunt and the mirror-scale distance was one half of the normal,  $1.6 \times 10^{-19}$  is the ionic charge expressed in coulomb. Since so many ions were adsorbed on the apparent surface of 0.111 cm.<sup>2</sup>, the fraction  $\theta$  covered by the mono-atomic layer must be

$$\theta = \frac{2.12 \times 10^{12}}{0.111 \times 4.8 \times 10^{14}} = 0.040.$$

According to Langmuir,<sup>(6)</sup> if  $\nu_p$  and  $\nu_a$  are respectively the numbers of ions and atoms evaporated in unit time from unit area of the surface which is in equilibrium with the impinging atoms, their ratio may be given by

$$\frac{\nu_p}{\nu_a} = \frac{1}{2} \exp. \left[ \frac{\epsilon(V_w - V_i - V_c)}{kT} \right] \quad (1).$$

$V_w$  is the work function of pure tungsten and  $V_i$  the ionization potential of potassium and  $V_c$  the contact potential of tungsten covered with potassium against pure tungsten.  $V_c$  varies with  $\theta$ . Now in the course of flashing at a temperature  $T$ , the surface concentration and consequently the contact potential, change continuously. Equation (1) holds only for a minimum amount of potassium atoms evaporated. Let us define the differential ionization efficiency for the surface with a certain  $\theta$  and  $V_c$  by equation (2), where  $N = \nu_p + \nu_a$ :

$$\frac{d\nu_p}{dN} = \frac{\frac{1}{2} \exp. \left[ \frac{\epsilon(V_w - V_i - V_c)}{kT} \right]}{1 + \frac{1}{2} \exp. \left[ \frac{\epsilon(V_w - V_i - V_c)}{kT} \right]} \quad (2).$$

This equation shows that the ionization efficiency is highest when  $V_c$  is nil and decreases as  $V_c$  increases.

The total ionization  $\nu_p$ , which is proportional to the galvanometer deflection may be obtained by integrating equation (2) with respect to  $\theta$  from  $\theta$  to zero,  $N$  and  $V_c$  being expressed in terms of  $\theta$ .  $N$  is obviously equal to  $N_0 \theta$ , where  $N_0 = 4.8 \times 10^{14}$  is the number of atoms in 1 cm.<sup>2</sup> of the mono-atomic layer on tungsten. If  $V_c$  is assumed to be proportional to

(6) I. Langmuir, *J. Am. Chem. Soc.*, **54** (1932), 2825.

$\theta$ , i.e.  $V_c = c\theta$ , as will be discussed below, the integration gives

$$\nu_p = AN_0 \frac{kT}{c\varepsilon} \left[ \log \left( 1 + \frac{1}{2} \exp. [\varepsilon(V_w - V_i)/kT] \right) - \log \left( 1 + \frac{1}{2} \exp. [\varepsilon(V_w - V_i - c\theta)/kT] \right) \right] \quad (3),$$

where  $A = 0.111 \text{ cm.}^2$  the area of the deposit.

We see from this equation that the total ionization will show a linear increase for a considerably wide range of  $\theta$ , if  $V_w - V_i$  is so large that 1 can be neglected against the exponential term, for in this case equation (3) is reduced to  $\nu_p = N_0 \theta$ . This means the complete ionization for this range of  $\theta$ .

The general form of the curve is determined solely by the second term, which can be put in the form  $\log(1 + e^x)$  and is graphically

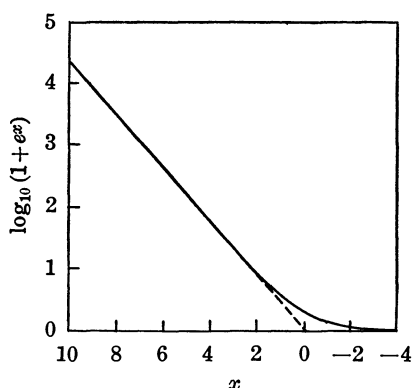


Fig. 8.

represented in Fig. 8. The comparison with the experimental curve (Fig. 7) shows that its linear portion corresponds to the range of  $x$  from 4 to 2, an appreciable deviation from the linearity beginning at about 2, or at

$$\varepsilon(V_w - V_i - V_c)/kT = 2.$$

Now if we put in equation (2)  $V_w = 4.52 \text{ V.}$   $V_i = 4.32 \text{ V.}$   $T = 1.379^\circ \text{K.}$  and  $V_c = 0$ , the ionization efficiency will be found considerably less than 100 per cent:

$$\frac{\nu_p}{N} = 0.804.$$

Thus the value of  $V_w - V_i$  is not large enough to explain the straight portions of the curves shown in Figs. 5 and 6.

In their experiments on the surface ionization of potassium by tungsten, Copley and Phipps<sup>(7)</sup> found that the values of  $\nu_p/\nu_a$  which they found could be brought into conformity with equation (1) if the factor  $1/2$  was omitted.

As they pointed out, a factor  $(1 - r_p)/(1 - r_a)$  has been omitted in equation (1), where  $r_p$  and  $r_a$  are the reflection coefficients of ions and atoms. This factor is usually supposed to be unity but they assumed that it happened to cancel the factor  $1/2$ . This argument may not be accepted as it stands but the omission of  $1/2$  has the favourable effect of increasing the ionization efficiency. According to equation (3) the differential ionization efficiency is calculated to 89.2 per cent at  $\theta = 0$ . This value is, however, still too low to explain the experimental results. Further considerations in this point will be discussed in the next report.

(7) Copley and Phipps, *Phys. Rev.*, **45** (1934), 344.

### Summary.

In these experiments on the measurement of the intensity of potassium atomic beams with a tungsten ribbon, the following results have been obtained:

(1) The ribbon was used to catch potassium atoms at room temperature and the positive ions formed by flashing were measured with a ballistic galvanometer.

(2) The ribbon surface is uniform for the ionization of potassium atoms.

(3) For the evaporation in the form of ions of adsorbed potassium atoms, the ribbon must be heated higher than  $800^{\circ}\text{C}$ .

(4) When the ionization of adsorbed potassium atoms is effected by flashing, the ionization is complete, when the surface concentration is below 0.04; otherwise, the ionization is incomplete.

(5) The ionization efficiency as a function of the surface concentration of potassium atoms was calculated on simple assumption and was found to deviate from the value observed.

The author wishes to express his sincere thanks to Prof. Nobuji Sasaki for his kind suggestion. Thanks are also due to the Japan Society for the Promotion of Scientific Research for a grant to Prof. Sasaki, from which the expense has been defrayed; to Dr. T. Okada, Institute of Chemical Technology; to Mr. B. Imamura, of the Tokyo Denki Kabushiki Kaisha, for supplying him with tungsten ribbons; and to Professor C. Matsuda, Institute of Electrical Engineering for lending him an optical pyrometer.

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## On the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum-carbonyl.

By Isamu SANO.

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**Introduction.** It is generally accepted through experiences<sup>(1)</sup> for a long time, although there have been raised a number of objections<sup>(2)</sup> against the concept, that oxalic acid is decomposed in its aqueous solutions

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(1) G. Bizio, *Z. anal. Chem.*, **9** (1870), 392; A. Downes and T. P. Blunt, *Proc. Roy. Soc. (London)*, **29** (1879), 219; E. Duclaux, *Compt. rend.*, **103** (1886), 1011; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; A. Richardson, *J. Chem. Soc.*, **65** (1894), 450; H. de Vries, *Z. angew. Chem.*, **1899**, 521; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(2) T. Gigli, *Chem. Zentr.*, **64** (1893), I, 11.

by oxygen in the air to turn into carbon dioxide and water, if exposed to direct sun-light as well as (naturally in smaller extent) to diffused day-light for a certain space of time; while if not subjected to the agency of light (for instance, in the dark), it is quite stable.

It is thoroughly known as well, on the other hand, that oxalic acid is decomposed in its aqueous solutions by moulds,<sup>(3)</sup> no matter whether it may be present in the dark or in the light, and according to Wehmer<sup>(3)</sup> and Jorissen,<sup>(1),(3)</sup> the acid acts as a poison for the moulds if the concentration of the acid solution is greater than 2–3%. Dilute solutions can be conserved by means of sterilization or by adding 50 c.c. of concentrated sulphuric acid per litre, boric acid being scarcely effective. On the addition of manganese sulphate the decomposition of oxalic acid due to oxidation in its aqueous solutions is more accelerated in the presence of light.

S. Ishimaru<sup>(4)</sup> investigated the influences of purity of oxalic acid preparation, day-light, and sulphuric acid added on the preservation of aqueous solutions of oxalic acid during a long period extending over seven months, and established that a 0.01 N solution is stable when 50 c.c. of concentrated sulphuric acid per litre is added, irrespective of purity of preparation as well as day-light. A 0.1 N solution is decomposed in the light notwithstanding the addition of sulphuric acid, but stable in the dark without sulphuric acid. A 0.5 N solution is stable in the dark without sulphuric acid, solution of pure preparation being stable in the light.

O. Šulc<sup>(5)</sup> studied the effects of various metals in finely divided state such as palladium, silver, copper, and platinum on the decomposition of aqueous solutions of oxalic acid at room temperatures. The results obtained with palladium which was ascertained to be the most effective of the metals aforesaid, are tabulated below. A 100 c.c. of 0.1 N aqueous oxalic acid solution was mixed with 1.36 grams of palladium powder afresh ignited and cooled in the air prior to use in a closed flask in each run of the experiments and 10 c.c. was pipetted out from it at the desired inter-

| Time elapsed in days | Titre of the oxalic acid solution in c c. |       |                   |       |
|----------------------|-------------------------------------------|-------|-------------------|-------|
|                      | in the dark                               |       | in the light      |       |
|                      | without palladium                         | with  | without palladium | with  |
| 0                    | 10.05                                     | 10.05 | 10.04             | 10.04 |
| 4                    | —                                         | —     | 9.92              | 8.62  |
| 8                    | 10.03                                     | 8.79  | —                 | —     |
| 9                    | —                                         | —     | 9.00              | 6.78  |
| 19                   | 10.00                                     | 8.24  | 6.40              | 3.75  |
| 26                   | 9.90                                      | 8.31  | —                 | —     |
| 38                   | —                                         | —     | 0.34              | 0.25  |

(3) C. Neubauer, *Z. anal. Chem.*, **9** (1870), 392; W. N. Hartley, *Chem. News*, **37** (1878), 9; G. Fleury, *Chem. Zentr.*, **14** (1883), 547; O. Warburg, *Untersuch. botan. Inst. Tübingen*, **2** (1886–8), 117; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(4) S. Ishimaru, *J. Chem. Soc. Japan*, **43** (1922), 767; **53** (1932), 449; *Science Repts. Tôhoku Imp. Univ.*, Ser. I, **24** (1935), 411.

(5) O. Šulc, *Z. physik. Chem.*, **28** (1899), 719.

vals of time, mixed with a small quantity of sulphuric acid, warmed if necessary and titrated with a potassium permanganate solution.

In the preceding papers,<sup>(6)</sup> the author reported the formation and behaviour of a platinum-carbonyl sol of red colour obtainable from an aqueous solution of chloroplatinic acid by the action of carbon monoxide and the catalytic decomposition of hydrogen peroxide by the sol. The present communication deals with the experiments on the decomposition of oxalic acid in its aqueous solutions due to oxidation by the air, which is catalysed by the colloidal platinum-carbonyl as well as by the colloidal platinum obtainable from it.

On passing carbon monoxide through an aqueous solution of chloroplatinic acid at ordinary temperature for a while, the colour of the solution changes from yellow to red, the platinum-carbonyl sol being thus obtained. By dialyzing the red sol or letting it stand in the air, it turns black before long to produce a platinum sol as prepared by Bredig's method.

**Experimental Procedures and Results.** The oxalic acid solutions used were prepared by dissolving oxalic acid purified by means of recrystallization in distilled water. The red sol was prepared by passing carbon monoxide through a 0.05% aqueous solution of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) with nearly a constant velocity throughout the experiments, carbon monoxide being obtained by heating the mixture of oxalic acid and concentrated sulphuric acid and purified by passing through alkaline hydroxide solutions. The black sol was obtained from the red one by standing it in the air as already mentioned. Accordingly the sol, red or black, was inferred from calculation to contain 0.188 grams of platinum in one litre.

In each run of the experiments described below, the red sol and the black one added as catalyst are respectively used immediately after its formation, the red sol being obtained from the aqueous solution of chloroplatinic acid and the black one from the red sol, and both of them being not dialyzed.

The reactions were carried out at 25.0°C. as well as 50.0°C. under diffused day-light. The vessels were cleaned and steamed to the full before use. The results obtained are indicated in Table 1 to Table 12, where  $t$  denotes the time elapsed from the beginning in hours,  $c$  the titre of the reacting solution titrated with a 0.1 N barium hydroxide solution at time  $t$  in c.c., corrections being made for the portion of the titre attributable to hydrochloric acid in the sol added as catalyst, and  $t_r$  the time duration during which the sol remains red in the reaction mixture before it passes into black in hours. The meanings of  $c_k$  and  $t_k$  will be explained later. The procedures and results were as follows.

25.0°C.: A 20 c.c. of a 0.10 N oxalic acid solution was placed in a flask, 20 c.c. of the red sol was added to it and the solution thoroughly mixed by shaking. At the desired intervals of time, 10 c.c. was pipetted out from it and titrated with the barium hydroxide solution. The results are shown in Tables 1 and 2.

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(6) I. Sano, this Bulletin, **9** (1934), 320; **13** (1938), 118.



Table 1.

| $t$       | $c$             | $c_k (t_k = 14)$ |
|-----------|-----------------|------------------|
| 0         | 11.80 ( $c_0$ ) | —                |
| 2         | 11.75           | —                |
| 4         | 11.78           | —                |
| 6         | 11.80           | —                |
| 27        | 11.71           | 11.76            |
| 29        | 11.69           | 11.75            |
| 50        | 11.59           | 11.74            |
| 75        | 11.50           | 11.75            |
| 99        | 11.43           | 11.77            |
| 147       | 11.32           | 11.85            |
| 173       | 11.23           | 11.86            |
| 197       | 11.08           | 11.80            |
| 221       | 10.92           | 11.73            |
| 245       | 10.84           | 11.74            |
| 317       | 10.64           | 11.81            |
| 365       | 10.56           | 11.92            |
| 412       | 10.30           | 11.82            |
| 604       | 9.62            | 11.79            |
| $t_r = 3$ |                 |                  |

Table 2.

| $t$       | $c$             | $c_k (t_k = 6)$ |
|-----------|-----------------|-----------------|
| 0         | 14.14 ( $c_0$ ) | —               |
| 4         | 14.13           | —               |
| 5         | 14.15           | —               |
| 24        | 13.96           | 14.10           |
| 50        | 13.81           | 14.17           |
| 55        | 13.76           | 14.15           |
| 72        | 13.63           | 14.16           |
| 75        | 13.56           | 14.11           |
| 96        | 13.41           | 14.12           |
| 100       | 13.40           | 14.14           |
| 120       | 13.23           | 14.12           |
| 168       | 12.89           | 14.14           |
| 172       | 12.83           | 14.11           |
| 192       | 12.70           | 14.13           |
| 194       | 12.68           | 14.12           |
| 216       | 12.48           | 14.08           |
| 220       | 12.49           | 14.12           |
| 264       | 12.14           | 14.08           |
| $t_r = 4$ |                 |                 |

50.0°C.: The reacting mixtures consisting of 10 c.c. of aqueous solution of oxalic acid of a definite concentration and 2 c.c. of the red or black sol were placed in test-tubes provided with rubber stopper through which a capillary tube was inserted as a line of communication of the air. At the desired intervals of time, the test-tubes were, by turns, titrated with the barium hydroxide solution. The reacting solutions were, as in the other cases, agitated at short intervals. The results are given in Tables 3, 4, 5, 6, 7 and 8.

Table 3. Concentration of oxalic acid solution : 0.10 N  
Sol added as catalyst : red

| $t$       | $c$             | $c_k (t_k = 6)$ |
|-----------|-----------------|-----------------|
| 0         | 15.69 ( $c_0$ ) | —               |
| 1.5       | 15.79           | —               |
| 3         | 15.62           | —               |
| 6         | 15.48           | —               |
| 9         | 15.39           | 15.46           |
| 12        | 15.34           | 15.48           |
| 15        | 15.25           | 15.46           |
| 18        | 15.19           | 15.47           |
| 21        | 15.16           | 15.51           |
| 24        | 15.05           | 15.47           |
| 27        | 14.97           | 15.45           |
| 30        | 14.91           | 15.46           |
| $t_r = 2$ |                 |                 |

Table 4. Concentration of oxalic acid solution : 0.10 N  
Sol added as catalyst : red

| $t$       | $c$             | $c_k (t_k = 10)$ |
|-----------|-----------------|------------------|
| 0         | 12.06 ( $c_0$ ) | —                |
| 2         | 12.13           | —                |
| 4         | 11.95           | —                |
| 6         | 11.82           | —                |
| 8         | 11.71           | —                |
| 10        | 11.59           | —                |
| 12        | 11.55           | 11.60            |
| 16        | 11.45           | 11.60            |
| 20        | 11.34           | 11.59            |
| 24        | 11.17           | 11.52            |
| 28        | 11.16           | 11.61            |
| 32        | 11.05           | 11.60            |
| 35        | 10.98           | 11.60            |
| $t_r = 2$ |                 |                  |

Table 5. Concentration of oxalic acid solution : 0.10 N  
Sol added as catalyst : black

| $t$       | $c$             | $c_k(t_k = 2)$ |
|-----------|-----------------|----------------|
| 0         | 12.07 ( $c_0$ ) | —              |
| 1         | 11.80           | —              |
| 2.5       | 11.57           | 11.61          |
| 4         | 11.45           | 11.60          |
| 6         | 11.35           | 11.64          |
| 9         | 11.02           | 11.52          |
| 12        | 10.87           | 11.58          |
| 16        | 10.70           | 11.69          |
| 21        | 10.35           | 11.67          |
| 24        | 10.12           | 11.63          |
| 28        | 9.80            | 11.55          |
| 30        | 9.77            | 11.67          |
| $t_r = -$ |                 |                |

Table 6. Concentration of oxalic acid solution : 0.05 N  
Sol added as catalyst : red

| $t$       | $c$            | $c_k(t_k = 2)$ |
|-----------|----------------|----------------|
| 0         | 5.65 ( $c_0$ ) | —              |
| 2         | 5.69           | —              |
| 4.5       | 5.42           | 5.61           |
| 6         | 5.32           | 5.60           |
| 8         | 5.25           | 5.69           |
| 10        | 5.10           | 5.68           |
| 12        | 4.91           | 5.62           |
| 16        | 4.73           | 5.71           |
| 21        | 4.39           | 5.67           |
| 24        | 4.11           | 5.53           |
| 27        | 4.05           | 5.67           |
| 32        | 3.76           | 5.64           |
| $t_r = 2$ |                |                |

Table 7. Concentration of oxalic acid solution : 0.05 N  
Sol added as catalyst : black

| $t$       | $c$            | $c_k(t_k = 2)$ |
|-----------|----------------|----------------|
| 0         | 6.12 ( $c_0$ ) | —              |
| 1         | 5.88           | —              |
| 2.5       | 5.64           | 5.70           |
| 4         | 5.54           | 5.76           |
| 6         | 5.30           | 5.73           |
| 9         | 4.97           | 5.70           |
| 12        | 4.78           | 5.81           |
| 16        | 4.33           | 5.70           |
| 21        | 4.02           | 5.83           |
| 24        | 3.73           | 5.74           |
| 27        | 3.52           | 5.74           |
| 30        | 3.38           | 5.85           |
| $t_r = -$ |                |                |

Table 8. Concentration of oxalic acid solution : 0.025 N  
Sol added as catalyst : red

| $t$       | $c$            | $c_k(t_k = 2)$ |
|-----------|----------------|----------------|
| 0         | 3.05 ( $c_0$ ) | —              |
| 2         | 3.10           | —              |
| 4         | 2.84           | 3.05           |
| 6         | 2.68           | 3.10           |
| 8         | 2.50           | 3.11           |
| 10        | 2.31           | 3.08           |
| 12        | 2.16           | 3.10           |
| 16        | 1.87           | 3.10           |
| 21        | 1.79           | 3.56           |
| 24        | 1.35           | 2.99           |
| 27        | 1.27           | 3.13           |
| 30        | 1.12           | 3.08           |
| $t_r = 2$ |                |                |

One run was carried out at 50.0°C. in hermetically sealed test-tubes. The results obtained are indicated in Table 9.

With the view of investigating the extent to which the light has influence upon the decomposition of oxalic acid in its aqueous solution, a number of runs were made under the conditions as already described without the sol being added. The results are shown in Tables 10, 11 and 12. From these results it can be concluded that aqueous solutions of oxalic acid are not decomposed in the least under the conditions concerned.

Table 9. Concentration of oxalic acid solution : 0.05 N  
Sol added as catalyst : black

| $t$       | $c$            | $c_k(t_k = 1.5)$ |
|-----------|----------------|------------------|
| 0         | 6.07 ( $c_0$ ) | —                |
| 1         | 5.79           | —                |
| 2.5       | 5.69           | 5.76             |
| 4         | 5.54           | 5.72             |
| 6         | 5.38           | 5.70             |
| 9         | 5.24           | 5.78             |
| 12        | 4.98           | 5.71             |
| 20        | 4.75           | —                |
| 24        | 4.72           | —                |
| 27        | 4.66           | —                |
| 30        | 4.66           | —                |
| $t_r = -$ |                |                  |

**Discussion of the Results.** The above results indicated in the tables (Table 1 to Table 9 inclusive) are graphically depicted below in terms of the relationship between  $\log(c_0/c)$  and  $t$  in Fig. 1, 2, 3 and 4 (Curve 1 to Curve 9 inclusive). If the decomposition of oxalic acid due to oxidation in its aqueous solutions, which is accelerated by colloidal platinum-carbonyl as well as colloidal platinum should, in the course of reaction, come to proceed in accordance with the formula for uni-molecular reaction

$$-dc/dt = kc \quad \text{or} \quad \log(c_0/c) = kt,$$

where  $c_0$  is the initial concentration and  $k$  the velocity constant, it may be

anticipated that there must be a portion of straight line in the curve indicating the relation between  $\log(c_0/c)$  and  $t$ .

Table 10.  
Concentration of oxalic acid solution : 0.10 N  
Temperature : 25.0°C.

| $t$ | $c$             |
|-----|-----------------|
| 0   | 14.32 ( $c_0$ ) |
| 20  | 14.31           |
| 24  | 14.31           |
| 43  | 14.28           |
| 68  | 14.27           |
| 72  | 14.36           |
| 92  | 14.40           |
| 96  | 14.37           |
| 116 | 14.35           |
| 164 | 14.35           |
| 188 | 14.38           |
| 216 | 14.38           |
| 260 | 14.36           |
| 356 | 14.35           |
| 358 | 14.34           |
| 456 | 14.29           |
| 457 | 14.30           |

Table 11.  
Concentration of oxalic acid solution : 0.10 N  
Temperature : 50.0°C.

| $t$ | $c$             |
|-----|-----------------|
| 0   | 12.17 ( $c_0$ ) |
| 4   | 12.16           |
| 9   | 12.12           |
| 12  | 12.16           |
| 18  | 12.15           |
| 24  | 12.17           |
| 30  | 12.12           |

Table 12.  
Concentration of oxalic acid solution : 0.05 N  
Temperature : 50.0°C.

| $t$ | $c$            |
|-----|----------------|
| 0   | 6.14 ( $c_0$ ) |
| 4   | 6.15           |
| 9   | 6.22           |
| 12  | 6.16           |
| 18  | 6.18           |
| 24  | 6.16           |
| 30  | 6.16           |

In the case where the red sol is added as catalyst, the apparent concentration of oxalic acid solution remains nearly constant over a certain space of time and the reacting solution is of red tint throughout the period, suggesting the sol to exist unchanged. In time, however, the solution will lose the red colour to become tinged with black and then the decomposition will begin abruptly and proceed smoothly. The induction period

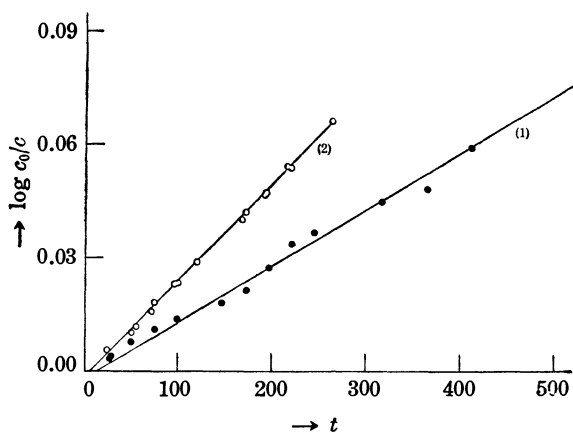


Fig. 1.

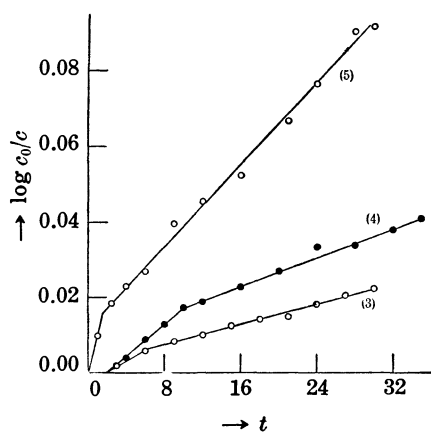


Fig. 2.

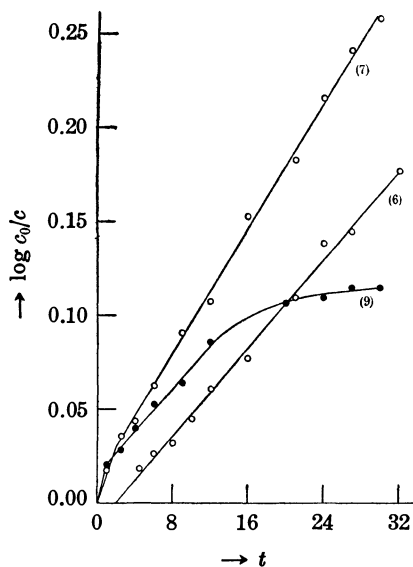


Fig. 3.

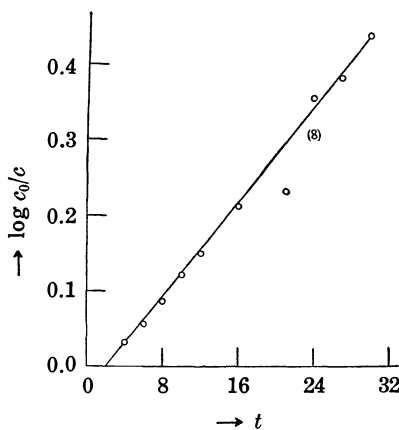


Fig. 4.

mentioned above is distinctly shown by the former parts of Curves 1, 2, 3, 4, 6 and 8; while the latter parts of the curves concerned are linear, indicating the reaction to proceed as unimolecular.

On adding the red sol to aqueous solutions of oxalic acid, carbon monoxide ratiocinated from various facts already established<sup>(7)</sup> to be held in the colloidal particle as its essential constituent will vanish gradually from it through volatilization as well as oxidation, since the sol is diluted with oxalic acid solution loaded with dissolved oxygen. Sooner or later, carbon monoxide constituting the particle will reach a certain limiting amount, when the particle may be reasonably regarded as colloidal

(7) I. Sano, this Bulletin, 9 (1934), 320.

platinum rather than as colloidal platinum-carbonyl; in other words, a sol of platinum of black colour will be formed and hereupon, the induction period will be over.

In the case where the black sol obtained from the red one is added as catalyst, the decomposition of oxalic acid in its aqueous solutions takes place immediately after mixing and proceeds without any delay. Although the former part of the curve standing for the relation between  $\log(c_0/c)$  and  $t$  makes a bend in due course of time, the latter part of it assumes a rectilinear figure during the time duration concerned as shown by Curves 5, 7 and 9.

The transition period above mentioned—in the case of the red sol, it follows in the wake of the induction period as seen from Curves 3 and 4—may probably result from coagulation of the sol due to electrolyte. Since the sol under consideration is negatively charged, its coagulation must be caused by positive charge and in consequence, the catalytic activity of colloidal particles must be decreased to some extent. On passing this stage, there may scarcely occur any change in the catalytic activity of the particles. The coagulation may be assumed to proceed the more rapidly as well as strongly, the more concentrated the oxalic acid solution is.

This can be seen by comparing one another the magnitudes of the velocity constant,  $k$ , for the straight portion of the curve, calculated from the diagram. It is clear from the table that  $k$  increases definitely as the

| Number of table | Temperature at which the reaction was carried out (°C.) | Sol added as catalyst | $t_r$ | Concentration of aqueous solution of oxalic acid (N) | $k$ (hour <sup>-1</sup> ) |
|-----------------|---------------------------------------------------------|-----------------------|-------|------------------------------------------------------|---------------------------|
| 1               | 25.0                                                    | red                   | 3     | 0.10                                                 | 0.000150                  |
| 2               | 25.0                                                    | red                   | 4     | 0.10                                                 | 0.000249                  |
| 3               | 50.0                                                    | red                   | 2     | 0.10                                                 | 0.000658                  |
| 4               | 50.0                                                    | red                   | 2     | 0.10                                                 | 0.000956                  |
| 5               | 50.0                                                    | black                 | —     | 0.10                                                 | 0.00275                   |
| 6               | 50.0                                                    | red                   | 2     | 0.05                                                 | 0.00586                   |
| 7               | 50.0                                                    | black                 | —     | 0.05                                                 | 0.00850                   |
| 8               | 50.0                                                    | red                   | 2     | 0.025                                                | 0.0157                    |
| 9               | 50.0                                                    | black                 | —     | 0.05                                                 | 0.00563                   |

concentration of aqueous solution of oxalic acid decreases. It was observed, in fact, at 50.0°C. that in dilute solutions, the sol added is practically stable and remains black as it was throughout one run of the experiments; while in concentrated solutions, it coagulates to a marked degree in several hours from the commencement to settle at the bottom. Consequently, it appears that coagulation of the sol may be more influenced by electrolyte than by heat.

The value of  $c_k$  tabulated previously was calculated from  $k$  thus obtained in accordance with the formula for unimolecular reaction

$$\log(c_k/c) = kt,$$

where  $c$  is the concentration of oxalic acid solution at time  $t$  elapsed from a specified starting-point of reckoning indicated by  $t_k$  in the tables. It might be anticipated for  $c_k$  to assume a constant value in each run of the experiments if the reaction should proceed as unimolecular.

It has been stated already that oxalic acid is decomposed in its aqueous solutions in the presence of oxygen. The effect can be seen distinctly from Curve 9. In this run the reaction was carried out in test-tubes hermetically sealed in order to keep out the air from the outside. It can be seen that drift occurs in the final stage from want of oxygen.

In connection with what has been mentioned above, some theoretical consideration will be made as follows.

It may be supposed on the whole that chemical reactions will occur between molecules adsorbed on adjacent spaces of the catalyst surface, and the rate of reaction is slow in comparison with the rate at which molecules of reactants condense upon and evaporate from the surface; that is to say, the rate of reaction will not affect to any appreciable extent the equilibrium between the adsorbed layer and the surrounding medium.

If  $\theta_1$  represents the fraction of the available surface covered unimolecularly with molecules of oxalic acid and  $\theta_2$  with molecules of oxygen at any instant, it will follow that for equilibrium between the adsorbed layer consisting of both molecules of oxalic acid as well as oxygen and those in the surrounding medium, under the assumption that each molecule of these may occupy one elementary space of the surface and the presence of solvent may be left out of consideration,

$$a_1\mu_1(1-\theta_1-\theta_2) = \nu_1\theta_1 \quad \text{and} \quad a_2\mu_2(1-\theta_1-\theta_2) = \nu_2\theta_2,$$

$a_1$  and  $a_2$  being the fractions of the numbers of molecules of oxalic acid and oxygen,  $\mu_1$  and  $\mu_2$ , striking the surface in unit time which condense, and  $\nu_1\theta_1$  and  $\nu_2\theta_2$  the numbers of molecules of oxalic acid and oxygen which evaporate from the surface in unit time. Reference must be made to that oxalic acid may be treated as non-electrolyte for the sake of simplicity, the state of the molecule adsorbed on the catalyst surface being not taken into consideration both for dissociated as well as undissociated molecule.

If the surface is covered so sparsely by molecules of both of them that  $\theta_1 \ll 1$  and  $\theta_2 \ll 1$  and accordingly  $\theta_1 + \theta_2 \ll 1$ , then  $1 - \theta_1 - \theta_2$  may be put as approximately equal to unity; hence, it follows that

$$a_1\mu_1 = \nu_1\theta_1 \quad \text{and} \quad a_2\mu_2 = \nu_2\theta_2$$

$$\text{or} \quad \theta_1 = \mu_1 \cdot a_1 / \nu_1 \quad \text{and} \quad \theta_2 = \mu_2 \cdot a_2 / \nu_2.$$

Since it may be presumed for the rate of reaction,  $v$ , to be proportional to the amounts of reactants adsorbed on the available surface, it will be given by

$$v = k\theta_1\theta_2,$$

$k$  being the velocity constant. Substituting the values for  $\theta_1$  and  $\theta_2$ , it follows that

$$v = k\mu_1\mu_2\cdot\alpha_1\alpha_2/\nu_1\nu_2.$$

Considering  $\mu$  to be proportional to the concentration,  $c$ , of the reactant, this may be written in the form

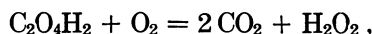
$$v = k'c_1c_2,$$

$k'$  being made up of a combination of various constants such as  $k$ ,  $\alpha$  and  $\nu$ . The formula thus obtained reduces to the formula for unimolecular reaction

$$v = k''c_1,$$

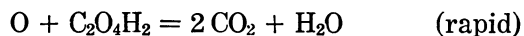
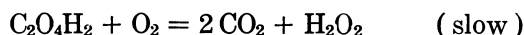
where  $k'' = k'c_2$ , provided that  $c_2$  is constant throughout the experiment, and this is actually the case as the reacting system is supplied with oxygen from the outside.

On studying the influence of light on the decomposition of oxalic acid in its aqueous solutions due to oxidation by oxygen in the air, Richardson<sup>(1)</sup> concluded that during the decomposition of the acid in the presence of light and oxygen, the carbon in each molecule is oxidized to carbon dioxide and the hydrogen to hydrogen peroxide, if oxygen is in excess, in accordance with the equation

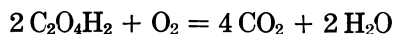


although the peroxide found by analysis falls, in general, far short (it rarely reaching one-tenth) of that calculated from the equation, on account of the decomposition of the acid occurring at the expense of the peroxide to some extent.

From the above-mentioned, the decomposition of oxalic acid due to oxidation in its aqueous solutions by colloidal platinum will be explained in the following manner. Whenever oxalic acid is decomposed by oxygen on the catalyst surface to produce carbon dioxide and hydrogen peroxide, atomic oxygen will be liberated then and there from hydrogen peroxide since it is readily decomposed by colloidal platinum as a well-known fact, and in quick succession, this will act on molecules of oxalic acid adsorbed on adjacent spaces of the catalyst surface and oxidize them; namely,



Hence, the reaction



will proceed unimolecularly.

### Summary.

(1) The decomposition of aqueous solutions of oxalic acid (0.10, 0.05, 0.025 N) due to oxidation accelerated by colloidal platinum-carbonyl of red colour as well as colloidal platinum of black colour obtainable from

it was, in the presence of oxygen and diffused day-light, studied during a period extending several hundred hours at 25.0°C. and thirty hours at 50.0°C.

(2) In the case where the red sol is added as catalyst, the reaction proceeds as unimolecular after it passed through an induction period and subsequently a transition period, while in the case where the black sol is added, it proceeds as the above after a transition period, no induction period presenting itself.

(3) The more dilute the acid solution, the more stable is the sol throughout the course of the experiment and consequently, the larger is the velocity constant.

(4) The mechanism of the reaction was discussed on these facts.

The author wishes to express his sincere thanks to Prof. J. Same-shima for his kind guidance and encouragement throughout the work. The expense of it has been defrayed from the Committee on Catalysis in the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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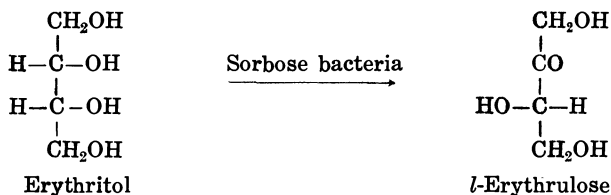


## The Formation of *d*-Erythrulose.

By Koichi IWADARE.

(Received March 13, 1939.)

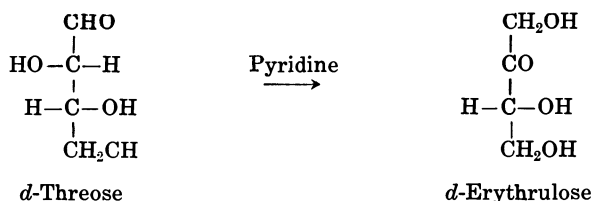
The syntheses of monoses were recently much investigated, and all the aldo- and keto-sugars of hexoses and pentoses, whose existence is supposed by theory, have already been prepared. As for tetroses, among the six theoretically possible forms, *d*-erythrulose has been the only sugar hitherto not synthesized. Its antipode, *l*-erythrulose, or *l*-2-keto-tetrose, was prepared by G. Bertrand<sup>(1)</sup> by oxidative fermentation of erythritol with sorbose bacteria (*bacterium xylinum*) about forty years ago, and its crystalline derivative was prepared by H. Müller, C. Montigel and T. Reichstein<sup>(2)</sup> in recent year. This biochemical method, however, is of course unavailable for the formation of *d*-form.



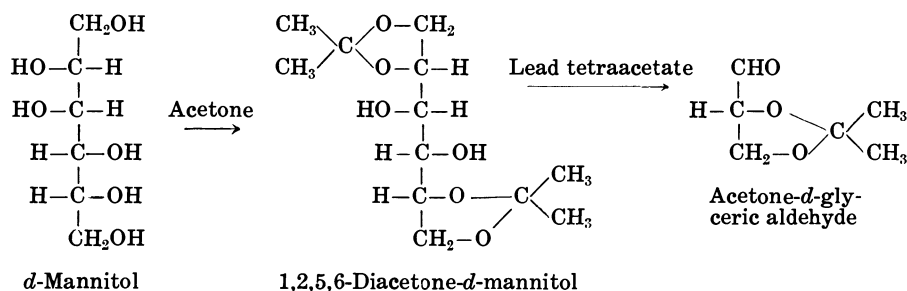
(1) G. Bertrand, *Compt. rend.*, **130** (1900), 1330. In this literature the sugar is written as *d*-erythrulose by old nomenclature, but it is quite clear from the reduction product that it should be *l*-form.

(2) H. Müller, C. Montigel, and T. Reichstein, *Helv. Chim. Acta*, **20** (1937), 1468.

In general, aldoses can be partly transformed to ketoses by heating them with organic bases such as pyridine or quinoline.<sup>(3)</sup> So *d*-threose was heated with pyridine at various temperatures in order to obtain *d*-erythrulose by epimerization. However, the mixture soon became quite dark, and *d*-erythrulose could not be obtained by this way.



So the method of R. Prince, K. Gätzi, and T. Reichstein<sup>(4)</sup> for preparing ketose by the addition of diazo-methane on the acetone derivative of glyconic acid chloride, which has one carbon atom less than the ketose to be obtained, was used successfully for this preparation of *d*-erythrulose. For this purpose, first of all, acetone-*d*-glyceric aldehyde is prepared from *d*-mannitol according to the method of H. O. L. Fischer and E. Baer.<sup>(5)</sup> That is, *d*-mannitol is shaken mechanically with acetone adding hydrochloric acid for condensing agent, then the mixture is neutralized with lead carbonate, and, after the removal of the solvent by distillation, 1,2,5,6-diacetone-*d*-mannitol is separated from triacetone-mannitol. The former is oxidized with lead tetraacetate, and thus acetone-*d*-glyceric aldehyde is obtained, the boiling points of which are 54° at 12 mm. and 63° at 20 mm.



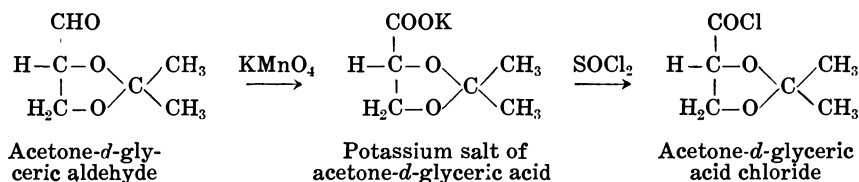
Acetone-*d*-glyceric aldehyde thus prepared is oxidized by potassium permanganate in alkaline solution, and the potassium salt of acetone-*d*-glyceric acid is obtained in colourless crystalline powder. Its specific rotatory power is  $[\alpha]_D^{15} = +23.7^\circ$  ( $c = 2.11$  in water). The potassium salt of acetone-*d*-glyceric acid is heated with thionyl chloride in ether solution and acetone-*d*-glyceric acid chloride is obtained. Freshly distilled chloride has specific rotatory power  $[\alpha]_D^{15} = +14.9^\circ$  ( $c = 1.6$  in ether). Acetone-*d*-glyceric acid amide is prepared by pouring the chloride into ammonia

(3) S. Danilow, E. V. Danilowa, and P. Schantorowitsch, *Ber.*, **63** (1930), 2271; K. Iwadare and B. Kubota, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34** (1938), 183.

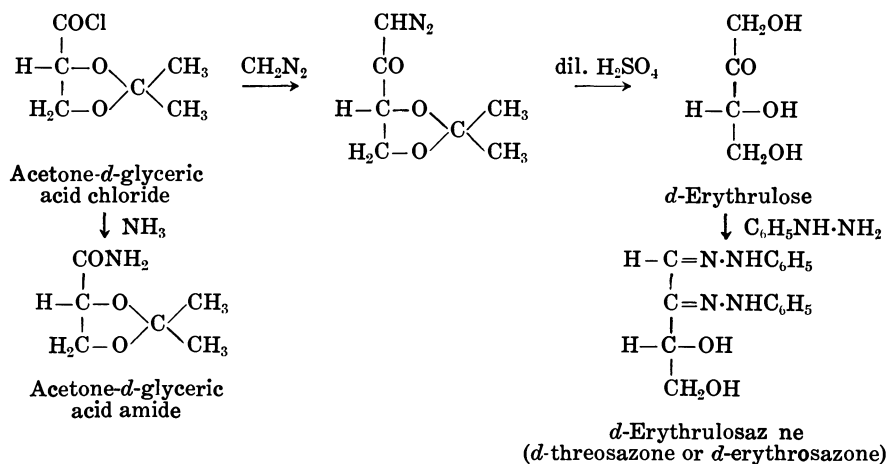
(4) K. Gätzi and T. Reichstein, *Helv. Chim. Acta*, **21** (1938), 186; R. Prince, Diss. Zürich, 1937.

(5) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **17** (1934), 622.

in ether solution. It melts at 72–73° and has specific rotatory power  $[\alpha]_D^{16} = +39.1^\circ$  ( $c = 0.8$  in water).



Ether solution of acetone-*d*-glyceric acid chloride is slowly poured into diazo-methane solution in ether, cooled with freezing mixture. After a day's standing, the solution is evaporated, and the residual diazo-ketone is submitted to hydrolysis by heating with dilute sulphuric acid. *d*-Erythrulose thus obtained is distilled in vacuo. Colourless syrup with specific rotatory power  $[\alpha]_D^{15} = -11 \pm 3^\circ$  in dilute solution. This value is in good agreement with that of *l*-erythrulose ( $[\alpha]_D^{15} = +11.4^\circ \pm 1^\circ$ ), which was reported by H. Müller, C. Montigel, and T. Reichstein.<sup>(2)</sup> *d*-Erythrulose solution reduces Fehling's solution at once in the cold. Its osazone melts at 168°. (Found: N, 18.64. Calc. for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_4$ : N, 18.72%). This melting point agrees with that of *d*-threosazone, which was prepared from *d*-threose by the author. So we may be able to say that *d*-erythrulose is now formed.



### Experimental.

**Acetone-*d*-glyceric aldehyde.** Three hundred grams of *d*-mannitol were mechanically shaken with 6 kg. of acetone and 150 c.c. of concentrated hydrochloric acid for about four hours, excess of lead carbonate or potassium carbonate was added, and the mixture was stirred mechanically. After neutralization, it was filtered, and acetone was removed by distillation. The residual crystalline mass was dissolved in 200 c.c. of alcohol and poured into 2 or 3 litres of water with stirring. The mixture was filtered and evaporated in vacuo, and the residue was dissolved in water. It was again filtered and evaporated. Thus about 100 g. of crude diacetone-mannitol was obtained. It was dissolved in 5 l. of petroleum benzine and filtered as soon as the solution was cooled to room temperature. Yield, about 25 g.

Thirty grams of diacetone-*d*-mannitol was dissolved in 1 litre of benzene, and 50 g. of lead tetraacetate was added. After an hour it was filtered and neutralized with diazo-methane, and the greater part of the solvent was removed by distillation. Then it was fractionally distilled at diminished pressure. Acetone-*d*-glyceric aldehyde distilled at 54° at 12 mm., and 63° at 20 mm. Yield, 13 g.

**Potassium salt of acetone-*d*-glyceric acid.** Ten grams of aldehyde were dissolved in 600 c.c. of water and the solution of 6.5 g. of potassium hydroxide and 10 g. of potassium permanganate in 600 c.c. of water was added drop by drop to it, the mixture being stirred vigorously. After two hours it was filtered, and the filtrate was neutralized with dilute sulphuric acid and evaporated in vacuo to dryness. It was dissolved in absolute alcohol, filtered from inorganic salt, again evaporated to thin syrup, and ether was added to it. Precipitated potassium salt was filtered and recrystallized from alcohol. Its specific rotatory power is  $[\alpha]_D^{15} = +23.7^\circ$  ( $c = 2.11$  in water). (Found: K, 21.63. Calc. for  $C_6H_9O_4K$ : K, 21.23%).

**Acetone-*d*-glyceric acid chloride.** Five grams of potassium salt was suspended in 40 c.c. of ether and 3 g. of thionyl chloride added. The mixture was boiled on a water bath for two hours and filtered. From the filtrate ether and the most of thionyl chloride were removed by distillation, and the residue was fractionally distilled at diminished pressure. The chloride distilled at 61° at 15 mm. It is a clear colourless liquid, with  $[\alpha]_D^{15} = +14.9^\circ$  ( $c = 1.6$  in ether). Yield, 1 g.

**Acetone-*d*-glyceric acid amide.** To an excess of ethereal solution of ammonia, 0.3 g. of chloride was added. It was then filtered from ammonium chloride and evaporated to syrup. The latter was dissolved in benzene, and soon crystallized. Recrystallized from benzene its melting point was 72–73°.  $[\alpha]_D^{16} = +39.1^\circ$  ( $c = 0.8$  in water). (Found: N, 9.78. Calc. for  $C_6H_{11}O_3N$ : N, 9.65%).

***d*-Erythrulose.** One gram of acetone-*d*-glyceric acid chloride was dissolved in 150 c.c. of absolute ether and poured into 1.5 g. diazo-methane dissolved in 60 c.c. of ether, cooling with freezing mixture. After a day's standing, the solution was filtered and evaporated, and the yellow syrup of diazo-ketone was hydrolysed by heating with 100 c.c. of 1% sulphuric acid on the water bath for two hours. Then it was neutralized with freshly precipitated barium carbonate and filtered with active charcoal. The filtrate was evaporated in vacuo to syrup and *d*-erythrulose distilled at 68° at 0.01 mm., the temperature of the bath being 100–105°. Its specific rotatory power was  $[\alpha]_D^{15} = -11^\circ \pm 3^\circ$ .

***d*-Erythrosazone.** *d*-Erythrulose was dissolved in water and heated with excess of phenylhydrazine and acetic acid for three hours. The separated oily substance was crystallized from alcohol. Melting point, 168° (Found: N, 18.64. Calc. for  $C_{16}H_{18}O_2N_4$ : N, 18.72%).

### Summary.

(1) *d*-Erythrulose was formed by the hydrolysis of diazo-ketone which was obtained by condensing diazo-methane with acetone-*d*-glyceric acid chloride.

(2) Potassium salt of acetone-*d*-glyceric acid ( $[\alpha]_D^{15} = +23.7^\circ$ ), acetone-*d*-glyceric acid chloride ( $[\alpha]_D^{15} = +14.9^\circ$ ) and acetone-*d*-glyceric acid amide ( $[\alpha]_D^{16} = +39.1^\circ$ ) were obtained.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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## Die Kolloidchemische Untersuchung der Systeme von drei flüssigen Komponenten III.<sup>(1)</sup> Über Emulgierung zwei-flüssiger Systeme mit gleichen spezifischen Gewichte.

Von Naoyasu SATA und Haruhiko OKUYAMA.

(Eingegangen am 13. März 1939.)

(1) **Einleitung.** Wenn das spezifische Gewicht disperser Phase und Dispersionsmittels eines disperses Systems gleich wäre, müsste das System theoretisch unendlich beseändig sein.<sup>(2)</sup> Aber in Wirklichkeit hängen, bekanntlich, noch viele andere Faktoren damit zusammen. Wegen der Leichtigkeit des Experimentes, wurden die Untersuchungen an dieser Richtung meistens mit Emulsionen ausgeführt. So sind z.B. nach Donnan und seine Mitarbeitern,<sup>(3)</sup> für die Beständigkeit einer Emulsion, ausser der Verschiedenheit der spezifischen Gewichte zwischen disperser Phase und Dispersionsmittel, noch die Viskosität, die Grenzflächenspannung,  $\zeta$ -Potential usw. massgebend, von denen sie das  $\zeta$ -Potential am wichtigsten gefunden haben. Bhatnagar<sup>(4)</sup> hat den Versuch angestellt an Anilin-Wasser System bei 46°C., wo die spezifische Gewichte beider Schichten den gleichen Wert ergeben. Dadurch wurde bestätigt, dass das Vorhandensein kleiner Menge fremder Substanz, als Emulgator oder Stabilisator, die entscheidende Rolle spielt. Während der Experimente vorhergehender Versuche<sup>(1)</sup> haben wir gefunden, dass es möglich ist, durch Kombinieren geeigneter drei Flüssigkeiten zwei-flüssige Systeme mit gleichen spezifischen Gewichte herzustellen. Man kann dabei nach Wahl der Komponenten noch Viskosität, Grenzflächenspannung usw. einigermassen willkürlich regulieren. Im folgenden haben wir untersucht die Emulgierungserscheinung und Eigenschaften der Emulsionen, welche aus den Flüssigkeitspaaren gleicher spezifischen Gewichte entstanden sind. Es wurde zum Versuch besonders solche Kombinationen der Komponenten ausgewählt, dass es zwischen ihnen die chemische Reaktion ausgeschlossen ist und dadurch hervorgerufene Nebenwirkung auf Emulsion auch vernachlässigbar ist.

(2) **Wahl der Versuchsmaterialien.** Berücksichtigend die Mischbarkeit und spezifische Gewichte der Flüssigkeiten, ist es nicht schwer die Kombinationen von drei Flüssigkeiten auszuwählen, welche bei geeigneter Konzentration zwei-flüssige Systeme mit gleicher spezifischen Gewichte ergeben würden. Nachstehendem Versuch haben wir folgende Kombinationen benutzt.

System A: Wasser-Benzol-Tetrachlorkohlenstoff.

System B: Wasser-Amylalkohol (iso)-Chloroform.

System C: Wasser-Methylalkohol-Benzol.

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(1) Sata und Kimura, dies Bulletin **10** (1935), 409; Sata und Niwase, *ibid.*, **12** (1937), 86.

(2) W. Clayton, "The Theory of Emulsions and Their Technical Treatment", 121, London (1935).

(3) *ibid.*, 27.

(4) Bhatnagar, *Trans. Faraday Soc.*, **16** (1921), Appendix, 27.

Da die Grenzflächenspannung zwischen nicht mischbaren Flüssigkeiten an vielen Beispielen bekannt sind,<sup>(5)</sup> könnte man die Grenzflächenspannung nach dem Zufügen dritter Flüssigkeit ordnungsmässig abschätzen und zwar in obengenannten Systemen sollte die Reihenfolge der Grenzflächenspannung:  $A > B > C$  sein. Es wurde die Vermutung tatsächlich experimentell bestätigt, wie in Tabelle 1 zu ersehen sind. Das System von zwei Flüssigkeitsschichten mit gleicher spezifischen Gewichte wurde dann folgendermassen hergestellt: Man nimmt je 300 bis 400 ccm. nicht mischbarer Flüssigkeit in einer Flasche mit geschliffenem Stöpsel, welche im Thermostat von 25°C. gestellt ist. Das dritte Komponent wurde dann in kleinen Portionen zugefügt, bis die spezifische Gewichte beider Schichten den gleichen Wert ergeben. Das spezifische Gewichte wurde, von Zeit zu Zeit, mit Ostwaldschem Pyknometer kontrolliert. Die Resultate sind auch in Tabelle 1 angegeben.

(3) **Messung der Grenzflächenspannung und Viskosität.** Weil das spezifische Gewicht beider Schichten gleich ist, die brauchbare Messanordnung wurde ziemlich beschränkt. Wir haben nach Bartell und Miller,<sup>(6)</sup> Kidokoro<sup>(7)</sup> usw. den Apparat in U-Form benutzt, wie in Abb. 1 skizziert ist. Die Grenzflächenspannung ( $\sigma$ ) zwischen der Flüssigkeiten  $L_1/L_2$  wird gegeben durch die Formel,

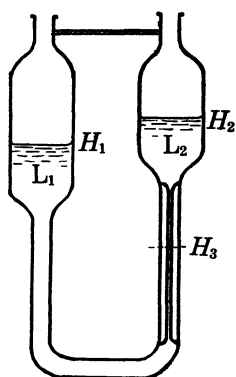


Abb. 1.

$$\sigma = \frac{gr}{2} (d_2 h - d_1 h'); \quad \begin{aligned} h &= H_2 - H_3 \\ h' &= H_1 - H_3 \end{aligned}$$

wobei,

$r$ : Kapillarhalbmesser.

$d_1, d_2$ : Spezifisches Gewicht von  $L_1$  bzw.  $L_2$ .

$H_1, H_2$ : Höhe der Oberfläche von  $L_1$  bzw.  $L_2$ .

$H_3$ : Höhe der Grenzfläche  $L_1/L_2$ .

$g$ : Erdbeschleunigung,

bedeuten. Setzt man nach unserer Bedingung  $d_1 = d_2 = d$ , so wird die Formel einfach  $\sigma = \frac{dgr}{2} (h - h')$ . Aber die Messung selbst wird dadurch viel schwerer, denn die Flüssigkeitsgrenze  $H_3$ , unter dieser Bedingung, sehr leicht ausser der Kapillare verschoben wird, was die Messung unmöglich macht. Die Viskosität wurde gemessen an  $L_1$  und  $L_2$  separat mit Ostwaldschem Viskosimeter. Die erhaltene physikalische Konstanten sind in Tabelle 1 zusammengestellt. Nun könnte man mit diesen Systemen die Wirkung der Erdbeschleunigung und auch die chemische Reaktionen bei gewöhnlicher Temperatur ausschliessend annehmen. Weil deswegen Stabilisator bzw. Emulgator zu betrachtende Substanzen vollkommen nicht vorhanden sind, wird die Untersuchung der Emulgierungserscheinung ohne Nebenerscheinung damit ermöglicht werden.

(5) "International Critical Tables", IV, 436, New York (1928).

(6) Bartell und Miller, *J. Am. Chem. Soc.*, **50** (1928), 1961; **54** (1932), 936; **55** (1933), 2419.

(7) Kidokoro, *dies Bulletin*, **7** (1932), 280.

Tabelle 1.

|   | Komponent                                      | Schicht-Zeichen | Spezifisches Gewicht (25°C.) | Viskosität | Grenzflächen-spannung |
|---|------------------------------------------------|-----------------|------------------------------|------------|-----------------------|
| A | Wasser<br>Benzol<br>Tetrachlor-<br>kohlenstoff | W.              | 0.9972                       | 1.00       | 36.6                  |
|   |                                                | NW.             | 0.9972                       | 0.75       |                       |
| B | Wasser<br>Amylalkohol (iso)<br>Chloroform      | W.              | 0.9955                       | 1.09       | 11.4                  |
|   |                                                | NW.             | 0.9955                       | 2.03       |                       |
| C | Wasser<br>Methylalkohol<br>Benzol              | W.              | 0.8701                       | 1.29       | 3.6                   |
|   |                                                | NW.             | 0.8699                       | 2.76       |                       |

\* W., NW.: Abkürzung von „wässeriger“ und „nicht wässeriger“ Schicht.

#### (4) Allgemeines über Vorgang des Emulgierens und Koagulierens.

Wenn die chemisch wirkende Faktoren ganz ausgeschlossen sind, wie in unserem Fall, so ist leicht zu erwarten dass man dann die Grenzflächen-spannung zuerst berücksichtigen muss. Wirklich das System C mit kleiner Grenzflächenspannung, lässt sich sehr leicht emulgieren durch schwaches Umrühren, wie z.B. durch nur einmaliges Umdrehen der Flasche. Wohingegen das System A, dessen Grenzflächenspannung am grössten ist, muss man mässig kräftig hin und her schütteln um zu emulgieren, unter dieselber Bedingung. Daraus ersieht man, dass die Emulgierung desto leichter vor sich geht je kleiner die Grenzflächen-spannung ist. Trotz der Gleichheit der spezifischen Gewichte, sind die entstandene Emulsionen so unbeständig, dass sie schon in einigen Minuten nach dem Schütteln zu einem klaren zwei-flüssigen System, wie vorher, sich trennen. Da in diesem Fall die Trennung wegen der Verschiedenheit der spezifischen Gewichte zwischen disperser Phase und Dispersions-mittels praktisch vernachlässigbar ist, als die Ursache der Trennung, musste man die Koagulation durch Zusammenstoss der Tropfen in erster Linie in Betracht nehmen. Weil die Wahrscheinlichkeit des Zusammenstosses den Tröpfchenzahlen oder der Konzentration abhängig ist, haben wir die konzentrierte und verdünnte Emulsion separat behandelt. Die konzentrierte bedeutet die Emulsionen, welche aus annähernd gleichem Volum von Dispersionsmittel und disperser Phase entstanden sind, d.h. die Volumkonzentration 40 bis 60%. Die verdünnte versteht man die Volumkonzentration unter 10%. Selbstverständlich die Sache hängt ausserdem noch ab, von dem Emulsionstyp,<sup>(8)</sup> der Dispersität, der Homogenität der Tröpfchen usw., auf denen wir später wieder zurückkommen werden. Im folgenden wurden die Versuchsergebnisse nach 1–2 minutigen kräftigen Handschütteln beschrieben.

(a) *Konzentrierte Systeme.* Durch einfaches Handschütteln, lässt das System, in allen Fällen, zu einer ziemlich homogenen Emulsion dispergieren. Ihre Dispersität ist aber sehr grob. Die Tröpfchen sind,

(8) D.h. die Feststellung, welche Schicht des Systems (W. oder NW.) als disperse Phase in die andere dispergiert hat.

sofort nach dem Schütteln, schon einige zehntel mm. gross, welche mit blossen Augen leicht erkennbar sind. Die Vergrösserung der Tröpfchen durch Koagulation geht ziemlich schnell vor sich und nach 4–5 Minuten trennt sich die Emulsion zum klaren zwei-flüssigen System wie vorher. Trotzdem verläuft sich der Vorgang, wegen Gleichheit des spezifischen Gewichtes viel langsamer als anderer Fall, wie z.B. der Fall des Systems reines Wassers und Benzol usw., bei denen die Trennung schon in einigen Sekunden nach dem Schütteln erzogen wird, dass man kaum von dem Vorgang etwas beobachten kann. Wohingegen in unserem Fall, hat man doch genug Zeit den Koagulationsvorgang genau zu beobachten und einigen Schluss davon zu ziehen. Nun durch obenausgeführten Versuch wurde folgendes erkannt. Beim System B bzw. C mit kleinerer Grenzflächenspannung, wachsen die einzelne Tröpfchen langsamer zu, um dann die Flüssigkeitsmasse abzuspalten; während beim System A mit grösserer Grenzflächenspannung, die Tröpfchen sich schneller vergrössern und die Flüssigkeitsmasse scheidet sich auch viel früher aus. Der Vorgang wurde schematisch wie Abb. 2 bezeichnet. Dadurch überzeugt man sich darauf,

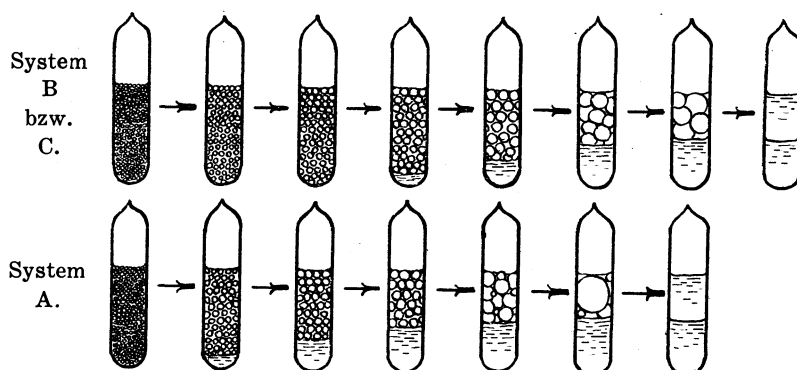


Abb. 2.

dass die Koagulation (oder der Rückgang der Emulgierung) wieder mit der Grenzflächenspannung abhängt, wenn sonstige chemisch wirkende Faktoren ausgeschlossen sind, wie in diesem Fall.

(b) *Verdünnte Systeme.* Verdünntes System lässt sich durch gewöhnliches Handschütteln kaum emulgieren. Wir haben die USW.<sup>(9)</sup> benutzt, um es zu emulgieren. Dazu schmilzt man 0.5 ccm. NW.-Flüssigkeit mit 4.5 ccm. W.-Flüssigkeit in einem Probiergläschen vom inneren Durchmesser 17 mm. zu und beschallt die USW. für eine Minute. Obwohl eine Schicht nur 10% beträgt, dispergiert sie niemals vollkommen in die anderen hinein, wie schon von Söllner und Bondy hingewiesen wurde.<sup>(10)</sup> Die W.-Schicht ergibt jedenfalls nach der Beschallung eine weiss trübe Emulsion ziemlich hoher Dispersität.<sup>(10)</sup> Der Zusammenhang von Beständigkeit der Emulsion mit Grenzflächenspannung und Viskosität des

(9) Abkürzung von Ultraschallwellen; siehe auch L. Bergmann, „Der Ultraschall“, Berlin (1937); N. Sata und N. Naruse, *Kolloid-Z.*, **86** (1939), 102; N. Sata und Y. Niwase, *Kolloid-Z.*, **81** (1937), 294, usw.

(10) K. Söllner und C. Bondy, *Trans. Faraday Soc.*, **32** (1936), 616; **31** (1935), 835, 843.



Dispersionsmittels ist in Tabelle 2 ersichtlich. Also hier ist das System desto beständiger, je grösser die Grenzflächenspannung ist. Wie schon anfangs erwähnt, wenn man annimmt, dass die Grenzflächenspannung mit der Mischbarkeit (Löslichkeit) antiparallel zu betrachten ist, dann gibt es folgende Erklärungsmöglichkeit. Wir haben eben gesehen, dass durch USW. hergestellte Emulsion ziemlich fein dispers ist. Bekanntlich in einem dispersen System mässiger Dispersität findet die Löslichkeitserhöhung disperser Phase statt, durch dessen Folge die Vergrösserung grösserer dispersen Teilchen auf Kosten feinerer dispersen Teilchen

Tabelle 2.

| System                      | A                                              | B                                         | C                                       |
|-----------------------------|------------------------------------------------|-------------------------------------------|-----------------------------------------|
| Komponent                   | Wasser<br>Benzol<br>Tetrachlor-<br>kohlenstoff | Wasser<br>Amylalkohol (iso)<br>Chloroform | Wasser<br>Methylalkohol<br>Benzol       |
| Grenzflächen-<br>spannung   | 36.6                                           | 11.4                                      | 3.65                                    |
| Viskosität von<br>W-Schicht | 1.00                                           | 1.09                                      | 1.29                                    |
| Beständigkeit               | Nach 4 Tagen,<br>noch Spur trübe               | Nach 1 Tage,<br>ganz klar                 | Nach 4-5<br>Stunden, schon<br>ganz klar |

geschehen wird.<sup>(11)</sup> Dann solche Erscheinung selbstverständlich leichter im System C als im System A zu geschehen ist, welche die Unbeständigkeit der Emulsion verursachen könnte; denn die gegenseitige Löslichkeit beider flüssigen Schichten vom System C grösser als vom System A ist. Hier kann man aber nicht einfach bestimmtes sagen, weil unter 10%-Emulsion eines Flüssigkeitspaares zwei Sorten der Emulsionstypen, namentlich NW/W- und W/NW-Typ zu verstehen sind. Der Versuch muss unter besonderer Rücksicht des Emulsionstyps ausgeführt werden. Wenn man daran denkt, dass die Viskosität des Dispersionsmittels die Bewegung der dispersen Teilchen verhindern kann, ist die Parallelität zwischen Viskosität des Dispersionsmittels und Beständigkeit leicht zu verstehen.

(Fortsetzung folgt.)

(11) H. Freundlich, „Kapillarchemie“, I, 218, Leipzig (1930).

# Chemical Studies by Means of Molecular Beams. VIII.\* A Method of Measuring the Intensity of Potassium Atomic Beams with an Incandescent Tungsten Surface. Part 2.

By Kumasaburo KODERA.

(Received March 10, 1939.)

**Relation between the Surface Concentration of Adsorbed Atoms and the Ionization Efficiency.** In the preceding report it was shown that the efficiency of ionization which was obtained by flashing the potassium atoms deposited on the tungsten surface differed considerably from what to be expected from the simple considerations as to the magnitudes of the work function and the contact potential of the tungsten used.

Now let us examine more closely the conditions of the tungsten surface and adsorbed potassium atoms. The tungsten ribbon was, as stated previously, heated to 1400–1500°C. This heat treatment is sufficient to get rid of the alkali contamination but not of the adsorbed oxygen, although it may completely eliminate the tungsten oxide. For the perfect removal of the adsorbed oxygen, the tungsten ribbon should be heated over 2900°K. In our experiments, therefore, we have always to do with a surface partly covered with oxygen, i.e. an incomplete W–O surface. The W–O surface has a very large electron work function, though its exact value has not yet been determined. Kingdon<sup>(1)</sup> takes the value to be about 9.2 V. and Reimann<sup>(2)</sup> about 6.2 V. and Bosworth and Rideal<sup>(3)</sup> about 6.3 V. At any rate in our experiments  $V_w$  must be valued at somewhat higher than 4.52 V.

Since our measurements indicate that the surface ionization curves show an appreciable departure from the linear course at  $\theta = 0.04$ , which corresponds to  $x = \varepsilon(V_w - V_i - V_c)/kT = 2$ , as we have already mentioned in the preceding report, we may estimate  $V_w$  if we know  $V_c$ , the contact potential of a potassium covered surface against the original surface. When potassium atoms are adsorbed on the W–O or W surface they are ionized there and adsorbed as ions, as long as  $\theta$  is not too large. These adsorbed ions induce the negative charges under the metal surface and form the dipoles therewith. These dipoles produce the contact potential difference  $V_c$  according to the following equation:

$$V_c = 2\pi \sigma_0 \theta \mu, \quad (1)$$

where  $\sigma_0 = 3.56 \times 10^{14}$  is the number of atoms adsorbed per cm<sup>2</sup> of the true surface at  $\theta = 1$  and  $\mu$  is the average dipole moment. According

\* Preceding papers were published in Japanese in the *J. Chem. Soc. Japan*, **57** (1936), **58** (1937).

(1) K. H. Kingdon, *Phys. Rev.*, **24** (1924), 510.

(2) A. L. Reimann, *Phil. Mag.*, **20** (1935), 594.

(3) R. C. L. Bosworth and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A**, **162** (1937), 1.

to de Boer<sup>(4)</sup>  $\mu$  can be theoretically calculated by the equation:

$$\frac{\mu}{2} = \varepsilon r - \frac{\alpha \varepsilon}{(2r)^2}, \quad (2)$$

where  $\varepsilon$  is the electronic charge and  $r$  the radius and  $\alpha$  the polarizability of the potassium ion. Their values are respectively  $4.8 \times 10^{-10}$ ,  $1.33 \times 10^{-8}$  and  $0.88 \times 10^{-24}$  and equation (2) gives then the value of  $\mu$  to be

$$\mu = 11.36 \times 10^{-18} \text{ e. s. u.}$$

With this value of  $\mu$  and  $\theta = 0.04$ ,  $V_c$  is calculated from equation (1):

$$V_c = 300 \times 2\pi \times 3.56 \times 10^{14} \times 0.04 \times 11.36 \times 10^{-18} = 0.305 \text{ V.}$$

As stated before,  $V_w - V_i - V_c = 2kT/\varepsilon = 0.238$ , when  $\theta = 0.04$ , so that  $V_w - V_i = 0.543 \text{ V}$  or  $V_w = 4.86 \text{ V}$ , since  $V_i = 4.32 \text{ V}$ . On the other hand, Bosworth and Rideal<sup>(3)</sup> found the dipole moment of potassium on W-O surface at  $\theta = 0.04$  to be  $20.5 \times 10^{-18} \text{ e. s. u.}$  which gives  $V_c = 0.55 \text{ V}$ , so that  $V_w = 5.11 \text{ V}$ .

These latter values of  $V_c$  and  $V_w$  seem to be more reliable than the former, since they are based on the actual experimental data of  $\mu$ , but there is no definite evidence for this. Accordingly, we shall continue our discussion taking both values into consideration. In equation (1)  $V_c$  is proportional to  $\theta$ . In reality, however, as  $\theta$  increases, the mutual depolarizing force of anions begins to be operative and gradually causes to slacken the increasing rate of  $V_c$ , so that the  $V_c - \theta$  curve will pass a maximum and decrease to approach a constant value of solid potassium. Since in our experiments the value of  $\theta$  is small, we may use equation (1) or

$$V_c = c\theta, \quad (3)$$

where  $c$  is equal to  $2\pi\sigma_0\mu$  and found to be either 7.6 or 13.8, according as the theoretical or the experimental value of  $\mu$  is used.

With either of these values and  $T = 1379^\circ\text{K}$  for the ribbon temperature or  $\varepsilon/kT = 8.4$  and  $A = 0.111 \text{ cm}^2$ , the total ionization can be calculated numerically by means of equation (3) in the preceding report<sup>(5)</sup> from which  $1/2$  is omitted:

$$\nu_p = AN_0 \frac{kT}{e\varepsilon} \left[ \log(1 + \exp. [\varepsilon(V_w - V_i)kT]) - \log(1 + \exp. [\varepsilon(V_w - V_i - c\theta)/kT]) \right]$$

The total ionization curves are shown in Figs. 1 and 2 with full lines. The experimental points represented by  $\times$  and  $\odot$  correspond to those in Fig. 6 in the preceding report.

The agreement of the experimental points with the theoretical curves is not good in either case, but in the region of larger values of  $\theta$ , it is better in Fig. 2 than in Fig. 1.

(4) J. H. de Boer, "Electron Emission and Adsorption Phenomena." 85, Cambridge (1935).

(5) K. Kodera, this Bulletin, 14 (1939), 114.

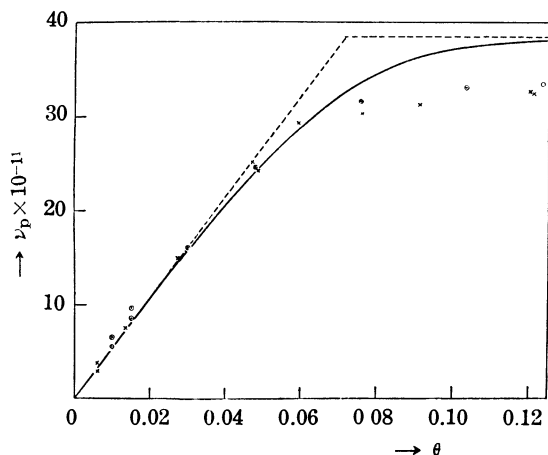


Fig. 1.

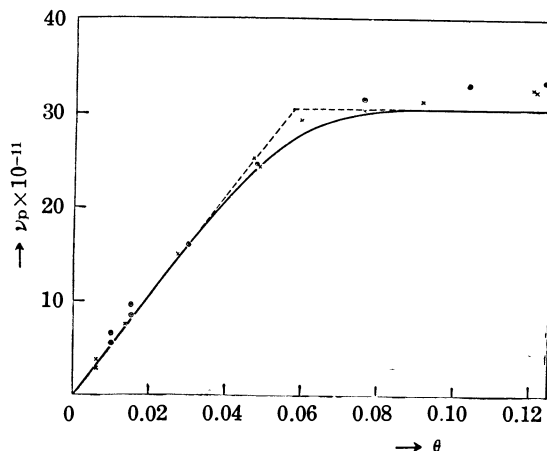


Fig. 2.

Now turning to our assumption  $V_c = c\theta$ , it must be noted that for larger values of  $\theta$  this relation holds no longer good on account of the mutual depolarizing force. This argument makes plausible the deviation of the theoretical curves from the experimental points. It is therefore desirable to know a more precise relation between  $V_c$  and  $\theta$  in this region of  $\theta$ . Bosworth and Rideal<sup>(3)</sup> have determined  $\mu$  for a wide range of  $\theta$ , from which  $V_c$  is obtained as a function of  $\theta$  (Fig. 3). With these values of  $V_c$  the differential ionization is calculated by equation (2) in the preceding report<sup>(5)</sup> with the factor  $1/2$  dropped:

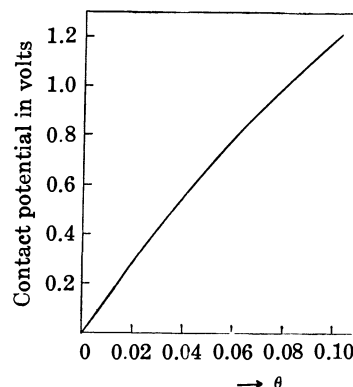


Fig. 3.

$$\frac{d\nu_p}{dN} = \frac{\exp. [\varepsilon(V_w - V_i - V_c)/kT]}{1 + \exp. [\varepsilon(V_w - V_i - V_c)/kT]}$$

The results is shown in Fig. 4. The total ionization curve may be obtained from Fig. 4 by graphical integration. The result (Fig. 5) is seen to be in sufficient agreement with the experimental values.

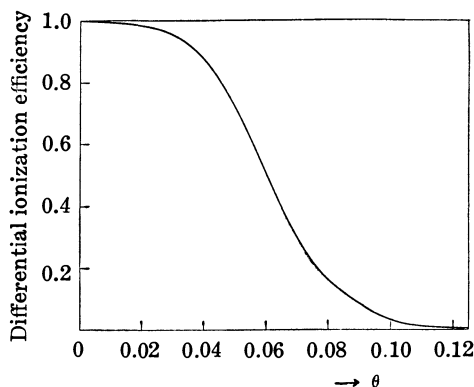


Fig. 4.

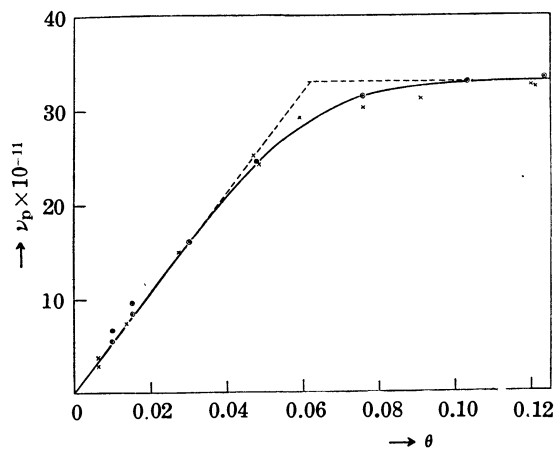


Fig. 5.

**The Surface Migration of the Adsorbed Atoms.** In our experiments, adsorbed atoms are at first confined to a very small portion of the ribbon surface. If the surface migration can take place, the site of the adsorbed atoms will gradually spread out and the surface concentration will accordingly become smaller. It must therefore be possible, by taking advantage of this phenomenon, to reduce a high surface concentration and bring about better or even complete ionization.

The phenomenon of surface migration is not significant when the ribbon is kept at room temperature but becomes noticeable at higher temperatures. (Bosworth and Rideal<sup>(3)</sup> have, however, reported that even at room temperature they observed the migration to occur when  $\theta$  was large.) To examine this effect, deposits having a certain  $\theta$  larger than 0.04 were preheated to 600–700°C. for different intervals of time, the cathode being kept at a higher potential to suppress the evaporation of ions. If the surface migration has occurred, the flashing should give a larger ion current than without preheating.

The results obtained in these experiments are shown in Figs. 6 and 7 in which the ordinate represents the galvanometer deflection and the

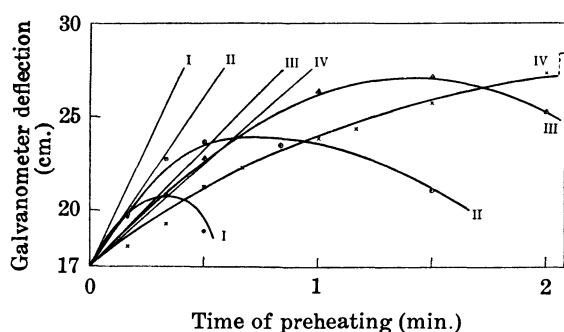


Fig. 6.

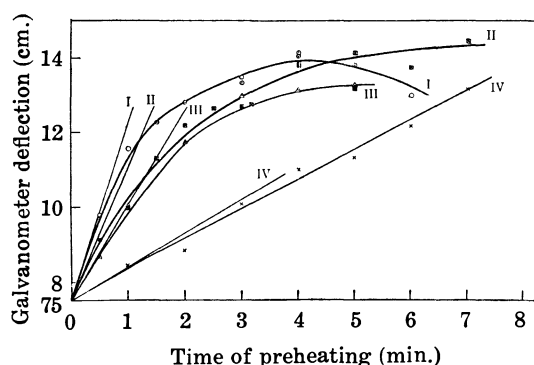


Fig. 7.

abscissa, the time of preheating. The existence of the surface migration is evident in all the curves. Curves I–IV in Fig. 6 were obtained respectively with the temperatures of 756, 704, 651 and 634°C. for preheating. Each of these curves has a maximum, the height of which decreases as the temperature of preheating rises. This is probably attributable to the fact that some fraction of the adsorbed atoms is evaporated while being preheated. That the rise of the curves is more rapid at a higher temperature of preheating is due to the greater migration velocity of the atoms. The dotted line in the figure represents the galvanometer deflection corresponding to the perfect ionization. The maximum of IV is equal to 94 per cent of that value. When the adsorbed atoms were heated at 580°C. for 6–7 minutes, a 100 per cent ionization was effected. In case  $\theta$  was smaller than 0.04, the preheating caused no change in the ionization efficiency. This is self-evident since the ionization efficiency is 100 per cent from the outset.

This surface migration explains also the behaviour of curve II in Fig. 4 in the preceding report.<sup>(5)</sup> If a low flashing temperature of the

ribbon is effected with a small electric current, the rise of the ribbon temperature is comparatively slow, so that there is ample time for the surface migration to take place and improve the ionization efficiency in the region  $\theta > 0.04$ . But the migration velocity increases as temperature rises, so that, as exemplified in curve II, an optimum will be reached at a temperature where these opposing effects just balance. Making use of the surface migration, the portion of the linear increase in the initial part of the curve in Fig. 6 in the preceding report may be extended to the larger values of  $\theta$ .

**Energy of Activation of the Surface Migration.** It would be interesting to correlate the preceding experimental results with the migration velocity of the adsorbed ions, although the experiments were not undertaken for this special purpose. Especially it should be mentioned that the data relating to the temperature are inexact, for the range with which we are here concerned lies outside the limit of direct measurement with an optical pyrometer.

Let us assume that the migration or diffusion coefficient of the potassium ion on the tungsten surface is a function of the temperature only and not of the surface concentration, although this assumption is only approximately right<sup>(6)</sup>.

If a certain deposit of potassium atoms begins to expand at a certain temperature, the distribution of the surface concentration after a time  $t$  will be given by a function in which the diffusion coefficient  $D$  and the time  $t$  occur everywhere in the form of product  $Dt$ .

If then equal deposits simultaneously start the migration at different temperatures, they will attain the identical distribution of concentration successively in time  $t$  given by the relation  $Dt = \text{constant}$ . Although the total number of potassium atoms remains constant, every stage of expansion of the deposit is characterized by the corresponding amount of ions liberated upon flashing, since, as we have seen, the ionization efficiency is a function of the surface concentration. The same state of expansion to be attained at different temperatures may then be recognized by the equality of the galvanometer deflection obtained on flashing.

As to the actual determination of  $t$  from the curves in Figs. 6 and 7 use was made of the tangents drawn at the initial points with the purpose of avoiding the effect of the loss of potassium caused by evaporation during the preheating and of the change of contact potential with the surface concentration. The heat of activation  $Q$  for the migration may then be obtained from the inclination of the  $\log t - T^{-1}$  straight line, provided the diffusion constant is expressible in the form  $Ae^{-\frac{Q}{RT}}$

The value of  $Q$  was thus determined for two cases of different initial surface concentrations  $\theta = 0.10$  and  $0.20$  of the deposit.  $Q$  was found greater for the smaller surface concentration. The magnitudes of  $Q$  are fairly similar to those obtained by Bosworth,<sup>(6)</sup> who, by following the expansion of the deposit by the photoelectric activity, determined  $D$  for different temperatures and different surface concentrations and then  $Q$

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(6) R. C. L. Bosworth *Proc. Roy. Soc. (London)*, A, **154** (1936), 112.

from the  $\log D-T^{-1}$  lines. Since, however, the probable error is large, it would be reasonable not to give our  $Q$  values but to associate to the curves the tangents whose relative inclinations were conversely determined from the value of  $Q$  as given by Bosworth, i.e.  $Q = 0.59$  V. for  $\theta = 0.10$ ;  $Q = 0.53$  V. for  $\theta = 0.20$ . One will see in Figs. 6 and 7 that they are fairly in line with the curves.

Thus we see that the procedure we have just mentioned permits a convenient determination of the activation energy of surface migration though not the migration coefficient itself. Refined measurements would yield more accurate values.

**Advantages of the Method of Flashing.** This method of flashing with a tungsten ribbon has its own limit of application. If a measurement of the intensity at a point or along a line on the cross section of an atomic beam is required, it is more convenient to use a filament. On the contrary, for the measurement of the intensity of an atomic beam as a whole or of a very spacious portion of it, this method is preferable. One important precaution to be taken is to keep the specific surface concentration always below 0.04. Even if we take advantage of the surface migration, 0.1 would be the highest allowable surface concentration in practical use. For this reason, this method is more suitable for measuring weak atomic beams with a large cross section. An atomic beam of a high intensity can be measured with the ribbon kept at a flashing temperature, but this process generates much heat which may give rise to many troubles in the apparatus. Of atomic beams with the same total intensity, those with larger cross sections are more suitable for measuring than those with smaller cross sections.

An example will make this point clear. When a surface concentration of 0.04 is produced within a circle of radius 0.1 mm., the number of atoms adsorbed is:

$$4.8 \times 10^{14} \times 0.04 \times \pi (1 \times 10^{-2})^2 = 6.0 \times 10^9$$

where  $4.8 \times 10^{14}$  is the number of atoms adsorbed on each  $\text{cm}^2$  of the apparent area when  $\theta$  is 1. The quantity of electricity to be obtained when all these atoms are ionized is:

$$1.6 \times 10^{-19} \times 6.0 \times 10^9 = 0.96 \times 10^{-9} \text{ coulombs,}$$

where  $1.6 \times 10^{-19}$  is the charge of an ion in coulomb. By dividing this value by the sensitivity of the galvanometer used,  $3.77 \times 10^{-10}$  coulomb per 1 mm. deflection, the value of the galvanometer deflection is found to be

$$0.96 \times 10^{-9} / 3.77 \times 10^{-10} = 2.55 \text{ mm.}$$

Thus we see that the maximum allowable surface concentration within a circle of radius 0.1 mm. can give rise to only 2.5 mm. deflection of the galvanometer.

### Summary.

In these experiments on the measurement of the intensity of potassium atomic beams with a tungsten ribbon, the following results have

been obtained:

(1) The ionization efficiency of adsorbed potassium atoms by flashing is found to be in good agreement with the calculated one, if the correct values of the work function and those of the contact potential of the tungsten surface are used.

(2) Adsorbed potassium atoms begin to migrate on the surface of the ribbon when the latter is heated to 500–700°C. This effect enables us to obtain a perfect ionization even with a concentration higher than  $\theta = 0.04$ .

(3) A simple method of determining the heat of activation of the surface migration is proposed.

From the above facts, it has been concluded that this method is the most suitable for measuring all at one time weak atomic beams of large cross sections.

The author expresses his sincere thanks to Prof. Nobuji Sasaki, at whose suggestion the present investigation has been undertaken. Thanks are also due to the Japan Society for the Promotion of Scientific Research for a grant to Prof. Sasaki, from which the expense has been defrayed.

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**Die kolloidchemische Untersuchung der Systeme von drei flüssigen Komponenten. III. Über Emulgierung zwei-flüssiger Systeme mit gleichen spezifischen Gewichte.**

(Fortsetzung und Schluss,\*)

Von Naoyasu SATA und Haruhiko OKUYAMA.

(Eingegangen am 13. März, 1939.)

(6) **Über den Emulsionstyp und das Volumverhältnis.** Das Verhalten der zwei-flüssigen Systeme gleicher spezifischen Gewichte nach dem Emulgieren, d. h. der Koagulationsverlauf, die Beständigkeit usw. wurden vorher erwähnt. Dahingegen tritt die Erscheinung der Emulgierung viel verwickelter auf, worauf wir weiter eingehend untersucht haben. Hierbei kommt der Emulsionstyp vorerst in Frage; nämlich, wie erwähnt, welche Flüssigkeitsschicht (W- oder NW-) dispergiert in die andere und bildet darin Emulsionströpfchen? Selbstverständlich hängt das Volumverhältnis beider Schichten unmittelbar damit zusammen. Zur Untersuchung dieser Fragestelle, haben wir einige Proben verschiedener

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\* Fortsetzung aus S. 139 dieses Bandes.

Volumverhältnissen hergestellt, welche in den Probiergläsern gleicher Grösse zugeschmolzen sind. Eine Serie dieser Proben wurde dann durch kräftiges Schütteln emulgiert und beobachtet. Den Emulsionstyp kann man nach einiger Übungen und Erfahrungen, einfach vom Aussehen der Emulsionen, leicht feststellen. Obwohl die W- und NW- Schicht von gleichem spezifischen Gewicht sind, unterscheiden sie sich voneinander in ihrer Brechungsvermögen, Viskositäten usw.. Deswegen lässt sich der Emulsionstyp, von dem Glanz der Tröpfchen oder der Mobilität des Systems, leicht erkennen. Die Versuchsergebnisse sind in Tabelle 3 zusammengestellt.

Tabelle 3.

|                                          |      |     |      |     |      |      |     |     |     |
|------------------------------------------|------|-----|------|-----|------|------|-----|-----|-----|
| Volum der W-Schicht (c.c.)               | 0.5  | 1.0 | 1.5  | 2.0 | 2.5  | 3.0  | 3.5 | 4.0 | 4.5 |
| Volum der NW-Schicht (c.c.)              | 4.5  | 4.0 | 3.5  | 3.0 | 2.5  | 2.0  | 1.5 | 1.0 | 0.5 |
| Wasser-Benzol-Tetrachlor-<br>kohlenstoff | W/NW |     |      |     |      | NW/W |     |     |     |
| Wasser-Amylalkohol (iso)-<br>Chloroform  | W/NW |     |      |     | NW/W |      |     |     |     |
| Wasser-Methylalkohol-<br>Benzol          | W/NW |     | NW/W |     |      |      |     |     |     |

Daraus ersieht man, dass im allgemeinen eine Phase mit kleinerem Volum als disperse Phase, in die andere mit grösserem Volum dispergiert, wie von Wa. Ostwald<sup>(12)</sup> und anderen hingewiesen wurde. Aber beim Volumverhältnis in der Nähe 1:1, d. h., wo das System aus annähernd gleichem Volum disperser Phase und Dispersionsmittels besteht, merkt man, dass der Emulsionstyp, je nach den Komponenten des Systems, die charakteristische Tendenz vor sich zeigt. Nämlich das System A neigt sich mehr in W/NW- Typ zu emulgieren, während das System B und C die Tendenz haben, leichter NW/W-Typ zu ergeben.

(7) **Einfluss der Gasphase und der Gefässwand.** Durch oben ausgeführten Versuch wurde bestätigt, dass der Emulsionstyp eine charakteristische Tendenz vor sich zeigt, wenn das Volumverhältnis 1:1 annähert. An diesem Punkte wurde wiederum einen Versuch angestellt, unter besonderer Berücksichtigung der Gasphase und der Gefässwand.

Stamm und Kraemer<sup>(13)</sup> beschreiben dass wenn zwei unmischbare Flüssigkeiten umgerührt werden, treten zwei gegeneinander umgekehrte Erscheinungen auf. Namentlich einerseits, emulgiert sich eine Flüssigkeit in die andere und andererseits, koagulieren sich die entstandenen Tröpfchen durch Zusammenstösse. Sie nahmen an, dass dabei Volumverhältnis, Grenzflächenspannung, Viskosität usw. darüber massgebend sein. So haben sie experimentell bewiesen dass die Flüssigkeit höherer Viskosität die Tendenz hat, sich in die der niedrigeren Viskosität hinein zu emul-

(12) Wa. Ostwald, *Kolloid-Z.*, **6** (1910), 103; **7** (1910), 64; **32** (1923), 77; **47** (1929), 131.

(13) A. J. Stamm und E. O. Kraemer, *J. Phys. Chem.*, **30** (1926), 992.

gieren und Tröpfchen bilden. Da sie den Versuch an den Systemen vom Wasser und Benzol, Nitrobenzol oder Tetrachlorkohlenstoff ausgeführt haben, lässt es sich vermuten, dass die Beobachtung nicht so einfach erzeugt war: denn die spezifische Gewichte der Komponenten waren so verschieden, dass die Trennung der Emulsion fast sofort nach dem Schütteln geschehen sein müsste. In unserem Falle wurde der Versuch, wegen Gleichheit des spezifischen Gewichtes, viel erleichtert. Ausserdem möchten wir noch darauf aufmerksam machen, dass man bei der Untersuchung der Emulgierungserscheinung mit gewöhnlicher Versuchsanordnung, den Einfluss der Gasphase und der Gefässwand nicht übersehen dürfen. Nämlich bei der Emulgierung, soweit sie in gewöhnlicher Weise durch mechanisches Schütteln oder Umrühren durchgeführt wird, ist es kaum möglich das Hineinmischen der Gasphase (Luft) in die flüssige Phase auszuschliessen. Ferner, ob die Flüssigkeit die Gefässwand benetzen oder nicht, könnte auch die Emulgierung beeinflussen.

Um die genannten Abhängigkeiten klar zu machen, haben wir folgendermassen versucht. Wir nahmen eine im Reagenzröhrchen zugeschmolzene Probe vom Volumverhältnis 1:1 und beobachteten genau den Einfluss obengenannter Faktoren auf Emulgierung bzw. Koagulierung. Die Resultate sind in Tabelle 4 zusammengestellt.

Tabelle 4.

| Komponenten                   | Möglicher Emulsions-typ | Viskosität des Dispersionsmittels | Entstandene Emulsions-typ | Tröpfcheneigenschaften     | Zustand an der Grenzfläche          |                                     |
|-------------------------------|-------------------------|-----------------------------------|---------------------------|----------------------------|-------------------------------------|-------------------------------------|
|                               |                         |                                   |                           |                            | Luft/L <sub>1</sub> /L <sub>2</sub> | Wand/L <sub>1</sub> /L <sub>2</sub> |
| Wasser — Benzol —             | W/NW                    | 0.75                              | W/NW                      | Klein und homogen          |                                     |                                     |
| Tetrachlorkohlenstoff         | NW/W                    | 1.00                              | —                         | Heterogen mit Luftbläschen |                                     |                                     |
| Wasser — Amylalkohol- (iso) — | W/NW                    | 2.03                              | W/NW                      | Klein und homogen          |                                     |                                     |
| Chloroform                    | NW/W                    | 1.09                              | —                         | Heterogen mit Luftbläschen |                                     |                                     |
| Wasser — Methylalkohol —      | W/NW                    | 2.76                              | —                         | Heterogen mit Luftbläschen |                                     |                                     |
| Benzol                        | NW/W                    | 1.29                              | NW/W                      | Klein und homogen          |                                     |                                     |

Spalte 2 und 3 zeigen die möglichen Emulsionstypen und die Viskosität des Dispersionsmittels entsprechendes Emulsionstyps.

Spalte 4 ergeben die beim Volumverhältnis 1:1 entstandenen Emulsionstypen.

In Spalte 5 wurde die Charakteristik der Emulsionströpfchen beschrieben. Selbstverständlich entsteht mit Volumverhältnis 1:1 nur ein Typ der Emulsion, wie in Spalte 4 ersichtlich ist. Aber durch Änderung des Volumverhältnisses könnte man auch einen anderen Typ erhalten. (Siehe Tabelle 3).

In Spalte 6 wurde die Stellung, welche ein Tröpfchen der dispersen Flüssigkeit ( $L_1$ ) an der Grenzfläche zwischen Dispersionsmittel ( $L_2$ ) und Luft genommen hat, skizziert. In anderen Worten, das Kennzeichen ist dargestellt, ob eine Flüssigkeit auf der Oberfläche der anderen sich verbreitet hat oder nicht. Natürlich ist es mit der Tröpfchengrösse abhängig. Die Abbildung gibt die Stellung eines Tröpfchens ähnlicher Grösse schematisch an.

In Spalte 7 sind die Grenzfläche beider Flüssigkeitsschichten gegen Gefässwand gezeichnet, welche mit der Benetzbarkeit der Flüssigkeiten zusammenhängen. Man sieht, dass der Grenzwinkel Wand/ $L_1$ / $L_2$  beim System A am kleinsten und beim C am grössten ist. Wenn man nun, die entstandenen Typen (Spalte 4) mit aderen Eigenschaften der Systemvergleicht, findet man interessante Tatsachen. Zuerst merkt man, dass zwischen der Viskosität (Spalte 3) oder dem Benetzungsproblem und entstandenem Type (Spalte 4) gar keine Abhängigkeit zu finden ist.

Dahingegen, die Tröpfcheneigenschaften und Grenzflächenzustände Luft/ $L_1$ / $L_2$  (Spalte 5 und 6) zeigen eine ausgesprochene Regelmässigkeit mit dem entstandenen Emulsionstyp. Es entsteht der W/NW-Typ aus System A bzw. B und NW/W-Typ aus System C. In diesen Fällen sind die Emulsionströpfchen gleichmässig in ihrer Grösse und haften gar keine Luftbläschen daran. Das einzelne Tröpfchen bleibt kugel-förmig auf der Oberfläche anderer Flüssigkeit und breitet sich nicht aus (siehe Spalte 6). Dahingegen sind die Tröpfchengrösse bei den nicht entstandenen Typen oder unbeständigen Typen ungleichmässig und man sieht dass feine Luftbläschen daran anhaften. Einzelnes Tröpfchen bleibt nicht kugel-förmig auf der Oberfläche des Dispersionsmittels, sondern es verbreitet sich linsen-förmig aus.

Wenn man sich hier daran erinnert, dass beim kräftigen Schütteln oder Umrühren unter gewöhnlichen Bedingungen, Hineinmischen der Luft (Gas-Phase) nicht zu vermeiden ist, könnte man folgendes schliessen. Da beim Schütteln, die flüssige Phase jedem Moment an erneuerte grosse Grenzfläche mit Luft begegnet,<sup>(14)</sup> die emulgierte Tröpfchen auf dieser Grenzfläche je nach ihren Eigenschaften, entweder linsen-förmig sich verbreiten oder unverändert kugel-förmig bleiben. Dann ist es, wie die Skizzen in Abb. 3 zeigen, leicht verständlich, dass die linsen-förmige Tröpfchen auf der Oberfläche viel leichter zu einer Flüssigkeitsmasse zusammenschmelzen als die kugel-förmigen, womit die Verschiedenheit der Beständigkeit zu erklären ist. Dass die Tröpfchen unbeständiger Emulsion die feinen Luftbläschen anhaften, scheint die Affinität zwischen

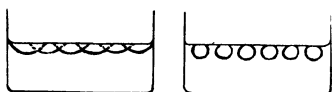


Abb. 3.

Flüssigkeit und Luft zu tun haben, worüber noch eingehend untersucht werden müssen. Jedenfalls ist es dabei klar, dass diese Luftbläschen das scheinbare spezifische Gewicht der Tröpfchen vermindern, und sodann auch die Trennung der Emulsion beschleunigen können.

(8) **Über das Umrühren ohne Gasphase.** Wie erwähnt, beim Umrühren oder Schütteln, ist das Zusammenmischen der Gasphase gewöhn-

(14) A. von Buzagh, "Kolloidik," 282, Dresden und Leipzig (1936).

lich nicht vermeidlich. Aber die obenausgeführte Untersuchung hat uns gezeigt, dass das Verhalten der Tröpfchen auf der Oberfläche gegen Luft (Gasphase) eine wichtige Rolle über den Emulsionstyp und die Beständigkeit spielt. Jetzt ist es uns erwünscht die Emulgierungserscheinung zu untersuchen, welche nur zwischen zwei Flüssigkeiten geschieht und das Eintreten der Gasphase dabei vollkommen ausgeschlossen ist. Dazu nimmt man ein langes Reagenzglas (25 cm.) und füllt es mit gleichen Volumen beider Flüssigkeiten ein. Obwohl sie in ihrer spezifischen Gewichte gleich sind, bilden sie meistens zwei flüssiges System mit der Grenzfläche in der Mitte. Das kommt vielleicht davon, weil die Benetzungsaffinität der beiden Flüssigkeiten gegen Gefäßwand nicht ganz gleich ist. Man stellt dann einen Rührer an, welcher einigen cm. um die Flüssigkeitsgrenze auf und ab bewegt. Da die obere flüssige Schicht hoch genug ist, bleibt der Effekt des Rührens nur um die Flüssigkeitsgrenze herum, so dass das Hineinmischen der Luft ausgeschlossen ist. Die Vorrichtung ist schematisch in Abb. 4 ersichtlich. Der Versuch zeigt tatsächlich, dass die beiden Flüssigkeiten ohne Luftbläschen umgerührt werden. Dabei hat man keine Feststellung, welcher Emulsionstyp, d.h. entweder NW/W-Typ oder W/NW-Typ leichter zu entstehen ist. Hier scheint dass nur die mechanische oder hydrodynamische Bedingung des Rührens und höchstens die Viskosität damit zu tun haben.

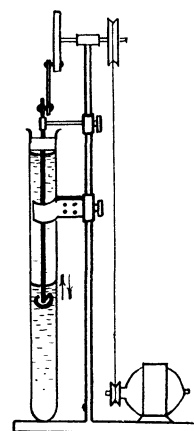


Abb. 4.

(9) **Über die Wirkung der USW.** Die emulgierende und koagulierende Wirkung der USW. an flüssig-flüssigen Systeme wurde von Söllner und Bondy<sup>(10)</sup> eingehend untersucht. Mit den Systemen der Flüssigkeitspaaren gleicher spezifischen Gewichte haben wir auch durchschnittlich ähnliches Resultat erhalten. Weil die Emulgierung durch USW. von der Grenzflächenzerstreuung und Kavitation hervorgerufen wird, entstehen dadurch die Emulsionen umgekehrter Typen in gleicher Zeit. Abb. 5 stellt das Verhalten schematisch dar. Bei der USW.-Emulgierung spielt

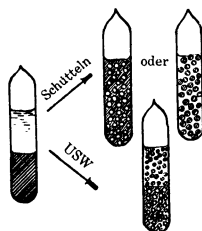


Abb. 5.

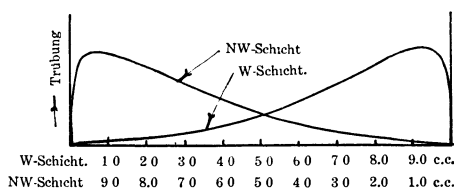


Abb. 6.

das Volumverhältnis wieder die wichtige Rolle. Und zwar der Versuch an Proben verschiedener Volumverhältnissen hat gezeigt, dass die Trübung der Flüssigkeitsschicht bei geeignetem Volumverhältnis einen Maximum ergibt. In Abb. 6 sind die Trübungskurven der W- und NW-Schicht mit

einem Maximum beim Volumverhältnis von etwa 1:9 übergetragen. Wir möchten hier darauf aufmerksam machen, dass die Erscheinung eine Art der Bodenkörperregel<sup>(15)</sup> zu betrachten ist. Nach Söllner und Bondy findet die USW.-Koagulation der Emulsionen im Bauche der stationären USW. statt, wenn die disperse Flüssigkeit leichter als Dispersionsmittel ist, wie z.B. Toluol im Wasser. Wohingegen, wenn das Gewichtsverhalten umgekehrt, wie Quecksilber im Wasser der Fall ist, geschieht die Koagulation im Knoten. Wie es mit unserem Fall von Flüssigkeitspaaren mit gleichen spezifischen Gewichte wird, soll eine interessante Aufgabe zukünftiger Untersuchung sein.

### Zusammenfassung.

(1) Es wurde die Emulgierungserscheinung zwischen zwei Flüssigkeiten mit gleichen spezifischen Gewichte untersucht.

(2) Solche zwei-flüssige Systeme wurden hergestellt durch Kombinationen von drei Flüssigkeiten verschiedener Mischbarkeit und spezifischen Gewichte.

(3) Die Systeme „Benzol-Wasser-Tetrachlorkohlenstoff“; „Wasser-Amylalkohol (iso)-Chloroform“ und „Wasser-Methylalkohol-Benzol“ wurden untersucht. Sie ergeben bei geeigneter Konzentration zwei-flüssige Systeme, welche in spezifischen Gewichte gleich sind aber in Grenzflächenspannung usw. verschieden sind.

(4) Die Emulgierung und Koagulation sind trotz der Gleichheit der spezifischen Gewichte, noch von Grenzflächenspannung, Viskosität, Volumverhältnis abhängig.

(5) Ein Versuch mit besonderer Rücksicht an Emulsionstyp wurde ausgeführt, welcher bei Emulgierungserscheinung ausser obengenannten Faktoren eine wichtige Rolle spielt.

(6) Dadurch wurde festgestellt, dass man zum Emulgierungsproblem noch den Einfluss der Gasphase und Gefäßwand in Betracht nehmen muss.

(7) Die USW.-Emulgierung ergab fast das gleiche Resultat wie in dem Falle des Systems des Flüssigkeitspaares nicht gleicher spezifischen Gewichte.

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(15) Wo. Ostwald, *Kolloid-Z.*, **43** (1927), 227, 249, 277.

## Zur Mikrobestimmung des Selens in organischen Verbindungen.

Von Sumio UMEZAWA.

(Eingegangen am 20. März, 1939.)

Wrede<sup>(1)</sup> hat das Selen in organischen Verbindungen, wie bei der Schwefelbestimmung nach Pregl, unter Benutzung von Perlenrohr und Platinkontaktsternen bestimmt und dabei wurde die entstandene selenige Säure mit Alkali titriert. Enthält aber die Substanz Stickstoff oder Halogene, so ist die massanalytische Methode nicht ausführbar.

Danach haben Drew und Porter<sup>(2)</sup> die Substanz im Cariusröhrchen mit Salpetersäure oxydiert, die selenige Säure in salzsaurer Lösung mit Schwefeldioxyd reduziert, und das Selen in elementarer Form gewogen. Doch scheint hier, dass der Gebrauch konzentrierter Salpetersäure bei der Oxydation im Bombenröhrchen und die Fällung des Selens mit Schwefeldioxyd möglichst vermieden werden soll.

In vorliegender Mitteilung empfehle ich eine allgemein ausführbare Methode, die für die Selenbestimmungen von Halogen- und Nitroderivaten des Selenophens<sup>(3)</sup> und der Selenophthene<sup>(4)</sup> verwendet wird. Ich habe Spiralenrohr nach Pregl benutzt, die selenige Säure in stark salzsaurer Lösung mit Natriumsulfit reduziert, und das Selen gravimetrisch bestimmt.

**Ausführung.** Man verfährt im allgemeinen folgendermassen. Man wägt die Substanz, so dass sie 3–5 mg. Selen enthält.<sup>(5)</sup> Die Spirale<sup>(6)</sup> wird zuerst vor der Verbrennung mit reinem Wasser benetzt, um die selenige Säure aufzufangen. Die Platinkontaktsterne werden in den leeren Rohrantel eingeführt. Zuerst substituiert man die Luft im Rohre durch Sauerstoff in 3–5 Minuten und bringt dann die im Platinschiffchen abgewogene Substanz in das Rohr ein. Hierauf vollzieht man sehr langsam die Verbrennung im Sauerstoffstrom. (40–50 Blasen in 1 Minute).<sup>(7)</sup> Nach beendeter Verbrennung verlöscht man die Flammen und lässt im Sauerstoffstrom erkalten. Man entfernt den Kautschukstopfen und zieht das Schiffchen und die beiden Platinkontakte aus dem Rohre. Dann spannt man das Spiralenrohr unter einem spitzen Winkel gegen die Vertikale so ein, dass die Spitze des Spiralenrohres im Inneren des weiten Reagensglases<sup>(8)</sup> endet, und wäscht vorsichtig den Spiralenan-

(1) F. Wrede, *Z. physiol. Chem.*, **109** (1920), 272; H. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," V. Aufl., 205.

(2) H.D.K. Drew und C.R. Porter, *J. Chem. Soc.*, **1929**, 2091.

(3) H. Sugimoto und S. Umezawa, *dies Bulletin*, **11** (1936), 157; S. Umezawa, *dies Bulletin*, **11** (1936), 777.

(4) Noch nicht veröffentlicht.

(5) Für die Abwägung von flüchtigen Flüssigkeiten verwendet man Capillaren. Siehe F. Pregl, "Die quantitative organische Mikroanalyse," IV. Aufl., 62, (1935).

(6) Siehe F. Pregl, *loc. cit.*, 115.

(7) Verwendet wurde ein Blasenähler von gleicher Grösse wie der von F. Pregl (*loc. cit.*, 26.) bei der Kohlenstoff-Wasserstoff-Bestimmung benutzte.

(8) F. Pregl, *loc. cit.*, 119.

teil mit destilliertem Wasser dreimal. Zu der gesamten Flüssigkeit von etwa 30 c.c. versetzt man 7 c.c. reiner konzentrierter Salzsäure und erhitzt 5 Minuten im siedenden Wasserbade. Zu der abgekühlten Lösung fügt man dann 3 c.c. gesättigte Natriumsulfitlösung<sup>(9)</sup> hinzu, wobei sich das Selen zuerst als amorphe rote Modifikation abscheidet. Durch Erhitzen aufs neue im siedenden Wasserbade während 30–40 Minuten ballt sich die schwarze Selenmodifikation und ist nach einstündigem Stehenlassen filtrierbar. Für die Filtration habe ich wie Drew und Porter das Filtrerröhrchen nach Pregl benutzt und sie mit Hilfe eines Hebers, ebenso wie bei der Halogenbestimmung nach Pregl, durchgeführt. Nach beendeter Filtration wäscht man das Innere des Filtrerröhrchens mit destilliertem Wasser und dann mit Alkohol dreimal. Nun wird im Regenerierungsblock 10 Minuten auf 105–110° getrocknet und nach Ablauf von 20 Minuten nach dem Abwischen gewogen.

Berechnung der Analyse:  $\log \% \text{ Se} = \log (\text{gef. Selen}) + (1 - \log \text{ Substanz})$

#### Beispiele.

| Nr. | Substanz in mg.           |                                              |        | Gef. Se<br>mg. | Gef. Se<br>% | Fehler<br>in % |
|-----|---------------------------|----------------------------------------------|--------|----------------|--------------|----------------|
| 1   | Selenophen                | $\text{C}_4\text{H}_4\text{Se}$              | 4.848  | 2.909          | 60.01        | –0.27          |
| 2   | Monochlorselenophen       | $\text{C}_4\text{H}_3\text{ClSe}$            | 11.421 | 5.420          | 47.46        | –0.25          |
| 3   | Tetrabromselenophen       | $\text{C}_4\text{Br}_4\text{Se}$             | 29.251 | 5.172          | 17.68        | –0.04          |
| 4   | $\beta$ -Nitroselenophen  | $\text{C}_4\text{H}_3\text{O}_2\text{NSe}$   | 8.895  | 4.008          | 45.06        | +0.17          |
| 5   | Monobromdinitroselenophen | $\text{C}_4\text{HO}_4\text{N}_2\text{BrSe}$ | 15.816 | 4.137          | 26.22        | –0.15          |

Bei dem beschriebenen Verfahren ist es wichtig die Substanz, die 3–5 mg. Selen enthält, zu wägen. Die Anwesenheit von Halogenen oder Stickstoff (!) beeinträchtigt nicht dieses Verfahren.

Es sei mir erlaubt, Herrn Prof. H. Suginome für seine Ratschläge zu dieser Arbeit meinen herzlichen Dank auszusprechen.

*Chemisches Institut  
der Kaiserlichen Hokkaido-Universität,  
Sapporo.*

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(9) Reines Präparat von Merck wurde verwendet.



## Synthetische Versuche in der Selenophen-Gruppe. IV. Einführung von Seitenketten in den Selenophen-Kern.

Von Sumio UMEZAWA.

(Eingegangen am 20, März 1939.)

In den vorhergehenden Mitteilungen<sup>(1)</sup> wurden die Grund-Substitutionsreaktionen, die den Selenophenkern im allgemeinen als aromatisch kennzeichnen, mitgeteilt. Nun habe ich mich damit beschäftigt, Seitenketten in das Selenophen einzuführen.

Zu diesem Zwecke wurde zunächst die Fittigsche Synthese auf die Selenophen-Gruppe zu übertragen versucht, um womöglich zu den Selenophenhomologen zu gelangen, was aber bisher erfolglos blieb. Auch wurden die Halogen-selenophene<sup>(2)</sup>, darunter auch das 2-Jodselenophen<sup>(3)</sup> mit Magnesium kaum grignardiert, auch wenn verschiedene Aktivierungsmethoden auf Magnesiumspäne angewendet wurden. Aus diesen Beobachtungen dürfte wenigstens geschlossen werden, dass diese grosse Reaktionsträgheit des Halogenatoms im Selenophen auf der eigentümlichen Struktur des letzteren beruht.

Infolge seiner besonderen Unbeständigkeit gegen Aluminiumchlorid bietet auch die Synthese nach Friedel-Crafts eine ausserordentliche Schwierigkeit, wobei das angewendete Selenophen sich gänzlich zersetzt. Doch gelingt die Darstellung der verschiedenen Selenenylketone mit mässiger Ausbeute, wenn man nach dem Prinzip der Stadnikoffschen Synthese<sup>(4)</sup> Zinntetrachlorid an Stelle von Aluminiumchlorid verwendet.

Besonders glatt verläuft die Kondensation zwischen aliphatischen Säurechloriden und Selenophen; lässt man Zinntetrachlorid in thiophenfreiem, wasserfreiem Benzol oder Schwefelkohlenstoff auf ein Gemisch von ebenso reinem Benzol oder Schwefelkohlenstoff, Selenophen und Acetylchlorid unter Kühlung einwirken, so kann man das  $\alpha$ -Acetoselenenon (IV) vom Siedep.  $107^{\circ}/14.5$  mm. erhalten, das mit Phenylhydrazin ein Phenylhydrazon vom Schmelzp.  $116^{\circ}$  ergibt. Kondensiert man das  $\alpha$ -Acetoselenenon mit Benzaldehyd bei Gegenwart von Chlorwasserstoff, so bildet sich das 2-Cinnamoylselenophen (VII), d. h. Styryl- $\alpha$ -selenenylketon vom Schmelzp.  $81-82.5^{\circ}$ , welches das dem Chalkon entsprechende Selenophenderivat ist und durch Einwirken von Brom in das Dibromid  $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO \cdot C_4H_9Se$  vom Schmelzp.  $155.5-156^{\circ}$  übergeht. Beim Eintragen von Zinntetrachlorid in eine Benzol- oder Schwefelkohlenstofflösung von Propionsäurechlorid und Selenophen entsteht unter denselben Bedingungen ebenso das Propioselenenon (II) vom Siedep.  $115^{\circ}/14$  mm., das ein Semicarbazon vom Schmelzp.  $175-176^{\circ}$  ergibt. Beachtenswert ist,

(1) Frühere Mitteilungen: dies Bulletin, **11** (1936), 157; **11** (1936), 775; **12** (1937), 4.

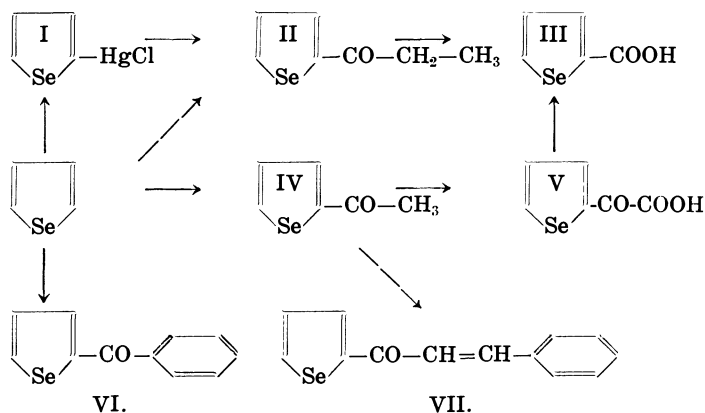
(2) H. Suginome und S. Umezawa, dies Bulletin, **11** (1936), 157.

(3) S. Umezawa, noch nicht veröffentlicht.

(4) G. Stadnikoff und W. Rakowsky, *Ber.*, **61** (1928), 268; Siehe auch *Ber.*, **61** (1928), 1996.

dass bei diesen Reaktionen, wie schon Stadnikoff<sup>(5)</sup> erwähnt hat, die Ausbeute an Selenenylketonen von den angewendeten Lösungsmitteln abhängt und beim Gebrauch von Benzol am grössten ist. Da es vorkommt, dass bei der Oxydation des Propioselenenons die später erwähnte  $\alpha$ -Selenophensäure (III) am leichtesten zugänglich ist, so wurde die Reaktion zwischen  $\alpha$ -Chlormercuri-selenophen (I) und Propionylchlorid versucht, um wenn möglich, die Ausbeute noch mehr zu erhöhen; doch ergab sich keine Verbesserung.

Die Kondensation des Selenophens mit Benzoylchlorid bei Gegenwart von Zinntetrachlorid in denselben Lösungsmitteln geht nicht so glatt wie bei der Darstellung der aliphatischen Selenenylketone; jedoch bildet sich dabei das Phenylselenenylketon (VI) vom Schmelzpt.  $57-8^\circ$ , das auch ein Phenylhydrazon vom Schmelzpt.  $175-176.5^\circ$  ergibt. Beim Erhitzen von Selenophen mit Benzoylchlorid und wenig Phosphorpentoxyd, das, wie schon Steinkopf<sup>(6)</sup> beobachtet, katalytisch einwirkt, entsteht auch das Phenylselenenylketon, allerdings mit geringer Ausbeute. Alle diese Ketone verhalten sich weit beständiger als das Selenophen selbst und geben Phenylhydrazon oder Semicarbazon als ihre funktionellen Derivate.



Von diesen Ketonen, zumal von acetyliertem Selenophen, ist die grosse synthetische Bedeutung für die Selenophen-Gruppe, wie in der Thiophenreihe, zu erwarten, dass die Acetylierung ein bequemes Mittel bietet, kohlenstoffhaltige Seitenketten einzuführen, welche man dann in  $-\text{COOH}$ ,  $-\text{CO-COOH}$ ,  $-\text{CHO}$ , Alkylrest etc. verwandeln kann. Hier möchte ich über die Oxydation der Ketone berichten.

Oxydiert man das 2-Propionyl-selenophen mit stark verdünnter alkalischer Kaliumpermanganatlösung, so entsteht die  $\alpha$ -Selenophensäure (III) vom Schmelzpt.  $122-124^\circ$ , in einer ziemlichen Ausbeute. Die  $\alpha$ -Selenophensäure ist in ihren Eigenschaften der Benzoesäure ähnlich und ergibt die Indophenin-Reaktion in ausgezeichneter Weise beim Erhitzen mit konzentrierter Schwefelsäure und Isatin.

(5) G. Stadnikoff und I. Goldfarb, *Ber.*, **61** (1928), 2341.

(6) W. Steinkopf, *Ann.*, **413** (1917), 343.

Auffallend ist, dass bei der Oxydation des Acetoselenenons mit verdünnter alkalischer Kaliumpermanganatlösung unter bestimmten Bedingungen fast einheitlich die  $\alpha$ -Selenenylglyoxylsäure (V) vom Schmelzp. 92–94° ohne Nebenentstehung<sup>(7)</sup> der  $\alpha$ -Selenophensäure erhalten wird. Lässt man die Säure aus wasserhaltigem Äther krystallisieren, so nimmt sie, wie bei der Glyoxylsäure, ein Molekül Wasser auf, das über Schwefelsäure oder Alkali im Vakuum leicht verloren wird; die wasserhaltige Selenenylglyoxylsäure schmilzt bei 44–46.5°. Ähnlich wie beim Chlorhydrat kann man auch bei Selenenylglyoxylsäure eine chemische Bindung von einem Molekül Wasser annehmen und so für dieselbe zur Strukturformel  $C_4H_3Se \cdot C(OH)_2 \cdot COOH$  einer Dioxyessigsäure gelangen, doch scheint die Formel  $C_4H_3Se \cdot CO \cdot COOH + H_2O$  ausreichend zur Erklärung der Eigenschaften dieser Säure zu sein. Die  $\alpha$ -Selenenylglyoxylsäure ist eine sehr starke Säure und ergibt das Semicarbazon vom Schmelzp. 192–193°, welches einen ziemlich starken Säurecharakter zeigt und aus seiner alkalischen Lösung durch Essigsäure in Gegenwart von überschüssigem Natriumacetat nicht oder nur unvollkommen gefällt wird, worüber Bougault<sup>(8)</sup> bei der Darstellung des Phenylglyoxylsäure-semicarbazons berichtet hat. Zur Darstellung des  $\alpha$ -Selenenylglyoxylsäure-semicarbazons wurde die Ketosäure direkt mit Semicarbazidchlorhydrat, sogar in stark salzsaurer Lösung behandelt. Die  $\alpha$ -Selenenylglyoxylsäure kann man weiterhin mit Wasserstoffsuperoxyd fast quantitativ in die  $\alpha$ -Selenophensäure (III) verwandeln.

Ob die Substituenten in den verschiedenen Verbindungen tatsächlich die angegebene Stellung einnehmen, konnte nicht direkt bewiesen werden. Wenn man jedoch die grosse Ähnlichkeit<sup>(9)</sup> des Selenophens mit dem Thiophen in Betracht zieht, so erscheint der Analogieschluss erlaubt zu sein, dass sich die beiden Körper auch in Bezug auf die chemische Reaktionsweise übereinstimmend verhalten werden.

Herrn Prof. H. Suginome möchte ich an dieser Stelle für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank aussprechen. Gleichzeitig bin ich für die Gewährung eines Stipendiums der Kaiserlichen Akademie zu Dank verpflichtet.

### Beschreibung der Versuche.

$\alpha$ -Acetoselenenon ( $\alpha$ -Methylselenenylketon) (IV). Zu einer eisgekühlten Lösung von 6 c.c. Selenophen, 5.4 c.c. Acetylchlorid und 50 c.c. thiophenfreiem, gut getrocknetem Benzol tropft man eine Mischung von 8 c.c. Zinntetrachlorid in 10 c.c. ebenfalls reinem Benzol unter Umschütteln in Eiswasser ein. Das Reaktionsgemisch färbt sich sofort dunkelbraun. Man giesst es dann in Eiswasser, lässt es über Nacht stehen, um dabei entstandene Komplexverbindung zu zerlegen, äthert es aus und trocknet über Glaubersalz. Nach Eindampfen der Lösungsmittel unterwirft man das erhaltene braungefärbte Öl der Wasserdampfdestillation. Man äthert es wieder aus, trocknet über Glaubersalz, dampft ein und fraktioniert dann. Das  $\alpha$ -Acetoselenenon ging als ein schwachgelbes stark lichtbrechendes Öl, bei 107°/14.5 mm. oder 103.5°/12 mm. über.

(7) Bei der Oxydation des Acetothienons entsteht als Nebenprodukt immer  $\alpha$ -Thiophensäure. Siehe W. P. Bradley, *Ber.*, **19** (1886), 2115.

(8) J. Bougault, *Chem. Zentr.*, **1916**, II, 742; *J. pharm. chim.*, [7], **11**, 5.

(9) Siehe auch Umezawa, *dies Bulletin*, **12** (1937), 4.

Ausbeute 5 g., 42% der Theorie.  $d_4^{25}$ : 1.5530;  $n_D^{18}$ : 1.601. Gefunden: C, 41.47; H, 3.24; Se, 45.53. Berechnet für  $C_6H_6OSe$ : C, 41.61; H, 3.49; Se, 45.78%.

Wird eine Spur Acetoselenenon mit Isatin und Schwefelsäure erhitzt, so tritt die Indophenin-Reaktion in schöner Weise ein. Bei mässiger Oxydation in der Kälte wird es zu Selenenylglyoxylsäure oxydiert, wie später beschrieben ist.

**$\alpha$ -Acetoselenenon-phenylhydrazon**,  $C_4H_5SeC(CH_3)=N \cdot NH \cdot C_6H_5$ . Molekulare Mengen von Acetoselenenon, salzsaurem Phenylhydrazin und essigsaurem Natron werden in wässriger Lösung zusammengebracht und öfters umgeschüttelt. An der Wand des Gefässes scheidet sich dann eine Krystallmasse ab. Aus Alkohol umkrystallisiert bildet das Acetoselenenon-phenylhydrazon hellgelb gefärbte, büschelförmig gruppierte Nadelchen vom Schmp. 114–116°. Gefunden: N, 10.76. Berechnet für  $C_{12}H_{11}N_2Se$ : N, 10.65%. Dies zersetzt sich vollständig nach einigen Wochen unter Bräunung.

**$\alpha$ -Propioselenenon (II)**. Ein eisgekühltes Gemisch aus 3.9 c.c. Zinntetrachlorid und 4 c.c. thiophenfreiem, gut getrocknetem Benzol wird zu einem Gemisch aus 3 c.c. Selenophen, 3 c.c. Propionylchlorid und 30 c.c. ebenso reinem Benzol unter Umschütteln in Eiswasser nach und nach eingetragen. Das dunkelbraune Reaktionsgemisch wird sofort in Eiswasser gegossen, über Nacht stehen gelassen und wie beim  $\alpha$ -Acetoselenenon aufgearbeitet. Das  $\alpha$ -Propioselenenon siedet bei 115°/14 mm. und ist fast farblos. Ausbeute 2.3 g., 36% der Theorie.  $d_4^{25}$ : 1.4687;  $n_D^{14}$ : 1.587. Gefunden: C, 44.56; H, 4.01. Berechnet für  $C_7H_8OSe$ : C, 44.91; H, 4.31%.

**$\alpha$ -Propioselenenon-semicarbazon**,  $C_7H_8SeC(CH_3)=N \cdot NH \cdot CO \cdot NH_2$ . Das  $\alpha$ -Propioselenenon wurde in wenig Alkohol gelöst und dazu einige Tropfen einer gesättigten wässrigen Lösung von gleichen Gewichtsteilen salzsaurem Semicarbazid und Kaliumacetat gegeben. Nach Stehen über Nacht wurde das auskrystallisierte Produkt aus wässrigem Alkohol umkrystallisiert. Farblose Fadenbüschel vom Schmp. 175–176°. Gefunden: N, 17.21. Berechnet für  $C_8H_{11}N_3OSe$ : N, 17.29%. Leicht löslich in Aceton, schwer löslich in Äther, auch in der Wärme; in Benzol löslich, unlöslich in Ligroin.

**$\alpha$ -Chlormercuriselenophen (I)**. Die Darstellung der Quecksilberverbindungen von Selenophen wurde schon von Briscoe und seinen Mitarbeitern<sup>(10)</sup> untersucht. Das Monochlormercuriselenophen ist aber noch nicht beschrieben.

Ein Gemisch von 3 c.c. Selenophen, 20 c.c. Alkohol und Natriumacetatlösung (10 g. Natriumacetat in 20 c.c. Wasser) wurde mit einer gesättigten Sublimatlösung (9.5 g. Sublimat in ungefähr 130 c.c. Wasser) versetzt. Das ganze Reaktionsgemisch wurde tüchtig über Nacht durchgeschüttelt, wobei ein weisser krystallinischer Niederschlag ausschied, der abfiltriert wurde. Das Filtrat lässt in der Regel bei längerem Stehen noch ziemlich viel des gleichen Niederschlags ausfallen. Nach dem Auswaschen mit kaltem Wasser wurde der Niederschlag mit reichlichen Mengen von Alkohol wiederholt ausgekocht, so lange die Lösung beim Erkalten noch Krystalle abschied. Die heisse alkoholische Lösung wurde mit dem Heisswassertrichter filtriert. Das  $\alpha$ -Quecksilberchloridselenophen krystallisiert beim Erkalten in farblosen Tafeln, welche in der Flüssigkeit fast wie blankes Silber glänzen und nach dem Trocknen ein weisses Pulver darstellen. Es schmilzt bei 201–202° unter Aufschäumen. Ausbeute 7 g. Gefunden: Cl, 9.13. Berechnet für  $C_6H_5ClSeHg$ : Cl, 9.68%. Beim Aufbewahren färbt sich das  $\alpha$ -Chlormercuriselenophen allmählich, und wird beim Durchführen von Schwefelwasserstoff in alkoholischer Lösung zersetzt, wobei sich schwarzes Quecksilbersulfid niederschlägt.

**Reaktion zwischen  $\alpha$ -Chlormercuriselenophen und Propionylchlorid**. 4.5 g.  $\alpha$ -Quecksilberchloridselenophen wurden mit 1 c.c. Propionylchlorid gemischt und im Wasserbade am Rückflusskühler kurze Zeit erwärmt. Die Masse färbt sich anfangs fleischrot, dann schwarz. Nach dem Erkalten wurde das Reaktionsgemisch in Eiswasser gegossen und mit Natriumcarbonat neutralisiert. Nach Abfiltrierung des gelben Quecksilberoxyds wurde das Filtrat ausgeäthert und aufgearbeitet. Das nach dem Abdunsten des Äthers hinterbliebene braune Öl wurde mit Semicarbazid behandelt, wobei

(10) H.V.A. Briscoe, J. B. Peel und G.W. Young, *J. Chem. Soc.*, 1929, 2589.

das Semicarbazon des  $\alpha$ -Propioselenenons sich bildet, welches durch Mischprobe mit dem durch die Zinntetrachloridmethode erhaltenen Präparat festgestellt wurde.

**$\alpha$ -P-enylselenenylketon (VI).** Hier möchte ich bemerken, dass bei Verwendung von Schwefelkohlenstoff die Kondensation des Selenophens mit Benzoylchlorid bei Gegenwart von Zinntetrachlorid zu etwas besserer Ausbeute führt als bei Verwendung von Benzol als Lösungsmittel.

Zu einer Lösung von 2 c.c. Selenophen, 2.7 c.c. Benzoylchlorid und 20 c.c. Schwefelkohlenstoff wurden 2.6 c.c. Zinntetrachlorid in 5 c.c. Schwefelkohlenstoff unter Umschütteln in Eiswasser hinzugefügt, wobei die Reaktion nicht so heftig als bei der Kondensation des Acetylchlorids war. Das Aufarbeiten wurde wie bei der Darstellung des Acetoselenenons ausgeführt. Ausbeute 0.05 g. Umkrystallisiert aus Alkohol, schwach grünliche Nadeln vom Schmp. 57–58°. Gefunden: C, 55.93; H, 3.83. Berechnet für  $C_{11}H_8OSe$ : C, 56.17; H, 3.44%.

**$\alpha$ -Phenylselenenylketon-phenylhydrazon,**  $C_6H_5SeC(C_6H_5)=N-NH-C_6H_5$ . Das Phenylselenenylketon wurde in wenig Alkohol gelöst und dazu mit einigen Tropfen Phenylhydrazin erhitzt. Dann wurde die Lösung mit heissem Wasser verdünnt. Der ausgeschiedene Krystallbrei wurde abfiltriert und aus Alkohol umkrystallisiert. Schwach gelbe feine Nadeln, Schmp. 175–176.5°. Gefunden: N, 8.86. Berechnet für  $C_{17}H_{11}N_2Se$ : N, 8.62%.

**Die Bildung von 2-Phenylselenenylketon aus Selenophen und Benzoylchlorid bei Gegenwart von wenig Phosphorpentoxyd.** 1 c.c. Selenophen, 1.4 c.c. Benzoylchlorid und ungefähr 0.03 g. Phosphorpentoxyd wurden im Ölbad unter Rückfluss erhitzt. Bei etwa 90° (Bad) entwickelt sich Chlorwasserstoff sehr heftig und die Lösung färbt sich dunkelbraun. Die Reaktion wurde 15 Stunden lang bei etwa 100° fortgesetzt, bis die Chlorwasserstoffentwicklung praktisch aufgehört hatte. Das Reaktionsgemisch wurde in verdünnte Sodalösung eingebracht und ungefähr eine Stunde lang auf dem Wasserbade degeneriert. Ausgeäthert, Äther getrocknet, und verjagt. Rückstand war eine dickflüssige Masse, die beim Erkalten erst, wenigstens zum grössten Teile, erstarrte. Auf Ton gepresst, aus Alkohol umkrystallisiert. Schwach graue Nadeln vom Schmp. 57–58°. Mischschmelzpunkt stimmt mit dem durch Zinntetrachloridmethode erhaltenen Präparat überein. Die Ausbeute betrug 0.17 g., etwa 7% der Theorie.

**2-Cinnamoylselenophen (Styryl- $\alpha$ -selenenylketon) (VII).** Diese Verbindung wurde, analog der Claisenschen Darstellungsmethode<sup>(11)</sup> des Chalkons durch Kondensation von Acetoselenenon und Benzaldehyd auf folgende Weise gewonnen: Ein Gemisch von 2.5 c.c. Acetoselenenon und 1.6 c.c. Benzaldehyd war unter Abkühlung (ungefähr –10°) mit Salzsäure gesättigt und mehrere Tage sich selbst überlassen. Schon nach einigen Stunden wird die Flüssigkeit dunkel und syrupartig, um schliesslich zu einem unansehnlichen braunschwarzen Harz zu erstarren. Dieses wurde zur Entfernung der Salzsäure auf dem Wasserbade erwärmt und mit Ligroin unter Zusatz von Tierkohle mehrere Male extrahiert. Beim Einengen und dann Erkalten der Lösung erhält man schöne, schwachgelbe, gruppierte Prismen. Dreimal aus Ligroin umkrystallisiert, schwachgelbe gruppierte Prismen, Schmp. 81–82.5°. Gefunden: C, 59.93; H, 4.13. Berechnet für  $C_{13}H_{10}OSe$ : C, 59.75; H, 3.86%. Das 2-Cinnamoylselenophen ist in heissem Alkohol und Ligroin leicht löslich und ergibt kein Pikrat mit Pikrinsäure in Alkohol oder Äther.

**Cinnamylselenenyl-dibromid,**  $C_6H_5Se-CO-CHBr-CHBr-C_6H_5$ . Das Cinnamylselenenyl wurde in Schwefelkohlenstoff aufgelöst und zu der Lösung wurde eine Schwefelkohlenstofflösung von Brom nach und nach in etwas Überschuss zugesetzt. Nach ungefähr zehn Minuten wurden der Schwefelkohlenstoff und überschüssiges Brom in Vakuum über Paraffin und Alkali eingedunstet, wobei eine schwachgefärbte krystallinische Masse zurückblieb. Umkrystallisiert aus Alkohol unter Zusatz von Tierkohle. Rautenförmige Kryställchen. Schmp. 155.5–156°. Gefunden: Br, 38.25. Berechnet für  $C_{18}H_{10}OBr_2Se$ : Br, 37.97%.

(11) L. Claisen und A. Claperède, *Ber.*, **14** (1881), 2463.

**$\alpha$ -Selenophensäure (Selenophencarbonsäure-(2)) (III).** Zur Darstellung der Säure ist die Oxydation des  $\alpha$ -Propionylselenophens am besten, welches vor der Acetylverbindung den Vorzug hat, dass bei der Oxydation die Säure direkt (ohne die Stufe der Selenenylglyoxylsäure) fast rein erhalten wird.

4.2 g. Kaliumpermanganat in 400 c.c. Wasser wurden zu einem Gemisch von 3 c.c. 50%ige Natronlauge in 230 c.c. Wasser und 2.4 c.c. Propioselenenon unter Umrühren im Laufe von 2 Stunden nach und nach eingetragen. Versuchstemperatur 20–24°. Das Reaktionsgemisch wurde dann vom Braunstein abfiltriert und bis auf ein kleines Volumen im Vakuum eingeeengt. Säuert man dann die Lösung mit konzentrierter Salzsäure unter Abkühlung im Eiswasser, so scheidet sich die  $\alpha$ -Selenophensäure in schwachbraun gefärbter krystallinischer Masse ab. Ausbeute 0.9 g., 41% der Theorie. Umkrystallisiert aus Wasser, schöne farblose Nadeln. Schmp. 122–124°. Gefunden: C, 34.28; H, 2.71. Berechnet für  $C_6H_4O_2Se$ : C, 34.30; H, 2.30%.

Die  $\alpha$ -Selenophensäure ist in ihren Eigenschaften der Benzoesäure ähnlich. Mit Schwefelsäure und Isatin erhitzt, erzeugt sie eine schöne blaue Lösung.

**$\alpha$ -Selenophensaures Silber,  $C_6H_4Se \cdot CCOAg$ .** Dieses wird in Form glänzender, durchsichtiger Blättchen erhalten, wenn man heisse verdünnte Lösungen von  $\alpha$ -selenophensaurem Ammonium und Silbernitrat vermischt und erkalten lässt. Man filtriert es ab, wäscht mit kaltem Wasser und trocknet über Chlorcalcium im Vakuum. Gefunden: Ag, 38.27. Berechnet für  $C_6H_4O_2AgSe$ : Ag, 38.85%.

**$\alpha$ -Selenenylglyoxylsäure (V).** Man kann sie durch partielle Oxydation des Acetoselenenons rein erhalten. Man wendet am besten die folgenden Verhältnisse an. 2.5 c.c. Acetoselenenon werden mit einer Lösung von 6.7 g. Kaliumpermanganat und 1.6 g. Natriumhydroxyd in 530 c.c. Wasser in der Eiskühlung so lange tüchtig umgerührt, bis die anfangs rote, dann grüne Farbe der Lösung vollständig verschwunden ist, was ungefähr eine Stunde in Anspruch nimmt. Die alkalische Flüssigkeit wird von dem ausgeschiedenen Braunstein abfiltriert und das Filtrat wird unter Erwärmen im Vakuum eingeeengt. Die hinlänglich abgedampfte Lösung wurde behufs Entfernung des unveränderten Acetoselenenons mit Äther einigemal ausgeschüttelt. Die ätherhaltige Lösung wurde sofort mit 2 N Salzsäure angesäuert und mit Äther bis zur Erschöpfung unter Zusatz von Kochsalz extrahiert. Der nach Eindampfen des Lösungsmittels gewonnene, ölige Rückstand krystallisiert nach kurzer Zeit bei der Abkühlung. Ist die Säure nur gut zwischen Filtrierpapier abgepresst worden, so schmilzt sie schon bei 42–45°. Ausbeute 1 g. Über Schwefelsäure, oder Alkali im Vakuum nimmt sie aber für einige Zeit einen fortwährend steigenden Schmelzpunkt an, und zwar liegt derselbe nach einem Tage bei ungefähr 85–90°. Umkrystallisierung zweimal aus Schwefelkohlenstoff, hellgelbe Prismen, Schmp. 92–94°.

**Wasserbestimmung:** Die getrocknete reine Säure wurde in wasserhaltigem Äther aufgelöst und bis zum Eindampfen stehen gelassen. Die auskrystallisierte Säure wurde auf Ton sorgfältig abgepresst; Schmp. 44–46.5°. Die wasserhaltige Säure wurde sofort gewogen und über Alkali—die Säure scheint über Schwefelsäure gefärbt—im Vakuum gestellt. Nach ungefähr 30 Stunden war Gewichtskonstanz eingetreten, und die Säure schmolz bei 92–94°. Gefunden:  $H_2O$ , 8.54. Berechnet für  $C_6H_4O_3Se \cdot H_2O$ , 8.15%. Gefunden: C, 35.35; H, 1.98. Berechnet für  $C_6H_4O_3Se$ : C, 35.55; H, 1.99%.

Die von Claisen<sup>(12)</sup> für Phenylglyoxylsäure angegebene, auf Zusatz von konz. Schwefelsäure und thiophenhaltigem Benzol entstehende Farbenreaktion ist undeutlich, da sich die Selenenylglyoxylsäure selbst in der konz. Schwefelsäure unter Färbung auflöst.

**$\alpha$ -Selenenylglyoxylsäure-semicarbazon,  $(C_6H_4Se) \cdot C : (N-NH-CO-NH_2)COOH$ .** Das Semicarbazon der Selenenylglyoxylsäure besitzt einen hohen Schmelzpunkt und schmilzt unter Gasentwicklung. Er ist fast unlöslich in dem meisten organischen Lösungsmitteln und zeigt einen ziemlich starken Säurecharakter. Zur Darstellung dieses Semicarbazons wurde die  $\alpha$ -Selenenylglyoxylsäure in wenig Wasser gelöst und dazu einige Tropfen einer gesättigten wässrigen Lösung von gleichen Gewichtsteilen salzsaurem Semicarbazid und Kaliumacetat gegeben. Da nach Stehen über Nacht kein

(12) L. Claisen, *Ber.*, 12 (1879), 1505.

krystallinischer Körper sich ausgeschieden hatte, setzte man einige Tropfen konzentrierter Salzsäure unter Eiskühlung zu. Das sofort ausgeschiedene  $\alpha$ -Selenenylglyoxylsäure-semicarbazon wurde abgesaugt, mit Wasser sorgfältig gewaschen, getrocknet über Chlorcalcium im Vakuum und dann analysiert. Schmp. 192–193°, unter heftigem Aufschäumen und Bräunung. Gefunden: N, 15.81. Berechnet für  $C_7H_7O_3N_3Se$ : N, 16.16%.

**$\alpha$ -Selenenylglyoxylsaures Barium**,  $C_4H_3SeCO \cdot COO\frac{1}{2}Ba \cdot \frac{1}{2}H_2O$ . Die  $\alpha$ -Selenenylglyoxylsäure wurde in wenig Wasser gelöst und mit Bariumcarbonat gesättigt. Die Lösung wurde von überschüssigem Bariumcarbonat abfiltriert und über Chlorcalcium im Vakuum eingedampft. Das ausgeschiedene Bariumsalz der  $\alpha$ -Selenenylglyoxylsäure wurde aus Wasser umkrystallisiert. Gruppierte dünne Tafeln wurden über Chlorcalcium im Vakuum getrocknet und dann analysiert. Gefunden:  $H_2O$ , 2.97. Berechnet für  $C_6H_3O_3Se\frac{1}{2}Ba \cdot \frac{1}{2}H_2O$ :  $H_2O$ , 3.22%. Gefunden: Ba, 25.57. Berechnet für  $C_6H_3O_3Se\frac{1}{2}Ba$ : 25.37%..

**Oxydation der  $\alpha$ -Selenenylglyoxylsäure zur  $\alpha$ -Selenophensäure.** 0.3 g.  $\alpha$ -Selenenylglyoxylsäure wurden in 4 c.c. Wasser aufgelöst und die Lösung wurde mit 5 Tröpfchen Perhydrol bei Zimmertemperatur versetzt, wobei fast keine Kohlendioxydentwicklung stattfand. Erhitzt man dann die Lösung bis auf 90°, so entfärbt sie sich und entwickelt heftig Kohlendioxyd. Beim Erkalten der Lösung scheiden farblose Nadeln der Selenophensäure aus, die in kaltem Wasser wenig löslich sind. Ausbeute ist fast quantitativ. Sie wurden aus Wasser umkrystallisiert. Schmp. 122–124°. Mischschmelzpunkt mit dem authentische Präparat, das aus  $\alpha$ -Propioselenenon erhalten wurde, zeigte keine Depression.

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Sapporo.*

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**Über die chemische Natur des Papains. III. Mitteilung.<sup>(1)</sup>  
Über die Wirkungsweise der Blausäure auf Papain.**

Von Shigeo OKUMURA.

(Eingegangen am 28. März, 1939.)

In seiner II. Mitteilung<sup>(2)</sup> hat der Verfasser eine Reinigungsmethode des Papains mittels Taka-Amylase beschrieben und dabei erwähnt, dass bei dem so gewonnenen Papain-Präparat die SH-Reaktion mit Nitroprussidnatrium weder vor noch nach dem Behandeln mit Blausäure positiv verläuft, das Papain-Präparat aber durch Blausäure aktivierbar ist. Aus diesem Umstand hat der Verfasser abgeleitet, dass die Blausäureaktivierung des Papains nicht auf der Aufspaltung der in dem Enzymkomplex enthaltenen -S-S-Gruppen in SH-Gruppen, sondern auf der Entfernung des Hemmungskörpers beruht, der im Laufe der Verdauung entsteht oder im Papain-Präparat vorkommt.

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(1) I. Mitteilung; dies Bulletin, **12** (1937), 319.

(2) dies Bulletin, **13** (1938), 534.



Auf Grund der oben erwähnten Tatsachen hat der Verfasser gemäss der vorliegenden Mitteilung Versuche über die Wirkungsweise der Blausäureaktivierung durchgeführt. Dabei wurde die Vorstellung des Verfassers über die Natur der Blausäure-Aktivierung durch den Befund, der in Abb. 1 und Tabelle 1 wiedergegeben ist, experimentell bestätigt. Es wurde nämlich, nachdem Gelatine durch ein mit Amylase gereinigtes Papain 24 Stunden lang verdaut worden war, abermals Gelatine zugesetzt. Dabei war der Anstieg der Verdauungskurve beim Papain-Gelatine-System (Kurve I) sehr gering, beim HCN-Papain-Gelatine-System (Kurve II) jedoch sehr deutlich.

Aus diesem Befund kann man den Schluss ziehen, dass das Papain beim HCN-Papain-Gelatine-System, da es infolge der Schutzwirkung der Blausäure vor einer Hemmungswirkung der Abbauprodukte behütet wird, die frisch zugesetzte Gelatine gut verdauen kann, während das Papain bei Abwesenheit von Blausäure durch Protein-Abbauprodukte gehemmt wird.

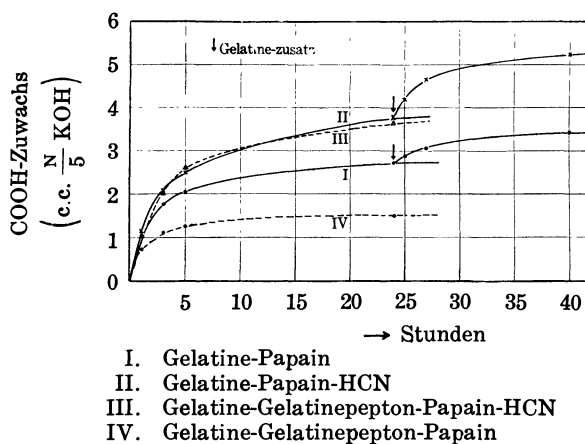
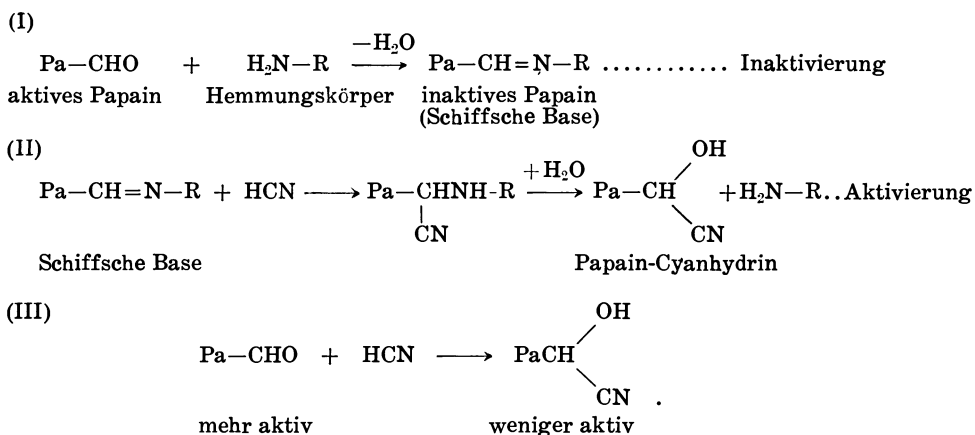


Abb 1.

Um seine Annahme weiter zu verstärken, hat der Verfasser einen Versuch angestellt, bei dem er gefunden hat, dass das Papain beim Papain-Gelatine-System (Kurve IV) bereits von Anfang der Verdauung an stark, beim HCN-Papain-Gelatine-System (Kurve III) dagegen nicht gehemmt wird, wenn man das vorher hergestellte Protein-Abbauprodukt schon auf das Papain einwirken lässt, bevor dieses zur Gelatine gemischt wird. Demnach möchte der Verfasser annehmen, dass die Blausäureaktivierung des Papains nicht auf der Erweiterung der Spezifität, sondern auf der Beseitigung schädlichen Einflusses von Seiten des Hemmungskörpers beruht.

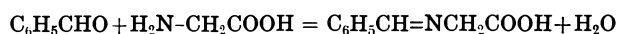
Der gleiche Hemmungseffekt auf Papain konnte man auch bei Glycyl-l-leucin beobachten. Die Hemmungswirkung dieses Peptides lässt sich gleichfalls durch Blausäure beseitigen (Tabelle 3). Dieser Befund legt die Vermutung nahe, dass der Hemmungskörper vielleicht ein spezielles Peptid sei. Zieht man die Tatsache in Betracht, dass das Papain ein eine Aldehyd-Gruppe tragendes Protein ist, wie der Verfasser schon in der I. Mitteilung mitgeteilt hat, so wird man zu dem Schluss kommen, dass

die Hemmungserscheinungen auf einer Schiffsch-Base-Bildung durch die Kondensation der Aldehyd-Gruppen des Papains mit den Amino-Gruppen der Peptide beruhe, und die Blausäureaktivierung daher ihren Grund in einer Behinderung dieser Kondensation und einer Regeneration der Aldehyd-Gruppen des Papains aus der bereits entstandenen Schiffsch-Base bestehe. Dieser Vorgang kann folgendermassen formuliert werden:



Nach der obigen Formulierung nimmt der Verfasser an, dass das Papain-Cyanhydrin mit Gelatine schwerer zu verbinden ist als das Papain, dass daher die Anfangsaktivität des Papain-Cyanhydrins niedriger, seine proteolytische Wirkung jedoch dauernder ist.

Über die Kondensation von Aldehyden mit Aminosäuren bzw. Peptiden sind Untersuchungen von Gerngross und Zühlke<sup>(3)</sup>, Scheibler und Baumgarten<sup>(4)</sup> und Bergmann<sup>(5)</sup> angestellt worden. Die Aminosäuren bzw. Peptide werden nämlich schon durch Schütteln mit den Aldehyden in wässrigem alkalischen Medium leicht kondensiert. Z. B. entsteht aus Benzaldehyd und Glycin Benzyliden-Glycin.



Vor allem stellte M. Bergmann zahlreiche Aldehyd-Aminosäure-Verbindungen folgender Typen dar,



Me<sup>I</sup> = einwertiges Metall oder Radikal

Me<sup>II</sup> = zweiwertiges Metall

und erhielt die Ausgangsaminosäuren bzw. Peptide durch Spaltung mittels Mineralsäure wie Schwefelsäure, Salzsäure und Salpetersäure zurück.

Um den Wirkungsmechanismus der Blausäure zu prüfen, hat der Verfasser als Modellversuch das Benziliden-Glycin-Barium nach Angaben

(3) Gerngross, *Biochem. Z.*, **108** (1920), 89; Gerngross, Zühlke, *Ber.*, **57** (1924), 1482.

(4) Scheibler, Baumgarten, *Ber.*, **55** (1922), 1358.

(5) M. Bergmann, *Ber.*, **58** (1925), 1034; Bergmann, Zervas, *Z. Physiol. Chem.*, **152** (1926), 293, **172** (1927), 286.

von Bergman dargestellt und sowohl mittels 5N-Schwefelsäure als auch 20%ige Blausäure<sup>(6)</sup> aufgespalten. Dabei hat er beobachtet, dass das Benziliden-Glycin-Barium in Blausäurelösung leicht löslich und gleichzeitig unter Benzaldehyd-Abspaltung leicht zersetzlich ist.

Wenn der durch den Modellversuch dargestellte Vorgang wirklich stattfindet, dann liegt die Möglichkeit nahe, dass sich die durch Blausäure gespaltenen Hemmungskörper  $H_2N-R$  nach Schema (II) isolieren lassen soll, was sich experimentell leicht nachprüfen lässt. Nachdem das vorgereinigte<sup>(2)</sup> Papain in Wasser gelöst und mit Blausäure aktiviert worden ist, wird die Enzymlösung mittels Kollodiumhülle gegen destilliertes Wasser dialysiert. Aus der Aussenlösung der Dialyse wird durch Eindampfen im Vakuum eine dunkle braune Masse gewonnen, welche die Ninhydrin-Reaktion sehr deutlich zeigt und keine proteolytische Wirkung besitzt. Dabei ist es bemerkenswert, dass die Aktivität des Papains durch Beseitigung des Hemmungskörpers verstärkt wird. Wie in der Tabelle 4 ersichtlich ist, kann dieser dunkle braune Hemmungskörper die Wirkung des Papains hemmen, das letztere aber durch Zusatz der Blausäure reaktiviert werden.

Der Verfasser glaubt hiermit, dass, auf Grund der oben beschriebenen experimentellen Tatsachen, der Mechanismus der Blausäureaktivierung des Papains einigermassen geklärt worden sei.

### Beschreibung der Versuche.

**Versuchsreihe I.** Zum Versuche wurde das mit Amylase gereinigte Papain angewandt. Ansätze: Nr. 1; 1%ige Papainlösung 10 c.c. (N-Acetatpuffer-Lösung ( $pH = 5$ )) + 5%ige Gelatine-Lösung 80 c.c. + Wasser 10 c.c. Nr. 2; 1%ige Papainlösung 10 c.c. + 5%ige Gelatine-Lösung 80 c.c. + 3%ige Blausäure-Lösung 10 c.c. Dann wurden nach einer bestimmten Zeitspanne 10 c.c. abpipettiert und deren Aktivität geprüft, nach 24 Stunden wieder 20 c.c. 5%ige Gelatine-Lösung zugesetzt, 12 c.c. abpipettiert und titriert. Nr. 3; 1%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 4; 1%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 15 c.c. + 3%ige Blausäure 5 c.c. Nr. 5; 1%ige Papainlösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 5%ige Gelatine-Pepton-Lösung 10 c.c. + Wasser 10 c.c. Nr. 6; 1%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 5%ige Gelatine-Pepton-Lösung 10 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 5 c.c. Die Aktivität wurde mit jeweils 10 c.c. geprüft.

Tabelle 1. COOH-Zuwachs (c.c. N/5 KOH)

| Stunde |       |                  | 1/6  | 1    | 3    | 5    | 24   | Nachträgliche Zugabe von Gelatine |      |      |
|--------|-------|------------------|------|------|------|------|------|-----------------------------------|------|------|
|        |       |                  |      |      |      |      |      | 25                                | 27   | 40   |
| A      | Nr. 1 | ohne Zusatz      | 0.35 | 1.04 | 1.80 | 2.03 | 2.80 | 2.90                              | 3.05 | 3.48 |
|        | Nr. 2 | +HCH             | 0.32 | 1.15 | 2.10 | 2.55 | 3.75 | 4.20                              | 4.70 | 5.30 |
| B      | Nr. 3 | ohne Zusatz      | 0.28 | 1.14 | 1.66 | 2.00 | 2.71 | —                                 | —    | —    |
|        | Nr. 4 | +HCN             | —    | 1.08 | 1.99 | 2.43 | 3.53 | —                                 | —    | —    |
|        | Nr. 5 | +Gelatine-Pepton | 0.16 | 0.72 | 1.13 | 1.28 | 1.74 | —                                 | —    | —    |
|        | Nr. 6 | Nr. 5+HCN        | —    | 1.04 | 2.03 | 2.51 | 3.65 | —                                 | —    | —    |

(6) Gesättigte Lösung von gasförmiger Blausäure, die aus  $Na_3Fe(CN)_6$  und  $H_2SO_4$  entwickelt worden war.

Dieselbe Erscheinung wurde natürlich auch bei dem vorgereinigten Papain<sup>(2)</sup> beobachtet. Die Versuchsergebnisse sind in Tabelle 2 und 3 zusammengestellt.

**Versuchsreihe II.** Ansätze: Nr. 1; 5%ige Papain-Lösung (N-Acetat-Puffer-Lösung ( $pH = 5$ )) 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 2; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 15 c.c. Nr. 3; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 4%ige Witte-Pepton-Lösung 10 c.c. + Wasser 10 c.c. Nr. 4; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 4%ige Witte-Pepton-Lösung 10 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 5 c.c. Nr. 5; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 6; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Gelatine-Pepton-Lösung 10 c.c. + Wasser 10 c.c. Nr. 7; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Gelatine-Pepton-Lösung 20 c.c. Die Aktivität wurde mit jeweils 10 c.c. geprüft.

Tabelle 2. COOH-Zuwachs (c.c. N/5 KOH)

| Stunde |       |                   | 1    | 3    | 5    | 24   |
|--------|-------|-------------------|------|------|------|------|
| A      | Nr. 1 | ohne Zusatz       | 1.73 | 2.37 | 2.62 | 3.58 |
|        | Nr. 2 | +HCN              | 2.05 | 2.87 | 3.20 | 4.63 |
|        | Nr. 3 | +Witte-Pepton     | 1.59 | 2.10 | 2.20 | 2.67 |
|        | Nr. 4 | +HCN+Witte-Pepton | 2.48 | 3.58 | 4.10 | 6.20 |
| B      | Nr. 5 | ohne Zusatz       | 1.33 | 1.70 | 1.92 | 2.26 |
|        | Nr. 6 | +Gelatine-Pepton  | 0.96 | 1.20 | 1.28 | 1.70 |
|        | Nr. 7 | +Gelatine-Pepton  | 0.90 | 1.06 | 1.10 | 1.42 |

**Versuchsreihe III.** Ansätze: Nr. 1; 2.5%ige Papain-Lösung (in N-Acetat-Puffer-Lösung ( $pH = 5$ )) 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 2; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Glycyl-L-leucin 0.55 g. + Wasser 20 c.c. Nr. 3; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Glycyl-L-leucin 1.1 g. + Wasser 10 c.c. Nr. 4; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + Wasser 10 c.c. Nr. 5; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 5 c.c. Nr. 6; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + Wasser 10 c.c. + Glycyl-L-leucin 1.1 g. Nr. 7; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 10 c.c. + Glycyl-L-leucin 1.1 g. Die Aktivität wurde mit jeweils 10 c.c. geprüft.

Tabelle 3. COOH-Zuwachs (c.c. N/5 KOH)

| Stunde |       |                               | 1    | 3             | 5             | 24   |
|--------|-------|-------------------------------|------|---------------|---------------|------|
| A      | Nr. 1 | ohne Zusatz                   | 1.33 | 1.70          | 1.92          | 2.26 |
|        | Nr. 2 | +Glycyl-L-leucin (0.1 g.)     | 1.06 | 1.49          | 1.58          | 1.98 |
|        | Nr. 3 | +Glycyl-L-leucin (0.2 g.)     | 0.88 | 1.00 (2 Std.) | 1.13 (4 Std.) | 1.67 |
| B      | Nr. 4 | ohne Zusatz                   | 2.40 | 3.09          | 3.41          | 4.74 |
|        | Nr. 5 | +HCN                          | 2.37 | 3.41          | 3.95          | 5.78 |
|        | Nr. 6 | +Glycyl-L-leucin (0.2 g.)     | 1.78 | 2.35          | 2.59          | 3.83 |
|        | Nr. 7 | +Glycyl-L-leucin (0.2 g.)+HCN | 2.10 | 2.86          | 3.40          | 5.58 |

**Isolierung des Hemmungskörpers.** Wenn das vorgereinigte Papain in Wasser gelöst, mit Blausäure 24 Stunden lang aktiviert und schliesslich 48 Stunden lang mittels Kolloidiumhülle gegen destilliertes Wasser dialysiert worden ist, wird die Aus-sen-Lösung im Vakuum engedampft und getrocknet. Die Innen-Lösung wird im Vakuum eingeengt und auf ihre Aktivität geprüft.

Tabelle 4. COOH-Zuwachs (c.c. N/5 KOH)

| Stunde |       |                      | 1/6  | 1    | 3    | 24   |
|--------|-------|----------------------|------|------|------|------|
| A      | Nr. 1 | Ausgangs-Enzymlösung | 0.40 | 1.02 | —    | —    |
|        | Nr. 2 | Innen-Lösung         | 0.68 | 1.40 | —    | —    |
|        | Nr. 3 | Nr. 2+Hemmungskörper | 0.54 | 1.12 | —    | —    |
| B      | Nr. 4 | Innen Lösung         | —    | —    | 2.24 | 2.94 |
|        | Nr. 5 | Nr. 4+Hemmungskörper | —    | —    | 1.96 | 2.60 |
|        | Nr. 6 | Nr 5+HCN             | —    | —    | 2.06 | 3.34 |

An dieser Stelle möchte ich Herrn Prof. S. Akabori für seine lebens-würdigen Ratschläge und freundliche Unterstützung meinen herzlichsten Dank aussprechen.

*Chemisches Institut der Kaiserlichen  
Universität zu Osaka.*

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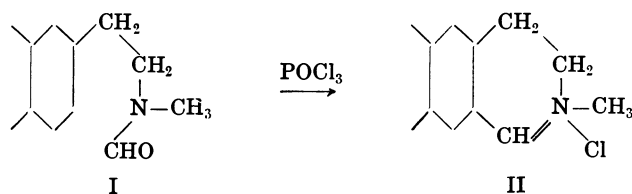
## Über die Synthese aromatischer Aldehyde.

Von Shiro AKABORI und Yoshinori SENOH.

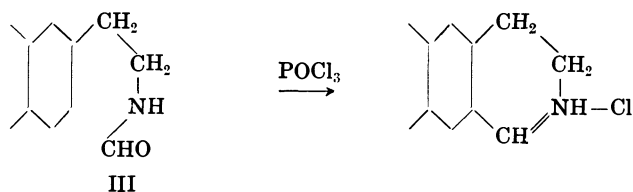
(Eingegangen am 28. März 1939.)

Die vorliegende Mitteilung beschreibt Versuche über eine neue, für Laboratoriumszwecke geeignete Synthese aromatischer Aldehyde.

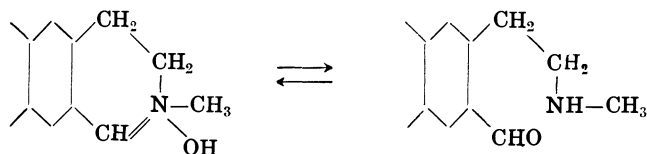
Vor dreizehn Jahren hat der eine der Verfasser (S. Akabori)<sup>(1)</sup> gefunden, dass die bei der Kondensation von Formyl-phenyläthylamin-derivaten zu 3,4-Dihydroisochinoliniumsalzen (II) mittels Phosphoroxychlorid viel bessere Ausbeuten der Formyl-*N*-methylphenyläthylamin-derivate (I) gaben als die der Formyl-derivate (III), bei denen die Methylgruppe fehlt.



(1) dies Bulletin, **1** (1926), 96.



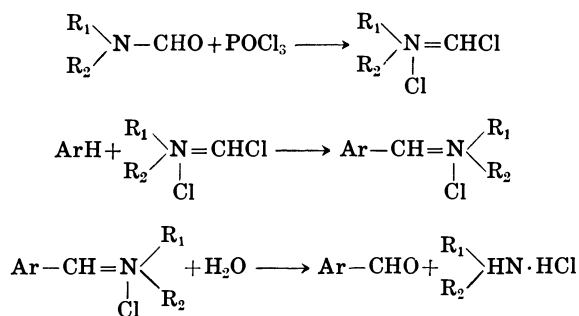
Für die freie Base von *N*-Methyl-3,4-dihydroisochinolin liegt ein Gleichgewicht wie folgt vor:



deswegen reagiert sie wie ein Aldehyd, indem sie nämlich leicht mit Hydroxylamin zum Oxim kondensiert.

Demnach ist die oben erwähnte inneremolekulare Kondensation von Formyl-*N*-methyl-phenyläthylamin zum Dihydro-isochinoliniumsalz und darauffolgende Hydrolyse nichts anderes als die Umkettung der mit dem Stickstoff verknüpften Formylgruppe an den Benzolkern.

Wenn sich eine derartige Kondensation zwischenmolekular erzielen lässt, so ist wohl durch Hydrolyse des Kondensationsprodukts Aldehyd zu gewinnen. In der Tat ist uns die Synthese einiger aromatischer Aldehyde nach dem obigen Prinzip gelungen. Wir konnten aus Anisol und Formylpiperidin Anisaldehyd, aus Veratrol und Formylpiperidin Veratrumaldehyd und aus Resorcin-dimethyläther und Formyldiäthylamin Resorcylaldehyd-dimethyläther darstellen. Der Reaktionsmechanismus lässt sich wohl durch folgende Reaktionsreihe wiedergeben.



Als Kondensationsmittel kann man ausser Phosphoroxychlorid auch Phosphortrichlorid benutzen.

Eine ganz ähnliche Synthese aromatischer Aldehyde mittels Formylanilin wurde schon von Dimroth und Zoeppritz<sup>(2)</sup> beschrieben. Diese Synthese lässt sich aber nur bei Phenolen, die leicht am Kern substituierbar sind, wie Resorcin oder Pyrogallol anwenden, nicht aber bei Phenol-

(2) *Ber.*, **35** (1902), 993.

äthern. Unsere Methode ist dagegen für Phenoläther geeignet, aber nicht für Phenole.

### Beschreibung der Versuche.

**Anisaldehyd aus Anisol und Formylpiperidin.** 10 g. Formylpiperidin und 20 g. Anisol wurden in einem Rundkolben zusammengegossen und zu dem Gemisch unter Eiskühlung 10 g. Phosphoroxchlorid langsam hinzugefügt. Das Reaktionsgemisch wurde 12 Stunden lang bei Zimmertemperatur stehen gelassen und dann 6 Stunden auf dem Wasserbad erhitzt, wobei sich die Masse intensiv gelb färbte. Nachdem sie abgekühlt worden war, wurde eine grössere Menge Petroläther zugefügt um das überschüssige Anisol aufzunehmen. Das am Boden des Kolbens ausgeschiedene Reaktionsprodukt wurde von dem Petroläther getrennt und langsam mit eiskaltem Wasser versetzt. Die Hydrolyse fand sofort statt und die Ausscheidung von Anisaldehyd machte sich durch dessen Geruch bemerkbar. Der Aldehyd wurde mit Äther ausgeschüttelt, die ätherische Lösung mit wasserfreiem Natriumsulfat getrocknet und der Äther abdestilliert. Das zurückbleibende Öl wurde unter vermindertem Druck destilliert. Die Fraktion, die bei 130–140°/35 mm. überging, erweis sich als Anisaldehyd. Ausbeute 3.5 g. (21% der Theorie).

Das Kondensationsprodukt mit Dimethylbarbitursäure schmolz bei 147–148° (Nach Akabori<sup>(3)</sup> schmilzt Anisal-dimethylbarbitursäure bei 147–148°). (Gef.: N, 10.23. Ber. für  $C_{14}H_{11}N_2O_4$ : N, 10.21%).

**Veratrumaldehyd aus Veratrol und Formylpiperidin.** 15 g. Veratrol, 8 g. Formylpiperidin und 13 g. Phosphoroxchlorid wurden unter Eiskühlung vermischt, bei Zimmertemperatur über Nacht stehen gelassen und dann 8 Stunden auf den siedenden Wasserbad erhitzt. Das so gewonnene Kondensationsprodukt wurde mit eiskaltem Wasser versetzt und mit Äther ausgezogen. Die ätherische Lösung wurde mit Natriumbisulfid-Lösung geschüttelt um den Aldehyd in die wässrige Schicht überzuführen. Letztere wurde mit Natriumcarbonat versetzt und wieder mit Äther ausgezogen. Die ätherische Lösung wurde dann mit Natriumsulfat getrocknet, der Äther abdestilliert und das zurückbleibende Öl unter vermindertem Druck destilliert. Die bei 171–173°/21 mm. übergegangene Fraktion wurde aus Ligroin umkrystallisiert. Schmp. 45°. Ausbeute 5.0 g. (33% der Theorie).

Zur Identifizierung wurde Veratrumaldehyd-semicarbazon dargestellt, das bei 179.5° schmolz. (Gef.: N, 18.94. Ber. für  $C_{10}H_{13}N_3O_3$ : N, 18.84%).

**Resorcyaldehyd-dimethyläther aus Resorcin-dimethyläther und Formyldiäthylamin.** Das Gemisch von 15 g. Resorcin-dimethyläther und 8 g. Formyldiäthylamin wurde unter Eiskühlung mit 12 g. Phosphortrichlorid versetzt, bei Zimmertemperatur über Nacht stehen gelassen und dann auf dem Wasserbad 8 Stunden lang erhitzt. Das Reaktionsgemisch wurde genau so wie bei der Synthese von Veratrumaldehyd weiter verarbeitet. Das aus 95%igem Alkohol umkrystallisierte Produkt schmolz bei 71°. Ausbeute 7 g. (40% der Theorie).

Das Oxim aus dem nach oben synthetisierten Resorcyaldehyd-dimethyläther schmolz bei 103–104°. (Gef.: N, 7.44. Ber. für  $C_8H_{11}NO_2$ : N, 7.74%).

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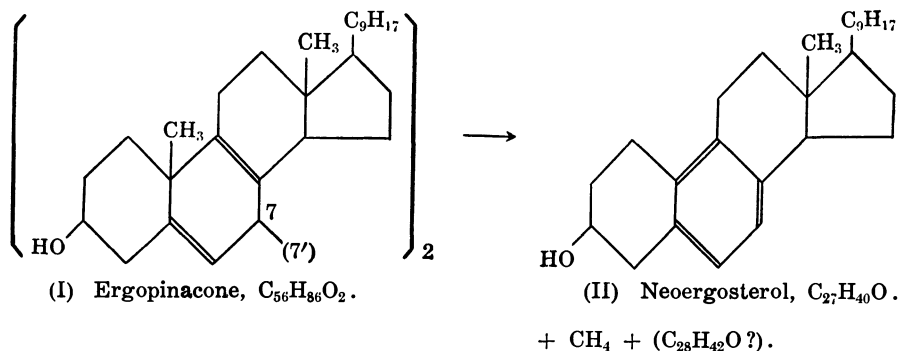


## Iso-dehydroergosterol as A Component of Iso-neoergosterol, A Molecular Compound Obtained from the Pyrolysis of Ergopinacone.

By Toshio ANDO.

(Received March 29, 1939.)

Ergosterol,  $C_{28}H_{44}O$ , as found by Windaus and Borgeaud,<sup>(1)</sup> undergoes dehydrogenation when its alcoholic solution containing eosin is exposed to light in the absence of oxygen. The product,  $C_{56}H_{86}O_2$ , has been inappropriately called ergopinacone. Ergopinacone suffers a characteristic decomposition on submitting it to distillation in vacuum or on heating it with acetic anhydride.<sup>(2)</sup> In this decomposition methane is eliminated, and neoergosterol,  $C_{27}H_{40}O$ , has been the only other fragment to be characterized, although Inhoffen<sup>(3)</sup> suggested that ergopinacone and its decomposition might be formulated as follows:



Some time ago Urushibara and the present author<sup>(4)</sup> obtained a new compound besides neoergosterol from the pyrolysis followed by distillation in vacuum of ergopinacone, and named it iso-neoergosterol, since it then appeared to be an isomeride of neoergosterol. Subsequently,<sup>(5)</sup> on acylation with 3,5-dinitrobenzoyl chloride and pyridine it gave equal quantities of two different dinitrobenzoates, one being neoergosteryl 3,5-dinitrobenzoate melting at 227–228° (corr.) with decomposition and the other a 3,5-dinitrobenzoate with the presumable composition  $C_{35}H_{44}O_6N_2$  melting at 187.5–189.5° (corr.) with decomposition. The latter corresponded in composition to the dinitrobenzoate of a compound with the formula  $C_{28}H_{42}O$ . However, the dinitrobenzoate was not identical with dehydroergosteryl dinitrobenzoate with the same composition and the same melting point. Thus the author was led to presume that iso-neoergosterol was a

(1) A. Windaus and P. Borgeaud, *Ann.*, **460** (1928), 235.

(2) H. H. Inhoffen, *Ann.*, **497** (1932), 130.

(3) H. H. Inhoffen, *Naturwissenschaften*, **25** (1937), 125.

(4) Y. Urushibara and T. Ando, *this Bulletin*, **11** (1936), 757.

(5) T. Ando, *ibid.*, **13** (1938), 371.

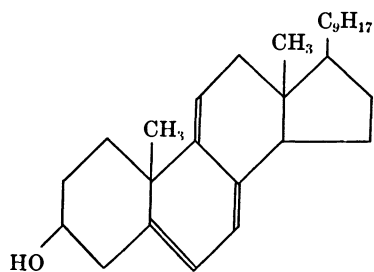
molecular compound of neoergosterol and an isomeride of dehydroergosterol. The latter component has now been isolated in free state. The author proposes the name "iso-dehydroergosterol" for this new sterol derivative, because it is most probably an isomeride of dehydroergosterol.

Careful hydrolysis of the 3,5-dinitrobenzoate melting at 187.5–189.5° with 1% alcoholic potash and recrystallization of the product from methanol gave free iso-dehydroergosterol in colourless aggregated needles with a melting point 128–129.5° (corr.) and a specific rotation  $[\alpha]_D^{10} = -102^\circ$  in chloroform. The substance is easily soluble in organic solvents, and gives instantly an insoluble addition compound with digitonin. It is thus shown that iso-neoergosterol owes its pronounced precipitability with digitonin to this component.

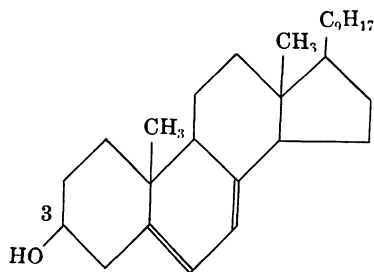
On account of great difficulty in drying completely the substance due to unstability to heat and of the hygroscopic nature of the dried substance, analyses gave no satisfactory results. However, it was possible to decide between two alternative formulas,  $C_{28}H_{44}O$  and  $C_{28}H_{42}O$ : By taking advantage of the fact that the hydrogen content is hardly affected by the addition of water ( $H_2O$  requires  $H = 11.19\%$ ) to the ergosterol formula ( $C_{28}H_{44}O$  requires  $H = 11.19\%$ ) and of a molecule or a fraction of water to the dehydroergosterol formula ( $C_{28}H_{42}O$  requires  $H = 10.74$  and  $C_{28}H_{42}O + H_2O$   $H = 10.75\%$ ), it could be shown that the dehydroergosterol formula is preferable to the ergosterol formula (Found:  $H = 10.96, 10.85\%$ ). The analyses of the dinitrobenzoate also corresponded to the dehydroergosterol formula more satisfactorily than to the ergosterol formula.<sup>(5)</sup> Lack of the material made it unable to determine the number of double bonds by any other method.

Iso-dehydroergosterol is not stable in air nor to heat, gives distinctly the colour reactions of Liebermann-Burchard and of Rosenheim, and shows sharp absorption maxima at 280, 270  $m\mu$ , and indistinct one at 252  $m\mu$ .<sup>(6)</sup>

Comparison of the free alcohols also indicates clearly that iso-dehydroergosterol is different from dehydroergosterol (III). The latter melts at 146° and gives  $[\alpha]_D^{18} = +149^\circ$  and an absorption maximum at 320  $m\mu$  corresponding to the three conjugate double bonds.<sup>(7)</sup>



(III) Dehydroergosterol.



(IV) Ergosterol.

(6) The author thanks Dr. K. Yamasaki for taking absorption spectra.

(7) A. Windaus and O. Linsert, *Ann.*, **465** (1928), 148.

As for the constitution of iso-dehydroergosterol, its properties as described above indicates that a hydroxyl group is situated at carbon atom 3 with the same configuration as in ergosterol (IV), and further may suggest that, of the three double bonds in the ring system, two are conjugated probably in one ring and another is isolated in one of the other rings. However, it is hardly possible to infer the positions or the distribution of these three double bonds from the data of absorption spectra, rotatory power, and colour reactions, because there are no sufficient materials to formulate any rules for compounds with three double bonds in the ring system. Even if Inhoffen's formula (I) for ergopinacone is assumed, it would give no reference for knowing the positions of the double bonds in the product from such a destructive change as pyrolysis.

Iso-neoergosterol can be synthesized from components: When neoergosterol and iso-dehydroergosterol in equal quantities were dissolved in and crystallized from acetone, the molecular compound separated out. Recrystallization gave colourless needles melting at 138–139° (corr.) alone and in admixture with the specimen obtained from the pyrolysis of ergopinacone. The synthetic compound showed a specific rotation  $[\alpha]_D^{11} = -66.1^\circ$  while the other  $[\alpha]_D^{20} = -59.1^\circ$ .<sup>(5)</sup> The synthetic iso-neoergosterol, as a molecular compound, showed a depression in the melting point when mixed with a small amount of either component.

The isolation of iso-dehydroergosterol,  $C_{28}H_{42}O$ , from the pyrolysis of ergopinacone substantiates Inhoffen's hypothetical equation for this reaction. On recrystallizing the crude product from this reaction neoergosterol crystallizes out first, and then iso-neoergosterol follows. Iso-neoergosterol is the molecular compound of neoergosterol and iso-dehydroergosterol, but cannot be separated into components by mere recrystallization. Hence, it is clear that in this reaction more neoergosterol is formed than iso-dehydroergosterol, while Inhoffen's equation requires equimolecular amounts of neoergosterol and a compound or a group of compounds with the formula  $C_{28}H_{42}O$ . It seems, therefore, that iso-dehydroergosterol either is formed by a secondary change from the direct product of the pyrolysis or suffers partly a transformation during distillation. Or otherwise, a number of compounds with the formula  $C_{28}H_{42}O$  may be formed side by side. In any case, at least one more compound with the formula  $C_{28}H_{42}O$  may be expected, unless the primary product suffers such a change as to alter its composition.

### Experimental.

**The Isolation of Iso-dehydroergosterol.** Iso-dehydroergosteryl 3,5-dinitrobenzoate was obtained from iso-neoergosterol in the same way as described in the previous paper.<sup>(5)</sup> For the experiments recorded in this paper 87 mg. of a specimen of the dinitrobenzoate melting at 187–189.5° (corr.) and 91 mg. of another melting at 184.5–187° (corr.) were available. The dinitrobenzoate was carefully saponified as follows:

The dinitrobenzoate (87 mg.) of the melting point 187–189.5° was dissolved in benzene (14 c.c.), and the solution was added drop by drop to boiling 1% alcoholic potash (0.06 g. potassium hydroxide in 6 g. alcohol), while the benzene was instantly distilled off. The resulting brown solution was concentrated under a slightly diminished pressure and water was added to the concentrate, when a dark brown viscous matter separated. It was extracted with ether, and the ethereal solution was washed with dilute acetic acid and with water, dried with anhydrous sodium

sulphate, and evaporated. The remaining orange-coloured mass, after dried over caustic potash in vacuum, was crystallized from hot methanol in almost colourless needles (46 mg.) melting at 130–131.5° (corr.). Repeated recrystallization from methanol containing a small amount of water gave pure iso-dehydroergosterol in colourless aggregated small needles (21 mg.). It melts at 126.5–128° (uncorr.) or 128–129.5° (corr.) to a colourless liquid, and shows  $[\alpha]_D^{10} = -102^\circ$  (7.35 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{10} = -0.75^\circ$ ) and ultraviolet absorption maxima in 0.036% hexane solution at 280, 270 (both sharp), and 252  $m\mu$  (indistinct). An additional yield (9 mg.) was obtained from the mother liquors of recrystallization.

In the same way the other specimen (91 mg.) of the dinitrobenzoate melting at 184.5–187° gave another crop of iso-dehydroergosterol (35 mg.) in colourless aggregated small needles showing melting point 125.5–128° (uncorr.) or 127–129.5° (corr.), and ultraviolet absorption maxima in 0.035% hexane solution at 280, 270 (both sharp), and 254  $m\mu$  (indistinct), an additional yield (11 mg.) being obtained from the mother liquors.

The substance is unstable in air and must be kept in vacuum or in the atmosphere of carbon dioxide. It rapidly became yellow when it was dried at 100° in vacuum over phosphorus pentoxide. For analysis the substance was dried in vacuum at room temperature over calcium chloride.

|                                     |                        |
|-------------------------------------|------------------------|
| Found:                              | (1) C, 82.69; H, 10.96 |
|                                     | (2) C, 81.49; H, 10.85 |
| Calculated for $C_{28}H_{42}O$ :    | C, 85.21; H, 10.74     |
| $C_{28}H_{42}O + \frac{1}{2}H_2O$ : | C, 83.30; H, 10.75     |
| $C_{28}H_{42}O + H_2O$ :            | C, 81.47; H, 10.75     |
| $C_{28}H_{44}O$ :                   | C, 84.76; H, 11.19     |
| $C_{28}H_{44}O + \frac{1}{2}H_2O$ : | C, 82.87; H, 11.19     |
| $C_{28}H_{44}O + H_2O$ :            | C, 81.08; H, 11.19%    |

**Reactions of Iso-dehydroergosterol.** In the Liebermann-Burchard test iso-dehydroergosterol gives red, violet, and deep blue colours, while in the Rosenheim test instantly pink, light violet after five minutes, then blue, and finally dark violet colours.

When iso-dehydroergosterol (3 mg.) dissolved in a few drops of 95% alcohol was mixed with a 1% alcoholic solution of digitonin (10 mg.), precipitation of the digitonide took place instantly and was completed in a few minutes.

**The Synthetic Preparation of Iso-neoergosterol from Neoergosterol and Iso-dehydroergosterol.** When equal quantities (12 mg. each) of neoergosterol (m.p. 153.5–154.5°, corr.) and iso-dehydroergosterol (m.p. 127–129.5°, corr.) were dissolved together in a small amount of acetone with warming and the solution was cooled, there occurred separation of fine colourless needles (19 mg.) melting at 138.5–140° (corr.). Recrystallization gave iso-neoergosterol in colourless fine needles melting at 138–139° (corr.) alone and in admixture with the specimen obtained from the pyrolysis of ergopinacone. The synthetic product showed a specific rotation  $[\alpha]_D^{10} = -66.1^\circ$  (6.8 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{10} = -0.45^\circ$ ).

A depression of the melting point was observed when the synthetic iso-neoergosterol was melted with a very small quantity of either neoergosterol (mixed melting point 135–138°, corr.) or iso-dehydroergosterol (mixed melting point 128.5–134.5°, corr.).

The author's cordial thanks are due to Prof. Y. Urushibara for his kind guidance and encouragement. The author expresses his gratitude also to Mr. Y. Yamaguchi and to Oji Seishi Co. for generous help.

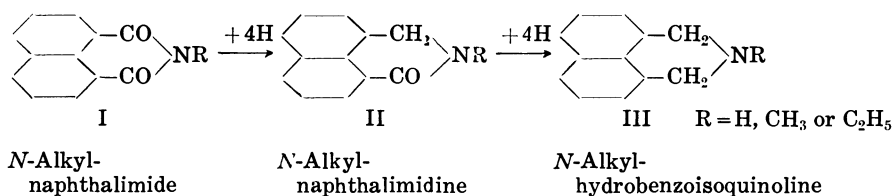
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## Electrolytic Reduction of Naphthalimide and its Derivatives.

By Buhei SAKURAI.

(Received April 10, 1939.)

So far as the author is aware, no one has yet succeeded in reducing naphthalic acid imides by purely chemical means. Electrolytically, however, both carbonyls in the imides may successfully be reduced as in the case of other dibasic acid imides, when zinc amalgam<sup>(1)</sup> is used as the cathode.



In the reduction experiments E. Späth<sup>(2)</sup> and his collaborator used lead cathode in a 50% sulphuric acid solution passing the current of 45 amp. per 100 sq. cm., and reported to have obtained 15% hydrobenzoisoquinoline as the final reduction product. By working under exactly the same condition the author could procure no reduction product, and even with the cathode of zinc amalgam the result was not much improved.

In order to find out better conditions for electrolytic reduction several experiments were performed by controlling concentration of sulphuric acid, current density, temperature of electrolyte, etc., but all were fruitless. Influence of alcohol added to the electrolyte with the object of increasing the solubility of the imide was found out to bring no better results.

In the case of its derivatives such as *N*-methyl-naphthalimide and *N*-ethyl-naphthalimide reduction took place with much ease. They were reduced with fairly good yield in sulphuric acid solution with cathode and produced *N*-methyl-naphthalimidine and *N*-ethyl-naphthalimidine respectively. The reduction stopped here without going further than this stage. For their complete reduction cathode of much stronger reducing power, such as zinc amalgam was required.

### Experimental.

The materials used in the experiment were prepared in the following way.

Naphthalic acid was first prepared from acenaphthene by oxidizing it with powdered potassium bichromate in a warm glacial acetic acid solution, and naphthalic acid anhydride thus obtained (yellow powder, melting at 270°) was heated in a retort to which a current of ammonia was constantly passed and then cooled till it became

(1) B. Sakurai, this Bulletin, **7** (1932), 155; **10** (1935), 311.

(2) E. Späth and F. Brausch, *Univ. Wien, Monatschr.*, **50** (1928), 349.

a lump. The lump was taken out and crushed into powder and recrystallized from alcohol. Naphthalimide was thus prepared as reddish-brown powder, melting at 300°.

Methyl-naphthalimide was prepared by mixing naphthalic acid anhydride and methylamine in equivalent amount and recrystallized from alcohol after it was gradually heated on the water bath (yellow brown needle-like crystals, melting at 205°). Ethyl-naphthalimide (yellow needle-like crystals, m.p. 148°) was prepared in the same manner using ethylamine instead of methylamine.

**I. Naphthalimide** (I, R=H). Naphthalimide and its derivatives are insoluble in sulphuric acid solution. When one or both of two carbonyl groups are reduced into methylene groups, the basicity of molecules increases considerably, and in consequence they become soluble in the acidic electrolyte forming soluble salt. Thus the progress of reduction is clearly indicated by gradual disappearance of the imides suspended in the electrolyte. The experiments were conducted with lead cathode by controlling concentration of sulphuric acid (30–90%), temperature (26–60°), and current density (5–12 amp. per 100 sq. cm.), in various manners, but in no case the material was seen to dissolve in electrolyte. As the reduction was perceived to take place with zinc amalgam cathode, the best conditions of electrolysis were sought as follows. Cathode: zinc amalgam, 16 sq. cm. of area. Catholyte: mixture of 50 c.c. of 90%  $\text{H}_2\text{SO}_4$  and 50 c.c. of alcohol and 1 g. of naphthalimide was added to it. Anode: cylindrical lead plate. Anolyte: 90%  $\text{H}_2\text{SO}_4$ . Current density: 105.3 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 1234.9 F. per mol. Temperature: 30°.

Into the anolyte contained in a cylindrical biscuit vessel a cell containing catholyte was dipped, and a spiral lead tube was inserted into the cathode chamber. Cold water was passed through the tube to cool catholyte from inside, while the electrolyte bath itself was cooled all the time from outside with cold water. After 10 hours' electrolysis the catholyte still containing a considerable amount of undissolved substance was taken out and heated on the water bath to drive off alcohol. It was then diluted with about three times as much water and filtered. 0.69 g. of unreduced substance was obtained. The acidic solution was then shaken with ether several times in order to extract original imide remaining unreduced. About 0.14 g. of another unreduced substance was obtained. The aqueous solution was then made alkaline with caustic soda and treated with ether yielding thereby a small quantity of a brownish substance.

The platinum double chloride of this substance melted at 198° with decomposition. (Found: Pt, 26.04. Calculated for  $[\text{C}_{12}\text{H}_{11}\text{N}]_2\text{H}_2\text{PtCl}_6$ : Pt, 26.10%). The yield of the dihydrobenzoisquinoline was found to be 8%.

**II. N-methyl-naphthalimide** (I, R= $\text{CH}_3$ ). (1) *Reduction with lead cathode.* With the view of obtaining N-methyl-naphthalimidine, reduction was conducted in sulphuric acid solution with lead cathode under the following conditions. Cathode: cylindrical lead plate, 100 sq. cm. of area. Catholyte: 1 g. of imide was suspended in 100 c.c. of 50%  $\text{H}_2\text{SO}_4$ . Anode: cylindrical lead plate. Anolyte: 50%  $\text{H}_2\text{SO}_4$ . Current density: 5 amp. per 100 sq. cm. Current quantity: 393.6 F. per mol. Temperature: 40°.

The electrolysis was carried out by cooling the electrolytic bath from outside with cold water, keeping the catholyte always in a vigorous agitation. The imide appeared to have dissolved fairly well. But 10 hours' electrolysis seemed to have been still insufficient as 0.57 g. of the original imide was detected remaining unchanged. This was filtered, and the filtrate was extracted with ether, when 0.059 g. of some other unreduced substance was obtained. The solution was made alkaline with caustic soda solution and again extracted with ether. About 0.3 g. of brown oily substance with a peculiar smell was obtained. This was easily soluble in hydrochloric acid solution and formed white needle-like crystals. Its platinum double chloride formed orange-coloured crystals melting at 172° with decomposition. (Found: Pt, 24.27. Calculated for  $[\text{C}_{13}\text{H}_{11}\text{NO}]_2\text{H}_2\text{PtCl}_6$ : Pt, 24.28%). The substance is thus regarded undoubtedly as N-methyl-naphthalimidine.

In the electrolysis with lead cathode reduction seems not to proceed further than the first stage. As the concentration of sulphuric acid has a close relation to reduction rate, a series of experiments were carried out by varying the concentration of sulphuric acid, results of which are summarised in Table 1.

From the table it is seen that the amount of unreduced substance decreases, as the concentration of sulphuric acid increases, making the reduction rate more than 30% in 50% solution of sulphuric acid. If, however, the concentration of sulphuric acid exceeds 50%, the yield of the reduced substance shows no remarkable increase despite the considerable decrease of the undissolved substance. Perhaps this is due to the fact that the imide partly polymerises into an unreducible substance on account of the high concentration of sulphuric acid. A resinous substance which may be regarded as such a polymer was always obtained, when electrolysis was conducted with the catholyte containing more than 70% of sulphuric acid.

As *N*-methyl-naphthalimide is slightly soluble in alcohol, though it is insoluble in sulphuric acid, electrolysis was carried out with a solution to which an equal volume of alcohol was added. The results are shown in Table 2.

As is seen from the table, the solution containing 40% of sulphuric acid gives the best results. When sulphuric acid becomes more concentrated the reduction rate falls rapidly, which shows that the effect of alcohol is rather harmful. Probably alcohol acts to enhance the resinification of the material, which is responsible for the rapid increase of ether extract from acidic medium containing more than 70% sulphuric acid.

(2) *Reduction with zinc amalgam cathode.* For the purpose of obtaining the complete reduction product of *N*-methyl-naphthalimide, i.e. *N*-methyl-hydrobenzoisoquinoline, zinc amalgam was taken as the cathode under the following conditions. Cathode: zinc amalgam 16 sq. cm. Catholyte: 100 c.c. of 50%  $\text{H}_2\text{SO}_4$  in which 1 g. of imide was suspended. Anode: cylindrical lead plate. Anolyte: 50% sulphuric acid. Current density: 75 amp. per 100 sq. cm. Time of electrolysis: 6 hours. Current quantity: 566.9 F. per mol. Temperature: 34°.

Electrolysis was carried out by cooling the electrolytic bath, from outside with cold water and from inside by passing cold water through a spiral lead tube inserted to the catholyte, which was always kept vigorously stirring. Though the imide did not readily dissolve in the electrolyte, yet its amount was observed to diminish by degrees. At the beginning of electrolysis the experiment was much disturbed by hydrogen bubbles evolved at cathode, but it was soon found that this was easily prevented by dropping a small quantity of alcohol into it. After 6 hours' electrolysis the catholyte was diluted with about double volume of water and then filtered, when about 0.55 g. of insoluble substance was isolated. The filtrate was then treated with ether, and from the ether extract a small amount of light yellow fine needle-like crystals was obtained. This substance melted at 205° and was found to be unreduced material.

Table 1.

| Conc. of $\text{H}_2\text{SO}_4$ (%) | Undissolved material (%) | Ether extract from acidic medium (%) | <i>N</i> -methyl-naphthalimide (%) |
|--------------------------------------|--------------------------|--------------------------------------|------------------------------------|
| 20                                   | 91                       | —                                    | 4.5                                |
| 30                                   | 75                       | —                                    | 14                                 |
| 40                                   | 67                       | —                                    | 23                                 |
| 50                                   | 57                       | 5                                    | 32                                 |
| 60                                   | 55                       | 9                                    | 30                                 |
| 70                                   | 30                       | 21                                   | 36                                 |
| 80                                   | 20                       | 35                                   | 33                                 |

Table 2.

| Conc. of $\text{H}_2\text{SO}_4$ (%) | Undissolved material (%) | Ether extract from acidic medium (%) | <i>N</i> -methyl-naphthalimide (%) |
|--------------------------------------|--------------------------|--------------------------------------|------------------------------------|
| 40                                   | 25                       | 10                                   | 49                                 |
| 50                                   | 30                       | 11                                   | 27                                 |
| 60                                   | 42                       | 15                                   | 19                                 |
| 70                                   | 10                       | 60                                   | 20                                 |
| 80                                   | 13                       | 51                                   | 18                                 |
| 90                                   | 11                       | 59                                   | 22                                 |

Now the remaining solution was made alkaline with caustic soda solution and then subjected to steam distillation. After making the distillate acidic with dilute hydrochloric acid it was evaporated to dryness. 0.2 g. of a substance in the form of white powder was left as the residue. That this substance was nothing but the hydrochloride of desired *N*-methyl-hydrobenzoisoquinoline was proved by analysing its platinum double salt obtained as beautiful orange-coloured crystals melting at 212° under decomposition. (Found: Pt, 25.15. Calculated for  $[\text{C}_{13}\text{H}_{13}\text{N}]_2\text{H}_2\text{PtCl}_6$ : Pt, 25.15%).

The solution, from which *N*-methyl-hydrobenzoisoquinoline was extracted with ether, was distilled with steam to drive off the base still remaining, and again treated with ether. After evaporating ether from the ether extract the aqueous solution was acidified with hydrochloric acid and evaporated to dryness. 0.05 g. of white powder was yielded. The platinum double chloride of this substance, melting at 170°, was identified as the double salt of *N*-methyl-naphthalimidine formed by electrolysis at lead cathode.

With the view of investigating the relation between the concentration of sulphuric acid and the reduction rate, a series of experiments was carried out by using as catholyte a mixture of equal volume of alcohol and sulphuric acid solution of various concentrations. Each electrolysis was continued for ten hours and the results are as shown in Table 3.

Table 3.

| Conc. of $\text{H}_2\text{SO}_4$ (%) | Undissolved material (%) | Ether extract from acidic medium (%) | <i>N</i> -methyl-hydrobenzo-isoquinoline (%) | <i>N</i> -methyl-naphthalimidine (%) |
|--------------------------------------|--------------------------|--------------------------------------|----------------------------------------------|--------------------------------------|
| 50                                   | 31                       | 20                                   | 21                                           | 5.0                                  |
| 60                                   | 17                       | 20                                   | 26                                           | 4.5                                  |
| 70                                   | 13                       | 21                                   | 29                                           | 5.9                                  |
| 80                                   | 20                       | 23                                   | 27                                           | 4.4                                  |
| 90                                   | 14                       | 29                                   | 38                                           | 4.5                                  |

As is seen from the above table, the greater was the concentration of acid the less was the undissolved material, and at the same time the more the yield of *N*-methyl-hydrobenzoisoquinoline. The concentration of sulphuric acid seems to exert no influence upon the yield of *N*-methyl-naphthalimidine, which remains almost constant. When the concentration of sulphuric acid becomes more than 70%, the quantity of the ether extract from acidic medium is observed to increase gradually. This is probably due to polymerization of the material, as was stated above.

III. *N*-ethyl-naphthalimide (I,  $\text{R}=\text{C}_2\text{H}_5$ ). (1) *Reduction with lead cathode.* In order to get the reduction product of the first stage, i.e. *N*-ethyl-naphthalimidine, electrolysis was tried with lead cathode under the following conditions. Cathode: cylindrical lead plate, 100 sq. cm. of area. Catholyte: 100 c.c. of 60% sulphuric acid solution in which 1 g. of imide was added. Anode: cylindrical lead. Anolyte: 50% sulphuric acid. Current density: 6.5 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 546 F. per mol. Temperature: 35°.

Electrolysis was conducted just in the same manner as in the case of the methyl derivative. When electrolysis stopped, a great quantity of insoluble substance still remained suspended in the solution. This was filtered off and 0.68 g. of unreduced substance was obtained. The filtrate was then treated with ether and from the ether extract 0.10 g. of unreduced substance was further produced. The electrolyte was then made alkaline with caustic soda and treated with ether, when a small amount of a yellowish oily substance soluble in hydrochloric acid was obtained. Its platinum double chloride was formed as yellow-brown crystals, melting at 165° with decomposition. (Found: Pt, 23.44. Calculated for  $[\text{C}_{14}\text{H}_{13}\text{NO}]_2\text{H}_2\text{PtCl}_6$ : Pt, 23.46%).



This reduction product was identified to be *N*-ethyl-naphthalimidine. The reduction rate was calculated to be 15.4%.

The results of investigation carried out to determine the relation between the concentration of sulphuric acid and the reduction rate are summarized in Table 4.

As 80-90% sulphuric acid solution caused foaming of catholyte, which made electrolysis very troublesome, a little amount of alcohol was added to catholyte. In consequence, insoluble substance remarkably decreased, while the part extracted with ether from acid solution increased. The concentration of 60% was found to be most favourable for reduction.

The results of the electrolysis showing the relation of the concentration of sulphuric acid to the reduction rate, when worked with catholyte containing an equal volume of alcohol, are shown in Table 5.

Table 4.

| Conc. of $\text{H}_2\text{SO}_4$ (%) | Undissolved material (%) | Ether extract from acidic medium (%) | <i>N</i> -ethyl-naphthalimidine (%) |
|--------------------------------------|--------------------------|--------------------------------------|-------------------------------------|
| 40                                   | 82                       | 8                                    | 4.5                                 |
| 50                                   | 78                       | 10                                   | 6.3                                 |
| 60                                   | 68                       | 10                                   | 15.4                                |
| 70                                   | 75                       | 8                                    | 9.1                                 |
| 80                                   | 47                       | 30                                   | 9.1                                 |
| 90                                   | 45                       | 35                                   | 10.9                                |

Table 5.

| Conc. of $\text{H}_2\text{SO}_4$ (%) | Undissolved material (%) | Ether extract from acidic medium (%) | <i>N</i> -ethyl-naphthalimidine (%) |
|--------------------------------------|--------------------------|--------------------------------------|-------------------------------------|
| 40                                   | 92                       | 3                                    | 1                                   |
| 50                                   | 70                       | 19                                   | 2                                   |
| 60                                   | 72                       | 15                                   | 3                                   |
| 70                                   | 68                       | 15                                   | 2                                   |
| 80                                   | 70                       | 16                                   | 2                                   |
| 90                                   | 71                       | 18                                   | 2                                   |

(2) *Reduction with zinc amalgam cathode.* With the view of obtaining the complete reduction product electrolysis was carried out with zinc amalgam cathode under the same conditions as were used in reduction of the corresponding methyl derivative. They were as follows. Cathode: zinc amalgam, 16 sq. cm. of area. Catholyte: mixture of 50 c.c. of 50%  $\text{H}_2\text{SO}_4$  and 50 c.c. of alcohol in which 1 g. of the imide was introduced. Anode: cylindrical

lead plate. Anolyte: 50%  $\text{H}_2\text{SO}_4$ . Current density: 75 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 103.7 F. per mol. Temperature: 26°.

The material dissolved readily in the course of electrolysis and reduction seemed to take place far more smoothly than with lead cathode. But its dissolution was not completed even at the end of electrolysis. The catholyte was heated on the water bath to drive off alcohol and then it was diluted with double volume of water. 0.3 g. of undissolved material thus precipitated was filtered, and the filtrate was treated with ether, when 0.3 g. of unreduced substance was extracted. The filtrate was now made alkaline with caustic soda solution, and subjected to steam distillation, collecting the distillate in dilute hydrochloric acid solution as long as it continued to react alkaline. The hydrochloric acid solution was then evaporated to dryness on the water bath, when 0.21 g. of white powder was left as the residue. The platinum double chloride prepared from the residue was beautiful orange-coloured crystals melting at 197° with decomposition. (Found: Pt, 24.29. Calculated for  $[\text{C}_{11}\text{H}_{11}\text{N}]_2\cdot\text{H}_2\text{PtCl}_6$ : Pt, 24.28%).

On treating the remaining solution after steam distillation with ether a small amount of oily substance was extracted. Its platinum double chloride melted at 165° and was identified as *N*-ethyl-naphthalimidine. The yield was 5.4%. In order to obtain the relation of the reduction rate to the concentration of acid, a series of

electrolyses were carried out by varying the concentration of acid. The results are summarized in Table 6.

Table 6.

| Conc. of<br>H <sub>2</sub> SO <sub>4</sub> (%) | Undissolved<br>material (%) | Ether extract<br>from acidic<br>medium (%) | N-ethyl-hydro-<br>benzo-iso-<br>quinoline (%) | N-ethyl-<br>naphthal-<br>imidine (%) |
|------------------------------------------------|-----------------------------|--------------------------------------------|-----------------------------------------------|--------------------------------------|
| 30                                             | 47                          | 19                                         | 24                                            | 5.1                                  |
| 40                                             | 37                          | 25                                         | 18                                            | 2.2                                  |
| 50                                             | 30                          | 30                                         | 21                                            | 5.4                                  |
| 60                                             | 25                          | 31                                         | 14                                            | 5.4                                  |
| 70                                             | 23                          | 31                                         | 15                                            | 5.4                                  |
| 80                                             | 21                          | 33                                         | 17                                            | 5.4                                  |
| 90                                             | —                           | 30                                         | 44                                            | 6.1                                  |

As is seen from the table, the greater was the concentration of the acid, the more soluble became the material, and at 90% it completely dissolved, but the ether extract did not increase in the same proportion. The yield of the complete reduction product remarkably increased at 90%. The yield of *N*-ethyl-naphthalimidine, independent of the concentration of acid, remained nearly constant, as in the case of the corresponding methyl derivative.

The author expresses his sincere thanks to Dr. Motooki Matsui, Professor emeritus of the Kyoto Imperial University, for his cordial suggestions.

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# Studies on Rhythmic Precipitates.

By Toshizo ISEMURA.

(Received November 24, 1938.)

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## I. Introduction.

In 1896 Liesegang discovered that when silver nitrate solution was allowed to diffuse into a gel impregnated with a small quantity of potassium dichromate, the deposition of the silver chromate in the gel was not continuous but marked by gaps or empty spaces at regular intervals.<sup>(1)</sup> Percieving the importance of the phenomenon he studied this phenomenon systematically<sup>(2)</sup> which was then followed by many other investigators.<sup>(3)</sup> As the result of their investigations, it was observed that not only silver chromate but also some other scarcely soluble substances form rhythmic precipitates. It was ascertained, that in many precipitation reactions rhythmic bands are obtained, when two reactive substances are brought in contact with each other, by diffusing one of the substances into a solution of the other in a gel. Since then it attracted the interest of the investigators in the question: what mechanism the phenomenon is produced by? At first, Wilh. Ostwald proposed a theory to explain this phenomenon, which is known to-day as the "super-saturation theory".<sup>(4)</sup> Ever since many other theories were presented by different authors,<sup>(5)</sup> yet this phenomenon cannot be fully explained by these hitherto proposed theories.

The present author studied the rhythmic precipitates from various standpoints, the description of which is given in the following pages. A number of new examples were obtained in the course of study, and it was made clear that in several examples the rhythmic precipitates, which are considered hitherto as Liesegang phenomenon, are produced by the periodic changes of external conditions such as light or temperature. It has been studied on the effect of the varieties of gel, the electrolytes, the hydrogen ion concentration, the presence of impurities and other substances, the ageing of gel, the light and the temperature on the formation of rhythmic precipitates. It was also studied a general regularity with regard to the intervals of the bands.

## II. Various Influences on the Formation of Rhythmic Precipitates.

**The Influence of the Nature of Gel.** Rhythmic precipitates are formed not only in a gel but also in places such as capillary tubes or narrow aperture between two glass plates where no gel is present. The formation of rhythmic precipitates in a gel will be described first.

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(1) Liesegang, *Naturw. Wochschr.*, **11** (1896), 353; *Photographisches Archiv*, (1896), 221.

(2) Liesegang, *Kolloid-Z.*, **2** (1898), 70; *Z. physik. Chem.*, **88** (1914), 1; "Chem. Reaktionen in Gallerten" Düsseldorf, (1898); "Geologische Diffusionen", Dresden, (1913).

(3) See Hedges, "Liesegang rings"; S. Veil, "Les Phénomènes Périodiques de la Chimie" Paris, (1934).

(4) *Z. physik. Chem.*, **23** (1897), 365; "Lehrbuch der Allgemeinen Chemie" II, 2, 777, Leipzig, (1911).

(5) Bradford, *Kolloid-Z.*, **30** (1922), 364; Chatterji and Dhar, *Kolloid-Z.*, **31** (1922), 15; *ibid.*, **37** (1925), 2, 89; Wo. Ostwald, *Kolloid-Z.*, **36** (Zsigmondy-Festschrift) (1925), 380; Holmes, *J. Am. Chem. Soc.*, **40** (1918), 1187; Fischer and McLaughlin, *Kolloid-Z.*, **30** (1922), 13; Traube and Takehara, *Kolloid-Z.*, **35** (1924), 245; Michaleff, Nikiforoff and Schemjakin, *Kolloid-Z.*, **66** (1934), 197; Christiansen and Wulff, *Z. physik. Chem.*, B, **26** (1934), 187.

As Liesegang<sup>(1)</sup> had first found, the rhythmic precipitation of silver chromate is well developed in a gelatine jelly, but generally not in an agar-agar or in a silicic acid gel. This is known as a specific influence of a gel on the formation of rhythmic bands. Moreover, even though a gel is made of gelatine, the same results may not be obtained with various gelatines from different manufacturers.

The present author carried out three series of experiments. In the first series, five kinds of gelatines were used, two of which, being the products of our country, were purchased from Takeda Pure Chemicals & Co. and were denoted by A and B, while the others were also purchased from Takeda but manufactured by Coignet Père et Fils & Co. in Belgium and were denoted by A, D, and No. 1. In the gels which were made from these gelatines under entirely the same conditions, it was tried to make rhythmic precipitate of silver chromate. 3% gelatine solutions containing 0.1% potassium dichromate were made and introduced into test tubes (diameter about 10 mm.) to the height of 7 cm. After the gel set firmly, 5% silver nitrate solution was poured on it. The test tubes were kept in a dark room.

In Japanese gelatine A no distinct rhythmic bands were formed but at the transition zone from the fine brick-red precipitates to the relatively coarse dark violet precipitates, some faint bands were seen. In Japanese gelatine B, 8~9 distinct bands were found under a continuous zone of brick-red precipitate, beneath which a layer was formed of uniformly scattered dark violet precipitate, and in the lower part of the test tube there were 6 violet bands which consisted of relatively coarse precipitate. On the other hand, in all other three gelatines, which were made in Belgium, the typical rhythmic precipitate of brick-red silver chromate was well developed. In gelatine A of Coignet, 25 bands were formed. In this case, the intervals between two succeeding bands were the shortest among the three examples. In gelatine No. 1. of Coignet, 21 bands were formed. In gelatine D of Coignet, 20 bands were formed and the intervals between them were the longest among these three.

The second series of experiment were conducted in the same manner, with seven samples of photographic gelatines, A, B, and C for the manufacture of positive cinematographic film and A, B, C and D for negative film. These photographic gelatines were placed at the author's disposal by the kindness of Fuji Photo Film Co. Ltd. The conditions were entirely the same as those of the first series. The results were as follows. In gelatine A for positive film, 15 bands were recognised, though seven of which were very faint. In gelatine B for positive film, 26 bands were formed, the lower the position of the band formed in the gel was, the smaller the diameter of the disc of band. The density of the band formation was large. In gelatine C for positive film, 26 distinct bands were formed, and in this case also, the lower the position of the band the smaller the diameter of the disc. In gelatin A for negative film, 12 bands were formed, though all were faint, four of them were especially very faint. In gelatine B for negative film, 30 bands were formed. The band was too dense and a part of the banded precipitate was blurred. The banding was the same type with gelatine B for positive film. In gelatine C for negative film 15 bands were formed, seven of

which being very faint. The appearance of this rhythmic precipitate was similar to that in gelatine A for positive film. In gelatine D for negative film, 17 bands were formed, the typical rhythmic precipitate being well developed.

In the third series, an attempt was made to make bands of magnesium hydroxide in these photographic gelatines. In this case, the specific influence of gelatines was more or less indistinct. In gelatine A for positive film, 2 bands and a band of saturn structure were formed. In gelatine B for positive film, 2 bands and a ring were formed. In gelatine C for positive film, 2 bands and a ring were formed. In gelatine A for negative film also, 2 bands and a ring were formed, but in this case the intervals between the bands were somewhat larger than the cases of gelatine B and C for positive film. In gelatine B for negative film, 2 bands and a ring were formed, the intervals between them were the same as in the cases of gelatine B and C for positive film. In gelatine C for negative film, 2 bands and a band of saturn structure were formed and in gelatine D for negative film, 3 bands were formed. The differences of bands in the case of magnesium hydroxide caused by the varieties of gelatine were somewhat obscure but recognisable.

Thus the different gelatines give entirely diverse results. It seems that these effects may be chiefly referred to the hydrogen ion concentration of the gel and to the impurities contained in gelatine. Liesegang<sup>(6)</sup> concluded that the specific influences of gelatines on the formation of rhythmic precipitates are referred to the content of gelatose, a hydrolytic product of gelatine.

By the author's experiment, however, it was recognised that the influence of the difference of gelatose content is not so large, for the banding was scarcely influenced by the addition of a small quantity of gelatose to the gel. Accordingly, the influence of the species of gelatines is not referred only to the gelatose content.

Certain rhythmic precipitate is formed in gelatine, in agar-agar, or in silicic acid gel, irrespective of the species of the medium, or even in the complete absence of gel. For example, the rhythmic precipitate of calcium phosphate is the case. It is well known that calcium phosphate forms rhythmic precipitate in gelatine, in agar-agar or in the complete absence of gel. The author could obtain the rhythmic bands of this substance also in silicic acid gel.<sup>(7)</sup>

On the other hand, it is well known that silver chromate gives a typical rhythmic precipitate in gelatine jelly but not in agar-agar or in silicic acid gel. Bradford<sup>(8)</sup> obtained silver chromate bands in an agar-agar gel which contained somewhat large quantity of potassium citrate with potassium dichromate. Hatschek<sup>(9)</sup> had succeeded in obtaining the bands of silver chromate in a silicic acid gel, which was prepared by the unusual method, based on the fact that silicic acid is gelatinised on mixing

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(6) Liesegang, *Kolloid-Z.*, **2** (1907), 70.

(7) Isemura, this Bulletin, **13** (1938), 493.

(8) Bradford, "Alexander's Colloid Chemistry, Theoretical and Applied" Vol. I, 790, New York (1926).

(9) Hatschek, *Kolloid-Z.*, **38** (1926), 151.

a solution of sodium silicate with somewhat large quantity of a solution of potassium dichromate.

As reported in a previous communication,<sup>(10)</sup> the present author had also succeeded in obtaining more distinct rhythmic bands of silver chromate in a silicic acid gel which was prepared by the usual procedure. A sol was prepared by mixing a solution of sodium silicate with some acids and then potassium dichromate was added. After the gel set firmly, a strong silver nitrate solution was put on it and let diffuse into the gel. Silver chromate bands in a silicic acid gel were thus obtained. In this case, hydrogen ion concentration of the gel plays an important rôle, and the range of pH where the rhythmic precipitates are made, is very narrow. So, it was believed by many investigators, that silver chromate cannot be obtained in bands in silicic acid gel and they insisted upon the non-formation of bands as being the specific effect of gel. The rhythmic precipitates of the same substance are produced in various jellies by modifying the conditions in certain degree.

Lead chromate does not form rhythmic bands in an ordinary silicic acid gel, but forms bands in the presence of some glucose in the gel.<sup>(11)</sup> Lead iodide in a silicic acid gel does not form rhythmic precipitate in an ordinary condition and fern-like fronds grow down into the gel, mixed with many hexagonal plates. But it was found in rare cases that the rhythmic precipitate of this substance occurred accidentally. When the crystal became relatively small, the rhythmic precipitate was generally formed. The increase of the concentration of inner and outer electrolytes is favourable for making the deposited crystals small. In order to make sure of the formation of the rhythmic precipitate of lead iodide a third substance has to be added, which makes the crystals of lead iodide very small. Citrate and tartrate fit for this purpose. The typical rhythmic bands of lead iodide in a silicic acid gel were obtained by the presence of a small quantity of citrate or tartrate.<sup>(12)</sup> These results will be described later in detail.

It seems from the above-mentioned results that the nature of gel has a great influence on the formation of periodic precipitate but rhythmic bands are produced in any gel when we modify the condition appropriately. Generally the precipitates formed in gelatine are especially small in size. The precipitates formed in silicic acid gel on the contrary, are often well-developed crystals, and the bands are often blurred by the growth of too large crystals which came in contact with each other.

The presence of a gel is favourable in many cases but not always necessary for the formation of bands. This was already shown by Dreaper<sup>(13)</sup> and others.<sup>(14)</sup> In their experiments rhythmic precipitation was observed in a capillary tube or in a narrow aperture between two glass plates and the formed rhythmic bands are always microscopic. We can recognise from these facts, that the gel has an important signifi-

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(10) Isemura, this Bulletin, **13** (1938), 489

(11) Isemura, *ibid.*, **8** (1933), 11.

(12) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 58.

(13) Dreaper, *Kolloid-Z.*, **14** (1914), 163.

(14) Wo. Ostwald, *Kolloid-Z.*, **40** (1926), 144; Notboom, *ibid.*, **32** (1923), 247; Morse, *J. Phys. Chem.*, **34** (1930) 1554; Ghosh, *J. Indian Chem. Soc.*, **7** (1930), 509.

cance to prevent the disturbances caused by heat convection or by mechanical shocks. If the reactions are undertaken in a viscous fluid and mechanical shock is prevented and the sudden change of temperature is avoided, then rhythmic bands may be produced in an ordinary test tube in the absence of jelly. When the density of the precipitate produced by such reaction in the viscous fluid is large, the precipitate settles down by gravity so that the bands blur.

In some colour reactions, however, bands are preserved for a long time. For example, the reaction which is known as Lunge's reaction for nitrate ion, gives often rhythmic bands when the system is kept from disturbances. A dilute potassium nitrate solution is gently run down the side of a test tube on a diphenylamine solution in concentrated sulphuric acid, and the tube is allowed to stand for several days. Blue rhythmic bands, are formed in sulphuric acid. Similar rhythmic colourings were observed in some other colour reactions. Reaction between an aqueous solution of egg albumin and a solution of  $\alpha$ -naphthol or thymol in sulphuric acid, which is called Molisch's reaction for sugar in protein, gives violet or red-brown bands. The reaction of an aqueous solution of egg albumin with a solution of glyoxylic acid in sulphuric acid, that is known as the Hopkins and Cole's reaction for protein, gives blue violet rhythmic colouring in the entire absence of disturbance. Fig. 1 shows the rhythmic colouring of the reaction of protein with  $\alpha$ -naphthol and thymol. The left photograph is obtained by the reaction of protein with thymol and the right by the reaction with  $\alpha$ -naphthol. When we carefully protect the test tubes from shocks and sudden change of temperature, we can preserve these bands for a long period.

**The Influence of Inner Electrolyte and its Concentration.** The range of the concentration of inner and outer electrolytes for the formation of the Liesegang rings is rather narrow. Accordingly, it gives the general appearance that the formation of rhythmic precipitate is limited to some special substances. In the author's opinion, however, the formation of periodic precipitate is a general phenomenon.

The concentration of inner electrolyte has especially a profound influence on the formation of bands. The concentration of electrolyte beyond a certain limit is necessary for the formation of bands. The increase of the concentration of inner electrolyte beyond this limit makes the banding more dense. The distance from the top of the gel to the first separated band becomes large with the increase of the concentration of inner electrolyte. On the other hand, if the concentration exceeds certain upper limit, bands can no more be obtained.

The increase of the concentration of inner electrolyte hinders the diffusion of outer electrolyte into a gel, while the inner electrolyte diffuses in the opposite direction, so that there remains little reactant at the bottom of the test tube. Consequently, the distance between the last formed band and the top of the gel becomes short when the bands deposit closely each other. The relation between the density of bands and the change of concentration of inner electrolyte was shown in the previous communications.<sup>(15)</sup> Some of the results are given in the following tables.

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(15) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 301, 629.



Table 1.  
Bands of Silver Carbonate.

| Conc. of sodium carbonate (inner electrolyte) (%) | Number of bands    |
|---------------------------------------------------|--------------------|
| 0.25                                              | continuous precip. |
| 0.23                                              | continuous precip. |
| 0.20                                              | 10                 |
| 0.15                                              | 5                  |
| 0.12                                              | 4                  |
| 0.10                                              | 3                  |
| 0.08                                              | 0                  |
| 0.06                                              | 0                  |

Gelatine 2.8%.  
Outer electrolyte: silver nitrate 5%.  
Temperature: 5°C.

Table 2.  
Bands of Silver Carbonate.

| Conc. of ammonium carbonate (inner electrolyte) (%) | Number of bands |
|-----------------------------------------------------|-----------------|
| 2.3                                                 | 13              |
| 1.4                                                 | 15              |
| 0.9                                                 | 12              |
| 0.6                                                 | 9               |
| 0.5                                                 | 8               |
| 0.4                                                 | 7               |
| 0.3                                                 | 5               |
| 0.2                                                 | 6               |
| 0.1                                                 | 3               |

Gelatine 2.8%.  
Outer electrolyte: silver nitrate 5%.  
Temperature 5°C.

Table 3. Bands of Silver Iodate.

| Conc. of silver nitrate (inner electrolyte) (%) | Total number of bands | Number of bands * |
|-------------------------------------------------|-----------------------|-------------------|
| 0.17                                            | 20                    | 15                |
| 0.13                                            | 22                    | 14                |
| 0.09                                            | 22                    | 13                |
| 0.07                                            | 22                    | 12                |
| 0.04                                            | 10                    | 3                 |

Gelatine 2.8%. Outer electrolyte: potassium iodate 5%. Temperature: 5°C.

The asterisk denotes the number of bands formed from 10 to 40 mm. from the contact surface of the diffusing solution and gel. (The same in Tables 3, 5, 7, 12, 14, 16).

Table 4. Bands of Silver Arsenite.

| Conc. of sodium arsenite (inner electrolyte) (%) | Total number of bands | Number of bands ** |
|--------------------------------------------------|-----------------------|--------------------|
| 1.8                                              | 23                    | 16                 |
| 1.0                                              | 29                    | 18                 |
| 0.7                                              | 27                    | 19                 |
| 0.3                                              | 26                    | 18                 |
| 0.2                                              | 20                    | 17                 |
| 0.1                                              | 14                    | 11                 |

Gelatine 2.5%. Outer electrolyte: silver nitrate 5%. Temperature: 10°C.

\*\* denotes the number of bands formed 30 to 60 mm apart from the contact surface of the gel and the diffusing electrolyte. (The same in Tables 4 8, 13, 17).

Table 5. Bands of Lead Iodate.

| Conc. of potassium iodate<br>(inner electrolyte) (%) | Number of bands* |
|------------------------------------------------------|------------------|
| 2.0                                                  | 23***            |
| 1.8                                                  | 25               |
| 1.6                                                  | 23               |
| 1.4                                                  | 22               |
| 1.2                                                  | 20               |
| 1.0                                                  | 20               |
| 0.8                                                  | 19               |
| 0.6                                                  | 17               |
| 0.4                                                  | 14               |
| 0.1                                                  | 8                |

Gelatine 2%. Outer electrolyte: lead acetate 0.5 mol.  
Temperature: 15°C.

\*\*\* A continuous precipitate was formed to a point of 12 mm. from the contact surface and the bands could not be counted in the part 10 to 12 mm. apart from the surface.

In these cases, the effects of concentration of inner electrolyte were investigated keeping other conditions in same. Experiments were conducted in test-tubes the inner diameter of which being 1.2 cm. and the length, 11 cm. These test tubes were filled with the gel to the height of 6.5 cm. Fig. 2 shows the effect of concentration of inner electrolyte in the case of silver carbonate bands. These photographs correspond to the third to seventh experiments shown in Table 1.

The influence of the concentration of inner electrolyte was studied subsequently with barium chromate, lead carbonate in gelatine, lead carbonate, cobalt sulphide, ferric ferrocyanide, cobalt phosphate, copper iodate, copper carbonate and bismuth chromate bandings in silicic acid gels. These experimental results will be described later in details.

The appearance of the rhythmic precipitate of a certain substance, produced by the action of the various salts as the inner electrolyte, differs profoundly according to the kind of salt. For instance, when we make silver carbonate bands in gelatin, we can use ammonium carbonate as well as sodium carbonate. But the appearance of the obtained rhythmic bands is quite different in these cases. In the case of ammonium carbonate the bands are obtained for relatively wide range of the concentration of inner electrolyte, namely 0.1~2.3%, while in the case of sodium carbonate the range of concentration is rather narrow. Moreover the bands of silver carbonate which were made by using sodium carbonate as the inner electrolyte looked like tablets and were separated from each other with considerable intervals. The bands which were made by using ammonium carbonate, grew relatively close as seen in Table 2 and each band was often incomplete and had the appearance of a net-work or an assemblance of fragments of crescent-shaped precipitate. It seems that the influence

of the varieties of inner electrolyte is referred to the effect of the soluble reaction products, such as sodium nitrate or ammonium nitrate, on the solubility and growth of the precipitate.

**The Influence of Outer Electrolyte and its Concentration.** On the formation of rhythmic precipitate it is necessary that the outer electrolyte diffuses into the gel. So the concentration of the outer electrolyte must be high. At least it must be hypertonic to that of the inner electrolyte. The effect of the concentration of the outer electrolyte on the formation of periodic bands is similar in many cases. The higher the concentration is, the larger the number of bands becomes. The larger the ratio of concentration of outer electrolyte to that of inner electrolyte becomes, the closer the intervals between the bands, generally become. So, if the conditions, excepting the concentration of the outer electrolyte are maintained constant, it is obvious that the higher the concentration is, the larger the number of the formed bands and the smaller the intervals between the bands become. The importance of the concentration as to whether bands are formed or not, is smaller in this case than in the case of inner electrolyte, that is the range of concentration that can form rhythmic bands is very wide. But too concentrated solution is often unfavourable for the rhythmic banding. If the concentration becomes too high, the bands stand too close together, so a part of precipitate appears only like a column of precipitate and has not a periodic structure. At the same time, if too concentrated solution of outer electrolyte was used, it often peptised the gel. For example, when silver chromate bands are made in gelatine, too concentrated silver nitrate solution peptises the gelatine at the contact surface of the gel with the solution. For these reasons, the concentration of outer electrolyte is somewhat restricted, but in general, the concentration of outer electrolyte for the rhythmic banding has a relatively small significance. The results of the experiments on the influence of the concentration of outer electrolyte, were also shown in the previous communication.<sup>(15)</sup> Some of the results are given in the following tables.

Table 6.

Bands of Silver Carbonate.

| Conc. of silver nitrate (outer electrolyte) (%) | Number of bands |
|-------------------------------------------------|-----------------|
| 20                                              | 9               |
| 15                                              | 8               |
| 10                                              | 7               |
| 5                                               | 6               |

Gelatine 2.8%.

Inner electrolyte:

sodium carbonate 0.17%.

Temperature 5°C.

Table 7. Bands of Silver Iodate.

| Conc. of potassium iodate (outer electrolyte) (%) | Total number of bands | Number of bands* |
|---------------------------------------------------|-----------------------|------------------|
| Saturated solution                                | 22                    | 13               |
| 5.0                                               | 21                    | 12               |
| 4.0                                               | 17                    | 9                |
| 3.0                                               | 13                    | 6                |
| 2.0                                               | 12                    | 2                |

Gelatine 2.8%.

Inner electrolyte: silver nitrate 0.1%.

Temperature 5°C.

Table 8. Bands of Silver Arsenite.

| Conc. of silver nitrate<br>(outer electrolyte) (%) | Number of<br>bands** |
|----------------------------------------------------|----------------------|
| 15                                                 | 15                   |
| 10                                                 | 26                   |
| 5                                                  | 15                   |

Gelatine 2.5%.

Inner electrolyte:

sodium arsenite 0.67%.

Temperature: 10°C.

When a 15% silver nitrate solution was added the formed continuous precipitate came down to a distance of 43 mm. from the surface of the gel. Therefore, the bands decreased in number, but in reality they stood close by in the highest degree.

Table 9. Bands of Lead Iodate.

| Conc. of lead acetate<br>(outer electrolyte) (mol.) | Number of<br>bands* |
|-----------------------------------------------------|---------------------|
| 1.00                                                | 22                  |
| 0.75                                                | 21                  |
| 0.50                                                | 20                  |
| 0.25                                                | 18                  |

Gelatine 2.0%.

Inner electrolyte:

potassium iodate 1.2%.

Temperature: 15°C.

Fig. 3 shows the change of the closeness with the concentration of outer electrolyte in the case of silver carbonate bands.

The influence of the concentration of outer electrolyte was subsequently studied with lead carbonate, copper iodate, and cobalt sulphide bandings in silicic acid gels. In the case of calcium phosphate bands in the silicic acid gel, some peculiar results were obtained. While the concentration of outer electrolyte is relatively low, the general rule—the higher the concentration is, the larger the number of bands formed becomes or the smaller the intervals between the bands become—holds in this case also. But if the concentration exceeds a certain limit, the influence is scarcely observed as shown in Table 10. The rhythmic precipitates which were obtained by the diffusion of calcium chloride, the concentration of which were beyond a certain limit, are entirely identical<sup>(16)</sup>.

Table 10. Calcium phosphate in silicic acid gel.

| Conc. of calcium chloride<br>(outer electrolyte) (%) | Number of bands |                                                                                 |
|------------------------------------------------------|-----------------|---------------------------------------------------------------------------------|
| 30                                                   | 8               | } These three coincide and showed no difference.                                |
| 25                                                   | 8               |                                                                                 |
| 20                                                   | 8               |                                                                                 |
| 15                                                   | 8               | } The bands were close in proportion to the concentration of outer electrolyte. |
| 10                                                   | 8               |                                                                                 |
| 5                                                    | 7               |                                                                                 |

Inner electrolyte: sodium phosphate 0.5%.

As described in the foregoing paragraphs, bands of different appearance are obtained under the same experimental conditions when the

(16) Isemura, this Bulletin, **13** (1938), 493.

species of the inner electrolyte are different. Similarly, different bands are obtained, when the species of outer electrolyte differs. This is proved in the cases, for example, of the formation of periodic precipitates of lead iodate in gelatine, where lead nitrate and lead acetate solutions of the same concentration are used as the outer electrolyte respectively. When lead nitrate is used, the bands are thinner and their number is larger and the intervals between them become shorter than the case of lead acetate. Fig. 4 shows such a case, the left being obtained by diffusion of lead nitrate and the right by lead acetate. The bands stood so close in the case of lead nitrate, that scarcely any strata were discriminated in the upper part of the figure. This fact is not to be referred to the difference of the diffusibility of lead nitrate and lead acetate. It must preferably be referred to the influence of the solubility of the precipitate in the formed soluble salts such as potassium nitrate and potassium acetate. Because, the effects of the temperature or the concentration of gel, which affect considerably the diffusibility, give smaller difference of bandings than the effect of the outer electrolyte. Even when a half concentrated solution of lead nitrate to that of lead acetate is used still closer the bands are formed than those formed by the diffusion of the lead acetate solution.

Rhythmic precipitates of bismuth chromate in silicic acid gel, obtained by diffusing bismuth nitrate and bismuth chloride have quite different appearances. In this case, the acid which is used to prepare the gel has also some effects on the bands. So this case will be treated later again.

Contrary to the effects of the concentration of outer electrolyte previously described, there are a number of cases in which, when the concentration of outer electrolyte increases, the intervals between the bands increase and the bands become more distinct. This is the case of gold banding. Indeed, gold bands are not formed as a true "Liesegang phenomenon" but as a reflex of the rhythms of external conditions. This will be described in the later part.

According to Lincoln and Hillyer,<sup>(17)</sup> if the ratio of the concentrations of outer and inner electrolyte is constant, the same distribution of the layers of rhythmic precipitate is obtained, providing that the gel concentration and the temperature are constant. By the decrease of the concentration of inner electrolyte the formation of precipitate becomes slower, and on the other hand, by the decrease of that of outer electrolyte, it diffuses more slowly, so the influences of the decrease of the concentration of both inner and outer electrolyte become relatively small, for both affect oppositely. But it seems that both influences are not completely compensated by each other. The present author studied this fact by using the bands of silver chromate in gelatine and calcium phosphate in silicic acid gel. These rhythmic precipitates, however, did not obey the above rule. So, it seems that the fact pointed out by Lincoln and Hillyer has no generality.

**Interchange of Inner and Outer Electrolytes.** When a rhythmic precipitate obtained by the interaction of two substances in a gel, either

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(17) Lincoln and Hillyer, *J. Phys. Chem.*, **38** (1934), 907.

of the two may well become an inner electrolyte or an outer electrolyte. In many experiments by various authors, in which silver chromate bands are made in gelatine, potassium dichromate is usually dissolved in gelatine as an inner electrolyte and silver nitrate is allowed to diffuse into the gel. But, inversely, by diffusion of potassium dichromate into the gelatine containing silver nitrate, we can also obtain the rhythmic precipitate of silver chromate.

Accordingly, the interchange of inner and outer electrolytes has no concern with the formation of rhythmic precipitate as a general rule.

It is often impossible to add salts of heavy metals to the silicic acid gel, for silicic acid is partially coagulated. On the other hand, when silver carbonate bands are formed in gelatine containing ammonium carbonate by the diffusion of silver nitrate, a rhythmic precipitate which often consists of crescent-shaped bands is obtained. When the bands are formed reversely in gelatine containing silver nitrate as an inner electrolyte, we shall meet an interesting fact. At first silver carbonate bands have formed, but with the progress of diffusion to the lower part of the gel, the upper bands successively re-dissolved by the formation of a more soluble double or complex salt with the excess of diffusing ammonium carbonate. Owing to the deposition of precipitate in gel, the gel is broken at these parts of deposition. Later, being separated, these parts do not cohere again. There remain rhythmic cracks.

When lead iodide bands in a silicic acid gel are formed by the diffusion of potassium iodide into a gel containing lead acetate, well-developed rhythmic bands are obtained, although a part of lead iodide re-dissolve, forming a soluble complex salt at the top of the gel. But inversely, if lead acetate diffuses into a gel containing potassium iodide, lead iodide is formed at first, but it is immediately converted into a white double salt with successively coming lead acetate. In this case the bands are not so distinct.

In some cases the rhythmic bands of quite different appearances are obtained by the interchange of the inner and outer electrolytes. This is the case with rhythmic bands of silver iodate in gelatine. When a gel containing potassium iodate was covered with silver nitrate solution a rhythmic precipitate is obtained as shown in Fig. 5, the bands of which consist of flocculent clusters of crystals. On the contrary, when a gel containing silver nitrate was covered with the potassium iodate solution the formed rhythmic precipitate is very peculiar in shape, showing a greatly different form from any rhythmic precipitates which the author had ever seen. Fig. 6 shows this rhythmic precipitate. In this case, the structure is rather complicated, thus, band consisting of scattered coarse crystals, thin band consisting of very small crystals and relatively thick band consisting of coarse crystals and empty interspace were repeatedly observed.

**The Influence of the Concentration of Gel.** The concentration of gel has a remarkable influence on rhythmic precipitate. In many cases, if the concentrations of inner and outer electrolyte are kept constant, the number of formed bands decreases and the intervals between them increase with the increase of gel concentration. The distance from the

top of the gel to the last formed band also decreases, in general, with the concentration of the gel. The influence of gel concentration had been investigated on the rhythmic precipitates of silver carbonate, silver iodate, silver arsenite and lead iodate in gelatine gels. The results are shown in the following tables (Table 11-15).

Table 11.  
Bands of Silver Carbonate.

| Conc. of gelatine (%) | Number of bands |
|-----------------------|-----------------|
| 5.0                   | 2               |
| 4.0                   | 4               |
| 3.0                   | 5               |
| 2.0                   | 9               |

Inner electrolyte: sodium carbonate 0.17%.  
Outer electrolyte: silver nitrate 5%.  
Temperature: 5°C.

Table 12.  
Bands of Silver Iodate.

| Conc. of gelatine (%) | Total number of bands | Number of bands* |
|-----------------------|-----------------------|------------------|
| 5.0                   | 21                    | 12               |
| 4.0                   | 23                    | 13               |
| 3.0                   | 25                    | 12               |
| 2.8                   | 25                    | 13               |
| 1.5                   | 25                    | 14               |

Inner electrolyte: silver nitrate 0.13%.  
Outer electrolyte: potassium iodate 5%.  
Temperature: 5°C.

Table 13. Bands of Silver Arsenite.

| Conc. of gelatine (%) | Number of bands** |
|-----------------------|-------------------|
| 4.4                   | 16                |
| 3.5                   | 17                |
| 3.1                   | 18                |
| 2.7                   | 19                |
| 2.3                   | 21                |

Inner electrolyte: sodium arsenite 0.67%.  
Outer electrolyte: silver nitrate 5%.  
Temperature: 10°C.

Table 14. Bands of Lead Iodate.

| Conc. of gelatine (%) | Number of bands |
|-----------------------|-----------------|
| 6.0                   | 16              |
| 4.8                   | 18              |
| 3.0                   | 20              |
| 2.0                   | 23              |

Inner electrolyte: potassium iodate 1.6%.  
Outer electrolyte: lead acetate 0.5 mol.  
Temperature: 15°C.

Fig. 7 shows the effect of the concentration of gel in the case of silver carbonate bands in gelatine. The intervals between bands increase and the number of formed bands decreases with the concentration of gel. The influence of gel concentration was first investigated quantitatively by Popp<sup>(18)</sup> with rhythmic precipitate of magnesium hydroxide in gelatine. According to her experiment, the band itself and the intervals between bands increased with gel concentration, but the number of bands formed was unchanged. In a concentrated gel, the diffusion proceeds slowly and the gel acts to prevent the separation of precipitates. The above results seemed to show that the increase of gel concentration forced to decrease the diffusion velocity and to increase the action which prevents considerably the separation of precipitates.

(18) K. Popp, *Kolloid-Z.*, **36** (1925), 208.

There is an exceptional rhythmic precipitate that gives a reverse result to the above mentioned general rule. This is the case of silver chromate in gelatine. The results are shown in Table 15.

Table 15.

## Bands of Silver Chromate.

| Conc. of gelatine (%) | Number of bands |
|-----------------------|-----------------|
| 10.0                  | 35              |
| 7.5                   | 31              |
| 5.0                   | 27              |
| 2.5                   | 19              |

Inner electrolyte: potassium dichromate 0.13%.

Outer electrolyte: silver nitrate 30%.

Room temperature.

In this case the number of bands increases and the intervals between bands decrease by the increase of gel concentration.

Indeed, there is a significance in the existence of gel for the prevention of the disturbance caused by convection and removing unfavourable effects caused by shocks. Rhythmic precipitate is generally obtainable either in dilute or concentrated gel. For the quickness of diffusion of outer electrolyte it is convenient to use a dilute gel which has the "form-stability" beyond a certain limit. In some special cases, however, it is better to

use the concentrated gel, for it favours the accumulation of the precipitate. One of the example of this case is the gold banding in silicic acid gel. Gold bands are well developed in the gel which is prepared by mixing equal volumes of a 1.16 density water glass solution and a 3 N solution of sulphuric acid, but only faint bands are obtained in the gel prepared by mixing a solution of water glass ( $d = 1.06$ ) and a 0.5 N sulphuric acid.

**The Influence of Light.** Experiments have been done on the rhythmic precipitates of various examples in the light and dark place, and it has been known that, in general, the rhythmic bands appear in light as well as in dark. But in one of the previous communication,<sup>(19)</sup> the author has reported that the light has a profound influence on certain rhythmic precipitate such as that of silver chromate in gelatine jelly. Light has an effect only on the photo-sensitive systems such as chromate-gelatine and an essential significance on the diurnally formed system.

Küster<sup>(20)</sup> stated that no band of silver chromate was obtained in the dark, while Davies<sup>(21)</sup> obtained good bands. Blair<sup>(22)</sup> reported that the bands formed in complete darkness show irregularity. The experiment carried out by the present author are as follows. Three samples of gelatine solutions were prepared, the first sample was made in complete darkness while the second and the third in an ordinary room. The first and the second were set in the dark place and the third, in an ordinary room. Three days later, silver nitrate solution was poured on these gels. After standing the former two in the dark and the latter in the light for a week, rhythmic precipitates of silver chromate were recognised in

(19) Isemura, this Bulletin, **8** (1933), 108.

(20) Küster, *Kolloid-Z.*, **13** (1913), 192.

(21) Davies, *J. Am. Chem. Soc.*, **44** (1922), 2698.

(22) S. Blair, *Phil. Mag.*, **49** (1925), 90.



all three test tubes and no irregularity was noticed. From this fact it has been ascertained that the formation of bands is not affected by the darkness.

According to Blair the bands become irregular when the gel has been irradiated with visible light. But Cluzet and Kofmann<sup>(23)</sup> stated that the formation of rhythmic precipitates was unaffected by visible light. The author found that the radiation of visible ray has an important effect on the formation of bands though the bands do not become irregular even by the strong irradiation of direct sun light. The experiment was done as follows: 2.5% gelatine gel containing potassium dichromate (0.1%) as an inner electrolyte was allowed to set in test tubes and they were kept in a dark place. After the gel set firmly, it was covered with 15% silver nitrate solution. Then each of the test tubes was exposed to direct sun light for different interval of time. The light was filtered through the layer of water to avoid the effect of heat ray. In this case, the number of the formed bands increases in proportion to the time of exposure. But when a certain time interval was exceeded, the bands formed too close to each other and the whole appeared as a dark brown column. Analogous results were obtained by the influence of diffused light.

We can conclude from these results, that the visible light caused to increase the number of bands and to decrease the distance between bands. It seems that these changes which are caused by the exposure to light, are due to the transformation of gel structure and to the interaction of gelatine and potassium dichromate. After long exposure, gel becomes somewhat difficultly soluble and does no more reset. From this fact, it is probable that the gel changes somewhat in its structure or at least the micelle of gelatine suffers some changes.

The author conceives, from these facts, that at first the gelatine reacts with potassium dichromate on exposure to light and changes to insoluble modification. This modification has a less protective action from crystallisation of silver chromate than before. So the bands become closer and the number of them increases.

Blair, studied the effect of visible light by the exposure to the radiation from a half watt lamp, instead of sun light, at very short distance (6 in. range), and recognised that the bands become irregular. In writer's opinion, by the radiation from a short distance as in Blair's experiment, the energy of light delivered to the gel system does not distribute equally as in the case of parallel ray as sun light. Hence the irregular bands were formed.

According to Blair, ultra-violet ray from quartz mercury lamp makes the formation of bands impossible even in a few hours, while Cluzet and Kofmann found that the formation of Liesegang rings was retarded by ultra-violet light. The retardation of formation of rings is also recognised by the author's experiment. And rings became finer and closer each other than in the non-illuminated case.

Recently Köhn and Mainzhausen<sup>(24)</sup> have published an interesting results on the influence of light. According to their result, the influence

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(23) Cluzet and Kofmann, *Compt. rend. soc. biol.*, **104** (1931), 1001.

(24) Köhn and Mainzhausen, *Kolloid-Z.*, **79** (1937), 316.

of light is recognised when a photo-sensitive substance such as silver chloride is formed in the gel. Subsequently, the author has repeated the experiment on the influence of light that was reported in formerly published work using the gelatine purified by the method of Loeb.<sup>(25)</sup> Most impurities in gelatine were desorbed, and it was verified by Lüppo-Cramer's method.<sup>(26)</sup> The gelatine thus purified was almost perfectly free from chlorine or other halogen ions. The obtained results were the same with the former one. The number of bands formed was increased according to the time of exposure to light before superposing the diffusing electrolyte, and the intervals between them became short. It seems that the variation of the distance between bands and the number of them have no concern with the content of chlorine or halogen ions. It gives a very important suggestion on this problem whether rhythmic precipitate of chromate of any metal which does not form a photo-sensitive salt, are affected or not by the irradiation of light. The effect of light on barium chromate bands was studied using the purified gelatine. In this case, the effect of light is also considerable. The experiment was done as follows: a 3% gelatine gel containing 0.5% potassium dichromate as the inner electrolyte was allowed to set in three test tubes in a dark place. The first tube was exposed to direct sun light for about two hours, the second kept in an ordinary room for a day, and the third kept in the dark throughout. A 1 N barium chloride solution was poured on the gels and all three tubes were kept in the darkness. In the test tube exposed to direct sun light the bands became close and blurred and in the test tube kept in diffused light the bands also became close but each band was distinguishable.

Analogous results were also obtained by the influence of ultra-violet ray which is shown in Fig. 8. A gelatine solution which was prepared as above described, was poured into three test tubes of fused silica. One was exposed directly to a quartz mercury lamp, the other exposed to ultra-violet ray filtered from visible rays by a special filter, and the last kept in the dark throughout. The lamp used for this experiment was "Acme"mercury quartz lamp which was made by Shimazu factory. Input of the current applied to the apparatus was 110 volts and 10.2 amperes and the distance between the test tubes and the lamp was about 20 cm. In the photograph, the left is one which was exposed directly to the mercury quartz lamp and the middle to ultra-violet ray and the right unexposed one.

According to the author's opinion, the tanning effect of light plays an important rôle in these cases. This is clear from another fact that light has no influence on the rhythmic banding of the system which does not cause the photochemical reaction between medium and inner electrolyte. For example, lead iodate bands in gelatine are not influenced by light when it was experimented in the condition entirely similar to that of the above described silver chromate system. Also, copper chromate bands in a silicic acid gel are not affected at all by irradiation, for silicic acid and potassium chromate do not react photochemically with each other. On the other hand, there are some rhythmic precipitates on

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(25) Loeb, *J. Gen. Physiol.*, **1** (1918), 237.

(26) Lüppo-Cramer, *Kolloid-Z.*, **5** (1909), 249.

the formation of which light has an essential significance. This is the case, for example, with a rhythmic precipitate of gold. Davies<sup>(29)</sup> has found first that light has an essential effect on the rhythmic banding of gold. The author considered that red-blue-green zones are probably formed by the variation of external irradiation. This assumption was confirmed by the following experiment: To 20 c.c. of a mixture of equal volumes of a 1.158 density sodium silicate solution and 3 N sulphuric acid, it was added 0.8 c.c. of 1% auric chloride. The gel set in a day or two. This gel was kept in a thermostat and covered with a saturated solution of oxalic acid and irradiated with a 60 watt lamp from 50 cm. distance. As oxalic acid diffused into the gel, auric chloride was reduced. The reduced gold was scattered uniformly, but in transmitted light, many bands could be distinguished in the red violet coloration of colloidal gold. These bands may be formed either by the variation of the light intensity or by the true periodic precipitation. Experiment was done under the irradiation of constant light intensity, which was obtained by using accumulators of large capacity as an electric source. By the continuous irradiation of lamp which was supplied by a current from the accumulators, colloidal gold was separated out and scattered uniformly, and no band was observed in it. So it must be referred to the fact that the bands formed by irradiation with the lamp, are produced by the variation of the intensity of light. A rhythmic precipitate of gold differed from so-called Liesegang ring which is formed by the periodic precipitation of entirely chemical cause, and is only a reflex of external rhythms.

**The Effect of Temperature.** It is reasonable that the solubility of a precipitate and the diffusion velocity of reactants are affected by temperature. The formation of a rhythmic precipitate on which the solubility and the diffusion velocity have a serious influence, may also be affected by the temperature. In many cases, the lower the temperature is the larger the number of bands formed, and the smaller the intervals between the bands, if the conditions are kept constant excepting temperature. For example, rhythmic precipitates such as silver iodate, silver arsenite and lead iodate in gelatine gels are the cases. The results are shown in the following tables (Table 16-18). Nevertheless, in certain

Table 16.  
Band of Silver Iodate.

| Temperature (°C.) | Total number of bands | Number of bands* |
|-------------------|-----------------------|------------------|
| 5                 | 18                    | 12               |
| 13                | 18                    | 10               |
| 18                | 20                    | 6                |

Inner electrolyte:  
silver nitrate 0.13%.  
Outer electrolyte:  
potassium iodate 5%.  
Gelatine 2.8%.

Table 17. Bands of  
Silver Arsenite.

| Temperature (°C.) | Number of bands** |
|-------------------|-------------------|
| 5                 | 16                |
| 13                | 14                |
| 18                | 13                |

Inner electrolyte:  
sodium arsenite 0.67%.  
Outer electrolyte:  
silver nitrate 5%.  
Gelatine 4.0%.

Table 18.  
Bands of Lead Iodate.

| Temperature (°C.) | Number of bands* |
|-------------------|------------------|
| 5                 | 20               |
| 15                | 15               |
| 20                | 13               |

Inner electrolyte:  
potassium iodate 0.4%.  
Outer electrolyte:  
lead acetate 0.5 mol.  
Gelatine 2.0%.

(27) Davies, *J. Am. Chem. Soc.* **44** (1922), 2700; *ibid.*, **45** (1923), 2261.

rhythmic precipitates the inverse results were obtained, i.e. the higher the temperature is, the smaller the intervals between bands become. Examples of this case are the rhythmic precipitates of silver carbonate and magnesium hydroxide in gelatine. In the case of silver carbonate, the experiment was carried as follows: sodium carbonate was dissolved in a concentration of 0.17% in 2.5% gelatine and a 5% solution of silver nitrate was placed on it as an outer electrolyte. The experiments were made at 5, 13, and 18°C. In these experiments, the number of bands formed were the same, as shown in Table 19, but in the samples at lower temperatures, the intervals between

Table 19.  
Bands of Silver Carbonate.

| Temperature (°C.) | Number of bands |
|-------------------|-----------------|
| 5                 | 7               |
| 13                | 7               |
| 18                | 7               |

Inner electrolyte: sodium carbonate  
0.17%.

Outer electrolyte: silver nitrate 5%.  
Gelatine 2.5%.

bands became wider. Popp found that the distance between bands of magnesium hydroxide in gelatine increased as the temperature was lowered.<sup>(18)</sup> The effects of temperature on the bands differ in case to case, which may be principally caused by the degree of change of diffusibility of ion and solubility of the formed precipitate. On the whole, the diffusibilities of ions increase with temperature and it seems that the degree of change of diffusibility are not so great and almost of the same extent with various ions, while the difference of degrees of solubility change has a serious significance. The changes of solubilities of the above mentioned substances with temperature are tabulated in the following.

Table 20.  
Silver Carbonate.

| Temperature (°C.) | Solubility (mol./l.)                  |
|-------------------|---------------------------------------|
| 15                | $1.18 \times 10^{-4}$ <sup>(28)</sup> |
| 25                | $1.16 \times 10^{-4}$ <sup>(29)</sup> |

Table 21.  
Magnesium Hydroxide.<sup>(30)</sup>

| Temperature (°C.) | Solubility (%)       |
|-------------------|----------------------|
| 15.5              | $2.8 \times 10^{-2}$ |
| 100               | $4.0 \times 10^{-3}$ |

The solubility of silver carbonate is almost unchanged by the variation of temperature, while that of magnesium hydroxide decreases as temperature is elevated. In general, however, the solubilities of solids increase with the rise of temperature. So, the increase of solubility causes a rhythmic precipitate of large intervals. When the solubility does not change with the change of temperature, the effect of the change of diffusibility is recognised.

(28) Kremers, *Pogg. Ann.*, **85** (1852), 42.

(29) Spencer and M. le Pla, *Z. anorg. Chem.*, **65** (1909), 11.

(30) Fyfe, "Gmelin Handbuch der anorganischen Chemie", II 1, 429.

The author pointed in the foregoing paragraphs, that there are rhythmic bands which are caused by the rhythmical irradiation of light. Similarly, there are bandings which are caused by the rhythmical change of temperature. So-called diurnal bands are made by the rhythms of temperature as well as by those of light. Rhythmic banding of mercuric iodide in a silicic acid gel, which had been presented by Holmes,<sup>(31)</sup> is an example of such a type. By the author's experiment, it was found that this banding is caused by the rhythmical change of temperature. According to Holmes' description, in a U-tube with a silicic acid gel (obtained by mixing equal volumes of a 1.06 density water glass solution and 1 N acetic acid) filling the bend, 0.5 N mercuric chloride in one arm and 0.1 N potassium iodide in the other, sharp red bands of mercuric iodide followed the curve like ranks of soldiers pivoting in regular formation. The present author noticed, at first that the bands formed are greatly influenced by the weather, and so it was supposed that the bands may be formed by the light. But it was observed that the rhythmic bands have formed even if the U-tube was cut off from any light. Next, the reaction was tried in a thermostat in a dark place, no band was formed and crystals of mercuric iodide were uniformly distributed in the gel. When the U-tube in which the bands were growing, was transferred into a thermostat in a dark place, then the banding has stopped. An example thus obtained is shown in Fig. 9. Diurnal bands are sometimes caused by intermittent light, but many diurnal bands of substances excepting photo-sensitive ones are caused by the change of temperature.

**The Influence of the Presence of Impurities or Third Substances.** Impurities in gels have often profound influences on the periodic precipitation and the bands formed. It was already pointed that the formed bands are greatly affected by the species of gelatine. This fact is partly referred to the quantities of the species of impurities in the gels. Chlorides and phosphates are contained in the ordinary gelatine as impurities. In the case of silver chromate bands, these impurities form the so-called secondary rhythmic bands by the reaction with silver nitrate. In a gelatine gel which was dialysed and the hydrogen ion concentration regulated adequately, rhythmic precipitates free from secondary bands could be obtained. The secondary band will be treated again in later pages. The existence of a very small quantity of potassium ferrocyanide in gelatine hindered the formation of silver chromate bands and red brown precipitate has deposited uniformly in the gel. The impurities in the gel react with the diffusing electrolyte and form insoluble precipitate which does not form the rhythmic bands. These precipitates hindered the formation of band. For this reason lead iodate, silver arsenite, barium chromate, silver iodate, barium carbonate and lead sulphate are not obtained as rhythmic precipitates in commercial non-dialysed gelatine. The following curious result was obtained in the formation of rhythmic precipitate of lead iodate. A 3% non-dialysed gelatine sol containing previously as much of potassium iodate as to be 1% in concentration was gelatinised and then lead acetate was allowed

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(31) H. N. Holmes, *J. Am. Chem. Soc.*, **40** (1918). 1187.

to diffuse into the gel. Continuous white precipitate was formed for the first several days. But a few days later, the first band was formed a little distant from the continuous precipitate. After an interval of one or two days, the second band appeared. When this second band began to appear, the first increased its width and got near enough to touch the continuous precipitate. Then a little later the second band grew and grew, when the first band completely joined the continuous precipitate. When the growth of the second band became prominent, the third began to appear. When the third developed, the second also joined the continuous precipitate. This course was repeated on in order, and finally all the bands were joined into one continuous precipitate. Upon observing this continuous precipitate by holding to a reflective light, it apparently contained the discontinuous parts, which ranged at regular intervals and varied in whiteness.

Therefore, originally, lead iodate must be regarded as to precipitate rhythmically in gelatine. But this result seems to be ascribable to the presence of impurities of such a kind as to produce a white precipitate, probably of phosphate and chloride, by their action on lead ion in the gelatine. It is certified that lead iodate forms a very distinct rhythmic precipitate in a purified gelatine. On the other hand, silver chromate has an entirely different colour from that of silver chloride and silver phosphate which are formed in gelatine by the reaction between impurities and the diffusing electrolyte, silver nitrate. So the bands of silver chromate are formed irrespective of the existence of such impurities.

There are often cases in which the presence of a third substance is favourable for the formation of rhythmic bands. The precipitate of silver chromate becomes very fine in the presence of some potassium citrate, and sharp and thick well-developed bands of orange red colour are observed.<sup>(11)</sup> This effect, of citrate, is caused by the increase of metastable limit of the solubility of silver chromate in the existence of a salt of polyvalent acid. The author tried to make silver chromate bands in gelatine in the presence of aconitate of the same concentration, being a salt of tervalent organic acid as citrate. Bands have been formed better in the presence of aconitate than in its absence. The particles of silver chromate are fine and bands are sharp and thinner than in the case of the presence of citrate. It is well known that silver chromate does not form bands in agar-agar. Bradford succeeded, however, in obtaining silver chromate bands in an agar-agar gel when the gel contained relatively large quantity of potassium citrate with potassium dichromate. Bradford recommended the following procedure; 2 N silver nitrate solution is allowed to diffuse into a 1% agar-agar gel containing N/100 of potassium dichromate and N/55 of potassium citrate.<sup>(8)</sup> In the same condition, the author substitute aconitate for citrate and tried to obtain the bands but the trial failed. Accordingly, even if we use an analogous substance, we can not expect the similar results. So it seems that every third substance has its specific effect.

The addition of potassium citrate to the gel is effective for the banding in many examples. When a rhythmic precipitate is indistinct by the deposition of coarse crystals in the interspaces between bands, then the addition of a small quantity of citrate often brings the bands

very distinct. Bands of cobalt phosphate, lead phosphate, silver iodate and lead iodide in silicic acid gels are examples of such cases. It is a well-known fact that when potassium iodide diffuses into a silicic acid gel which contains lead acetate, fern-like fronds grow down into the gel, mixed with many large hexagonal plates. As it was mentioned above, lead iodide makes occasionally a rhythmic precipitate even in silicic acid gel when its crystals are relatively small. We can obtain well-developed bands of lead iodide if there is a third substance which makes the crystals of lead iodide small. Citrate and tartrate are fit for this purpose. Experiments were conducted as follows: At first 0.7–2.0 c.c. of 1 N lead acetate, then 0.05–1.00 c.c. of a 3% solution of potassium citrate were added to a silicic acid gel, which was prepared by mixing 10 c.c. of a 1.06 density solution of water glass and an equal volume of 1 N acetic acid. The gels were prepared in about 100 different conditions. A 2 N solution of potassium iodide was poured on these gels. When both lead acetate and potassium citrate were small in quantity, the separated crystals were relatively coarse and scattered, so that the formation of the bands could not be recognised. When they were large in quantity, a white compound, probably lead citrate, was produced in the sol and precipitated at the bottom of the test-tube. There are, therefore, some limits in adding quantities of lead acetate and potassium citrate. Formation of the rhythmic precipitate was recognised within the limits of 0.4–0.6 c.c. in potassium citrate and of 0.85–1.1 c.c. in lead acetate. The most favourable result was obtained in 0.55 c.c. of potassium citrate and 0.9 c.c. of lead acetate, when 2 N potassium iodide was used as a diffusing electrolyte. Tartrate ion is weaker than citrate ion in the ability of making the crystals of lead iodide finer. Accordingly, in producing the bands of lead iodide by the aid of tartrate ion, a relatively large amount of the ion should be mixed. But in the presence of a large amount of tartrate ion, it produces white precipitate by acting on the ion in the sol. There is naturally some limit in its use. A 2 N solution of potassium iodide was diffused into gel, which was prepared by adding 1.2 c.c. of a lead acetate solution (1 N) and 0.8 c.c. of 3% tartaric acid to a sol prepared by mixing 10 c.c. of sodium silicate solution ( $d = 1.06$ ) and an equal volume of acetic acid (1 N). In this case the most favourable result could be obtained. In comparison with the case of citrate ion, the crystals were coarse, which stood close and formed thin bands. In Fig. 10, the left shows a typical precipitate, fern-like fronds, of lead iodide in silicic acid gel, the middle a rhythmic precipitate occasionally obtained and the right a rhythmic precipitate in gel containing citrate.

In a preceding communication, the author already reported that the presence of a small quantity of some alcohols, fatty acids or amino acids has a considerable effect on the formation of silver chromate bands.<sup>(32)</sup> The formation of bands was often strongly inhibited by the presence of a small quantity of fatty acids. The number of bands generally increases in the presence of alcohol but decreases in the presence of amino acids such as glycine and alanine. Koenig<sup>(33)</sup> pointed out that the

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(32) Isemura, this Bulletin, **9** (1934), 236.

(33) Koenig, *J. Phys. Chem.*, **24** (1920), 466.

diffusion and the solubility of the reaction product are so affected and consequently the rhythmic precipitate in a silicic acid gel is also profoundly influenced when alcohols, urea or sugars were added to the gel. When a small quantity of some salts such as potassium iodide or potassium bromide was added to a gel containing soluble phosphate and calcium nitrate was diffused into the gel, a rhythmic precipitate of calcium phosphate in the silicic acid gel will be obtained. In this case, the first four or five bands, consisting of relatively large crystals, were apart but the following bands were blurred, for the crystals were too coarse. The coarseness of the crystals are caused by the fact that the solubility of calcium phosphate is increased in some salts solutions. At the upper part of the gel the ion which forms a rhythmic precipitate is in excess, so the precipitation occurs easily. But, at the lower part of the gel, the small difference of the solubility will largely affect the separation of precipitate. In general, the crystals separate more slowly from more soluble media and the size of the crystals are large. It seems that this is the cause of indistinctness and irregularity of the bands.

In the case of the experiments on the rhythmic precipitation in a silicic acid gel, the gel is usually prepared by mixing a solution of water glass with some acid, and it is used without dialysis. Such a gel always contains a sodium salt of the acid which is formed on the double decomposition of sodium silicate by the acid. These salts as a third substance may have a profound influence on the banding. According to Holmes, the gel which was prepared by mixing a solution of sodium silicate with sulphuric acid, is adequate to the bading of gold but the gel prepared by mixing a solution of water glass with hydrochloric acid or acetic acid is inadequate to the same purpose. The present author, however, obtained good gold bands in the gel prepared by hydrochloric or acetic acid. The appearance of bands is somewhat different from the gel prepared with sulphuric acid.

Holmes said that bands of mercuric iodide are blurred in the presence of chlorine ion, so the use of hydrochloric acid is inadequate to prepare the gel for the formation of those bands. In this case, the gel which was prepared by mixing water glass with acetic acid is adequate. In the case of a rhythmic precipitate of silver chromate in a silicic acid gel, the best developed bands were formed in the gel prepared by mixing water glass with nitric acid. These facts may be considered as the influence of a third substance which is indifferent to the reaction.

Bismuth chromate banding is obtained, when bismuth chloride was forced to diffuse into a silicic acid gel which was prepared by mixing water glass solution with hydrochloric acid. Fig. 11 shows such bands. If the gel was prepared by mixing water glass with acetic acid, bands are difficult to obtain. When bismuth nitrate is allowed to diffuse into the gel prepared by mixing water glass with hydrochloric acid, no band can be obtained. In this case coarse globular precipitate, probably of bismuthy chloride is deposited. In the gel prepared from water glass and acetic acid, on the contrary, a well-developed banding is obtained, while its appearance is quite different from that of the banding by the diffusion of bismuth chloride. This is another example of the fact that a third substance has an important significance on the formation of rhythmic bands.



**The Effect of Ageing.** It is interesting that the banding is affected with the age of jellies before superimposing the diffusing electrolyte. Schleussner<sup>(34)</sup> recommended to keep a gelatine gel for twenty four hours before pouring the diffusing solution. The most remarkable observation which has ever been done, is that of Scott Blair.<sup>(22)</sup> He has made measurements which show that the distance of the last bands from the upper end of jelly increases regularly with the age of gel. This result has been reproduced by the present author.

The author has found another interesting fact. The effect of ageing on the formation of bands did not appear if the experiment was carried as follows. The gelatine solution was prepared and poured into several test-tubes and allowed to set. Then, after different time intervals, each of the test-tubes excepting one, was warmed, melted the gel and allowed again to reset. In this manner, the gels of different age were prepared. Then silver nitrate solution was poured on them. In this case, the formed bands in the respective tubes appeared quite equal and identical to that of unmelted gel, i.e. the most aged gel. From these results the author concludes that the ageing effect of gel on the formation of Liesegang rings is not caused by the change of structure of gel as Scott Blair considered, but by the change of modification of gelatine into less protective one by an interaction of potassium dichromate and this change proceeds with the age. It is considered, moreover, that the decrease of potassium dichromate after ageing was not recognised as Scott Blair observed, for this change of modification is probably caused by spending very small amount of potassium dichromate.

The effect of ageing was also studied on the system of copper chromate in silicic acid gel within the range of three months. The remarkable results as in the case of silver chromate was not seen. According to Koenig,<sup>(33)</sup> a fresh silicic acid gel gives best bands while the gel kept before diffusion gives irregular results. In the author's experiments on copper chromate, however, even the three months aged gel also gave good regular bands and showed no essential difference from that in a freshly prepared gel.

Subsequently, the author's view was confirmed by some other experiments. The effect of ageing was tested with a rhythmic precipitate in a gel which does not react with the inner electrolyte. Lead iodate bands in a gelatine gel and calcium phosphate bands in a silicic acid gel were investigated. The sol containing the adequate concentration of the inner electrolyte was poured into several test tubes. Then the test tubes were kept in a thermostat. After the gel set, the diffusing electrolyte was superposed on the gel in one of the test tubes. After a while, the diffusing electrolyte was poured on the gel of the second test tube and later on the gel of the third, and so on. After the outer electrolyte had diffused to the bottom of the test tubes, the formed rhythmic precipitates were compared with each other. No recognisable differences were observed. Thus, when the inner electrolyte does not react with the gel, the effect of ageing of gel is not recognisable, so that the effect of ageing is not referred to the change of structure of gels by age.

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(34) Schleussner, *Kolloid-Z.*, **31** (1922), 347.

**The Influence of the Hydrogen Ion Concentration.** In general, the solubility of a salt is considerably influenced by the hydrogen ion concentration of the solution. In many cases, its solubility increases with the hydrogen ion concentration of the medium. It is considered that the Liesegang's phenomenon will be strikingly affected by the hydrogen ion concentration of the gel, because the solubility of the salt is an important factor in the formation of rhythmic precipitates and for the formed bands. However, in many experiments which were hitherto conducted by many investigators, little attention was paid to the hydrogen ion concentration. In view of this point, the author studied thoroughly the influence of hydrogen ion concentration of the medium.

First, silver chromate bands in gelatine was tested. It is well known that the rhythmic precipitate of silver chromate is well developed in an ordinary commercial gelatine. When a small quantity of alkali is added to the gel, the intervals between bands become short and the number of formed bands increases. Inversely, when a small quantity of acid is added in the gel, the intervals between the bands become large, the bands consist of relatively coarse precipitate and have often imperfect appearance and the number of formed bands decreases. On the other hand, the well-developed bands of silver chromate are difficult to obtain in a gelatine which was purified by dialysis. Also it is difficult to obtain in a gelatine of the highest quality. These facts are ascribed by Liesegang<sup>(35)</sup> to the presence of gelatose, the hydrolytic product of gelatine in an ordinary commercial gelatine. But in the author's opinion, the concentration of hydrogen ion in gelatine jelly is a more significant factor than the presence of gelatose. Ordinary commercial gelatines have the *pH* ranging from 5.5 to 6.4, but pure dialysed gelatines have the *pH* ranging about its isoelectric point that is about 4.7. Accordingly, the author considered that the hydrogen ion concentration of the gel is rather more important than the presence of gelatose. In the jelly which was prepared with "gelatine alba pulvis" from Merck, well-developed bands of silver chromate were formed. But in the jelly which was prepared with the ash-free gelatine (the same gelatine purified by Loeb's method), no bands or only two or three imperfect bands were obtained. However, if a small quantity of caustic soda is added to thus purified gelatine, silver chromate bands were again obtained in such a gel. When too much alkali was added, the bands became close to each other and blurred. A result of a series of experiments with purified gelatine is shown in Table 22. Table 23 is a result of a series of experiments with purified gelatine, the manufacturer of which is unknown. These cases give coincident results. The bands are formed best at the *pH* range of 5.5–6.0. When the influence of the species of gel on the banding was described in the preceding paragraphs, it was pointed out that the banding is markedly affected by the species of gelatine. The author measured the values of *pH* of those gelatines in its 3% solutions. The results are shown in Table 24. The formation of band, however, can not be referred only to the *pH* of gelatine. Because the band are not the same, even in the same *pH* with different gelatines. The *pH* of the photographic gelatines was also

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(35) Liesegang, *Z. physik. Chem.*, **88** (1914), 1.

measured and shown in Table 25. With these gelatines, rhythmic precipitates were easily obtainable in the range of  $pH$  which is somewhat larger than the preceding examples.

Table 22.

## Bands of Silver Chromate.

| Sodium hydroxide<br>(0.25 N) added (c.c.) | Number of bands |
|-------------------------------------------|-----------------|
| 0.00                                      | 4               |
| 0.10                                      | 16              |
| 0.20                                      | 27              |
| 0.30                                      | 39              |

Inner electrolyte: potassium dichromate 0.15%. Outer electrolyte: silver nitrate 5%. 3.2% gelatine 7 c.c.

Table 23.

## Bands of Silver Chromate.

| Sodium hydroxide<br>(0.25 N) added (c.c.) | Number of bands |
|-------------------------------------------|-----------------|
| 0.00                                      | 0               |
| 0.10                                      | 10              |
| 0.15                                      | 12              |
| 0.20                                      | 26              |
| 0.25                                      | 32              |

Inner electrolyte: potassium dichromate 0.15%. Outer electrolyte: silver nitrate 5%. 3.0% gelatine 7 c.c.

Table 24.

| Species           | $pH$ |
|-------------------|------|
| Home production A | 6.40 |
| Home production B | 6.30 |
| Coignet A         | 5.75 |
| Coignet D         | 5.55 |
| Coignet No. 1.    | 5.60 |

Table 25.

| Species                  | $pH$ |
|--------------------------|------|
| Gelatine A for pos. film | 5.90 |
| Gelatine B for pos. film | 6.30 |
| Gelatine C for pos. film | 5.90 |
| Gelatine A for neg. film | 5.95 |
| Gelatine B for neg. film | 5.65 |
| Gelatine C for neg. film | 6.50 |
| Gelatine D for neg. film | 5.70 |

Barium chromate bands in gelatine are greatly influenced by the hydrogen ion concentration. When a cobalt acetate solution was diffused into a gel containing a small quantity of trisodium phosphate as an inner electrolyte, rhythmic precipitate of cobalt phosphate in gelatine are formed while no band is formed in a gel containing secondary sodium phosphate. This fact is also ascribed to the effect of hydrogen ion concentration.

In a gel of organic colloid, such as gelatine,  $pH$  value of the gel is in a narrow range, if some acid or alkali is not added to the gel. But in the case of a silicic acid gel,  $pH$  value of the gel will vary widely by the quantities of acid and water glass, which were used to prepare the gel. Accordingly, it seems that the effect of the hydrogen ion concentration on the rhythmic banding in a silicic acid gel is still more remarkable than in the case of gelatine gel. Holmes showed that rhythmic precipitates of copper chromate and basic mercuric chloride are formed in somewhat basic gels of silicic acid. The basic gel contains, in

general, some undecomposed sodium silicate in a small extent. When a solution of a salt of heavy metal diffuses into such a gel, it reacts with undecomposed sodium silicate and forms precipitate of silicate of the heavy metal. There deposits such a precipitate of silicate side by side with the precipitate that forms the rhythmic bands. For example, silver chromate bands in a silicic acid gel are the case. It has long been considered that silver chromate does not make rhythmic bands in the silicic acid gel. This must be ascribed also to the effect of hydrogen ion concentration. In the gel of relatively low hydrogen ion concentration, silver silicate is formed side by side with silver chromate and often hinders the rhythmic banding. When the hydrogen ion concentration is high, the silicic acid does not set to a gel. So the range of hydrogen ion concentration favourable for the formation of typical rhythmic bands is very narrow which has been already pointed out by the present author.<sup>(10)</sup>

Table 26 shows the results obtained in the gels which have been made by mixing equal volumes of sodium silicate solution (density = 1.06) and nitric acid of different concentrations. With more concentrated nitric acid than 0.70 N, the silicic acid does not gelatinise.

Table 26. Silver Chromate Bands in Silicic Acid Gel.

| Concentration of $\text{HNO}_3$ (N) | Nature of rhythmic bands                                                                                                                                                                                              |
|-------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0.67                                | Typical rhythmic precipitates consisting of relatively coarse crystals of red black plates were obtained. The intervals between bands were large.                                                                     |
| 0.63                                | Typical rhythmic precipitates were obtained. Crystals were small needles.                                                                                                                                             |
| 0.58                                | At the top of the gel Liesegang bands accompanied by dendrites were recognised. In the middle, only dendrites were seen, and at the bottom again rhythmic bands appeared but they were those formed by diurnal cause. |
| 0.55                                | The result was analogous to the case of 0.58N. But the number of formed Liesegang bands was less.                                                                                                                     |
| 0.50                                | No Liesegang band was formed. Dendrites and diurnal bands were seen.                                                                                                                                                  |

Outer electrolyte:  $\text{AgNO}_3$  5%. Gel: 6.0 c.c. of  $\text{Na}_2\text{SiO}_3$  solution ( $d = 1.06$ ) + 6.0 c.c. of  $\text{HNO}_3$  + 0.4 c.c. of 5%  $\text{K}_2\text{Cr}_2\text{O}_7$  as inner electrolyte.

It is desirable that the gel prepared with plenty of acid, is dialysed thoroughly, though it accompanies some difficulties in addition of the inner electrolyte. In many experiments which were carried out by the present author, the gel which was prepared by mixing equal volumes of a sodium silicate solution ( $d = 1.06$ ) with 0.7 N nitric acid, 0.7 N sulphuric acid or 0.75 N acetic acid, was favourable for various bandings. The author<sup>(36)</sup> reported, previously, the banding of nickel dimethylglyoxime in a silicic acid gel. It was studied in the gels of the value of pH ranging

(36) Isemura, *J. Chem. Soc. Japan*, **57** (1936), 546.

from 3.90 to 8.00. The rhythmic precipitate was formed in the  $pH$  range between 4.80 and 6.40. Relatively long needles were formed in the region of the  $pH$  value below 4.80, while very minute crystals were formed continuously and no bands were obtained in the region above 6.40. The crystals were large, the thickness of every band was also large and the number of formed bands was small in the lower  $pH$  region between 4.80 and 6.40. On the contrary, in the higher  $pH$ , crystals formed were minute, bands were sharp and thin, the number of band was large and the intervals were narrow.

How was the banding influenced, in a silicic acid gel, when the bands were formed as tablets instead of bands consisting of relatively large crystals? On this problem, bands of calcium phosphate were investigated.<sup>(7)</sup> The results obtained on this rhythmic precipitate are tabulated in Table 27. As shown by this table, it was found that the rhythmic

Table 27. Calcium Phosphate Bands in Silicic Acid Gel.

| Concentration of acetic acid (N) | $pH$ of gel | Number of bands          |
|----------------------------------|-------------|--------------------------|
| 0.60                             | 8.98        | A continuous precipitate |
| 0.70                             | 7.72        | A continuous precipitate |
| 0.75                             | 7.04        | 9                        |
| 0.80                             | 6.01        | 7                        |
| 0.90                             | 5.50        | 4                        |
| 1.00                             | 5.30        | 3                        |
| 2.00                             | 4.67        | 0                        |

Outer electrolyte:  $CaCl_2$  30%. Inner electrolyte:  $Na_2HPO_4$  0.4%.  
 $Na_2SiO_3$  ( $d = 1.06$ ).

Equal volumes of  $Na_2SiO_3$  and acetic acid were mixed to make a gel. As much of the gel was taken as to fill to a height of 6 cm. of a test tube of 1.2 cm. internal diameter and 11 cm. in length.

precipitate of calcium phosphate could be formed in the range of  $pH$  between 5.30 and 7.04. The precipitation of calcium phosphate was difficult below 5.30, while the precipitation occurred continuously and no band was formed above 7.04. In the range between 5.30 and 7.04 the smaller the value of  $pH$  is, the larger the intervals between bands and the smaller the number of formed bands becomes. The distance between the surface of gel and the last formed band becomes large with the value of  $pH$  of the gel. That is to say, the higher the acidity of the gel is, the more difficult the banding is.

Besides these, the formation of many other rhythmic precipitates, especially such as copper iodate etc., in silicic acid gel were strongly affected by the hydrogen ion concentration. The effect of the concentration of acid which was used to prepare a gel, to the banding was studied, and the results will be given in Part V in this paper.

The hydrogen ion concentration of the diffusing electrolyte as well as that of the gel, has also a profound influence on the rhythmic pre-

precipitation. On the formation of rhythmic bands of bismuth chromate, the bismuth nitrate solution in nitric acid of various concentration was used as the outer electrolyte. With bismuth nitrate in dilute nitric acid, bands were formed from the top of gel; the number of them was large and the interspaces between them were very small. On the contrary, with bismuth nitrate in concentrated nitric acid, the band was not formed at the top of the gel but appeared at a certain depth from the surface. The number of formed bands were small and interspaces between them were large. The distance from the top of the gel to the first formed band was increased with the concentration of nitric acid. The distance to the last formed band from the surface of the gel was also increased with the concentration of nitric acid. These results are all referred to the increase of solubility of formed bismuth chromate with increasing acidity.

### III. Regularity of the Intervals Between Bands.

It is an established fact that in the Liesegang phenomenon the intervals between bands become larger as the distance increases from the contact surface with the outer electrolyte solution. Schleussner<sup>(37)</sup> said that the interval of the  $n$ th band and that of the  $(n+1)$ th band stood in a constant ratio. The author<sup>(38)</sup> experimentally proved that the intervals of bands beared a relation of a quadratic equation to the numbers of the formed bands. When the interval of  $n$ th band is shown by  $\Delta X_n$ , we can obtain as equation.

$$\Delta X_n = a + bn + cn^2 \quad (1)$$

in which  $a$ ,  $b$  and  $c$  are constants.

Bauer,<sup>(39)</sup> supposing that an equation of the same form as the partial differential equation of heat conduction could be applied in the diffusion of ion into a gel, set up the equation:

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial X^2}$$

where  $u$  means the concentration of the ion to diffuse from an external liquid into the gel;  $t$  the time;  $x$  the interval; and  $a^2$  the diffusion constant. From this equation he theoretically drew a conclusion from the standpoint of super-saturation theory that the ratio of the interval of  $n$ th band to that of  $(n+1)$ th band could be shown by

$$\frac{\Delta X_{n+1}}{\Delta X_n} = 1 + p$$

in which  $p$  is

$$\frac{\Delta X}{x^*} \sim \frac{\Delta t}{2t^*} = p \sim \text{const.}$$

(37) Schleussner, *Kolloid-Z.*, **34** (1924), 338.

(38) *J. Chem. Soc. Japan*, **55** (1934), 809.

(39) *Kolloid-Z.*, **64** (1933), 181.

where  $t^*$  is the time required to form precipitates and  $x^*$  is the distance to the locality where the precipitate is formed.

If the interval between the stopper\* and the first band is shown by  $\Delta X_0$ , we can obtain and can set up in order

$$\begin{aligned}\frac{\Delta X_1}{\Delta X_0} &= 1 + p \\ \frac{\Delta X_2}{\Delta X_1} &= 1 + p \\ \frac{\Delta X_3}{\Delta X_2} &= 1 + p \\ &\dots\dots\dots \\ \frac{\Delta X_n}{\Delta X_{n-1}} &= 1 + p .\end{aligned}$$

Multiplication in each side of the equations gives the following relation

$$\frac{\Delta X_n}{\Delta X_0} = (1 + p)^n .$$

If the right side of this equation is expanded by the binominal theorem, we obtain

$$\frac{\Delta X_n}{\Delta X_0} = \left\{ 1 + np + \frac{n(n-1)}{2!} p^2 + \frac{n(n-1)(n-2)}{3!} p^3 + \dots \right\} .$$

As  $p$  is a number of small value, we may neglect the higher terms of  $p$  and we get

$$\Delta X_n = \Delta X_0 \left\{ 1 + np + \frac{n(n-1)}{2} p^2 \right\}$$

or

$$\Delta X_n = \Delta X_0 + \Delta X_0 \left( 1 - \frac{p}{2} \right) pn + \frac{\Delta X_0}{2} p^2 n^2 . \quad (2)$$

As  $\Delta X_0$  and  $p$  are constants, we may denote,

$$\Delta X_0 = a , \quad \Delta X_0 \left( 1 - \frac{p}{2} \right) p = b , \quad \frac{\Delta X_0}{2} p^2 = c .$$

Now this equation is identical with the above-mentioned empirical formula

$$\Delta X_n = a + bn + cn^2 .$$

In Table 28, as an example, the results are shown on the rhythmic precipitate of copper chromate in a silicic acid gel. Second column shows the observed values and the fourth column the values which were obtained by the empirical equation (1), and the fifth column the values

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\* The word stopper means the german "Propfen" after Popp. (*Kolloid-Z.*, **36** (1925), 208).

which were obtained by the equation (2) in which  $a$ ,  $b$  and  $c$  were calculated from the experimentally determined  $p$  and  $\Delta X_0$ .

Table 28. Copper Chromate in a Silicic Acid Gel.

| No. | $\Delta X_{\text{obs.}}$ | $1+p=k$       | $\Delta X_{\text{calc. by}}$<br>empir. formula | $\Delta X_{\text{calc. by}}$<br>theor. formula |
|-----|--------------------------|---------------|------------------------------------------------|------------------------------------------------|
| 1   | 0.09                     | 1.11          | 0.09                                           | 0.09                                           |
| 2   | 0.10                     | 1.20          | 0.10                                           | 0.10                                           |
| 3   | 0.12                     | 1.08          | 0.11                                           | 0.12                                           |
| 4   | 0.13                     | 1.08          | 0.13                                           | 0.13                                           |
| 5   | 0.14                     | 1.14          | 0.14                                           | 0.14                                           |
| 6   | 0.16                     | 1.14          | 0.16                                           | 0.16                                           |
| 7   | 0.18                     | 1.11          | 0.18                                           | 0.17                                           |
| 8   | 0.20                     | 1.10          | 0.20                                           | 0.19                                           |
| 9   | 0.22                     | 1.09          | 0.23                                           | 0.21                                           |
| 10  | 0.24                     | 1.13          | 0.26                                           | 0.23                                           |
| 11  | 0.27                     |               | 0.28                                           | 0.25                                           |
|     |                          | Average 1.117 |                                                |                                                |

In the empirical formula (1), calculation was made in taking  $a = 0.080$ ,  $b = 0.075$ , and  $c = 0.001$ . In the theoretical formula (2), it was made by using the constants  $a$ ,  $b$  and  $c$  which were calculated from  $\Delta X_0 = 0.083$  and  $p = 0.117$ . It was ascertained that both formulas gave almost identical values.

Subsequently, the formula was applied on other rhythmic precipitates namely, those of calcium phosphate in silicic acid gel, silver arsenite in gelatine, and lead iodate in gelatine. The distances between bands calculated from the theoretical formula were fairly concordant with the experimental data. But the calculated values of the higher number is always somewhat smaller than observed values.

Table 29 gives the results obtained with calcium phosphate in a silicic acid gel. The values of the fourth column were obtained from the assumption of  $a = 0.173$ ,  $b = 0.00241$ , and  $c = 0.00029$ , and those of the fifth column calculated from  $\Delta X_0 = 0.176$  and  $p = 0.154$ .

Table 29. Calcium Phosphate in a Silicic Acid Gel.

| No. | $\Delta X_{\text{obs.}}$ | $1+p=k$       | $\Delta X_{\text{calc. by}}$<br>empir. formula | $\Delta X_{\text{calc. by}}$<br>theor. formula |
|-----|--------------------------|---------------|------------------------------------------------|------------------------------------------------|
| 1   | 0.20                     | 1.15          | 0.20                                           | 0.20                                           |
| 2   | 0.23                     | 1.17          | 0.23                                           | 0.23                                           |
| 3   | 0.27                     | 1.15          | 0.27                                           | 0.27                                           |
| 4   | 0.31                     | 1.13          | 0.31                                           | 0.31                                           |
| 5   | 0.35                     | 1.11          | 0.37                                           | 0.35                                           |
| 6   | 0.39                     | 1.15          | 0.42                                           | 0.40                                           |
| 7   | 0.45                     | 1.20          | 0.48                                           | 0.45                                           |
| 8   | 0.54                     | 1.13          | 0.55                                           | 0.51                                           |
| 9   | 0.61                     | 1.20          | 0.62                                           | 0.57                                           |
| 10  | 0.73                     |               | 0.71                                           | 0.63                                           |
|     |                          | Average 1.154 |                                                |                                                |



Table 30 gives the results obtained with silver arsenite in gelatine, which were calculated on the assumption;  $a = 0.083$ ,  $b = 0.0049$ ,  $c = 0.000145$ ,  $\Delta X_0 = 0.083$ ,  $p = 0.0611$ .

Table 30. Silver Arsenite in Gelatine.

| No. | $\Delta X_{\text{obs.}}$ | $1+p=k$        | $\Delta X_{\text{calc. by}}$<br>empir. formula | $\Delta X_{\text{calc. by}}$<br>theor. formula |
|-----|--------------------------|----------------|------------------------------------------------|------------------------------------------------|
| 1   | 0.087                    |                | 0.087                                          | 0.087                                          |
| 2   | 0.091                    | 1.046          | 0.092                                          | 0.092                                          |
| 3   | 0.099                    | 1.088          | 0.098                                          | 0.098                                          |
| 4   | 0.101                    | 1.020          | 0.104                                          | 0.104                                          |
| 5   | 0.110                    | 1.087          | 0.110                                          | 0.110                                          |
| 6   | 0.120                    | 1.091          | 0.117                                          | 0.117                                          |
| 7   | 0.122                    | 1.017          | 0.123                                          | 0.123                                          |
| 8   | 0.129                    | 1.058          | 0.130                                          | 0.130                                          |
| 9   | 0.138                    | 1.070          | 0.138                                          | 0.138                                          |
| 10  | 0.147                    | 1.068          | 0.146                                          | 0.146                                          |
| 11  | 0.151                    | 1.028          | 0.153                                          | 0.153                                          |
| 12  | 0.165                    | 1.100          | 0.162                                          | 0.162                                          |
|     |                          | Average 1.0611 |                                                |                                                |

Table 31 gives the results obtained with lead iodate in gelatine, which were calculated on the assumption:  $a = 0.132$ ,  $b = 0.01006$ ,  $c = 0.00075$ ,  $\Delta X_0 = 0.131$ ,  $p = 0.096$ .

Table 31. Lead Iodate in Gelatine.

| No. | $\Delta X_{\text{obs.}}$ | $1+p=k$       | $\Delta X_{\text{calc. by}}$<br>empir. formula | $\Delta X_{\text{calc. by}}$<br>theor. formula |
|-----|--------------------------|---------------|------------------------------------------------|------------------------------------------------|
| 1   | 0.143                    |               | 0.143                                          | 0.144                                          |
| 2   | 0.156                    | 1.189         | 0.155                                          | 0.157                                          |
| 3   | 0.168                    | 1.078         | 0.169                                          | 0.172                                          |
| 4   | 0.180                    | 1.070         | 0.184                                          | 0.189                                          |
| 5   | 0.201                    | 1.116         | 0.201                                          | 0.206                                          |
| 6   | 0.218                    | 1.085         | 0.219                                          | 0.225                                          |
| 7   | 0.232                    | 1.064         | 0.239                                          | 0.244                                          |
| 8   | 0.254                    | 1.095         | 0.260                                          | 0.265                                          |
| 9   | 0.281                    | 1.107         | 0.283                                          | 0.286                                          |
| 10  | 0.325                    | 1.157         | 0.308                                          | 0.311                                          |
|     |                          | Average 1.096 |                                                |                                                |

As seen from these four tables, the values of  $\Delta X$  obtained by the empirical formula and those calculated from the theoretical formula are in good concordance.

#### IV. Classification and Secondary Bands.

**Classification of Rhythmic Precipitates.** Among the banded precipitates which are known commonly as rhythmic precipitates, some are produced by different causes from that of the so-called Liesegang phenomenon. So, the rhythmic precipitates can and must be arranged at least into the following three classes.

- (1) Rhythmic precipitate as a Liesegang phenomenon.
- (2) Rhythmic precipitate as the reflex of external rhythms.
- (3) Compound rhythmic precipitate.

Silver chromate bands in gelatine are a typical Liesegang phenomenon. Many rhythmic precipitates such as lead iodate, magnesium hydroxide, silver carbonate in gelatine, copper chromate, calcium phosphate in silicic acid gel, etc. belong to this type. By the aspects of the bands formed, this class can be further divided into two sub-classes. These two sub-classes have been indicated as the two classes of rhythmic precipitate by Chatterji and his collaborators,<sup>(40)</sup> the classification of which is based on the shape and not on the nature. The classification based on structure will be described later.

A rhythmic precipitate formed as the reflex of external rhythms may be obtained in many precipitating reactions. It is caused by the change of diffusion velocity or by the furtherance and the hindrance of precipitation by external rhythms. External rhythms occur naturally with the change of day and night, which brings the periodical change of light and temperature. For example, the rhythmic banding of gold is caused by the rhythm of light intensity while that of mercuric iodide in a silicic acid gel is produced by the rhythm of temperature. The characteristic of this type of rhythmic precipitate is that one band is formed by one rhythm and that the intervals between bands become smaller with the advance of band formation. It is because diffusion velocity becomes gradually slow that the intervals become smaller. At the bottom of the gel, the inner electrolyte is exhausted and the intervals between bands become large again. Accordingly, rhythmic precipitates made by external rhythms often have minimum intervals between bands in the lower part of the gel.

In a rhythmic precipitate of gold, there exists several secondary bands which are caused by the change of intensity of irradiation. A band always consists of red-violet-blue-green-yellow zones. This fact is connected with the change of light intensity of morning, noon and evening.

Compound rhythmic precipitate is the one composed of true Liesegang phenomenon and the rhythmic precipitate of diurnal causes. For example, lead iodide in a silicic acid gel containing a small quantity of citrate formed often this type of rhythmic precipitate. In this case diurnal black bands caused by the partial decomposition of lead iodide by light and diurnal bands caused by the change of temperature were

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(40) Chatterji and Dhar, *J. phys. Chem.*, **28** (1924), 41; *Kolloid-Z.*, **40** (1926), 97; Mukherjee and Chatterji, *Kolloid-Z.*, **50** (1930), 147.

formed in addition to a rhythmic precipitate as a Liesegang phenomenon. These three banding appeared simultaneously. This is a good example of compound rhythmic precipitate.

Rhythmic precipitates may be classified according to the structure as follows:

- (1) Banded precipitate (or Liesegang rings)
  - Sub-class I
  - Sub-class II
- (2) Helicoidal precipitate. (or spiral precipitate)
- (3) Banded precipitate with bands of saturn structure.
- (4) Radial precipitate.<sup>(41)</sup>
- (5) Complicated modification.

Ordinary rhythmic precipitates form bands in test tube, while they form rings on glass plate. This class may be divided into two sub-classes: I, the tablet-like bands separated by marked gaps or empty spaces and II, the rhythmic precipitate of the type which has deposition maxima. In the former the precipitate is often paste-like, but in the latter, it is often well-defined crystals. As examples of type I, we can indicate calcium phosphate in silicic acid gel and magnesium hydroxide in gelatine, and as an example of II type, lead iodide in silicic acid gel.

A helicoidal precipitate is obtained in a test tube, while a spiral precipitate is obtained on a glass plate. If the diffusing electrolyte is superposed on a gel before it sets firmly enough, a helicoidal precipitate is often formed. So, it is closely connected with the deformation of the gel, which is mechanically caused by the addition of the diffusing electrolyte. Bands of saturn structure are, of course, obtained only in a test tube, while a radial precipitate is obtained on a glass plate. It seems, the formation of bands of saturn structure depends on the ease of precipitation along the glass wall and active diffusion in the center of the test tube. Other forms of band are special cases. These can be included in the complicated modifications.

**Secondary Bands.** When a rhythmic precipitate of silver chromate is formed in gelatine, many thin faint layers are usually observed in the interspaces between brick red bands of silver chromate. These layers are known as secondary bands, and ascribed, by Köhler,<sup>(42)</sup> to the rhythmic precipitation of ammonium nitrate or potassium nitrate which is formed by the interaction of ammonium dichromate or potassium dichromate and silver nitrate. On the other hand, Schleussner<sup>(43)</sup> insists that these secondary bands are caused by silver chloride or phosphate which is formed by the interaction of the diffusing silver nitrate and chloride or phosphate contained in gelatine as an impurity. The author support Schleussner's consideration from the standpoint of the following experiments.

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(41) Veil, *Compt. rend.*, **196** (1933), 1491.

(42) Köhler, *Kolloid-Z.*, **19** (1916), 65.

(43) Schleussner, *Kolloid-Z.*, **31** (1922), 347.

When silver nitrate solution is allowed to diffuse into gelatine without any inner electrolyte, then there are obtained a number of thin bands. In this case the bands must consist of silver salt, for such a soluble salt as potassium nitrate or ammonium nitrate is generally difficult to obtain in a rhythmic precipitate. It is interesting that with increasing  $pH$  the intervals between silver chromate bands decrease but the intervals between secondary bands increase. This change of the intervals of secondary bands with  $pH$  is inverse to the cases of general rhythmic precipitates. In gelatine without chromate, however, the intervals between secondary bands decrease with increasing  $pH$ . So, it seems that in gelatine of large  $pH$ , more silver ion is consumed by the precipitation of silver chromate bands, and in such a gel, the secondary bands have larger intervals because silver ion decreases and the result obtained is exactly the same as by the decrease of concentration of the diffusing electrolyte.

The author experimented on the formation of silver chromate bands with gelatines which were dialysed in different degrees. In the less dialysed gelatine, the number of the secondary bands formed is large and the intervals between them are small, but in well-dialysed gelatine, the number of secondary bands is small and the intervals between them become large.

## V. Special Part.

**Conditions for the Formation of Some New Examples.** In the course of the present study, the author found many new examples of rhythmic precipitates. Some detailed description of these examples will be given in the followings. Conditions for banding have also been investigated of some rhythmic precipitates which were hitherto reported by other authors giving no detailed description. Among the following experiments, those with bismuth chromate, bismuthyl chloride, bismuthyl nitrate, calcium phosphate, and lead iodide in silicic acid gel were conducted in the test tubes of internal diameter of 1.5 cm., while the other experiments were all conducted in the test tubes of internal diameter of 1.2 cm.

**Barium Chromate in Gelatine Gel.** When a solution of barium chloride was poured on a pure ash-free gelatine jelly containing potassium dichromate as the inner electrolyte, bands were obtained of pale yellow relatively coarse particles of barium chromate. It is remarkable that these bands formed only in purified gelatine, but not in ordinary non-dialysed gelatine. This may be explained by the fact that the impurities contained in gelatine react with barium chloride and form insoluble salt distributing uniformly in the gel and prevent the band formation of barium chromate.

In the test tube the gelatine jelly is dehydrated, probably, by the tanning action of barium chloride and the meniscus of the jelly is depressed in the centre. Accordingly every band has remarkably concave form in its central part. At the top of the gel the bands are thin, but in the lower part of the gel they are thick consisting of relatively large

crystals. The conditions for the banding are summarised in the following table. In this table, the 1st column expresses the number of experiment, the 2nd, the volume of 3.2% gelatine solution, the 3rd, the water added to the gelatine to make the definite volume of gel, the 4th, the inner electrolyte, and the 5th, the added alkali.

Table 32.

| No. | Gel                             |                    |                                                                                          |                             | Outer electrolyte     | Results                 |
|-----|---------------------------------|--------------------|------------------------------------------------------------------------------------------|-----------------------------|-----------------------|-------------------------|
|     | Gelatine solution (3.2%) (c.c.) | Water added (c.c.) | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution (5.0%) (inner electrolyte) (c.c.) | NaOH solution (1.0%) (c.c.) |                       |                         |
| 1   | 5.00                            | 0.00               | 2.00                                                                                     |                             | BaCl <sub>2</sub> 1 N | Diffused bands.         |
| 2   | 5.00                            | 1.00               | 1.00                                                                                     |                             | "                     |                         |
| 3   | 5.00                            | 1.50               | 0.50                                                                                     |                             | "                     |                         |
| 4   | 5.00                            | 1.90               | 0.10                                                                                     |                             | "                     | Typical rhythmic bands. |
| 5   | 5.00                            | 1.95               | 0.05                                                                                     |                             | "                     | Some faint bands.       |
| 6   | 7.20                            | 0.30               | 0.80                                                                                     | 0.00                        | "                     | No band formation.      |
| 7   | 7.20                            | 0.20               | 0.80                                                                                     | 0.10                        | "                     |                         |
| 8   | 7.20                            | 0.10               | 0.80                                                                                     | 0.20                        | "                     |                         |
| 9   | 7.20                            | 0.00               | 0.80                                                                                     | 0.30                        | "                     |                         |

No. 1 and No. 2 gave bands, which were thin and compact at the top of the gel while they became diffuse and they consisted of coarse crystals in the lower part. No. 3 was the most favourable condition and gave typical bands. In No. 4, the concentration of the inner electrolyte was too dilute to form a distinct rhythmic precipitate. Consequently, faint bands have formed only at the top of the gel. No. 5 gave no bands, but a scattered precipitate. From No. 6 to No. 9, there appears the influence of the acidity of the gel. In an acidic gel such as No. 6, the bands consisted of coarse crystals and were somewhat indistinct. The less acidic the gel became, the more easily the precipitation occurred; and the more distinct the bands became, within the extent of the above experiments. As already stated, this banding is strongly affected by the irradiation of visible or ultraviolet light before superposing the diffusing electrolyte.

**Lead Carbonate in Gelatine Gel.** Lead acetate or lead nitrate solution is diffused into a gel, which has been prepared from gelatine purified by Loeb's method and contains sodium carbonate or ammonium carbonate as the inner electrolyte. Then well-developed rhythmic bands consisting of a somewhat coarse globular precipitate are obtained. In the case of relatively low concentration of the inner electrolyte the bands consisting of crescent shaped fragments are obtained. In gels containing somewhat more concentrated inner electrolytes, bands of saturn structure are often formed. In the presence of a sufficient quantity of inner electrolyte in the gel good typical bands are obtained. Conditions for

the experiments are given in Table 33.\* The meaning of the data in the table is quite the same with the former table.

In the experiment No. 1 many crescent shaped fragments of bands were formed, which was so incomplete that they were scarcely perceived as a rhythmic precipitate. From No. 2 to No. 4, there were many bands of saturn structure in the lower part of gel. No. 5 gave typical bands. As seen from the table (No. 2–No. 7), the number of formed bands in-

Table 33.

| No | Gel                             |                    |                                                      |     | Outer electrolyte                                  | Number of bands | Results                      |
|----|---------------------------------|--------------------|------------------------------------------------------|-----|----------------------------------------------------|-----------------|------------------------------|
|    | Gelatine solution (3.0%) (c.c.) | Water added (c.c.) | Inner electrolyte (c.c.)                             |     |                                                    |                 |                              |
| 1  | 5.0                             | 0.6                | Na <sub>2</sub> CO <sub>3</sub> (5%)                 | 0.4 | Pb(CH <sub>3</sub> COO) <sub>2</sub> 1 N           |                 | Fragmental bands.            |
| 2  | 5.0                             | 0.5                | „                                                    | 0.5 | „                                                  | 12              | } Bands of saturn structure. |
| 3  | 5.0                             | 0.4                | „                                                    | 0.6 | „                                                  | 15              |                              |
| 4  | 5.0                             | 0.3                | „                                                    | 0.7 | „                                                  | 15              |                              |
| 5  | 5.0                             | 0.2                | „                                                    | 0.8 | „                                                  | 22              | } Typical rhythmic bands.    |
| 6  | 5.0                             | 0.1                | „                                                    | 0.9 | „                                                  | 29              |                              |
| 7  | 5.0                             | 0.0                | „                                                    | 1.0 | „                                                  | 31              |                              |
| 8  | 5.0                             | 0.6                | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> (5%) | 0.4 | „                                                  |                 | } Typical bands.             |
| 9  | 5.0                             | 0.2                | „                                                    | 0.8 | „                                                  |                 |                              |
| 10 | 5.0                             | 0.5                | Pb(CH <sub>3</sub> COO) <sub>2</sub> (1 N)           | 0.5 | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 5% |                 |                              |
| 11 | 5.0                             | 0.5                | „                                                    | 0.5 | Na <sub>2</sub> CO <sub>3</sub> 5%                 |                 |                              |

creases with the concentration of the inner electrolyte. No. 8 gave bands consisting of coarse crystals. In this case thin white bands were formed at first, which then converted into bands consisting of coarse crystals. In No. 9 the first four bands were distinct and all convex, but those in the lower part of the gel were blurred. No. 10 and No. 11 gave also typical bands which indicate that the interchange of inner and outer electrolytes gave small influence on the banding. The right photograph in Fig. 12 is an example of this rhythmic precipitate.

**Lead Carbonate in Silicic Acid Gel.** When lead acetate or lead nitrate solution diffuses into a silicic acid gel containing sodium carbonate as inner electrolyte, lead carbonate bands are obtained. As it was already mentioned in the preceding paragraphs, the rhythmic bands of lead carbonate in gelatine consisted of globular particles. In silicic acid gel, however the bands consisted of relatively long needles, sometimes accompanied by a small amount of globular particles. The length of the needles obtained often attained several millimeters in a gel of somewhat high acidity. The conditions of the experiments are summarised in Table 34.

Table 34.

| No. | Gel                                                       |                                                   |                                                             |                    | Outer electrolyte                                     |  | Number of bands | Results                          |
|-----|-----------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------------|--------------------|-------------------------------------------------------|--|-----------------|----------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | CH <sub>3</sub> CO <sub>2</sub> H solution (c.c.) | Inner electrolyte (c.c.)                                    | Water added (c.c.) |                                                       |  |                 |                                  |
| 1   | 3.0                                                       | 0.75 N 3.0                                        | Na <sub>2</sub> CO <sub>3</sub> (5.0%) 0.2                  | 0.8                | Pb(NO <sub>3</sub> ) <sub>2</sub> 1 N                 |  | 12              | Typical rhythmic bands           |
| 2   | 3.0                                                       | „ 3.0                                             | „ 0.4                                                       | 0.6                | „                                                     |  | 14              |                                  |
| 3   | 3.0                                                       | „ 3.0                                             | „ 0.6                                                       | 0.4                | „                                                     |  | 26              |                                  |
| 4   | 3.0                                                       | „ 3.0                                             | „ 0.8                                                       | 0.2                | „                                                     |  | 36              |                                  |
| 5   | 3.0                                                       | „ 3.0                                             | „ 1.0                                                       | 0.0                | „                                                     |  | 45              |                                  |
| 6   | 3.0                                                       | „ 3.0                                             | „ 0.6                                                       | 0.4                | Pb(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> 1 N |  | 18              |                                  |
| 7   | 3.0                                                       | „ 3.0                                             | „ 0.8                                                       | 0.2                | „                                                     |  | 40              |                                  |
| 8   | 3.0                                                       | „ 3.0                                             | „ 1.0                                                       | 0.0                | „                                                     |  | 50              |                                  |
| 9   | 3.0                                                       | 0.60 N 3.0                                        | „ 0.5                                                       | 0.5                | Pb(NO <sub>3</sub> ) <sub>2</sub> 1 N                 |  |                 | Close bands                      |
| 10  | 3.0                                                       | „ 3.0                                             | „ 0.5                                                       | 0.5                | Pb(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> 1 N |  |                 |                                  |
| 11  | 3.0                                                       | 0.65 N 3.0                                        | „ 0.5                                                       | 0.5                | Pb(NO <sub>3</sub> ) <sub>2</sub> 1 N                 |  |                 |                                  |
| 12  | 3.0                                                       | „ 3.0                                             | „ 0.5                                                       | 0.5                | Pb(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> 1 N |  |                 |                                  |
| 13  | 3.0                                                       | 0.70 N 3.0                                        | „ 0.5                                                       | 0.5                | Pb(NO <sub>3</sub> ) <sub>2</sub> 1 N                 |  |                 | Typical bands                    |
| 14  | 3.0                                                       | „ 3.0                                             | „ 0.5                                                       | 0.5                | Pb(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> 1 N |  |                 |                                  |
| 15  | 3.0                                                       | 1.0 N 3.0                                         | „ 0.3                                                       | 0.7                | Pb(NO <sub>3</sub> ) <sub>2</sub> 1 N                 |  | 1               | Only one band was obtained       |
| 16  | 3.0                                                       | „ 3.0                                             | „ 0.5                                                       | 0.5                | „                                                     |  | 3               |                                  |
| 17  | 3.0                                                       | „ 3.0                                             | „ 0.7                                                       | 0.3                | „                                                     |  | 3               |                                  |
| 18  | 3.0                                                       | „ 3.0                                             | „ 0.9                                                       | 0.1                | „                                                     |  | 5               | Bands consisted of long crystals |
| 19  | 3.0                                                       | „ 3.0                                             | „ 1.0                                                       | 0.0                | „                                                     |  | 6               |                                  |
| 20  | 3.0                                                       | 0.75 N 3.0                                        | Pb(NO <sub>3</sub> ) <sub>2</sub> (1 N) 0.3                 |                    | Na <sub>2</sub> CO <sub>3</sub> 5.0%                  |  | 4               | Some diffused bands              |
| 21  | 3.0                                                       | „ 3.0                                             | Pb(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> (1 N) 0.3 |                    | „                                                     |  | 3               |                                  |

In No. 1. typical rhythmic bands were obtained, which consisted of needles and were separated by large clear interspaces. No. 2 also gave a typical rhythmic precipitate, the crystals of which were distributed more densely. In No. 1–No. 8, the number of bands formed increased with the concentration of inner electrolyte. In No. 3–No. 8, every band that consisted of globular precipitate was sharp at the lower surface on which the needles grew. At the bottom of the gel two or three bands have deposited which were consisted only of globular precipitate. In No. 9, there formed a white continuous precipitate down to the middle part of the gel, while many indistinct bands formed from the middle to the bottom of the gel. They were complicated probably by the formation of lead silicate. In No. 10, at the middle of the gel close bands and at the bottom of the gel distinct ones were formed. The bands did not consist of needles. No. 11 was analogous to No. 9, the bands being more distinct. No. 12 was analogous to No. 10, the bands being also more distinct. Both No. 13 and No. 14 gave typical rhythmic bands. At the middle of the

gel, the bands blurred by the growth of crystals, but at the bottom the bands became distinct again, because the intervals between them increased. In No. 15 only a band was obtained consisting of small globules at 1.2 cm. from the top of the gel. No. 16–No. 18 gave bands similar to those of No. 15, but they consisted of somewhat shorter needles. No. 19, gave bands formed by the cluster of long crystals. No. 20 and No. 21 did not give good bands. In No. 15–No. 19, the effect of the concentration of the inner electrolyte was observed as usual.

It is seen from the foregoing results that a rhythmic precipitate of long crystals is well developed in a gel which is prepared by mixing an equal volumes of a 1.06 density water glass solution with a 0.7 N or more concentrated solution of acetic acid. In a gel which is prepared by mixing equal volumes of a water glass solution ( $d = 1.06$ ) and 0.65 N or less concentrated acetic acid, banding is not good. The appearance of crystals is quite different by the acidity of the gel. This is caused probably by the formation of lead silicate and lead carbonate. In Fig. 12, the middle photograph shows a typical rhythmic precipitate of lead carbonate in silicic acid gel and the left an example of the bands consisting of long needles.

Even if the inner electrolyte is interchanged with the outer electrolyte, the rhythmic bands still formed. But when sodium carbonate or ammonium carbonate is allowed to diffuse into the gel, the bands are not so distinct as the case where the lead salts diffuses into the gel.

**Bismuth Chromate in Silicic Acid Gel.** When a solution of bismuth nitrate or bismuth chloride diffuses into a silicic acid gel containing potassium chromate as inner electrolyte, yellow bands of bismuth chromate are obtained. The appearance of this rhythmic precipitate is greatly affected by the kind of acid which was used to prepare the gel, by the species of the diffusing electrolyte, and by the acidity of the diffusing solution and of the gel itself. The conditions for obtaining this rhythmic precipitate are shown in Table 35.

In this table,  $\text{Bi}(\text{NO}_3)_3$  I indicates a 0.5 mol solution of bismuth nitrate in 3 N nitric acid, and  $\text{Bi}(\text{NO}_3)_3$  II, a 0.5 mol solution in the least concentration of nitric acid that does not cause hydrolysis. The rhythmic precipitate has better developed by the diffusion of bismuth nitrate than that of bismuth chloride. The solution of bismuth chloride which was used in the present experiments is a 1 mol solution in hydrochloric acid. The rhythmic bands formed by the diffusion of bismuth nitrate were yellow and had many pores in the bands. The precipitate grew at the interface between the glass and the gel, and the bands in the lower part of the gel were cloaked with this yellow film of the precipitate.

When the rhythmic precipitate was made by the diffusion of a bismuth nitrate solution in relatively concentrated nitric acid, the band was first formed at a point somewhat distant from the top of the gel. In No. 1, the first band formed at a point 1.3 cm. distant from the top of the gel; in No. 2, 1.7 cm.; in No. 3, 2.2 cm.; and in No. 4, 2.4 cm. In No. 5–No. 8, only several faint bands formed at the top of the gel, then a globular precipitate uniformly formed and no bands and no precipitate formed from the middle to the bottom. In No. 9–No. 12, we



Table 35.

| No. | Gel                                                       |                                               |                                             |     | Outer electrolyte                                            | Number of bands | Results                                      |
|-----|-----------------------------------------------------------|-----------------------------------------------|---------------------------------------------|-----|--------------------------------------------------------------|-----------------|----------------------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | Acid (c.c.)                                   | Inner electrolyte (c.c.)                    |     |                                                              |                 |                                              |
| 1   | 6.5                                                       | CH <sub>3</sub> CO <sub>2</sub> H 6.5 (0.5 N) | K <sub>2</sub> CrO <sub>4</sub> 1.0 (1 mol) | 1.0 | Bi(NO <sub>3</sub> ) <sub>3</sub> I                          | 5               | Typical rhythmic precipitates were formed.   |
| 2   | 6.5                                                       | " 6.5                                         | " 0.8                                       | 0.8 | "                                                            | 3               |                                              |
| 3   | 6.5                                                       | " 6.5                                         | " 0.5                                       | 0.5 | "                                                            | 3               |                                              |
| 4   | 6.5                                                       | " 6.5                                         | " 0.2                                       | 0.2 | "                                                            | 3               |                                              |
| 5   | 6.5                                                       | " 6.5                                         | " 1.0                                       | 1.0 | BiCl <sub>3</sub>                                            |                 | Faint rhythmic bands were formed.            |
| 6   | 6.5                                                       | " 6.5                                         | " 0.8                                       | 0.8 | "                                                            |                 |                                              |
| 7   | 6.5                                                       | " 6.5                                         | " 0.5                                       | 0.5 | "                                                            |                 |                                              |
| 8   | 6.5                                                       | " 6.5                                         | " 0.2                                       | 0.2 | "                                                            |                 |                                              |
| 9   | 6.5                                                       | " 6.5                                         | " 1.3                                       | 1.3 | Bi(NO <sub>3</sub> ) <sub>3</sub> II                         | 15              | Typical rhythmic bands were formed.          |
| 10  | 6.5                                                       | " 6.5                                         | " 1.0                                       | 1.0 | "                                                            | 18              |                                              |
| 11  | 6.5                                                       | " 6.5                                         | " 0.8                                       | 0.8 | "                                                            | 22              |                                              |
| 12  | 6.5                                                       | " 6.5                                         | " 0.5                                       | 0.5 | "                                                            | 18              |                                              |
| 13  | 6.5                                                       | HCl (0.85 N) 6.5                              | " 1.0                                       | 1.0 | BiCl <sub>3</sub>                                            |                 | No bands were obtained.                      |
| 14  | 6.5                                                       | " 6.5                                         | " 1.0                                       | 1.0 | Bi(NO <sub>3</sub> ) <sub>3</sub> I                          |                 |                                              |
| 15  | 6.5                                                       | " 6.5                                         | " 1.0                                       | 1.0 | Bi(NO <sub>3</sub> ) <sub>3</sub> II                         |                 |                                              |
| 16  | 6.5                                                       | HCl (0.5 N) 6.5                               | " 0.5                                       | 0.5 | Bi(NO <sub>3</sub> ) <sub>3</sub> I                          |                 |                                              |
| 17  | 6.5                                                       | HCl (0.5 N) 6.5                               | " 0.5                                       | 0.5 | Bi(NO <sub>3</sub> ) <sub>3</sub> II                         |                 | Well developed rhythmic bands were obtained. |
| 18  | 6.5                                                       | " 6.5                                         | " 1.3                                       | 1.3 | BiCl <sub>3</sub>                                            | 2               |                                              |
| 19  | 6.5                                                       | CH <sub>3</sub> CO <sub>2</sub> H 6.5 (0.5 N) | " 0.5                                       | 0.5 | Bi(NO <sub>3</sub> ) <sub>3</sub> I                          | 6               |                                              |
| 20  | 6.5                                                       | " 6.5                                         | " 0.5                                       | 0.5 | Bi(NO <sub>3</sub> ) <sub>3</sub> II<br>2 N HNO <sub>3</sub> | 6               |                                              |
| 21  | 6.5                                                       | " 6.5                                         | " 0.5                                       | 0.5 | Bi(NO <sub>3</sub> ) <sub>3</sub><br>1 N HNO <sub>3</sub>    | 19              |                                              |

obtained the best bands. Fig. 13 shows an example of this type of rhythmic precipitate. In No. 13, there formed many large spherulites, but no bands. In No. 14–No. 17, the results were analogous to that of No. 13. In No. 18, a stopper of the precipitate and two large bands, separated by large interspaces formed and these all consisted respectively of secondary rhythmic bands.

Thus the bands which were obtained by the diffusion of bismuth chloride in a gel prepared with hydrochloric acid were quite different to those formed by the diffusion of bismuth nitrate in a gel which was prepared with acetic acid. Fig. 11 shows an example of this type of rhythmic precipitate. This is partly referred to the fact that bismuth chloride hydrolyses more easily than bismuth nitrate. The bands formed by bismuth chloride is always accompanied by bismuthyl chloride. They seemed to be a compound rhythmic precipitate of bismuth chromate and bismuthyl chloride.

In the examples of No. 5–No. 8 and No. 13–No. 17, many globular particles are seen. These are not bismuth chromate but probably bismuthyl chloride. The formation of bismuthyl chloride and bismuthyl nitrate bands in silicic acid gel will be treated later again. The rhythmic bands of bismuth chromate are never formed by the diffusion of bismuth nitrate into the gel prepared with hydrochloric acid. It has already been stated that when bismuth nitrate diffused into a gel prepared with acetic acid like in the experiments No. 1–No. 4, bands having many pores were obtained. Moreover, the bands often showed the saturn type or more complicated structures. When this rhythmic precipitate are stood for a long time (five to six months), the crystallisation of bismuth chromate occurred, and orange clusters of crystals have deposited by the further advance of the diffusion. With the growth of these crystals the bands began to chip, and crescent shaped bands formed. At last, the bands disappeared entirely and several somewhat large spherical clusters of crystals remained.

**Bismuthyl Chloride and Bismuthyl Nitrate in Silicic Acid Gel.** The author studied the formation of rhythmic precipitates of bismuthyl chloride and bismuthyl nitrate in silicic acid gel, for bismuth chloride and bismuth nitrate are both readily hydrolysable. When bismuth chloride or bismuth nitrate diffuses into a silicic acid gel which contains no inner electrolyte, a white rhythmic precipitate is formed. The best bands were formed when bismuth chloride is allowed to diffuse in the gel prepared with hydrochloric acid. The conditions for the experiments are summarised in Table 36.

Table 36.

| No. | Gel                                                                      |                                               |                                      | Results                       |
|-----|--------------------------------------------------------------------------|-----------------------------------------------|--------------------------------------|-------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution<br>( <i>d</i> =1.06)<br>(c.c.) | Acid (c.c.)                                   | Outer electrolyte                    |                               |
| 1   | 7.0                                                                      | CH <sub>3</sub> CO <sub>2</sub> H (0.5 N) 7.0 | BiCl <sub>3</sub>                    | } No bands were formed.       |
| 2   | 7.0                                                                      | „ 7.0                                         | Bi(NO <sub>3</sub> ) <sub>3</sub> I  |                               |
| 3   | 7.0                                                                      | HCl (0.5 N) 7.0                               | BiCl <sub>3</sub>                    |                               |
| 4   | 7.0                                                                      | HCl (0.42 N) 7.0                              | „                                    | } Rhythmic bands were formed. |
| 5   | 7.0                                                                      | CH <sub>3</sub> CO <sub>2</sub> H (0.5 N) 7.0 | Bi(NO <sub>3</sub> ) <sub>3</sub> II |                               |

The concentrations of the diffusing electrolyte were the same as in the case of bismuth chromate. In No. 1, a white globular precipitate formed uniformly all through the test tube. In No. 2, there is no band and a small amount of precipitate formed sparsely. In No. 3–No. 5 rhythmic bands were formed. In No. 4 four compact bands and one consisting of globular particles were formed, each band being consisted of far smaller crystals than in the case of No. 3. In No. 5 eight bands were formed, each of which consisted of a small amount of scattered crystals.

From the foregoing results we can conclude that no band is formed in a gel which is prepared by mixing a water glass solution and acetic acid when bismuth chloride is chosen as diffusing electrolyte. Bismuth nitrate is less hydrolysable than bismuth chloride, so when  $\text{Bi}(\text{NO}_3)_3$  I diffuses in a gel there is no band formation. But when  $\text{Bi}(\text{NO}_3)_3$  II diffuses, rhythmic bands form, because  $\text{Bi}(\text{NO}_3)_3$  I is difficultly hydrolysable in an excess of nitric acid.

**Cobalt Phosphate in Silicic Acid Gel.** When cobalt acetate diffused into a gel containing a small quantity of soluble phosphate as inner electrolyte, a red rhythmic precipitate of cobalt phosphate were formed. Every band was thick while the particles forming the bands were considerably coarse. The bands were not so distinct because the particles forming them were coarse and scattered. When a very small quantity of citrate was added to the gel, well developed bands such as shown in Fig. 14 was obtained. The left photograph is an example of cobalt phosphate bands in a silicic acid gel. The experimental conditions are summarised in Table 37 and the results are given in the following lines.

Table 37.

| No. | Gel                                                          |       |                                                              |                                        | Outer electrolyte                    | Results                                          |
|-----|--------------------------------------------------------------|-------|--------------------------------------------------------------|----------------------------------------|--------------------------------------|--------------------------------------------------|
|     | $\text{Na}_2\text{SiO}_3$ solution<br>( $d=1.06$ )<br>(c.c.) | Water | $\text{CH}_3\text{CO}_2\text{H}$ solution<br>(1 N)<br>(c.c.) | Inner electrolyte<br>(c.c.)            |                                      |                                                  |
| 1   | 3.0                                                          | 0.6   | 2.4                                                          | $\text{Na}_3\text{PO}_4$<br>(0.5 mol)  | 0.2                                  | Bands consisting of coarse crystals were formed. |
| 2   | 3.0                                                          | 0.7   | 2.3                                                          | "                                      | 0.2                                  |                                                  |
| 3   | 3.0                                                          | 0.8   | 2.2                                                          | "                                      | 0.2                                  |                                                  |
| 4   | 3.0                                                          | 0.9   | 2.1                                                          | "                                      | 0.2                                  | Somewhat indistinct bands were formed.           |
| 5   | 3.0                                                          | 1.0   | 2.0                                                          | "                                      | 0.2                                  |                                                  |
| 6   | 3.0                                                          | 1.1   | 1.9                                                          | "                                      | 0.2                                  |                                                  |
| 7   | 3.0                                                          | 1.2   | 1.8                                                          | "                                      | 0.2                                  |                                                  |
| 8   | 3.0                                                          | 1.3   | 1.7                                                          | "                                      | 0.2                                  | Distinct bands were formed.                      |
| 9   | 3.0                                                          | 1.4   | 1.6                                                          | "                                      | 0.2                                  |                                                  |
| 10  | 3.0                                                          | 0.8   | 2.2                                                          | $\text{Na}_2\text{HPO}_4$<br>(0.5 mol) | 0.7                                  | A few bands and a long stopper were formed.      |
| 11  | 3.0                                                          | 0.8   | 2.2                                                          | "                                      | 0.5                                  |                                                  |
| 12  | 3.0                                                          | 0.9   | 2.1                                                          | "                                      | 0.5                                  | Irregular bands were formed.                     |
| 13  | 3.0                                                          | 0.6   | 2.2                                                          | "                                      | 0.5                                  |                                                  |
|     |                                                              |       |                                                              | + Citrate (3%)                         | 0.2                                  | Very distinct bands were formed.                 |
| 14  | 3.0                                                          | 1.2   | 1.8                                                          | $\text{Na}_2\text{HPO}_4$<br>(0.5 mol) | 0.5                                  | Close bands were formed.                         |
| 15  | 3.0                                                          | 0.9   | 2.1                                                          | Phosphate mixture                      | 1.0                                  |                                                  |
| 16  | 3.0                                                          | 1.1   | 2.1                                                          | "                                      | 0.8                                  | A few bands were formed.                         |
| 17  | 3.0                                                          | 1.3   | 2.1                                                          | "                                      | 0.6                                  |                                                  |
| 18  | 3.0                                                          | 1.5   | 2.1                                                          | "                                      | 0.4                                  | Some indistinct bands were formed.               |
| 19  | 3.0                                                          | 1.8   | 2.1                                                          | "                                      | 0.1                                  |                                                  |
| 20  | 3.0                                                          | 0.9   | 2.1                                                          | $\text{Co}(\text{NO}_3)_2$<br>(5%)     | 0.5                                  | No band was formed.                              |
|     |                                                              |       |                                                              |                                        | $\text{Na}_2\text{HPO}_4$<br>0.5 mol |                                                  |
|     |                                                              |       |                                                              |                                        |                                      | A stopper and two bands were formed.             |

The bands of cobalt phosphate were often irregular. The bands and the large stopper of precipitate were influenced by diurnal cause. In No. 1, five bands consisting of relatively coarse crystals were formed. In No. 2, seven bands were formed, being somewhat irregularly distributed. No. 3–No. 7 gave what seemed to be compound bands of cobalt phosphate and probably of cobalt silicate. In these cases seven or eight rather indistinct bands were formed. In No. 8 and No. 9, the precipitate deposited continuously from the top to the middle part of the gel and eight bands were formed at the bottom. No. 10 gave a stopper 18 mm. long and five bands of relatively coarse crystals. No. 11 gave a stopper of 19 mm. long and three distinct bands consisting of coarse crystals, every band being about 3 mm. thick. In No. 12, five irregular bands were formed. In No. 13, a stopper 18 mm. long and three very distinct bands were formed as shown in Fig. 14. In No. 14, bands were close to each other and a precipitate grew even in the interspaces between bands.

The phosphate mixture, which was used in the experiments of No. 15–No. 19, was a mixture of six volumes of 0.5 mol secondary sodium phosphate and four volumes of 0.5 mol primary potassium phosphate. In this mixture, hydrogen ion concentration was almost the same with that of a neutral solution. The effect of the concentration of inner electrolyte were investigated in these experiments. In No. 15 a stopper and three distinct bands were formed, and in No. 16 a stopper and three bands were obtained. In No. 17 and No. 18 a stopper and four bands were formed, and the crystals were so coarse and so widely scattered, that the bands were very indistinct. No. 19 gave no bands. In No. 20, a stopper of 14 mm. length and two thick bands, 4 mm. and 8 mm. thick respectively, were obtained. The interchange of the inner and the outer electrolyte was possible in this case.

**Cobalt Phosphate in Gelatine Gel.** The formation of rhythmic bands of cobalt phosphate in silicic acid gel has already been described in a preceding paragraph. The formation of a similar rhythmic precipitate in gelatine was subsequently examined. Five percent solution of cobalt nitrate was poured on a gelatine gel (3%), which was made from purified ash-free gelatine and contained the secondary sodium phosphate as its inner electrolyte. The gel was made by mixing 5.5 c.c. of gelatine solution with 0.5 c.c. of 0.5 mol solution of secondary sodium phosphate. In this case we obtained two imperfect bands consisted of scattered crystals. This result was due to the relatively large acidity of the gel, and to the fact that cobalt phosphate has a considerable solubility in such an acidic gel.

If tertiary sodium phosphate was added to the gel instead of secondary one, a well-developed rhythmic precipitate of cobalt phosphate can be obtained. It seems, from this result, that acidity of the gel was favourable to the formation of rhythmic bands. The right photograph in Fig. 14 shows the rhythmic precipitate of cobalt phosphate in gelatine.

**Cobalt Sulphide in Silicic Acid Gel.** When a barium sulphide solution diffuses into a gel containing cobalt acetate or nitrate as inner

electrolyte, very close black bands are obtained. Riegel<sup>(44)</sup> had experimented on this subject, who placed a silicic acid containing sodium sulphide on a solid silicic acid gel containing cobalt nitrate, and obtained the rhythmic bands of cobalt sulphide. In this case, however, the sodium sulphide finally destroys the silicic acid gel. So sodium sulphide is inadequate as an outer electrolyte to obtain this rhythmic precipitate. The present author, therefore, used barium sulphide as the diffusing electrolyte instead of sodium sulphide, and obtained very close but sharp bands. Thus more than 20 bands were often counted in the range of 10 mm. which situated at the depth of 30 to 40 mm. from the top of the gel. The conditions and the results are shown in Table 38.

Table 38.

| No. | Gel                                                       |                                                   |                          |                                             | Outer electrolyte                    | Results                                     |
|-----|-----------------------------------------------------------|---------------------------------------------------|--------------------------|---------------------------------------------|--------------------------------------|---------------------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | CH <sub>3</sub> CO <sub>2</sub> H solution (c.c.) | Inner electrolyte (c.c.) |                                             |                                      |                                             |
| 1   | 3.0                                                       | 0.75 N                                            | 3.0                      | Co(NO <sub>3</sub> ) <sub>2</sub> (5%) 0.20 | Saturated solution of BaS            | Close black, distinct bands were formed.    |
| 2   | 3.0                                                       | „                                                 | 3.0                      | „ 0.10                                      | „                                    |                                             |
| 3   | 3.0                                                       | „                                                 | 3.0                      | „ 0.05                                      | „                                    |                                             |
| 4   | 3.0                                                       | „                                                 | 3.0                      | Co(NO <sub>3</sub> ) <sub>2</sub> (1%) 0.20 | „                                    |                                             |
| 5   | 3.0                                                       | „                                                 | 3.0                      | „ 0.15                                      | „                                    |                                             |
| 6   | 3.0                                                       | „                                                 | 3.0                      | „ 0.10                                      | „                                    | No band was formed.                         |
| 7   | 3.0                                                       | 1.0 N                                             | 3.0                      | Co(NO <sub>3</sub> ) <sub>2</sub> (5%) 0.10 | „                                    | Many bands of saturn structure were formed. |
| 8   | 3.0                                                       | 0.75 N                                            | 3.0                      | Sat. solution of BaS 0.12                   | Co(NO <sub>3</sub> ) <sub>2</sub> 5% | Somewhat incomplete banding occurred.       |
| 9   | 3.0                                                       | „                                                 | 3.0                      | Co(NO <sub>3</sub> ) <sub>2</sub> (5%) 0.20 | Saturated solution of BaS            | Close typical bands were formed.            |
| 10  | 3.0                                                       | „                                                 | 3.0                      | „ 0.20                                      | 3/4 sat. solution of BaS             |                                             |
| 11  | 3.0                                                       | „                                                 | 3.0                      | „ 0.20                                      | 1/2 sat. solution of BaS             |                                             |
| 12  | 3.0                                                       | „                                                 | 3.0                      | „ 0.20                                      | 1/4 sat. solution of BaS             |                                             |

The intervals between the bands became larger with the decrease of the inner electrolyte. In No. 1, the bands were so close that we could scarcely see them even by transmitted light. In the order of No. 2, No. 3, and No. 4, the bands were separated by progressively larger interspaces. The number of bands formed became very small in No. 5, and no bands formed in No. 6. In such a gel of high acidity as in No. 7, the bands were separated from each other and often many bands of saturn structure were formed. The influence of the concentration of outer electrolyte was remarkable. The number of bands between 30 mm. and

(44) Riegel, *J. Phys. Chem.*, **35** (1931), 1675.

60 mm. depths from the surface of the gel was counted in No. 9–No. 12, and obtained 72, 54, 49, and 45 bands in No. 9, No. 10, No. 11 and No. 12 respectively.

The interchange of the inner and outer electrolytes was tried in No. 8. When barium sulphide was dissolved in the gel as an inner electrolyte, rhythmic bands were also obtained. But the bands were not so well-developed as in the case in which the cobalt salt was contained in the gel. In this case diurnal bands were also recognised in the lower part of the gel.

**Copper Iodate in Silicic Acid Gel.** When copper sulphate solution diffused into silicic acid gel containing potassium iodate as an inner electrolyte, a rhythmic precipitate of copper iodate which was different from an ordinary one, was obtained. The bands often consisted of a bluish white stopper of precipitate, a few bluish white compact bands and one or two diffuse blue bands. The conditions for this rhythmic precipitation are given in Table 39.

Table 39.

| No. | Gel                                                       |              |                                               |                           | Outer electrolyte     | Results                                    |
|-----|-----------------------------------------------------------|--------------|-----------------------------------------------|---------------------------|-----------------------|--------------------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | Water (c.c.) | Acid (c.c.)                                   | Inner electrolyte (c.c.)  |                       |                                            |
| 1   | 4.0                                                       | 1.9          | CH <sub>3</sub> CO <sub>2</sub> H 2.4 (1 N)   | KIO <sub>3</sub> 0.2 (5%) | CuSO <sub>4</sub> 2 N | A stopper and a diffuse band was formed.   |
| 2   | 4.0                                                       | 1.6          | " 2.4                                         | " 0.5                     | " "                   |                                            |
| 3   | 4.0                                                       | 1.3          | " 2.4                                         | " 0.8                     | " "                   |                                            |
| 4   | 4.0                                                       | 0.6          | " 2.4                                         | " 1.5                     | " "                   |                                            |
| 5   | 4.0                                                       | 0.1          | " 2.4                                         | " 2.0                     | " "                   |                                            |
| 6   | 3.0                                                       | 0.9          | " 2.1                                         | " 1.0                     | " "                   | A stopper and a few bands were formed.     |
| 7   | 3.0                                                       | 1.0          | " 2.0                                         | " 1.0                     | " "                   |                                            |
| 8   | 3.0                                                       | 1.1          | " 1.9                                         | " 1.0                     | " "                   |                                            |
| 9   | 3.0                                                       | 1.2          | " 1.8                                         | " 1.0                     | " "                   |                                            |
| 10  | 3.0                                                       | 1.3          | " 1.7                                         | " 1.0                     | " "                   |                                            |
| 11  | 3.0                                                       | 1.4          | " 1.6                                         | " 1.0                     | " "                   | Many close bluish white bands were formed. |
| 12  | 3.0                                                       | 1.5          | " 1.5                                         | " 1.0                     | " "                   |                                            |
| 13  | 3.0                                                       | 1.7          | " 1.3                                         | " 1.0                     | " "                   |                                            |
| 14  | 4.0                                                       |              | CH <sub>3</sub> CO <sub>2</sub> H 4.0 (0.6 N) | " 1.0                     | CuSO <sub>4</sub> 2 N |                                            |
| 15  | 4.0                                                       |              | " 4.0                                         | " 1.0                     | " 1.5 N               |                                            |
| 16  | 4.0                                                       |              | " 4.0                                         | " 1.0                     | " 1.0 N               | A stopper and a few bands were formed.     |
| 17  | 4.0                                                       |              | " 4.0                                         | " 1.0                     | " 0.5 N               |                                            |
| 18  | 4.0                                                       |              | " 4.0                                         | " 1.0                     | " 0.25 N              |                                            |
| 19  | 4.0                                                       |              | HCl (0.7 N) 4.0                               | " 1.3                     | CuSO <sub>4</sub> 2 N | No band was formed.                        |

In No. 1, a stopper of 2.5 cm. in length and a faint band were formed. As the concentration of the inner electrolyte was increased, the length

of the stopper decreased and the number of the bands formed increased. In No. 2, a stopper of 2.0 cm. in length, a distinct and compact band and two diffuse bands consisting of scattered spherulites were formed. In No. 3, the length of the stopper was 1.6 cm., and a distinct band and two thick diffuse bands were formed. In No. 4, stopper of 1.4 cm. in length, a sharp band and three spherulite bands were obtained. In No. 5, no stopper was formed and at a depth of 0.8 cm. from the top of the gel a band 0.5 cm. thick, two other sharp bands and two diffuse spherulite bands were formed. The influence of the acidity of the gel was observed in No. 6–No. 13. The stopper was thin or entirely missing in the more acidic gels, while it was thick in the more basic gels. No. 6 gave no stopper but three bands below the depth of 3 mm. from the top of the gel successively and one more far apart from them. Analogous results were obtained in No. 7 and No. 8, though every band was thicker than those of No. 6. Both No. 9 and No. 10 gave a stopper of 1.5 cm. in length and three globular bands. No. 11 gave two sharp and three spherulite bands and a stopper in which two bands were recognised. In No. 12, a thick stopper, in which also two bands were recognised, and two sharp and three diffuse bands were formed. No. 13 gave many bluish white bands but the banding was irregular. No. 14 gave a stopper of 1.6 cm in length and one sharp and two spherulite bands. No. 15 and No. 16 gave analogous results to No. 14 but the stopper was shorter in No. 15 and still shorter in No. 16. In No. 17 a thin stopper and two spherulite bands, and in No. 18 a still thinner stopper and a spherulite band were formed. In a gel which was prepared by mixing a sodium silicate solution ( $d = 1.06$ ) and hydrochloric acid, copper iodate did not form bands. No. 19 showed this result.

In short, the bands become shorter and the number of sharp compact bands increases with the increase of the concentration of inner electrolyte. With the increase of acidity, the stopper becomes thinner. The number of the bands formed becomes larger in the less acidic gels and in such a basic gel as shown in No. 13, many bluish white bands are formed. These bands are a compound rhythmic precipitate of copper iodate accompanying copper hydroxide and copper silicate. The formation of bands becomes difficult with the decrease of the concentration of copper sulphate, as the compact bands turn into a spherulite bands.

**Copper Carbonate in Silicic Acid Gel.** A rhythmic precipitate of copper carbonate was obtained by the diffusion of copper sulphate solution into a silicic acid gel containing ammonium carbonate. The bands were not so sharp and the upper and lower surfaces of each band seemed diffuse. The intervals between the bands were large and the thickness of every band was also large. An irregular banding was produced in a basic gel. This seemed also to be due to the formation of copper carbonate accompanied by copper hydroxide and copper silicate. In a fairly acidic gel, the carbonate in the gel was decomposed and escaped from it. Concentrated acid is also inadequate to the rhythmic precipitation. The conditions of the experiments are given in Table 40.

In gels of the same acidity, the larger the concentration of the inner electrolyte is, the thicker the stopper becomes. This was seen from

Table 40.

| No. | Gel                                                                      |                                                      |                                                                | Outer electrolyte     |  | Results                                  |
|-----|--------------------------------------------------------------------------|------------------------------------------------------|----------------------------------------------------------------|-----------------------|--|------------------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution<br>( <i>d</i> =1.06)<br>(c.c.) | CH <sub>3</sub> CO <sub>2</sub> H solution<br>(c.c.) | Inner electrolyte<br>(c.c.)                                    |                       |  |                                          |
| 1   | 3.0                                                                      | 0.5 N 3.0                                            | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> 1.0<br>(0.5 N) | CuSO <sub>4</sub> 2 N |  | Irregular bands were formed.             |
| 2   | 3.0                                                                      | 0.6 N 3.0                                            | „ 0.2                                                          | „                     |  | } Rhythmic bands were formed.            |
| 3   | 3.0                                                                      | „ 3.0                                                | „ 0.5                                                          | „                     |  |                                          |
| 4   | 3.0                                                                      | „ 3.0                                                | „ 1.0                                                          | „                     |  |                                          |
| 5   | 3.0                                                                      | 0.73 N 3.0                                           | „ 1.0                                                          | „                     |  | } No band and only a stopper was formed. |
| 6   | 3.0                                                                      | 0.75 N 3.0                                           | Na <sub>2</sub> CO <sub>3</sub> 0.3<br>(5%)                    | „                     |  |                                          |

No. 2–No. 4. No. 1 gave an irregular banding of bluish white precipitate. No. 2 gave a thin stopper and four bands. In No. 3, a stopper 15 mm. long, two distinct bands, and a faint band were formed. In No. 4, a stopper 17 mm. long, two distinct bands, and two faint bands were formed. In No. 5, three bands which were separated by very large intervals, were formed. Under the same conditions, excepting the acidity of the gel, the stopper was thinner in the more acidic gels. In an acidic gel, the intervals between the bands become larger and the precipitate become greenish. On the other hand, the increase of the concentration of the inner electrolyte tends to shorten the intervals between the bands and change the colour of the bands from greenish blue to bluish white. The most adequate condition for the preparation of a gel for this purpose is attained by mixing a sodium silicate solution (*d* = 1.06) with an equal volume of 0.60–0.73 N acetic acid.

**Silver Carbonate in Gelatine Gel.** Silver carbonate forms a rhythmic precipitate in ordinary gelatine, which become more distinct in purified gelatine. The conditions for the banding were studied thoroughly,<sup>(45)</sup> and the results were partly shown in the preceding paragraphs. The most favourable condition was obtained by superposing a 5% silver nitrate solution to a 2.8% gelatine gel in which as much of sodium carbonate had previously been added as to be 0.2% in concentration. This condition gave the rhythmic precipitate in which the distances between bands were very large and it looked as if white tablets were placed in the test tube. These white bands of silver carbonate were tinged with light yellow with the lapse of days, which became black even by diffused light after a long duration.

As an inner electrolyte ammonium carbonate may also be used. In this case, however, the formed rhythmic precipitate differs a little in appearance from that obtained by sodium carbonate. In addition, it was known that the rhythmic bands were formed with ammonium carbonate

(45) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 629.



in varying the concentration in a considerably wide range. The bands in this case did not take the perfect tablet-like forms as in the case of sodium carbonate, but looked like incomplete net-works or cracked plates.

Silver nitrate may be used as an inner electrolyte. When sodium carbonate solution was poured on the gel containing silver nitrate, bands were not so much manifested and sharp as in the case where silver nitrate was allowed to diffuse. When ammonium carbonate was used as an outer electrolyte, the rhythmic bands were formed which dissolved subsequently in order, and remained the rhythmic cracks.

**Silver Arsenite in Gelatine Gel.** Silver arsenite does not produce rhythmic bands in a commercial non-dialysed gelatine, while it makes distinct bands in a well dialysed one as in the case of lead iodate. The conditions for the formation were studied thoroughly.<sup>(45)</sup> The most favourable condition for producing this rhythmic precipitate was as follows. As much of sodium arsenite had been added to 2.0% dialysed gelatine as to be 0.1% in concentration. After the gel set firmly, 5–10% solution of silver nitrate was allowed to diffuse into the gel. In this case a yellow continuous precipitate was formed in the range of about 20 mm. from the top of the gel and many thin and sharply defined bands were formed in a further forward part. This was a very beautiful rhythmic precipitate and sensitive to light, readily changing its colour into dark yellowish green and finally into black by the diffused light.

Contrariwise, silver nitrate may be used as the inner electrolyte. A 10% solution of sodium arsenite was poured on 3% gelatine gel containing silver nitrate at the concentrations of 0.1–1.0%. In this condition, the rhythmic precipitate was always formed. Scarcely any difference was found between the rhythmic precipitate produced by this method and that by diffusion of silver nitrate.

**Silver Iodate in Gelatine Gel.** It had been reported in a previous communication that the silver iodate make rhythmic precipitate in a well-dialysed gelatine, while it does not, in non-dialysed commercial gelatine.<sup>(45)</sup> The most favourable condition for producing a rhythmic precipitate of this substance is as follows. A 5% potassium iodate solution was allowed to diffuse into 2.8% gelatine gel, in which as much of silver nitrate had been dissolved as to be 0.1% in concentration. The rhythmic precipitate produced in this case was very peculiar in shape, showing a greatly different form from any rhythmic precipitate which the author had ever seen. That is, one band was a thin disc composed of very fine crystals and an annexed band was above it, which consisted of a small number of extremely fine precipitate. A layer of the same precipitate as one above the thin disc was annexed below. In the lower part, as going downward from it, the precipitated particles became coarse and there was formed a layer of massive particles. These series of layers formed one periodic structure and adjoined the next series across a clear space. The precipitate produced between this thin band and the subsequent one did not originate from the impurities in the gelatine, being different from the so-called secondary bands present between the rhythmic precipitate of silver chromate. It was apparent from the facts

that even though potassium iodate was allowed to diffuse into the dialysed gelatine, which was used for the experiment, no precipitate was produced in the absence of inner electrolyte and the band of coarse particles between two successive bands was always only one. Fig. 6 shows an example of this rhythmic precipitate.

In experiment as to whether silver iodate could produce the rhythmic precipitate, the author employed at first, reversely to the above mentioned method, silver nitrate as the diffusing agent and potassium iodate as the inner electrolyte. In this case, the rhythmic bands of utterly different kind from the above mentioned was obtained. The particles of thus obtained rhythmic precipitate was coarse and did not gather close into a tablet-like band. The bands were coarse and uneven, so that they were inevitably indistinct. In addition, scarcely any clear spaces between successive bands was observed. Fig. 5 shows this type of the bands.

**Silver Capronate in Gelatine Gel.** Silver capronate forms a well defined rhythmic precipitate in gelatine jelly. Well dialysed gelatine, freed from chlorides and phosphates, was dispersed into 4% sol, the acid was added and then allowed to set. The concentration of the acid was 0.05–0.1 mol. per litre. After the gel set firmly, 20% silver nitrate solution was poured on it. White thin bands with relatively large distances were obtained.

**Silver Phosphate in Silicic Acid Gel.** When a silver nitrate solution was allowed to diffuse into a silicic acid gel which contained sodium phosphate, rhythmic precipitate of silver phosphate was obtainable if the acidity of the gel was adequate to the reaction. In a gel of low acidity, silver silicate would probably have formed accompanying the silver phosphate and yellowish brown close bands were formed. The conditions for the experiments are shown in Table 41.

Table 41.

| No. | Gel                                                    |                 |                                                     |                                                | Outer electrolyte     | Results                                                          |
|-----|--------------------------------------------------------|-----------------|-----------------------------------------------------|------------------------------------------------|-----------------------|------------------------------------------------------------------|
|     | Na SiO <sub>3</sub> solution<br>( $d=1.06$ )<br>(c c.) | Water<br>(c c.) | CH <sub>3</sub> CO <sub>2</sub> H<br>(1N)<br>(c.c.) | Inner electrolyte<br>(c c.)                    |                       |                                                                  |
| 1   | 3.0                                                    | 0.8             | 2.2                                                 | Na <sub>2</sub> HPO <sub>4</sub> 0.3<br>(8.4%) | AgNO <sub>3</sub> 10% | Typical rhythmic precipitate was formed.                         |
| 2   | 3.0                                                    | 0.8             | 2.2                                                 | „ 0.3                                          | AgNO <sub>3</sub> 5%  | Rhythmic bands were formed.                                      |
| 3   | 3.0                                                    | 0.9             | 2.1                                                 | „ 0.3                                          | „ „                   |                                                                  |
| 4   | 3.0                                                    | 1.0             | 2.0                                                 | „ 0.3                                          | „ „                   |                                                                  |
| 5   | 3.0                                                    | 1.1             | 1.9                                                 | „ 0.3                                          | „ „                   |                                                                  |
| 6   | 3.0                                                    | 1.2             | 1.8                                                 | „ 0.3                                          | „ „                   | Bands were formed and below bands crystals were scattered about. |
| 7   | 3.0                                                    | 1.3             | 1.7                                                 | „ 0.3                                          | „ „                   |                                                                  |
| 8   | 3.0                                                    | 1.4             | 1.6                                                 | „ 0.3                                          | „ „                   |                                                                  |
| 9   | 3.0                                                    | 1.5             | 1.5                                                 | „ 0.3                                          | „ „                   | Faint bands were formed.                                         |

In No. 1, well-developed yellow bands of silver phosphate were formed. In No. 2 and No. 3, seven or eight bands consisting of relatively coarse crystals were formed at the top of the gel and below the last formed band crystals were scattered. In No. 4, the best rhythmic bands were obtained. In a gel which was less acidic, silver silicate would probably have formed accompanying silver phosphate. The bands were closer, and in the lower part of the gel, crystals were coarse and no band was recognisable. No. 5 and No. 6 are the cases. In No. 7 and No. 8, finer close yellowish brown bands were formed, consisting probably of silver phosphate and silicate. No. 9 was inadequate to the banding, for, in this case only faint bands were formed at the top of the gel, and below these there was spread the precipitate uniformly. In short, the conditions from No. 1 to No. 4 were favourable to form a rhythmic precipitate of silver phosphate in a silicic acid gel.

**Silver Arsenate in Silicic Acid Gel.** It is expected that silver arsenate forms rhythmic precipitate in silicic acid gel, by the analogy of silver phosphate. Silver arsenate bands in gelatine gel was already reported by Rayleigh.<sup>(46)</sup> The present author has examined on this substance in silicic acid gel. A sodium arsenate solution (0.3 c.c. of 10% solution) was added to a sol which was prepared by mixing 3.0 c.c. of a water glass solution ( $d = 1.06$ ) with an equal volume of 0.6–0.75 N acetic acid. After the sol set firmly to a gel, 5 or 10% solution of silver nitrate was poured on the gel and let diffuse in it. A chocolate brown precipitate deposited rhythmically. The bands were in contact with each other at the top of the gel, while at the bottom of the gel they were distinct and separated by marked gaps. In an ordinary room, the silver salt was decomposed by light and the rhythmic precipitate was blackened, so this experiment was favourably conducted in a dark room.

**Silver Iodate in Silicic Acid Gel.** The formation of a rhythmic precipitate of silver iodate in a gelatine jelly was already reported in a preceding paragraph. Now, its formation in a silicic acid gel will be described. By the diffusion of silver nitrate into a silicic acid gel containing potassium iodate as inner electrolyte, somewhat curious white bands consisting of flocculent clusters of relatively coarse crystals were formed. As the diffusion proceeded down, the crystals became coarser and accordingly each of the flocks which formed the bands grew considerably large and the bands became indistinct and uneven. We could see, however that the precipitate had the nature of bands, from the fact that the bands separated by marked interspaces by the addition of a small quantity of citrate to the gel. The conditions for the experiments are summarised in Table 42.

No. 1 and No. 2 gave such bands as described above. About 40 bands were formed within 50 mm. from the surface of gel. In No. 3, no band but yellow precipitate was formed at the top of the gel, which was probably silver iodate accompanying silver silicate, while in the lower part of the gel complicated yellow bands were formed. In No. 4,

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(46) Rayleigh, *Phil. Mag.*, **38** (1919), 738.

Table 42.

| No. | Gel                                                       |                                                   |                                            |             | Outer electrolyte      | Results                          |
|-----|-----------------------------------------------------------|---------------------------------------------------|--------------------------------------------|-------------|------------------------|----------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | CH <sub>3</sub> CO <sub>2</sub> H solution (c.c.) | Inner electrolyte (c.c.)                   |             |                        |                                  |
| 1   | 3.0                                                       | 0.75 N 3.0                                        | KIO <sub>3</sub> (5%)                      | 0.65        | AgNO <sub>3</sub> (5%) | } Rhythmic bands were formed.    |
| 2   | 3.0                                                       | 0.70 N 3.0                                        | „                                          | 0.65        | „                      |                                  |
| 3   | 3.0                                                       | 0.60 N 3.0                                        | „                                          | 0.65        | „                      |                                  |
| 4   | 3.0                                                       | 0.50 N 3.0                                        | „                                          | 0.65        | „                      | No band was formed.              |
| 5   | 3.0                                                       | 0.75 N 3.0                                        | „<br>+citrate (3%)                         | 0.65<br>0.3 | „                      | Most distinct bands were formed. |
| 6   | 3.0                                                       | 0.75 N 3.0                                        | KIO <sub>3</sub> (5%)+<br>aconitate (1.5%) | 0.65<br>0.3 | „                      | Distinct bands were formed.      |
| 7   | 3.0                                                       | 0.50 N 3.0                                        | KIO <sub>3</sub> (5%)                      | 0.65        | „                      | Irregular bands were formed.     |

however, a yellow precipitate was formed from the top to the bottom of the gel, and no band was recognisable. As it was already stated, the presence of a small quantity of citrate in the gel favours the formation of these rhythmic bands. In No. 5, the best bands were obtained. Each band consisted of many flocculent clusters of crystals separated by marked gaps. The effect of aconitate in making the crystals small is less than that of citrate. In No. 6, the bands were less distinct than in No. 5. In No. 7, a result analogous to No. 3 was obtained.

In a gelatine jelly, when the inner electrolyte was interchanged with the outer electrolyte, that is to say, by the diffusion of potassium iodate into a gel containing silver nitrate, a rhythmic precipitate of an entirely different appearance was formed. In a silicic acid gel, however we cannot dissolve silver nitrate, because it reacts with silicic acid and precipitation occurs. So the interchange of the electrolytes is impossible in a silicic acid gel.

**Calcium Phosphate in Silicic Acid Gel.** Several reports have already published in regard to the formation of rhythmic precipitate of calcium phosphate in other medium than the silicic acid gel. But the banding in the silicic acid gel have never been reported. The present author therefore has tried an experiment in order to know whether the Liesegang phenomenon of calcium phosphate could be caused or not in the silicic acid gel.<sup>(16)</sup> And it was certified that calcium phosphate produced an extremely prominent rhythmic precipitate even in the silicic acid gel, and that the banding was closely related to the hydrogen ion concentration of the medium. The results were partly described in the preceding part of this paper.

The following is one of the most favourable conditions. That is, for dissolving phosphate in the gel, 1 c.c. of a 8% solution of secondary

sodium phosphate was added to 10 c.c. of a 0.75 N acetic acid and then 10 c.c. of a solution of sodium silicate ( $d = 1.06$ ) was added to it and allowed to stand to gelatinise. After the gel set firmly, 2 mol solution of calcium nitrate was superposed on it.

For dissolving calcium salt in the gel, after a sodium silicate solution ( $d = 1.06$ ) was mixed with 10 c.c. of 0.75 N acetic acid and 1.0 c.c. of a 10% calcium chloride solution was added to the mixture, while stirring up. After the gel set firmly, 8% secondary sodium phosphate was poured on it. White sharp bands were formed in both cases spacing regular intervals.

**Calcium Oxalate in Silicic Acid Gel.** Calcium oxalate forms a rhythmic precipitate in silicic acid gel. The adequate condition for the banding is as follows: To 5 c.c. of sodium silicate solution ( $d = 1.06$ ) add 5 c.c. of a mixture of acetic acid and oxalic acid (0.5 N, ratio of the two acids; 1:1 or 1:3). The silicic acid gel set in one night. Then ca. 5 c.c. of calcium chloride solution (10–25% solution) are poured on the gel. The rhythmic bands are formed which has an appearance like an opal. Clear spaces between bands are so narrow that the bands can better be seen by the transmitted light. Too large or too small quantity of oxalic acid prevents the formation of calcium oxalate bands.

**Strontium Oxalate in Silicic Acid Gel.** Strontium oxalate forms a rhythmic precipitate in silicic acid gel in the presence of potassium citrate as the third substance. The condition for the banding is as follows: To 5 c.c. of sodium silicate solution ( $d = 1.06$ ) add equal volume of the mixed acid above described and 0.01–0.02 g of potassium citrate. After setting the gel, put 5 c.c. of 25% strontium nitrate solution on it. About a week later, the formation of bands is observed by the transmitted light. Citrate accelerates, in this case, the formation of nucleus of the crystals. No strata were formed when no citrate was added in the gel. The nucleus formation is accelerated by the presence of the citrate and accordingly the formation of strata will become easier. The author found the formation of dense, white bands of strontium oxalate by adding a small quantity of citrate to the mixture before setting.

**Nickel Dimethylglyoxime in Silicic Acid Gel.** When an alcoholic solution of dimethylglyoxime is added to a solution of nickel salt, a red voluminous precipitate of nickel dimethylglyoxime is produced. Such a complex compound forms also rhythmic bands in a silicic acid gel.<sup>(47)</sup> Five cubic centimeters of a solution of sodium silicate ( $d = 1.06$ ), was taken into test tube and mixed with 5 c.c. of 1 N acetic acid and then 0.25 c.c. of a saturated solution of dimethylglyoxime in alcohol was added to it and the mixture was left quiet until it set. A 15% solution of nickel sulphate was poured on the gel. Red rhythmic precipitate was formed which consisted of dendrites of fine crystals.

If the used quantity of dimethylglyoxime was smaller than 0.1 c.c. the precipitate was so coarse that no bands were produced. If the

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(47) Isemura, *J. Chem. Soc. Japan*, **57** (1936), 546.

quantity was larger than 0.5 c.c., the bands were so dense that the formation of a rhythmic precipitate was rather indistinct. If the solution of nickel sulphate was smaller than 7.5% in concentration, the formed bands were smaller in number and the crystals of nickel dimethylglyoxime became coarse, so that the bands blurred. The adequate concentration of nickel sulphate, therefore, should be 10–20%. The formation of bands of this precipitate was strongly affected by the hydrogen ion concentration of the medium. The most adequate pH value for the formation of this rhythmic precipitate was about 5.0–5.5.

**Lead Chromate in Silicic Acid Gel.** It has generally been considered that the lead chromate forms bands in agar-agar gel but not in silicic acid gel. But the author has obtained the rhythmic bands of this substance in silicic acid gel by modifying the conditions appropriately. It is doubtful, however, whether the bands obtained in this case are the Liesegang phenomenon or not. They are probably the diurnal bands. The condition of the banding is as follows: In 5 c.c. of sodium silicate solution ( $d = 1.06$ ) dissolve 0.01–0.005 g. of potassium chromate as inner electrolyte and 0.03–0.05 g. of glucose. To this solution add an equal volume of a half normal solution of acetic acid. After setting, 10% lead nitrate solution is superposed on the gel as outer electrolyte. Ten or more days later, it was observed that many thin and crowded bands were formed. If too much potassium chromate was added, the dendrites were also formed simultaneously, and if too little, the bands became very vague.

H. N. Holmes<sup>(34)</sup> has found, in the periodic precipitate of mercuric iodide in silicic acid gel, that the presence of glucose in the gel makes the bands very much sharper. The author has found, in the same manner, that the addition of glucose makes the periodic structure of the lead chromate much sharper. In this case, two periodicities exist just as the case of silver chromate banding in gelatine containing small amount of soluble chlorides and phosphates. Larger periodicity is easily recognised while smaller one is often difficult to observe without a magnifying glass. At the lower part of the tube, however, both can easily be recognised with the naked eyes. It is interesting that in this case the upper part of the jelly is coloured yellow, the subsequent layer, orange, and the lower, brown. The banding appears under this part and becomes yellow again at the lowermost part. It seems that such a colour change is caused by the difference of the size of formed crystals.

**Lead Iodide in Silicic Acid Gel.** When potassium iodide solution diffuses into silicic acid gel containing lead acetate, fern-like fronds grow down in the gel, mixing with hexagonal plates. It is believed that the lead iodide does not form rhythmic precipitate in the silicic acid gel. But it was found, in rare cases, that the rhythmic precipitate of this substance occurred accidentally. The author studied the condition under which the rhythmic precipitates are formed,<sup>(12)</sup> and found that when the crystals become relatively small, the rhythmic precipitates are generally formed. The increase of the inner and outer electrolyte is favourable to the formation of small crystals. A third substance must be added which makes the crystals of lead iodide small in order to make sure

the formation of rhythmic bands. Citrate and tartrate are fit to this purpose as already mentioned in the preceding paragraph. One normal acetic acid containing 0.9 c.c. of 1 N lead acetate and 0.55 c.c. of 3% potassium citrate to every 10 c.c. was mixed with the equal volume of water glass solution ( $d = 1.06$ ) and poured into a test tube. After the silicic acid had set firmly, it was covered with 2 N potassium iodide solution. By this procedure good rhythmic bands from fine crystals were always formed. Similarly, to make the gel, 1 N acetic acid containing 1.2 c.c. of 1 N lead acetate and 0.8 c.c. of 3% tartaric acid to every 10 c.c. was mixed with the water glass solution. Then the gel was covered with 2 N potassium iodide solution. Beautiful well-defined rhythmic precipitates consisting of relatively large crystals were produced. These results show that the formation of bands is the true Liesegang's phenomenon. But the crystallisation of lead iodide is much influenced by the temperature and the light. The crystallisation of this substance is faster in day time than in night. Moreover, lead iodide is decomposed by bright light, especially in the presence of citrate and the colour of crystals changes to black. For these reasons, two other periodic deposition of diurnal nature, which are caused by the change of temperature and light, are produced as the reflex of the external periodicities. Frequently, these three rhythms, Liesegang's and two diurnal bandings, appear at the same time in one test tube and the complicated bands are obtained.

**Lead Iodate in Gelatine Gel.** As already mentioned, lead iodate is hardly obtained as rhythmic precipitate in non-dialysed gelatine. Because the rhythmic bands of lead iodate becomes undistinguishable by a continuous, white precipitate probably consisting of chloride and phosphate of lead in ordinary commercial gelatine, which contains always some impurities of chloride and phosphate. Very beautiful and well-defined rhythmic precipitate is formed by using the gelatine purified by electro-dialysis or by Loeb's method.<sup>(48)</sup> One of the most favourable conditions for the banding is as follows: a 0.5 mol solution of lead acetate was allowed to diffuse into a 2% purified gelatine gel containing as much of potassium iodate as to be 4% in concentration. This rhythmic precipitate is one of the most distinct and beautiful example which the author have ever seen. Lead iodate makes often the helicoidal precipitate. The reason for the formation of helicoidal precipitate is not thoroughly clear but probably it is ascribed to the deformation of gel by the pouring of diffusing electrolyte on it. The conditions for the banding and the effect of various influences were studied and the results were partly shown in the preceding paragraphs. Light has no influences on this rhythmic precipitate and the ageing of gel also has no influences.

**Lead Iodate in Silicic Acid Gel.** It was already reported in the preceding paragraph, that if lead acetate diffuse into a gelatine gel containing potassium iodate, a very beautiful well-defined rhythmic precipitate is formed. But on standing this rhythmic precipitate for a long time, more lead acetate diffuse into the gel, reacts with the already formed

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(48) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 301.

lead iodate, and transforms the bands into those consisting of large crystals. It seems that the band of coarse crystals are composed of a double salt of relatively high solubility. This transformation from fine well-defined bands to incomplete bands of coarse crystals is far faster in silicic acid gel than in gelatine. The bands were scarcely observed in silicic acid gel after the transformation, because the crystals formed were large scattered globules. The quick transformation is probably due to the lack of protective action of the silicic acid gel. Six c.c. of a sol which was prepared by mixing equal volumes of a sodium silicate solution ( $d = 1.06$ ) and 0.70–0.75 N acetic acid solution is added with 0.6 c.c. of 5% potassium iodate solution. After the gel set firmly, a lead acetate solution (1 N) was poured on the gel. About ten bands were formed after 24 hours but these transformed, successively, from the top, into bands consisting of large globules, which blurred within two or three days.

**Lead Phosphate in Silicic Acid Gel.** It was examined whether lead phosphate was precipitated in rhythmic bands or not in silicic acid gel. A sol which was prepared by mixing 3.0 c.c. of a ( $d = 1.06$ ) solution water glass with an equal volume of 0.75 N acetic acid, is added with 0.5 c.c. of a 0.5 mol solution of sodium phosphate. After the sol set firmly to a gel, 1 N solution of lead acetate or lead nitrate was superposed on the gel. The banding was indistinct. Somewhat long needles were formed and it seems that these needles distribute to make faint bands. When 0.3 c.c. of a 3% potassium citrate solution was added beforehand to the gel, distinct rhythmic bands were formed. When a lead acetate solution (1 N) diffused into the gel, more than twenty bands were recognised. But in the case of the diffusion of lead nitrate, the bands were often imperfect and consisted of fragments.

**Lead Phosphate in Gelatine Gel.** The lead phosphate precipitates in silicic acid gel as somewhat long needles and the rhythmic nature of this precipitate is, as already mentioned, indistinct. In the presence of a small quantity of citrate, however, the crystals became smaller and they appeared as a rhythmic precipitate. It is known that crystals formed in gelatine are generally smaller than those formed in a silicic acid gel. So, it is expected that lead phosphate forms rhythmic bands in gelatine. The author made an experiment on it. Sodium phosphate (0.5 c.c. of 0.5 mol solution) was dissolved in 6 c.c. of a 3% solution of purified ash-free gelatine. After the gel set firmly, 1 N solution of lead acetate was poured on the gel as the outer electrolyte. Seven white bands were formed and then the crystals deposited uniformly below these bands.

**Cerium Iodate in Silicic Acid Gel.** The bands of cerium iodate were obtained by the diffusion of cerium nitrate into silicic acid gel containing potassium iodate as inner electrolyte. The condition for the banding was as follows. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ( $d = 1.06$ ) with an equal volume of 0.7 N acetic acid was added with 1.0 c.c. of a saturated solution of potassium iodate. After the sol set firmly to the gel, 5% solution of cerium nitrate was superposed on it. White beautiful bands were obtained. Every band formed close to each



other. For the first 2.5 cm. from the top of the gel, a continuous white precipitate was formed and for the next 2.5 cm. 15 bands were recognised, separated by narrow clear gaps.

**Silver Ferrocyanide in Silicic Acid Gel.** A rhythmic precipitate of silver ferrocyanide was obtained by the diffusion of silver nitrate into silicic acid gel containing potassium ferrocyanide. The bands were very close to each other. More than 15 bands were often formed in one centimeter. This banding was already studied by Mukherjee and Chatterji.<sup>(49)</sup> They concluded that the intervals between bands become smaller with the advance of diffusion. But in the present experiments all of the bands were separated by almost equal intervals. It is doubtful that these bands were formed as a Liesegang phenomenon. This banding is influenced by the acidity of the gel. Some conditions and the results obtained are given in Table 43 and follows.

Table 43.

| No. | Gel                                                       |                                                   |                                             |     | Outer electrolyte (5%) | Results                                     |
|-----|-----------------------------------------------------------|---------------------------------------------------|---------------------------------------------|-----|------------------------|---------------------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | CH <sub>3</sub> CO <sub>2</sub> H solution (c.c.) | Inner electrolyte (c.c.)                    |     |                        |                                             |
| 1   | 3.0                                                       | 0.6 N 3.0                                         | K <sub>4</sub> Fe(CN) <sub>6</sub> 0.3 (2%) | 0.3 | AgNO <sub>3</sub>      | A yellow continuous precipitate was formed. |
| 2   | 3.0                                                       | 0.7 N 3.0                                         | „                                           | 0.3 | „                      | A grey continuous precipitate was formed.   |
| 3   | 3.0                                                       | 0.8 N 3.0                                         | „                                           | 0.3 | „                      | } Close rhythmic bands were formed.         |
| 4   | 3.0                                                       | 0.9 N 3.0                                         | „                                           | 0.3 | „                      |                                             |
| 5   | 3.0                                                       | 1.0 N 3.0                                         | „                                           | 0.3 | „                      |                                             |
| 6   | 3.0                                                       | 1.0 N 3.0                                         | „                                           | 0.7 | „                      |                                             |

In a gel of low acidity such as No. 1, yellow precipitate was formed uniformly and no band was recognised. In No. 2, also, no band was formed but a white precipitate formed uniformly. In No. 3–No. 5 many close bands were obtained. These bands were type of sub-class II (class II of Chatterji). Generally, the intervals between bands were large in a gel of high acidity. In No. 5, the intervals between bands were larger than those in No. 3 and in No. 4. In No. 6, the bands were very close to each other owing to the relatively high concentration of the inner electrolyte.

**Ferric Ferrocyanide in Silicic Acid Gel.** Rhythmic bands of ferric ferrocyanide were obtained by the diffusion of ferric chloride into silicic acid gel containing potassium ferrocyanide as an inner electrolyte. These rhythmic bands were indistinct, showing a blue continuous precipitate by reflected light but many bands were seen by transmitted light. The banding was sub-class II type (class II type of Chatterji). The conditions are given in Table 44.

(49) Mukherjee and Chatterji, *Kolloid-Z.*, **50** (1930), 147.

Table 44.

| No. | Gel                                                       |                                                   |     |                                             | Outer electrolyte    | Results                                                      |
|-----|-----------------------------------------------------------|---------------------------------------------------|-----|---------------------------------------------|----------------------|--------------------------------------------------------------|
|     | Na <sub>2</sub> SiO <sub>3</sub> solution (d=1.06) (c.c.) | CH <sub>3</sub> CO <sub>2</sub> H solution (c.c.) |     | Inner electrolyte (c.c.)                    |                      |                                                              |
| 1   | 3.0                                                       | 0.5 N                                             | 3.0 | K <sub>4</sub> Fe(CN) <sub>6</sub> 0.1 (2%) | FeCl <sub>3</sub> 5% | Faint bands were formed.                                     |
| 2   | 3.0                                                       | "                                                 | 3.0 | " 0.3                                       | "                    | No band and only a stopper was formed.                       |
| 3   | 3.0                                                       | 1.0 N                                             | 3.0 | " 0.1                                       | "                    |                                                              |
| 4   | 3.0                                                       | "                                                 | 3.0 | " 0.3                                       | "                    |                                                              |
| 5   | 3.0                                                       | "                                                 | 3.0 | " 0.7                                       | "                    | Blue rhythmic precipitate was observed by transmitted light. |
| 6   | 3.0                                                       | 0.6 N                                             | 3.0 | " 0.3                                       | "                    |                                                              |
| 7   | 3.0                                                       | 0.7 N                                             | 3.0 | " 0.3                                       | "                    |                                                              |
| 8   | 3.0                                                       | 0.8 N                                             | 3.0 | " 0.3                                       | "                    |                                                              |
| 9   | 3.0                                                       | 0.9 N                                             | 3.0 | " 0.3                                       | "                    | No band was formed.                                          |
| 10  | 3.0                                                       | 0.8 N                                             | 3.0 | " 0.1                                       | "                    |                                                              |

When the concentration of potassium ferrocyanide was small, either the banding was indistinct or no band was formed as in the cases of No. 1, No. 3, and No. 4. In No. 2, brown bands were formed which were thinner in the lower part and separated by small interspaces. These were probably diurnal bands of ferric basic chloride or ferric hydroxide. At the bottom of the gel some rhythmic bands of prussian blue were formed. No. 3 gave no band and only a brown stopper. In No. 4, many blue bands were observed by transmitted light but no band by reflected light. No. 5 gave brown diurnal bands but blue bands were not observed even by transmitted light for the precipitation was too dense. In No. 6–No. 9 blue rhythmic bands were well observed by transmitted light. No. 10 gave no band. A brown band was always observed at the top of the gel in these banded precipitates. These were probably formed by basic chloride of iron, ferric hydroxide or basic ferric acetate which was produced by the hydrolysis of ferric chloride or its interaction with acetic acid. These brown bands were formed simultaneously with bands of prussian blue, and were affected by external rhythms. So the banding was always very irregular. Moreover, this rhythmic precipitate was affected by the acidity of the gel. In a gel of high acidity, many bands were formed in the lower part of the gel, situating close to each other. This was probably due to the fact that the diffusing ferric chloride was not easily hydrolysable in the more acidic gels and so the consumption of ferric chloride by hydrolysis was small. Accordingly, ferric chloride of the same concentration acts as if it were a concentrated solution in the more acidic gels.

**Uranyl Phosphate in Silicic Acid Gel.** A rhythmic precipitate of uranyl phosphate was obtained by the action of uranyl acetate with soluble phosphate in silicic acid gel. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ( $d=1.06$ ) with an equal volume of 0.75 N acetic acid was added with 0.3 c.c. of a 8.74% solution of sodium phosphate. After the gel set firmly, 2% solution of uranyl acetate was superposed on it. Pale yellow bands consisting of relatively coarse crystals were formed. The appearance was entirely analogous to the

bands of uranyl arsenate which will be described later. Coarse crystals have been deposited under the last band. The bands belong to the category of the type of sub-class II.

**Uranyl Arsenate in Silicic Acid Gel.** The precipitating reaction of uranyl arsenate is analogous to the case of uranyl phosphate. So the formation of rhythmic precipitate of uranyl arsenate in a silicic acid gel was experimented, and a similar result was obtained. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ( $d = 1.06$ ) with an equal volume of 0.75 N acetic acid was added with 0.3 c.c. of a 10% solution of sodium arsenate. After the gel set firmly, 2% solution of uranyl arsenate was superposed on it. Several bands of pale yellow uranyl arsenate were obtained. The crystals forming the bands became coarse with the advance of diffusion. Almost no crystals formed below the last band. These bands were also the sub-class II type.

### Summary.

(1) The conditions of the formation of various examples of rhythmic precipitates have been studied. The effects were tested of the change of species and concentrations of gel, inner electrolyte and outer electrolyte, the temperature, the light intensity and the hydrogen ion concentrations of medium and outer electrolyte solution.

(2) The regularity of spacing between bands has been studied. The distance between bands is expressed empirically by the quadratic equation concerning the ordinal number of it. The same equation was deduced from a theoretical standpoint, the physical meaning of the equation being considered.

(3) Classification of the rhythmic precipitates by the cause of formation and by the structure has been proposed. Secondary bands were investigated and discussed.

(4) New examples of rhythmic precipitate have been described, i.e. barium chromate, cobalt phosphate, lead carbonate, lead phosphate, lead iodate, silver arsenate, silver carbonate, silver iodate and silver capronate in gelatine gel, and bismuth chromate, bismuthyl chloride, bismuthyl nitrate, cobalt phosphate, cobalt sulphide, copper carbonate, copper iodate, cerium iodate, calcium phosphate, calcium oxalate, strontium oxalate, ferric ferrocyanide, lead carbonate, lead iodate, lead phosphate, nickel dimethylglyoxime, silver arsenate, silver ferrocyanide, silver phosphate, silver iodate, uranyl phosphate and uranyl arsenate in silicic acid gel. The conditions for the formation of these rhythmic precipitates have been thoroughly investigated.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices and encouragement throughout the work.

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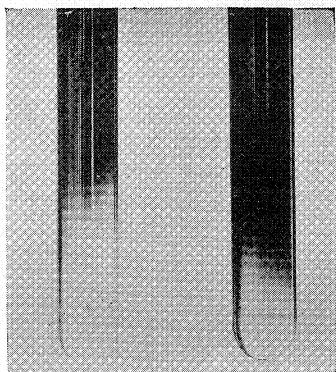


Fig. 1.

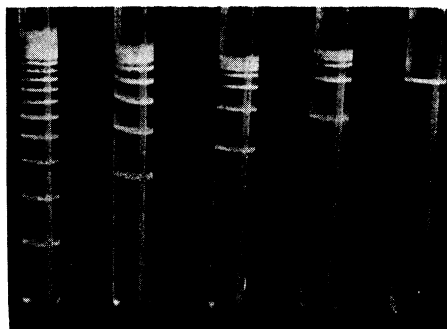
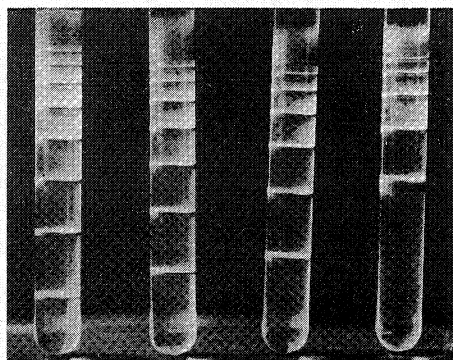
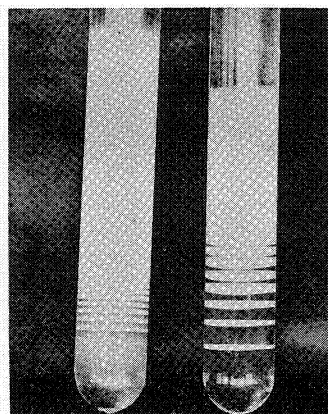
Fig. 2.  $\text{Na}_2\text{CO}_3$  (conc.)  $\rightarrow$   $\text{Na}_2\text{CO}_3$  (dil.)Fig. 3.  $\text{AgNO}_3$  (conc.)  $\rightarrow$   $\text{AgNO}_3$  (dil.)

Fig. 4.

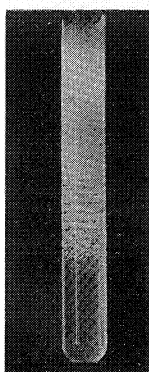


Fig. 5.

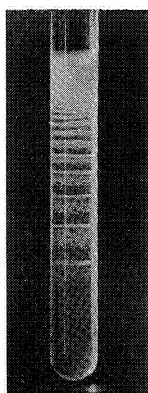
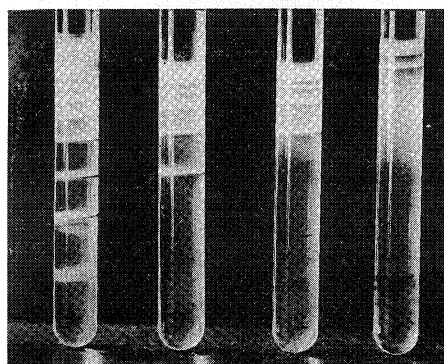


Fig. 6.

Fig. 7. Gelatine (dil.)  $\rightarrow$  Gelatine (conc.)

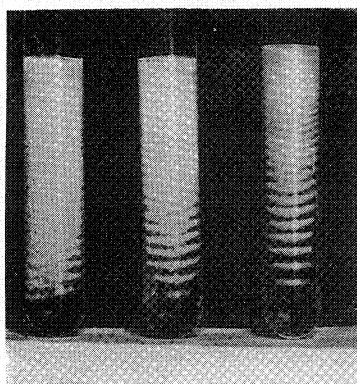


Fig. 8.

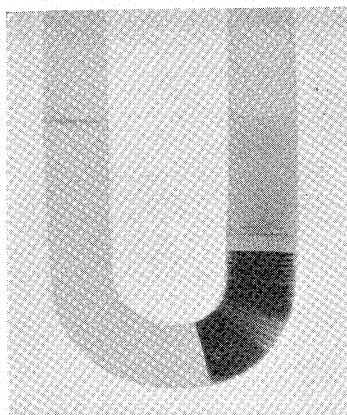


Fig. 9.

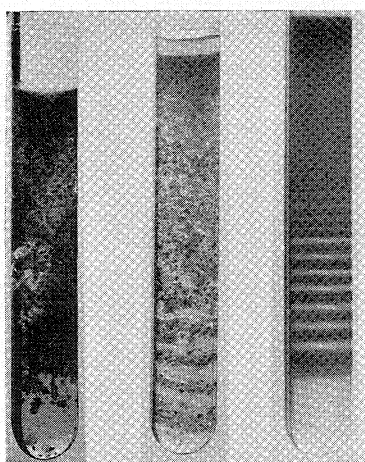


Fig. 10.

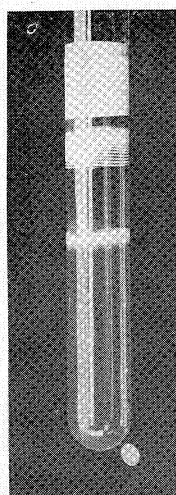


Fig. 11.

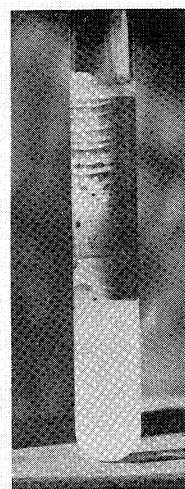


Fig. 13.

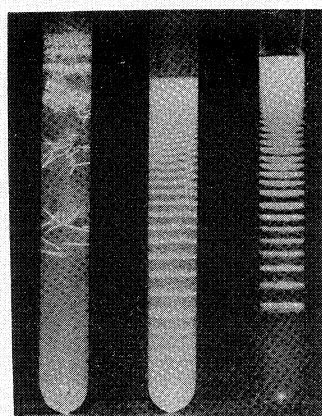


Fig. 12.

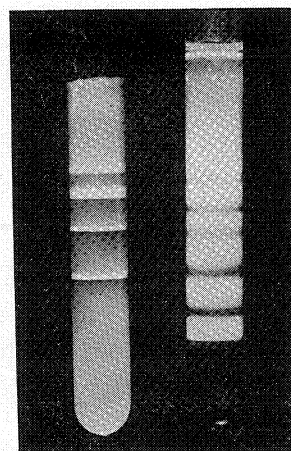


Fig. 14.

# Chemical Studies of the Western Pacific Ocean. IV. The Refractive Index of Sea Water.

By Yasuo MIYAKE.

(Received April 11, 1939.)

The refractive index of sea water was measured for the first time by J. Soret and Ed. Sarasin<sup>(1)</sup> in 1889. In 1900, H. Tornøe<sup>(2)</sup> studied the same subject and expressed the relation between salinity and refractive index by the next empirical formula:

$$\log n_D^{17.5}/S = 6.14340 - 0.00006 \cdot S,$$

where  $n$  is the refractive index and  $S$ , the salinity. Apparently it seems possible to determine the salinity by applying this equation without resorting to the tedious volumetric method; however, it is to be regretted that the accuracy of the results thus obtained is far too inferior.

After Tornøe, attempts by O. Krümmel<sup>(3)</sup> and other later investigators in improving the new method to the state of practical application for determination of salinity proved fruitless. For instance, M. C. Vauraburg<sup>(4)</sup> obtained a convenient formula expressing the relation between refractive index and density of sea water at various temperatures, however, the accuracy of the results obtained by this formula barely approaches the order of that of an ordinary aerometer. In 1924, C. Pape<sup>(5)</sup> finally succeeded in the exact determination of salinity from the refractive index of water by measuring the minute differences between the refractive indices of standard water and samples with an interferometer of high precision. By this method, we can easily determine the salinity very precisely and in a few minutes. The chief object of the present work lies not in the determination of salinity but in a study leading to a stoichiometrical explanation of the refractive index of sea water.

**Experimental.** The Pulfrich's refractometer made by Fuess was used throughout the experiments. Sea water collected on March 16th, 1938 at N 42°38', E 145°14', was divided into ten samples of various chlorinities by dilution with water. The refractive index of each sample was carefully measured with Mazda's sodium lamp at 25°C. The results of the measurements are shown in Table 1.

As shown in Fig. 1, the relation between refractive index and chlorinity is almost linear and may be represented by the next empirical formula:

$$n_D^{25} = .1.33249_7 + 0.000334 \text{ Cl} \quad (1).$$

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(1) J. Soret and Ed. Sarasin, *Compt. rend.*, **108** (1889), 1248.

(2) H. Tornøe, *Rep. Norw. Fish. Mar. Invest.*, **1** (1900), No. 6.

(3) O. Krümmel, "Handbuch der Ozeanographie", I, Stuttgart (1907).

(4) M. C. Vauraburg, *Compt. rend.*, **172** (1921), 863.

(5) C. Pape, *Ann. d. Hydrog.*, **53** (1924), 249; Schumacher, *Z. Ges. Erdk.* I, **47** (1926), 251.

Table 1. The Relation between Refractive Index and Chlorinity.

| $n$     | Cl‰   | $n$     | Cl‰  |
|---------|-------|---------|------|
| 1.33863 | 18.54 | 1.33498 | 7.53 |
| 1.33812 | 16.73 | 1.33437 | 5.66 |
| 1.33742 | 14.80 | 1.33369 | 3.79 |
| 1.33681 | 13.07 | 1.33303 | 1.90 |
| 1.33629 | 11.23 | 1.33250 | 0.00 |
| 1.33559 | 9.37  |         |      |

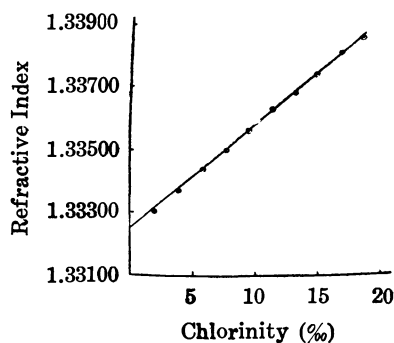


Fig. 1.

For the refractive index of pure water at 25°C., the average of the three values, 1.33251 (Hall and Payne), 1.33248 (Baxter and Burgess) and 1.33250 (measured by the author), was adopted.

**The Refractive Index of Artificial Sea Water.** It seems to be evident that the difference between the refractive index of pure water and sea water depends mainly upon the salts contained in the latter. It is of interest to know whether the refractive index of an artificial sea water is identical or not with that of a natural sea water of the same degree of chlorinity. An artificial sea water was prepared with chlorinity equivalent to 18.54‰ and its refractive index was measured. As shown in Table 2, the refractive index of the artificial sea water was in good agreement with that of natural sea water.

Table 2. A Comparison between the Refractive Index of Artificial and Natural Sea Waters of the same Chlorinity. Cl‰ 18.54.

| Sea Water  | Artificial | Natural |
|------------|------------|---------|
| $n_D^{25}$ | 1.33863    | 1.33863 |

In the next place, we may expect that when we dissolve the respective salts individually in water and measure the refractive index  $\nu$  of each solution, the relation shown in the next formula should hold.

$$n = n_0 + \sum (\nu - n_0) \quad (2),$$

where  $n$  is the refractive index of sea water;  $\nu$ , the refractive index of each solution;  $n_0$ , the refractive index of distilled water.

Table 3 shows the results of the experiment.

Table 3.

| Salt                           | g/l     | $\nu$   | $\nu - n_0$ |
|--------------------------------|---------|---------|-------------|
| NaCl                           | 26.4738 | 1.33707 | 0.00457     |
| KCl                            | 0.6922  | 1.33259 | 0.00009     |
| MgCl <sub>2</sub>              | 3.4112  | 1.33294 | 0.00044     |
| MgSO <sub>4</sub>              | 2.1825  | 1.33336 | 0.00086     |
| CaSO <sub>4</sub>              | 1.2838  | 1.33277 | 0.00027     |
| CaCO <sub>3</sub>              | 0.2170  | 1.33250 | 0.00000     |
| $\Sigma (\nu - n_0) = 0.00623$ |         |         |             |

$$n = n_0 + \Sigma (\nu - n_0) = 1.33250 + 0.00623 = 1.33873$$

$$n_{\text{observed}} = 1.33863.$$

The results of the measurements described above, prove experimentally that the refraction of sea water is a summation of the individual refractions of pure water and dissolved salts. In the next paragraph, a more theoretical discussion will be given.

**A Theoretical Consideration.** Inasmuch as sea water is a dilute solution of inorganic salts, the greater part of each salt is dissociated into its ions. So, when refraction of sea water is mentioned, we must usually deal with the ionic refraction instead of molecular refraction. Therefore, since the values of the ionic refraction introduced from the theory of Lorenz-Lorentz have been calculated by Heydweiller<sup>(6)</sup> and K. Fajans,<sup>(7)</sup> we can easily obtain the equivalent refraction of sea water completely. According to the Lorenz-Lorentz's theory, the equivalent refraction (*E.R.*) of sea water is represented by the next formula:

$$E.R. = \frac{1000 d}{d} \frac{n^2 - 1}{n^2 + 2} \quad (3),$$

where  $n$  is the index of refraction of sea water and  $d$ , its density. On the other hand, *E.R.* is the sum of the refraction of pure water and of ions of the solute.

Then,

$$E.R. = \frac{1000 d - S}{d_0} \frac{n_0^2 - 1}{n_0^2 + 2} + N_{\text{Cl}} R_{\text{Cl}} + N_{\text{Na}} R_{\text{Na}} + N_{\text{SO}_4} R_{\text{SO}_4} + N_{\text{Mg}} R_{\text{Mg}} + N_{\text{Ca}} R_{\text{Ca}} + N_{\text{K}} R_{\text{K}} \quad (4),$$

where  $S$  is the quantity of salt per litre of sea water ;  
 $d_0$ , the density of pure water at 25°C. ;  
 $n_0$ , the refractive index of pure water at 25°C. ;  
 $N$ , the number of mols of each ion ;  
and  $R$ , the refraction of each ion.

(6) A. Heydweiller, *Ann. Physik*, **41** (1913), 499.

(7) K. Fajans and G. Joos, *Z. Physik*, **23** (1924), 1.



The first term of this formula is the refraction of pure water. Therefore, by knowing every  $N$  and  $R$ , we may completely evaluate the above formula.

In Table 4, the numerical values of  $N$  and  $R$  are given.

Table 4.

| Ion             | $N$ mol/l | $R$ c.c. | $N \times R$ c.c. |
|-----------------|-----------|----------|-------------------|
| Na              | 0.4542    | 0.200    | 0.0908            |
| Cl              | 0.5352    | 9.00     | 4.8168            |
| SO <sub>4</sub> | 0.0276    | 14.63    | 0.4038            |
| Mg              | 0.0541    | -1.57    | -0.0850           |
| Ca              | 0.0108    | 0.68     | 0.0731            |
| K               | 0.0093    | 2.23     | 0.0207            |
| Total           |           |          | 5.3202            |

The first term is ;

$$\frac{1000 d - S}{d_0} \frac{n_0^2 - 1}{n_0^2 + 2} = 203.533 \text{ c.c.}$$

where,

$$d, \quad 1.022222 \text{ (25°C., Cl } \rho_{\%}^{\circ} 18.54);$$

$$d_0, \quad 0.997069 \text{ (25°C.)};$$

$$S, \quad 34.26 \text{ g/l};$$

and

$$n_0, \quad 1.33249_7 \text{ (25°C., Na D-line).}$$

Then, the calculated value of  $E.R.$  is ;

$$E.R._{\text{calc.}} = 208.853 \text{ c.c.}$$

On the other hand the value of  $E.R.$  obtained from Formula (3) becomes ;

$$E.R._{\text{obs.}} = 208.846 \text{ c.c.} \quad (n = 1.33863).$$

The two results are in quite good agreement. Thus we have been able to demonstrate theoretically that the refraction of sea water is a sum of the refractions of pure water and of solute ions.

It is interesting to note that 90% of the ionic refraction is due to the chloride ion. There is a parallelism between molecular refraction and molecular volume; probably in this case, the chloride ion may be the one which occupies the largest space in sea water.

### Summary.

(1) Refractive indices of sea water of various chlorinities were measured and the following empirical formula was obtained:

$$n_D^{25} = 1.33249_7 + 0.000334 \text{ Cl}$$

(2) An assumption that the refraction of sea water is a summation of the individual refractions of pure water and dissolved salts, was proved both experimentally and theoretically.

In conclusion, the author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

*Central Meteorological Observatory of Japan.*

## Studies on the Effect of Electric Field on the Viscosity of Liquids.

By Osamu KIMURA.

(Received April 19, 1939.)

**Introduction.** Many experiments have been done on the effect of electric field on the viscosity of liquids,<sup>(1)</sup> but few, on the viscosity of solutions.<sup>(2)</sup> This paper deals with the effect of electric field on the viscosity of the following solutions. As the solutes, a homologous series of fatty acids (lauric, myristic, palmitic, and stearic acids) and an alcohol (cetyl alcohol) were used. In this homologue the number of carbon of an acid increases from the next lower one by two, or the length of the molecule increases regularly according to the number of carbon of acid. While this electro-viscose effect seems to depend upon the length of the molecule of solute, and if so, it is interesting to examine how this effect depends upon the length of molecule of solute. For this purpose the homologue of fatty acid is selected here. As the solvents, benzene and hexane, both of which are non-polar and show no electro-viscose effect, were used. The author reports here the results of the measurement, using special viscosimeter, of the viscosity of solutions which are prepared by combining these solutes and solvents. One of these solutions, i.e. benzene solution of stearic acid has been investigated and reported in the previous paper.<sup>(3)</sup>

**Apparatus.** The author has devised for this experiment a special viscosimeter which is similar to that of L. Herzog and S. Sokolow.<sup>(1)</sup> The principle of measurement is the same as Ostwald's viscosimeter, but the modified capillary part in applying electric field, is composed of two pieces of electrodes, of which the gap is very narrow and has rectangular section. The whole apparatus is shown in Fig. 1 and the section of the capillary part, in Fig. 1a. As we see in the figure, the apparatus is composed of three parts, i.e. glass bulb A, capillary C and the glass tube B. The volume of A is about 2 c.c. The electrodes are made of aluminium block, the surface of which is covered by electrolytic oxide film in order to make it a good insulator of electricity. Between two electrodes, two thin pieces of glass are inserted. Then we get a capillary of rectangular section, the dimension of which is  $0.3 \times 0.02$  cm.<sup>2</sup>, and the length of capillary is

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(1) W. Krönig, *Wied. Ann.*, **25** (1885), 618. W. Duff, *Phys. Review*, **1896**, 23. G. Quincke, *Wied. Ann.*, **62** (1897), 1. G. Pacher and L. Finazzi, *Atti, Re Ist Ven.*, **59**, 2 (1889-1900), 389. A. Pocchettino, *Atti. D. Real. Accad. dei Linc.*, V. **12**, 2 (1903), 389. Ercollini, *Il. Nuovo Cimento*, **5** (1903), 249. Ph. Lenard, *Ann. Physik.*, (4) **61** (1920), 715. R. Herzog, H. Kudar, and E. Paersch, *Naturwissenschaften*, **21** (1933), 622., *Physik. Z.*, **35** (1934), 466. E. D. Alock, *Physics*, **7** (1936), 126. Y. Björnsthål, *Physics*, **6** (1935), 257. S. Dobinski, *Physik. Z.*, **14** (1935), 509. P. Sokolow and S. Sosinski, *Acta Physicochimica*, U.R.S.S., **5** (1936), 433, 691., *Ber. Akad. U.R.S.S.*, **4** (1935), 123.

(2) A. Passynski, *Kolloid-Z.*, **70** (1935), 180. Y. Björnsthål and K. O. Snellman, *Kolloid-Z.*, **78** (1937), 258.

(3) O. Kimura, this Bulletin, **12** (1937), 147.

6 cm. It is naturally very important to keep the apparatus at constant temperature as the viscosity of liquid is much affected even by a slight fluctuation of temperature. For this purpose, the apparatus must be set up in a thermostat. Since the liquid thermostat is inconvenient, the author has preferred air thermostat, of which the fluctuation of temperature is below  $0.1^{\circ}\text{C}$ . The time is measured by a stop-watch, which is accurate to one tenth of a second. The source of high voltage electricity is obtained by the usual means of a step up A.C. 100 volt transformer and rectifying it to direct current.

Table 1.

| Solvent | Solute        | Molar fraction | Gram % |
|---------|---------------|----------------|--------|
| benzene | lauric acid   | 0.01           | 2.272  |
| "       | "             | 0.02           | 4.591  |
| "       | "             | 0.04           | 9.393  |
| "       | myristic acid | 0.01           | 2.590  |
| "       | "             | 0.02           | 5.233  |
| "       | "             | 0.04           | 10.69  |
| "       | palmitic acid | 0.01           | 2.909  |
| "       | "             | 0.02           | 5.877  |
| "       | "             | 0.04           | 12.00  |
| "       | stearic acid  | 0.01           | 3.227  |
| "       | "             | 0.02           | 6.520  |
| "       | "             | 0.04           | 13.32  |
| "       | cetyl alcohol | 0.01           | 2.750  |
| "       | "             | 0.02           | 5.557  |
| "       | "             | 0.04           | 11.34  |
| hexane  | "             | 0.04           | 11.72  |

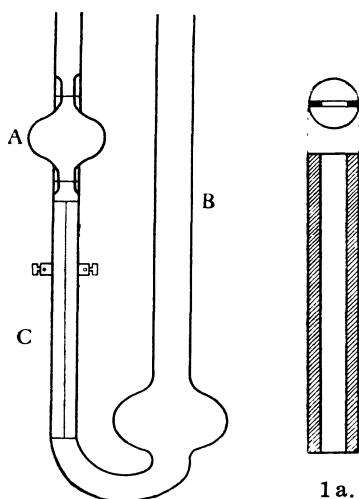


Fig. 1.

**Experiment.** The solvents, benzene and hexane, were first purified and then dried by distilling them over pieces of sodium. Lauric acid and cetyl alcohol are of Takeda's pure chemical, and stearic, palmitic, myristic acid are of Merck's. As the unit of concentration, molar fraction is used. The determination was done in all cases on the solution of following three concentrations, namely; 0.01, 0.02, 0.04. The relation of molar fraction with gram percent is shown in Table 1. The temperature is kept at  $20^{\circ}\text{C}$ . throughout the experiment. The measurement of viscosity was proceeded first from pure benzene and hexane. These non-polar solvents did not show any change of viscosity in electric field, as found by the earlier investigators. Then the measurement was carried out on the above-mentioned solutions. In this case, the increase of viscosity occurs when the electric field is applied, and the reproducibility of this effect has been checked by the successive observations of the time of transpiration with or without electric field. The applied voltage varies from zero to thousand volts. The voltage per centimeter may hardly be calculated as the distribution of potential in oxide film is unknown. Therefore here is described only the applied voltage. As the distance of electrode is 0.02 cm., if we assume

the layer of oxide film very thin, the approximate voltage can be estimated by multiplying the applied voltage by 50.

The movement of liquid in a capillary tube of rectangular section is calculated by Rowell and Finlayson,<sup>(4)</sup> that is

$$Q = \frac{4}{3} \cdot \frac{II}{\eta} \cdot b h^3 \left( 1 - x \cdot \frac{h}{b} \right) t$$

$$\text{where } x = \frac{192}{\pi^5} \cdot \sum_{n=1}^{\infty} \left( \frac{1}{n^5} \cdot \tanh \frac{\pi n b}{2h} \right) \text{ with } n \text{ odd,}$$

and  $Q$  is the volume of the transpired liquid in  $t$  seconds, the viscosity,  $b$  and  $h$  two sides of rectangle,  $II$  pressure,  $x$  number only referring to  $b$  and  $h$ . In this apparatus since  $Q, II, b$  and  $h$  are constant, we can get the following relation;

$$\eta \propto t$$

This is the same as found in Ostwald's viscosimeter, therefore we can assume that the time of transpiration is proportional to viscosity.

Now the results are shown in Tables 2-7 and Figs. 2-6.

Table 2. Lauric acid  
( $C_{11}H_{23}COOH$ ) in benzene.

| Concentration | Voltage | $t''$ | $\frac{\Delta t}{t} \times 100$ |
|---------------|---------|-------|---------------------------------|
| 0.01          | 0       | 48.2  | 0.00                            |
| "             | 300     | 48.2  | 0.00                            |
| "             | 400     | 48.3  | 0.21                            |
| "             | 500     | 48.4  | 0.42                            |
| "             | 600     | 48.5  | 0.62                            |
| "             | 700     | 48.6  | 0.83                            |
| 0.02          | 0       | 47.3  | 0.00                            |
| "             | 300     | 47.4  | 0.21                            |
| "             | 500     | 47.5  | 0.42                            |
| "             | 600     | 47.6  | 0.63                            |
| "             | 700     | 47.7  | 0.85                            |
| "             | 800     | 47.8  | 1.06                            |
| 0.04          | 0       | 51.0  | 0.00                            |
| "             | 300     | 51.1  | 0.20                            |
| "             | 400     | 51.2  | 0.39                            |
| "             | 500     | 51.3  | 0.59                            |
| "             | 600     | 51.4  | 0.78                            |
| "             | 700     | 51.5  | 0.98                            |
| "             | 800     | 51.6  | 1.18                            |

Table 3. Myristic acid  
( $C_{13}H_{27}COOH$ ) in benzene.

| Concentration | Voltage | $t''$ | $\frac{\Delta t}{t} \times 100$ |
|---------------|---------|-------|---------------------------------|
| 0.01          | 0       | 68.4  | 0.00                            |
| "             | 300     | 68.4  | 0.00                            |
| "             | 400     | 68.5  | 0.15                            |
| "             | 500     | 68.6  | 0.29                            |
| "             | 600     | 68.7  | 0.44                            |
| "             | 700     | 68.8  | 0.59                            |
| "             | 800     | 69.0  | 0.88                            |
| 0.02          | 0       | 49.6  | 0.00                            |
| "             | 200     | 49.7  | 0.20                            |
| "             | 300     | 49.8  | 0.40                            |
| "             | 400     | 50.0  | 0.81                            |
| "             | 500     | 50.3  | 1.41                            |
| "             | 600     | 50.5  | 1.82                            |
| "             | 700     | 50.8  | 2.42                            |
| "             | 800     | 51.2  | 3.23                            |
| 0.04          | 0       | 55.3  | 0.00                            |
| "             | 300     | 55.5  | 0.36                            |
| "             | 400     | 55.7  | 0.72                            |
| "             | 500     | 56.1  | 1.44                            |
| "             | 600     | 56.5  | 2.17                            |
| "             | 700     | 56.9  | 2.89                            |
| "             | 800     | 57.3  | 3.62                            |
| "             | 900     | 58.0  | 4.88                            |

(4) *Engineering*, **126** (1928), 249, 385., see also G. Barr, "A Monograph of Viscometry", 145, (1931).

Table 4. Palmitic acid  
( $C_{15}H_{31}COOH$ ) in benzene.

| Concentration | Voltage | $t''$ | $\frac{\Delta t}{t} \times 100$ |
|---------------|---------|-------|---------------------------------|
| 0.01          | 0       | 47.7  | 0.00                            |
| "             | 100     | 47.8  | 0.21                            |
| "             | 200     | 48.9  | 0.42                            |
| "             | 300     | 49.0  | 0.63                            |
| "             | 500     | 49.1  | 0.84                            |
| "             | 600     | 49.1  | 0.84                            |
| "             | 800     | 49.1  | 0.84                            |
| 0.02          | 0       | 55.1  | 0.00                            |
| "             | 150     | 55.2  | 0.18                            |
| "             | 300     | 55.3  | 0.36                            |
| "             | 500     | 55.4  | 0.54                            |
| "             | 800     | 55.5  | 0.73                            |

The solution of 0.04 molar fraction cannot be obtained due to its solubility restriction.

Table 6. Cetyl alcohol  
( $C_{15}H_{31}CH_2OH$ ) in benzene.

| Concentration | Voltage | $t''$ | $\frac{\Delta t}{t} \times 100$ |
|---------------|---------|-------|---------------------------------|
| 0.01          | 0       | 45.0  | 0.00                            |
| "             | 300     | 45.1  | 0.22                            |
| "             | 500     | 45.2  | 0.44                            |
| "             | 600     | 45.2  | 0.44                            |
| "             | 700     | 45.2  | 0.44                            |
| "             | 800     | 45.2  | 0.44                            |
| 0.02          | 0       | 48.6  | 0.00                            |
| "             | 100     | 48.7  | 0.21                            |
| "             | 200     | 48.9  | 0.62                            |
| "             | 300     | 49.1  | 1.03                            |
| "             | 500     | 49.1  | 1.03                            |
| "             | 800     | 49.1  | 1.03                            |
| 0.04          | 0       | 54.5  | 0.00                            |
| "             | 100     | 55.9  | 0.73                            |
| "             | 200     | 56.8  | 2.39                            |
| "             | 300     | 57.3  | 5.14                            |
| "             | 400     | 57.4  | 5.32                            |
| "             | 500     | 57.4  | 5.32                            |
| "             | 550     | 57.8  | 6.05                            |
| "             | 600     | 58.2  | 6.78                            |
| "             | 700     | 58.5  | 7.34                            |
| "             | 800     | 58.5  | 7.34                            |
| "             | 800     | 58.9  | 8.08                            |
| "             | 900     | 59.3  | 8.80                            |
| "             | 1000    | 60.0  | 10.10                           |

Table 5. Stearic acid  
( $C_{17}H_{35}COOH$ ) in benzene.

| Concentration | Voltage | $t''$ | $\frac{\Delta t}{t} \times 100$ |
|---------------|---------|-------|---------------------------------|
| 0.01          | 0       | 48.2  | 0.00                            |
| "             | 300     | 48.3  | 0.21                            |
| "             | 500     | 48.4  | 0.42                            |
| "             | 800     | 48.4  | 0.42                            |
| 0.02          | 0       | 49.7  | 0.00                            |
| "             | 200     | 49.9  | 0.40                            |
| "             | 300     | 50.1  | 0.80                            |
| "             | 400     | 50.2  | 1.01                            |
| "             | 500     | 50.3  | 1.21                            |
| "             | 600     | 50.3  | 1.21                            |
| "             | 700     | 50.3  | 1.21                            |
| "             | 800     | 50.3  | 1.21                            |
| 0.04          | 0       | 61.7  | 0.00                            |
| "             | 100     | 62.0  | 0.49                            |
| "             | 200     | 62.5  | 1.30                            |
| "             | 300     | 64.2  | 4.05                            |
| "             | 400     | 65.0  | 5.35                            |
| "             | 500     | 65.0  | 5.35                            |
| "             | 600     | 65.0  | 5.35                            |
| "             | 700     | 65.0  | 5.35                            |
| "             | 800     | 65.0  | 5.35                            |

Table 7. Cetyl alcohol in hexane.

| Concentration | Voltage | $t''$ | $\frac{\Delta t}{t} \times 100$ |
|---------------|---------|-------|---------------------------------|
| 0.04          | 0       | 41.0  | 0.00                            |
| "             | 100     | 41.1  | 0.93                            |
| "             | 200     | 42.2  | 2.93                            |
| "             | 300     | 42.2  | 3.42                            |
| "             | 400     | 42.4  | 3.42                            |
| "             | 500     | 42.4  | 3.42                            |
| "             | 600     | 42.4  | 3.42                            |
| "             | 650     | 42.4  | 3.42                            |
| "             | 700     | 42.7  | 3.14                            |
| "             | 750     | 42.7  | 3.14                            |
| "             | 800     | 42.8  | 4.39                            |
| "             | 850     | 42.9  | 4.64                            |
| "             | 900     | 43.1  | 5.12                            |

In the earlier experiments, the remarkable electro-viscose effect was observed when the liquid touches electrodes directly; and little effect was observed when the liquid is insulated from electrode, say by glass

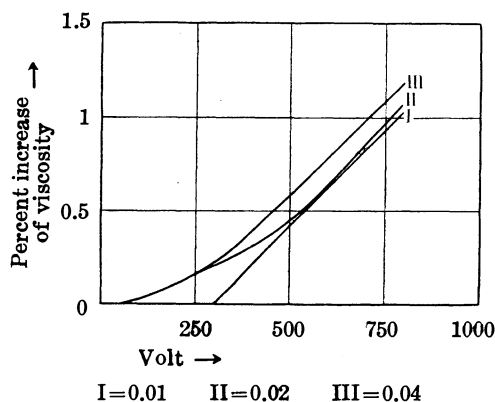


Fig. 2. Lauric acid in benzene.

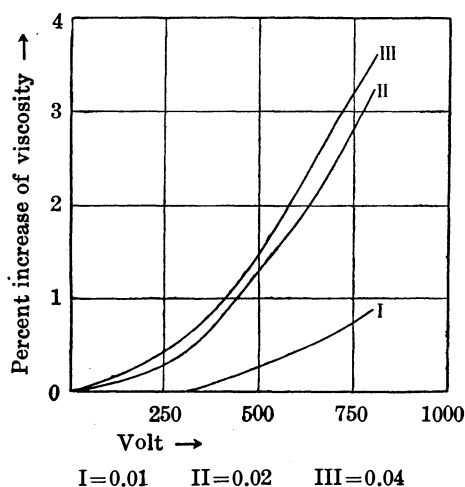


Fig. 3. Myristic acid in benzene.

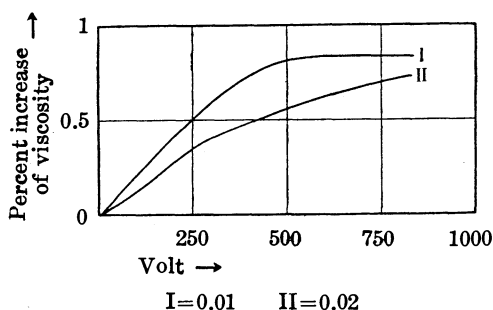


Fig. 4. Palmitic acid in benzene.

layer. This is partially due to the enormous drop of voltage in glass layer, and partially to the movement of ion in liquid. In fact, Sokolow<sup>(1)</sup> proved that this effect remarkably depends upon the conductivity of liquid, while electrolysis occurs at the same time when the liquid touches electrode directly, and may have some influences. Accordingly, in this case, the phenomenon is too complicated to give the proper interpretation. Therefore to minimize such disturbing influences it is necessary to insulate liquid from electrodes. It is for this reason that in the experiment the electrode was covered by oxide film to insulate it from liquid. The result of experiment clearly shows that in general the viscosity increases with voltage, but the way of increase is characteristic in each solution. This result is remarkable, considering that these substances are homologue. First, in the case of lauric acid, in which the number of carbon is least; the increase of viscosity is less noticeable than others, and is in linear relation with voltage. Next, in myristic acid in which the number of carbon is two more than that of lauric acid, the nature of curve is almost the same, but the increase is more noticeable. Although palmitic acid comes next, let us first take up the case of stearic acid. The form of curve is quite different, and viscosity increases proportionally with the increase of electric field so long as it is weak, but when it reaches a certain limiting value, the viscosity no

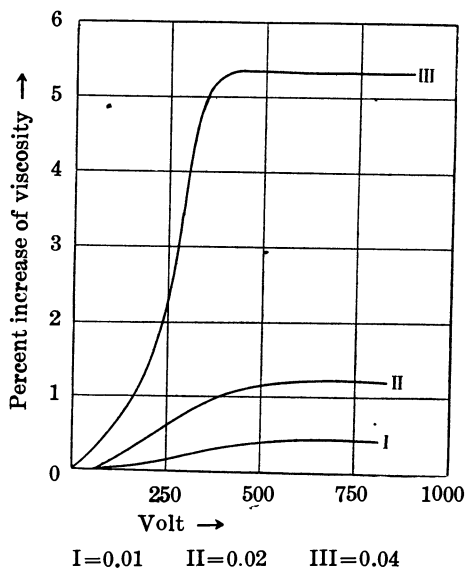


Fig. 5. Stearic acid in benzene.

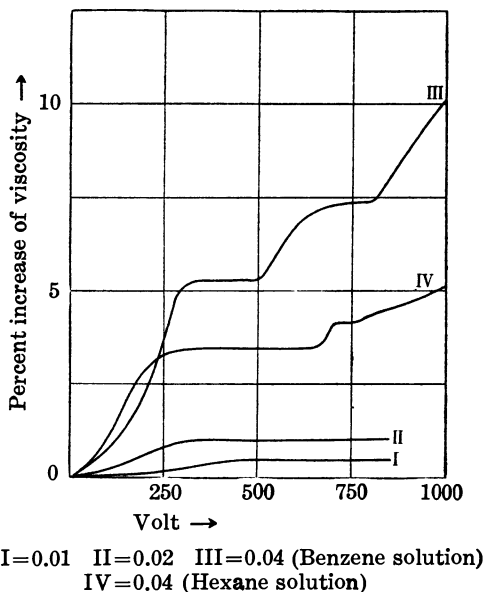


Fig. 6. Cetyl alcohol in benzene and hexane.

longer increases. This phenomenon is common in three different concentrations. The break point in the curves practically coincides with one another. Now let us consider palmitic acid, which lies between myristic and stearic acid in their number of carbon. The nature of curve again seems to be similar with those of two acids and lie between those of two acids. Now the curve of cetyl alcohol is the most characteristic as compared to the rest; in this case, as we see in the figure, the viscosity increases stepwise, and in the horizontal part of the curve for benzene solution corresponds with that of hexane solution, which shows that electroviscose effect is almost independent of the nature of solvent. Thus we can say that in homologue series, the longer the molecule of solute and the more concentrated a solution is, the greater the effect appears.

In general, if the solute has a dipole moment, the electric field will tend to orient the solute molecule in a direction which is parallel to the field. If  $F$  be the field strength and  $\mu$  the electric dipole moment of the molecule, the energy of the molecule due to the electric field will be  $\mu F \cos \alpha$ , where  $\alpha$  is the angle between the dipole axis and the direction of the electric field. There are also thermal energy and energy due to viscous flow associated with molecule. Thermal energy does not depend upon angle between the dipole axis and the direction of the electric field, hence it will cause no orientation of the molecules. Neglecting the viscous stress, we can compare the magnitude of electrical energy with that of thermal energy, as mentioned in the previous paper,<sup>(3)</sup> and obtain the following result that the number of molecules, which orients to the direction of electric field, is very few at the voltage which is realized in this experiment, and so if we raise the field intensity, the number of oriented molecules must increase, and also the viscosity. The above interpretation agrees with experimental results of lauric and myristic acids, and the

results for palmitic acid slightly deviates from the theory, while in stearic acid much more deviation is observed; hence it may be stated that longer the chain, the greater the deviation. This suggests us that the phenomenon may be influenced by some other additional factors. It is more complicated in the case of cetyl alcohol. The reason of this discrepancy from the theory is that the above-mentioned assumption is too simple to be applied in this case. The association of the molecule of solute may be an explanation. The fact that the greater the molecular weight, the easier to form associated molecules, agrees with these experimental results; and that in the case of cetyl alcohol the effect is independent of solvent also supports this theory.

### Summary.

(1) A capillary viscosimeter is made, to which electric field can be applied.

(2) By means of this viscosimeter, the viscosity of benzene and hexane solution of lauric, myristic, palmitic, and stearic acid and of cetyl alcohol is measured in the presence of electric field.

(3) The viscosity of these solutions generally increases in electric field, and the stronger the field the greater the increase. The acid with longer chain shows much more effect than one with the shorter. In a solution the effect is proportional to concentration.

(4) In lauric acid, the increase of viscosity shows a linear relation. In stearic acid, the increase ceases at a certain voltage.

(5) In cetyl alcohol the viscosity increases stepwise and the form of the viscosity-field intensity curve is independent of the nature of solvent.

(6) This electro-viscose effect is due to the orientation of molecules of solute.

(7) The irregularity of curves in stearic acid and cetyl alcohol seems to be the result from association.

In conclusion, the author wishes to express his sincere gratitude to Professor N. Sata who has been kind enough to give him guidance and encouragement throughout this research.

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## On the Nature of Foam. VI. Emulsion and Foam Formation of Ternary System, Ethyl Alcohol—Ethyl Ether—Water.

By Tunetaka SASAKI.

(Received April 24, 1939.)

It was indicated in the preceding papers<sup>(1)(2)</sup> that in ternary systems of acetic acid—ethyl ether—water (AEW) and acetic acid—benzene—water (ABW), the diagram showing the relation between foam formation and composition has two maxima, one of which being situated in the region where the system shows critical opalescence or anomalous viscosity. In the case of ternary system of ethyl alcohol—ethyl ether—water (EEW), however, it has been known that there exists no region of such critical opalescence.<sup>(3)</sup> It is interesting, therefore, to investigate whether this system has or lacks the maximum of foam formation corresponding to the absence of critical opalescence. Present paper describes the foam formation and the nature of emulsion of EEW-system.

**Experiments.** In ternary system of EEW, ethyl alcohol is soluble in all proportions both in ether and in water, while ethyl ether is hardly miscible with water. The mutual solubility curve of this system was obtained by the measurements of volume compositions of limiting turbid mixtures.<sup>(1)</sup> The data and the diagram are shown in Table 1 and in Fig. 1. Tie-lines were determined from a volume ratio of upper and lower

Table 1.

| Volume composition of limiting turbid mixture (c.c.) |             |       |
|------------------------------------------------------|-------------|-------|
| Ethyl alcohol                                        | Ethyl ether | Water |
| 0                                                    | 1.15        | 8.85  |
| 0                                                    | 9.80        | 0.20  |
| 1.45                                                 | 1.30        | 7.25  |
| 1.55                                                 | 7.75        | 0.70  |
| 2.40                                                 | 1.59        | 6.01  |
| 2.45                                                 | 6.12        | 1.43  |
| 2.52                                                 | 5.90        | 1.58  |
| 2.81                                                 | 2.52        | 4.67  |
| 2.81                                                 | 4.93        | 2.26  |
| 2.88                                                 | 3.52        | 3.60  |
| 2.92                                                 | 3.66        | 3.42  |

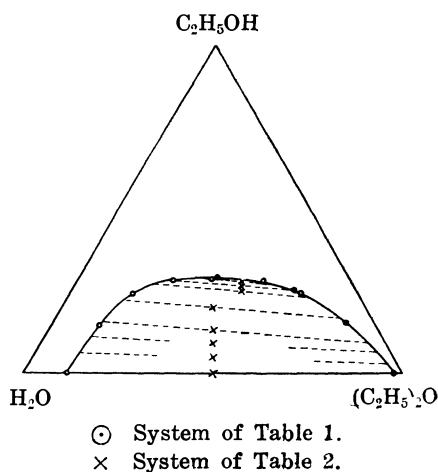


Fig. 1.

(1) Sasaki, this Bulletin, **13** (1938), 669.

(2) Sasaki, this Bulletin, **14** (1939), 3.

(3) Sata and Kimura, this Bulletin, **10** (1935), 409.

liquid layers ( $V_u$  and  $V_l$  respectively) coexisting in a heterogeneous system, as described in the preceding paper.<sup>(1)</sup> The data are shown in

Table 2 and are also depicted in Fig. 1.

Table 2.

| Composition in volume (c.c.) |             |       | Volume ratio |             |
|------------------------------|-------------|-------|--------------|-------------|
| Ethyl alcohol                | Ethyl ether | Water | Upper layer  | Lower layer |
| 0                            | 5.00        | 5.00  | 0.818        | 1.000       |
| 0.48                         | 4.76        | 4.76  | 0.763        | 1.000       |
| 0.90                         | 4.55        | 4.55  | 0.742        | 1.000       |
| 1.30                         | 4.35        | 4.35  | 0.707        | 1.000       |
| 2.00                         | 4.00        | 4.00  | 0.700        | 1.000       |
| 2.50                         | 4.50        | 3.00  | 1.334        | 1.000       |
| 2.65                         | 4.41        | 2.94  | 1.390        | 1.000       |
| 2.79                         | 4.33        | 2.88  | 1.630        | 1.000       |

The measurements of the foam stability were then undertaken for homogeneous and heterogeneous systems of EEW, using the same shaking apparatus and on the same conditions as described in the preceding paper.<sup>(1)</sup> A constant volume (10 c.c.) of liquid for measurement is introduced in a test tube of 1.5 cm. in diameter and 15 cm. in length, and is shaken 300 times for 10 seconds with amplitude of 12 cm. The time required from immediately after the stop of shaking to the complete collapse of foam zone was measured and was considered to be the stability of foam. The height of foam was not measured for the sake of simplicity. Some of the results of measurements are shown in Table 3, the data of which are shown diagrammatically in Fig. 2.

Table 3.

| Composition in volume (c.c.) |             |       | Stability of foam (second) | Composition in volume (c.c.) |             |       | Stability of foam (second) |
|------------------------------|-------------|-------|----------------------------|------------------------------|-------------|-------|----------------------------|
| Ethyl alcohol                | Ethyl ether | Water |                            | Ethyl alcohol                | Ethyl ether | Water |                            |
| 0                            | 1.15        | 8.85  | 0                          | 2.60                         | 3.70        | 3.70  | 1.3                        |
| 0                            | 9.80        | 0.20  | 0                          | 2.70                         | 3.10        | 4.20  | 0                          |
| 0.25                         | 0           | 9.75  | 6.1                        | 2.86                         | 2.80        | 4.34  | 0                          |
| 0.50                         | 0           | 9.50  | 7.3                        | 2.90                         | 3.40        | 3.70  | 1.8                        |
| 0.50                         | 0.50        | 9.00  | 2.2                        | 2.93                         | 3.70        | 3.40  | 0                          |
| 0.50                         | 1.00        | 8.50  | 1.7                        | 2.90                         | 5.10        | 2.00  | 3.1                        |
| 0.98                         | 1.22        | 7.80  | 1.8                        | 3.00                         | 2.00        | 5.00  | 10.6                       |
| 1.00                         | 0.50        | 8.50  | 4.6                        | 3.00                         | 2.50        | 4.50  | 17.9                       |
| 1.20                         | 5.80        | 3.00  | 0                          | 3.00                         | 3.00        | 4.00  | 36.9                       |
| 1.50                         | 0           | 8.50  | 3.9                        | 3.00                         | 3.50        | 3.50  | 22.4                       |
| 1.50                         | 1.00        | 7.50  | 1.8                        | 3.00                         | 4.00        | 3.00  | 22.2                       |
| 1.50                         | 7.00        | 1.50  | 1.2                        | 3.00                         | 4.50        | 2.50  | 6.8                        |
| 1.90                         | 1.40        | 6.70  | 0                          | 3.50                         | 0           | 6.50  | 2.6                        |
| 2.00                         | 0.50        | 7.50  | 2.3                        | 3.50                         | 3.00        | 3.50  | 4.2                        |
| 2.00                         | 1.00        | 7.00  | 8.9                        | 3.50                         | 3.80        | 2.70  | 3.0                        |
| 2.00                         | 5.50        | 2.50  | 1.4                        | 4.00                         | 1.00        | 5.00  | 2.6                        |
| 2.20                         | 3.90        | 3.90  | 0.5                        | 4.50                         | 3.00        | 2.50  | 1.5                        |
| 2.50                         | 1.00        | 6.50  | 2.9                        | 5.00                         | 5.00        | 0     | 0                          |
| 2.50                         | 4.50        | 3.00  | 1.7                        | 6.00                         | 2.00        | 2.00  | 0.5                        |
| 2.50                         | 6.00        | 1.50  | 2.6                        | 7.50                         | 2.50        | 0     | 0                          |
| 2.50                         | 7.50        | 0     | 0                          |                              |             |       |                            |



Table 4.

| Composition in volume (c.c.) |             |       | Type of emulsion produced by shaking of the mode |        |
|------------------------------|-------------|-------|--------------------------------------------------|--------|
| Ethyl alcohol                | Ethyl ether | Water | (1)                                              | (2)    |
| 2.90                         | 3.70        | 3.40  | O-in-W                                           | O-in-W |
| 2.80                         | 3.40        | 3.80  | O-in-W                                           | O-in-W |
| 2.79                         | 3.75        | 3.46  | O-in-W                                           | W-in-O |
| 2.75                         | 3.30        | 3.95  | O-in-W                                           | W-in-O |
| 2.71                         | 3.93        | 3.36  | W-in-O                                           | W-in-O |
| 2.70                         | 3.65        | 3.65  | O-in-W                                           | W-in-O |
| 2.59                         | 3.89        | 3.52  | W-in-O                                           | W-in-O |
| 2.55                         | 3.04        | 4.41  | O-in-W                                           | W-in-O |
| 2.45                         | 3.30        | 4.25  | O-in-W                                           | W-in-O |
| 2.40                         | 2.60        | 5.00  | O-in-W                                           | O-in-W |
| 2.35                         | 2.75        | 4.90  | O-in-W                                           | W-in-O |
| 2.18                         | 3.27        | 4.55  | O-in-W                                           | W-in-O |
| 2.14                         | 3.39        | 4.47  | W-in-O                                           | W-in-O |
| 1.80                         | 2.50        | 5.70  | O-in-W                                           | O-in-W |
| 1.75                         | 2.72        | 5.53  | O-in-W                                           | W-in-O |
| 1.54                         | 3.59        | 4.87  | O-in-W                                           | W-in-O |
| 1.50                         | 3.75        | 4.75  | W-in-O                                           | W-in-O |
| 1.00                         | 2.80        | 6.20  | O-in-W                                           | O-in-W |
| 0.98                         | 2.94        | 6.08  | O-in-W                                           | W-in-O |
| 0.88                         | 3.68        | 5.44  | O-in-W                                           | W-in-O |
| 0.86                         | 3.84        | 5.30  | W-in-O                                           | W-in-O |
| 0.50                         | 3.00        | 6.50  | O-in-W                                           | O-in-W |
| 0.48                         | 3.27        | 6.25  | O-in-W                                           | W-in-O |
| 0.44                         | 3.86        | 5.70  | O-in-W                                           | W-in-O |
| 0.43                         | 4.02        | 5.55  | W-in-O                                           | W-in-O |
| 0                            | 4.35        | 5.65  | W-in-O                                           | W-in-O |
| 0                            | 4.12        | 5.88  | C-type*                                          | W-in-O |
| 0                            | 3.86        | 6.14  | C-type*                                          | W-in-O |
| 0                            | 3.75        | 6.25  | O-in-W                                           | O-in-W |

\* Complex type i.e. the upper layer is W-in-O type and the lower layer, O-in-W type.

results are shown in Table 4. These data are depicted in Fig. 3. In this figure, A and B represent the region in which systems show only one type of emulsion, W-in-O and O-in-W types respectively, whatever the modes of shaking, and C represents the region in which systems show the tendency to produce both types of emulsions according to the above two modes of shaking.

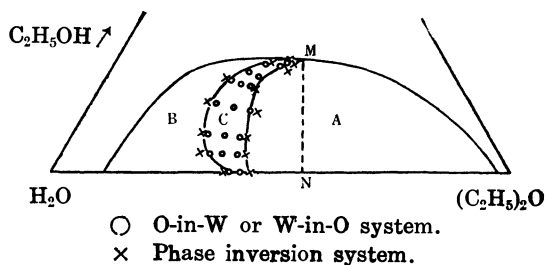


Fig. 3.

In the phase inversion zone, a series of systems, varying in volume ratio of upper and lower liquid layers of nearly definite compositions respectively, were investigated in order to see the effect of volume to the nature of emulsion produced by shaking. In this measurements, 10 c.c. of a system is taken in a test tube and the following three modes of shaking are applied to it.

- (1) The mode of shaking described in (1) of Table 4.
- (2) The mode of shaking described in (2) of Table 4.
- (3) Usual up-and-down shaking only is applied from the beginning.

The type of emulsion produced by above three modes of shaking are determined from the behaviours of breaking up of emulsion in the same manner as described before. The stability of emulsion, that is, the time required from immediately after shaking to the complete collapse of emulsion droplets, was also measured. The results are shown in Table 5.

**Discussion.** The diagram of the foam stability of EEW-system, as a whole, is similar in the shape to that of ABW-<sup>(2)</sup> and especially to AEW-system.<sup>(1)</sup> In the homogeneous region, surface of the diagram is steep along ethyl alcohol-water line and particularly the steepest along a portion of mutual solubility curve, while it has a gentle slope towards ethyl ether-ethyl alcohol line. The stability of foam shows maxima at three points P, Q and R in Fig. 2. Point P corresponds to the maxima of foam stability of binary mixture, ethyl alcohol-water, which has already been determined from the measurement of foam stability by another method.<sup>(6)</sup> The maximum point Q is situated along the mutual solubility curve and the degree of stability at this point far more exceeds that at P. These relations are quite similar to AEW-system.<sup>(1)</sup>

It was suggested in AEW-<sup>(1)</sup> and especially in ABW-system<sup>(2)</sup> that such region of remarkable foam stability and the region of critical opalescence or anomalous viscosity take the same position. Such regions are also near the point of intersection (M in Fig. 2) made by the mutual solubility curve and the locus of middle points of tie-lines. In the heterogeneous system near this point, the physical properties of upper and lower liquid layers closely resemble each other and the system shows the nature of colloidal solution when shaken. The maximum of foam formation as well as critical opalescence and anomalous viscosity was explained from this colloidal nature in the preceding papers.<sup>(1)(2)</sup> In the present case of EEW-system, the foam stability shows its maximum at point Q, although it is known that critical opalescence is absent in this system.<sup>(3)</sup> The point Q is also situated in the vicinity of the point of intersection (M) made by the mutual solubility curve and the locus of middle points of tie-lines. Maximum of foam stability can also be seen at point R, but it is rather uncertain as the vicinity of this point was not precisely investigated.

The diagram of foam stability in the heterogeneous region of EEW-system, like that of AEW-system, consists of two parts, foamy and non foamy regions which are represented as A' and B', respectively, in Fig. 2.

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(6) Sasaki, this Bulletin, **13** (1938), 517.

In a heterogeneous system of A' region, foam can be produced on shaking, because a lower liquid layer of larger surface tension and smaller volume is dispersed in an upper one, and the foam formation was not prevented by these emulsion drops as was described in the preceding paper.<sup>(1)</sup> In a heterogeneous system of B' region, an upper liquid layer of smaller surface tension and smaller volume is dispersed in a lower one on shaking.<sup>(1)</sup> In such conditions, the film of foam is destroyed by emulsion droplets and the system does not foam on shaking. Frequently, emulsion droplets containing air bubbles are obtained on shaking in the case where emulsion droplets have considerably smaller surface tension than the dispersing medium as in the case of AEW-system.

The heterogeneous region is divided into three portions A, B and C, referring to the type of emulsion produced by shaking as shown in Fig. 3. In a heterogeneous system of A region, the upper liquid layer is generally excessive in volume compared with the lower one and the system shows the tendency of the lower layer being dispersed in the upper one, namely, W-in-O emulsion results whatever the modes of shaking.<sup>(4)</sup> A heterogeneous system of B region, in the same manner, shows the tendency of the upper layer being dispersed in the lower one and O-in-W emulsion results, independent of the modes of shaking. The region A also involves systems in which a lower layer is slightly excessive in volume than the upper one, and yet the former is dispersed in the latter. The system of C region shows the tendency of producing both types of emulsion according to the two different modes of shaking. The modes of shaking described in (1) favours to produce O-in-W emulsion and the shaking of the mode (2) favours to produce W-in-O emulsion. These relations between mode of shaking and type of resulting emulsion is similar to those of AEW- and ABW-systems, and they can also be explained in the same manner.<sup>(4)</sup> The region C is also called the zone of phase inversion by shaking. It can be seen that this zone of phase inversion is not situated along the line MN. It is not necessary for the phase inversion system that volumes of upper and lower layers are equal, as in the case of AEW-<sup>(4)</sup> and ABW-systems.<sup>(5)</sup> The behaviours of a system belonging to the zone of phase inversion was precisely studied and are tabulated in Table 5. It can be seen in this table that the behaviours of phase inversion systems to the shaking gradually change with relative volume ratio of coexisting upper and lower liquid layers.

The phase inversion system (a) which has relatively smaller value of  $V_u/V_l$ , namely, which is situated close to the region B, shows a strong tendency to become O-in-W emulsion by shaking of the modes (1) and (3). W-in-O emulsion which is produced only by careful shaking of the mode (2), readily turns to O-in-W emulsion by a slight up-and-down shaking. In system (b) and (c) which have a little larger value of  $V_u/V_l$  than that of the system (a), O-in-W emulsion becomes also selectively produced by the usual up-and-down shaking of the mode (3) as in the system (a), but the tendency to produce W-in-O is more remarkable in (b) and (c) than in (a). W-in-O emulsion produced in the systems (b) and (c) by shaking of the mode (2) can be inverted to O-in-W emulsion only by a strong shaking. This tendency is even more conspicuous in the system (d). In this system, both types of emulsion once established by shakings

of the modes (1) and (2) cannot be inverted each other, even by a violent shaking. In the system (d), however, there is still difference between the tendency of producing O-in-W emulsion and that of W-in-O emulsion. Emulsion of the former type is selectively produced by the usual up-and-down shaking. The tendency of producing W-in-O emulsion becomes still more marked until, at last, in system (e) and (f) which have more higher values of  $V_u/V_l$  than that of (d), the tendencies of producing both types of emulsions become equal. In such systems, two possible types of emulsions produced by shaking of the modes (1) and (2) cannot of course be inverted each other by any shaking. Moreover, usual up-and-down shaking occasionally produces both types of emulsions. Thus, in systems (e) and (f), two types of emulsions are utterly equal in their tendencies of formation on shaking. These system are, therefore, considered to be the true intermediate or boundary systems between W-in-O and O-in-W regions (A and B regions), but it is not necessary that these systems should be equally distant from both of these regions. The tendency of producing W-in-O emulsion overcomes that of O-in-W emulsion as we go further from (f) to (i) (namely, as a system approaches A region), and the emulsion of the former type is selectively

Table 5.

| System | Composition in volume (c.c.) |             |       | Volume ratio |             | Type and stability of emulsion produced by shaking of the mode |     |            |
|--------|------------------------------|-------------|-------|--------------|-------------|----------------------------------------------------------------|-----|------------|
|        | Ethyl alcohol                | Ethyl ether | Water | Upper layer  | Lower layer | (1)                                                            | (2) | (3)        |
| (a)    | 1.50                         | 2.70        | 5.80  | 0.259        | 1.000       | { O-in-W $\longleftrightarrow$ W-in-O<br>$S_e = 8$ $S_e = 10$  |     | O-in-W     |
| (b)    | 1.50                         | 2.80        | 5.70  | 0.293        | 1.000       | { O-in-W $\longleftarrow$ W-in-O<br>$S_e = 8$ $S_e = 11$       |     | O-in-W     |
| (c)    | 1.50                         | 3.00        | 5.50  | 0.348        | 1.000       | { O-in-W $\longleftarrow$ W-in-O<br>$S_e = 8$ $S_e = 12$       |     | O-in-W     |
| (d)    | 1.50                         | 3.10        | 5.40  | 0.372        | 1.000       | { O-in-W $\longleftrightarrow$ W-in-O<br>$S_e = 9$ $S_e = 14$  |     | O-in-W     |
| (e)    | 1.50                         | 3.20        | 5.30  | 0.380        | 1.000       | { O-in-W $\longleftrightarrow$ W-in-O<br>$S_e = 7$ $S_e = 12$  |     | both types |
| (f)    | 1.50                         | 3.30        | 5.20  | 0.400        | 1.000       | { O-in-W $\longleftrightarrow$ W-in-O<br>$S_e = 8$ $S_e = 14$  |     | both types |
| (g)    | 1.50                         | 3.40        | 5.10  | 0.448        | 1.000       | { O-in-W $\longleftrightarrow$ W-in-O<br>$S_e = 10$ $S_e = 15$ |     | W-in-O     |
| (h)    | 1.50                         | 3.45        | 5.05  | 0.470        | 1.000       | { O-in-W $\longleftrightarrow$ W-in-O<br>$S_e = 10$ $S_e = 16$ |     | W-in-O     |
| (i)    | 1.50                         | 3.50        | 5.00  | 0.485        | 1.000       | { O-in-W $\longrightarrow$ W-in-O<br>$S_e = 9$ $S_e = 15$      |     | W-in-O     |

$S_e$  denotes the stability of emulsion in second.

$\longleftrightarrow$  inversion with ease by shaking of the mode (3).

$\longleftarrow$  inversion with difficulty.

$\longleftrightarrow$  no inversion.

established by up-and-down shaking. The tendency of inversion from O-in-W to W-in-O also increases as the system approaches the region A. These relations can be seen in Table 5 and in Fig. 4.

In the heterogeneous binary system of ethyl ether and water, phase inversion by shaking does not occur, but some systems exhibit complex dispersion, producing both types of emulsions simultaneously by shaking.

It can also be pointed out that the stability of emulsion ( $S_e$ ) is not always parallel to its tendency of formation.<sup>(4)</sup> In Table 4, W-in-O emulsion is more stable than O-in-W emulsion throughout all systems of phase inversion zone, but in systems of (a), (b), (c) and (d), unstable O-in-W emulsion is selectively produced by usual up-and-down shaking. It is noted further that the tendency of producing W-in-O emulsion increases with its stability, but the increase of the tendency of producing O-in-W emulsion is not parallel to its stability.

In the heterogeneous system of EEW, there exists foam-nonfoam system, that is, the system which behaves both foamy and non foamy according to the different modes of shaking. It was indicated in the preceding paper<sup>(4)</sup> that the existence of the foam-nonfoam system is restricted in such a portion of foamy region in the heterogeneous system as it makes, at the same time, a portion of phase inversion zones. In Fig. 4, A' surrounded by dotted line shows the foamy region of heterogeneous system of EEW, and C represents the zone of phase inversion. Hatched portion, therefore, indicates the foam-nonfoam region. The situation and nature of phase inversion system of EEW is just similar to that of AEW.<sup>(4)</sup> It foams when it is shaken by the mode (2), while it does not foam by the shaking of the mode (1).

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his valuable advice and the inspection of this paper. The expense for the experiment is defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

### Summary.

(1) The mutual solubility curve, tie-lines and the foam stability of homogeneous and heterogeneous system of ethyl alcohol-ethyl ether-water (EEW) were measured. The diagram was established to show the relation between the foam stability and the composition. It shows two maxima of foam stability, one of which is situated along the mutual solubility curve, and the other is on the line of ethyl alcohol-water. The former is more remarkable in its magnitude than the latter as in the system of acetic acid-ethyl ether-water (AEW). The diagram shows the third maximum of foam stability but it is uncertain.

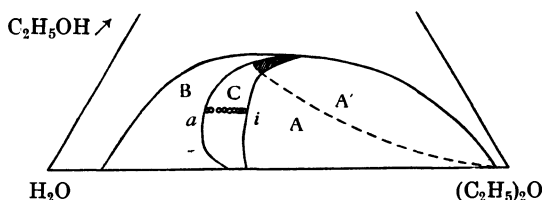


Fig. 4.



(2) Heterogeneous system of EEW is divided into three portions referring to the type of emulsion produced by shaking, namely, W-in-O region, O-in-W region and phase inversion zone. In W-in-O or O-in-W region, a system simply produces W-in-O or O-in-W emulsion respectively, whatever the modes of shaking, while in the phase inversion zone, a system occasionally produces both types of emulsion according to the two different modes of shaking. In the phase inversion zone, the tendency to produce W-in-O emulsion gradually decreases and the tendency to produce O-in-W emulsion increases as a system changes in composition from those near W-in-O region to those near O-in-W region.

(3) Foam-nonfoam system can also be observed in this system as in AEW or acetic acid-benzene-water system. The region of its existence was determined.

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## The Effect of the Silent Electrical Discharge on the Synthesis of Monochloroacetic Acid.

By Yutaka ISOMURA.

(Received May 2, 1939.)

### I. Red Phosphorus as Catalyser.

Monochloroacetic acid has been simply prepared with catalysers such as red phosphorus,<sup>(1)</sup> iodine,<sup>(1)</sup> sulphur,<sup>(2)</sup> etc., by bubbling vigorously gaseous chlorine into acetic acid in direct sun-light and its yield has never exceeded 60.6%.<sup>(3)</sup> In the present research, instead of direct sun-light, the silent electrical discharge was applied for the activation of chlorine and it was found that the discharge is so effective as to increase 15–100% of the best yield of monochloroacetic acid ever obtained.

*Apparatus.* The usual apparatus (Fig. 1) was improved as shown in Fig. 2, to increase the effect of the discharge. An induction coil is used (primary circuit: constant current of 3 A., 8 V.; secondary circuit: 0.25 mA., 14000 V.).

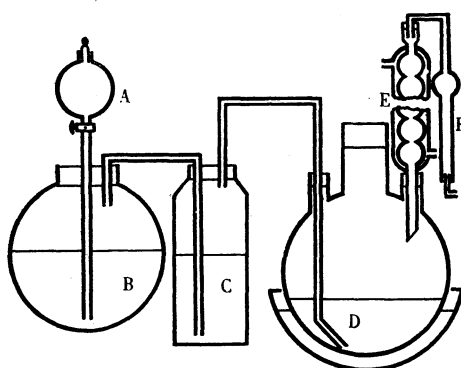
*Experimental.* At every run of experiments the followings have been kept the same: temperature, 100°C., 7 g. of red phosphorus, and 70 c.c. of acetic acid (99–100%), while the volume of chlorine passed

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(1) H. Müller, *Ann.*, **133** (1865), 156.

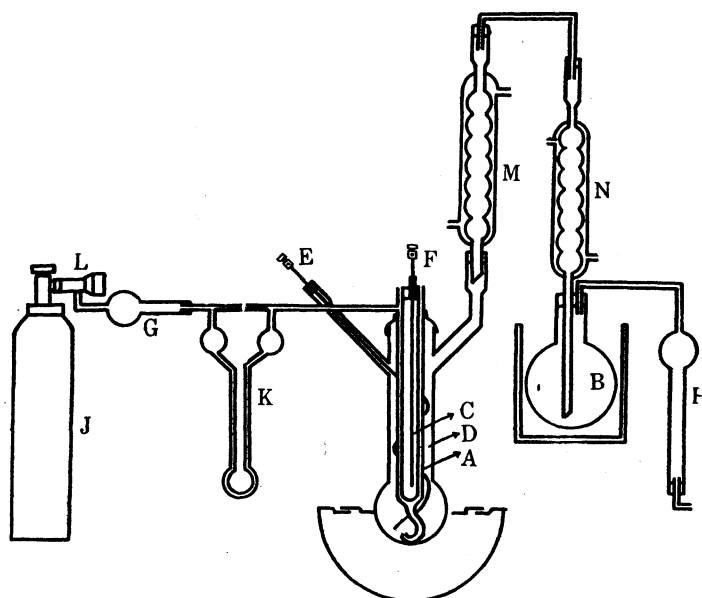
(2) Anger and Behall, *Bull. s. c. chim.*, [3], **2** (1889), 145.

(3) Cohen, "Practical Organic Chemistry", 106, London (1930).



A: Conc.  $\text{H}_2\text{SO}_4$                       D:  $\text{CH}_3\text{COOH}$  + catalyser  
 B:  $\text{CaOCl}_2$                               E: 50 cm. Liebig Condenser  
 C: Conc.  $\text{H}_2\text{SO}_4$                       F:  $\text{CaCl}_2$  tube.

Fig. 1.



A: Outside electrode.                      G, H:  $\text{CaCl}_2$  tube.  
 B:  $\text{CH}_3\text{COCl}$  collector. (cooled by  
     immersing in ice water)              J:  $\text{Cl}_2$  bomb.  
 C: Inner electrode in dil.  $\text{H}_2\text{SO}_4$ .      K:  $\text{Cl}_2$  flowmeter.  
 D:  $\text{CH}_3\text{COOH}$  + catalyser.              L: Microdrive auxiliary valve.  
 E: To the earth.                            M: 50 cm. Liebig condenser.  
 F: To the secondary circuit of the      N: 40 cm. Liebig condenser.  
     induction coil.

Fig. 2.

into acetic acid in unit time and the duration of the reaction have been varied. The experimental results are shown in Table 1-3, and Fig. 3-8.

There is a linear relation between the pressure difference of chlorine in the flowmeter and the volume of chlorine bubbled into acetic acid per minute, as is shown in Fig. 3.

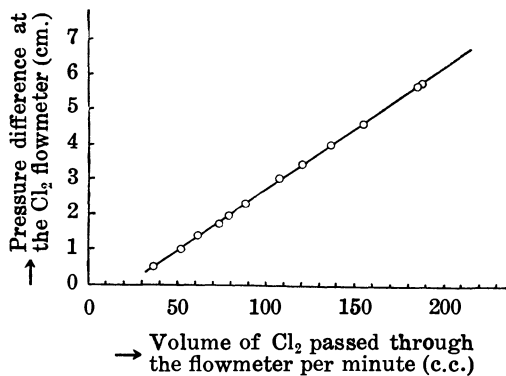


Fig. 3.

Careful observations of the reaction permit attention to the following points as to the mechanism of the reaction.

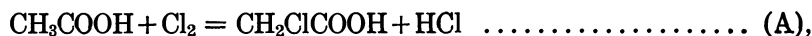
(1) An abundant quantity of acetyl chloride is formed in the reaction.

(2) The behaviour of phosphorus as catalyser is not a simple carrier of chlorine and it is often dissolved completely into the reacting system. By the quantitative analysis on the residue of the distillation, the

following substance are found in the extracts by water.



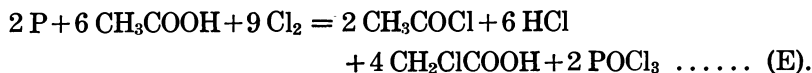
(3) The equation which was formerly believed to explain the reaction being



the values  $\frac{\text{Observed yield of monochloroacetic acid}}{\text{Theoretical yield by the equation (A)}} \times 100$  and

$\frac{\text{Volume of chlorine calculated from the yield of monochloroacetic acid by the equation (A)}}{\text{Total chlorine bubbled into the system}} \times 100$  (for example, the yield of monochloroacetic acid by passing 222 c.c. of chlorine per minute for four hours with the discharge), are too small to explain the completion of the reaction as is shown in Table 3.

To clear up these points and to modify the former views about the mechanisms of the reaction, the following new equation is proposed by the author. The equation is made up in a simple form from many individual processes which were previously investigated by Brückner<sup>(4)</sup>. That is



Judging from the values calculated by the equation (E) in the Table 1-3 and in Fig. 4-8, it will be found that the above mentioned points are cleared up by this equation. Though it may not be of an exclusive nature, it will at least indicate the principal mechanism of the reaction.

(4) Brückner, *Z. angew. Chem.*, **50** (1928), 226.

Table 1. Acetic acid : 70 c.c. ; Duration of reaction : 2 hours ; Catalyser : red phosphorus 7 g.

| No. of experiments                                                                                | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    |
|---------------------------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Preess. diff. at the Cl <sub>2</sub> flowmeter (cm.)                                              | 3     | 3     | 4     | 4     | 4.5   | 5     | 5     | 6     | 6     | 7     | 7     | 7     |
| Duration of electric discharge (hours)                                                            | —     | 2     | —     | 2     | 2     | —     | 2     | —     | 2     | —     | 2     | 2     |
| Total vol. of Cl <sub>2</sub> passed<br>at 0°, 1 atm. (litres)                                    | 12.2  | 12.2  | 15.2  | 15.2  | 16.85 | 18.55 | 18.55 | 21.71 | 22.63 | 25.13 | 25.13 | 25.15 |
| Total yield of CH <sub>3</sub> ClCOOH (g.)                                                        | 4     | 6     | 8     | 11    | 14    | 9     | 15    | 11    | 19    | 14    | 26    | 22    |
| $\frac{\text{CH}_3\text{ClCOOH produced}}{\text{CH}_3\text{COOH taken}} \times 100$               | 5.55  | 8.17  | 10.85 | 15.0  | 19.1  | 12.2  | 20.5  | 15.0  | 27.2  | 19.1  | 35.5  | 29.9  |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$                        | 3.44  | 5.15  | 6.88  | 9.5   | 12.05 | 7.75  | 12.9  | 9.5   | 17.2  | 12.05 | 22.3  | 18.93 |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$                        | 5.18  | 7.78  | 10.35 | 14.18 | 18.2  | 11.62 | 19.5  | 14.18 | 26.0  | 18.2  | 33.7  | 28.5  |
| Yield per litre of Cl <sub>2</sub> (g.)                                                           | 0.33  | 0.49  | 0.53  | 0.73  | 0.85  | 0.48  | 0.82  | 0.51  | 0.88  | 0.56  | 1.03  | 0.87  |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (A)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 7.78  | 11.66 | 12.2  | 17.14 | 19.7  | 14.46 | 19.17 | 15.3  | 20.82 | 13.2  | 24.52 | 20.74 |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (E)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 17.48 | 26.2  | 28.06 | 38.55 | 44.32 | 25.85 | 43.1  | 34.37 | 46.83 | 29.7  | 55.15 | 46.6  |
| CH <sub>3</sub> COCl in the collector (g.)                                                        | 2     | 2     | 2     | 2     | 2     | 2     | 3     | 3     | 3     | 3     | 4     | 4     |

Table 2. Acetic acid : 70 c.c. ; Duration of reaction : 3 hours ; Catalyser : red phosphorus 7 g.

| No. of experiments                                                                                | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13   |
|---------------------------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| Press. diff. at the Cl <sub>2</sub> flowmeter (cm.)                                               | 2     | 2     | 3     | 3     | 4     | 4     | 5     | 5     | 6     | 6     | 6     | 7     | 7    |
| Duration of electric discharge (hours)                                                            | —     | 3     | —     | 3     | —     | 3     | —     | 3     | —     | 3     | 3     | —     | 3    |
| Total vol. of Cl <sub>2</sub> passed<br>at 0°, 1 atm. (litres)                                    | 13.52 | 13.52 | 18.34 | 18.56 | 22.95 | 22.65 | 27.93 | 28.38 | 32.37 | 32.91 | 32.91 | 37.10 | 37.8 |
| Total yield of CH <sub>3</sub> ClCOOH (g.)                                                        | 10    | 17    | 18    | 23    | 25    | 35    | 34    | 45    | 40    | 48    | 49    | 45    | 54   |
| $\frac{\text{CH}_3\text{ClCOOH produced}}{\text{CH}_3\text{COOH taken}} \times 100$               | 13.6  | 23.2  | 24.5  | 38.2  | 34.0  | 47.7  | 46.0  | 61.2  | 53.6  | 65.3  | 66.8  | 61.2  | 73.5 |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$                        | 8.6   | 14.7  | 15.4  | 24.1  | 21.5  | 30.1  | 29.2  | 38.7  | 34.4  | 41.3  | 42.1  | 38.7  | 46.6 |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$                        | 12.95 | 22.1  | 23.3  | 36.3  | 32.3  | 45.5  | 44.0  | 58.5  | 52.0  | 62.2  | 63.5  | 58.5  | 70.0 |
| Yield per litre of Cl <sub>2</sub> (g.)                                                           | 0.74  | 1.25  | 0.99  | 1.51  | 1.09  | 1.55  | 1.22  | 1.58  | 1.24  | 1.46  | 1.49  | 1.21  | 1.43 |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (A)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 17.53 | 29.81 | 23.10 | 35.8  | 25.8  | 36.6  | 23.9  | 37.6  | 29.3  | 34.52 | 35.3  | 28.8  | 33.8 |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (E)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 39.3  | 67.06 | 52.35 | 80.46 | 57.83 | 82.4  | 64.9  | 84.5  | 65.9  | 77.8  | 79.4  | 64.7  | 76.2 |
| CH <sub>3</sub> COCl in the collector (g.)                                                        | 3     | 3     | 5     | ?     | 8     | 8     | 10    | 8     | 10    | 10    | 6     | 4     | 5    |

Table 3. Acetic acid : 70 c.c. ; Duration of reaction : 4 hours ; Catalyser : red phosphorus 7 g.

| No. of experiments                                                                                | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    |
|---------------------------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Press. diff. at the Cl <sub>2</sub> flowmeter (cm.)                                               | 1.4   | 1.4   | 2     | 2     | 2     | 2     | 2.75  | 2.75  | 2.75  | 2.75  | 4     |
| Duration of electric discharge (hours)                                                            | —     | 4     | —     | —     | 4     | 4     | —     | —     | 4     | 4     | —     |
| Total vol. of Cl <sub>2</sub> passed<br>at 0°, 1 atm. (litres)                                    | 13.97 | 14.01 | 17.47 | 17.92 | 17.83 | 17.93 | 22.31 | 21.96 | 22.30 | 22.14 | 30.59 |
| Total yield of CH <sub>3</sub> ClCOOH (g.)                                                        | 5     | 12    | 9     | 12.2  | 19.8  | 18    | 15    | 17    | 32.3  | 34.3  | 30.5  |
| $\frac{\text{CH}_3\text{ClCOOH produced}}{\text{CH}_3\text{COOH taken}} \times 100$               | 6.8   | 16.3  | 12.2  | 16.6  | 26.9  | 24.5  | 20.3  | 23.0  | 43.7  | 46.4  | 41.5  |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$                        | 4.3   | 10.3  | 7.7   | 10.5  | 17.0  | 15.5  | 12.9  | 14.6  | 27.8  | 29.5  | 26.2  |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$                        | 6.5   | 15.6  | 12.2  | 16.1  | 25.7  | 23.3  | 19.4  | 22.2  | 42.0  | 44.0  | 39.5  |
| Yield per litre of Cl <sub>2</sub> (g.)                                                           | 0.36  | 0.86  | 0.52  | 0.67  | 1.11  | 1.0   | 0.67  | 0.78  | 1.44  | 1.56  | 0.99  |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (A)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 8.48  | 20.3  | 12.2  | 16.1  | 26.3  | 26.5  | 15.9  | 18.4  | 34.4  | 36.8  | 23.6  |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (E)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 19.1  | 45.7  | 27.5  | 36.3  | 59.2  | 53.5  | 35.9  | 41.3  | 77.3  | 82.6  | 53.2  |
| CH <sub>3</sub> COCl in the collector (g.)                                                        | 3     | 5     | 5     | 8     | 8     | 8     | 8     | 8     | 8     | 10    | 15    |
| No. of experiments                                                                                | 12    | 13    | 14    | 15    | 16    | 17    | 18    | 19    | 20    | 21    |       |
| Press. diff. at the Cl <sub>2</sub> flowmeter (cm.)                                               | 4     | 4     | 4     | 5     | 5     | 6     | 6     | 6     | 7     | 7     |       |
| Duration of electric discharge (hours)                                                            | —     | 4     | 4     | —     | 4     | —     | 4     | 4     | —     | 4     |       |
| Total vol. of Cl <sub>2</sub> passed<br>at 0°, 1 atm. (litres)                                    | 30.66 | 30.37 | 30.70 | 37.74 | 36.78 | 43.78 | 43.18 | 43.2  | 50.86 | 49.73 |       |
| Total yield of CH <sub>3</sub> ClCOOH (g.)                                                        | 29    | 47    | 46    | 40    | 62    | 49    | 70    | 68    | 54    | 73    |       |
| $\frac{\text{CH}_3\text{ClCOOH produced}}{\text{CH}_3\text{COOH taken}} \times 100$               | 39.4  | 63.9  | 62.7  | 53.1  | 87.0  | 67.0  | 95.2  | 92.5  | 73.7  | 99.3  |       |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$                        | 25.0  | 40.4  | 39.5  | 34.4  | 56.0  | 42.3  | 60.2  | 58.5  | 46.5  | 62.8  |       |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$                        | 37.6  | 61.0  | 59.6  | 51.8  | 80.5  | 63.5  | 91.0  | 88.0  | 70.0  | 94.5  |       |
| Yield per litre of Cl <sub>2</sub> (g.)                                                           | 0.94  | 1.52  | 1.50  | 1.06  | 1.68  | 1.12  | 1.62  | 1.57  | 1.06  | 1.47  |       |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (A)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 22.4  | 36.7  | 35.5  | 25.1  | 40.0  | 26.5  | 38.4  | 37.4  | 25.5  | 34.8  |       |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (E)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 50.5  | 82.5  | 79.9  | 56.5  | 89.9  | 59.6  | 86.5  | 83.9  | 56.6  | 78.3  |       |
| CH <sub>3</sub> COCl in the collector (g.)                                                        | 15    | 3     | 5     | 10    | 10    | 15    | 10    | 15    | 15    | 15    |       |

In Fig. 4-11

- ⊙ 2 hours' reaction with discharge
- 2 hours' reaction without discharge
- 3 hours' reaction with discharge
- ◐ 3 hours' reaction without discharge
- ⊗ 4 hours' reaction with discharge
- ◑ 4 hours' reaction without discharge

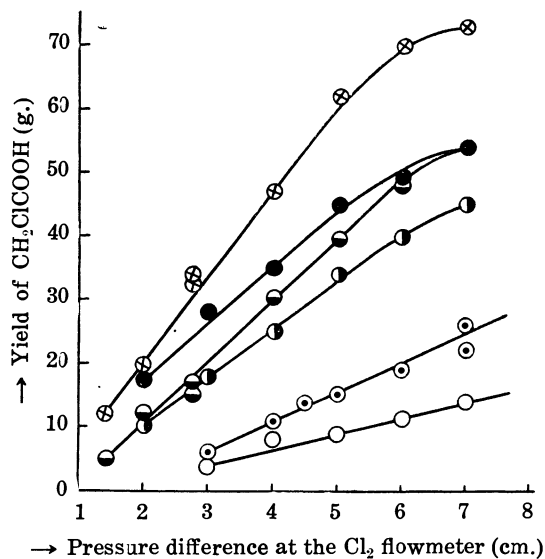


Fig. 4.

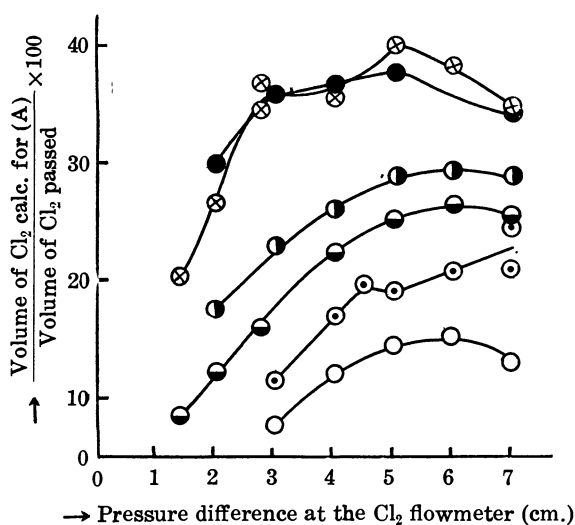


Fig. 5.

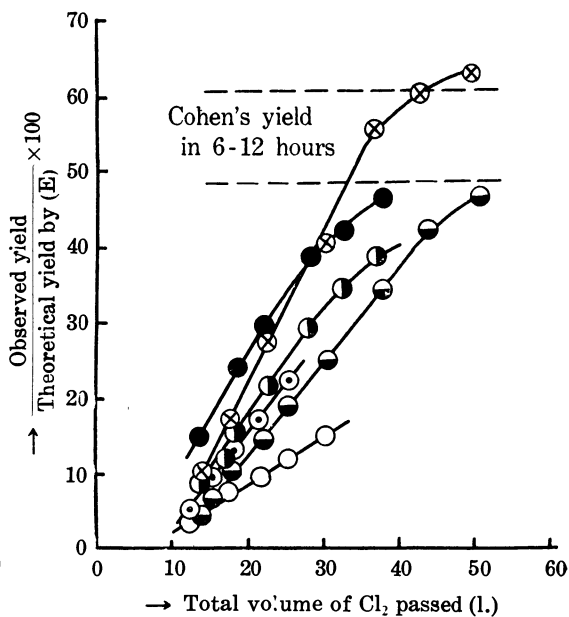


Fig. 6.



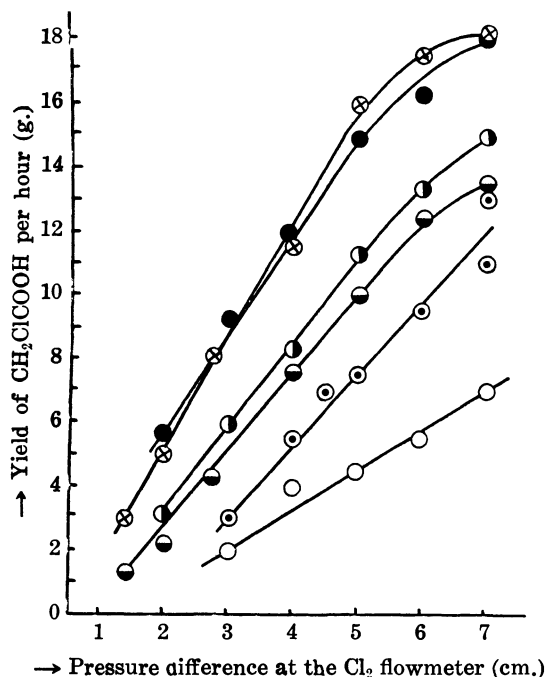


Fig. 7.

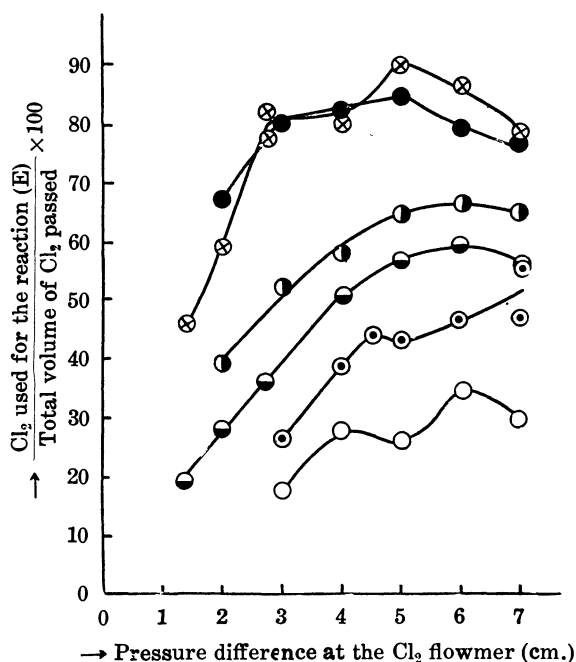


Fig. 8.

## II. Iodine, Red Phosphorus, and Phosphorus Pentachloride as Catalyser.

Brückner<sup>(4)</sup> reported that he obtained 66% of monochloroacetic acid in four hours by using 1 g.  $I_2$  + 2 g.  $P_4$  + 2 g.  $PCl_5$  as catalyser and bubbling 245 c.c. of chlorine per minute through acetic acid. This result was so amazing that even now this catalyser maintains its industrial application.

The experiments were carried out by the present author with the same catalyser in much the same way as was previously mentioned and the same results as those of Brückner were obtained. However, by using 1 g. of iodine for 70 c.c. of acetic acid, a great deal of difficulties were found to eliminate iodine vapour from every fraction of the distillation. The amount of iodine was then diminished from 1 g. to 0.2 or 0.1 g. so far as the yield of monochloroacetic acid was not affected. With the modified catalyser, that is 0.1–0.2 g.  $I_2$  + 2 g.  $P_4$  + 2 g.  $PCl_5$ , the experiments were carried out to see the effect of the silent electrical discharge on the synthesis of monochloroacetic acid. As the result, the yield of monochloroacetic acid was increased in a great extent and the elimination of iodine from the product was satisfactory by carrying out the distillation at 180–190°C.<sup>(5)</sup>

(5) Even if 0.1 or 0.2 g. of iodine is used for 70 c.c. of acetic acid, the distillates between 180 and 190°C. have sometimes pinc tint. It is found that 0.5–1% of active charcoal is effective enough to decolourize such a small quantity of iodine in monochloroacetic acid. Iodine is completely adsorbed by charcoal at the temperature between 180 and 190°C.





Table 6. Acetic acid : 70 c.c. ; Duration of reaction : 4 hours ; Catalyser :  
0.1 g. iodine + 2 g. red phosphorus + 2 g. phosphorus pentachloride.

| No. of experiments                                                                                | 1     | 2     | 3     | 4     | 5     | 6     | Brückner<br>(Acetic acid : 100 c.c.<br>1g. I <sub>2</sub> + 2g. P <sub>4</sub> + 2g. PCl <sub>5</sub> ) |
|---------------------------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|---------------------------------------------------------------------------------------------------------|
| Press. diff. at the Cl <sub>2</sub> flowmeter (cm.)                                               | 3     | 3     | 4     | 4     | 5     | 5     | 7.9                                                                                                     |
| Duration of electric discharge (hours)                                                            | —     | 4     | —     | 4     | —     | 4     | —                                                                                                       |
| Total vol. of Cl <sub>2</sub> passed<br>at 0°, 1 atm. (litres)                                    | 24.43 | 24.43 | 30.46 | 30.46 | 36.94 | 36.91 | 58.8                                                                                                    |
| Total yield of CH <sub>2</sub> ClCOOH (g.)                                                        | 68    | 74    | 84    | 88    | 90    | 93    | 104                                                                                                     |
| $\frac{\text{CH}_2\text{ClCOOH produced}}{\text{CH}_3\text{COOH taken}} \times 100$               | 92.6  | 100.6 | 114   | 119.5 | 122.5 | 126.5 | 104                                                                                                     |
| $\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$                        | 58.5  | 63.5  | 72.0  | 75.5  | 77.4  | 80.0  | 66.0                                                                                                    |
| Yield per hour (g.)                                                                               | 17    | 18.5  | 21    | 22    | 22.5  | 23.3  | 19.1                                                                                                    |
| Yield per litre of Cl <sub>2</sub> (g.)                                                           | 2.78  | 3.03  | 2.76  | 2.89  | 2.43  | 2.52  | 1.77                                                                                                    |
| $\frac{\text{Vol. of Cl}_2 \text{ calc. for (A)}}{\text{Vol. of Cl}_2 \text{ passed}} \times 100$ | 66.0  | 71.8  | 65.4  | 68.5  | 57.7  | 59.7  | 41.9                                                                                                    |
| CH <sub>3</sub> COCl in the collector (g.)                                                        | 3     | 3     | 3     | 3     | 3     | 3     | ?                                                                                                       |

From the experiments the followings can be perceived.

(1) Iodine is dissolved in acetic acid as  $\text{ICl}$  or  $\text{ICl}_3$  and thus serves for the equal distribution of chlorine in the system. By the thermal decomposition in the distillation, iodine is again set free from  $\text{ICl}$  or  $\text{ICl}_3$  and is mixed in every distillate.

(2) The yield of acetyl chloride is far less than that of the previous experiment (only 2.5 g in four hours).

(3) Phosphorus pentachloride serves to produce acetyl chloride in adequate amount and velocity.

(4) Sometimes a part of phosphorus is dissolved, but in the majority of the experiments it maintains its initial amount, and the yield of monochloroacetic acid never fluctuates as it does otherwise by the diminution of the amount of phosphorus.

From the above mentioned facts we may conclude that the main mechanism of the reaction is expressed by the equation (A), and that the added substances take rôle of the catalyser.

Not only from the above mentioned facts, but also from the values calculated by the equation (A) as is shown in Table 4-6, and Fig. 9-11, the equation seems to be correct.

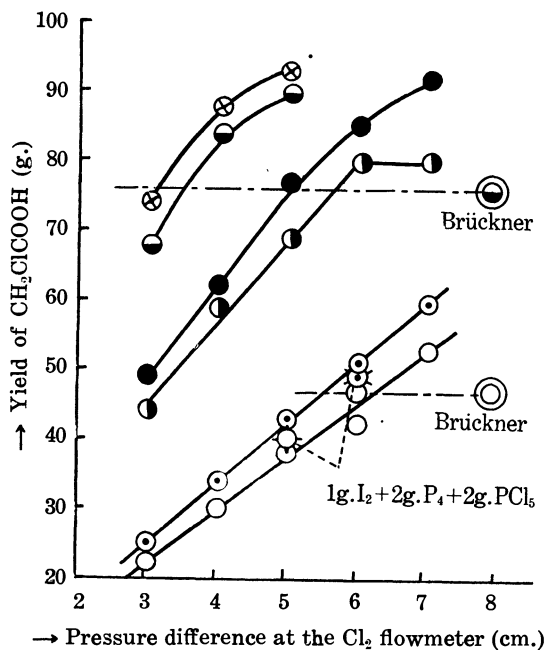


Fig. 9.

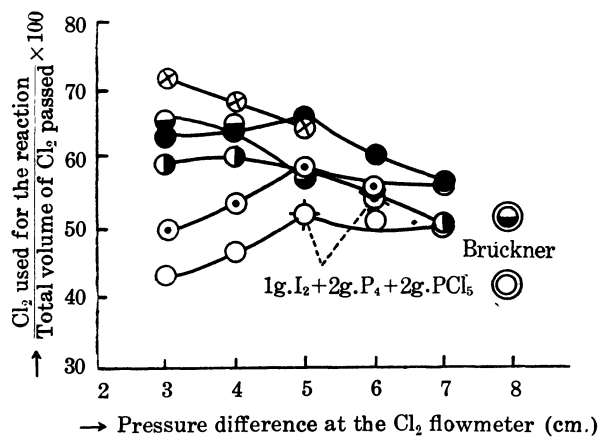


Fig. 10.

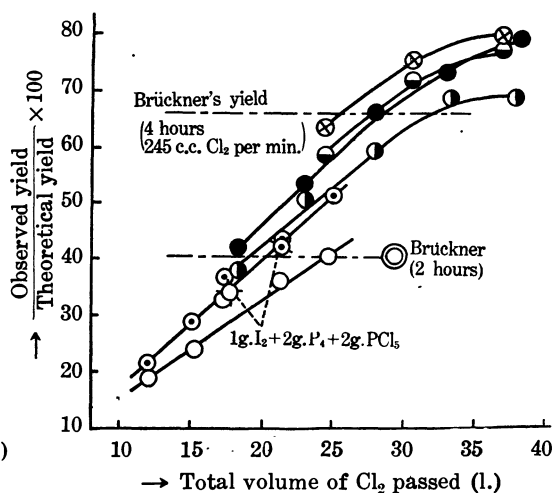


Fig. 11.

### Summary.

(1) Silent electrical discharge is very effective to produce monochloroacetic acid from acetic acid and chlorine by using red phosphorus as catalyser, and it increases 15–100% of the yield of monochloroacetic acid compared with the formerly obtained results. The yield of 62.8% in four hours running is one of the best record that is attained in the experiment using red phosphorus (10%) as catalyser. A new equation (E) is proposed to clear up several questions involved in the formerly believed equation (A).

(2) The reaction between acetic acid and chlorine was carried out under the influence of the silent electrical discharge, using iodine, red phosphorus, and phosphorus pentachloride as catalyser. The reaction is expressed by the equation (A). The yields of 79.2% in the reaction for three hours discharge and 80.0%, for four hours discharge, are far better than the yield of 66% reported by Brückner. This is chiefly due to the effect of the new modified catalyser and of the silent electrical discharge.

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## Studies on the Oiliness of Liquids. VII. Measurements of the Static Friction Coefficients of Esters, Ketones and Glycerine.

By Toshizo ISEMURA.

(Received May 23, 1939.)

The measurements of the static friction of glass surfaces, when various organic liquids are present as lubricant, have already been reported in the previous papers.<sup>(1)</sup> The liquids tested contain polar compounds as well as non-polar ones. The former consists, mostly, of alcohol and normal acids, which have the polar group at one end of their molecules. It is interesting to know whether the shape of the molecule has the effect on the lubricating activity or not. In the present experiments, therefore, esters and ketones have been tested as lubricating liquids. These compounds have the polar group at the middle part of the molecule. Glycerine was also tested, which has three polar groups in a relatively small molecule. We have reported in the preceding papers, that the friction coefficients of water<sup>(2)</sup> and methyl alcohol<sup>(3)</sup> are 0.75 and 0.62 respectively. These

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(1) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659 ; H. Akamatu and J. Sameshima, *ibid.*, **11** (1936), 791 ; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127 ; H. Akamatu, *ibid.*, **13** (1938), 127.

(2) H. Akamatu, *ibid.*, **13** (1938), 131.

(3) J. Sameshima, M. Kidokoro and H. Akamatu, *ibid.*, **11** (1936), 663.

data have been revised and found that they are somewhat too low. The results will be described in the following lines.

The experiment was pursued by the balance method. The friction surfaces consisted of a flat glass and a glass with a spherical surface. They were cleaned sufficiently prior to each experiment by the same method as described in the former paper. The purest samples available were used in the experiments. All esters and ketones were sufficiently dried with quick lime or anhydrous potassium carbonate and then distilled before the experiment. Glycerine was distilled six times in vacuum to expel the last trace of water contained in it. The measurements were conducted at room temperature without any special adjustment of temperature because the coefficient of friction is not seriously affected by the change of temperature. The results obtained are summarised in Table 1. Fig. 1 shows the relations between the friction coefficient and the number of carbon atoms in the molecule of the substance.

Table 1.

| Lubricant                | <i>W</i> | <i>F'</i> | $\mu$ | Lubricant               | <i>W</i> | <i>F'</i> | $\mu$ |
|--------------------------|----------|-----------|-------|-------------------------|----------|-----------|-------|
| Methyl acetate           | 21.55    | 18.52     | 0.86  |                         | 29.30    | 22.38     | 0.76  |
|                          | 21.55    | 18.52     | 0.86  |                         | 29.30    | 21.80     | 0.74  |
|                          | 23.85    | 20.90     | 0.88  |                         | 37.70    | 27.88     | 0.75  |
|                          | 23.85    | 21.70     | 0.91  |                         |          |           | 0.74  |
|                          | 27.00    | 22.88     | 0.85  | <i>n</i> -Octyl acetate | 21.55    | 15.54     | 0.72  |
|                          | 27.00    | 22.18     | 0.82  |                         | 23.85    | 17.05     | 0.72  |
|                          | 29.30    | 26.95     | 0.92  |                         | 27.00    | 19.33     | 0.72  |
|                          |          |           | 0.87  |                         | 29.30    | 21.64     | 0.74  |
| Ethyl acetate            | 21.55    | 17.50     | 0.81  |                         | 35.40    | 25.78     | 0.72  |
|                          | 25.40    | 21.12     | 0.83  |                         | 37.70    | 28.90     | 0.77  |
|                          | 27.00    | 21.60     | 0.80  |                         |          |           | 0.73  |
|                          | 29.30    | 23.70     | 0.81  | Ethyl propionate        | 14.10    | 11.90     | 0.85  |
|                          | 29.40    | 24.18     | 0.82  |                         | 15.70    | 13.20     | 0.84  |
| <i>n</i> -Propyl acetate | 14.50    | 12.00     | 0.83  |                         | 19.30    | 15.05     | 0.78  |
|                          | 17.00    | 13.18     | 0.78  |                         | 23.35    | 17.70     | 0.76  |
|                          | 19.30    | 15.55     | 0.81  |                         | 29.30    | 23.10     | 0.79  |
|                          | 19.30    | 15.15     | 0.79  |                         | 30.05    | 23.80     | 0.79  |
|                          | 27.00    | 21.30     | 0.79  |                         | 33.35    | 26.10     | 0.79  |
|                          | 29.30    | 24.25     | 0.83  |                         |          |           | 0.80  |
|                          |          |           | 0.81  | Ethyl butylate          | 15.00    | 12.20     | 0.81  |
| <i>n</i> -Butyl acetate  | 19.40    | 15.43     | 0.80  |                         | 16.60    | 13.10     | 0.79  |
|                          | 23.85    | 19.08     | 0.80  |                         | 23.85    | 19.50     | 0.82  |
|                          | 27.00    | 20.64     | 0.77  |                         | 27.00    | 21.60     | 0.80  |
|                          | 29.30    | 22.40     | 0.77  |                         | 27.90    | 22.02     | 0.79  |
|                          | 31.70    | 23.99     | 0.76  |                         | 29.30    | 23.10     | 0.79  |
|                          | 35.40    | 26.50     | 0.75  |                         | 31.55    | 24.98     | 0.79  |
|                          | 37.70    | 31.40     | 0.83  |                         |          |           | 0.80  |
|                          |          |           | 0.78  | Acetone                 | 14.35    | 12.54     | 0.88  |
| <i>n</i> -Amyl acetate   | 21.55    | 15.60     | 0.73  |                         | 17.30    | 14.80     | 0.86  |
|                          | 23.55    | 17.30     | 0.74  |                         | 18.35    | 14.89     | 0.81  |
|                          | 23.85    | 17.70     | 0.74  |                         | 21.05    | 18.25     | 0.87  |
|                          | 27.70    | 19.48     | 0.72  |                         | 27.02    | 23.20     | 0.86  |
|                          |          |           |       |                         |          |           | 0.86  |



Table 1.—(Concluded)

| Lubricant           | <i>W</i> | <i>F</i> | $\mu$ | Lubricant      | <i>W</i> | <i>F</i> | $\mu$ |
|---------------------|----------|----------|-------|----------------|----------|----------|-------|
| Methyl ethyl ketone | 21.30    | 17.65    | 0.83  | Glycerine      | 25.70    | 21.43    | 0.84  |
|                     | 21.30    | 17.35    | 0.81  |                | 48.40    | 42.30    | 0.88  |
|                     | 24.30    | 19.20    | 0.79  |                |          |          | 0.86  |
|                     | 26.30    | 22.40    | 0.85  |                |          |          |       |
|                     | 26.30    | 21.70    | 0.83  | Water          | 16.05    | 14.35    | 0.89  |
|                     | 29.30    | 25.00    | 0.85  |                | 19.45    | 17.83    | 0.92  |
| Diethyl ketone      |          |          | 0.83  |                | 20.75    | 19.20    | 0.93  |
|                     | 17.00    | 13.85    | 0.82  |                | 20.80    | 19.50    | 0.94  |
|                     | 19.30    | 15.95    | 0.83  |                | 22.70    | 19.65    | 0.87  |
|                     | 19.30    | 15.96    | 0.83  |                | 24.50    | 21.30    | 0.87  |
|                     | 23.35    | 20.00    | 0.86  |                | 26.15    | 23.60    | 0.90  |
|                     | 27.00    | 23.12    | 0.86  |                |          |          | 0.90  |
|                     | 29.30    | 25.95    | 0.81  |                |          |          |       |
| Acetophenone        |          |          | 0.84  | Methyl alcohol | 17.10    | 13.79    | 0.81  |
|                     | 19.30    | 13.90    | 0.72  |                | 20.30    | 16.45    | 0.81  |
|                     | 27.00    | 19.15    | 0.71  |                | 20.85    | 15.98    | 0.77  |
|                     | 29.30    | 20.82    | 0.71  |                | 21.50    | 15.86    | 0.74  |
|                     | 29.30    | 22.18    | 0.76  |                | 23.70    | 18.47    | 0.78  |
|                     | 29.30    | 21.25    | 0.73  |                | 24.15    | 19.45    | 0.81  |
|                     | 31.05    | 22.40    | 0.72  |                |          |          | 0.79  |
|                     | 33.35    | 25.05    | 0.75  |                |          |          |       |
|                     | 33.85    | 24.01    | 0.71  |                |          |          |       |
|                     |          |          | 0.73  |                |          |          |       |

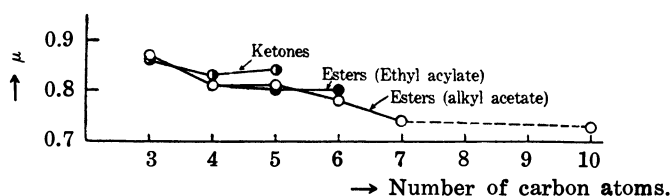


Fig. 1.

We know from Table 1, that all these substances—esters, ketones, and glycerine—give relatively high friction coefficients. So it may be concluded from these results, that substances which have the polar group at the middle part of the molecule do not serve as good lubricants. The polar molecule attaches to the friction surface with its polar group and presenting non-polar chain to the liquid interface, forming a monomolecularly orientated layer.<sup>(4)</sup> A substance serve as a better lubricant when molecules take regular arrangement on the sliding surface than they take irregular arrangement.<sup>(5)</sup> The esters and ketones have the polar group at the middle part of the molecule, with which they may anchor on the surface. It is recognisable from this fact that they take regular arrangement more difficultly than the molecules having polar group at the end of the molecule. This may be the reason of high friction coefficients of esters and ketones.

(4) Hardy and Doubleday, *Proc. Roy. Soc. (London)*, **A**, **104** (1923), 25; Akamatu, *this Bulletin*, **13** (1938), 127.

(5) H. Akamatu and J. Sameshima, *ibid.*, **11** (1936), 793.

As already reported in the preceding papers, the lower homologous are poorer lubricants than the higher homologous in the aliphatic alcohol series.<sup>(6)</sup> The analogous fact is also observed in the ester series, although they give always higher friction coefficients than alcohols. However, the effect of chain length of alkyl group in the ester is more predominated than the effect of that of acyl group.

The high static friction coefficient of glycerine is also ascribable to its molecular structure. When glycerine is placed on the sliding surface, it attaches to the surface with its three polar groups and the molecule can hardly be inclined according to the anchoring with these groups. Moreover, no flexibility can be considered of its molecule for the shortness of its chain. The friction coefficient of water was determined to be 0.9. It is the highest friction coefficient we ever obtained on the glass surface in the presence of lubricant. Hardy and Doubleday stated that water is neutral to the surfaces of glass or steel in that it neither lowers nor raises the friction.<sup>(7)</sup> This fact may be probably ascribable to the very short chain of the molecule.

In conclusion the author expresses his hearty thanks to Prof. J. Sameshima for his kind guidance and encouragement. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due. The author's acknowledgement is also due to Hattori Hokokwai for a grant.

### Summary.

- (1) The static friction coefficients have been measured when esters, ketones and glycerine are placed on the glass surface as lubricants.
- (2) The friction coefficients of these liquids are very high.
- (3) Some considerations have been made on the high friction coefficients of these liquids.
- (4) The friction coefficients of water and methyl alcohol have been revised.

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(6) J. Sameshima, M. Kidokoro and H. Akamatu, *ibid.*, **11** (1936), 659; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127.

(7) Hardy and Doubleday, *Proc. Roy. Soc. (London)*, **A**, **104** (1923), 34.

## Geochemische Untersuchungen der Vulkane in Japan. IX. Bestimmung des Schwerwassergehaltes von den in der Nähe des Vulkans Asama befindlichen Quellwasser.\*

Von Yuji SHIBATA, Kimio NOGUCHI, und Osamu KANEKO.

(Eingegangen am 24. Mai 1939.)

Über den Ursprung der aus den Kratern tätiger Vulkane oder aus den in ihren Nähen befindlichen Fumarolen ausgestossenen Wasserdämpfe sind bisher verschiedene Ansichten geäußert. Nämlich betrachtet man sie bald als juveniles Wasser, bald als vadoses Wasser oder bald als das Gemisch dieser beiden Wasserarten. Das ist ebenfalls der Fall bei der Auseinandersetzung über die Herkunft von Thermen und Pegen. Zwar einerseits vertrat Robert Bunsen die Vadoswassertheorie; als er im Jahre 1846 gelegentlich der Studienreise nach Island die Frage über die Entstehung dortiger Thermen erörterte, während andererseits Elie de Beaumont, A. Gautier u.a. behaupteten, dass das Thermalwasser im allgemeinen des magmatischen Ursprungs ist. Dagegen sind die amerikanischen Forscher, die neuerdings über die im Yellowstone Park befindlichen heißen Quellen eine interessante Untersuchung ausgeführt haben, wieder die erstere Bunsensche Theorie zu stützen geneigt.

In Bezug auf den Unterschied zwischen magmatischem (juvenilem) und vadossem Wasser wurde die folgende Ansicht von A. Gautier<sup>(1)</sup> im Jahre 1910 vorgebracht: das juvenile Wasser, seiner Meinung nach, enthält im wesentlichen Bicarbonate und Silikate von Alkali- und Schwermetalle, deren Gehalt von meteorologischen Bedingungen wenig beeinflusst wird, während das vadose Wasser überhaupt Carbonate, Sulfate und Chloride von Calcium und Magnesium auflöst, indem ihre Konzentration durch Niederschläge leicht verändert wird.

Jedoch wird die strenge Unterscheidung von diesem beiden Wasserarten im Sinne Gautiers nur schwierig durchführbar, weil das rein juvenile Wasser auf der Erdoberfläche sehr selten anzutreffen ist. Nimmt man aber an, dass die Verteilung von Wasserstoff- sowie Sauerstoff-Isotopen in juvenilem und vadossem Wasser nicht gleichartig sei, so könnte man einen sicheren Anhaltspunkt für die Erkennung dieser beiden Wasserarten gewinnen, indem man einen exakten Vergleich zwischen Dichten des zur Frage kommenden Naturwassers und des Leitungswassers, das als ein typisches vadoses Wasser betrachtet wird, anstellt.

Zahlreiche Untersuchungen von verschiedenen Forschern lehren uns tatsächlich, dass die an der Erdoberfläche weit verbreiteten vadosen Wasser (Seewasser, Flusswasser, Quellwasser, besonders Leitungswasser) immer ungefähr gleiche Dichte besitzen, während es noch keinen Beweis gibt für die Dichtegleichheit zwischen dem eben genannten Wasserart und dem von der Erdtiefe stammenden.

\* Übersetzung einer Mitteilung, die in *J. Chem. Soc. Japan*, **58** (1937), 1013. auf Japanisch beschrieben.

(1) A. Gautier, *Compt. rend.*, **150** (1910), 436.

Macht man nun eine Voraussetzung, die dahin geht, dass bei der allerersten Entstehung von mineralischen Bestandteilen des heutigen Erdballs, die leichteren Isotopen der chemische Elemente mit grösserer Leichtigkeit als die schweren miteinander in Bindung eingetreten wären, so könnte man wohl daran denken, dass auch das Wasser, das seit solchen Urzeiten in der Erdtiefe verborgen bleibt, eine reichlichere Menge der leichteren Molekülen enthält als das vadoso Wasser, das jetzt, wie bekannt, ein konstantes Verhältnis von leichten Molekülen zu schweren innehält.

Seit einigen Jahren sind wir mit der geochemischen Erforschung der tätigen Vulkane in Japan beschäftigt, und wir stellen z.Z. über die Gase, die Wasser, die Gesteine, die Asche u.s.w. vom Vulkan Asama, der sich seit 1935 im Zustande von lebhafter Aktivität befindet, vielseitige Untersuchungen an. Dabei haben wir auch die vergleichenden Dichtemessungen der verschiedenen Naturwasser, die hier und da in der Umgegend vom Vulkan Asama sprudeln, und des Leitungswassers von der Stadt Tokyo ausgeführt. Wie es unten näher beschrieben wird, wird es bestätigt, dass die in Frage kommenden Naturwasser meistens einige  $\gamma$  leichter sind als das Leitungswasser. Diese Resultate scheinen gewissermassen für unsere oben erwähnte Voraussetzung zu sprechen, aber wir wollen noch kein bestimmtes aussagen, bevor unsere weitere, mit zahlreichen Materialien fortzuführende Untersuchungen zum Abschluss kommen.

**Beschreibung der Versuche.** 1. *Messungsapparate.* Im wesentlichen haben wir für die Dichtemessung der Naturwasser die von M. Koizumi<sup>(2)</sup> ausgearbeitete Schwimmermethode angewandt, die aber von uns in einigen Punkten etwas verbessert wurde. Der Thermostat besteht aus einer Doppelwanne, deren äussere durch das im Kochsalz-Eis-Kältegemisch zirkulierende Wasser gekühlt ist. Die Temperatur der inneren Wanne ist somit bei etwa  $8^{\circ}$  innerhalb  $\pm 0.002^{\circ}$  konstant gehalten; dies entspricht einem Dichteunterschiede von  $0.1 \gamma$ . Der Schwimmer ist aus Quarz hergestellt, und sein Unterteil ist spindelförmig gemacht, so dass er im Probegefäss auf und ab ganz glatt bewegen kann. Die Kapazität des Probegefässes aus Pyrexglas beträgt 5 ccm.

2. *Reinigung des Probewassers.* Da die Naturwasser aus der vulkanischen Gegend im allgemeinen etwas sauer reagieren, so wird das Probewasser zuerst mit Natriumperoxyd neutralisiert und nötigenfalls filtriert. Dann wird es mit kleiner Menge von Natriumperoxyd und Kaliumpermanganat versetzt, unter Rückfluss gekocht und schliesslich vorsichtig destilliert.

Um die durch Fraktionieren verursachte Isotopentrennung zu vermeiden, wurden immer je 5 ccm. Wasser am Anfang und am Ende von jeder Destillation weggeschaffen. Das so vorläufig gereinigte Wasser wurde noch weiteren Destillationen unterworfen. Die Vorrichtung für dieses letztere Reinigungsverfahren besteht, wie in Abb. 1 gezeigt, aus drei Destillierkolben aus Pyrexglas, die von oben nach unten stufenweise angeordnet und mit Kühlern verbunden sind. Die Apparatur wurde vorher gut gewaschen und getrocknet, wobei man das ganze System hindurch die getrocknete und kohlensäurefreie Luft durchströmen lässt. Bei der

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(2) M. Koizumi, *J. Chem. Soc. Japan*, **56** (1935), 811.

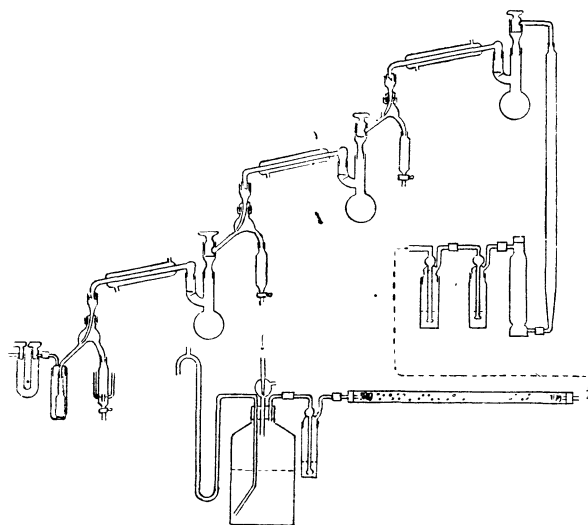


Abb. 1.

Destillation trägt man eine kleine Menge von  $P_2O_5$  in den ersten Kolben und wenig Bariumhydroxyd in den zweiten Kolben ein. Die allerletzte Destillation aus dem dritten Kolben wird ohne Zusatz sehr vorsichtig ausgeführt. Die Reinheit des so behandelten Wassers wurde durch die Messung der Leitfähigkeit geprüft, deren Werte  $0.6 \sim 2 \times 10^{-6}$  rezip. Ohm betragen.

### 3. Standardwasser.

Der Erfolg der Dichteunterschiedsmessung nach der Schwimmermethode

beruht überhaupt auf der strengen Unveränderlichkeit des Standardwassers. Deshalb haben wir am 15. April 1935, eine grosse Menge städtischen Leitungswassers in einer gut verschliessbaren Flasche aufbewahrt. Die Reinigung desselben wurde genau gleich wie beim Probewasser vorgenommen.

4. Gleichgewichtstemperatur. Die Bestimmung der Gleichgewichtstemperatur wurde nach der Briscoeschen Methode<sup>(3)</sup> ausgeführt; es handelt sich nämlich um die Tatsache, dass innerhalb der engen Temperaturgrenze von  $0.1^\circ$  die Geschwindigkeit von auf- oder abwärts bewegendem Schwimmer mit der Differenz zwischen der betreffenden Temperatur und der Gleichgewichtstemperatur in streng linearem Verhältnis steht. Demnach wird die Gleichgewichtstemperatur nach graphischer Methode verhältnismässig einfach ermittelt, wenn man die Geschwindigkeit des bewegendes Schwimmers bei einigen bestimmten Temperaturen genau

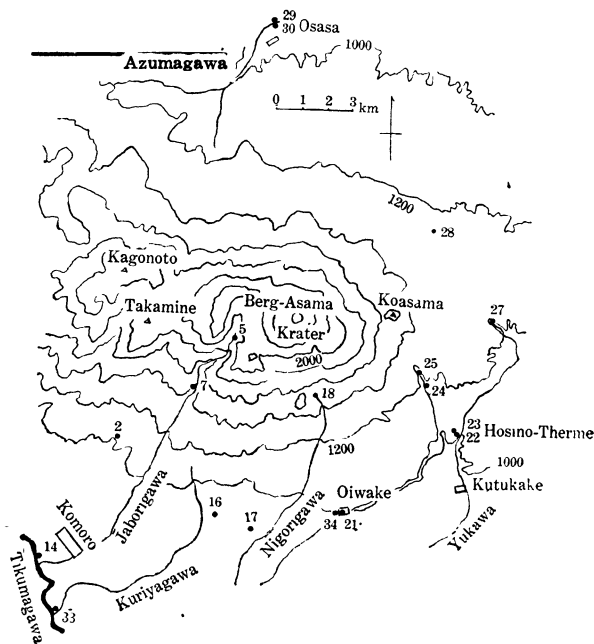


Abb. 2.

(3) H. V. A. Briscoe, *J. Chem. Soc.* **1934**, 1207.

notiert. Die Fehlergrenze beträgt dabei etwa  $\pm 0.5 \gamma$  in bezug auf Dichteunterschied.

**Ergebnisse der Dichtemessungen.** Auf der vereinfachten Karte vom Vulkan Asama (Abb. 2) wurden die Örtlichkeiten der Probenahme mit den Ziffern angezeigt, die sich auch auf die Tabelle beziehen. Obgleich einige der gewonnenen Werte für den Dichteunterschied innerhalb der Fehlergrenze liegen, ist es doch merkwürdig, dass es kein Quell-, Thermen- und Mineralwasser gibt, die schwerer sind als das Leitungswasser von der Stadt Tokyo.

Um weiter zu sehen, ob man imstande wäre, bestimmte Beziehungen zwischen den Dichten und den anderen Eigenschaften des Naturwassers ausfindig zu machen, haben wir sie graphisch dargestellt, indem der Dichteunterschied ( $D_{\text{Nat.}} - D_{\text{Leit.}}$ ) als Ordinaten und die anderen Werte, wie Wassertemperatur, Menge der Abdampfdruckstände, pH-Wert, Gehalt an gewissen Ionen u.s.w., als Abszissen aufgetragen sind. Kurze Besprechungen über die erhaltenen Kurven werden folgendermassen gegeben:

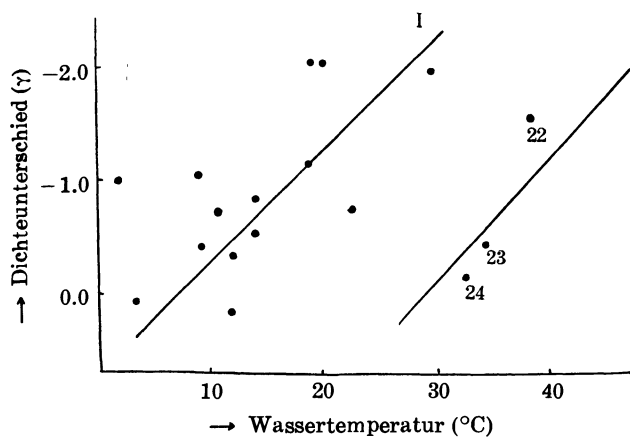


Abb. 3.

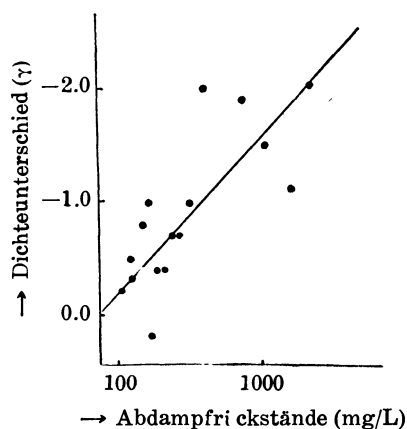


Abb. 4.

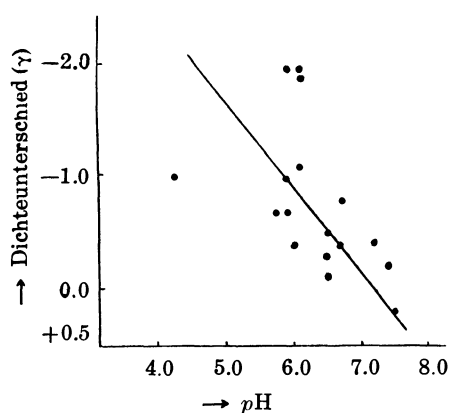


Abb. 5.

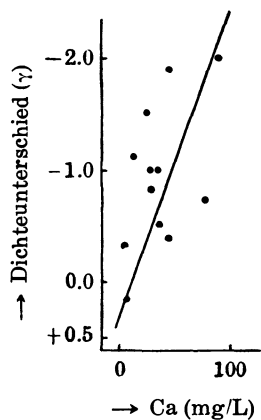


Abb. 6.

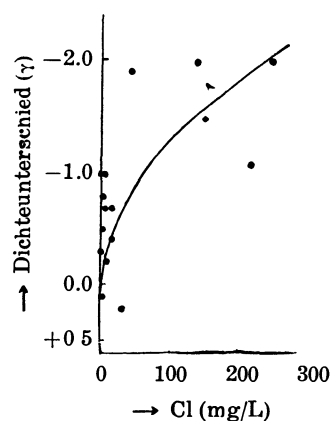


Abb. 7.

| Nr.            | Herkunft der Wasserprobe                     | Datum             | Dichteunterschied<br>( $D_{\text{Nat.}} - D_{\text{Leit.}}$ ) | Höhe von Meeres-<br>spiegel<br>m | Wasser-<br>temperatur<br>°C | pH   | Abdampf-<br>rückstände<br>mg/L | Fe<br>mg/L | Ca<br>mg/L | Cl<br>mg/L | SiO <sub>2</sub><br>mg/L |
|----------------|----------------------------------------------|-------------------|---------------------------------------------------------------|----------------------------------|-----------------------------|------|--------------------------------|------------|------------|------------|--------------------------|
| 25             | Wasserfall von Sengataki                     | 14. Juni 1935     | +0.2                                                          | 1180                             | 11.6                        | 7.5  | 315                            | 0.26       | 10.1       | 31.6       | 75                       |
| 5 <sub>1</sub> | Mineralwasser aus Jigokudani                 | 14. Oktober 1934  | +0.1                                                          | 1920                             | 3.2                         | 2.66 | 1692                           | 67.7       | 103.       | 3.9        | 37                       |
| 24             | Mineralwasser aus Sengataki                  | 14. Juni 1935     | -0.1                                                          | 1150                             | 32.0                        | 6.5  | 3217                           | 0.64       | 407.       | 731.       | 67                       |
| 14             | Flusswasser von Tikumagawa                   | 12. Juni 1935     | -0.2                                                          | 600                              | —                           | 7.4  | 140                            | 0.42       | —          | 8.7        | 91                       |
| 16             | Sprudel vom Sinrakuji-Teich                  | 12. Juni 1935     | -0.3                                                          | 910                              | 11.8                        | 6.5  | 185                            | 0.24       | 7.9        | 3.5        | 67                       |
| 23             | Thermalwasser (II) von der<br>Hosino-Therme  | 14. Juni 1935     | -0.4                                                          | 1000                             | 33.8                        | 7.2  | 1230                           | 0.20       | 47.8       | 176.3      | 63                       |
| 21             | Bohrungsquellwasser von<br>Yamaya (Oiwake)   | 22. August 1935   | -0.4                                                          | 990                              | —                           | 6.0  | 408                            | 3.31       | —          | 16.3       | 62                       |
| 34             | Bohrungsquellwasser von<br>Katayama (Oiwake) | 10. Dezember 1935 | -0.4                                                          | 990                              | 9.0                         | 6.7  | 376                            | 3.79       | —          | 15.7       | 43                       |
| 17             | Mineralwasser von Oyati                      | 12. Juni 1935     | -0.5                                                          | 870                              | 13.9                        | 6.5  | 183                            | 0.32       | 38.5       | 4.1        | 68                       |
| 18             | Quellwasser vom Fluss<br>Nigorigawa          | 26. April 1935    | -0.7                                                          | 1490                             | 10.5                        | 5.74 | 473                            | 77.3       | 78.3       | 12.5       | 74                       |
| 29             | Mineralwasser von Osasa                      | 15. Juni 1935     | -0.7                                                          | 970                              | 22.2                        | 5.9  | 490                            | 0.55       | 140.       | 10.7       | 75                       |
| 2              | Mineralwasser von Hisino                     | 9. Juni 1935      | -0.8                                                          | 1000                             | 13.8                        | 6.7  | 272                            | 1.08       | 32.0       | 3.7        | 71                       |
| 7              | Sprudel beim Fluss Jaborigawa                | 20. August 1935   | -1.0                                                          | 1400                             | 8.7                         | 5.9  | 303                            | 52.8       | 31.7       | 3.4        | 77                       |
| 5 <sub>2</sub> | Dasselbe wie (5 <sub>1</sub> )               | 28. April 1935    | -1.0                                                          | 1920                             | 1.8                         | 4.31 | 575                            | 37.6       | 36.4       | 4.5        | 64                       |
| 28             | Bohrungsquellwasser von<br>T. Utibori        | 14. Juni 1935     | -1.1                                                          | 1280                             | 18.3                        | 6.1  | 1202                           | 0.61       | 15.3       | 221.       | 68                       |
| 22             | Thermalwasser (I) von der<br>Hosino-Therme   | 14. Juni 1935     | -1.5                                                          | 1000                             | 37.7                        | 7.4  | 1042                           | 1.19       | 26.7       | 154.       | 77                       |
| 30             | Dasselbe wie (29), (II)                      | 15. Juni 1935     | -1.9                                                          | 970                              | 29.0                        | 6.1  | 906                            | 3.96       | 46.3       | 45.0       | 73                       |
| 27             | Quellwasser vom Fluss Yukawa                 | 27. April 1935    | -2.0                                                          | 1200                             | 18.5                        | 6.1  | 1336                           | 0.18       | 89.4       | 249.9      | 64                       |
| 33             | Mineralwasser von Yunose                     | 13. Mai 1936      | -2.0                                                          | 620                              | 19.5                        | 5.9  | 652                            | 3.64       | —          | 144.7      | 92                       |

*Wassertemperatur.* Wie man aus Abb. 3 ersieht, sind die von uns studierten Naturwasser in zwei Gruppen einzuteilen: die eine, die mit I bezeichnet ist, gehört zum natürlichen Quellwasser, während die andere II solche Wasser umfasst, die man durch Bohrung bekam. In diesen beiden Gruppen herrscht allerdings der gleiche Umstand, dass je höher die Wassertemperatur ist, umso leichter wiegt das Wasser.

*Abdampfrückstände.* Abgesehen von den Proben 5, 23 und 24, besteht bei allen Naturwassern eine Proportionalität zwischen dem Dichteunterschied und der Menge von Abdampfrückständen (Abb. 4).

*pH-Wert.* Von den Proben 5<sub>1</sub> und 22 abgesehen, verhält der Dichteunterschied sich umgekehrt wie pH-Werte, d.h. je sauer das Naturwasser reagiert, desto kleiner ist seine Dichte (Abb. 5).

Was den Ionengehalt anbelangt, so scheint es, auch eine Proportionalität zwischen dem Dichteunterschied und den Konzentrationen an Ca- sowie Cl-Ionen vorhanden zu sein, aber bezüglich anderer Ionen ist keine solche regelmässige Beziehung festzustellen.

Der Kaiserlichen Akademie der Wissenschaft sind die Autoren für ihre finanziellen Unterstützung zu der Arbeit zu besten Dank verpflichtet.

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**Geochemische Untersuchungen der Vulkane in Japan. XVIII.  
Dichtemessungen des durch Kondensation von Fumarolendampf  
erhaltenen Wassers.**

Von Shinya OANA.

(Eingegangen am 25. Mai 1939.)

In der IX. Mitteilung<sup>(1)</sup> von geochemischen Untersuchungen der japanischen Vulkane haben Y. Shibata, K. Noguchi und S. Kaneko die Ergebnisse der Dichtemessungen von zahlreichen natürlichen Wässern in Asama-Gegend berichtet. Diese Arbeit wurde, wie in dieser Mitteilung betont, unter einer Voraussetzung ausgeführt, dass die Moleküle des juvenilen Wassers reichlichere Menge der leichteren Wasserstoff- sowie Sauerstoffisotopen enthalten als die des vadosen Wassers; und die Resultate dieser Untersuchung wurden zwar in dem Sinne erreicht, dass die oben erwähnte Voraussetzung wohl gestützt ist.

Kurz nach der Veröffentlichung dieser Arbeit hat einer der oben genannten Autoren (Kaneko) die Dichte einer durch Kondensation des

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(1) Dieses Bulletin, **14** (1939), 274. Die früheren Mitteilungen (I~XVII) sind in J. chem. Soc. Japan auf Japanisch publiziert.

Fumarolendampfes von einem Vulkan "Yakeyama"\* in Yetigo-Provinz erhaltenen Wasserprobe gemessen.<sup>(2)</sup> Der berechnete Dichteunterschied zwischen diesem Wasser und dem Leitungswasser von der Stadt Tokyo betrug  $+2.0 \gamma$ , d.h. dieses magmatisch zu betrachtende Wasser aus der Fumarole war gegen die Shibatasche Hypothese etwas schwerer als das Leitungswasser (typisch vadoses Wasser). Dieses unerwartete Resultat musste damals etwas zweifelhaft angenommen werden, weil dies das einzige Beispiel vom Wasser aus der Fumarole darstellte.

Nun habe ich jetzt die gleichartige Untersuchung über die Wasserproben, die aus den Fumarolen vom Vulkan "Yakedake"\*\* in Sinano-Provinz und von "Iōyama" in der Therme-Gegend von Hakone in Sagami-Provinz durch Kondensation eigenhändig gesammelt wurden, ausgeführt. Überraschenderweise zeigten sich alle diese Wasserproben, ausgenommen nur eine, immer deutlich schwerer als das städtische Leitungswasser.

Ich habe alsdann die weiteren Dichtemessungen von verschiedenen Thermal- und Mineralwässern aus der Umgegend vom Vulkan "Yakedake" bewerkstelligt, um zu bestätigen, ob die an Wasser aus Fumarolendampf beobachtete anomale Erscheinung auch bei solchen Wasserarten wieder wahrzunehmen sei. Aber die letztere wiegen fast ausnahmslos leichter als das Leitungswasser, genau sowie die experimentellen Ergebnisse, die von Shibata, Noguchi und Kaneko bei den natürlichen Wässern von Asama-Gegend erhalten wurden. Konstatiert wurde also durch meine diesmalige Arbeit die Tatsache, dass das Wasser aus Fumarolendampf in der Regel schwerer ist als das vadoses Wasser, während Thermal- und Mineralwasser gegenteils immer leichter wiegen als das letztere.

Die Frage wird unten wieder weitgehend diskutiert werden.

**Beschreibung der Versuche.** *Dichtemessung.* Der Dichteunterschied zwischen natürlichem Wasser und dem Leitungswasser von der Stadt Tokyo ist gleicherweise wie derjenige, der von Shibata, Noguchi und Kaneko gearbeitet wurde, nach der Schwimmermethode ermittelt. Nur sei es erwähnt, dass die Fehlergrenze durch die Verbesserung hauptsächlich des Temperaturregulators im Thermostat bis zu  $\pm 0.1 \gamma$  erniedrigt werden konnte.

*Kondensieren der Fumarolendämpfe.* Man deckt das Mundloch der Fumarole mit einem Glasrichter, der mit etwa 10 m. langer Glasröhre in Verbindung steht. Am Ende dieser Röhre ist mit einer Reihe von einigen Glasflaschen versehen, um die Dämpfe völlig darin kondensieren zu lassen. In Sommerzeit muss man wenigstens die am Ende stehende Flasche mit dem Kältegemisch aus fester Kohlensäure und Alkohol und andere mit Wasser gut abkühlen, aber im Winter genügt die Wasserkühlung. Das so gewonnene Wasser wurde vorsichtig durch mehrmalige Destillationen gereinigt,<sup>(3)</sup> bis die spezifische Leitfähigkeit von der Wasserprobe einen Wert von  $3 - 5 \times 10^{-7}$  Mho. erreicht. Die gewonnenen Resultate sind in Tabelle 1 angegeben.

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(2) Nicht publiziert.

\* Ein ruhender Vulkan (Ruhig seit dem letzten Ausbruch in 1852).

\*\* Ein tätiger Vulkan (Die bedeutenden Ausbrüche fanden in 1909, 1911, 1915 und 1925 statt).

(3) Der Reinigungsprozess ist dasselbe wie die Arbeit von Shibata, Noguchi und Kaneko. Vergl. IX. Mittl.

Tabelle 1. Dichteunterschied zwischen den natürlichen Wässern und dem Leitungswasser von der Stadt Tokyo.

| Ort                                            | Art                                       | Datum         | Temperatur (°C) | pH  | Dichteunterschied |
|------------------------------------------------|-------------------------------------------|---------------|-----------------|-----|-------------------|
| 1. Yakedake (A)                                | Fumarolendampf                            | 2. Aug. 1938  | 170             | 2.2 | +5.4 $\gamma$     |
| 2. Yakedake (B)                                | „                                         | 6. Aug. 1938  | 210             | 2.3 | +5.1 $\gamma$     |
| 3. Yakedake (D)                                | „                                         | „             | 91              | 5.8 | +1.4 $\gamma$     |
| 4. Yakedake (C)                                | „                                         | „             | 80.2            | 5.8 | -2.7 $\gamma$     |
| 5. Iōyama                                      | „                                         | 27. Nov. 1938 | 85.0            | 5.9 | +1.9 $\gamma$     |
| 6. Therme-Kamikōti                             | Thermalwasser                             | 22. Juli 1937 | 51.0            | 7.3 | -2.0 $\gamma$     |
| 7. Therme Nakanoyu                             | „                                         | 25. Juli 1937 | 50.0            | 6.5 | -1.5 $\gamma$     |
| 8. Therme-Bokudenburg                          | „                                         | 22. Juli 1937 | 48.2            | 6.4 | -2.4 $\gamma$     |
| 9. Therme-Hotaka<br>(untere)                   | „                                         | 3. Aug. 1938  | 63.6            | 6.2 | -2.7 $\gamma$     |
| 10. Therme-Hotaka (obere)                      | „                                         | „             | 53.8            | 6.3 | -2.0 $\gamma$     |
| 11. Therme Yarimi                              | „                                         | „             | 47.0            | 6.3 | -1.4 $\gamma$     |
| 12. Gamadagawa bei<br>Therme-Hotaka            | Flusswasser                               | „             | 11.5            | 6.5 | -1.3 $\gamma$     |
| 13. Gamadagawa bei<br>Therme-Yarimi            | „                                         | „             | 14.0            | 6.6 | -1.9 $\gamma$     |
| 14. Therme-Hirayu (obere)                      | Thermalwasser                             | 5. Aug. 1938  | 81.5            | 6.7 | -1.2 $\gamma$     |
| 15. Therme-Hirayu<br>(untere)                  | „                                         | 4. Aug. 1938  | 69.0            | 6.3 | -2.2 $\gamma$     |
| 16. Ippōsui                                    | Kohlensäure-<br>haltiges<br>Mineralwasser | „             | 22.0            | 5.6 | -0.9 $\gamma$     |
| 17. Wasser von dem kleinen<br>Bach bei Ippōsui | „                                         | „             | 14.7            | 6.8 | -1.3 $\gamma$     |

Diese Orte sind in Abb. 1. gezeigt.

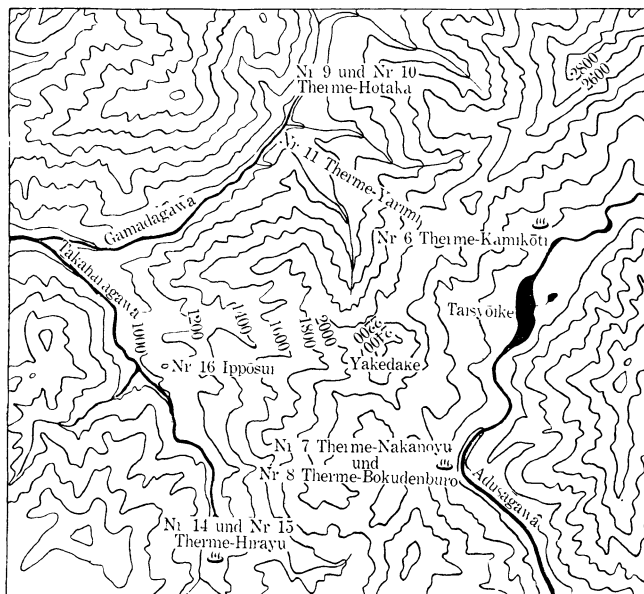


Abb. 1. Yakedake und seine Umgebung.

- (1) Obere und untere Therme-Hotaka sind voneinander etwa 50 m. entfernt.
- (2) Obere und untere Hirayu sind voneinander etwa 150 m. entfernt.
- (3) Bokudenburg steht in der Nähe von Nakanoyu etwa 40 m. entfernt.

**Diskussion der Ergebnisse.** Woran liegt denn die Ursache, dass das durch Kondensation von Fumarolendampf erhaltene Wasser immer schwerer ist als das vadoso Wasser? Die Antwort dafür ist keineswegs einfach und man möge vielleicht darüber verschieden bedenken. Vor allem aber ist es sehr wahrscheinlich, dass die schweren Wassermoleküle in Fumarolendämpfen meistens von  $\text{H}_2\text{O}^{18}$  bestehen, weil die Konzentrierung von den Deuterium haltenden Molekülen in natürlichem Wasser wenig denkbar ist.

Dann könnte man im wesentlichen die folgenden zwei Prozesse als die Ursache aufnehmen: (1) Die Austauschreaktion zwischen  $\text{O}^{16}$  in Wassermoleküle und  $\text{O}^{18}$  in Luftsauerstoff unter katalytischer Wirkung von der Oberfläche der Gesteinen bei der Temperatur von Fumarole, und (2) die Isotopentrennung durch die natürlichen langjährigen Destillation von magmatischem Wasser.

Die Beurteilung von diesen beiden Gedanken würde zu gewissem Grade durch Experiment gelangt und zwar bin ich in der Absicht zuerst die Versuche über Austauschreaktion auszuführen, indem die experimentellen Bedingungen möglichst die Natur nachahmend gewählt werden.

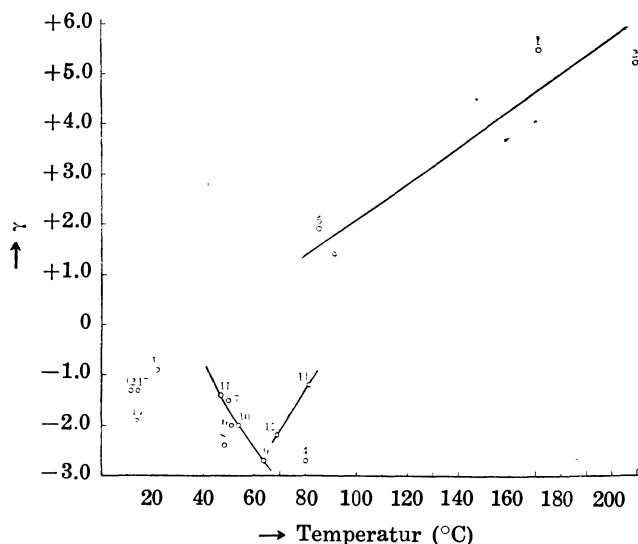


Abb. 2. Beziehung zwischen der Temperatur und dem Dichteunterschied des Wassers.

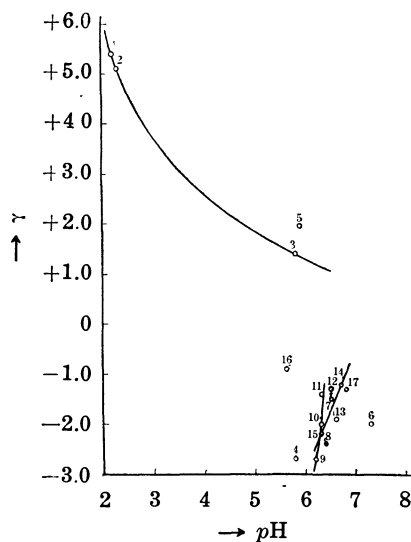


Abb. 3. Beziehung zwischen dem pH-Wert und dem Dichteunterschied des Wassers.

Nunmehr habe ich die oberen Ergebnisse graphisch dargestellt, wobei der Dichteunterschied des Wassers ( $D_{\text{Nat.}} - D_{\text{Leit.}}$ ) auf die Ordinaten und Wasser- oder Dampftemperatur und pH-Wert auf die Abszisse angesetzt. Wie man in Abb. 2 und 3 ersieht, wiegen die Wässer aus Fumarolendämpfen desto schwerer, je höher die Temperatur sind und je saurer sie reagieren, ausgenommen die Wasserprobe (C) von Yakedake-Fumarole. Diese letztere ist leichter als das Leitungswasser und zeigt sich etwas abweichend von den anderen in ihrem Charakter; nämlich enthält sie weder Schwefelwasserstoff, schweflige Säure noch Chlorywasserstoff und

ihre Temperatur ist verhältnismässig niedrig, und deshalb würde sie vielmehr in die heisse Quelle klassifiziert werden, während die Wasserproben Nrr. 1, 2, 3 und 5 immer  $\text{SO}_2$ -,  $\text{H}_2\text{S}$ - und  $\text{HCl}$ -haltig sind und ziemlich stark sauer reagierend.

Die oben genannten Beziehungen bei anderen Wasserarten wie Thermal- und Mineralwasser sind wenig regelmässig, weil solches Wasser mehr oder weniger von Niederschlägen beeinflusst wird. Aber wenn man darunter die miteinander in näherem Verhältnis stehenden aufnimmt, so findet man hier wieder eine Regel. So zum Beispiel sind die Thermalwässer Nrr. 9, 10 und 11, die entlang den Gamada-Fluss (Siehe Abb. 1) sprudeln, umso leichter, je höher ihre Temperatur und je stärker ihre Säurereaktion sind.

Diese Arbeit wird weiter über den Fumarolenwässern von verschiedenen Örtlichkeiten fortgesetzt werden.

Es sei mir gestattet, Herrn Prof. Yuju Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und Ratschläge, und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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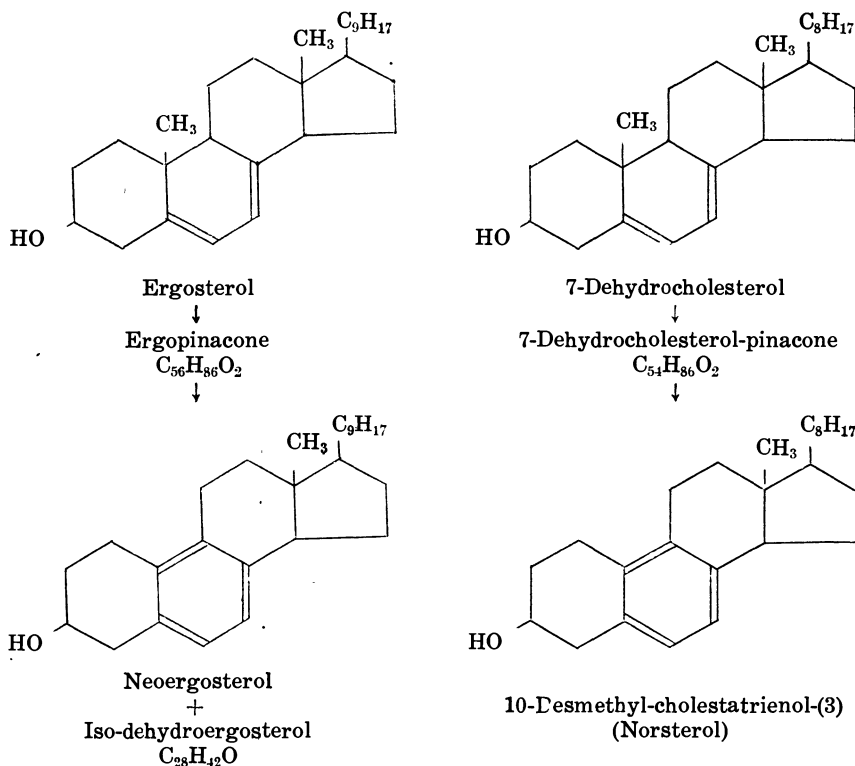
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# The Photochemical Dehydrogenation of Ergosterol and 7-Dehydrocholesterol.

By Toshio ANDO.

(Received March 31, 1939.)

Ergosterol undergoes dehydrogenation when its alcoholic solution containing eosin is exposed to light in the absence of oxygen.<sup>(1)</sup> The product,  $C_{56}H_{86}O_2$ , has been unappropriately called ergopinacone. It suffers a characteristic decomposition on submitting it to distillation in vacuum or on heating it with glacial acetic acid or decalin.<sup>(2)</sup> In this decomposition methane is eliminated, and neoergosterol is formed along with iso-dehydroergosterol,  $C_{28}H_{42}O$ , which has been isolated and characterized by the present author.<sup>(3)</sup>



The analogous photochemical dehydrogenation of 7-dehydrocholesterol, with a structure similar to that of ergosterol, to 7-dehydrocholesterol-pinacone, and the decomposition of the latter to 10-desmethyl-cholesta-

(1) A. Windaus and P. Borgeaud, *Ann.*, **460** (1928), 235.

(2) H. H. Inhoffen, *Ann.*, **497** (1932), 130.

(3) Y. Urushibara and T. Ando, this Bulletin **11** (1936), 757; T. Ando, *ibid.*, **13** (1938), 371; **14** (1939), 169.

trienol-(3) (norsterol) corresponding to neoergosterol have been reported independently by Urushibara and the present author<sup>(4)</sup> and by Schenck, Buchholz, and Wiese.<sup>(5)</sup> 7-Dehydrocholesterol-pinacone obtained by the present author had a lower melting point (m.p. of anhydrous substance 185.5–186°, corr.) and less water of crystallization ( $C_{54}H_{86}O_2 + H_2O$ ) than the substance described by the German authors ( $C_{54}H_{86}O_2 + 1\frac{1}{2}H_2O$ , m.p. 196–197°). The pyrolytic decomposition of 7-dehydrocholesterol-pinacone, however, yielded 10-desmethyl-cholestatrienol-(3) apparently identical with norsterol obtained by the German authors by boiling their 7-dehydrocholesterol-pinacone with acetic anhydride. Hence, it seemed possible that 7-dehydrocholesterol-pinacone exists either in two forms differing in the water of crystallization or in two isomerides differing in the configuration or in the positions of the double bonds, the differences having no influence on the constitution of the decomposition product. Ergopinacone has been often prepared in this laboratory, but the known form only has always been obtained.

In the preparation of 7-dehydrocholesterol-pinacone, the author dissolved 7-dehydrocholesterol and eosin in alcohol containing a little benzene and boiled the solution to remove air, while the German authors used alcohol solely and passed carbon dioxide. It was first assumed that such differences might have caused the production of different substances. Now the author has dehydrogenated not only 7-dehydrocholesterol but also ergosterol by these two different methods. The solutions prepared in the two ways were exposed to sunlight for several days. The specimens of the pinacones as well as their diacetates and dibenzoates which have been obtained in the two series of experiments are compared in the accompanying tables.

Table 1. Ergopinacone and Esters.

## (A) The boiling method.

| Substance                   | m.p. (corr.) | $[\alpha]_D$ | Absorption maxim.           |
|-----------------------------|--------------|--------------|-----------------------------|
| Ergopinacone <sup>(4)</sup> | 200–201°     |              |                             |
| Diacetate <sup>(6)</sup>    | 207–207.5°   | –209° (12°)  | 267–268 m $\mu$ (not sharp) |
| Dibenzoate                  | 206.5–207.5° | –160° (22°)  |                             |

## (B) The carbon dioxide method.

| Substance    | m.p. (corr.) | $[\alpha]_D$ | Absorption maxim.           |
|--------------|--------------|--------------|-----------------------------|
| Ergopinacone | 200–201°     |              |                             |
| Diacetate    | 206.5–207°   | –202° (16°)  | 267–275 m $\mu$ (not sharp) |
| Dibenzoate   | 206.5–207.5° | –160° (16°)  |                             |

(4) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802; **12** (1937), 495.

(5) F. Schenck, K. Buchholz, and O. Wiese, *Ber.*, **69** (1936), 2696.

(6) T. Ando, this Bulletin, **13** (1938), 373. The melting point of the diacetate was given formerly as 205.5–206° (corr.), but it became a little higher on further recrystallization.

(7) The sharp absorptions of the dibenzoates are undoubtedly due to the benzoyl groups.

Table 2. 7-Dehydrocholesterol-pinacone and Esters.

## (A) The boiling method.

| Substance                                 | m.p. (corr.) | $[\alpha]_D$                               | Absorption maxim.          |
|-------------------------------------------|--------------|--------------------------------------------|----------------------------|
| 7-Dehydrocholesterol-pinacone             | 184.5-185.5° | -175° (24°)<br>-171° (18°) <sup>(10)</sup> | 254 m $\mu$ . (indistinct) |
| Diacetate <sup>(8)</sup>                  | 190-190.5°   | -149° (26°)                                |                            |
| Dibenzoate <sup>(9)</sup> <sup>(10)</sup> | 183-183.5°   | -114° (17°)                                |                            |

## (B) The carbon dioxide method.

| Substance                     | m.p. (corr.) | $[\alpha]_D$  | Absorption maxim.                 |
|-------------------------------|--------------|---------------|-----------------------------------|
| 7-Dehydrocholesterol-pinacone | 184.5-185.5° | -159° (24°)   | 254 m $\mu$ . (indistinct)        |
| Diacetate <sup>(8)</sup>      | 191-191.5°   | -146° (26°)   |                                   |
| Dibenzoate                    | 182.5-183.5° | -113.5° (26°) |                                   |
| „ <sup>(9)</sup>              | 182.5-183.5° | -101° (25°)   | 280, 273 m $\mu$ . <sup>(7)</sup> |

There is no doubt that the substances in the two series A and B are identical each with each. In all cases the identities were confirmed by mixed melting points. 7-Dehydrocholesterol-pinacone showed the lower melting point irrespective of the methods of removing air from the solutions of 7-dehydrocholesterol and eosin.

The pinacones and their esters all showed the colour reactions of Liebermann-Burchard and of Rosenheim as shown in the experimental part.

Another difference in the methods of preparation of 7-dehydrocholesterol-pinacone may be found in the time of exposure to sunlight. The author exposed the solutions for several days, while the German authors for a few hours. Then it is possible that the higher melting product may be formed in short exposure but changeable to the lower melting form during a longer action of sunlight. A preliminary experiment has given an indication to the possibility that it is the case. Ten hours' exposure gave a product melting at 192.5-193.5° (corr.) with decomposition after repeated recrystallization and the melting point was lowered to 187-187.5° (corr.) in a month and to 185.5-186.5° (corr.) in a year, when the substance was reserved in vacuum. Further experiments are required to decide the matter conclusively.

## Experimental.

## Ergopinacone and Esters.

**Dibenzoate from Ergopinacone Prepared by the Boiling Method.** Benzoyl chloride (5 g.) was added slowly to a solution of ergopinacone (205 mg.) in pyridine (40 c.c.) with

(8) The diacetate of the German authors showed m.p. 201-202° and  $[\alpha]_D^{25}$  -161.2°.

(9) Prepared from 7-dehydrocholesteryl benzoate. All the other esters described in the tables were prepared from the pinacones.

(10) Y. Urushibara and T. Ando, this Bulletin, 12 (1937), 495.



cooling and occasional shaking. The mixture was left to stand at room temperature overnight, and poured into ice water. The separating red matter, which solidified completely in a few days, was collected, washed with dilute acetic acid and with water, recrystallized three times from benzene-95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless, extremely fine needles (167 mg.), m.p. 201.5-202.5° (uncorr.) or 206.5-207.5° (corr.) with decomposition (Found: C, 84.92; H, 9.82. Calculated for  $C_{70}H_{94}O_4$ : C, 84.12; H, 9.49%). A considerable depression of the melting point was observed when the substance was mixed with the diacetate with the same melting point, but no depression with the specimen of the dibenzoate described below.  $[\alpha]_D^{25} = -160^\circ$  (13.95 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{22} = -2.23^\circ$ ).

**Preparation of Ergopinacone by the Carbon Dioxide Method.** Carbon dioxide was passed through a solution of ergosterol (1 g.) and eosin (1 g.) in 95% alcohol (about 400 c.c.) for 20 minutes to remove air, and the solution was exposed to sunlight for four days. The separating needles were collected after further a week's standing, washed, and recrystallized twice from benzene-95% alcohol. Colourless silky needles (315 mg.), m.p. 200-201° (corr.) with decomposition. The substance showed the same colour reactions as the specimen prepared by the boiling method.

**Diacetate.** The above ergopinacone (150 mg.) was acetylated with acetic anhydride and pyridine, and the product was recrystallized twice from benzene-95% alcohol, colourless fine needles (139 mg.), m.p. 201.5-202° (uncorr.) or 206.5-207° (corr.) with decomposition (Found: C, 82.00; H, 10.64. Calculated for  $C_{60}H_{90}O_4$ : C, 82.31; H, 10.37%). Mixed melting point with the specimen from ergopinacone prepared by the boiling method 204.5-205.5° (corr.).  $[\alpha]_D^{16} = -202^\circ$  (11.45 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{16} = -2.31^\circ$ ). Ultraviolet absorption maximum about 267-275 m $\mu$  (indistinct) in 0.055% hexane solution. In the Liebermann-Burchard test the diacetate gives red, violet, blue, and bluish green colours, while in the Rosenheim test pink, violet, dark violet, and finally dark green colours.

**Dibenzoate.** Prepared from the above ergopinacone (250 mg.). Colourless fine needles (217 mg.), melting at 201.5-202.5° (uncorr.) or 206.5-207.5° (corr.) with decomposition alone or in admixture with the specimen described above (Found: C, 84.43; H, 10.16. Calculated for  $C_{70}H_{94}O_4$ : C, 84.12; H, 9.49%).  $[\alpha]_D^{16} = -160^\circ$  (14.4 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{16} = -2.31^\circ$ ). Ultraviolet absorption maxima in 0.041% hexane solution 280 and 273 m $\mu$  (both very sharp). In the Liebermann-Burchard test the dibenzoate gives instantly wine-red, bluish violet, and then bluish green colours, while in the Rosenheim test light pink, light violet, and bluish green colours.

### 7-Dehydrocholesterol-pinacone and Esters.

**Preparation of 7-Dehydrocholesterol-pinacone by the Boiling Method.** As described in the previous papers,<sup>(4)</sup> an alcohol-benzene solution of 7-dehydrocholesterol (383 mg.) and eosin (383 mg.) was boiled to remove air, and exposed to sunlight for several days. Silky long needles (117 mg.) were obtained, and recrystallization from benzene-alcohol gave colourless needles, m.p. 184.5-185.5° (corr.) with decomposition,  $[\alpha]_D^{24} = -175^\circ$  (6.8 mg. in 1 c.c. pyridine solution,  $l = 1$  dm.,  $\alpha_D^{24} = -1.19^\circ$ ). No depression of the melting point was observed when the substance was mixed with the specimen prepared by the carbon dioxide method. The melting point, however, was lowered to 180.5° (corr.) after standing in vacuum half a year.

**Diacetate.** The above 7-dehydrocholesterol-pinacone (35 mg.) was dissolved in pyridine (7 c.c.) and acetic anhydride (0.7 g.) was added. After standing at room temperature for ten days, the slightly yellowish mixture was poured into ice water, the separating crystals were collected after standing overnight, washed with water, with dilute acetic acid, and again with water, recrystallized twice from benzene-95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (30 mg.), m.p. 185.5-186° (uncorr.) or 190-190.5° (corr.) with decomposition (Found: C, 81.87; H, 10.53. Calculated for  $C_{58}H_{90}O_4$ : C, 81.81; H, 10.66%).  $[\alpha]_D^{26} = -149^\circ$  (6.7 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{26} = -1.00^\circ$ ). Ultraviolet absorption maximum in 0.052% hexane solution 254 m $\mu$  (narrow but indistinct), another very dim band at about 268 m $\mu$ . The substance showed no depression of the melting point when mixed with the specimen of the diacetate described below.

**Preparation of 7-Dehydrocholesterol-pinacone Dibenzoate from 7-Dehydrocholesteryl Benzoate by the Boiling Method.**<sup>(10)</sup> 7-Dehydrocholesterol-pinacone dibenzoate (38 mg.) was obtained from 7-dehydrocholesteryl benzoate (158 mg.) in a week's exposure to sunlight. M.p. 183-183.5° (corr.) with decomposition.  $[\alpha]_D^{17} = -114^\circ$ . No depression of the melting point was observed when the substance was mixed with the specimen of the dibenzoate described below. In the Liebermann-Burchard test the substance gives red, violet, blue, and after standing overnight dark green colours, while in the Rosenheim test pink, dark violet, dark green, and after standing overnight dark brownish violet colours.

**Preparation of 7-Dehydrocholesterol-pinacone by the Carbon Dioxide Method.** Carbon dioxide was passed through a solution of 7-dehydrocholesterol (383 mg.) and eosin (383 mg.) in 95% alcohol (150 c.c.) for 30 minutes to remove air, and the solution was exposed to sunlight for several days. Small needles which separated out were collected and washed, m.p. 182.5-183° (corr.), yield 180 mg. Recrystallized twice from benzene-alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless needles, m.p. 181-182° (uncorr.) or 184.5-185.5° (corr.) with decomposition,  $[\alpha]_D^{24} = -159^\circ$  (6.8 mg. in 1 c.c. pyridine solution,  $l = 1$  dm.,  $\alpha_D^{24} = -1.08^\circ$ ). The melting point was lowered to 182.5° (corr.) on standing in vacuum half a year.

**Diacetate.** Prepared from the above 7-dehydrocholesterol-pinacone (35 mg.). Colourless fine needles (33 mg.), m.p. 186.5-187° (uncorr.) or 191-191.5° (corr.) with decomposition (Found: C, 82.21, 82.28, 82.04; H, 10.40, 10.68, 10.97. Calculated for  $C_{58}H_{90}O_4$ : C, 81.81; H, 10.66%).  $[\alpha]_D^{26} = -146^\circ$  (7.25 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{26} = -1.06^\circ$ ). Ultraviolet absorption maximum in 0.050% hexane solution 254  $m\mu$  (narrow but indistinct), another extremely dim band at approximately 268  $m\mu$ . In the Rosenheim test the diacetate gives light pink, light violet, then dark green colours.

**Dibenzoate.** An ice-cooled solution of the above 7-dehydrocholesterol-pinacone (35 mg.) in pyridine (7 c.c.) was mixed with benzoyl chloride (0.8 g.) and the mixture was shaken occasionally for 20 minutes. After standing for a week at room temperature, the mixture was poured into ice water and left to stand for several days. The separating crystals were collected, washed, and recrystallized twice from benzene-alcohol. Colourless needles (31 mg.), m.p. 182.5-183.5° (corr.) with decomposition (Found: C, 83.92; H, 9.45. Calculated for  $C_{68}H_{91}O_4$ : C, 83.70; H, 9.72%).  $[\alpha]_D^{27} = -113^\circ$  (12.6 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{27} = -1.43^\circ$ ).

**Preparation of 7-Dehydrocholesterol-pinacone Dibenzoate from 7-Dehydrocholesteryl Benzoate by the Carbon Dioxide Method.** A solution of 7-dehydrocholesteryl benzoate (279 mg., m.p. 141.5-143°, clear at 187°, corr.) and eosin (279 mg.) in 95% alcohol (400 c.c.) was exposed to sunlight after removing air by passing carbon dioxide. After a week's irradiation the deposit was collected, washed, recrystallized twice from benzene-alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (109 mg.), m.p. 179-180° (uncorr.) or 182.5-183.5° (corr.) with decomposition (Found: C, 83.66; H, 9.51. Calculated for  $C_{68}H_{91}O_4$ : C, 83.70; H, 9.72%). No depression of the melting point was observed in admixture with other specimens of the dibenzoate described above.  $[\alpha]_D^{25} = -101^\circ$  (12.95 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{25} = -1.31^\circ$ ). Ultraviolet absorption maxima in 0.053% hexane solution 280 and 273  $m\mu$  (both very sharp). In the Rosenheim test the substance gives light pink, dark violet, dark green, and finally dark brownish violet colours.

**Preparation of 7-Dehydrocholesterol-pinacone by the Quick Method.** A solution of 7-dehydrocholesterol (227 mg.) and eosin (227 mg.) in 95% alcohol (100 c.c.) was exposed to sunlight after removing air by passing carbon dioxide. After ten hours' irradiation the deposit (75 mg., m.p. 189.5-190.5°, corr.) was collected, purified repeatedly, and dried as usual. Colourless fine needles, m.p. 189-190° (uncorr.) or 192.5-193.5° (corr.) with decomposition. In the Liebermann-Burchard test the substance gives red, violet, and blue colours, while in the Rosenheim test light pink, light red, reddish violet, and finally violet colours. The melting point was lowered with the lapse of time even though the substance was reserved in vacuum: It showed m.p. 187-187.5° (corr.) with decomposition after a month, and m.p. 185.5-186° (corr.) with decomposition after a year. The one year old substance showed a depression of the melting point when mixed with the specimen (m.p. 184.5-185.5°, corr.) prepared by the long 'exposure method (mixed m.p. 181.5-182.5, corr.).

### Summary.

Ergopinacone and 7-dehydrocholesterol-pinacone have been prepared by two different methods, viz., the boiling method and the carbon dioxide method. The products obtained by the two methods as well as diacetates and dibenzoates derived from them have been compared. It has been indicated that the two methods yield the same products.

In conclusion the author wishes to express his hearty thanks to Prof. Y. Urushibara for his kind guidance and encouragement. He acknowledges also his indebtedness to Dr. K. Yamasaki for his advice and kindness in taking absorption spectra, and to Mr. Yasohachi Yamaguchi and to Ozi Seisi Co. for generous help.

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## The Sorption of Gases on Reduced Nickel. II. Sorption of Gaseous Hydrogen Bromide and Hydrogen Chloride and Sorption of Hydrogen Bromide through a Liquid Medium.

By Matsuji TAKEBAYASHI.

(Received June 23, 1939.)

Reduced nickel reverses the direction of addition of hydrogen bromide to ethenoid compounds, and activates hydrogen bromide in the isomerization of a certain cis compound to its geometrical isomeride. Catechol inhibits the action of reduced nickel in either case. Since such an action of reduced nickel must be closely related to adsorption, the present work has been contemplated. In the previous paper<sup>(1)</sup> it was shown that at 20° reduced nickel adsorbs hydrogen bromide slowly but abundantly, giving an indication to an activated adsorption. The present paper records the results of experiments on the sorption of hydrogen bromide at 0°C., of hydrogen chloride, and of hydrogen bromide through carbon tetrachloride.

**Materials, Apparatus, and Methods.** Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. Hydrogen bromide was generated by the action of bromine on hot tetralin, passed through cold tetralin, anhydrous calcium bromide, anthracene, and a tube cooled with ice and salt, condensed in a vessel cooled with solid carbon

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(1) M. Takebayashi, this Bulletin, **14** (1939), 47.

dioxide and ether, recondensed in a vessel cooled with liquid air, and, after evacuating any uncondensable gases, vaporized, and only the middle fraction was used. Hydrogen chloride was prepared from concentrated hydrochloric acid and concentrated sulphuric acid, dried by passing through concentrated sulphuric acid, condensed in a receiver cooled with liquid air, and then fractionated. Carbon tetrachloride, the purest commercial material, was boiled with alkaline potassium permanganate, washed with water, dried over calcium chloride, and distilled over phosphorus pentoxide. Catechol used was a commercial pure material (Merck).

The apparatus was the same that was used in the previous work. In the experiments on the sorption from carbon tetrachloride a tube as shown in Fig. 1 was used instead of the simple one shown in Fig. 1 of the previous paper.<sup>(1)</sup>

In every experiment 1.00 g. of reduced nickel was used and treated with hydrogen at 350° as described in the previous paper. Sorption took place under 1 atmospheric pressure of the gases in the dark.

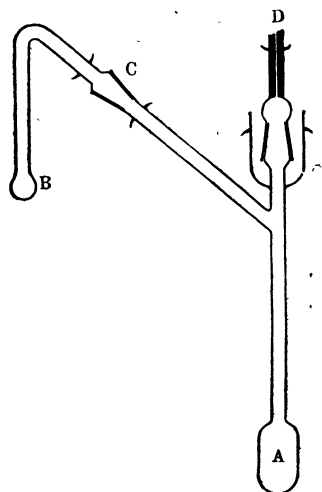


Fig. 1.

Table 1. The Sorption of Hydrogen Bromide on Reduced Nickel (1.00 g.) at 0°C.

| Time (min.) | Hydrogen bromide adsorbed (c.c., n.p.t.) |
|-------------|------------------------------------------|
| 1/2         | 1.90                                     |
| 1           | 2.20                                     |
| 2           | 2.28                                     |
| 3           | 2.35                                     |
| 5           | 2.47                                     |
| 10          | 2.67                                     |
| 20          | 2.86                                     |
| 30          | 3.00                                     |
| 50          | 3.20                                     |
| 70          | 3.30                                     |
| 100         | 3.42                                     |
| 130         | 3.52                                     |
| 160         | 3.62                                     |
| 190         | 3.69                                     |
| 1110        | 4.14                                     |
| 1230        | 4.12                                     |
| 1545        | 4.12                                     |
| 2580        | 4.14                                     |

**Sorption of Gaseous Hydrogen Bromide.** The sorption of hydrogen bromide on freshly reduced nickel was measured at 0°C. The result is given in Table 1. During the first few hours more, but in saturation less, hydrogen bromide is adsorbed at 0°C. than at 20°C. (compare Tables 5 and 6 of the previous paper). This may be another indication to an activated adsorption.

Desorption of hydrogen bromide proceeds slowly in vacuum at 0°C. The reduced nickel which adsorbed 4.14 c.c. of hydrogen bromide at 0°C. to saturation was placed in vacuum for three hours at room temperature; and hydrogen bromide was again introduced at 0°C., when the nickel adsorbed 0.91 c.c. in 1450 minutes and 1.12 c.c. in 1530 minutes. The

partial recovery of the capacity of sorption showed that a part of hydrogen bromide adsorbed on reduced nickel could be desorbed in three hours' evacuation.

**Sorption of Gaseous Hydrogen Chloride.** The sorption of hydrogen chloride on reduced nickel was observed at 20°C. and 0°C. The results are given in Tables 2, 3, and 4. At any time more hydrogen chloride is adsorbed on reduced nickel at 20°C. than at 0°C. and at either temperature more hydrogen bromide is adsorbed than hydrogen chloride.

The reduced nickel, which adsorbed 3.09 c.c. of hydrogen chloride at 0°C. to saturation and stood in vacuum for three hours, adsorbed at 0°C. 0.68 c.c. of hydrogen chloride in 1440 minutes and 0.78 c.c. in 1560 minutes. Thus it was shown that desorption takes place slowly in vacuum as in the case of hydrogen bromide.

**Sorption of Hydrogen Bromide on Reduced Nickel through Carbon Tetrachloride.** Since it is in liquid media that reduced nickel has been found to exert the peculiar influence on hydrogen bromide, it seemed desirable to study the sorption in such media. Carbon tetrachloride was chosen as the medium, and the sorption of hydrogen bromide on reduced nickel through this medium and the effect of catechol on the sorption were investigated.

The experimental procedure was as follows: Reduced nickel (1.00 g.), prepared as mentioned above, was taken in sorption tube A (Fig. 1), 1.0 c.c. of carbon tetrachloride or a carbon tetrachloride solution of catechol was poured into side tube B, the volume of the liquid was marked on the tube, and further 0.2 c.c. of pure carbon tetrachloride was added. The side tube was cooled with liquid air, and the whole apparatus was evacuated. Then the metal in the sorption tube was heated at 340–350°C. in the atmosphere of hydrogen to refresh the surface and then in vacuum for an hour to remove hydrogen, and cooled to room temperature. After the treatment of the metal was over, the excess of carbon tetrachloride in tube B was distilled off at room temperature through tube D. In this way any traces of water and air were removed. Then the cock nearest to sorption tube A was closed, tube B was revolved by 180° upward, and the contents of the tube were decanted into tube A, while tube A was cooled in liquid air. Then the sorption tube was warmed to 20°, and the sorption of hydrogen bromide was observed at 20°C.

It was first determined with the sorption apparatus that 1 c.c. of carbon tetrachloride absorbs 5.15 c.c. of hydrogen bromide of 1 atmospheric pressure at 20°C. Then 1 g. of reduced nickel was covered with 1 c.c. of pure carbon tetrachloride, and hydrogen bromide was introduced. The total amount of hydrogen bromide absorbed is given in Table 5. By subtracting the amount absorbed by carbon tetrachloride from the value given Table 5, the amount adsorbed on reduced nickel is found to be 4.27 c.c. The concentration of hydrogen bromide in carbon tetrachloride is about five times as large as in the gas, while reduced nickel adsorbed a little less hydrogen bromide from the carbon tetrachloride solution than from the gas.

Table 2. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 20°C.

| Time (min.) | Hydrogen chloride adsorbed (c.c., n.p.t.) |
|-------------|-------------------------------------------|
| 1/2         | 1.64                                      |
| 1           | 1.92                                      |
| 3           | 2.13                                      |
| 8           | 2.42                                      |
| 13          | 2.58                                      |
| 23          | 2.68                                      |
| 38          | 2.86                                      |
| 53          | 3.04                                      |
| 98          | 3.16                                      |
| 128         | 3.24                                      |
| 1418        | 3.92                                      |
| 1538        | 3.94                                      |

Table 3. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 20°C.

| Time (min.) | Hydrogen chloride adsorbed (c.c., n.p.t.) |
|-------------|-------------------------------------------|
| 1/2         | 1.68                                      |
| 1           | 1.90                                      |
| 4           | 2.18                                      |
| 9           | 2.38                                      |
| 19          | 2.54                                      |
| 29          | 2.67                                      |
| 49          | 2.77                                      |
| 69          | 2.84                                      |
| 99          | 2.93                                      |
| 129         | 2.98                                      |
| 159         | 3.02                                      |
| 189         | 3.06                                      |
| 1470        | 3.44                                      |

Table 4. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 0°C.

| Time (min.) | Hydrogen chloride adsorbed (c.c., n.p.t.) |
|-------------|-------------------------------------------|
| 1/2         | 1.47                                      |
| 1           | 1.71                                      |
| 3           | 1.89                                      |
| 5           | 2.03                                      |
| 10          | 2.16                                      |
| 20          | 2.26                                      |
| 30          | 2.36                                      |
| 50          | 2.52                                      |
| 70          | 2.54                                      |
| 100         | 2.59                                      |
| 130         | 2.63                                      |
| 190         | 2.69                                      |
| 1455        | 3.09                                      |
| 1590        | 3.09                                      |
| 1660        | 3.11                                      |
| 2630        | 3.09                                      |

Table 5. The Absorption of Hydrogen Bromide by Reduced Nickel (1.00 g.) and Carbon Tetrachloride (1.0 c.c.) at 20°C.

| Time (min.) | Hydrogen bromide absorbed (c.c., n.p.t.) |
|-------------|------------------------------------------|
| 1205        | 9.26                                     |
| 1440        | 9.38                                     |
| 1500        | 9.42                                     |

Table 6. The Absorption of Hydrogen Bromide by Reduced Nickel (1.00 g.) and Carbon Tetrachloride (1.0 c.c.) Containing Catechol (2 mg.) at 20°C.

|    | Time (min.) | Hydrogen bromide absorbed (c.c., n.p.t.) |
|----|-------------|------------------------------------------|
| I  | 1365        | 12.50                                    |
|    | 1440        | 12.58                                    |
|    | 1500        | 12.84                                    |
| II | 1320        | 12.19                                    |
|    | 1440        | 12.43                                    |
|    | 1520        | 12.52                                    |

It was first presumed that the inhibiting action of catechol on reduced nickel was caused by poisoning. Hence, the effect of catechol on the sorption of hydrogen bromide on reduced nickel was studied. Because of the small solubility of catechol in carbon tetrachloride, a solution containing 2 mg. of catechol in 1 c.c. was used. The solubility of hydrogen bromide in carbon tetrachloride was found to be hardly affected by such a small amount of catechol: 1 c.c. of the solution absorbed 5.56 c.c. of hydrogen bromide at 20°C. Then reduced nickel (1.00 g.) was covered with 1 c.c. of the solution and hydrogen bromide was introduced. The total amounts absorbed are shown in Table 6. More hydrogen bromide was absorbed in the presence of catechol, and a simple poisoning was not proved. These results as well as those obtained by O. Simamura in the experiments on the action of hydrogen bromide on catechol and reduced nickel will be interpreted by Y. Urushibara elsewhere.<sup>(2)</sup>

The author expresses his hearty thanks to Prof. Y. Urushibara for his kind guidance and encouragement. Thanks are also due to the Japan Society for the Promotion of Scientific Research and to Ozi Seisi Co. for grants.

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(2) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), No. 8.



## The Isomerization of Methyl Allo-cinnamate by Hydrogen Bromide and the Influence of Oxygen.

By Osamu SIMAMURA.

(Received July 1, 1939.)

In the previous report<sup>(1)</sup> an observation concerning the isomerization of dimethyl maleate to the fumarate caused by hydrogen bromide and chloride was described. It was shown that no participation of oxygen in addition to hydrogen bromide is necessary and this type of conversion of cis-trans isomerides was contrasted with that of isostilbene to stilbene<sup>(2)</sup>, which is brought about by the joint action of hydrogen bromide and either oxygen or reduced nickel but not by hydrogen bromide alone nor by hydrogen chloride under any condition at room temperature. In view of the essential function of the carbomethoxyl group in correlation to which were interpreted the experimental results and of hitherto attempted explanations of the nature of the catalysis by hydrogen halides in the

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(1) O. Simamura, this Bulletin, **14** (1939), 22.

(2) Y. Urushibara and O. Simamura, *ibid.*, **12** (1937), 507; **13** (1938), 566.

isomerization, a mechanism was tentatively suggested that the hydrogen halide associates with the ethenoid compound by the formation of hydrogen bond through the carbonyl oxygen atom, the accompanying displacement of the shared electrons in the molecule resulting in the more or less diminished rigidity of the double bond.

The scope of the research has since been extended to methyl allo-cinnamate, which has been, in conformity with the expectation from its structure, found to display the behaviour intermediate between dimethyl maleate and isostilbene. Thus, hydrogen bromide converted methyl allo-cinnamate to methyl cinnamate in the dark at room temperature with a slower rate than dimethyl maleate, and the isomerization was accelerated by the presence of oxygen, the action of which was suppressed by catechol added beforehand to the ester. Methyl allo-cinnamate was isomerized by hydrogen chloride very slowly even at an elevated temperature (55°). The formation of methyl cinnamate was also brought about by the addition of a drop of piperidine<sup>(3)</sup> to 0.1 c.c. of the allo-cinnamate (34% in the course of 24 hours).

These facts add to the possibility of the proposed mechanism of the catalysis by hydrogen halides, in which the presence of a carboalkoxyl group or rather of a carbonyl group conjugated with the double bond is essential. Further, in support of this view it is recorded in the literature that dibenzoyl-ethylene<sup>(4)</sup> and isobenzaldehyoxybenzoin<sup>(5)</sup> are easily converted by hydrogen chloride into their geometrical isomerides. According to the recent study by Y. Urushibara<sup>(6)</sup> bromine atoms play a deciding part as chain carriers in the addition of hydrogen bromide to allyl bromide in the presence of oxygen and in the isomerization of isostilbene by the co-operative action of hydrogen bromide and oxygen. As photo-sensitized bromine catalysis in the cis-trans isomerization is widely observed, it seems that the co-operation of hydrogen bromide and oxygen may be rather general irrespective of the nature of the substituents in the isomerizing molecule. In the case of dimethyl maleate the failure of detection of the influence of oxygen may be ascribed to the rapidity of the hydrogen bromide catalysis. With methyl allo-cinnamate the effectiveness of oxygen has been demonstrated.

**Materials.** The hydrogenation of methyl phenylpropiolate to methyl allo-cinnamate in methanol with palladium deposited on barium sulphate as catalyst yielded a mixture, which could not be easily handled. Then sodium phenylpropiolate was hydrogenated in aqueous solution with the same catalyst to allo-cinnamic acid (Yield 20%), which was converted into the silver salt and finally into the methyl ester by the action of methyl iodide upon the latter suspended in dry ether in the dark at room temperature.<sup>(7)</sup> The raw product was once distilled in vacuum, b.p. 94° under 1-1.5 mm.,  $n_D^{20}$  1.5541. Other materials were obtained and purified as described in the previous report.<sup>(1)</sup>

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(3) Compare G. R. Clemons and S. B. Graham, *J. Chem. Soc.*, **1930**, 213.

(4) C. Paal and H. Schulze, *Ber.*, **35** (1902), 168.

(5) H. Stobbe and K. Niedenzu, *ibid.*, **34** (1901), 3897.

(6) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), No. 8.

(7) C. Liebermann, *Ber.*, **23** (1890), 2510; **24** (1891), 1107.

**Experimental.** A clearing point curve of the binary mixture methyl allo-cinnamate—methyl cinnamate was constructed from the following data and subsequent analyses of reaction mixtures were effected by reference to the curve.

| Cinnamate (%)        | 0  | 10.9 | 17.7 | 30.9 | 39.7 | 55.4 | 72.6 | 85.0 | 100 |
|----------------------|----|------|------|------|------|------|------|------|-----|
| Clearing point (°C.) | −3 | −7   | −9   | −4   | 4.5  | 17   | 25.5 | 31.5 | 35  |

Experiments were carried out in the dark at room temperature, procedures being much the same as with dimethyl maleate. In a small glass bulb 0.1 c.c. of methyl allo-cinnamate was taken and after evacuation of the bulb 10 c.c. of hydrogen bromide was introduced, the bulb sealed off and left to stand for about two hours. Then the sealed end of the bulb was crushed in 1% aqueous potassium hydroxide, the oil was taken up in ether, the ether solution washed with water, dried and evaporated. The resulting ester mixture contained 71% of methyl cinnamate. When in addition to hydrogen bromide 3 c.c. of oxygen was admitted, as much as 82% of the allo-cinnamate was isomerized; and 15 mg. of catechol inhibited completely this accelerating action of oxygen, the conversion being 66%, which is about the same magnitude as without oxygen. In a separate experiment catechol was found ineffective in causing the isomerization.

In carbon tetrachloride solution (0.1 c.c. of the ester in 10 c.c.) contained in a tube of a 65 c.c. capacity 23% of the cinnamate was formed by hydrogen bromide (10 c.c.) in four hours. In the same vessel 0.1 c.c. of the allo-cinnamate in 5 c.c. of carbon tetrachloride was isomerized by 5 c.c. of hydrogen bromide in the presence of 20 c.c. of oxygen to the extent of 87% in 22.5 hours and the addition of 25 mg. of catechol reduced the conversion to 62%.

With hydrogen chloride the isomerization took place very slowly and when the reaction temperature was raised to 55°C. it amounted to 14% in the course of 7.5 hours. In carbon tetrachloride under essentially the same conditions as with hydrogen bromide, there was no appreciable formation of the cinnamate with 20 c.c. of hydrogen chloride, whether oxygen was present or not.

The author wishes to express sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragements throughout the work. Thanks are also due to the Japan Society for the Promotion of Scientific Research and to Ozi Seisi Company for grants.

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## Studies on the Oiliness of Liquids. VIII. Measurements of the Static Friction Coefficients for Silver Surfaces.

By Toshizo ISEMURA.

(Received May 23, 1939.)

The measurements of the coefficients of static friction of some pure chemical compounds as well as mixtures for glass surfaces were described in the preceding papers.<sup>(1)</sup> In the complete or film lubrication the surfaces are entirely separated by a thick film of lubricant and the friction depends only upon the nature of the lubricating liquid. It seems that the nature of surface material has no or little effect in this case. In boundary lubrication, however, the surfaces are in contact except for thin film which may be thick by only one molecule layer and the effect of the nature of the solid material can hardly be overlooked. It is important to measure the static friction coefficients with the surfaces of different materials. In the present paper, the measurement of the static friction coefficient for silver surfaces is described. The friction surfaces used consisted of a silver plate and a silver slider with convex spherical surface.

The experiments were pursued by the balance method. The cleanliness of the surfaces is of the utmost importance for the measurements of the static friction coefficients. The surfaces are cleaned in the following manner before each observation. The silver plate and the slider are polished with *rouge*-paper on a grinder, then with cloth and at last with leather or flannel to remove any scratches on the surfaces as completely as possible. After polishing, the surfaces are cleaned by electrolysis. A mixture of equal volumes of 1% aqueous solution of caustic soda and alcohol is taken as the electrolytic solution. The electrolytic cell consists of a platinum anode and a silver cathode. Electrolysis is conducted at 6 volts and less than 0.2 amp., for 30~60 minutes. After this treatment, the silver plate and the slider are rinsed with distilled water and then with drains of distilling alcohol and dried in a desiccator by passing a current of dry air. The silver surfaces cleaned by such a procedure are readily wetted with water and the friction coefficient of the surfaces with no lubricant is very high and fairly concordant in every experiment. It is a somewhat difficult matter to determine the cleanliness of the surface of silver. The friction coefficient itself is a very good criterion. The clean surfaces stick strongly and show a high friction coefficient. At first, the static friction coefficient of silver with no lubricant was determined. The results are shown in Table 1.

For the measurements of static friction coefficients of organic liquids, the friction coefficient of silver with no lubricant is measured prior to each experiment. If the value of the friction coefficient of silver surfaces

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(1) Sameshima, Kidokoro and Akamatsu, this Bulletins, **11** (1936), 659; Akamatsu and Sameshima, *ibid.*, **11** (1936), 791; Sameshima and Tsubuku *ibid.*, **12** (1937), 127; Akamatsu, *ibid.*, **13** (1938), 127; Isemura, *ibid.*, **14** (1939), 270.

is larger than 0.9, it was assumed that the surfaces are clean. The further measurements were conducted with these clean surfaces.

Table 1.

|              | W     | F     | $\mu$ |
|--------------|-------|-------|-------|
| No lubricant | 9.10  | 9.36  | 1.03  |
|              | 10.30 | 10.78 | 1.05  |
|              | 14.10 | 14.02 | 1.00  |
|              | 14.90 | 17.02 | 1.14  |
|              | 19.90 | 22.55 | 1.13  |
|              | 20.20 | 19.88 | 0.98  |
|              | 20.25 | 19.66 | 0.97  |
|              | 20.30 | 21.92 | 1.08  |
|              | 30.25 | 29.95 | 0.99  |
|              | 30.25 | 31.83 | 1.05  |
|              |       |       | 1.04  |

As to the cleaning of the steel surfaces, Hardy<sup>(2)</sup> wrote as follows: "Steel plates and sliders were cleaned by washing with soap and water, rubbing vigorously with the finger tips in a stream of tap water until water wetted the entire surface, rinsing with perfectly dry alcohol and allowing to drain in air." However, when the silver surfaces were washed with soap and rinsed with water, the surfaces entirely repelled water. The surface could not be wetted with water by rubbing the surface with finger tips in the stream of tap water. Probably, the soap molecules are strongly adsorbed by the surface and take orientation on it, the

polar group being attached to the surface. These surfaces show very low friction coefficients as shown in Table 2. The greater part of soap is removed rinsing the surfaces with alcohol. It is difficult however, to obtain sufficiently clean surface.

Table 2.

|                                               | W     | F     | $\mu$ |
|-----------------------------------------------|-------|-------|-------|
| Both plate and slider are washed with soap.   | 30.25 | 6.80  | 0.22  |
|                                               | 60.25 | 10.23 | 0.17  |
|                                               | 63.65 | 11.40 | 0.17  |
|                                               |       |       | 0.19  |
| Only plate is washed with soap, clean slider. | 30.25 | 5.13  | 0.17  |
|                                               | 38.65 | 7.18  | 0.19  |
|                                               |       |       | 0.18  |
| Only slider is washed with soap, clean plate. | 30.30 | 10.34 | 0.34  |

In the present experiment, the friction coefficients have been measured of water, alcohols, acids, hydrocarbons and esters. The purest samples available were used. Alcohols, acids and esters were distilled prior to each experiment, after sufficient drying with the appropriate drying agents. As already reported in the former paper,<sup>(3)</sup> the aliphatic hydrocarbons such as hexane, contain some unsaturated hydrocarbon as impurities.

(2) Hardy and Doubldray, *Proc. Roy. Soc. (London)*, **A**, **100** (1922), 550.

(3) Akamatu, this Bulletin, **13** (1938), 127.

These impurities cannot be removed merely by distillation. The samples containing these impurities give somewhat lower friction coefficients. So the hydrocarbons used in the present experiment were purified by shaking with fuming sulphuric acid for several days, dried over sodium metal and distilled.

The results obtained are shown in Table 3. The values of friction coefficient against the number of carbon atoms are plotted in Fig. 1 and Fig. 2.

Table 3.

|                | W     | F     | $\mu$ |                          | W     | F     | $\mu$ |
|----------------|-------|-------|-------|--------------------------|-------|-------|-------|
| Water          | 18.65 | 16.50 | 0.88  | Ethyl alcohol            | 18.65 | 16.05 | 0.86  |
|                | 20.25 | 16.85 | 0.83  |                          | 20.25 | 17.73 | 0.88  |
|                | 20.30 | 18.88 | 0.93  |                          | 23.65 | 20.10 | 0.85  |
|                | 30.25 | 28.40 | 0.94  |                          | 28.65 | 26.43 | 0.92  |
|                | 41.90 | 40.10 | 0.96  |                          | 30.25 | 26.20 | 0.87  |
|                |       |       | 0.91  |                          |       |       | 0.88  |
| Hexane         | 15.20 | 15.20 | 1.00  | <i>n</i> -Propyl alcohol | 28.64 | 22.80 | 0.80  |
|                | 18.70 | 16.92 | 0.90  |                          | 30.25 | 25.68 | 0.85  |
|                | 20.20 | 18.50 | 0.92  |                          | 30.25 | 23.98 | 0.79  |
|                | 20.30 | 19.20 | 0.95  |                          | 30.30 | 27.70 | 0.91  |
|                | 23.60 | 24.25 | 1.03  |                          |       |       | 0.84  |
|                |       |       | 0.96  |                          |       |       |       |
| Heptane        | 14.10 | 13.00 | 0.92  | <i>n</i> -Butyl alcohol  | 18.65 | 15.11 | 0.81  |
|                | 14.80 | 13.75 | 0.93  |                          | 19.10 | 14.90 | 0.78  |
|                | 17.50 | 16.75 | 0.96  |                          | 20.25 | 14.30 | 0.71  |
|                | 18.20 | 17.13 | 0.94  |                          | 20.25 | 15.68 | 0.77  |
|                | 19.10 | 18.05 | 0.95  |                          | 30.25 | 22.52 | 0.74  |
|                | 22.55 | 20.55 | 0.91  |                          | 30.25 | 22.50 | 0.74  |
|                |       |       | 0.94  |                          |       |       | 0.76  |
| Octane         | 14.10 | 14.28 | 1.01  | <i>n</i> -Amyl alcohol   | 20.25 | 13.23 | 0.65  |
|                | 14.90 | 13.72 | 0.92  |                          | 23.65 | 15.30 | 0.65  |
|                | 17.30 | 17.38 | 1.00  |                          | 29.90 | 20.20 | 0.68  |
|                | 17.50 | 16.90 | 0.97  |                          | 30.25 | 18.35 | 0.61  |
|                | 19.90 | 18.50 | 0.93  |                          |       |       | 0.65  |
|                |       |       | 0.97  |                          |       |       |       |
| Benzene        | 18.65 | 17.76 | 0.95  | <i>n</i> -Hexyl alcohol  | 14.10 | 9.42  | 0.67  |
|                | 20.25 | 19.13 | 0.95  |                          | 14.90 | 10.00 | 0.67  |
|                | 22.70 | 23.60 | 1.04  |                          | 17.50 | 10.82 | 0.62  |
|                | 23.20 | 22.60 | 0.95  |                          | 19.10 | 12.90 | 0.68  |
|                | 23.65 | 24.10 | 1.02  |                          | 22.50 | 14.48 | 0.64  |
|                | 25.65 | 24.10 | 0.94  |                          |       |       | 0.66  |
|                | 28.20 | 26.70 | 0.95  | <i>n</i> -Heptyl alcohol | 20.25 | 11.55 | 0.57  |
|                |       |       | 0.97  |                          | 28.65 | 15.92 | 0.56  |
|                |       |       |       |                          | 30.30 | 16.85 | 0.56  |
|                |       |       |       |                          | 38.70 | 21.00 | 0.54  |
|                |       |       |       |                          |       |       | 0.56  |
| Methyl alcohol | 14.10 | 11.82 | 0.84  | <i>n</i> -Octyl alcohol  | 19.10 | 10.69 | 0.56  |
|                | 14.90 | 13.38 | 0.90  |                          | 22.50 | 13.30 | 0.59  |
|                | 18.30 | 16.50 | 0.90  |                          | 23.70 | 11.65 | 0.49  |
|                | 18.30 | 17.05 | 0.93  |                          | 30.30 | 15.52 | 0.51  |
|                | 19.90 | 17.50 | 0.88  |                          | 30.30 | 14.73 | 0.49  |
|                | 23.30 | 21.73 | 0.93  |                          |       |       | 0.53  |
|                |       |       | 0.90  |                          |       |       |       |

Table 3.—(Concluded)

|                         | W     | F     | $\mu$ |                          | W     | F     | $\mu$ |
|-------------------------|-------|-------|-------|--------------------------|-------|-------|-------|
| Acetic acid             | 14.10 | 12.98 | 0.92  | Oleic acid               | 30.25 | 7.02  | 0.23  |
|                         | 18.65 | 17.78 | 0.95  |                          | 38.65 | 9.54  | 0.25  |
|                         | 20.30 | 17.68 | 0.87  |                          | 41.95 | 9.65  | 0.23  |
|                         | 28.65 | 25.70 | 0.90  |                          | 46.50 | 12.30 | 0.26  |
|                         | 30.30 | 27.66 | 0.91  |                          | 51.95 | 12.70 | 0.24  |
|                         |       |       | 0.91  |                          |       |       | 0.24  |
| Propionic acid          | 20.25 | 16.40 | 0.81  | Ethyl acetate            | 10.25 | 8.84  | 0.86  |
|                         | 28.65 | 23.35 | 0.82  |                          | 20.25 | 16.30 | 0.81  |
|                         | 30.25 | 25.78 | 0.85  |                          | 20.30 | 16.10 | 0.79  |
|                         | 38.65 | 33.42 | 0.86  |                          | 30.30 | 24.80 | 0.82  |
|                         |       |       | 0.84  |                          |       |       | 0.82  |
| Butyric acid            | 20.25 | 15.10 | 0.75  | <i>n</i> -Propyl acetate | 20.25 | 15.55 | 0.77  |
|                         | 20.30 | 13.40 | 0.66  |                          | 23.65 | 17.15 | 0.73  |
|                         | 30.25 | 21.12 | 0.70  |                          | 28.65 | 20.28 | 0.71  |
|                         | 30.30 | 22.10 | 0.73  |                          | 30.30 | 21.88 | 0.72  |
|                         |       |       | 0.71  |                          | 38.65 | 27.20 | 0.70  |
| Valeric acid            | 19.90 | 11.85 | 0.60  |                          | 38.65 | 28.12 | 0.73  |
|                         | 23.30 | 13.80 | 0.59  | <i>n</i> -Butyl acetate  |       |       | 0.73  |
|                         | 28.70 | 17.90 | 0.62  |                          | 20.25 | 14.00 | 0.69  |
|                         | 29.90 | 17.20 | 0.58  |                          | 28.65 | 19.70 | 0.69  |
|                         | 30.25 | 17.50 | 0.58  |                          | 28.70 | 19.98 | 0.70  |
|                         |       |       | 0.59  |                          | 30.25 | 20.25 | 0.67  |
| <i>n</i> -Caproic acid  | 20.25 | 11.20 | 0.55  |                          | 38.65 | 24.44 | 0.63  |
|                         | 23.65 | 12.40 | 0.52  |                          |       |       | 0.68  |
|                         | 28.65 | 14.81 | 0.52  | <i>n</i> -Amyl acetate   | 20.25 | 13.50 | 0.67  |
|                         | 30.25 | 16.44 | 0.54  |                          | 20.25 | 14.90 | 0.74  |
|                         | 30.25 | 17.12 | 0.57  |                          | 30.25 | 18.69 | 0.62  |
|                         | 38.65 | 21.20 | 0.55  |                          |       |       | 0.68  |
|                         |       |       | 0.54  |                          |       |       |       |
| <i>n</i> -Heptylic acid | 20.25 | 8.74  | 0.43  | <i>n</i> -Octyl acetate  | 20.30 | 12.90 | 0.64  |
|                         | 28.65 | 13.02 | 0.45  |                          | 20.30 | 13.13 | 0.65  |
|                         | 30.25 | 12.63 | 0.42  |                          | 28.65 | 17.48 | 0.61  |
|                         | 38.65 | 18.10 | 0.47  |                          | 30.30 | 19.20 | 0.63  |
|                         | 41.85 | 19.70 | 0.47  |                          | 38.65 | 22.40 | 0.58  |
|                         | 60.25 | 25.68 | 0.43  |                          |       |       | 0.62  |
|                         |       |       | 0.45  |                          |       |       |       |
| <i>n</i> -Caprylic acid | 41.85 | 13.82 | 0.33  | Ethyl propionate         | 14.10 | 11.62 | 0.82  |
|                         | 60.25 | 18.60 | 0.31  |                          | 17.50 | 14.22 | 0.81  |
|                         | 68.65 | 20.40 | 0.30  |                          | 18.30 | 15.18 | 0.83  |
|                         |       |       | 0.31  |                          | 23.30 | 19.53 | 0.84  |
|                         |       |       |       |                          |       |       | 0.83  |
| <i>n</i> -Nonylic acid  | 41.85 | 11.44 | 0.27  | Ethyl butyrate           | 20.25 | 15.46 | 0.76  |
|                         | 46.90 | 12.75 | 0.27  |                          | 20.30 | 15.88 | 0.78  |
|                         | 51.85 | 14.45 | 0.28  |                          | 30.25 | 22.90 | 0.77  |
|                         | 55.30 | 14.92 | 0.27  |                          |       |       | 0.77  |
|                         | 60.25 | 16.75 | 0.28  |                          |       |       |       |
|                         | 68.70 | 18.14 | 0.26  |                          |       |       |       |
|                         |       |       | 0.27  |                          |       |       |       |

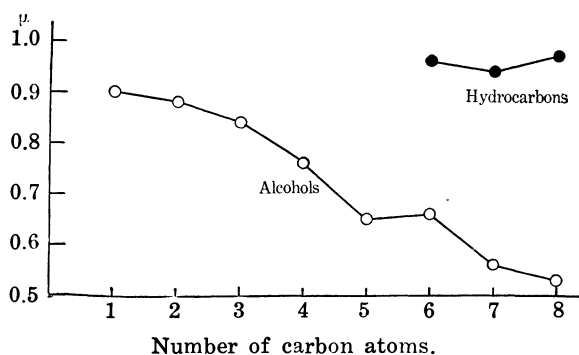


Fig. 1.

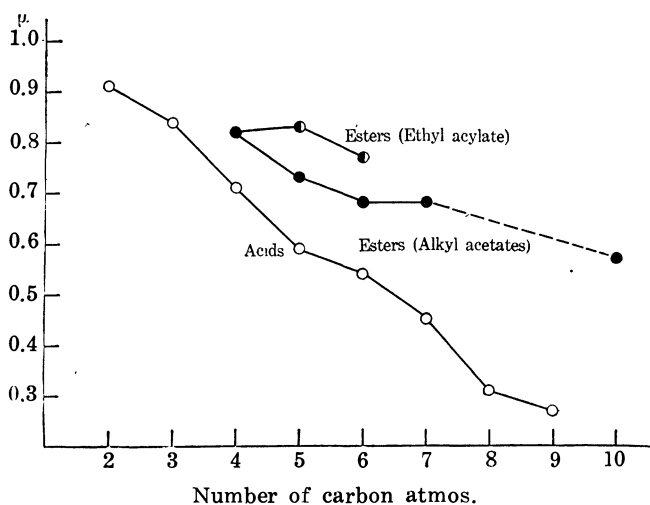


Fig. 2.

Hydrocarbon such as hexane, heptane, octane and benzene give very high friction coefficients. The  $\mu$ -values are almost the same with the value of clean surface. The lubricating activity is practically nil with these substances. The compounds of low molecular weight such as acetic acid, methyl alcohol, ethyl acetate and water are always poor lubricants irrespective to their species. In the cases of acids, alcohols and esters, the coefficients of friction are diminished as the length of the chains is increased. With lower homologues, there is no appreciable difference between the lubricating activities of acids, alcohols and esters. But with the compounds of fairly long chains acid is most efficient lubricant and alcohol comes next. Ester is most inefficient among the three. The results with alcohols and esters are almost comparable with the results on glass surfaces.<sup>(4) (5)</sup> Regarding to the  $\mu$ -values of acids, there is a

(4) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127.

(5) T. Isemura, *ibid.* **14** (1939), 270.



striking difference between the results obtained on glass surfaces and on silver surfaces. On the glass surfaces, the static friction coefficients of aliphatic acids are nearly constant,<sup>(4)</sup> while on silver surfaces, they diminish rapidly with the number of carbon atoms in the molecular formulae. For the washing with soap we know that the long chain molecules such as soap adhere to silver surface much better than to glass. The molecules take good orientation on the silver surface. The longer the molecules are, the better the orientation is taken. From these facts the long chain fatty acids serve as good lubricants. The regular arrangement of the molecules on the surface plays an important rôle on the oiliness. The effect of the arrangement of the molecules was already reported in the previous paper.<sup>(6)</sup> This is probably the reason why the long chain fatty acids shows the low friction coefficients.

In conclusion the author expresses his hearty thanks to Prof. J. Same-shima for his kind guidance and encouragement. The expense for the experiments has been defrayed from a grant given to Prof. Same-shima by Nippon Gakujutsu Shinkokai (Japan Society for the Promotion of Scientific Research), to which author's thanks are due. The author's acknowledgment is also due to Hattori Hokokwai for a grant.

### Summary

(1) Measurements of the static friction coefficients have been made to study the oiliness of liquids. The friction surfaces consisted of a silver plate and a silver piece of spherical surface.

(2) The static friction coefficients of water, hydrocarbons, aliphatic alcohols, aliphatic acids and esters have been measured.

(3) The static friction coefficients of these compounds excepting the acids are all comparable with the results obtained for the glass surfaces. The friction coefficients of acids diminish rapidly with the number of carbon atoms in the chain of the molecule for the silver surfaces, while they are nearly constant irrespective to the number of carbon atoms for glass surfaces.

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(6) Akamatu and Same-shima, this Bulletin, **11** (1936), 791.

## The Occurrence of Germanium in the Hot Springs of Senami.

By Kazuo KURODA.

(Received June 29, 1939.)

Germanium occurs in quite appreciable amounts in some mineral waters.<sup>(1)</sup> J. Bardet reported germanium to be present in the mineral waters of Vichy to the extent of one part in 40,000,000 parts of water. In this country, it was also found spectroscopically by Prof. K. Kimura in a large number of mineral waters.<sup>(2)</sup> In the present work the author attempted a spectroscopic estimation of the element in the hot springs of Senami, Niigata Prefecture.

**Arc Spectrographic Estimation of Germanium.** J. Papish and his collaborators<sup>(3)</sup> described a method of the arc spectrographic estimation of germanium, in which the germanium solution was placed on the lower electrode. In the present paper the author describes a method in which germanium is added to sodium chloride in various concentrations. 0.1441 g. of pure germanium dioxide was dissolved in water and the volume was made up to 100 c.c. Each c.c. of this solution contains 1 mg. of germanium. From this stock solution, solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg. of germanium per c.c. were prepared. 10 mg. of sodium chloride was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg of germanium respectively. The Hilger spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 1. In this table, s signifies that the line in question is strong, w that it is weak and f that it is faintly visible.

Table 1. Spectral Lines at Different Concentrations.

| $\lambda$ (Å) | 1 mg | 0.1 mg | 0.01 mg | 0.001 mg | 0.0001 mg | 0.00001 mg |
|---------------|------|--------|---------|----------|-----------|------------|
| 2198.7        | F    |        |         |          |           |            |
| 2314.2        | W    |        |         |          |           |            |
| 2327.9        | W    |        |         |          |           |            |
| 2338.6        | F    |        |         |          |           |            |
| 2379.1        | W    |        |         |          |           |            |
| 2394.1        | F    |        |         |          |           |            |
| 2397.9        | F    | F      |         |          |           |            |
| 2417.4        | S    | W      | W       | F        |           |            |
| 2498.0        | W    |        |         |          |           |            |

(1) J. Bardet, *Compt. rend.*, **157** (1913), 224; **158** (1914), 1278; A. P. Forjaz, *Compt. rend.*, **186** (1928), 1366; **189** (1929), 703.

(2) Not yet published.

(3) J. Papish, F. M. Brewer and D. A. Holt, *J. Am. Chem. Soc.*, **49** (1927), 3028.

Table 1.—(Concluded)

| $\lambda$ (Å) | 1 mg | 0.1 mg | 0.01 mg | 0.001 mg | 0.0001 mg | 0.00001 mg |
|---------------|------|--------|---------|----------|-----------|------------|
| 2533.2        | S    | W      |         |          |           |            |
| 2556.3        | W    |        |         |          |           |            |
| 2589.2        | W    | F      |         |          |           |            |
| 2592.6        | S    | W      | W       | F        |           |            |
| 2644.2        | W    | F      |         |          |           |            |
| 2651.1        | S    | S      | W       | W        | W         | F          |
| 2651.6        | S    | S      | W       | W        | F         |            |
| 2691.3        | S    | S      | W       | W        | F         |            |
| 2709.6        | S    | S      | W       | W        | F         |            |
| 2740.4        | S    | F      |         |          |           |            |
| 2754.6        | S    | S      | W       | W        | F         |            |
| 2793.9        | W    |        |         |          |           |            |
| 2829.1        | W    |        |         |          |           |            |
| 3039.1        | S    | S      | W       | W        |           |            |
| 3067.1        | W    |        |         |          |           |            |
| 3124.8        | W    | W      |         |          |           |            |
| 3269.5        | S    | W      | F       |          |           |            |

**Germanium Content of the Hot Springs of Senami.**<sup>(4)</sup> 500 c.c. of water sample was evaporated to complete dryness. Finely powdered residue in ten milligram portions was subjected to arc excitation. The following germanium lines were always found:—

| $\lambda$ (Å) | Intensity |
|---------------|-----------|
| 2651.1        | weak      |
| 2651.6        | faint     |
| 2691.3        | faint     |
| 2709.6        | faint     |
| 2754.6        | faint     |

This would seem to indicate that 0.0001 mg. of germanium was present in the zone of excitation. Expressed in percentages, the germanium content in the total residue is estimated to be 0.001. Expressed in terms of parts per million of the mineral water, it is supposed to be 0.03.

### Summary.

A method for the arc spectrographic detection and estimation of germanium was described.

The germanium content of the hot springs of Senami was estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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(4) According to R. Ishizu, the spring is classified as common salt spring.

## The Occurrence of Beryllium in the Hot Springs of Matunoyama.

By Kazuo KURODA.

(Received June 29, 1939)

Beryllium occurs in a great many minerals, but rarely in mineral waters.<sup>(1)</sup> Prof. K. Kimura found the occurrence of beryllium in the hot springs of Matunoyama, Niigata Prefecture, and in the present work the author attempted a spectroscopic estimation of the element.

**Arc Spectrographic Estimation of Beryllium.** Pure beryllium sulphate was dissolved in water. The beryllium content of this solution was determined gravimetrically and water was added to bring the concentration to 0.1 per cent. From this stock solution, solutions containing 0.01, 0.001, 0.0001, 0.00001, 0.000005, 0.0000025 and 0.000001 g. of beryllium per 100 c.c. were prepared. 10 mg. of sodium chloride was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001, 0.0001, 0.00005, 0.000025 and 0.00001 mg. of beryllium respectively. The Hilger quartz spectrograph of E2 type was used. The spectral lines observed at different concentrations are given in Table 1. In this table,

Table 1. Spectral Lines at Different Concentrations.

| $\lambda$ (Å) | 1 mg | 0.1 mg | 0.01 mg | 0.001 mg | 0.0001 mg | 0.00005 mg | 0.000025 mg | 0.00001 mg |
|---------------|------|--------|---------|----------|-----------|------------|-------------|------------|
| 2348.6        | S    | S      | S       | S        | W         | W          | F           |            |
| 2350.8        | S    | W      | F       |          |           |            |             |            |
| 2494.7        | S    | S      | S       | W        | F         |            |             |            |
| 2650.8        | S    | S      | S       | W        | F         |            |             |            |
| 2738.1        | F    |        |         |          |           |            |             |            |
| 2898.2        | W    |        |         |          |           |            |             |            |
| 2986.1        | F    |        |         |          |           |            |             |            |
| 3019.3        | F    |        |         |          |           |            |             |            |
| 3110.8        | W    | F      |         |          |           |            |             |            |
| 3130.4        | S    | S      | W       | W        | W         | W          | F           | F          |
| 3131.1        | S    | S      | W       | W        |           |            |             |            |
| 3187.3        | F    |        |         |          |           |            |             |            |
| 3321.1        | S    | S      | W       | W        | F         |            |             |            |
| 3321.4        | S    | S      | W       | W        | F         |            |             |            |

(1) A. Béchamp, *Compt. rend.*, **62** (1866), 1088; Pomier, *J. pharm. chim.* [2], **14** (1928), 199; M. Mazade, *Compt. rend.*, **32** (1851), 685.

s signifies that the line in question is strong, w that it is weak and f that it is faintly visible.

**Beryllium Content of the Hot Springs of Matunoyama.** 1600 c.c. of water sample was evaporated to complete dryness. The residue was treated with hydrochloric acid and filtered. The residue which mainly consisted of silica showed no beryllium when examined spectroscopically. The chloride solution was evaporated to dryness, heated to 130° in the air bath, and weighed. Finely powdered residue in ten milligram portions was subjected to arc excitation. The beryllium lines 2348.6 (weak) and 3130.4 (faint) were always found. This would seem to indicate that a quantity higher than 0.000025 mg and lower than 0.00005 mg of beryllium was present in the zone of excitation. Expressed in percentages, the beryllium content in the total residue is estimated to be between 0.00025 and 0.0005. Expressed in terms of parts per million of the mineral water it is supposed to be between 0.04 and 0.08.

### Summary

A method for the arc spectrographic detection and estimation of beryllium was described.

The beryllium content of the hot springs of Matunoyama was estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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# Vanadium, Chromium, and Molybdenum Contents of the Hot Springs of Japan.

By Kazuo KURODA.

(Received July 19, 1939.)

Aside from their well known mineral combinations, vanadium, chromium and molybdenum have long been known to occur in a great variety of rocks. They have been detected, however, rarely in mineral waters. The occurrence of vanadium, chromium and molybdenum in a large number of Japanese mineral waters has been recently found spectroscopically by Prof. K. Kimura, and their contents in the hot springs of Yunohanazawa, Hakone, Kanagawa Prefecture have been estimated by S. Oana.<sup>(1)</sup> In the present paper the author describes the results from the quantitative estimations of these elements in a number of hot springs of Japan.

**Methods of Analysis.** For the determinations of vanadium, chromium and molybdenum, Sandell's colorimetric method<sup>(2)</sup> was adopted. The analytical procedures will be briefly described in the following paragraphs.

(1) *Decomposition of Sample.* 2 to 5 g. of dry residue were first fused with anhydrous sodium carbonate. The melt was leached with water and ethyl alcohol was added to reduce  $\text{MnO}_4^-$ . Then it was filtered. The aqueous extract contains  $\text{CrO}_4^{2-}$ ,  $\text{VO}_3^-$  and  $\text{MoO}_4^{2-}$ , and the volume was made up to 100 c.c.

(2) *Vanadium.* A 30 c.c. portion was neutralized to methyl orange with 4N sulphuric acid and, after the addition of 8-hydroxyquinoline, vanadium was extracted by shaking with chloroform. The residue obtained by evaporating the chloroform solution was fused again with anhydrous sodium carbonate and the aqueous extract of this melt was treated with phosphotungstic acid: the yellow to orange colour was compared with that obtained with standard vanadium solutions.

(3) *Chromium.* A 10 c.c. portion was transferred to a small separating funnel, and neutralized to methyl orange with 4N sulphuric acid without using an indicator and, after the addition of 8-hydroxyquinoline, vanadium was removed by shaking with chloroform. Diphenylcarbazide and sulphuric acid were added: the red-violet colour was compared with that obtained with standard chromium solutions.

(4) *Molybdenum.* A 50 c.c. portion was transferred to a separating funnel. Concentrated hydrochloric acid, potassium thiocyanate solution and stannous chloride solution were added. The red-brown molybdenum thiocyanate was extracted with ether and the colour was compared with that obtained with standard molybdenum solutions.

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(1) Not yet published.

(2) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8** (1936), 336.

**The Results of the Analyses.** The results of the analyses are shown in Table 1.

Table 1. Vanadium Chromium and Molybdenum Contents of the Hot Springs of Japan.

| Hot Springs                                                    | Parts per million of the mineral water |       |        | % (per dry residue) |        |         |
|----------------------------------------------------------------|----------------------------------------|-------|--------|---------------------|--------|---------|
|                                                                | V                                      | Cr    | Mo     | V                   | Cr     | Mo      |
| (1) Mito, Sizuoka Prefecture                                   | 0.247                                  | 0.015 | 0.005  | 0.0190              | 0.0012 | 0.0004  |
| (2) "Daruma-Zigoku", Yunohanazawa, Hakone, Kanagawa Prefecture | 0.220                                  | 0.008 | 0.002  | 0.0105              | 0.0004 | 0.0001  |
| (3) Monkawa, Kanagawa Prefecture                               | 0.208                                  | 0.000 | 0.005  | 0.0007              | 0.0000 | 0.00002 |
| (4) "Kōbō-Yu", Yunohanazawa, Hakone, Kanagawa Prefecture       | 0.079                                  | 0.000 | 0.0004 | 0.0079              | 0.0000 | 0.00004 |
| (5) Matunoyama, Niigata Prefecture                             | 0.059                                  | 0.000 | 0.011  | 0.0004              | 0.0000 | 0.00008 |
| (6) Nanasure, Iwate Prefecture                                 | 0.054                                  | 0.000 | 0.010  | 0.0004              | 0.0000 | 0.00008 |
| (7) Kinkei, Totigi Prefecture                                  | 0.051                                  | 0.073 | 0.002  | 0.0024              | 0.0035 | 0.0001  |
| (8) "Umi-Zigoku", Beppu, Ōita Prefecture                       | 0.022                                  | 0.003 | 0.001  | 0.0006              | 0.0001 | 0.00003 |
| (9) Murasugi No. 3, Niigata Prefecture                         | 0.000                                  | 0.000 | 0.016  | 0.0000              | 0.0000 | 0.0095  |

The hot springs of Mito had the highest vanadium content, 0.0190% (per dry residue) and the mineral waters of Murasugi No. 3 the lowest, less than 0.001% (per dry residue). The average vanadium content of nine samples was 0.005% (per dry residue). It is supposed that vanadium is associated with iron and widely distributed in the mineral waters. The mineral waters of Kinkei had the highest chromium content, 0.0035% (per dry residue). Five samples (out of nine samples) contained less than 0.0001% (per dry residue) of chromium and the author could not detect it colorimetrically. Novokhatsky and Kalinin<sup>(3)</sup> reported molybdenum to be present in a number of hot springs in the Transilian Alatau Range in quantities varying from 0.001 to 0.06% (per dry residue). It is shown in Table 1 that the small amounts of molybdenum are widely distributed in the mineral waters of Japan. The Mineral waters of Murasugi No. 3 had the highest molybdenum content, 0.0095% (per dry residue). The molybdenum content of Murasugi No. 3 was also spectroscopically estimated by the present author to be 0.01% (per dry residue), as described below.

**Arc Spectrographic Detection and Estimation of Molybdenum in the Mineral Waters of Murasugi No. 3.** Prof. K. Kimura found the occurrence of molybdenum in the mineral waters of Murasugi No. 3 and an arc spectrographic estimation of the element was attempted by the present author. Solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg. of molybdenum per c.c. were prepared. 10 mg. of sodium chloride was added to 1 c.c. of each solution and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excita-

(3) *Compt. rend. acad. sci. U.R.S.S.*, **22** (1939), 323.

tion. The Hilger quartz spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 2. In this table, S signifies that the line in question is strong, W that it is weak and F that it is faintly visible.

Table 2. Spectral Lines at Different Concentrations.

| $\lambda$ (Å) | 1 mg. | 0.1 mg. | 0.01 mg. | 0.001 mg. | 0.0001 mg. | 0.00001 mg. |
|---------------|-------|---------|----------|-----------|------------|-------------|
| 3041.7        | W     | W       |          |           |            |             |
| 3112.1        | W     | W       | F        | F         |            |             |
| 3132.6        | S     | S       | W        | W         | F          | F           |
| 3158.2        | S     | S       | W        |           |            |             |
| 3170.3        | S     | S       | W        | W         | W          | F           |
| 3194.0        | S     | S       | W        | F         |            |             |
| 3208.9        | S     | S       | W        | W         | W          | F           |
| 3256.2        | W     | W       |          |           |            |             |
| 3289.0        | W     | W       |          |           |            |             |
| 3290.8        | W     | W       |          |           |            |             |
| 3325.7        | W     | W       |          |           |            |             |
| 3327.3        | W     | W       |          |           |            |             |
| 3340.2        | W     |         |          |           |            |             |
| 3344.8        | W     | W       |          |           |            |             |
| 3347.3        | W     | F       |          |           |            |             |
| 3358.1        | W     | W       |          |           |            |             |
| 3361.4        | W     | W       |          |           |            |             |
| 3363.8        | W     | W       |          |           |            |             |
| 3379.9        | W     | W       |          |           |            |             |
| 3382.5        | W     | W       |          |           |            |             |
| 3384.6        | W     | W       | W        | W         | W          | F           |
| 3404.4        | F     |         |          |           |            |             |
| 3405.9        | W     | W       |          |           |            |             |
| 3418.5        | F     |         |          |           |            |             |
| 3447.1        | W     | W       | F        |           |            |             |

500 c.c. of water sample was evaporated to complete dryness. Finely powdered residue in ten milligram portions was subjected to arc excitation. The following molybdenum lines were always found.

This would seem to indicate that 0.001 mg. of molybdenum was present in the zone of excitation. Expressed in percentages,<sup>(4)</sup> the molybdenum con-

| $\lambda$ (Å) | Intensity |
|---------------|-----------|
| 3112.1        | faint     |
| 3132.6        | weak      |
| 3170.3        | weak      |
| 3194.0        | weak      |
| 3208.9        | weak      |
| 3384.6        | weak      |

(4) Expressed in terms of parts per million of the mineral water it is supposed to be 0.02.



tent in the total residue of the mineral waters of Murasugi No. 3 is estimated to be 0.01, which is quite close to the value obtained by the colorimetric method.

### Summary.

(1) The vanadium, chromium and molybdenum contents in a number of hot springs of Japan were estimated.

(2) The molybdenum content of the mineral waters of Murasugi No. 3 was spectroscopically estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. It is also the author's pleasant duty to acknowledge the valuable advice offered by Mr. S. Oana. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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## Parachor, Dipolmoment, und Molrefraktion des Selenophens.

Von Bun-ichi TAMAMUSHI, Hajime AKIYAMA, und Sumio UMEZAWA.

(Eingegangen am 25. Juli 1939.)

Die physikalischen Konstanten des Selenophens—Dichte, Brechungsindex, Dampfdruck, Ausdehnungskoeffizient, Oberflächenspannung und Parachor—wurden von Briscoe und Peel<sup>(1)</sup> angegeben, die dieses Material durch Einwirkung von Acetylen auf Selen dargestellt haben. Einer von uns (S. U.), der nach der Angaben der genannten Autoren diese Darstellungsmethode bearbeitete,<sup>(2)</sup> erhielt das Material mit guter Ausbeute. Die Darstellungsmethode lautet folgenderweise: man lässt das Acetylen auf 20 g. Selen bei 350–370°C einwirken, das sich in einem Porzellanschiffe in einem Porzellanrohr befindet. Nach der Reaktion bleibt eine schwarze, teerartige Substanz im Schiffe. Man fraktioniert das rohe Öl mittels eines Ladenburgschen Kölbchens zweimal, wobei der Hauptanteil bei 110°C übergeht und darauf erhält man aus 192 g. rohem Öl 110 g. reines Selenophen. Durch mehrmalige Destillationen erhält man eine schwach gelblich gefärbte Flüssigkeit, deren Siedepunkt 110.3–111.2°C/754.2 mm. Dichte  $d_4^{25} = 1.6003$  und Brechungsindex  $n_D^{25} = 1.57689$  sind. Da dieses

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(1) H. V. A. Briscoe und J. B. Peel, *J. Chem. Soc.*, (London), **1928**, 1741.

(2) H. Suginome und S. Umezawa, *Dieses Bulletin*, **11** (1936), 157.

Präparat eine hohe Reinheit besitzen soll, was man aus den hohen Werten von Dichte und Brechungsindex ersehen kann,<sup>(3)</sup> kam es uns lohnend vor daran die physikalischen Konstanten neu zu bestimmen.

**Oberflächenspannung und Parachor.** Mit diesem Präparat versuchten wir zuerst die Kapillaritätskonstanten zu bestimmen. Die Oberflächenspannung wurde mittels der von einem von uns (B. T.) früher bearbeiteten Steighöhe-Methode<sup>(4)</sup> gemessen zwischen den Temperaturen von 25°C und 110°C. Der Durchmesser des gebrauchten Rohrs war bei dem engen Rohr 0,0370 cm und bei dem weiten 2 cm. Den Kontaktwinkel konnte man dadurch praktisch als null annehmen, dass man das Kapillarrohr bei jeder Messung mit Hilfe eines Magnets in die Flüssigkeit vollkommen hineintauchte. Der Messapparat befand sich in einem Wasser- bzw. Dampf-Thermostat. Die Steighöhe las man mittels eines Kathetometers mit Masstab-Ablesung von 0,005 cm ab. Die nach der Formel  $\sigma = \frac{1}{2} rhg(D-d)$  berechnete Oberflächenspannung wurde nach den Tabellen korrigiert, die von Sugden<sup>(5)</sup> angegeben sind. Die Ergebnisse werden in folgender Tabelle zusammengestellt.

Tabelle 1. Spezifische Kohäsion ( $\alpha^2$ ) und Oberflächenspannung ( $\sigma$ ) des Selenophens.

| $t$ C | $h$ (cm.) | $D-d$  | $\alpha^2$ (mm. <sup>2</sup> ) | $\sigma$ (dyn./cm.) |
|-------|-----------|--------|--------------------------------|---------------------|
| 25.0  | 2.476     | 1.6026 | 4.591                          | 36.05               |
| 35.1  | 2.403     | 1.5861 | 4.457                          | 34.63               |
| 56.4  | 2.262     | 1.5550 | 4.196                          | 31.96               |
| 63.6  | 2.214     | 1.5420 | 4.107                          | 31.02               |
| 77.5  | 2.100     | 1.5153 | 3.895                          | 28.92               |
| 94.5  | 1.998     | 1.4837 | 3.707                          | 26.95               |
| 110.2 | 1.895     | 1.4581 | 3.517                          | 25.12               |

Man berechnete hierauf die Molaroberflächenenergie  $\sigma \left( \frac{M}{D-d} \right)^{2/3}$  und deren Temperaturabhängigkeit ( $k$ ), indem man die bekannte Katayama'sche Gleichung:<sup>(6)</sup>

$$\sigma \left( \frac{M}{D-d} \right)^{2/3} = k(T_k - T)$$

anwendete. Der Mittelwert der Temperaturabhängigkeit ergab sich als 2,08 (Selenophen ist eine normale Flüssigkeit!), und unter Benutzung von diesem Wert berechnete man die kritische Temperatur, die sich im Mittelwert als 624.3°K ergab. Ferner bestimmte man das Parachor

(3) Vgl. mit Briscoe und Peelschen Daten:  $d_4^{15} = 1.5301$  und  $n_D^{15} = 1.568$ .

(4) B. Tamamushi, Dieses Bulletin, **1** (1926), 173.

(5) S. Sugden, *J. Chem. Soc.*, (London) **1921**, 1483.

(6) M. Katayama, *Sci. Rep. Tohoku Imp. Univ.*, **4** (1915), 373.

$P = \frac{M}{D-d} \sigma^{\frac{1}{4}}$ . Die Ergebnisse sind in Tabelle 2 gezeigt. Die hierbei verwendeten Dampfdichten wurden mittels der von Briscoe und Peel<sup>(1)</sup> angegebenen Daten von Dampfdruck berechnet.

Tabelle 2. Molaroberflächenenergie  $\left(\sigma \left(\frac{M}{D-d}\right)^{2/3}\right)$ , Temperaturkoeffizient ( $k$ ), Parachor ( $P$ ), und kritische Temperatur ( $T_k$ ).

| $t^\circ\text{K}$ | $\sigma \left(\frac{M}{D-d}\right)^{2/3}$ | $k$    | $P$     | $T_k^\circ\text{K}$ |
|-------------------|-------------------------------------------|--------|---------|---------------------|
| 298.0             | 679.1                                     | 2.20   | 200.3   | 624.7               |
| 308.1             | 656.9                                     |        | 200.4   | 623.9               |
| 329.4             | 614.3                                     | 2.00   | 200.4   | 624.2               |
| 336.6             | 599.6                                     | 2.04   | 200.5   | 625.3               |
| 350.5             | 565.6                                     | 2.44   | 200.5   | 622.4               |
| 367.5             | 534.4                                     | 1.83   | 201.2   | 624.3               |
| 383.2             | 504.0                                     | 1.94   | 201.2   | 625.5               |
|                   |                                           | (2.08) | (200.6) | (624.3)             |

Aus den grösseren Werten von Oberflächenspannung und Dichte folgt der kleinere Wert von Parachor im Vergleich mit den Briscoe und Peelschen Resultaten. Berechnet man aus diesen Werten von Parachor den Wert von Atomparachor des Selen, so bekommt man bei uns 58,3, während man dafür 68,0 bei Briscoe und Peel erhält, wobei man die folgenden Atom- bzw. Gruppen-Parachore verwendet.

$$C = 4.8 \quad H = 17.1 \quad \text{F} = 23.2 \quad \text{Se} = 8.5$$

Unter Benutzung der Messungsdaten an den fünf organischen Selen-Verbindungen (Diphenyl-Selenid usw.) hat zwar Sugden<sup>(7)</sup> für das Atomparachor des Selen den Wert 62.5 (im Mittelwert) angenommen, woraus man das Parachor des Selenophens berechnet und dabei 205.0 erhält. Dieser Wert liegt gerade zwischen dem von uns beobachteten Wert und dem von Briscoe und Peel beobachteten (210.6): die Übereinstimmung zwischen den berechneten und beobachteten ist jedoch bei uns näher, und zwar tritt bei uns eine Depression des Parachors hervor, dagegen eine Exaltation bei Briscoe und Peel. Es scheint noch fraglich, ob man zwischen der Depression des Parachors und dem aromatischen Charakter des Selenophenringes auf einen Zusammenhang schliessen kann, denn eine solche Depression lässt sich in anderen aromatischen Verbindungen noch nicht allgemeingültig erkennen.

**Dipolmoment.** Das Dipolmoment wurde durch die Messung der Dielektrizitätskonstante und Dichte der binären Flüssigkeitsgemische bestimmt, indem man für die dipolfreie Flüssigkeit einmal Benzol und

(7) S. Sugden, "The Parachor and Valency," S. 126 London (1930).

ein anderesmal Hexan verwendete. Die beiden Lösungsmittel waren sorgfältig gereinigte Präparate. Der für die Dielektrizitätskonstante (DK)-Messung gebrauchte Apparat war der elektrische Schwebungsapparat, dessen Sender auf einer Grundschiwingung von 200 m arbeitete. Die Kapazität des Präzisionskondensators war 150 mmf. mit Feinregulierung von 0,06 mmf. Den Messkondensator baute man nach Estermann<sup>(8)</sup>, indem man ein Platinblech in einem Glasrohr anlötete, und stellte ihn in einen Paraffin-Thermostat. Die ganze Apparatur war durch geerdete Metallumhüllung geschützt, durch welche nur das Führrohr des Messkondensators, die Feineinstellung der veränderlichen Kapazität und die Leitung des Telefons geführt waren.

Die Apparatur wurde empirisch geeicht und zwar zunächst mit Hilfe der verdünnten Lösungen von Äthyläther in Benzol: die Ergebnisse sind in folgender Tabelle angegeben, wobei man als DK des Benzols den von Williams<sup>(9)</sup> angegebenen Wert 2.282 (später unten 2.276) bei 25°C anwendete.

Tabelle 3. Molekulare Polarisation des Äthyläthers.  
In Benzol bei Temp. 25°C.

| $f_2$ (%) | $d_4^{25}$ | $\epsilon$ | $P_{1,2}$ | $P_2$ |
|-----------|------------|------------|-----------|-------|
| 0         | 0.8733     | 2.282      | 26.77     | 56.7  |
| 25        | 0.8312     | 2.752      | 34.11     | 56.4  |
| 50        | 0.7907     | 3.225      | 41.00     | 55.2  |
| 75        | 0.7494     | 3.809      | 48.45     | 55.7  |
| 100       | 0.7089     | 4.330      | 54.96     | 55.0  |

Die Kolonnen der Tabelle bedeuten von links nach rechts:  $f_2$  den Molenbruch des gelösten Stoffes,  $d_4^{25}$  die Dichte der Lösung,  $\epsilon$  die gemessene DK,  $P_{1,2} = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{f_1 M_1 + f_2 M_2}{d}$  die Molekularpolarisation der Lösung und  $P_2 = \frac{P_{1,2} - f_1 P_1}{f_2}$  die Molekularpolarisation des gelösten Stoffes.

Man kann mit Hilfe von der bekannten Debyeschen Grundformel aus der Molekularpolarisation  $P_2$  das elektrische Dipolmoment des gelösten Stoffes folgendermassen berechnen. Die Molekularpolarisation besteht aus zwei Teilen, nämlich der Polarisation infolge Ladungsverschiebungen  $P_2''$  und der Polarisation infolge der Orientierung fester Dipole  $P_2' = \frac{4\pi}{3} N \frac{\mu^2}{3kT}$  und demnach bekommen wir  $P_2' = P_2 - P_2''$ .

$P_2''$  wird nun annähernd berechnet nach der Lorenz-Lorentzschen Formel:  $P_2'' = \frac{n_0^2 - 1}{n_0^2 + 2} \cdot \frac{M}{d}$ , wobei  $n_0$  den Brechungsindex des gelösten Stoffes, extrapoliert für die Frequenz 0, bedeutet. Diese Extrapolation

(8) J. Estermann, *Ergeb. Exakt. Wiss.*, **8** (1929), 279.

(9) J. W. Williams, *Physik. Z.*, **29** (1928), 174; ebenda **32** (1931), 27.

kann zwar nur ausgeführt werden, wenn die Substanz keine ultraroten Absorptionen zeigt. Wenn dieses Vorgehen infolgedessen auch nicht als ganz exakt angesehen werden darf, so ergibt es doch manchmal einen genügend genauen Wert für den Teil  $P_2''$ . Der Einfachheit wegen nehmen wir noch für  $P_2''$ ,  $\frac{n_D^2-1}{n_D^2+2} \cdot \frac{M}{d}$  statt  $\frac{n_0^2-1}{n_0^2+2} \cdot \frac{M}{d}$ , was auch manchmal der Fall ist.

Für den Fall von Äthyläther fanden wir  $P_2'' = 22,5$ , woraus sich das Dipolmoment folgenderweise ausrechnen liess:

$$P_2' = P_2 - P_2'' = 55.8 - 22.5 = 33.3 \text{ cm.}^3$$

$$P_2' = \frac{4\pi}{3} N \frac{\mu^2}{3kT} = 33.3 \text{ cm.}^3$$

$$\mu = 1.26 \cdot 10^{-18} \text{ e. s. E.}$$

Tabelle 4 und 5 zeigen die Ergebnisse der Messung der Molekularpolarisation mit Selenophen. Man ermittelt hieraus nach der oben geschilderten Methode das elektrische Moment des Selenophens einmal in Benzol-Lösungen mit dem Ergebnis:  $\mu = 0.78 \cdot 10^{-18}$ , und ein andermal in Hexan-Lösungen mit dem Ergebnis:  $\mu = 0.77 \cdot 10^{-18}$ .

Tabelle 4. Molekulare Polarisation des Selenophens.  
In Benzol bei Temp. 25°C.

| $f_2$ (%) | $d_4^{25}$ | $\epsilon$ | $P_{1,2}$ | $P_2$  |
|-----------|------------|------------|-----------|--------|
| 0.000     | 0.8731     | 2.276      | 26.68     | (39.9) |
| 2.684     | 0.8908     | 2.305      | 27.05     | 40.6   |
| 4.058     | 0.8997     | 2.314      | 27.17     | 38.7   |
| 5.578     | 0.9101     | 2.324      | 27.27     | 37.1   |
| 7.427     | 0.9226     | 2.344      | 27.50     | 37.8   |
| 10.260    | 0.9424     | 2.370      | 27.77     | 37.3   |
| 24.670    | 1.0419     | 2.422      | 28.13     | 32.6   |

$$P_2'' = 27.1 \quad P_2' = 12.8 \quad \mu = 0.781 \cdot 10^{-18}$$

Tabelle 5. Molekulare Polarisation des Selenophens.  
In Hexan bei Temp. 25°C.

| $f_2$ (%) | $d_4^{25}$ | $\epsilon$ | $P_{1,2}$ | $P_2$  |
|-----------|------------|------------|-----------|--------|
| 0.000     | 0.6691     | 1.880      | 29.19     | (39.6) |
| 3.997     | 0.6924     | 1.908      | 29.50     | 36.8   |
| 7.324     | 0.7069     | 1.917      | 29.67     | 35.6   |
| 9.198     | 0.7246     | 1.936      | 29.62     | 33.8   |

$$P_2'' = 27.1 \quad P_2' = 12.5 \quad \mu = 0.772 \cdot 10^{-18}$$

Zum Vergleich tragen wir das oben bestimmte Dipolmoment des Selenophens mit den Dipolmomenten von Furan und Thiophen in die folgende Tabelle ein, woraus man sieht, dass das Dipolmoment des Selenophens etwas grösser als diejenigen von Furan oder Thiophen ist. Solange man aber die Bestimmungsmethode, die auf eine Vernachlässigung von Atompolarisation hinausläuft, anwendet, kann man einen Fehler kaum umgehen. Zur Bestimmung des genaueren Dipolmoments des Selenophens wäre es wünschenswert, wie Kubo<sup>(14)</sup> mit Thiophen getan hat, die Messung im Dampfzustand auszuführen.

Tabelle 6. Dipolmoment heterocyclischer Verbindungen.

| Substanz   | Dipolmoment (i. Debye E.) | Autor                      |
|------------|---------------------------|----------------------------|
| Furan      | 0.63 (Benzol)             | Partington <sup>(10)</sup> |
|            | 0.71 (Benzol)             | Smyth <sup>(11)</sup>      |
| Thiophen   | 0.63 (Benzol)             | Hassel <sup>(12)</sup>     |
|            | 0.54 (Hexan)              | Higashi <sup>(13)</sup>    |
|            | 0.58 (Dampf)              | Kubo <sup>(14)</sup>       |
| Selenophen | 0.78 (Benzol)             | Tamamushi, Akiyama, und    |
|            | 0.77 (Hexan)              | Umezawa                    |

Unter Annahme, dass im Ringe zwei Doppelbindungen existieren und dass man für den Valenzwinkel des Kohlenstoffes 125°C einsetzen kann, hat Smyth und Walls<sup>(11)</sup> den Valenzwinkel des Sauerstoffes bzw. des Schwefels auf mehr als 140°C abgeschätzt, der mit den kleinen Dipolmomenten dieser Stoffe entspricht. Unter der gleichen Annahme ergibt sich der Valenzwinkel des Selens aus dem beobachteten Dipolmoment als etwa 140°C (kleiner als bei Furan und Thiophen!), indem man für das Gruppenmoment C-Se = 1.1 anwendet.<sup>(15)</sup> Diese Betrachtungen sind aber nicht am Platz, denn die Feststellung, dass sowohl Furan oder Thiophen als auch Selenophen die gewöhnlichen Doppelbindungen enthalten, ist nach unseren heutigen Kenntnissen sehr unwahrscheinlich. Diese Sachlage wird noch aus der Depression in Molrefraktion dieser Stoffe wahrgenommen, wöüber unten berichtet werden soll.

**Molrefraktion.** Die Molrefraktion des Selenophens wurde bei 25°C bestimmt, indem man den Brechungsindex mittels einem Pulfrichschen Refraktometer mass: die Ergebnisse werden in Tabelle 7 angegeben.

Ermittelt man aus der erhaltenen Molrefraktion ( $MR_D$ ) die Atomrefraktion des Selens, wobei man die Eisenrohrschen Atom- bzw. Gruppen-Refractionen, nämlich: C = 2.418, H = 1.100,  $\overline{F}$  = 1.733 anwendet, so

(10) J. Partington und E. C. E. Hunter, *J. Chem. Soc.*, London, **1931**, 2062.

(11) C. P. Smyth und W. S. Walls, *J. Amer. Chem. Soc.*, **54** (1932), 3230.

(12) O. Hassel und E. Naeshagen, *Chem. Zentr.*, **1930**, 1956.

(13) K. Higashi, *Bull. Inst. Phys. Chem. Res.*, (Tokyo) **11** (1932), 729.

(14) M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.*, (Tokyo) **29** (1936), 122.

(15) Gruppenmoment: C-Se = 1.08, C-O = 0.94, C-S = 1.16. Siehe N. V. Sidgwick, "The Covalent Link in Chemistry," S. 150, New York (1933).

Tabelle 7. Molrefraktion des Selenophens bei 25°C.

|    | $n_D^{25}$ | $MR_D$ |
|----|------------|--------|
| C  | 1.57082    | 26.90  |
| D  | 1.57689    | 27.12  |
| F  | 1.59218    | 27.71  |
| G' | 1.60578    | 28.22  |

ergibt sich die Atomrefraktion:  $Se = 9.59$ . Dieser Wert der Atomrefraktion ist bedeutend kleiner als die Werte (10–11), die man für die Atomrefraktion des Selen aus den Daten von aliphatischen Seleniden oder von gesättigten cyclischen Selenverbindungen gefunden hat.<sup>(16)</sup> Dies deutet darauf hin, dass im Selenophen eine bedeutende Depression der Molrefraktion stattfindet. Diese Depression wird z. B. folgenderweise berechnet. Nach den von Morgan und Burstall<sup>(17)</sup> gewonnenen Daten ( $n_D^{18} = 1.5510$ ,  $d_4^{18} = 1.4816$ ) an Tetrahydroselenophen (eine gesättigte Verbindung des Selenophens), setzt man für die Molrefraktion dieses Stoffes  $MR_D = 29.08$ , woraus man für die Atomrefraktion des Selen  $Se = 10.61$  erhält. Berechnet man nun die Molrefraktion des Selenophens unter Benutzung der hier erhaltenen Atomrefraktion, so bekommt man 28.15, und demnach für die molekulare Exaltation  $EM_D = -1.03$  und für die spezifische Exaltation  $E\Sigma_D = -0.79$ .

Das Selenophen verhält sich also ähnlich wie andere heterocyclischen Verbindungen (Furan, Pyrrol, und Thiophen) oder Benzol, wobei auch die Depression in Molrefraktion mehr oder weniger zutage kommt. Die Tabelle 8 gibt die molekulare- bzw. spezifische Exaltation dieser heterocyclischen Verbindungen wieder.<sup>(18)</sup>

Tabelle 8. Molekulare- und spezifische Exaltation cyclischer Verbindungen.

| Substanz   | $EM_D$ | $E\Sigma_D$ |
|------------|--------|-------------|
| Benzol     | -0.17  | -0.22       |
| Furan      | -0.75  | -1.10       |
| Pyrrol     | -0.22  | -0.33       |
| Thiophen   | -1.08  | -1.31       |
| Selenophen | -1.03  | -0.79       |

(16) Atomrefraktion des Selen: z.B. 10.48 (aus Dimethylselenid) Y. Tanaka und Y. Nagai, *J. Soc. Chem. Ind.*, (Japan), **30** (1927), 171 B. 10.94 (aus Diäthylselenid) J. Zoppellari, *Gazz. Chim. Ital.*, **24**, II, 396. 10.85 (aus Methyläthylselenid) L. Tschgaeff, *Ber.*, **42** (1909), 49. 10.22 (aus Cycloselenohexan), 10.66 (aus Cycloselenopentan), 10.61 (aus Tetrahydroselenophen) G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, (London), **1929**, 2197, ebenda **1931**, 173.

(17) G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, (London), **1929**, 2197.

(18) Zusammengestellt von v. Auwers, *Lieb. Ann.*, **408** (1915), 257f.



Die Ursache dieser Depression in Molrefraktion dürfte man darin suchen, wie W. Hückel in seinem Lehrbuch angedeutet hat,<sup>(19)</sup> dass bei diesen cyclischen Verbindungen die Einflüsse endocyclischer Konjugation und der Störungen ganz anderer Art als bei acyclischen sind. Die Betrachtung, dass das Selenophen wie Thiophen oder Furan im allgemeinen einen aromatischen Charakter besitzen soll, steht mit unseren Erfahrungen die chemischen Eigenschaften dieses Stoffes betreffend im Einklang.<sup>(20)</sup> Das Selenophen verhält sich in der Tat sehr ähnlich wie Thiophen in der chemischen Reaktionsweise, obgleich das erstere zuweilen einen mehr ungesättigten Charakter als das zweite aufweist, indem das zweiwertige Selen zum vierwertigen übergeht.

Der aromatische Charakter des Pyrrols, Furans, und Thiophens, worin man eine quantenmechanische Resonanz zwischen zwei Formen annehmen kann, wurde von Bonino<sup>(21)</sup> in seinen Untersuchungen der Ramanspektren von diesen Stoffen konstatiert. Es wäre interessant das Ramanspektrum auch mit Selenophen zu untersuchen, was wir noch in Zukunft vornehmen möchten.

### Zusammenfassung.

An dem Selenophen-Präparat mit hoher Reinheit wurden die physikalischen Konstanten: Dichte  $d_4^{25} = 1.6003$ , Brechungsindex  $n_D^{25} = 1.57689$ , Molrefraktion  $MR_D = 27.12$ , Oberflächenspannung  $\sigma^{25} = 36.05$  dyn./cm., Temperaturabhängigkeit der Molaroberflächenenergie  $k = 2.08$ , Parachor  $P = 200.6$  und elektrisches Dipolmoment  $\mu = 0.78 \cdot 10^{-18}$  (in Benzol),  $\mu = 0.77 \cdot 10^{-18}$  (in Hexan) bestimmt.

Auf Grund dieser Daten wurde eine Diskussion über die Struktur dieses Stoffes dargelegt, insbesondere in Bezug auf den aromatischen Charakter dieses Stoffes.

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(19) W. Hückel, "Theoretische Grundlagen der organischen Chemie," II, S. 99, Leipzig (1931).

(20) S. Umezawa, *Dieses Bulletin*, **11** (1936), 157; **11** (1936), 775; **12** (1937), 4; **14** (1939), 155. W. Steinkopf, *Lieb. Ann.*, **532** (1937), 253.

(21) G. B. Bonino, R. Manzoni-Ansidei, und P. Pratesi, *Z. physik. Chem. B*, **22** (1933), 21; ebenda **25** (1934), 327.

## Dipolmoment und Struktur der isomeren Selenophthene.

Von Bun-ichi TAMAMUSHI, Hajime AKIYAMA und Sumio UMEZAWA.

(Eingegangen am 25. Juli 1939.)

In den synthetischen Untersuchungen in der Selenophengruppe gelang es einem von uns (S. U.) drei isomere Selenophthene  $C_6H_4Se_2$  rein zu gewinnen, die folgenderweise entstanden sind.

Destilliert man das durch die Einwirkung von Acetylen auf Selen entstandene schwarzbraune Oel, so gewinnt man Selenophen im Destillat, während sich aus dem Rückstand nach langer Zeit (über einen Monat) eine Substanz auskristallisiert, die aus Alkohol rekristallisiert wird. Diese Substanz, eine Form der Selenophthene, mit dem Schmelzpunkt  $123-124.5^\circ$  wird im folgenden mit dem Buchstaben (B) gekennzeichnet.

Das Filtrat teilt man durch Wasserdampfdestillation in zwei Teile, ein Pikrat-bildender Anteil und ein anderer Pikrat-nichtbildender. Der erste Anteil wird durch Ammoniak zersetzt und dann wird das dadurch wiedergewonnene Oel unter Vakuum destilliert. Nach wiederholter Rekristallisation mit Pikrat und Vakuumdestillation erhält man eine kristalline Substanz, die aus Alkohol rekristallisiert wird. Die Ausbeute ist zwar sehr gering. Diese Substanz, eine andere Form der Selenophthene, mit dem Schmelzpunkt  $51-51.5^\circ$  wird mit dem Buchstaben (A) bezeichnet.

Der Pikrat-nichtbildende Anteil wird nach mehrmaligen Wasserdampfdestillationen unter Vakuum destilliert, wobei man ein Oel von dem Siedepunkt  $93^\circ/14$  mm. gewinnt. Diese Substanz, eine dritte Form der Selenophthene, wird im folgenden mit (C) gekennzeichnet.

Die Eigenschaften dieser drei Isomeren und ihrer Derivate sind in Tabelle 1 zusammengestellt.

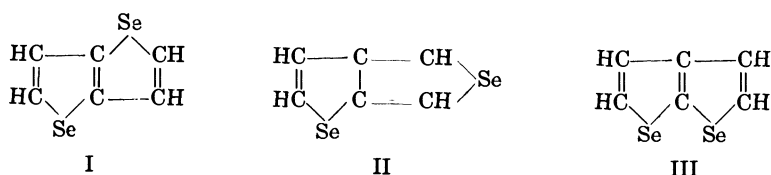
Tabelle 1. Konstanten der isomeren Selenophthene und ihrer Derivate.

| Selenophthen                  | Pikrat                   | Tetrabrom-Selenophthen           |
|-------------------------------|--------------------------|----------------------------------|
| (A) Schmp. $51-51.5^\circ$    | Schmp. $154-155.5^\circ$ | Schmp. $252.5-253^\circ$ (korr.) |
| (B) Schmp. $123-124.5^\circ$  | Schmp. $163-165^\circ$   | Schmp. $246-247.5^\circ$ (korr.) |
| (C) Sdp. $90-93^\circ/14$ mm. | —                        | Schmp. $271-272^\circ$ (korr.)   |

In Anbetracht der Challenger und Harrisonschen Untersuchungen<sup>(2)</sup> über die isomeren Thiophthene, könnte man nun für die oben isolierten Selenophthen-Isomeren folgende möglichen Strukturen aufstellen:

(1) S. Umezawa, Dieses Bulletin, **11** (1936), 197; **11** (1936), 775; **12** (1937), 4; **14** (1939), 155.

(2) F. Challenger und J. B. Harrison, *J. Inst. Petroleum Technologists*, **21** (1935), 135.



Es ist unsere Aufgabe zu bestimmen, welche von diesen Strukturen je einem von den oben erhaltenen drei Isomeren entspricht. Zu diesem Zweck haben wir die Methode der Dipolmoment-Bestimmung angewandt, die sich tatsächlich als zweckdienlich erwies.

Die Methode der Bestimmung des elektrischen Dipolmoments war dieselbe, die in der vorangehenden Arbeit<sup>(3)</sup> beschrieben worden ist. Die DK-Messungsapparatur arbeitete bei Frequenz von 200 m und die Messungen wurden bei 25°C und zwar in binären Gemischen in Benzol ausgeführt. Die Ergebnisse sind in Tabellen 2–4 angegeben, wobei  $f_2$  den Molenbruch des gelösten Stoffes,  $d_4^{25}$  die Dichte der Lösung,  $\epsilon$  die Dielektrizitätskonstante,  $P_{1,2}$  die Molekularpolarisation der Lösung,  $P_2$  die Molekularpolarisation des gelösten Stoffes,  $MR_{1,2}$  die Molrefraktion der Lösung und  $MR_2$  die Molrefraktion des gelösten Stoffes bedeutet.

Tabelle 2. Molekulare Polarisation des Selenophthens (C).  
In Benzol bei Temp. 25°C.

| $f_2$ (%) | $d_4^{25}$ | $\epsilon$ | $P_{1,2}$ | $P_2$  |
|-----------|------------|------------|-----------|--------|
| 0.000     | 0.8731     | 2.276      | 26.71     | (92.6) |
| 1.070     | 0.8896     | 2.316      | 27.35     | 86.9   |
| 2.039     | 0.9033     | 2.337      | 27.76     | 79.4   |
| 3.374     | 0.9221     | 2.367      | 28.30     | 73.8   |

$$P_2''(MR_D) = 44.6 \quad P_2' = 48.0 \quad \mu = 1.52 \cdot 10^{-18}$$

Tabelle 3. Molekulare Polarisation des Selenophthens (B).  
In Benzol bei Temp. 25°C.

| $f_2$ (%) | $d_4^{25}$ | $\epsilon$ | $P_{1,2}$ | $P_2$ | $n_D^{25}$ | $MR_{1,2}$ | $MR_2$ |
|-----------|------------|------------|-----------|-------|------------|------------|--------|
| 0.000     | 0.8731     | 2.276      | 26.71     | (75)  | 1.49664    | 26.17      | (51)   |
| 0.680     | 0.8841     | 2.295      | 27.00     | 70.5  | 1.49912    | 26.29      | 45.5   |
| 0.879     | 0.8861     | 2.299      | 27.13     | 76.2  | 1.50004    | 26.40      | 52.3   |
| 1.074     | 0.8882     | 2.306      | 27.27     | 76.3  | 1.50054    | 26.46      | 54.0   |
| 1.308     | 0.8930     | 2.309      | 27.27     | 71.1  | 1.50117    | 26.46      | 48.2   |
| 2.172     | 0.9062     | 2.327      | 27.60     | 67.7  | 1.50490    | 26.69      | 50.2   |

$$P_2''(MR_D) = 51 \quad P_2' = 24 \quad \mu = 1.07 \cdot 10^{-18}$$

(3) Dieses Bulletin, Diese Heft, S. 310.

Tabelle 4. Molekulare Polarisation des Selenophthens (A).  
In Benzol bei Temp. 25°C.

| $f_2(\%)$ | $d_4^{25}$ | $\epsilon$ | $P_{1,2}$ | $P_2$ | $n_D^{25}$ | $MR_{1,2}$ | $MR_2$ |
|-----------|------------|------------|-----------|-------|------------|------------|--------|
| 0.000     | 0.8731     | 2.276      | 26.71     | (52)  | 1.49664    | 26.17      | (56)   |
| 0.811     | 0.8355     | 2.282      | 26.85     | 43    | 1.50172    | 26.43      | 59     |
| 1.589     | 0.8950     | 2.292      | 27.11     | 52    | 1.50415    | 26.67      | 59     |
| 2.479     | 0.9131     | 2.329      | 27.53     | 62    | 1.50634    | 26.73      | 49     |

$$P_2''(MR_D) = 56$$

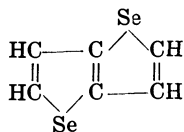
$$P_2' \cong 0$$

$$\mu \cong 0$$

Die Bestimmung der Molrefraktion wurde bei dem flüssigen Selenophthen (C) an der reinen Flüssigkeit durchgeführt mit dem Ergebnis:  $n_D^{25} = 1.6586$ ,  $d_4^{25} = 1.9354$  und demnach  $MH_D = 44.6$ , während sie bei den festen Präparaten (A) und (B) in benzoligen Lösungen ausgeführt wurde: die erhaltenen Daten sind in Kolonnen 6, 7, 8 in Tabelle 3 und 4 angegeben. In den letzten zwei Fällen liefert Extrapolation für die Konzentration null die Molrefraktion des gelösten Stoffes. Infolge der sehr geringen Ausbeute des erhaltenen Präparates bei den festen Isomeren, besonders bei der Form (A), war es schwierig die DK-Messungen sowie Brechungsindex-Messungen mit genügender Genauigkeit durchzuführen, man konnte sogar nicht die Messung wiederholen. Mit dem Präparat (B) konnte man indessen sowohl  $P_2$  als auch  $MR_2$  durch Extrapolation feststellen, während man mit dem Präparat (A) den Wert von  $P_2$  sowie  $MR_2$  nur als Mittelwert annähernd abschätzen konnte, indem man als Mittelwert sowohl von  $P_2$  als auch von  $MR_2$  einen gleichen Wert, etwa 50, aufnahm.

Wir stellten in dieser Weise das Dipolmoment folgendermassen fest: für den flüssigen Isomer (C)  $\mu = 1.52 \cdot 10^{-18}$ , für den einen festen Isomer (B)  $\mu = 1.07 \cdot 10^{-18}$  und für den andern festen Isomer (A)  $\mu \cong 0$ .

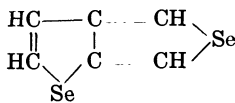
Wir nehmen nun an, dass ein Selenophthen-Molekül durch Kondensation von zwei regulär pentagonalen Selenophen-Ringen aufgebaut ist. Berechnet man unter dieser Annahme das elektrische Moment des Selenophthen-Moleküls, wobei man das in der vorangehenden Arbeit<sup>(3)</sup> festgestellte Gruppenmoment des Selenophen-Ringes benutzt, so erhält man folgende Dipolmomente je nach der Strukturformel (I), (II) und (III).



I

$$\mu_{\text{ber.}} = 0$$

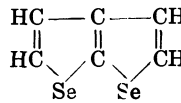
$$\mu_{\text{beo.}} = 0$$



II

$$\mu_{\text{ber.}} = 0.92 \cdot 10^{-18}$$

$$\mu_{\text{beo.}} = 1.07 \cdot 10^{-18}$$



III

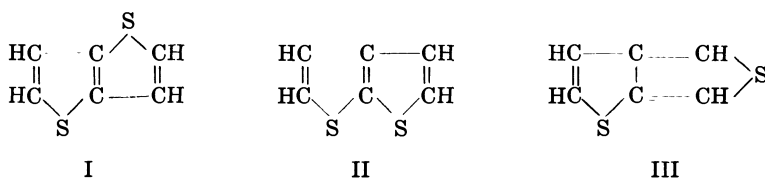
$$\mu_{\text{ber.}} = 1.48 \cdot 10^{-18}$$

$$\mu_{\text{beo.}} = 1.52 \cdot 10^{-18}$$

Hiernach findet man eine deutliche Uebereinstimmung zwischen den beobachteten und den berechneten Dipolmomenten. Es folgt nämlich, dass

der erste Isomer(A) der Struktur (I) d. h. eine trans-Form, der zweite Isomer(B) der Struktur (II) d. h. eine andere trans-Form und der dritte Isomer (C) der Struktur (III) d. h. eine cis-Form entspricht.

Zur Strukturbestimmung der isomeren Thiophthene haben auch Challenger und Harrison<sup>(2)</sup> die Methode der Dipolmoment-Messung in Betracht gezogen. Von drei Thiophthen-Isomeren wurden dabei einer im festen Zustand und die anderen im flüssigen, gewonnen. Das Dipolmoment des ersten war gleich null (Messung von Goss) gefunden, wodurch dieser der Struktur (I) entspricht, während die Dipolmomente der anderenflüssigen Isomeren gleich  $1.16 \cdot 10^{-18}$  bzw.  $1.03 \cdot 10^{-18}$  waren, welche demnach der Struktur (II) oder (III) zuzuordnen sind. Es scheint aber, dass die beiden flüssigen Verbindungen damals noch nicht ganz rein getrennt waren.



Bemerkenswert sind die analogen Beziehungen in den Thiophthen-Isomeren und in den Selenophthen-Isomeren. Es gibt indessen bei Selenophthen zwei feste (trans) und eine flüssige (cis) Verbindung, während bei Thiophthen eine feste (trans) und zwei flüssige (cis und trans) Verbindungen existieren. Die Schlussfolgerung aus Dipolmoment-Bestimmung über die Struktur dieser Verbindungen scheinen in den beiden Fällen schon sehr bedeutsam. Zur Struktur-Feststellung dieser Isomeren wäre es immerhin wünschenswert, weitere Kenntnisse zu erwerben sowohl bei Thiophthen als auch bei Selenophthen.<sup>(4)</sup> Die chemische Untersuchung in bezug auf die Selenophthene wird von einem von uns (S. U.) noch an anderer Stelle berichtet werden.

Die Molrefraktion des oben gewonnenen flüssigen Selenophthens (C) ist nach den Daten  $n_D^{25} = 1.6586$ ,  $d_4^{25} = 1.9354$  gleich 44.55 gesetzt. Die unter Anwendung von Atomrefraktion des Selen Se = 10.61 (ermittelt aus der Molrefraktion des Tetrahydroselenophens<sup>(5)</sup>) berechnete Molrefraktion des Selenophthens ist andererseits gleich 45.33. Demnach ist die molekulare Exaltation  $EM_D = -0.78$  und die spezifische Exaltation  $E_{ES_D} = -0.33$ . Es kommt also hier eine Depression hervor.

Bekanntlich zeigt Naphthalin eine deutliche Exaltation,<sup>(6)</sup> nämlich  $EM_D = 2.28$ , während Thionaphthen eine kleinere Exaltation  $EM_D = 0.93$  aufweist, was wahrscheinlich darauf beruht, dass der Einfluss der Exaltation in kondensierten Ringen durch den Einfluss der Depression im Thiophenring kompensiert wird. Bei Selenophthen, wo eher eine Depres-

(4) Bei Thiophthenen sind auch die Kenntnisse röntgenographischer Analyse an dem festen Isomer zur Struktur-Bestimmung benutzt worden (Challenger und Harrison).

(5) G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, (London), **1929**, 2197. Vgl. unsere vorangehende Arbeit, Diese Heft, S. 317.

(6) R. Kremann, "Physikalische Eigenschaften und chemische Konstitution," S. 78, Dresden (1937).

sion stattfindet, müssten die Einflüsse der Depression in den Selenophenringen superponiert stark zur Wirkung gelangen. Tabelle 5 gibt die molekulare- bzw. spezifische Exaltation der oben erwähnten kondensierten Ringverbindungen wieder.

Tabelle 5. Molekulare- und spezifische Exaltation von Naphthalin, Thionaphthen und Selenophthen.

| Substanz           | $EM_D$ | $E\Sigma_D$ |
|--------------------|--------|-------------|
| Naphthalin         | +2.28  | +1.78       |
| Thionaphthen       | +0.93  | +0.69       |
| Selenophthen (cis) | -0.78  | - 0.33      |

Das Selenophthen stellt jedenfalls ein interessantes Beispiel der kondensierten Ringverbindungen dar, in welchem eine Depression in Molrefraktion zur Erscheinung kommt.

#### Zusammenfassung.

Die Struktur der drei rein isolierten Isomeren des Selenophthens wurde mit Hilfe der Dipolmoment-Bestimmung festgestellt. Ein fester Isomer (Schmp. 51–51.5°) mit dem Dipolmoment  $\mu = 0$  entspricht der trans-Form, ein anderer fester Isomer (Schmp. 123–124.5°) mit dem Dipolmoment  $\mu = 1.07 \cdot 10^{-18}$  der anderen trans-Form und ein flüssiger Isomer mit dem Dipolmoment  $\mu = 1.52 \cdot 10^{-18}$  der cis-Form.

Es wurde auf die Depression in Molrefraktion des flüssigen Selenophthens aufmerksam gemacht.

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## The Mechanism of the Oxygen Effect on Hydrogen Bromide Reacting with Ethenoid Compounds.

By Yoshiyuki URUSHIBARA and Osamu SIMAMURA.

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**Introduction.**<sup>(1)</sup> In 1933, at the Dyson Perrins Laboratory, Oxford, one (Y.U.) of the authors had occasion to prepare 11-bromoundecanoic acid by adding hydrogen bromide to undecenoic acid according to the work by Walker and Lumsden.<sup>(2)</sup> Undecenoic acid was dissolved in toluene, a portion of toluene was distilled off to remove moisture, and hydrogen bromide was passed immediately into the cooled solution, when 10-bromoundecanoic acid was found to be the main product. On the other hand, when undecenoic acid was dissolved in toluene, both after being dried separately, and without distillation of the solvent hydrogen bromide was passed into the solution, the product was 11-bromoundecanoic acid. At that time it was assumed that the difference was caused by traces of moisture entering when the solution was prepared.<sup>(3)</sup>

Kharasch and Mayo<sup>(4)</sup> soon found that hydrogen bromide adds to pure allyl bromide in the absence of oxygen to give mainly 1,2-dibromopropane (normal reaction) while in the presence of peroxides or oxygen 1,3-dibromopropane is the main product (abnormal reaction). The effect was attributed to the action of peroxides and called "peroxide effect." The effect can be eliminated by the addition of antioxidants, e.g. diphenylamine and hydroquinone. Later Urushibara and Takebayashi<sup>(5) (6)</sup> showed that the effect of oxygen is caused by the action of molecular oxygen and suggested the possibility that the effect of peroxides might be due to the action of molecular oxygen generated by the decomposition of the peroxides. Further it was demonstrated that the abnormal reaction caused by oxygen is homogeneous.<sup>(7)</sup>

Ashton and Smith<sup>(8)</sup> studied the addition of hydrogen bromide to undecenoic acid in the light of Kharasch's observations and found that oxygen is the agent reversing the direction of addition also in this case.

Urushibara and Takebayashi,<sup>(9)</sup> studying the effects of various substances other than oxygen and peroxides, observed that ferromagnetic metals such as reduced nickel and reduced iron influence the addition of hydrogen bromide to allyl bromide quite in the same way as oxygen. Reduced nickel was found effective also in reversing the direction of

(1) Compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461.

(2) J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **79** (1901), 1191.

(3) Compare *Chemistry and Industry*, **52** (1933), 219.

(4) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

(5) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 798.

(6) *Idem, ibid.*, **12** (1937), 138.

(7) *Idem, ibid.*, **12** (1937), 173.

(8) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

(9) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51; **13** (1938), 400.

addition of hydrogen bromide to undecenoic acid in toluene solution.<sup>(10)</sup> While diphenylamine hardly affects the influence of reduced nickel and reduced iron, hydroquinone and catechol inhibit the action of reduced nickel to a great extent.<sup>(12) (13)</sup> Reduced nickel and reduced iron are stable to hydrogen bromide under the conditions of the experiments, while reduced cobalt is so liable to attack by hydrogen bromide that the effect of the metal is only moderately displayed.<sup>(11) (14)</sup>

The peculiar influence of oxygen and the ferromagnetic catalysts on hydrogen bromide has been observed further in the isomerization of isostilbene to stilbene, a reaction apparently quite different from the addition reactions. Kharasch and co-workers<sup>(15)</sup> found that in the dark pure isostilbene, dissolved in benzene, is not isomerized to stilbene by hydrogen bromide alone, but the addition of a peroxide to the mixture causes complete isomerization in a few minutes. The present authors<sup>(16) (17)</sup> extended Kharasch's observation to oxygen and to the ferromagnetic catalysts, viz., reduced nickel and reduced iron. Isostilbene, in the pure liquid state or in benzene solution, is isomerized to stilbene by hydrogen bromide in the presence of oxygen in the dark at room temperature. Reduced nickel and reduced iron also co-operate with hydrogen bromide to isomerize isostilbene, although the effect of hydrogen bromide in the presence of the ferromagnetic catalysts is much smaller than in the presence of oxygen under the conditions of the experiments. The strengths of the inhibiting actions of diphenylamine and catechol on oxygen and reduced nickel are quite parallel to those displayed in the cases of the addition reactions.<sup>(17)</sup>

A theory on the mechanism of the effect of oxygen or peroxides as outlined above have been presented by Kharasch and co-workers.<sup>(15) (18)</sup> The cis-trans isomerization caused by bromine and light is attributed to the action of bromine atoms.<sup>(19)</sup> Isostilbene is isomerized by hydrogen bromide not only in the presence of peroxides but also in sunlight, and hydroquinone inhibits the isomerization in either case.<sup>(15)</sup> Further the transformation of ethyl  $\alpha$ -bromoacetoacetate into ethyl  $\gamma$ -bromoacetoacetate by hydrogen bromide is accelerated by peroxides or oxygen as well as by light.<sup>(20)</sup> Kharasch assumes that bromine atoms are formed from hydrogen bromide by the action of peroxides or oxygen just as by the action of light and cause such effects. The effect of peroxides and oxygen on the addition of hydrogen bromide to ethenoid compounds was also explained on the assumption of bromine atoms.<sup>(18)</sup> Thus, the mechanism of the addition of hydrogen bromide to vinyl bromide, which was originally represented by electronic formulæ, may be put into ordinary formulæ as

(10) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331, 404, 574.

(11) *Idem, ibid.*, **11** (1936), 754.

(12) *Idem, ibid.*, **13** (1938), 400.

(13) *Idem, ibid.*, **13** (1938), 404.

(14) *Idem, ibid.*, **12** (1937), 51.

(15) M. S. Kharasch, J. V. Mansfield, and F. R. Mayo, *J. Am. Chem. Soc.*, **59** (1937), 1155.

(16) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507.

(17) *Idem, ibid.*, **13** (1938), 566.

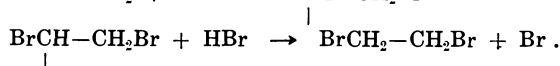
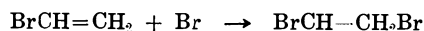
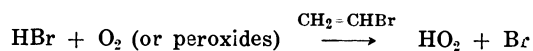
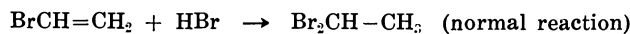
(18) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 238.

(19) A. Berthoud and Ch. Urech, *J. Chim. Phys.*, **27** (1930), 291.

(20) M. S. Kharasch, E. Sternfeld, and F. R. Mayo, *J. Am. Chem. Soc.*, **59** (1937), 1655.



follows:



The essential features of these representations are that in the normal reaction the bromide ion is directed toward the carbon atom with the lowest electron density to yield 1,1-dibromoethane, and that in the abnormal reaction the bromine atom is directed toward the carbon atom with the greater electron density to yield a 1,2-dibromoethyl free radical. This free radical then reacts with hydrogen bromide to yield 1,2-dibromoethane and another bromine atom, which is responsible for the propagation of the chain reaction. According to this mechanism the function of peroxides or oxygen is to produce bromine atoms acting as chain carriers.

Hey and Waters<sup>(21)</sup> also suggested that the addition process of the abnormal reaction is one requiring the transient production of neutral atoms of hydrogen and bromine from hydrogen bromide.

Winstein and Lucas,<sup>(22)</sup> to explain the directive influence of oxygen in the abnormal additions of hydrogen bromide to the double bonds, assumed the formation of an oxygen complex from the unsaturated molecule prior to the addition of hydrogen bromide. It will be, however, soon self-evident that this theory cannot explain the experimental facts.

Urushibara and Takebayashi<sup>(14) (6)</sup> also considered previously the mechanisms of the effects of oxygen and reduced nickel on the addition of hydrogen bromide to allyl bromide. The simplest explanation of the oxygen effect might be that the two reactions, one giving 1,2-dibromopropane and the other 1,3-dibromopropane, were simultaneous reactions proceeding without interfering with each other but with respective velocities determined by the concentrations of the reactants, oxygen accelerating the latter reaction only but being indifferent to the former. Such a simple explanation encounters at once serious difficulties. In the absence of oxygen 95% of the product is 1,2-dibromopropane. In the presence of oxygen 95% is 1,3-dibromopropane, while the total yield is not more than threefold in three days reaction. Assume that the two reactions were simultaneous reactions of the second order, then the following relations would exist:

$$x = y + z,$$

$$\frac{dy}{dt} = k_1(a-x)(b-x),$$

$$\frac{dz}{dt} = k_2(a-x)(b-x),$$

(21) D. H. Hey and W. A. Waters, *Chem. Rev.*, **21** (1937), 202.

(22) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60** (1938), 836.

$$\frac{dx}{dt} = (k_1 + k_2)(a - x)(b - x) \quad (1),$$

$$\frac{y}{z} = \frac{k_1}{k_2} \quad (2),$$

where  $a$  and  $b$  represent the initial amounts of allyl bromide and hydrogen bromide respectively,  $x$  the amount of allyl bromide which reacts in time  $t$ ,  $y$  and  $z$  the amounts of 1,2- and 1,3-dibromopropanes formed in time  $t$  respectively, and  $k_1$  and  $k_2$  constants. The above simple explanation requires only an increase of  $k_2$  to  $k_2'$  in the presence of oxygen. The ratio  $(k_1 + k_2')/(k_1 + k_2)$  can be evaluated from (1) and from (2) independently: Inserting the values obtained in the experiments,<sup>(5)</sup> values 3.3–5.4 are obtained from the relation (1) of the total reaction velocity while 19–22 from the relation (2) of the composition of the reaction product.

In the cases of vinyl bromide<sup>(23)</sup> and vinyl chloride<sup>(24)</sup> the reversal of the direction of addition by oxygen is more conspicuous: In the absence of oxygen the product is 100% ethylidene dihalide while in the presence of oxygen 100% ethylene dihalide. The fact that the normal reaction does not occur at all in the presence of oxygen cannot be explained on the assumption of the mere acceleration of the abnormal reaction by oxygen. Another difficulty is that the total yield of the products from allyl bromide and hydrogen bromide increases with the amount of oxygen admitted even after the proportion of 1,3-dibromopropane has reached the constant maximal value (95%); that is to say, the absolute yield of 1,2-dibromopropane decreases rapidly as the amount of oxygen increases until the latter reaches a certain amount and thence increases in the same rate as that of 1,3-dibromopropane.<sup>(5)</sup>

Smith<sup>(25)</sup> has briefly reported that the normal reaction of undecenoic acid and hydrogen bromide with thorough elimination of oxygen proceeded with a rate less than one-fiftieth of the speed of the abnormal reaction. It suffices, however, to point out that allyl bromide and hydrogen bromide give a product containing 95% 1,2-dibromopropane in a certain yield under a set of conditions and another product containing 95% 1,3-dibromopropane in a yield not more than three times as much under another set of conditions which differs from the former only in that a certain amount of oxygen is admitted. In the experiments by Urushibara and Takebayashi<sup>(10)</sup> on the addition of hydrogen bromide to undecenoic acid in toluene solution quantitative yields were always obtained regardless of the conditions and of the compositions of the products.

In the presence of reduced nickel which has never been in contact with air, allyl bromide and hydrogen bromide give a product containing 95% 1,3-dibromopropane in a total yield only twice as much as that obtained in the absence of the catalyst.<sup>(14)</sup> Reduced nickel is a heterogeneous catalyst, yet the normal reaction giving 1,2-dibromopropane is

(23) M. S. Kharasch, M. C. McNab, and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2521.

(24) M. S. Kharasch and C. W. Hannum, *ibid.*, **56** (1934), 712.

(25) J. C. Smith, *Chemistry and Industry*, **57** (1938), 464.

inhibited throughout the reacting system, the bulk of which is not in contact with the catalyst.

Thus Urushibara and Takebayashi<sup>(6)</sup> was led to assume that in the presence of a sufficient amount of oxygen (or reduced nickel) the catalyzed addition only takes place, and that the catalyzed addition yields a product consisting of 95% 1,3-dibromopropane and 5% 1,2-dibromopropane. The amount of oxygen just sufficient for producing the maximal proportion (95%) of 1,3-dibromopropane is 1.5 c.c. (n.p.t.) for 24 g. allyl bromide and 20 g. hydrogen bromide in a reaction vessel of 140 c.c. capacity.<sup>(5)</sup> Even if the whole oxygen were dissolved in the liquid, only one molecule of oxygen would be available for 3,000 molecules of allyl bromide. From a very fascinating speculation that the actions of oxygen and reduced nickel might be connected with their magnetic properties, it was assumed that each molecule of oxygen would exert some physical influence over at least 3,000 molecules of allyl bromide.

If the direction of addition of hydrogen bromide were decided according to the polarity of the allyl bromide molecule, how could one molecule of oxygen reverse totally the polarity of so many molecules of allyl bromide? Although it has been made probable that the substance to be influenced by oxygen and reduced nickel is hydrogen bromide,<sup>(16)</sup> it is non the less difficult to understand how one molecule of oxygen could exert a physical influence on thousands of molecules of hydrogen bromide. Thus the assumption of a chain mechanism seems necessary as in the case of a photochemical reaction with a great quantum yield.

Although Kharasch's theory of the chain reaction involving bromine atoms has obtained nearly no experimental evidence except an analogy with the photochemical reactions, no objection can be raised from the experimental results obtained by Urushibara and co-workers. On the contrary, the formation of stilbene dibromide in the experiment of isomerization of isostilbene by hydrogen bromide and oxygen in benzene solution seemed to favour Kharasch's theory.<sup>(17)</sup> Considering the very close resemblance of the effects of oxygen and reduced nickel, it may be presumed that the essential parts of the mechanisms of their actions are the same; yet there have been obtained no bases nor analogies to postulate the formation of bromine atoms from hydrogen bromide and reduced nickel. Thus the present authors have been led to carry out the experiments described below and elsewhere to discuss on Kharasch's theory on the one hand and to know the mechanism of the action of reduced nickel on the other, and, as for the mechanism of the oxygen effect, not only Kharasch's theory has been substantiated in principle but also a more comprehensive treatment of the matter has been made on the basis of the experimental results.

**Action of Hydrogen Bromide and Oxygen on Catechol.** As it seemed that the antioxidants would afford a clue to elucidation of the mechanism of the oxygen effect, the behaviour of catechol, the most effective of the antioxidants used in this laboratory, towards oxygen and hydrogen bromide was examined.

To a solution of 0.5 g. of catechol in 140 g. of carbon tetrachloride (catechol remained partly undissolved) a mixture of hydrogen bromide

and oxygen was passed for two hours in the dark at room temperature. No sign of change was noticeable and from the reaction mixture which had stood overnight the whole amount of catechol was recovered unchanged. Thus it was demonstrated that hydrogen bromide and oxygen do not unconditionally (or even in the presence of catechol) produce atoms or molecules of bromine. As it was then anticipated that the presence of an unsaturated compound might be essential for the formation of bromine atoms from hydrogen bromide and oxygen, the following experiments were carried out.

**Action of Hydrogen Bromide and Oxygen on Allyl Bromide.** Hydrogen bromide and oxygen do not react at room temperature as shown by the above experiment. Further it was previously observed that no peroxide was produced from allyl bromide and oxygen in the dark, but diffuse light caused the formation of a peroxide in a few days.<sup>(4)</sup>

Commercial allyl bromide was purified by washing with water and distilling in the dark, and a portion boiling at a constant temperature was used preferably immediately after distillation. Hydrogen bromide and oxygen were dried separately by passing over phosphorus pentoxide, mixed in a T-tube, and introduced into allyl bromide cooled with ice water in the dark (without cooling much heat was evolved causing the evaporation of allyl bromide). Changes were occasionally observed in dim light from an incandescent lamp. Much complicated reactions were perceived to occur during the passage of the gas mixture. There was no change in the beginning, but by and by the allyl bromide became turbid until drops of a liquid were distinctly observed on its surface. After a while it was noticed that the liquid became faintly yellow for a moment on shaking, indicating the liberation of bromine. The temporary coloration appearing on shaking grew deeper gradually but disappeared at once. Finally the coloration due to bromine persisted, but the liberation of bromine was not carried on beyond a certain extent on continuing the passage of the gas mixture.

The weight of the reaction products corresponded nearly to the amount expected from the addition of hydrogen bromide to allyl bromide, if it was taken into account that part of allyl bromide might have been carried away with the gas mixture. The liquid which separated on the surface was recognized as water. The colourless reaction mixture set free iodine from aqueous potassium iodide acidified with hydrochloric acid, showing that a peroxide had been formed in the reaction. The peroxide, however, is fairly stable and does not decompose easily, and the liberation of iodine from the iodide solution was not completed even when heat was applied. When the reaction mixture was shaken with water, the peroxide was found to shift partly to the aqueous layer as was shown by the liberation of iodine from the iodide solution. The liberation of iodine, however, was very slowly brought to completion even in the aqueous solution. Owing to such stability of the peroxide it was difficult to determine exactly its amount by titrating liberated iodine with a standard thiosulphate solution, but it was roughly estimated that the amount of the peroxide corresponded to 0.1 to 0.2 g. atom of iodine per 1 mole of allyl bromide used. The formation of the peroxide was detected

even after a few minutes' action of the gas mixture.

When the reaction mixture was washed with water, dried, and distilled under the atmospheric pressure, vigorous decomposition of the peroxide set in and hydrogen bromide was evolved. No fractions corresponding to allyl bromide and 1,2-dibromopropane were obtained and the temperature of the vapour rose abruptly, the greater part distilling near the boiling point ( $165^{\circ}$ ) of 1,3-dibromopropane. A fraction distilling above  $200^{\circ}$  was obtained in an amount corresponding to less than one-tenth of the whole products and a small amount of a carbonized matter remained in the flask. Thus 1,3-dibromopropane was found to form the greater part of the whole products.

As already mentioned, there occurs no change between allyl bromide and oxygen on the one hand and between hydrogen bromide and oxygen on the other. When hydrogen bromide was passed into allyl bromide in the same apparatus as used in the above experiment 1,3-dibromopropane was formed almost quantitatively (air being not excluded, the abnormal reaction took place), but neither water nor peroxide was produced. It is only when all three of allyl bromide, hydrogen bromide and oxygen are present that the reactions as described above take place.

Water seems to have been yielded from hydrogen peroxide which may have been primarily formed. The reasons are as follows: In general the first stage of the oxidation by molecular oxygen is the formation of peroxides. On passing hydrogen bromide and oxygen into allyl bromide a certain amount of bromine liberated remained unconsumed, thus suggesting that the oxidation of hydrogen bromide to bromine occurred to some extent even after the whole allyl bromide had reacted. Inasmuch as the organic peroxide is stable in the presence of much hydrogen bromide as mentioned above it could not be the oxidizing agent. The direct oxidation of hydrogen bromide by oxygen having been ruled out, the only remaining alternative is that the formation of water and bromine is caused by the action of hydrogen peroxide primarily formed on hydrogen bromide.

The bromine thus formed must enter into reaction with allyl bromide, yielding 1,2,3-tribromopropane (b.p.  $219-221^{\circ}$ ), which may have been contained in the fraction boiling above  $200^{\circ}$ . In a separate experiment 1,2,3-tribromopropane was prepared by adding bromine to allyl bromide and was found not to liberate iodine from aqueous potassium iodide acidified with hydrochloric acid.

It has been established by Bockemüller and Pfeuffer<sup>(26)</sup> that the simultaneous action of bromine and oxygen on allyl bromide gives a peroxide  $(\text{BrCH}_2)_2\text{CH-O-O-CH}(\text{CH}_2\text{Br})_2$  besides the tribromopropane. In the present case a part of the peroxide may have been resulted from allyl bromide, oxygen and the secondarily formed bromine by the same process as in the German investigators'; but that this is of subordinate importance is obvious on the following ground. Though the experiments by Bockemüller and Pfeuffer were performed under the conditions most favourable to the action of oxygen, the molar ratio of the oxygen consumed to the bromine which reacted was found as 1:6.5 ( $25^{\circ}$ ), corre-

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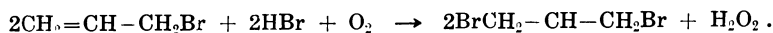
(26) W. Bockemüller and L. Pfeuffer, *Ann.*, **537** (1939), 178

sponding to the formation of less than one mole of the peroxide while five moles of the tribromopropane were produced. It was manifest in the present experiments that five times as much tribromopropane as the peroxide (as much as 0.4 mole of the tribromopropane for one mole of allyl bromide) and the corresponding amount of water (0.5 mole from one mole of allyl bromide) were not formed. In an experiment with 0.4 mole of allyl bromide the amount of water formed was estimated with the eye to amount only to a few tenths of 1 c.c.; and less than ten per cent of the whole products distilled near the boiling point of 1,2,3-tribromopropane. Hence, it must be concluded that the peroxide obtained in the present case was produced at least for the most part by the direct action of allyl bromide, oxygen and hydrogen bromide.

**Action of Hydrogen Bromide and Oxygen on Stilbene.** It has already been mentioned that in the isomerization of isostilbene by hydrogen bromide and oxygen in benzene solution a small amount of stilbene dibromide was formed.<sup>(17)</sup> To examine the action of hydrogen bromide and oxygen upon stilbene the gas mixture was passed into a benzene solution (50 c.c.) of stilbene (0.218 g.) under the same conditions as in the experiments with allyl bromide. After about fifteen minutes' passage of the gas mixture it was noticed that the solution had become yellow with bromine, and the coloration did neither fade on shaking nor become deeper on continuing the passage of the gas mixture. The gas was passed further for five minutes. When a sample from the reaction mixture was added to aqueous potassium iodide iodine was liberated and the benzene layer became violet. When the reaction mixture was evaporated in vacuum at room temperature there remained fine crystals embedded in an orange-coloured oil having an aromatic odour. The whole products weighed 0.433 g., while if all the stilbene used was to be converted into the dibromide it should give 0.412 g. A small volume of benzene was added to the mass and the crystalline substance was collected on a sheet of filter paper. It melted at 238° with decomposition and was identified as stilbene dibromide by the melting point of a mixture with an authentic specimen. The benzene extract contained a small amount of a peroxide as indicated by the test with ferrous ammonium sulphate and ammonium thiocyanate. The nature of the oily product was not further pursued.

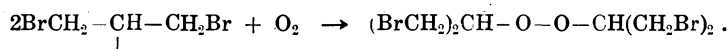
As a control experiment the gas mixture was passed into pure benzene (50 c.c.) for 25 minutes, but neither any coloration of the liquid nor the liberation of iodine on shaking the benzene with the iodide solution was observed.

**The Mechanisms of the Reactions of Hydrogen Bromide, Oxygen and the Ethenoid Compounds as well as the Mechanism of the Abnormal Addition in the Presence of Oxygen.** On the basis of the experimental results and the interpretation of them described above, the reactions in question seem to be represented by the schemes as shown below for the case of allyl bromide. The oxidation of hydrogen bromide by oxygen takes place with allyl bromide as a necessary acceptor of bromine atoms, giving rise to hydrogen peroxide and a dibromoisopropyl radical:

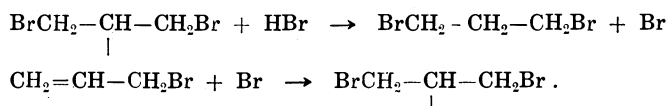


Here the diradical nature of oxygen comes into play, and the production of hydrogen peroxide may probably be preceded by the intermediate formation of a radical  $\text{HO}_2$ . Thus the above process may have to be further resolved into steps. An expression such as  $2\text{HBr} + \text{O}_2 \rightarrow 2\text{Br} + \text{H}_2\text{O}_2$ , however, should be avoided, because it is to be emphasized that the oxidation of hydrogen bromide by oxygen is only possible in the presence of an ethenoid compound.

Then the organic peroxide forms itself with all probability from the dibromoisopropyl radical and oxygen, and thus may be identical with that formed in the reaction of Bockemüller and Pfeuffer:

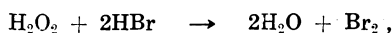


Even in the presence of much oxygen the greater part, and in the presence of a small amount of oxygen almost all, of the dibromoisopropyl radical starts the following chain reaction:

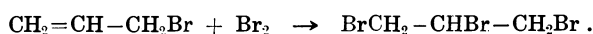


The abnormal additions of hydrogen bromide to ethenoid compounds can be considered to proceed by such chain processes.

The hydrogen peroxide oxidizes hydrogen bromide to produce bromine and water:



and the bromine set free adds probably for the most part to allyl bromide to yield 1,2,3-tribromopropane:



It may also be possible that the tribromopropane results from the addition of a second bromine atom to the dibromoisopropyl radical.

Inasmuch as the radicals and some of the compounds taking part in the above mechanism are to be considered as very reactive, there may be many other possibilities of reactions among them. For the sake of simplicity, however, only those processes that are necessary to explain what has been observed are considered. Minor particulars cannot be decided from the results so far obtained.

In the case of stilbene, the reaction seems to follow a course like the above in the main, but stilbene dibromide is the main product in this case and seems to be formed for the most part by the addition of two atoms of bromine in two steps.

The inhibiting action of the antioxidants on the abnormal addition reactions is considered to consist in capturing bromine atoms, thus interrupting the propagation of chains.

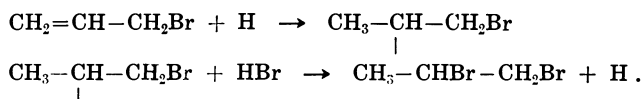
That the molecular bromine does not accelerate the abnormal addition has been shown by Smith.<sup>(27)</sup> In the addition of hydrogen bromide

(27) J. C. Smith, *Chemistry and Industry*, **57** (1938), 465.

to undecenoic acid in dilute benzene solution, the addition of much bromine caused the abnormal addition, but the necessary amount was very large compared with that of oxygen which was efficient enough in traces. In a concentrated solution hydrogen bromide added normally although bromine was consumed.

Thus not only Kharasch's hypothesis has been experimentally substantiated and it has been established that hydrogen bromide and oxygen give rise to bromine atoms in the presence of ethenoid compounds, but also the fate of hydrogen atoms and the reactions to proceed in the presence of much oxygen have been made clear.

**The Mechanism of the Normal Addition.** Since the double bond at the end of a chain, and especially the terminal unsaturated carbon atom, are associated with the least steric hindrance, it can be anticipated from a steric point of view that addition will take place at this carbon atom with the greatest ease. Thus, if hydrogen bromide adds by atoms, the atom adding first to the double bond, whether it may be the bromine atom or the hydrogen atom, will prefer the terminal position. No contradiction is tenable from the consideration of the electron density, because the atom, whether bromine or hydrogen, will be directed toward the terminal carbon atom with the greater electron density and it is hardly possible that the electron density should be affected by oxygen. If the initiative in addition, hence the terminal position, is taken exclusively by the bromine atom or by the hydrogen atom, then the product will contain a predominating proportion of either of the two isomerides. In the addition of hydrogen bromide to ethenoid compounds with terminal double bonds, e.g. allyl bromide and vinyl bromide, the products obtained under extreme conditions consist mainly or solely of either of the two possible isomerides. It must be noted here that in the above-mentioned examples oxygen exactly reverses the proportion of the two isomerides. An inspection of the constitutions of the main or sole products indicates at once that the initiative in addition is taken by the hydrogen atom in the normal reaction and by the bromine atom in the abnormal reaction. The abnormal reaction taking place in the presence of oxygen has just been explained on the basis of a chain mechanism involving the bromine atom and the radical formed by the addition of the bromine atom to the terminal carbon atom of the unsaturated molecule. The fact that the normal reaction is inhibited totally as the abnormal one becomes active, is well understood on the assumption that the normal reaction is also a chain reaction (see below). Thus the normal reaction may be represented by the following scheme:



Even in the presence of a sufficient amount of oxygen about 5% of the product from allyl bromide and hydrogen bromide is 1,2-dibromopropane, while in the absence of oxygen 1,3-dibromopropane is formed in a proportion of about 5%. Thus it can be assumed that about one-twentieth of the atoms, either bromine or hydrogen, taking the initiative in



addition add to the carbon atoms adjacent to the terminal carbon atoms rather than that the atoms adding first are all directed to the terminal carbon atoms and consist of 95% of one and 5% of the other, because in the cases of vinyl halides it must be concluded that all the atoms taking the initiative in addition are either bromine atoms or hydrogen atoms and add exclusively to the terminal carbon atoms, indicating that the compositions of the products obtained under extreme conditions depend entirely on the nature of the unsaturated molecules.

The accelerating effect of platinum black on the normal reaction may be attributed to the activation of the hydrogen atom of hydrogen bromide which takes the initiative in addition. The following facts support this idea: (1) While reduced nickel does not act as a hydrogenating catalyst at ordinary temperature, platinum black can activate hydrogen at ordinary temperature and pressure. (2) If hydrogen bromide is added to allyl bromide in the presence of both platinum black and oxygen, the composition of the product is intermediate and in this case bromine is liberated and remains free in spite of the presence of allyl bromide unchanged.<sup>(4)</sup> This may be interpreted as that the hydrogen atom activated by platinum black combines partly with oxygen while the unpaired bromine atom cannot add even to the unsaturated allyl bromide and is thrown off temporarily as a bromine molecule.

Since it seems that the normal reaction, or strictly speaking the reaction giving the same product as the normal reaction, accelerated by platinum black and the abnormal reaction caused by oxygen proceed side by side, the addition initiated by the hydrogen atom activated by platinum black is probably concluded by the combination of the remaining bromine atom to form 1,2-dibromopropane without commencing the chain reaction as shown above (further see below).

**The Cancelling of the Normal and the Abnormal Chains.** If the normal and the abnormal chains are brought into co-existence, the bromoisopropyl radical and the hydrogen atom of the former may combine with the bromine atom of the latter on the one hand, and, on the other, the dibromoisopropyl radical and the bromine atom of the abnormal chain may combine with the hydrogen atom of the normal chain. Thus cancelling of the two kinds of chains may occur and either kind remaining after this process will be propagated freely. After all the chains propagating in the system have become abnormal ones, the increase of the chains by increasing the amount of oxygen will cause only the increase of the reaction velocity without affecting the composition of the product. The experimental results are in perfect accordance with this.<sup>(5)</sup>

According to the above idea, the abnormal and the normal reactions cannot proceed side by side both in considerable intensities during a long time. Thus the fact that products of intermediate compositions are obtained under intermediate conditions needs an explanation. This affords, however, no indication that the two reactions should proceed side by side in a ratio that might be revealed by the compositions of the products. On the contrary, a simple calculation from the data obtained previously<sup>(5)</sup> makes it quite clear that under such conditions the normal chains pre-

dominate in the first stage of the reaction but are gradually supplanted by the abnormal chains.

| Amount of oxygen admitted (c.c.) | Total yield (%) |        |       | 1,3-Dibromopropane (%) in the product formed in |        |                               |
|----------------------------------|-----------------|--------|-------|-------------------------------------------------|--------|-------------------------------|
|                                  | 3 days          | 5 days | Diff. | 3 days                                          | 5 days | Last 2 days in 5 day reaction |
| 0*                               | 14              | 24     | 10    | 4                                               | 12     | 23                            |
| 0.5                              | 21              | 37     | 16    | 38                                              | 60     | 89                            |

\* A minute quantity of oxygen may have possibly been present, because the evacuation of air was effected with a rotary pump.

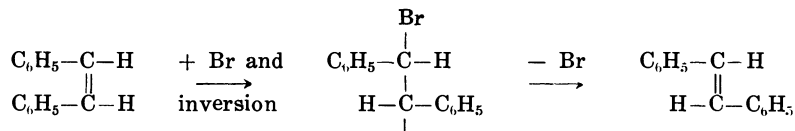
The accompanying table shows that the normal reaction is gradually supplanted by the abnormal reaction with the lapse of time. Such a phenomenon, which may be represented by the term "induction period," must occur also within 3 days, and it goes without saying that the more oxygen is present the quicker the abnormal reaction takes the place of the normal one. Thus the intermediate composition represents only the sum of products formed in the course of such rise and fall of the two reactions, and not the proportion with which the two reactions proceed all the time.

It is not impossible that oxygen may inhibit the normal reaction by catching the hydrogen atom carrying the normal chain; however, as the normal reaction can be eliminated by a very small amount of oxygen such a mechanism may not be responsible for the formation of water (or hydrogen peroxide) in the reaction of allyl bromide, hydrogen bromide and oxygen.

**The Mechanism of the Cis-trans Isomerization by Hydrogen Bromide and Oxygen.** It has already been suggested that the isomerization of isostilbene to stilbene by hydrogen bromide and oxygen may be closely related with the addition of hydrogen bromide to ethenoid compounds in the presence of oxygen. Thus it may reasonably be assumed that the first stage of the isomerization is the same as that of the addition, namely, the addition of the bromine atom formed from hydrogen bromide and oxygen to produce a bromo radical. Here the second stage of addition, namely, the formation of the completed addition product and another bromine atom, does not occur owing to the small concentration of hydrogen bromide and especially to the nature of the unsaturated linkage, but the bromine atom which has entered the unsaturated molecule goes out and moves to another molecule of the unsaturated compound. Thus the mechanism is quite analogous to that of the isomerization by bromine and light. However, the addition of a bromine atom to the double bond, free rotation about the single bond thus formed and elimination of the bromine atom, as postulated by Berthoud<sup>(19) (28)</sup>, do not explain the inversion of the geometrical isomerides. The addition (or the elimination)

(28) Compare further D. H. Hey and W. A. Waters, *Chem. Rev.*, **21** (1937), 169 and W. A. Waters, "Physical Aspects of Organic Chemistry," 139, London (1937).

of the bromine atom should be accompanied by an inversion of either of the unsaturated carbon atoms.<sup>(29)</sup> Then the isomerization of isostilbene by hydrogen bromide and oxygen may be represented as a chain reaction shown below:



The inhibiting action of antioxidants on the cis-trans isomerization by hydrogen bromide and oxygen can be attributed also to the break of the chains due to the capture of bromine atoms by them.

If much hydrogen bromide and oxygen be present, the bromo radical takes up another bromine atom to form stilbene dibromide rather than hydrogen atom from hydrogen bromide.

**Cases where the Effect of Oxygen is Undetectable.** It is beside the question of the present paper whether or not oxygen will affect the additions of hydrogen bromide proceeding by other mechanisms, e.g., ionic addition. The effect of oxygen, however, may be undetectable in certain cases of atomic additions by the chain mechanism.

Let the two unsaturated carbon atoms be designated as  $\alpha$  and  $\beta$ . If the  $\alpha$  carbon atom is terminal, any atom adding first will prefer it. In the case of allyl bromide 95% of the atoms adding first are directed to the  $\alpha$  carbon atoms, while in cases of vinyl halides all the atoms adding first combine with the  $\alpha$  carbon atoms. Here it may be pointed out again that, whether the atoms adding first are bromine or hydrogen, they are distributed between the  $\alpha$  and  $\beta$  positions in the same proportion.

If the double bond is not situated at the end of a chain and the  $\alpha$  and  $\beta$  carbon atoms are alike in their properties, the atoms adding first may tend to be distributed equally between the  $\alpha$  and  $\beta$  carbon atoms. In such a case the product may be near to a 50%:50% mixture of two isomerides, and irrespective of the kind of the atoms adding first the result of addition may be the same if seen from the composition of the product, and, therefore, the effect of oxygen may be difficult to detect.

Thus, Smith and co-workers<sup>(30)</sup> observed that the addition of hydrogen bromide to isoundecenoic acid or to the corresponding alcohol gives a mixture containing equal amounts of two isomerides either in the presence or in the absence of oxygen. Further Kharasch and co-workers<sup>(31)</sup> added hydrogen bromide to *cis*- and *trans*-pentene-(2) and obtained equal amounts of 2-bromopentane and 3-bromopentane regardless of the conditions of addition and of the spatial configuration of pentene-(2).

The distribution of the bromine atoms adding first between the  $\alpha$  and  $\beta$  carbon atoms may not always be equal to that of the hydrogen

(29) Compare R. L. Shriner, R. Adams, and C. S. Marvel, "Gilman's Organic Chemistry," Vol. I, 378, New York (1938).

(30) P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108; E. P. Abraham, E. L. R. Mowat, and J. C. Smith, *ibid.*, **1937**, 948.

(31) M. S. Kharasch, C. Walling, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1559.

atoms, and thus the normal and the abnormal reactions may not always give products with reciprocal compositions. In the special case where the distribution of the bromine atoms is a reciprocal of that of the hydrogen atoms, the compositions of the products will be equal in spite of the quite different modes of reactions. Such examples will be found in case the nature of the substituents exerts a decisive influence on the determination of the positions which the bromine atoms and the hydrogen atoms can take irrespective of the order of addition.

**Conclusion and Summary.** When hydrogen bromide acts on the ethenoid linkage in the presence of oxygen, the first change to be characterized is the formation of a bromo radical from the unsaturated molecule and the bromine atom formed from hydrogen bromide and oxygen. In the formation of the bromo radical, if the double bond is situated at the end of a chain, the bromine atom takes preferably the terminal position, and, if an asymmetric carbon atom is produced by the addition of the bromine atom, inversion is accompanied. In the second stage of the reaction the radical, according as its nature and the conditions, either takes up hydrogen atom from hydrogen bromide to form a completed addition product and another bromine atom or splits off the bromine atom to regenerate the double bond. In either case the cycle of the changes is propagated by a chain mechanism. The action of oxygen, therefore, resembles that of light quantum in a photochemical reaction proceeding with a great quantum yield.

The theory advanced in this paper is based on the experiments on the action of hydrogen bromide and oxygen on certain ethenoid compounds.

The effect of reduced nickel will be discussed in a separate paper on the basis of a quite similar mechanism.

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# On the Rhodanate Reaction of Molybdenum.

By Yasumitsu UZUMASA and Ken-ichi DOI.

(Received August 1, 1939.)

Since Braun<sup>(1)</sup> has reported the colour reaction of molybdenum produced by stannous chloride and rhodanate, the reaction has been in general adopted in the detection as well as in the estimation of the element. It is well known that the red colour once developed gradually disappears if the solution is treated with too much reducing agent. Thence some complex ions of *quinqivalent* molybdenum, such as  $\text{MoO}(\text{SCN})_5''$ , are considered to be responsible for the reaction. The fact is well recognized by some investigators but others are in the opinion that the red colour is due to the *tervalent* molybdenum, such as  $\text{Mo}(\text{SCN})_6''$ . The latter consideration still prevailing to a certain extent is by no means correct, however. The present writers<sup>(2)</sup> recently studied the absorption spectra of rhodanate- and chloro-complexes of molybdenum and have found that the solutions are, at least in the visible region, most hyperchromic when the element is in the *quinqivalent* state. And it was proved, moreover, that the solution of  $\text{K}_3[\text{Mo}(\text{SCN})_6]$ , which could be isolated in the crystalline state by the reaction between  $\text{K}_3[\text{MoCl}_6]$  and  $\text{KSCN}$ , had but a faint yellowish tinge, and that it became more hyperchromic only when some oxidizing agent was added.

It is often emphasized that *pH* of the solution in which molybdate-rhodanate reaction takes place should be very carefully controlled because the colour intensity depends largely upon the acidity of the medium. The reduction potential of a reducing agent, e.g., stannous chloride, is a function of the acid concentration of the solution so that *pH* should naturally play an important rôle in this colour reaction. Hurd and Allen<sup>(3)</sup> studied the effect of variables involved in the colorimetric determination of molybdenum. It is recommended by these authors that the concentration of hydrochloric acid should be kept at 5.0%, potassium rhodanate at 0.6%, and stannous chloride above 0.1%. To make a test of the molybdate-rhodanate reaction, stannous chloride is usually added to the solution of molybdate which already contains hydrochloric acid and rhodanate. In some books, however, the directions are given that the reducing agent should be added in advance and rhodanate be added afterwards. We thus notice that stress has never been laid on the order of priority in which the reagents are added. Nevertheless, this is a matter of no small importance. The colour intensity of the reaction products is not found to be identical when the order is reversed, even though the amounts of the reagents used are exactly the same. Experiments have therefore been carried out to elucidate what really causes this difference.

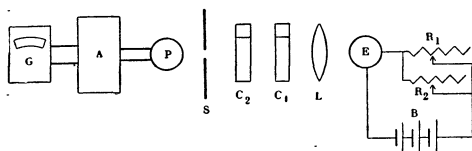
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(1) C. D. Braun, *Z. anal. Chem.*, **2** (1863), 36.

(2) Y. Uzumasa and K. Doi, *J. Chem. Soc. Japan.*, **59** (1938), 1047.

(3) L. C. Hurd and H. O. Allen, *Ind. Eng. Chem., Anal. Ed.* **7** (1935), 396.

**Experimental.** *Comparison of the colour produced by different procedures.* Two series of molybdate solutions each containing 1~24% hydrochloric acid were prepared. One series was coloured by adding rhodanate first and then stannous chloride (A), while the other coloured by the addition of stannous chloride followed by rhodanate (B). Both series were examined by means of a photoelectric colorimeter constructed by the writers. Its essentials are illustrated in Fig. 1.



- B: Lead storage batteries. 6V, Cap. 100A.  
 R<sub>1</sub>, R<sub>2</sub>: Slide resistances.  
 E: Mazda talkies-bulb. 5V, 5.5A.  
 L: Condensing lens.  
 C<sub>1</sub>, C<sub>2</sub>: Solution cells.  
 S: Slit.  
 P: Photocell. Elevam Cs-PV-65.  
 A: Amplifier.  
 G: Siemens box-type galvanometer.  
 0.25 × 10<sup>-6</sup>A.

Fig. 1.

A beam of light from the lamp E passes through the condensing lens L and the cell C<sub>1</sub> containing the filter liquid. The beam then traverses the second cell C<sub>2</sub> which contains the solution to be examined and enters the slit S by which it is defined. The unabsorbed light finally strikes the photocell P. The filter liquid is composed of an aqueous solution of cupric sulphate, the concentration of which is 20 mg. CuSO<sub>4</sub>/c.c. This solution serves for cutting off the infrared component of the light. The photoelectric current is amplified and can be read on a Siemens box-

type galvanometer G. The amplifier circuit applied by us is that proposed by Hogness, Zschelle, Jr. and Sidwell, Jr.<sup>(4)</sup> In this circuit the so-called "electrometer bulb" Mazda UX 54 is used by which a sufficient constancy of amplification during operation can be obtained.

Table 1. Transmission (%).<sup>\*</sup> Thickness: 1 cm.

| Procedure      |                               | A  |    |    |    |     | B  |    |    |    |     |
|----------------|-------------------------------|----|----|----|----|-----|----|----|----|----|-----|
| Conc<br>of HCl | <i>t</i> (min.) <sup>**</sup> | 1  | 30 | 60 | 90 | 120 | 1  | 30 | 60 | 90 | 120 |
|                |                               |    |    |    |    |     |    |    |    |    |     |
| 1              |                               | 36 | 66 | 73 | 75 | 88  | 91 | 85 | 87 | 87 | 88  |
| 2              |                               | 34 | 45 | 50 | 58 | 66  | 89 | 82 | 77 | 82 | 84  |
| 3              |                               | 32 | 38 | 45 | 47 | 56  | 35 | 58 | 54 | 62 | 67  |
| 5              |                               | 25 | 16 | 19 | 20 | 20  | 76 | 44 | 20 | 20 | 20  |
| 6              |                               | 26 | 15 | 22 | 23 | 23  | 76 | 43 | 25 | 28 | 30  |
| 8              |                               | 29 | 27 | 34 | 36 | 48  | 68 | 29 | 25 | 40 | 50  |
| 10             |                               | 27 | 28 | 35 | 40 | 65  | 51 | 39 | 45 | 68 | 73  |
| 15             |                               | 44 | 86 | 88 | 90 | 91  | 68 | 67 | 77 | 85 | 91  |
| 20             |                               | 52 | 90 | 91 | 91 | 91  | 82 | 86 | 90 | 91 | 91  |
| 24             |                               | 54 | 91 | 91 | 91 | 91  | 83 | 88 | 90 | 91 | 91  |

<sup>\*</sup> Distilled water: 93%. <sup>\*\*</sup> Time after the addition of the last reagent.

(4) T. R. Hogness, F. P. Zschelle, Jr. and A. E. Sidwell, Jr., *J. Phys. Chem.* **41** (1937), 379.

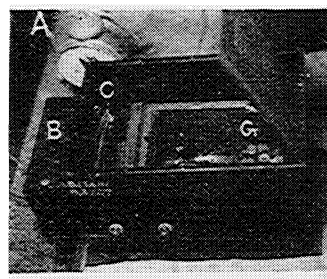
The results of the experiments carried out with two series of molybdate solutions coloured respectively in the manner described above are summarized in Table 1.

It has been recognized by a number of investigators that the colour produced by molybdenum and rhodanate undergoes considerable changes with the duration of time. With the object of following these changes, we constructed an apparatus by means of which any change in the colour of a given solution is autographically recorded. Fig. 2 shows the principal features of the apparatus.

The rays reflected from the mirror of the galvanometer are converged by a cylindrical lens C upon a sheet of bromide paper which is stretched round a drum held in a metallic box B. The shaft of the drum is, by means of a pair of cog-wheels, so connected with the shaft of the hour-hand of an alarm clock that the latter gives the former one complete turn in two hours. The difficulty of keeping either the light source or the amplifier at a constant condition often makes the autographic recording unsuccessful. To overcome this difficulty it is necessary not only that the storage batteries should be always kept in a perfect condition but also that as a light source a lamp which gives least fluctuation throughout the observation should be adopted. We found that the bulb used for automobile headlight was not suitable for the present purpose because of its unsteadiness of the filament. Instead, Mazda talkies-bulb is highly recommended, for its filament is extremely steady. As resistance in the main amplifying circuit, Nihonmusen Company's radio rheostats of variable type are used. These rheostats markedly, though not completely, excluded the possible fluctuation of the galvanometer.

Some autographical results are given in Fig. 3.

*Acid concentration and the formation of molybdenum brown.* We next studied at what concentration of hydrochloric acid molybdenum brown is most easily formed. To 1 c.c. of neutral molybdate solution



G: Shimazu box type galvanometer.  
C: Cylindrical lens.  
B: Metallic box containing a rotating drum.  
A: Alarm clock.

Fig. 2.

Table 2.

| <i>x</i> | <i>y</i> | Resultant conc. of HCl (%) | M/100 $K_2MoO_4$ | M/10 $K_2MoO_4$  |
|----------|----------|----------------------------|------------------|------------------|
| 0        | 8        | 1                          | brownish*        | yellowish brown* |
| 1        | 7        | 2                          | colourless       | yellowish        |
| 2        | 6        | 3                          | „                | colourless       |
| 3        | 5        | 4                          | „                | „                |
| 4        | 4        | 5                          | „                | „                |

\* These colorations indicate the formation of molybdenum brown.

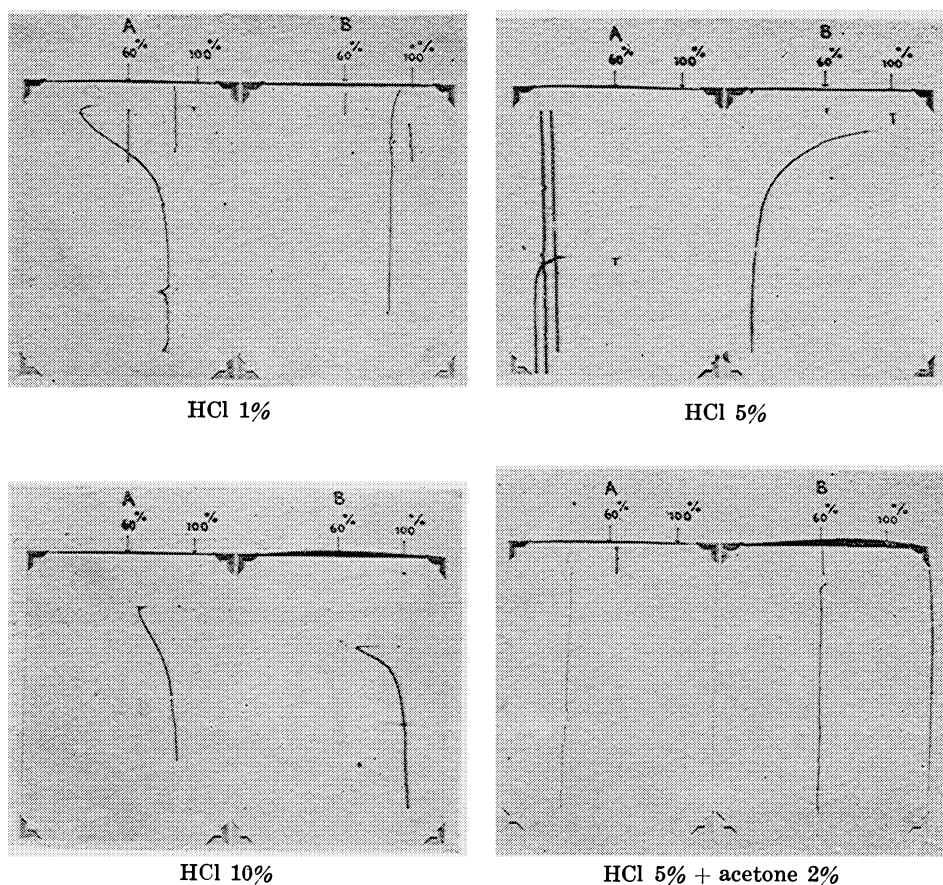


Fig. 3.

were added  $x$  c.c. of 10% hydrochloric acid and  $y$  c.c. of water. Each solution was then treated with 1 c.c. of 10% stannous chloride in 10% hydrochloric acid solution. The results are given in Table 2.

*Spectrographic examination of the reaction products.* In the next place, we examined spectrographically the reaction products of the procedure A and B. To the mixture of 1 c.c. of M/20 molybdate solution,  $x$  c.c. of 10% hydrochloric acid and  $y$  c.c. of water were added 1 c.c. of 10% KSCN, and then 1 c.c. of 10%  $\text{SnCl}_2^{(5)}$  (A); or 1 c.c. of 10%  $\text{SnCl}_2$  and then 1 c.c. of 10% KSCN (B). Ten minutes after the addition of the last reagent, 1 c.c. was pipetted out from each solution and diluted with a proper amount of water and hydrochloric acid so that the resultant solution might contain 1, 3, 5 or 8% HCl respectively. Their absorption spectra were then photographed with a small quartz spectrograph. The results are shown in Table 3.

(5) Stannous chloride should not be added more than this amount, because it has its own absorption in the ultraviolet region which masks the band of molybdenum in question.



Table 3.

| <i>x</i> | <i>y</i> | Resultant conc.<br>of HCl (%) | Absorption bands (Å) |          |
|----------|----------|-------------------------------|----------------------|----------|
|          |          |                               | A                    | B        |
| 0        | 7        | 1                             | 3100 + *             | 3000 + * |
| 2        | 5        | 3                             | 3150 ++              | 3000 ++  |
| 4        | 3        | 5                             | 3150 +++             | 3000 ++  |
| 7        | 0        | 8                             | 3150 +++             | 3000 +++ |

\* +, ++ and +++ indicate the relative intensities of the bands.

If the reaction products are shaken with ether, the coloured substance is extracted into the other layer, leaving stannous chloride in aqueous solution. The masking effect of stannous chloride may be thus avoided. The solutions obtained by the process A as well as by the process B were both allowed to stand for just ten minutes and then were extracted with 10 c.c. of ether. 1 c.c. was pipetted out from the ether layer, and diluted to 50 c.c. with ether. It was then observed spectrographically (Table 4). In case of A, the coloured substance was thoroughly extracted into ether, and the aqueous layer was almost colourless, while, in case of B, the extraction was always incomplete, the aqueous layer remaining more or less yellowish.

Table 4.

| Conc. of HCl (%) | Absorption bands (Å)        |                |
|------------------|-----------------------------|----------------|
|                  | A                           | B              |
| 1                | 3300 +                      | 2600 +         |
| 3                | 3300 ++, 3100 ++, 2600 +    |                |
| 4                | 3300 ++, 3100 ++, 2600 +    |                |
| 5                | 3300 +++, 3100 +++, 2600 ++ | 3300 +, 2600 + |
| 8                | 3300 +++, 3100 +++, 2600 ++ | 3300 +, 2600 + |

**Discussion of Results.** As it will be seen from Table 1 and also from the autographical results, the process A almost always develops a colour much more intense than the B. This is a fact which was hitherto disregarded. The optimum concentration of hydrochloric acid for the production of the maximum intensity of red colour is found to be approximately 5~6%. This is in accordance with the result of Hurd and Allen.<sup>(3)</sup>

Why the colour produced in the process A surpasses in intensity that produced in the process B may be explained in two ways.

I. In the process B, some intermediate compounds, e.g., molybdenum blue, molybdenum brown, etc., are expected to form, even when an excess of stannous chloride and hydrochloric acid is used. Those compounds are stable and may prevent the production of complexes of *quinqui-* or *tervalent* molybdenum.

II. When chloro-complexes of molybdenum, such as  $K_2[MoOCl_5]$ ,  $K_2[MoO_2Cl_3]$  or  $K_3[MoCl_6]$ , are once formed, their transmutation into corresponding rhodanate-complexes on the addition of potassium rhodanate may take place with considerable difficulty.

Our experiments indicate that, as shown in Table 2, the formation of molybdenum brown takes place only when the acid concentration is below 2%. The concentration of acid in which molybdenum blue is formed is likely to be much lower again; while the colour produced in the process B is weaker at *all* the concentration of acid than that produced in the process A (see Table 1). Consequently the formation of molybdenum blue or brown may not be responsible for the colour difference of the two processes.

Table 3 shows that the reaction products of the process A are always hyperchromic than those of the process B. The band of the former is situated between  $3100\text{\AA}$  and  $3150\text{\AA}$  while that of the latter is at  $3000\text{\AA}$ . It is also found that all the bands are more pronounced with increasing concentration of hydrochloric acid. According to our recent studies<sup>(2)</sup> on the absorption spectra of the molybdenum complexes,  $K_2[MoO(SCN)_5]$  has its band at  $3200\text{\AA}$  while  $K_2[MoOCl_5]$  has at  $2940\text{\AA}$ . The band produced by the process B is, therefore, ascribed to chloro-complexes of molybdenum. Probably these chloro-complexes may be rather stable and not easily changeable into rhodanate-complexes, even in a large excess of rhodanate.

The spectrographical examination of the ether extracts indicates that the more hydrochloric acid they contain, the more pronounced the bands appear. The extracts from the product of the process A are more hyperchromic than those from the process B (Table 4). When a solution of rhodanate complex of *quinqivalent* molybdenum,  $K_2[MoO(SCN)_5]$ , was acidified with hydrochloric acid and shaken with ether, a deep red extract was obtained which showed the absorption bands at  $3300\text{\AA}$  and  $3100\text{\AA}$ . These bands are in accord with those observed in the experiment with the ether extract from the process A.

On the basis of these results, it is concluded that the red colour observed in the rhodanate test for molybdenum is due to rhodanate complexes of *quinqivalent* molybdenum, possibly and chiefly  $K_2[MoO(SCN)_5]$ , and that when stannous chloride is added in advance, there may be formed some chloro-complexes, such as  $K_2[MoOCl_5]$  or  $K_2[MoO_2Cl_3]$ , which positively interfere the formation of red rhodanate compounds. The fact that the addition of potassium rhodanate to the aqueous solution of  $K_2[MoOCl_5]$  causes no remarkable coloration is in favour of this view. To make the test, therefore, it is always necessary to add ammonium or potassium rhodanate first and then some reducing agent, otherwise the sensitivity of the reaction might be more or less reduced.

The influence of acetone on this colour reaction was also studied. No doubt the presence of this organic solvent makes the colour developed more durable, but it neither increases the sensitivity of the reaction nor prevents undesirable effect of great excess of reducing agent. It is probable that the presence of acetone makes the reducing action milder and a long duration of time is necessary for over-reduction. The

coloured substances formed may thus remain much longer in the intermediate state of reduction. The colouring in the presence of acetone is also shown more constant in the records taken by the autographic apparatus.

#### Summary.

(1) By means of a photoelectric colorimeter, the reaction products between molybdenum and rhodanate under various conditions were examined. The colour changes with the duration of time were recorded by an autographic apparatus constructed by the writers.

(2) The spectrographic observations of the products were also carried out.

(3) The red colour observed in the rhodanate test for molybdenum is ascribed to rhodanate complexes of *quinqivalent* molybdenum, possibly and chiefly  $K_2[MoO(SCN)_5]$ .

(4) It is emphasized that, to attain the maximum sensitivity of the reaction, rhodanate should be added in advance of the reducing agent.

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## The Flow of Gases through Metallic Capillaries at Low Pressures.

By HIROSHI ADZUMI.

(Received August 5, 1939.)

It was reported by the present author<sup>(1)</sup> that the quantity of a gas flowing through a capillary in unit time and under unit pressure difference is expressed by the following formula:

$$K = 5.236 \times 10^2 \frac{1}{\eta} \frac{r^4}{l} p + \gamma \times 3.05 \times 10^4 \sqrt{\frac{T}{M}} \cdot \frac{r^3}{l}, \quad \dots\dots (1)$$

where  $\eta$  is the viscosity coefficient of the gas,  $M$  the molecular weight,  $p$  the mean pressure in mm. Hg,  $T$  the temperature,  $l$  and  $r$  respectively the length and the radius of the capillary and  $\gamma$  a coefficient equal to or smaller than unity. The flowing quantity  $K$  is measured by the product of the volume and the pressure of the gas. Coefficient  $\gamma$  of a gas is a function of pressure, but is constant at very low pressures, where it is equal to unity, and also constant at high pressures, where it is equal to about 0.9. This constant value of  $\gamma$  at high pressures is slightly different from gas to gas.

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(1) H. Adzumi, this Bulletin, **12** (1937), 292.

An interesting phenomenon about the flow of gases at low pressures is the existence of a minimum point on the  $K$ - $p$  curve. The theoretical interpretation of it has not yet been done, but if the nature of  $\gamma$  be cleared, the existence of a minimum will probably be explained. As stated above,  $\gamma$  is a coefficient depending on the nature of gases, but it is not known whether it depends on the nature of the capillary-wall or not. Almost all capillaries which were used by many authors to study the flowing phenomena of gases were made of glass. In order to know the effect of the material of the capillary-wall, the present experiments have been done.

**Experimental.** The procedure for measuring the quantities of flow of gases is the same as already described.<sup>(2)</sup> The material of capillaries used for experiments are glass, silver, aluminium, copper, and iron. The inner surfaces of these metallic capillaries were carefully made as smooth as possible. The internal diameters are about 0.054 ~ 0.058 cm. and lengths 5 ~ 10 cm. The exact dimensions of respective capillaries are shown in the accompanying tables. The quantities of hydrogen flowing in unit time and under unit pressure difference through various metallic capillaries at 15.5°C. are given in Table 1.

As the reproducibility of the quantities at pressures lower than about 0.05 mm. Hg was not good, the values of extremely low pressures are

Table 1. The Quantities of Flow of Hydrogen at 15.5°C.

Capillary : silver

( $l = 7.7$  cm.,  $r = 0.027$  cm.)

| $p_{\text{mm.}}$ | $K$     | $K-ap$ | $\gamma$ |
|------------------|---------|--------|----------|
| 1.517            | 1.456   | 0.844  | 0.89     |
| 1.210            | 1.329   | 0.841  | 0.89     |
| 1.109            | 1.290   | 0.846  | 0.90     |
| 0.8258           | 1.176   | 0.843  | 0.89     |
| 0.5850           | 1.080   | 0.844  | 0.89     |
| 0.5612           | 1.068   | 0.842  | 0.89     |
| 0.4022           | 1.004   | 0.842  | 0.89     |
| 0.2995           | 0.975   | 0.844  | 0.89     |
| 0.2229           | 0.952   | 0.862  | 0.91     |
| 0.1821           | 0.944   | 0.871  | 0.92     |
| 0.1646           | 0.941   | 0.874  | 0.92     |
| 0.1375           | 0.941   | 0.886  | 0.94     |
| 0.1018           | 0.939   | 0.898  | 0.95     |
| 0.0677           | 0.936   | 0.909  | 0.96     |
| 0.0578           | 0.937   | 0.914  | 0.97     |
| 0.0436           | 0.940   | 0.922  | 0.98     |
| 0.0329           | 0.939   | 0.926  | 0.98     |
| (0.000)          | (0.945) | 0.945  | 1.00     |

Capillary : aluminium

( $l = 5.4$  cm.,  $r = 0.029$  cm.)

| $p_{\text{mm.}}$ | $K$     | $K-ap$ | $\gamma$ |
|------------------|---------|--------|----------|
| 1.421            | 2.490   | 1.378  | 0.81     |
| 1.388            | 2.464   | 1.378  | 0.81     |
| 0.8951           | 2.073   | 1.372  | 0.81     |
| 0.8188           | 2.017   | 1.376  | 0.81     |
| 0.5431           | 1.801   | 1.376  | 0.81     |
| 0.4985           | 1.765   | 1.374  | 0.81     |
| 0.3434           | 1.655   | 1.387  | 0.82     |
| 0.3173           | 1.642   | 1.394  | 0.82     |
| 0.2217           | 1.590   | 1.416  | 0.83     |
| 0.2040           | 1.585   | 1.427  | 0.84     |
| 0.1449           | 1.567   | 1.454  | 0.86     |
| 0.1347           | 1.560   | 1.455  | 0.86     |
| 0.1156           | 1.560   | 1.469  | 0.87     |
| 0.1000           | 1.558   | 1.480  | 0.87     |
| 0.0718           | 1.561   | 1.505  | 0.89     |
| 0.0387           | 1.574   | 1.544  | 0.91     |
| 0.0237           | 1.588   | 1.569  | 0.92     |
| 0.0202           | 1.594   | 1.578  | 0.93     |
| (0.000)          | (1.699) | 1.699  | 1.00     |

(2) H. Adzumi, this Bulletin, **12** (1937), 285.

## Capillary : copper

 $(l = 9.8 \text{ cm.}, r = 0.030 \text{ cm.})$ 

| $p_{\text{mm.}}$ | $K$     | $K-ap$ | $\gamma$ |
|------------------|---------|--------|----------|
| 1.604            | 1.483   | 0.764  | 0.79     |
| 1.444            | 1.408   | 0.761  | 0.79     |
| 1.063            | 1.241   | 0.766  | 0.80     |
| 0.9690           | 1.192   | 0.758  | 0.79     |
| 0.7365           | 1.092   | 0.762  | 0.79     |
| 0.6801           | 1.065   | 0.760  | 0.79     |
| 0.5265           | 1.001   | 0.765  | 0.79     |
| 0.3230           | 0.914   | 0.769  | 0.80     |
| 0.2225           | 0.885   | 0.785  | 0.82     |
| 0.2181           | 0.888   | 0.790  | 0.82     |
| 0.1350           | 0.872   | 0.811  | 0.84     |
| 0.1175           | 0.870   | 0.817  | 0.85     |
| 0.0744           | 0.875   | 0.842  | 0.87     |
| 0.0645           | 0.876   | 0.847  | 0.88     |
| 0.0378           | 0.886   | 0.869  | 0.90     |
| 0.0376           | 0.892   | 0.875  | 0.91     |
| 0.0290           | 0.893   | 0.880  | 0.91     |
| 0.0185           | 0.901   | 0.893  | 0.93     |
| (0.000)          | (0.963) | 0.963  | 1.00     |

## Capillary : iron

 $(l = 9.96 \text{ cm.}, r = 0.029 \text{ cm.})$ 

| $p_{\text{mm.}}$ | $K$     | $K-ap$ | $\gamma$ |
|------------------|---------|--------|----------|
| 2.073            | 1.412   | 0.626  | 0.74     |
| 1.462            | 1.176   | 0.622  | 0.73     |
| 0.9332           | 0.971   | 0.617  | 0.73     |
| 0.6889           | 0.880   | 0.618  | 0.73     |
| 0.5291           | 0.821   | 0.620  | 0.73     |
| 0.4039           | 0.785   | 0.632  | 0.75     |
| 0.3951           | 0.784   | 0.634  | 0.75     |
| 0.3036           | 0.762   | 0.647  | 0.76     |
| 0.2815           | 0.755   | 0.648  | 0.77     |
| 0.2371           | 0.752   | 0.662  | 0.78     |
| 0.1864           | 0.739   | 0.668  | 0.79     |
| 0.1643           | 0.737   | 0.675  | 0.80     |
| 0.1464           | 0.738   | 0.683  | 0.81     |
| 0.0914           | 0.736   | 0.701  | 0.83     |
| 0.0720           | 0.737   | 0.710  | 0.84     |
| 0.0574           | 0.740   | 0.718  | 0.85     |
| 0.0440           | 0.744   | 0.727  | 0.86     |
| 0.0395           | 0.750   | 0.735  | 0.87     |
| (0.000)          | (0.846) | 0.846  | 1.00     |

obtained by calculation from formula (1) and are shown in brackets in the tables. The symbol  $ap$  in the third column of the tables indicates the first term of formula

(1). In Fig. 1,  $K$ 's are shown as functions of the mean pressures. These figures are similar to that in the case of capillary of glass and the existence of minimum points is also remarkable. As seen from the fourth columns of the tables,  $\gamma$ 's for various capillaries become respectively constant at high pressures. These constant values, which are denoted by  $\gamma_m$ , are shown in Table 2 in comparison with the value for the glass capillary.<sup>(1)</sup>

As seen from Table 2, the values of  $\gamma_m$  clearly depend upon the material of the capillary-wall.

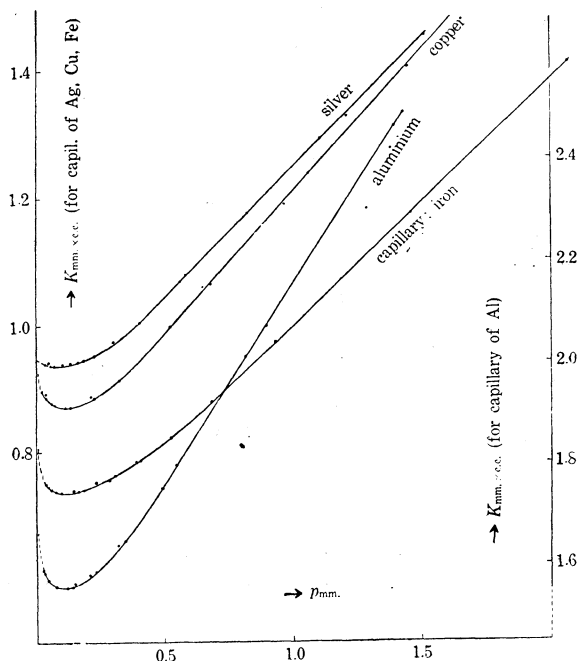


Fig. 1.

Table 2. Values of  $\gamma_m$  for Various Capillaries.

| Capillaries | Glass | Silver | Aluminium | Copper | Iron |
|-------------|-------|--------|-----------|--------|------|
| $\gamma_m$  | 0.91  | 0.89   | 0.81      | 0.79   | 0.73 |

**Discussion.** As stated above, the theoretical interpretation of the existence of a minimum point on the  $K$ - $p$  curve has not yet been done. Considering the dependence of  $\gamma_m$  upon the material of the capillary-wall and upon the flowing gas, the author advances the following argument. At very low pressures there are no molecules adsorbed on the surface of the capillary-wall but on increasing the pressure the adsorption will take place and the adsorbing area will be increased. At high pressures the surface will be saturated. Let us now consider the intermediate pressures at which the surface is not saturated. It is assumed that all the molecules which fall on the bare surface are adsorbed and that only some fraction of the molecules which fall on the already adsorbed molecules are reflected immediately. If this fraction of the reflected molecules is denoted by  $\beta$ , then  $1 - \beta$  is the fraction of molecules adsorbed. Therefore, of all the impinging molecules on the capillary-surface a fraction  $\rho$  will be adsorbed and this fraction is expressed as

$$\rho = \theta(1 - \beta) + (1 - \theta), \quad \dots\dots\dots (2)$$

where  $\theta$  is the fraction of the surface area already occupied, so that  $1 - \theta$  is that of the bare surface. When the surface is not saturated, the fraction  $\theta$  depends on the pressure, and this will increase only when molecules fall on the bare surface ( $1 - \theta$ ). Therefore,  $d\theta/dp$  is considered to be proportional to  $1 - \theta$ , then

$$\frac{d\theta}{dp} = c(1 - \theta),$$

where  $c$  is the proportionality constant. By integration

$$\theta = 1 - e^{-cp}, \quad \dots\dots\dots (3)$$

the integration constant being zero.

From (2) and (3),

$$\rho = 1 - \beta(1 - e^{-cp}). \quad \dots\dots\dots (4)$$

If only a fraction  $f$  of the impinging molecules leave the wall according to the cosine law (this is called 'diffuse emission') and the remainder,  $1 - f$ , are regularly reflected, some factor must be introduced into the formula of the molecular flow. This factor was given as  $f/(2 - f)$  by Gaede.<sup>(3)</sup>

Of all the impinging molecules, the adsorbed ones will be emitted after some stay in the adsorption layer, independently to the incident angle. So that the fraction of the diffuse emission ( $f$ ) is exactly equal to the fraction of adsorption ( $\rho$ ). Hence, by introducing the value of  $\rho$  to  $f$ ,  $\gamma$  is expressed as follows:

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(3) W. Gaede, *Ann. Physik*, (IV), **41** (1913), 289.

$$\gamma = \frac{f}{2-f} = \frac{1-\beta(1-e^{-cp})}{1+\beta(1-e^{-cp})}.$$

Thus the relation between  $\gamma$  and pressure is derived. At high pressures  $\gamma$  becomes constant,  $(1-\beta)/(1+\beta)$ , and at very low pressures it becomes approximately unity. At intermediate pressures  $\gamma$  depends on the pressure. This formula contains two unknown constants,  $\beta$  and  $c$ . In Table 3 are shown these constants calculated inversely from the observed data.

Table 3. Values of  $\beta$  and  $c$  for Hydrogen.

| Capillaries | Silver | Aluminium | Copper | Iron  |
|-------------|--------|-----------|--------|-------|
| $\beta$     | 0.058  | 0.104     | 0.117  | 0.156 |
| $c$         | 6.9    | 10.1      | 10.2   | 7.5   |

By using these calculated constants the flowing quantities  $K$  can be computed and these coincide satisfactorily with the experimental values. For example, the coincidence of these values of  $K$ 's in the case of iron capillary is indicated in Table 4 and Fig. 2.

Table 4.  
Values of  $K$  calculated.  
(Capillary : iron)

| $p_{\text{mm.}}$ | $K_{\text{obs.}}$ | $K_{\text{calc.}}$ |
|------------------|-------------------|--------------------|
| 1.0              | 0.998             | 0.997              |
| 1.7              | 0.884             | 0.883              |
| 0.5              | 0.813             | 0.812              |
| 0.3              | 0.760             | 0.766              |
| 0.2              | 0.744             | 0.739              |
| 0.1              | 0.736             | 0.733              |
| 0.05             | 0.742             | 0.779              |

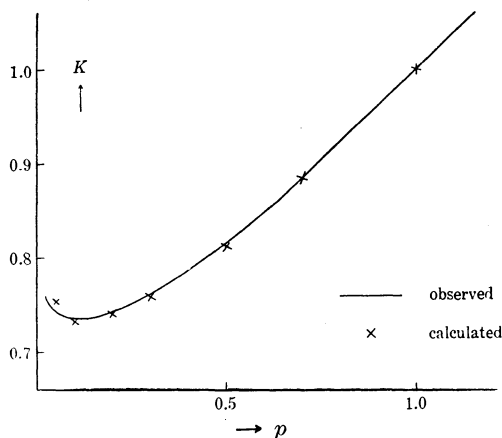


Fig. 2.

To summarize the preceding considerations, it can be said that, notwithstanding that the derived formula contains two unknown constants, the existence of a minimum point on the  $K$ - $p$  curve and the character of the factor  $\gamma$  in the flowing formula have been qualitatively interpreted.

In conclusion, the author wishes to express his cordial thanks to Professor Emeritus M. Katayama and Prof. H. Tominaga for their encouragement throughout this experiment. Thanks are due to the Japan Society for the Promotion of Scientific Research for a grant.

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## Viscosity Effect on the Rate of Solution of Calcium Carbonate in Hydrochloric Acid.

By Hitosi TOMINAGA, Hiroshi ADZUMI, and Taro ISOBE.

(Received August 15, 1939.)

In homogeneous reactions in solution, the viscosity effect on the rate is considered to be very small. In heterogeneous reactions, there are three processes occurring: (1) the solute molecules approach and collide with the solid surface, (2) there takes place a chemical reaction; and (3) finally the products recede from the interface into the bulk of the solution. The diffusion velocities of the reactants or reaction products depend on the viscosity of the solution and, therefore, if these velocities are not very much greater than that of the chemical reaction, the observed rate will be affected by the viscosity. When metals are attacked by aqueous acids or cadmium by aqueous iodine, the chemical change is rapid, and then the observed velocity is simply the velocity of diffusion. Thus the viscosity effect on the rate of dissolution of zinc in hydrochloric acid was already observed.<sup>(1)</sup>

On the other hand, according to Spring,<sup>(2)</sup> when marble dissolves in hydrochloric acid diffusion is rapid and the chemical change determines the observed rate. Spring's conclusion was drawn from the consideration of the apparent heat of activation. Brunner's experiments<sup>(3)</sup>, however, indicated the diffusion concerned. In order to examine these observations by measuring the viscosity effect, the following experiments have been done.

**Experimental.** The rate of reaction is obtained by measuring the volume of carbon dioxide evolved. A well polished disk of marble of 3 cm. diameter, which is attached to a glass shaft and covered with wax or enamel all the surfaces except one face of bottom side, is rotated 485 ~ 488 times per minute in hydrochloric acid. In order to keep the rotational velocity of the disk constant, a synchronous motor is used. Fifty cubic centimeters of the acid are contained in a bottle of capacity 250 c.c. This reaction bottle (Fig. 1) and a gas burette of carbon dioxide are placed in a thermostat of 25°C. Then the volume of carbon dioxide evolved is read at intervals of one minute after inserting the rotating disk into the acid solution. The initial concentration of hydrochloric acid varies between 0.1747 and 0.5317 N.

The relation between the velocity, that is, the volume of carbon dioxide evolved per minute, and the total volume is shown in Fig. 2. Fig. 3 and Table 1 show the effect of changing the viscosity of the acid

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(1) C. V. King and M. M. Braverman, *J. Am. Chem. Soc.*, **54** (1932), 1744.

(2) W. Spring, *Z. physik. Chem.*, **1** (1887), 209; and also Moelwyn-Huges, 'The Kinetics of Reactions in Solution', p.284 (1933).

(3) E. Brunner, *Z. physik. Chem.*, **47** (1904), 56.

solution by adding glycerine on the rate. The range of viscosities is 0.00909 (without glycerine)~0.01751.

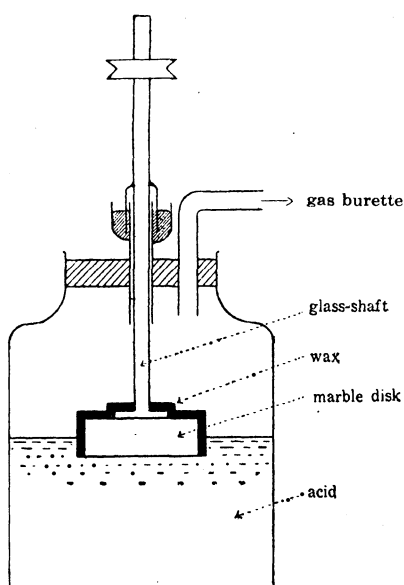


Fig. 1. Schematic View of the Reaction Bottle.

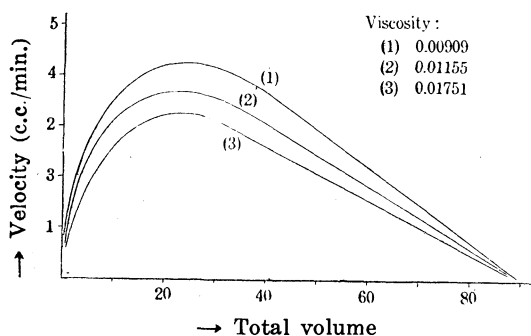


Fig. 3. Velocity Curves at Different Viscosities.

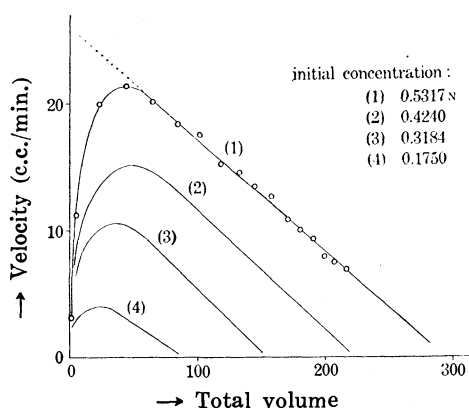


Fig. 2. Velocity Curves at Different Initial Concentrations.

Table 1. The Effect of Viscosity on the Velocity Constant.

| Glycerine % | $\eta$  | $k$    |
|-------------|---------|--------|
| —           | 0.00909 | 0.0495 |
| 3.78        | 0.00991 | 0.0475 |
| 5.37        | 0.01031 | 0.0433 |
| 9.77        | 0.01155 | 0.0411 |
| 14.51       | 0.01316 | 0.0377 |
| 19.16       | 0.01510 | 0.0369 |
| 23.85       | 0.01751 | 0.0344 |

Initial concentration of the acid :  
0.1750 N.

Rotational velocity of the disk :  
485 times per minute.

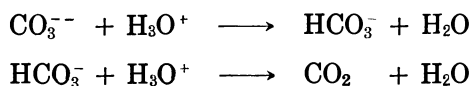
**Discussion.** As seen from Fig. 2, after about 30 c.c. of carbon dioxide has been evolved, the velocity changes linearly, which means the first order reaction occurs. The fore part of the reaction is an entirely different type. As seen from the figure, the maximum points of the velocity curves scarcely alter on using acids of different initial concentrations. The reaction before the maximum point is not simple, and there may be probably occurring following processes in this region. When the marble disk is inserted in the acid, carbon dioxide produced at the early stage will dissolve into the acid and when the neighbourhood of the disk is saturated, then for the first time bubbles of carbon dioxide are able to evolve. Further, there is time before the disk comes in perfect contact with the acid.

The reaction mechanism of the region before the maximum point seems to be very much complicated, and, therefore, only the region of the first order reaction is considered in this paper.

If the apparent reaction velocity of the linear part is denoted by  $v$ , it is proportional to the concentration of the acid,  $c$ , that is,

$$v = kc, \quad \dots\dots\dots (1)$$

where  $k$  is the velocity constant. As stated above, this heterogeneous reaction velocity consists of true chemical reaction velocity on the solid surface and the diffusion velocities of the hydroxonium ion in solution to the surface and of the reaction products to the bulk of the solution. True chemical change is considered to proceed in the two following stages:



The second reaction of the decomposition of bicarbonate may be assumed rapid, and, therefore, one molecule of carbon dioxide is produced for one hydrogen ion; namely, the true chemical reaction velocity  $v_1$  is proportional to  $c$ ,

$$v_1 = k_1c. \quad \dots\dots\dots (2)$$

As to the diffusion velocities of the individual components we may assume that Nernst's theory holds. Then

$$\text{diffusion velocity} = \frac{D \cdot A}{B \cdot \delta} c,$$

where  $D$  is the diffusion coefficient,  $A$  the area of the solid surface,  $B$  the volume of the solution, and  $\delta$  the thickness of the diffusion layer. In this reaction, notwithstanding the respective diffusion coefficients of  $\text{H}_3\text{O}^+$ ,  $\text{CO}_2$ , and  $\text{CaCl}_2$  may be concerned, all the constants are inversely proportional to the viscosity coefficient of the solution. Hence, the diffusion velocity  $v_2$ , in the lump, is expressed as follows:

$$v_2 = k_2 \frac{1}{\eta} c, \quad \dots\dots\dots (3)$$

where  $\eta$  is the viscosity coefficient.

On the marble surface, the chemical reaction takes place first, then diffusion follows. Hence, the apparent velocity  $v$  can be expressed as the sum of  $v_1$  and  $v_2$  added in series,

$$\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2}. \quad \dots\dots\dots (4)$$

From formulas (1)~(4),

$$\frac{1}{k} = \frac{1}{k_1} + \frac{\eta}{k_2}. \quad \dots\dots\dots (5)$$

As seen from formula (5),  $1/k$  is in general in the linear relation to the viscosity. If the chemical reaction is very rapid, the first term of formula (5) can be neglected and the line will cross the origin. On the contrary, if the diffusion is very rapid, the second term can be neglected and the line becomes parallel to the axis of viscosity. The actual results for this reaction are shown in Fig. 4.

As clearly seen, the velocities of the chemical reaction and the diffusion are both measurable, and according to the estimation from the figure these two processes concern in the same order under present conditions. This conclusion will be ascertained by following another experiment.

The rate of the same reaction has been measured by changing the rotational velocity of the disk. The results are shown in Table 2.

Table 2. The Effect of Rotational Velocity of the Disk on the Velocity Constant.

| $r$ (Number of rotation per minute) | 158     | 220     | 349     | 484     | 683     |
|-------------------------------------|---------|---------|---------|---------|---------|
| $k$                                 | 0.00633 | 0.00455 | 0.00287 | 0.00207 | 0.00146 |

Initial concentration of the acid: 0.1750 N. Viscosity: 0.00909.

The thickness of the diffusion layer  $\delta$  may depend on the rotational velocity  $r$ . If  $\delta$  is assumed to be inversely proportional to  $r$ , the diffusion velocity will be expressed as,

$$v_2 = k_3 r c . \quad \dots\dots\dots (6)$$

Hence,

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_3 r} . \quad \dots\dots\dots (7)$$

Similar to (5),  $1/k$  is in linear relation to  $1/r$ .

The graphical representation of the results is given in Fig. 4, and the cross point of the line with the axis, which indicates the value of  $1/k_1$ , coincides very well with that of the line of viscosity effect.

**On the Calculation of the Energy of Activation from the Temperature Coefficient of the Rate.** Moelwyn-Hughes<sup>(2)</sup> calculated the heat of activation of the reaction between marble and hydrochloric acid from the temperature coefficient of the rate which had been observed by

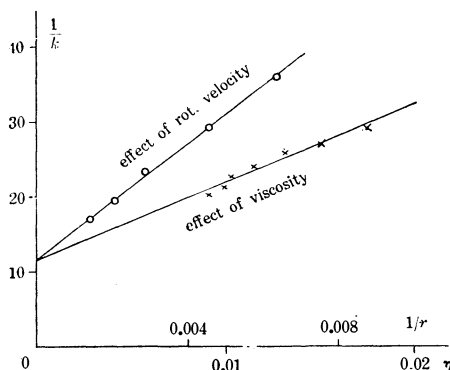


Fig. 4. Effects of Viscosity and Rot. velocity on the Velocity Constant.

Spring<sup>(2)</sup>, and found  $E_{15^{\circ}-35^{\circ}} = 6,300$  calories. In this calculation, however, the viscosity effect of this reaction was not taken into consideration. This is not correct. As stated above, this reaction is affected by viscosity, and by increasing temperature the viscosity is decreased. Hence, in the calculation of the apparent heat of activation from the temperature coefficient of the rate, the acceleration due to viscosity decrease must be eliminated.

Spring used a 5% acid solution and the observed ratio of the velocity constant of 35°C to that of 15°C was 2.05. The viscosity coefficients of this concentration are measured by the present authors as 0.00781 at 35°C and 0.01210 at 15°C. If the same amount of the viscosity effect as observed in the present experiment holds in the reaction in the 5% solution, the velocity constant of the latter reaction will become 1.23 times as much by changing the temperature from 15° to 35° owing only to the viscosity change. Hence, the increase of the rate in the ordinary meaning on raising the temperature becomes  $k_{35^{\circ}}/k_{15^{\circ}} = 1.82$ . By using this, the apparent heat of activation is corrected to 5,400 instead of 6,300 calories.

Generally, if a reaction is affected by viscosity, its effect must be taken into consideration in calculating the energy of activation from the temperature coefficient of the rate.

### Summary.

The viscosity effect on the rate of reaction between marble and hydrochloric acid has been measured. The mechanism of the reaction of the first order reaction has been considered and the results show that the true chemical reaction on the marble surface and the diffusions of the reactant and reaction products concern in the same order in this reaction. The same conclusion is obtained from the experiments of changing the rotational velocity of the marble disk. The apparent heat of activation, which was calculated by Moelwyn-Hughes from the temperature coefficient of the rate, has been corrected by considering the viscosity effect.

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## Austauschreaktion der Kernwasserstoffatome des Phenols. II. Austauschreaktion in saurer Lösung.<sup>(1)</sup>

Von Masao KOIZUMI.

(Eingegangen am 9. August 1939)

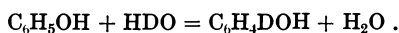
**Inhaltsübersicht.** Die Austauschreaktion der Kernwasserstoffatome des Phenols in der mit Salzsäure versetzten verdünnten sauren Lösung wird untersucht. Die Versuche, die bei konstanter Temperatur aber bei verschiedener Säurekonzentration ausgeführt werden, ergeben, dass die Beziehung zwischen der Geschwindigkeitskonstanten  $\bar{k}$  und der Säurekonzentration  $c$  durch die Formel wiedergegeben werden kann:

$$\log (\bar{k} / 2.303) = 1.26 \log c - 1.48 .$$

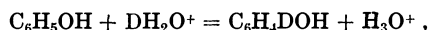
Die Reaktion ist nämlich in Bezug auf die H-Ionen von 1.26-Ordnung. Die Geschwindigkeitskonstante, die bei einer bestimmten Säurekonzentration (d.h. bei 0.0417 N und 0.0078 N) aber bei verschiedenen Temperaturen bestimmt wird, lässt sich dagegen durch die Formeln gut wiedergeben:

$$\begin{aligned} \log \bar{k}(0.0417 \text{ N}) &= (9.6 \pm 0.4) - \frac{27,400 \pm 0.600}{4.574 T} \quad (\text{Mol/Liter})^{-1} (\text{Sek.})^{-1}, \\ \log \bar{k}(0.0078 \text{ N}) &= (8.66 \pm 0.2) - \frac{27,200 \pm 0.300}{4.574 T} \quad (\text{Mol/Liter})^{-1} (\text{Sek.})^{-1}. \end{aligned}$$

Diese Konstante  $\bar{k}$  entspricht aber der stöchiometrischen Gleichung:



Da aber die wirkliche Reaktion höchstwahrscheinlich zwischen undissoziierten Phenolmolekülen und Hydroxoniumionen verlaufen muss:



wird die oben angegebene Formel für die scheinbare Geschwindigkeitskonstante  $\bar{k}$  für diese grundlegende Reaktion umgerechnet. Wenn man dabei die oben angegebene Beziehung zwischen der Geschwindigkeitskonstanten und H-Ionenkonzentration zu Grunde legt, dann ergibt sich für die wahre Geschwindigkeitskonstante  $k_0$  der grundlegenden Reaktion die Formel:

$$k_0 = 10^{12.5 \pm 0.3} \exp \left( - \frac{27,300 \pm 0.400}{RT} \right) \quad (\text{Mol/Liter})^{-1} (\text{Sek.})^{-1} .$$

Die vorliegenden Versuchsergebnisse werden im Vergleich mit den früher in alkalischer Lösung gewonnenen diskutiert.

**Einleitung.** Titani und ich haben früher die Austauschreaktion der Kernwasserstoffatome des Phenols in der mit Alkali versetzten Lösung untersucht (vgl. I. Mittl.). Dabei kamen wir zu dem Ergebnis, dass die Geschwindigkeitskonstante  $k_0$  für die grundlegende Reaktion (1) durch die Formel (2) wiedergegeben werden kann:



$$\bar{k}_0 = 10^{1.08} \exp \left( - \frac{24,800}{RT} \right) \quad (2)$$

---

(1) I. Mittl.: dies Bulletin, **13** (1938), 681.

insofern als die Menge des versetzten Alkalis im Vergleich mit dem Phenol viel geringer ist. Die Aktivierungsenergie für Reaktion (1) beträgt nämlich 24.8 Kcal. Aber weil nach dem Versuch von Geib<sup>(2)</sup> die Aktivierungsenergie für die Austauschreaktion der Kernwasserstoffatome des Resorcins in saurer Lösung sich ebenso hoch wie in alkalischer Lösung belief, liegt nun nahe, die Austauschreaktion des unsubstituierten Phenols auch in saurer Lösung zu untersuchen und ihre Aktivierungsenergie mit dem oben gefundenen Wert in alkalischer Lösung zu vergleichen.

**Versuchsanordnung.** Etwa 2 g. Phenol wird zusammen mit etwa 1 g. verdünntes schweres (ca. 4-prozentiges) Wasser, das aber durch Zusatz verschiedener Menge von Salzsäure angesauert worden ist, in einem zugeschmolzenen und gut evakuierten Glasrohr bei verschiedener Temperatur verschiedene Zeitlängen erwärmt. Nach dieser Behandlung wird das Wasser auf ähnliche Weise wie in I. Mittl. beschrieben wurde, vom Phenol und Säure abgesondert und die Dichte des so abgesonderten schweren Wassers, nach gründlicher Reinigung, mittels eines Quarzschwimmers mit der des gewöhnlichen Wassers verglichen. Das Austauschäquivalent  $na$  des Phenols bei der in Rede stehenden Versuchsdauer und -temperatur, das wie üblich durch Gl. (3) definiert wird, wird dann mit Hilfe der Gl. (4) berechnet:

$$na = \sum n_i a_i \quad (3)$$

$$na = \frac{2(D_a - D_e)}{D_e} \frac{M_w}{M_{ph}} \quad (4).$$

In diesen Gln. bedeutet  $n_i$  und  $a_i$  die Anzahl und den Verteilungsquotienten der H-Atome in einem Phenolmolekül, die unter den angegebenen Versuchsbedingungen gegen die des Wassers ausgetauscht worden sind,  $D_a$  und  $D_e$  den Dichteüberschuss des schweren Wassers vor und nach dem Versuch, und  $M_w$  und  $M_{ph}$  die Molzahl des verwendeten schweren Wassers und Phenols. Die Summation in Gl. (3) muss dabei für alle austauschbaren Arten der H-Atome in einem Phenolmolekül ausgeführt werden.

Wenn auf diese Weise das Austauschäquivalent  $na$  bei verschiedener Versuchsdauer  $t$  bestimmt worden ist, lässt sich die mittlere Geschwindigkeitskonstante  $\bar{k}$  für die Austauschreaktion der Kernwasserstoffatome des Phenols, deren Anzahl in einem Molekül offensichtlich drei beträgt, unter Benutzung der folgenden Gln. (5) und (6) graphisch ermitteln:<sup>(3)</sup>

$$-X \log Y = \frac{\bar{k}}{2.303} t \quad (5),$$

$$X = \frac{V}{4.2 M_{ph} + 2.2 M_w} \quad \text{und} \quad Y = \frac{1 - \frac{na - 1.25}{2.7}}{1 + \frac{na - 1.25}{\frac{2M_w}{M_{ph}} + 1.07}} \quad (6).$$

(2) K. H. Geib, *Z. physik. Chem.*, **A180** (1937), 211.

(3) Über die Ableitung dieser Gln. und die graphische Ermittlung von  $\bar{k}$  vgl. M. Koizumi und T. Titani, *dies Bulletin*, **13** (1938), 595.

Das zur Berechnung von  $X$  benötigte Volumen  $V$  der Lösung wird mit Hilfe des direkt gemessenen und in Tabelle 1 wiedergegebenen spezifischen Volumens der Lösung, eventuell durch kleine Inter- bzw. Extrapolation, rechnerisch gefunden.

Tabelle 1. Spezifisches Volumen der Lösung.<sup>(4)</sup>

| Zusammensetzung der Lösung                    | Temp. °C. | spez. Volumen in c.c. |
|-----------------------------------------------|-----------|-----------------------|
| 2 g. Phenol in 1 g. 0.125 N HCl-saures Wasser | 90        | 1.006                 |
|                                               | 100       | 1.015                 |
|                                               | 110       | 1.024                 |
|                                               | 120       | 1.033                 |
| 2 g. Phenol in 1 g. 1 N HCl-saures Wasser     | 90        | 1.000                 |
|                                               | 100       | 1.010                 |
|                                               | 110       | 1.020                 |
|                                               | 120       | 1.030                 |

**Abhängigkeit der Austauschgeschwindigkeit von der H-Ionenkonzentration in Lösung.** Unter Benutzung der oben beschriebenen Methode wird zunächst der Einfluss der HCl-Konzentration der Lösung auf die Austauschgeschwindigkeit untersucht, indem man den Austauschversuch bei einer konstanten Temperatur, nämlich bei 100°C., aber in verschiedenen starken HCl-Lösungen ausführt. Die dabei gewonnenen Versuchsergebnisse sind in Tabelle 2 zusammengestellt. In dieser Tabelle bedeutet HCl (in H<sub>2</sub>O) die Konzentration von HCl im verwendeten schweren Wasser, dagegen HCl (in Lösung) die in dem damit hergestellten Reaktionsgemisch. Dabei wird die letztere durch die Dividierung der ersteren mit der Zahl drei gefunden, weil das Volumen des zum Versuch benutzten und von vornherein durch den Zusatz von HCl angesäuerten schweren Wassers sich dem der damit hergestellten Lösung durchschnittlich wie 1:3 verhält. Die Versuchsnr. in der ersten Vertikalreihe der Tabelle drückt die zeitliche Reihenfolge der einzelnen Versuche aus.

Tabelle 2. Einfluss der HCl-Konzentration auf die Austauschgeschwindigkeit.

| Versuchs-<br>beingung     | Versuchs-<br>nr. | Versuchs-<br>dauer in Min. | $M_w$  | $M_{ph}$ | $D_a - D_e$<br>in $\gamma$ | $D_e$<br>in $\gamma$ | $n\alpha$ |
|---------------------------|------------------|----------------------------|--------|----------|----------------------------|----------------------|-----------|
| HCl (in H <sub>2</sub> O) | 28               | 60                         | 0.0549 | 0.0216   | 1517                       | 2063                 | 3.74      |
| = 1.00 N,                 | 2                | 120                        | 0.0547 | 0.0216   | 1526                       | 2054                 | 3.78      |
| HCl (in Lösung)           | 1                | 300                        | 0.0547 | 0.0222   | 1616                       | 1964                 | 4.05      |
| = 0.333 N.                |                  |                            |        |          |                            |                      |           |
| HCl (in H <sub>2</sub> O) | 32               | 40                         | 0.0545 | 0.0214   | 1119                       | 2655                 | 2.14      |
| = 0.666 N,                | 31               | 80                         | 0.0546 | 0.0216   | 1252                       | 2522                 | 2.51      |
| HCl (in Lösung)           | 39               | 85                         | 0.0545 | 0.0216   | 1482                       | 2292                 | 3.27      |
| = 0.222 N.                |                  |                            |        |          |                            |                      |           |

(4) Bei dieser Bestimmung des spezifischen Volumens der Lösung wurde gewöhnliches Wasser verwendet. Da aber das zum Hauptversuch verwendete schwere Wasser sehr verdünnt war, darf man das so bestimmte spezifische Volumen der Lösung in gewöhnlichem Wasser ohne weiteres zur Berechnung des Volumens der Lösung beim Hauptversuch benutzen.



Tabelle 2.—(Fortsetzung)

| Versuchs-<br>bedingung                                                     | Versuchs-<br>nr. | Versuchs-<br>dauer in Min. | $M_w$  | $M_{ph}$ | $D_a - D_e$<br>in $\gamma$ | $D_e$<br>in $\gamma$ | $n\alpha$ |
|----------------------------------------------------------------------------|------------------|----------------------------|--------|----------|----------------------------|----------------------|-----------|
| HCl (in H <sub>2</sub> O)<br>= 0.500 N,<br>HCl (in Lösung)<br>= 0.167 N.   | 7                | 60                         | 0.0543 | 0.0224   | 1274                       | 2890                 | 2.14      |
|                                                                            | 4                | 120                        | 0.0545 | 0.0218   | 1527                       | 2637                 | 2.90      |
|                                                                            | 6                | 200                        | 0.0541 | 0.0217   | 1678                       | 2486                 | 3.36      |
|                                                                            | 3                | 330                        | 0.0540 | 0.0219   | 1774                       | 2390                 | 3.76      |
|                                                                            | 5                | 900                        | 0.0542 | 0.0216   | 1832                       | 2332                 | 3.96      |
| HCl (in H <sub>2</sub> O)<br>= 0.353 N,<br>HCl (in Lösung)<br>= 0.118 N.   | 36               | 60                         | 0.0562 | 0.0216   | 1015                       | 2921                 | 1.81      |
|                                                                            | 37               | 120                        | 0.0561 | 0.0216   | 1215                       | 2721                 | 2.32      |
|                                                                            | 33               | 180                        | 0.0561 | 0.0218   | 1358                       | 2578                 | 2.83      |
| HCl (in H <sub>2</sub> O)<br>= 0.250 N,<br>HCl (in Lösung)<br>= 0.083 N.   | 8                | 120                        | 0.0553 | 0.0215   | 1278                       | 3068                 | 1.93      |
|                                                                            | 29               | 180                        | 0.0555 | 0.0216   | 1361                       | 2985                 | 2.34      |
|                                                                            | 10               | 240                        | 0.0555 | 0.0216   | 1511                       | 2835                 | 2.74      |
|                                                                            | 9                | 360                        | 0.0554 | 0.0216   | 1622                       | 2724                 | 3.06      |
| HCl (in H <sub>2</sub> O)<br>= 0.125 N,<br>HCl (in Lösung)<br>= 0.042 N.   | 15               | 0                          | 0.0558 | 0.0216   | 793                        | 3469                 | 1.22      |
|                                                                            | 11               | 240                        | 0.0556 | 0.0216   | 1181                       | 3081                 | 1.95      |
|                                                                            | 13               | 480                        | 0.0556 | 0.0216   | 1357                       | 2905                 | 2.40      |
|                                                                            | 12               | 900                        | 0.0554 | 0.0214   | 1625                       | 2637                 | 3.20      |
| HCl (in H <sub>2</sub> O)<br>= 0.0706 N,<br>HCl (in Lösung)<br>= 0.0235 N. | 38               | 910                        | 0.0557 | 0.0216   | 1292                       | 2754                 | 2.42      |
|                                                                            | 29               | 1800                       | 0.0556 | 0.0215   | 1533                       | 2513                 | 3.15      |
|                                                                            | 35               | 2700                       | 0.0555 | 0.0216   | 1645                       | 2401                 | 3.30      |
| HCl (in H <sub>2</sub> O)<br>= 0.0235 N,<br>HCl (in Lösung)<br>= 0.0078 N. | 41               | 2430                       | 0.0558 | 0.0218   | 1332                       | 3181                 | 2.14      |
|                                                                            | 40               | 3660                       | 0.0558 | 0.0218   | 1451                       | 3062                 | 2.42      |

Tabelle 3. Austauschgeschwindigkeitskonstante  $\bar{k}$   
bei verschiedener HCl-Konzentration  $c$  in Lösung.

| Konzentration $c$<br>von HCl in Lösung<br>in N. | $\log c$ | Geschwindigkeits-<br>konstante $\bar{k}/2.303$<br>(Mol/Liter) <sup>-1</sup> (Stunde) <sup>-1</sup> | $\log (\bar{k}/2.303)$ |
|-------------------------------------------------|----------|----------------------------------------------------------------------------------------------------|------------------------|
| 0.222                                           | -0.654   | 0.00525~0.000550                                                                                   | -2.270                 |
| 0.167                                           | -0.777   | 0.00362                                                                                            | -2.441                 |
| 0.118                                           | -0.928   | 0.00215~0.00220                                                                                    | -2.661                 |
| 0.083                                           | -1.081   | 0.00145~0.00150                                                                                    | -2.839                 |
| 0.042                                           | -1.377   | 0.00060                                                                                            | -3.222                 |
| 0.0235                                          | -1.629   | 0.000313                                                                                           | -3.505                 |
| 0.0078                                          | -2.108   | 0.000078                                                                                           | -4.108                 |

Die Austauschgeschwindigkeitskonstante  $\bar{k}$ , die unter Benutzung der oben in Tabelle 2 angegebenen Daten graphisch ermittelt wurde, ist zusammen mit der entsprechenden HCl-Konzentration in Lösung in Tabelle 3 wiedergegeben. Dabei werden die Daten bei 0.333 N (d.h. bei der konzentriertesten Lösung, die wir benutzten) nicht aufgenommen, weil in diesem Fall die Austauschgeschwindigkeit zu gross war, um die Geschwindigkeitskonstante genau zu bestimmen. Man muss ferner darauf achten, dass die Zeiteinheit für  $\bar{k}$  in Tabelle 3 nicht Minute wie in Tabelle 2 sondern Stunde ist.

Die in Tabelle 3 angegebenen Ergebnisse können wir nun durch die Formel gut wiedergeben:

$$\log(\bar{k}/2.303) = 1.26 \log c - 1.48 \quad (7)$$

wie man dies aus der nebenstehenden Abb. 1 ersieht, wo  $\log(\bar{k}/2.303)$  gegen  $\log c$  eingetragen ist.

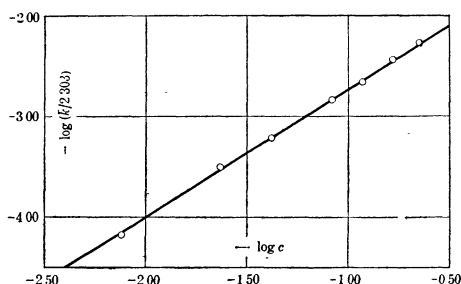


Abb. 1. Abhängigkeit der Geschwindigkeitskonstante  $\bar{k}$  von der HCl-Konzentration  $c$  in Lösung.

**Abhängigkeit der Austauschgeschwindigkeit von der Temperatur. Aktivierungsenergie.** Es wird oben gefunden, dass die Geschwindigkeitskonstante  $\bar{k}$  nicht, wie bei der gewöhnlichen säurebasekatalytischen Reaktion zu erwarten ist, mit der ersten Potenz der H-Ionenkonzentration sondern mit deren 1.26-Potenz zunimmt. Die Ursache für diese Abnormalität ist entweder in der Abhängigkeit des Stossfaktors  $Z$  bzw. der Aktivierungsenergie  $A$  der H-Ionenkonzentration zu suchen:

$$\bar{k} = Z \cdot e^{-\frac{A}{RT}} \quad (8).$$

Um zwischen diesen beiden Möglichkeiten zu einem Entscheid zu kommen, wird nun die Geschwindigkeitskonstante  $\bar{k}$  in zwei verschieden starken HCl-Lösungen resp. bei verschiedenen Temperaturen bestimmt und daraus die Aktivierungsenergie für die Reaktion in beiden Arten der Lösung ermittelt. Die dabei gewonnenen Versuchsergebnisse sind in Tabelle 4 und 5 wiedergegeben, wo die Einheit für  $\bar{k}$  ebenso wie in Tabelle 3 (Mol/Liter)<sup>-1</sup> (Stunde)<sup>-1</sup> ist.

Diese beiden in Tabelle 4 und 5 angegebenen Versuchsergebnisse sind auch in Abb. 2 graphisch wiedergegeben, wo  $\log(\bar{k}/2.303)$  gegen das Reziproke der absoluten Temperatur d.h.  $1/T$  dargestellt ist. Die beiden Kurven (I) und (II) in Abb. 2 können aber durch die Formeln gut wiedergegeben werden:

$$(I) \quad \log(\bar{k}/2.303) = (12.8 \pm 0.4) - \frac{27,400 \pm 0.600}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Std.})^{-1},$$

$$(II) \quad \log(\bar{k}/2.303) = (11.85 \pm 0.2) - \frac{27,200 \pm 0.300}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Std.})^{-1}. \quad (9).$$

Tabelle 4. Abhängigkeit der Geschwindigkeitskonstante  $\bar{k}$   
von der Temperatur in 0.042 N HCl-Lösung.

HCl (in H<sub>2</sub>O) = 0.125 N,

HCl (in Lösung) = 0.042 N

| Versuchs-<br>nr. | Versuchs-<br>dauer in Min. | $M_w$  | $M_{ph}$ | $D_a - D_e$<br>in $\gamma$ | $D_e$<br>in $\gamma$ | $n\alpha$ | $\bar{k}/2 \cdot 303$ | Versuchs-<br>temp.<br>°C. |
|------------------|----------------------------|--------|----------|----------------------------|----------------------|-----------|-----------------------|---------------------------|
| 21               | 480                        | 0.0558 | 0.0215   | 1053                       | 3209                 | 1.71      | 0.000208              | 90.5                      |
| 23               | 900                        | 0.0558 | 0.0215   | 1243                       | 3019                 | 2.12      |                       |                           |
| 26               | 1560                       | 0.0558 | 0.0215   | 1415                       | 2847                 | 2.57      |                       |                           |
| 11               | 240                        | 0.0556 | 0.0216   | 1181                       | 3081                 | 1.95      | 0.000600              | 100.0                     |
| 13               | 480                        | 0.0556 | 0.0216   | 1357                       | 2905                 | 2.40      |                       |                           |
| 27               | 690                        | 0.0555 | 0.0216   | 1496                       | 2766                 | 2.78      |                       |                           |
| 12               | 900                        | 0.0554 | 0.0214   | 1265                       | 2637                 | 3.20      |                       |                           |
| 14               | 120                        | 0.0555 | 0.0216   | 1243                       | 3019                 | 2.12      | 0.00173               | 110.5                     |
| 17               | 240                        | 0.0556 | 0.0216   | 1493                       | 2769                 | 2.78      |                       |                           |
| 16               | 360                        | 0.0558 | 0.0216   | 1655                       | 2607                 | 3.28      |                       |                           |
| 19               | 100                        | 0.0559 | 0.0212   | 1478                       | 2784                 | 2.80      | 0.00400               | 120.0                     |
| 25               | 170                        | 0.0554 | 0.0216   | 1670                       | 2592                 | 3.31      |                       |                           |

Tabelle 5. Abhängigkeit der Geschwindigkeitskonstante  $\bar{k}$   
von der Temperatur in 0.0078 N HCl-Lösung.

HCl (in H<sub>2</sub>O) = 0.235 N,

HCl (in Lösung) = 0.0078 N

| Versuchs-<br>nr. | Versuchs-<br>dauer in Min. | $M_w$  | $M_{ph}$ | $D_a - D_e$<br>in $\gamma$ | $D_e$<br>in $\gamma$ | $n\alpha$ | $\bar{k}/2 \cdot 303$ | Versuchs-<br>temp.<br>°C. |
|------------------|----------------------------|--------|----------|----------------------------|----------------------|-----------|-----------------------|---------------------------|
| 41               | 2430                       | 0.0558 | 0.0218   | 1332                       | 3181                 | 2.14      | 0.000077              | 100.0                     |
| 40               | 3660                       | 0.0558 | 0.0218   | 1451                       | 3062                 | 2.42      | ~0.000079             |                           |
| 43               | 1200                       | 0.0560 | 0.0215   | 1417                       | 3096                 | 2.39      | 0.000238<br>~0.000240 | 111.0                     |
| 42               | 1800                       | 0.0550 | 0.0216   | 1623                       | 2890                 | 2.87      |                       |                           |
| 44               | 2400                       | 0.0550 | 0.0215   | 1669                       | 2844                 | 3.05      |                       |                           |
| 46               | 936                        | 0.0560 | 0.0216   | 1693                       | 2820                 | 3.12      | 0.000565<br>~0.000575 | 120.0                     |
| 45               | 1296                       | 0.0560 | 0.0215   | 1774                       | 2739                 | 3.38      |                       |                           |

Oder wenn man die Zeiteinheit von Stunde in Sekunde umrechnet und ferner den Koeffizient 2.303 im Nenner der Geschwindigkeitskonstante wegnimmt, erhält man die Formeln:

$$(I) \quad \log \bar{k}(0.042 \text{ N}) = (9.6 \pm 0.4) - \frac{27,400 \pm 0.600}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1},$$

$$(II) \log \bar{k}(0.0078N) = (8.7 \pm 0.2) - \frac{27,200 \pm 0.300}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1}, \quad (10).$$

Aus diesen Versuchsergebnissen ersieht man, dass die Aktivierungsenergie in den beiden Reihen der Versuche miteinander befriedigend gut übereinstimmt, d.h. sie von der H-Ionenkonzentration fast unabhängig ist. Dagegen nimmt der Stossfaktor mit der Säurekonzentration in Lösung zu. Dies kommt offensichtlich von der katalytischen Wirkung der H-Ionen her. Bei der Ermittlung der Geschwindigkeitskonstante  $\bar{k}$  wird stillschweigend angenommen, dass die Reaktion als die bimolekulare Reaktion zwischen den neutralen Phenolmolekülen und schweren Wasser gemäss der stöchiometrischen Gl. (11) verläuft:

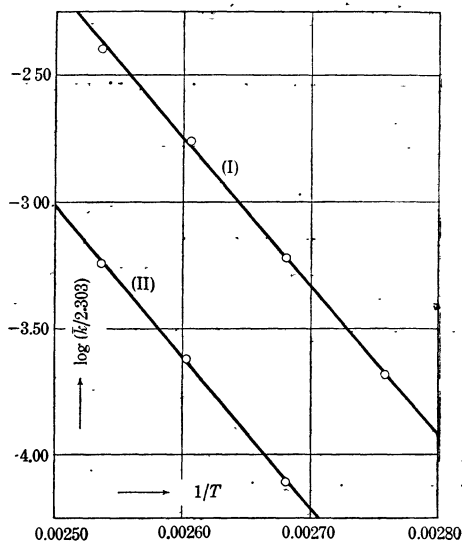
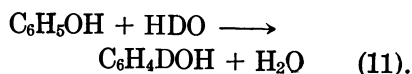


Abb. 2. Abhängigkeit der Geschwindigkeitskonstante  $k$  von der absoluten Temperatur  $T$ .

Aber die wirkliche Reaktion muss höchstwahrscheinlich zwischen den neutralen undissoziierten Phenolmolekülen und Hydroxoniumionen (bzw. Deuteroxoniumionen) nach dem Schema verlaufen:



Nimmt man deshalb an, dass die Geschwindigkeit dieser grundlegenden Reaktion (12) einfacherweise mit der ersten Potenz der Konzentration der einzelnen Reaktionsteilnehmer zunimmt, dann besteht zwischen der Geschwindigkeitskonstante  $\bar{k}$  für die stöchiometrische Reaktion (11) und der  $\bar{k}_0$  für die grundlegende Reaktion (12) die Beziehung:

$$\bar{k}_0 = \bar{k} \frac{2}{3} \frac{[[\text{C}_6\text{H}_5\text{OH}]] [[\text{H}_2\text{O}]]}{[\text{C}_6\text{H}_5\text{OH}] [\text{H}_3\text{O}^+]} \quad (13).$$

In dieser Gl. (13) bedeutet  $[[\text{C}_6\text{H}_5\text{OH}]]$  und  $[[\text{H}_2\text{O}]]$  resp. die gesamte (analytische) Konzentration von Phenol und Wasser, dagegen  $[\text{C}_6\text{H}_5\text{OH}]$  und  $[\text{H}_3\text{O}^+]$  die wirkliche Konzentration von undissoziierten Phenolmolekülen und Hydroxoniumionen in Lösung. Für den praktischen Zweck können wir aber offensichtlich  $[\text{C}_6\text{H}_5\text{OH}] = [[\text{C}_6\text{H}_5\text{OH}]]$  und  $[\text{H}_3\text{O}^+] = c$  (vgl. oben) setzen. Wenn man auf diese Weise mit Hilfe der Beziehung (13) die oben angegebenen Formeln (10) für die scheinbare Geschwindigkeitskonstante  $k$  in die wahre Geschwindigkeitskonstante  $\bar{k}_0$  umrechnet, dann ergeben sich die Formeln:

$$(I) \log \bar{k}_0(0.042N) = (12.1 \pm 0.4) - \frac{27,400 \pm 0.600}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1},$$

$$(II) \log \bar{k}_0(0.0078N) = (11.9 \pm 0.2) - \frac{27,200 \pm 0.300}{4.574 T} \quad ,, \quad ,, \quad (14).$$

Der Stossfaktor in diesen beiden Formeln hängt aber, wie beide Formeln zeigen, noch von der H-Ionenkonzentration ab und zwar nimmt er mit der letzteren allmählich zu. Die Ursache für diese Diskrepanz ist in der bei der Ableitung von Gln. (14) angenommenen einfachen Voraussetzung zu suchen, dass die Austauschgeschwindigkeit mit der ersten Potenz der Reaktionsteilnehmer, insbesondere mit der H-Ionen, zunimmt. Diese Voraussetzung trifft aber in Wirklichkeit nicht zu. Wir haben nämlich bei dem oben angegebenen Vorversuche gefunden, dass die wirklich Austauschgeschwindigkeit nicht mit der ersten Potenz der H-Ionenkonzentration sondern mit deren 1.26-Potenz zunimmt, wobei die vorliegende Austauschreaktion betreffend der H-Ionen als die Reaktion von der 1.26-Ordnung aufzufassen ist. Wenn wir deshalb bei der Umrechnung der Formeln (10) für  $\bar{k}$  in die Formeln für die wahre Geschwindigkeitskonstante  $\bar{k}_0$  dieser Tatsache Rechnung tragen und statt der Beziehung (13) die folgende Beziehung (15) benutzen, dann ergeben sich aus den beiden Formeln (12) die Formeln (16):

$$\bar{k}_0 = \bar{k} \frac{2}{3} \frac{[[C_6H_5OH]] [[H_2O]]}{[C_6H_5OH] [H_3O^+]^{1.26}} \quad (15),$$

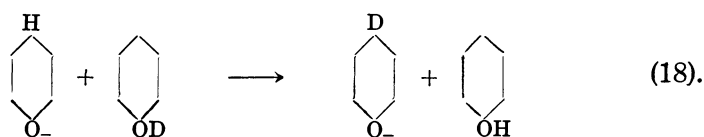
$$(I) \log \bar{k}_0(0.042N) = (12.5 \pm 0.4) - \frac{27,400 \pm 0.600}{4.574 T} \quad (\text{Mol/Liter})^{-1}(\text{Std.})^{-1},$$

$$(II) \log \bar{k}_0(0.0078N) = (12.5 \pm 0.2) - \frac{27,200 \pm 0.200}{4.574 T} \quad ,, \quad ,, \quad (16).$$

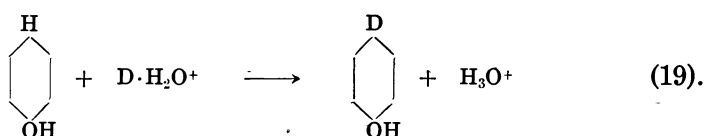
Der Stossfaktor in beiden Formeln (I) und (II) stimmt nun miteinander sehr gut überein. Man kann deshalb diese beiden Formeln (I) und (II) in einer einzigen von der H-Ionenkonzentration unabhängigen Formel vereinigen, die folgendermassen lautet:

$$\bar{k}_0 = 10^{12.5 \pm 0.3} \exp\left(-\frac{27,300 \pm 0.400}{RT}\right) \quad (17).$$

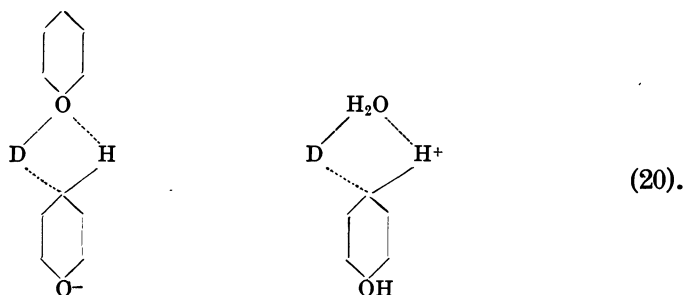
**Diskussion.** Die in dem vorliegenden Versuche gefundene Aktivierungsenergie für die Reaktion in saurer Lösung, die durchschnittlich 27.3 Kcal. beträgt, ist untrüglich grösser als die in alkalischer Lösung. Diese letztere beträgt nämlich, wie aus vorhergehendem Versuche (I. Mittl.) ersichtlich, 24.8 Kcal. Dieser Unterschied der Aktivierungsenergie ist aber offensichtlich auf die Verschiedenheit des Aktivierungsprozesses der beiden Arten der Reaktion zurückzuführen. Bei der Reaktion in alkalischer Lösung wird angenommen, dass der geschwindigkeitsbestimmende Prozess sich in der Reaktion zwischen dissoziierten Phenolationen und undissoziierten Phenolmolekülen befindet:



Zu dieser Annahme kommt man durch die Experimentaltatsache, dass die Austauschgeschwindigkeit mit der Konzentration von Alkali und Phenol, und zwar mit deren ersten Potenz, zunimmt.<sup>(5)</sup> Dagegen kann man über den Mechanismus der vorliegenden Reaktion in saurer Lösung nicht so ohne weiteres einen Schluss ziehen, weil in diesem Fall die Reaktionsgeschwindigkeit nicht einfach mit der ersten Potenz sondern mit der 1.26-Potenz der H-Ionenkonzentration wächst. Aber die naheliegendste Annahme ist, wie schon oben erwähnt, dass die Reaktion zwischen undissoziierten Phenolmolekülen und Hydroxoniumionen in folgender Weise verläuft:



Wenn dies wirklich der Fall ist, dann muss der zwischenbildende aktivierte Komplex für beide Reaktionen (18) und (19) die folgende Form I bzw. II besitzen.



I (in alkalischer Lösung).      II (in saurer Lösung).

Der Versuch zeigt, wie bereits oben erwähnt, dass die Aktivierungsenergie für die Reaktion in alkalischer Lösung geringer als die in saurer Lösung ist. Dies bedeutet, dass zur Bildung des aktivierten Komplexes I in alkalischer Lösung geringere Energie erforderlich ist als für den Komplex II in saurer Lösung. Man kann deshalb den Unterschied der Aktivierungsenergie für beide Arten der Reaktion durch die wahrscheinliche Annahme erklären, dass die Energie, die zur Bildung des Komplexes I in alkalischer Lösung erforderlich ist, hauptsächlich dazu verbraucht wird, um die Valenzstruktur des zu deuterierenden Phenolionenrestes zu verändern, während die zur Bildung des Komplexes II in saurer Lösung erforderliche Energie hauptsächlich zur Valenzänderung des ebenfalls

(5) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 631 (vgl. Tabelle 4).

zu deuterierenden neutralen Phenolmolekülrestes verbraucht wird. Da aber der Phenolionenrest überschüssige (negative) Ladung in sich selbst trägt, liegt die Annahme nahe, dass die Valenzänderung in demselben geringere Energie in Anspruch nehmen dürfte als die im neutralen Phenolmolekülrest in saurer Lösung.

Es wird weiter gefunden, dass der Stossfaktor für die Reaktion in saurer Lösung ( $= 10^{12.5}$ ) deutlich grösser ist als der in alkalischer Lösung. Dieser letztere ergibt sich nämlich aus dem letzten Versuch  $10^{10.8}$  (vgl. Gl. (2)). Diese Vergrösserung des Stossfaktors in saurer Lösung als in alkalischer darf aber wohl dadurch erklärt werden, dass die Reaktions- bzw. Stossteilnehmer in beiden Arten der Reaktion verschieden sind. Bei der Reaktion in alkalischer Lösung wirkt nämlich das neutrale undissoziierte Phenolmolekül, dagegen in saurer Lösung das Hydroxoniumion (bzw. Deuterixoniumion) als das Deuterierungsmittel und zwar derart, dass dies sein an O gebundenes D-Atom gegen das Kernwasserstoffatom des Phenolation (in alkalischer Lösung) bzw. des neutralen Phenolmoleküls (in saurer Lösung) austauscht. Aber diese Art der Austauschreaktion, wie im allgemeinen angenommen wird (elektrophile Substitutionsreaktion!), findet vorzüglich an solch einer Stelle des Benzolkerns des Phenolations bzw. Phenolmoleküls statt, wo die Elektronen mehr oder weniger angehäuft sind. Deshalb liegt die Annahme nahe, dass das positiv geladene Oxoniumion mit dem Phenolmolekül an seiner reaktionsfähigen, d.h. mehr oder weniger negativ geladenen, Stelle häufiger zusammenstösst als dies das neutrale Phenolmolekül mit dem Phenolation an derselben reaktionsfähigen Stelle des letzteren tut. Auf diese Weise kann man vielleicht die Vergrösserung des Stossfaktors bei der Reaktion in saurer Lösung erklären.

Zum Schluss möchte ich Herrn Prof. T. Titani für seine freundlichen Ratschläge und Hilfe bei der Ausführung der vorliegenden Arbeit meinen wärmsten Dank aussprechen. Der Nippon Gakujutsu-Shinkokai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkokai (der Hattori-Stiftung) bin ich auch für ihre finanzielle Unterstützung zu grösstem Dank verpflichtet.

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und chemische Forschung  
und*

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## Synthese der kondensierten Selenophene durch Einwirkung von Acetylen auf Selen.

Von Sumio UMEZAWA.

(Eingegangen am 24. August 1939.)

Unter den mehrkernigen kondensierten Selenophen-Systemen ist nur das Selenonaphthen, d.h. Benzoselenophen bekannt, über das zuerst von Mazza und Solazzo<sup>(1)</sup> in ihren Untersuchungen über die Einwirkung von Acetylen auf Selen berichtet wurde und dessen Darstellung dann kürzlich von Komppa und Nyman<sup>(2)</sup> durch Reduktion des 3-Oxyselenonaphthens sicher gestellt worden ist. Da vor einiger Zeit Challenger und Harrison<sup>(3)</sup> durch die Einwirkung von Acetylen auf Schwefeldampf die isomeren Thiophthene erhalten haben, und da weiterhin bei der Reaktion zwischen Acetylen und Selen Briscoe und seine Mitarbeiter<sup>(4)</sup> eine himmelblaue Flüssigkeit vom Siedep. 240–250° mit etwa 20 Prozent Selen abgetrennt haben, die sie als das unreine Selenophthen vermuteten, ist es von Interesse, den hochsiedenden Anteil des Reaktionsprodukts, das bei der Einwirkung von Acetylen auf Selen in einem elektrischen Ofen gewonnen wurde, auf seine Bestandteile hin zu untersuchen.

Wenn man unter bestimmten Bedingungen<sup>(5)</sup> gereinigtes Acetylen auf Selen einwirken liess, so wurde ein unangenehm riechendes Öl vom spez. Gew. 1.47 erhalten, welches 57 prozentiges Selenophen enthielt. Liess man den höhersiedenden Anteil, der durch Destillation unter atmosphärischem Druck vom Selenophen so vollständig wie möglich abgetrennt wurde, von einigen Tagen bis zu einen Monat lang in der Dunkelkammer stehen, so kristallisierten zahlreiche grosse Nadeln nach und nach heraus, welche 6.7 Prozenten des Ausgangsöls entsprachen. Nach Umkrystallisierung aus Alkohol zeigten sie den Schmelzp. 123–124.5° und ergaben schöne Indophenin-Reaktion beim Zusammenbringen mit Isatin und konzentrierter Schwefelsäure. Aus Alkohol kamen sie in Rautenform heraus. (Abb. 2) Die Ergebnisse ihrer Molekulargewichtsbestimmungen und Analysen lassen mit aller Deutlichkeit das Selenophthen  $C_6H_4Se_2$  erkennen. Wie die meisten kernkondensierten Verbindungen wird das Selenophthen leicht in sein Pikrat,  $C_6H_4Se_2 \cdot C_6H_2(NO_2)_3OH$ , vom Schmelzp. 163–5° übergeführt, das beim Behandeln mit ziemlich konzentriertem wässrigem Ammoniak leicht zerlegt wird. Beim Behandeln des Selenophthens mit überschüssigem Brom in einer Schwefelkohlenstofflösung bei tiefer Temperatur kann man die flüchtige Entstehung des schönen gelben krystallinischen Bromadditionsprodukts,

(1) F. P. Mazza und L. Solazzo, *Chem. Zentr.*, **100** (1929), I, 1454; *Rend. Accad. Sci. (Napoli)*, Serie 3a, **33** (1927), 236.

(2) G. Komppa und G. A. Nyman, *J. prak. Chem.*, **139** (1934), 229.

(3) F. Challenger und J. B. Harrison, *J. Inst. Petroleum Technologists*, **21** (1935), 135; *Chem. Zentr.*, **1935**, II, 1548.

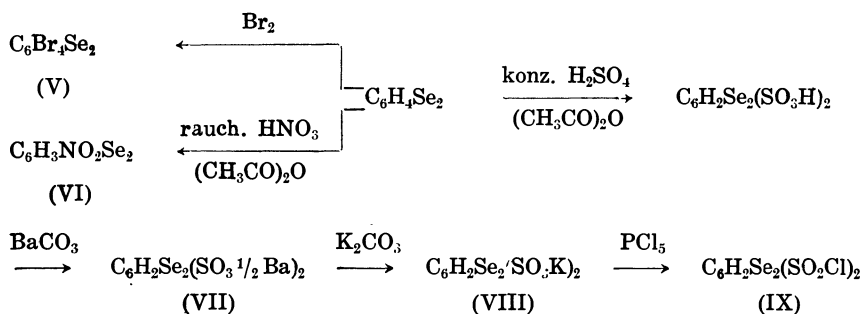
(4) H. V. A. Briscoe, J. B. Peel und P. L. Robinson, *J. Chem. Soc.*, **1928**, 2628.

(5) H. Suginome und S. Umezawa, *dies Bulletin*, **11** (1936), 162.

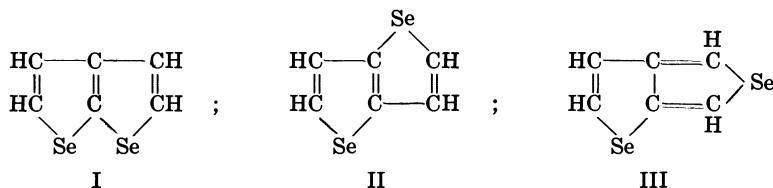


wie bei derselben Behandlung des Selenophens<sup>(6)</sup>, bemerken und kann schliesslich das Tetrabromselenophthen  $C_6Br_4Se_2$  (V) vom Schmelz.  $247.5^\circ$  (korr.) erhalten.

Um die Ähnlichkeit der chemischen Eigenschaften mit denen des Selenophens weiter klar zu stellen, versuchte ich das Selenophthen zu nitrieren und zu sulfonieren. Auf Selenophthen wirkt konzentrierte oder rauchende Salpetersäure mit grosser Heftigkeit oxydierend wie beim Selenophen<sup>(7)</sup>, doch gelang die direkte Nitrierung bei der Verdünnung mit Essigsäureanhydrid bei tiefer Temperatur und mit berechneter Menge der rauchenden Salpetersäure wurde ein Mononitroselenophthen (VI),  $C_6H_3NO_2Se_2$ , vom Schmelzp.  $108-109.5^\circ$  gewonnen, allerdings in nur mässiger Ausbeute, welches mit Methanol und Kalilauge keine Farbenreaktion ergibt. Auch wirkt konzentrierte Schwefelsäure zersetzend auf Selenophthen. Wenn man aber das Selenophthen in Essigsäureanhydrid mit berechneter Menge konzentrierter Schwefelsäure behandelt, so bildet sich eine Selenophthendisulfonsäure, welche in Bariumsalz (VII), Kaliumsalz (VIII) und in Sulfochlorid (IX) vom Schmelzp.  $234-6^\circ$  übergeführt wurde, wie im folgenden dargestellt wird.



Auf Grund der oben beschriebenen Tatsachen wird einwandfrei festgestellt, dass diese Verbindung vom Schmelzp.  $123-124.5^\circ$ , die aus dem Reaktionsprodukt zwischen Acetylen und Selen isoliert wurde, eine dem Thiophthen entsprechende Selenverbindung, d.h. ein Selenophthen ist. Handelt es sich um die Struktur des Selenophthens, so sind jedoch die Formeln I, II und III in Betracht zu ziehen.



Ich konzentrierte mein Interesse besonders darauf, aus dem höher-siedenden Anteil, der von Selenophen und einem festen Selenophthen abgetrennt wurde, noch weiter die Strukturisomeren des Selenophthens zu isolieren. Wie zu erwarten ist, kann man in der Tat noch zwei Selenophthene gewinnen.

(6) H. Sugimoto und S. Umezawa, a. a. O., S. 164.

(7) S. Umezawa, dies Bulletin, 11 (1936), 775.

Der übrigbleibende, unangenehm riechende Teer (110 g.) wurde der fraktionierten Destillation unterworfen, wobei die folgenden schwachgelb gefärbten Fraktionen erhalten wurden:

Tabelle 1.

|   | Sdp. (bei 14 mm.) | Gewicht | Se-Gehalt in % |
|---|-------------------|---------|----------------|
| 1 | 93–100°           | 30 g.   | 61.6           |
| 2 | 100–113°          | 30 g.   | 63.2           |
| 3 | 123–130°          | 9 g.    | 42.2           |

Hier schien die erste und zweite Fraktion hauptsächlich aus Selenophthen und wenig Selenonaphthen und Naphthalin zu bestehen. Wie schon bekannt, bilden Selenonaphthen und Naphthalin gut krystallisierende Pikrate mit Pikrinsäure, während das flüssige Selenophthen kein beständiges Pikrat ergibt, obgleich in alkoholischer Lösung eine Vertiefung der Lösungsfarbe stattfindet. Destilliert man die zweite Fraktion im Vakuum nach Beseitigung des Selenonaphthens und Naphthalins durch Pikratbildung, so ging fast das Ganze bei 90°–93° unter 14 mm. über.

Dieses fast farblose, starklichtbrechende Öl ergibt die Indophenin-Reaktion in ausgezeichneter Weise und verändert sich beim Schütteln mit wässriger Quecksilberacetatlösung in eine schwachgelbe amorphe Substanz, die wahrscheinlich ein Selenophthen-quecksilberacetat ist. Auch scheidet es sofort beim Schütteln mit alkoholischer wässriger Sublimatlösung einen für ein Selenophthen-quecksilberchlorid gehaltenen krystallinischen Körper heraus. Die Ergebnisse der Molekulargewichtsbestimmung und der Analyse dieses Öls lassen mit aller Deutlichkeit auch ein Selenophthen  $C_6H_4Se_2$  erkennen.

Dafür sprechen neben dem chemischen Verhalten besonders auch die Ergebnisse der optischen Untersuchung. Für das Selenophthen berechnet sich aus den im experimentellen Teil beschriebenen Konstanten unter Anwendung der Lorenz-Lorentzschen Formel die Molekularrefraktion für Natriumlicht,  $MR_D$ , zu 44.55. Für die Formel  $C_6H_4Se_2$  des Selenophthens berechnet sich  $MR_D$  zu 45.33. Bei dieser Berechnung ist die Differenz zwischen der aus den Konstanten von Morgan und Burstall<sup>(8)</sup> abgeleiteten  $MR_D$  des Tetrahydroselenophens und dem Wert für  $C_4H_8$  als wahrscheinlichste Atomrefraktion des Selen gebraucht. Da es schon von v. Auwers,<sup>(9)</sup> Brühl und anderen einwandfrei klar gestellt worden ist, dass sich bei den heterocyclischen Verbindungen Furan, Thiophen und Pyrrol eine Depression der Molekularrefraktion findet, könnte man die hier gefundene Depression der Molekularrefraktion ( $E\Sigma_D = -0.33$ ) der besonderen Konstitution des Selenophthens zur Last legen. In diesem Selenophthen auch würde der Selenophthenkern seine spektrochemische

(8) G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, **1929**, 1098.

(9) Zusammenstellung bei K. v. Auwers, *Ann.*, **408** (1915), 257.

Eigenart in ausgesprochener Weise geltend machen, wie v. Auwers<sup>(10)</sup> beim Cumaron und Thionaphthen klar gefunden hat.

Weiterhin konnte man noch das andere Selenophthen krystallinisch erhalten, welches sich in seinen Eigenschaften dem zuerst krystallinisch gewonnenen Selenophthen bzw. dem Thiophthen als nahe stehend ergeben hat. Aus später beschriebenen Gründen schlage ich hier für dieses die Bezeichnung *trans*-Selenophthen vor. Die Isolierung des *trans*-Selenophthens aus dem Rückstand, welchen die Gewinnung von Selenophen und Selenophthen vom Schmelzp. 123–124.5° zurückliess, gelingt wie folgt. Wenn man den schwach gefärbten Rückstand, der vorher mit Wasserdampf destilliert wurde, der fraktionierten Vakuumdestillation unterwirft, so geht, wie oben erwähnt, ein Hauptanteil zwischen ungefähr 93°–100° unter 14 mm. über (siehe Tabelle 1), der natürlich eine grosse Menge von flüssigem Selenophthen enthält, das bei etwas höherer Temperatur überzudestillieren scheint. Die Fraktion wurde deshalb über Pikrat gereinigt, das der fraktionierten Krystallisation unterworfen wurde, wobei ein grosser Anteil konstant bei 155.5–156.5° (korr.) schmolz. Ich glaubte anfangs Selenonaphthen-pikrat<sup>(2)</sup> in Händen zu haben, der Mischschmelzpunkt mit diesem vom Schmelzp. 156–7° (korr.) zeigte aber eine auffallende Depression. Die Zerlegung des Pikrats mit Ammoniak ergab farblose Krystalle vom Schmelzpunkt 51–51.5°. Deren Analyse und Molekulargewichtsbestimmung stimmten gut für ein Selenophthen. Merkwürdig ist es hier, dass das *trans*-Selenophthen einen dem Selenonaphthen, über dessen Gewinnung aus der dritten Fraktion später beschrieben wird, überraschend nahe liegenden Schmelzpunkt zeigt.

Was Krystallformen des *trans*-Selenophthens und des bei 123–124.5° schmelzenden Selenophthens anbelangt, so wurde das erstere aus absolutem Alkohol in zwei Spitzen auslaufende Nadeln (Abb. 1), das letztere aus demselben Lösungsmitteln in Rauten (Abb. 2) erhalten.

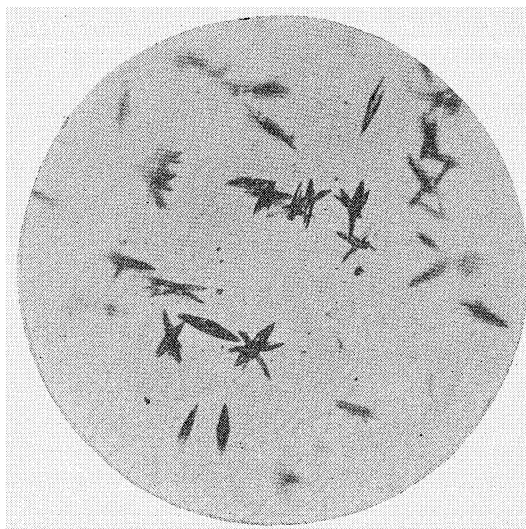


Abb. 1. *trans*-Selenophthen.  
Vergrösserung 50-fach.

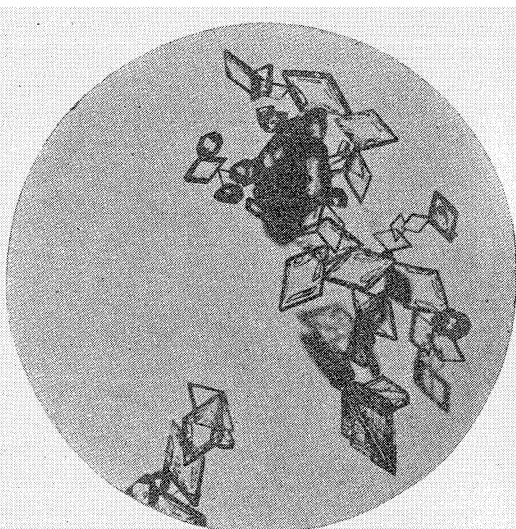


Abb. 2. Iso-Selenophthen vom Schmp.  
123–124.5°. Vergrösserung 100-fach.

(10) K. v. Auwers, a. a. O., S. 263.

Um solche strukturisomere Zusammenhänge der Selenophthene klarer zu stellen, wurden die letzteren jeder für sich im Schwefelkohlenstoff erschöpfend bromiert, wobei drei Tetrabromselenophthene abgeleitet wurden. Ihre Schmelzpunkte sind zusammen mit den Pikraten in Tabelle 2 zusammengestellt.

Tabelle 2.

| Selenophthene                              | Schmp. der Pikrate | Schmp. der Tetrabromselenophthene |
|--------------------------------------------|--------------------|-----------------------------------|
| Selenophthen vom Schmp. 123-124.5°         | 163-165°           | V. 246-247.5° (korr.)             |
| Selenophthen vom Sdp. 90-93°/14 mm.        | —                  | X. 271-272° (korr.)               |
| <i>trans</i> -Selenophthen Schmp. 51-51.5° | 154-155.5°         | XI. 252.5-253° (korr.)            |

Wir<sup>(11)</sup> haben die Dipolmomentmessungen der Selenophthene ausgeführt, die in diesem Falle das am leichtesten zugängliche Mittel darstellen, um die Strukturbeziehungen der drei Isomere klar zu stellen.

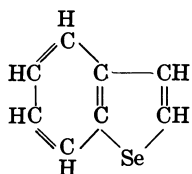
Das Ergebnis dieser Untersuchung ist, dass das *trans*-Selenophthen vom Schmelzpunkt 51-51.5°, wie im Falle des Thiophthens vom Schmelzpunkt 56°, das Challenger und Harrison<sup>(3)</sup> gewonnen hat, das Moment  $\mu \approx 0$  hat. Daraus kann man für das *trans*-Selenophthen mit Sicherheit auf Formel II schliessen. Für das Selenophthen vom Schmelzpunkt 123-124.5° und das flüssige Isomer werden die Momente  $\mu = 1.07 \times 10^{-18}$  e.s.E. (Benzol-Lösung) bzw.  $\mu = 1.52 \times 10^{-18}$  e.s.E. (Benzol-Lösung) gefunden. Da sich auch ergeben hat, dass das Selenophen ein Moment von  $\mu = 0.78 \times 10^{-18}$  e.s.E. (Benzol- und Hexan-Lösung) hat, kann man durch vektorielle Addition die Momente für Struktur I und II näherungsweise vorausberechnen—als Moment der Struktur I errechnet sich so  $\mu = 1.48 \times 10^{-18}$  e.s.E. und für das der Struktur III  $\mu = 0.92 \times 10^{-18}$  e.s.E. Auf Grund der Grösse der Dipolmomente ergeben sich damit als wahrscheinlichste Formeln für Selenophthen vom Schmelzp. 123-124.5° die Formel III und für das flüssige Isomer die Formel I d.h. die der *cis*-Form. Das erstere von der Formel III bezeichne ich als *iso*-Selenophthen.

Was die Synthese des Selenonaphthens betrifft, so ist sie schon von Mazza und Solazzo<sup>(1)</sup> durch Einwirkung von Acetylen auf Selen versucht worden und der Schmelzpunkt des Selenonaphthens wird von ihnen zu 53-4° angegeben. Sie haben jedoch für die Konstitution ihres Selenonaphthens keinen Beweis geliefert und irgendwelche Derivate beschrieben. Danach haben Komppa und Nyman<sup>(2)</sup> im Jahre 1933 das Selenonaphthen mit Sicherheit synthetisiert und es einer eingehenden Untersuchung unterworfen. Die Synthese von Komppa und Nyman besteht darin, dass man das 3-Oxy-selenonaphthen, das nach dem Verfahren von Lesser und Weiss<sup>(12)</sup> erhalten wurde, mit Natriumamalgam in alkoholischer Lösung reduziert.

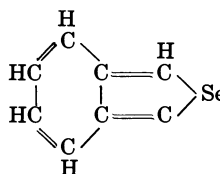
(11) B. Tamamushi, S. Umezawa und H. Akiyama, dies Bulletin **14** (1939), 318.

(12) R. Lesser und R. Weiss, *Ber.* **45** (1912), 1835; **46** (1913), 2640.

Wenn man nun die Struktur des Selenonaphthens, im Falle dass es bei der Einwirkung von Acetylen auf Selen gewonnen wird, überlegt, so sind jedoch die folgenden zwei Formeln möglich.



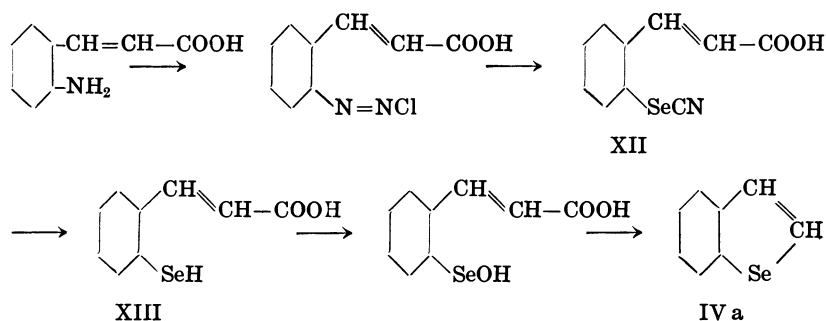
IV a



IV b

Es wurde schon von Komppa und Nyman<sup>(2)</sup> bemerkt, dass die Identität ihres Präparats vom Schmelzpunkt 50–51° (korr.) mit der Substanz, die von Mazza und Solazzo<sup>(1)</sup> gewonnen wurde, zweifelhaft erscheinen muss.

Wie ich schon beschrieb, zeigt der Selengehalt beim Übergang von der zweiten zur dritten Fraktion der Vakuum-Destillation des rohen Öls wieder eine Abnahme (siehe Tabelle 1). Gelegentlich konnte ich aus dem bei 123–130° unter 14 mm. übergehenden Destillat ein Pikrat vom Schmelzpunkt 154.5–156° erhalten, aus dem das Selenonaphthen vom Schmelzpunkt 50–51° (korr.) durch Zerlegung mit Ammoniak gewonnen wurde. Zur Feststellung der betreffenden Struktur habe ich das Selenonaphthen von der Formel IVa dargestellt. Die neue Selenonaphthensynthese ist völlig von der von Komppa und Nyman<sup>(2)</sup> verschieden und schlägt von *o*-Amino-zimtsäure ausgehend, den folgenden leicht verständlichen Weg ein.



Nach Diazotierung der *o*-Amino-zimtsäure wurde in üblicher Weise die überschüssige Mineralsäure mit Natriumacetat neutralisiert und die Diazoverbindung mit Selencyankalium umgesetzt. Charakteristisch für die bisher noch nicht beschriebene *o*-Selencyan-zimtsäure (XII) ist die Leichtigkeit, mit der sie sich schon in der Kälte durch Alkalien zu der entsprechenden *o*-Selenolzimtsäure (XIII) aufspalten lässt, die in alkalischer Lösung anders wie die Selensalicylsäure keine Neigung zeigt, sich zu den Diseleniden zu oxydieren. Da im allgemeinen<sup>(13)</sup> die Selenophenole durch Oxydation an der Luft sich leicht zu polymerisieren scheinen,

(13) Z. B.: H. Bauer, *Ber.*, **46** (1913), 93; S. Keimatsu u. I. Satoda, *J. Pharm. Soc. Japan*, **55** (1935), 19.

könnte man die Beständigkeit der *o*-Selenolzimtsäure von der Affinitätswirkung des Orthosubstituenten auf die Reaktionsfähigkeit der benachbarten Selenol-gruppe herleiten. Die alkalische Lösung der *o*-Selenolzimtsäure trübt sich schon in der Kälte durch Einwirkung von rotem Blutlaugensalz und die Bildung von Selenonaphthen (IVa) ist schon bei der Anwendung von ausserordentlich geringen Mengen durch den charakteristischen Geruch zu erkennen. Das hier erhaltene bei 50–51° (korr.) schmelzende Selenonaphthen zeigte keine Depression beim Mischen mit dem Präparat, das durch Einwirkung von Acetylen auf Selen erhalten wurde.

Hier ist folglich mit Sicherheit festgestellt, dass unter den Produkten der thermischen Reaktion zwischen Acetylen und Selen ausser dem Selenophen und strukturisomeren Selenophthenen sich noch das Selenonaphthen vom Formel IVa bildet.

Zum Schluss möchte ich Herrn Prof. Dr. H. Suginome für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank aussprechen. Gleichzeitig bin ich der Kaiserlichen Akademie für die Gewährung eines Stipendiums zu Dank verpflichtet.

### Beschreibung der Versuche.

**Iso-Selenophthen (III) und seine Derivate.** *Isolierung des iso-Selenophthens* (III). Der unangenehm riechende Teer, der durch Einwirkung von Acetylen auf Selen in einem elektrischen Ofen erhalten wird, ist dunkel rotbraun leichtflüssig und enthält wenig freien Kohlenstoff. 317 g. Teer wurden unter gewöhnlichem Druck destilliert, wobei am Anfang das Selenophen bei ungefähr 110° schwach gefärbt überging. Sobald das Selenophen grösstenteils überdestilliert ist, stieg die Temperatur schnell an. Die Destillation unter gewöhnlichem Druck wurde dann eingestellt, weil das übergegangene Öl sich dunkel braun zu färben anfang. Der hier erhaltene ölige Rückstand betrug ungefähr 150 g. Liess man ihn eine Woche bis einen Monat lang in der Dunkelkammer stehen, so schieden sich viele dunkel gefärbte grosse Nadeln aus, die von dem öligen Anteil abgetrennt und auf Ton sorgfältig getrocknet wurden. Das noch nicht umkrystallisierte Präparat schmolz bei 115–120°. Ausbeute, 21 g., d.h. 6.7% des Ausgangsteers. Sie wurde aus Alkohol unter Zusatz von Tierkohle mehrmal umkrystallisiert. Aus Alkohol kommen kleine rautenförmige Krystalle (Abb. 2.), Schmp. 123–124.5°. Gefunden: C, 30.81, 31.09; H, 1.96 2.11; Se, 67.19 Berechnet für  $C_{10}H_7Se_2$ : C, 30.77; H, 1.72; Se, 67.52%. 0.263 mg. Subst. in 2.377 mg. Campher:  $\Delta = 18.5^\circ$ . Gef. *M*, 239. Ber. *M*, 234.

Das Selenophthen ist leicht löslich in Schwefelkohlenstoff, etwas schwerer in heissem Alkohol, schwer in Aether und kaltem Alkohol. Beim Zusammenbringen mit Isatin und konzentrierter Schwefelsäure fand Violettfärbung in schöner Weise statt. Das Selenophthen hat einen charakteristischen Geruch, der einigermaßen am Naphthalin erinnert.

**Pikrat.** 0.52 g. des oben beschriebenen festen Selenophthens wurden in wenig Benzol gelöst und in die kalte Lösung wurde kalt gesättigte Benzol-Lösung von Pikrinsäure (0.51 g.) eingetropft. Nach einiger Zeit krystallisierte das Pikrat in schönen, langen, gelben Nadeln aus. Es wurde aus heissem Benzol und dann aus einer geringen Menge von heissem Methylalkohol umkrystallisiert. Gelbe Nadelbüschel. Schmp 163–5°. Gefunden: N, 9.27. Berechnet für  $C_{10}H_7Se_2 \cdot C_6H_3O_7N_3$ : 9.07%. Das Pikrat des festen Selenophthens ist sehr leicht löslich in Alkohol und wird durch ziemlich konzentriertes Ammoniak leicht zerlegt.

**Iso-Tetrabromselenophthen (V).** 1.5 g. Selenophthen wurden in wenig Schwefelkohlenstoff gelöst und in die Lösung wurde eine 30%-ige Lösung von 8 c.c. Brom unter Umschütteln im Eiswasser aus dem Tropftrichter nach und nach eingetropft. Am

Anfang schieden gelbe Krystalle, vermutlich<sup>9)</sup> ein Bromadditionsprodukt, ohne Bromwasserstoffentwicklung aus. Wenn ungefähr ein Drittel der Bromlösung versetzt war, verschwand das gelbe Bromadditionsprodukt und es entwickelte sich heftig Bromwasserstoff. Die Lösung wurde unter Feuchtigkeitsausschluss bei Zimmertemperatur zur vollständigen Einwirkung des Broms einige Tage stehen gelassen, wobei sich schwer lösliche säulenförmige Krystalle nach und nach ausschieden. Das ganze Reaktionsgemisch wurde dann mit verdünnter Kalilauge genügend gewaschen. Die ausgeschiedenen Säulen wurden abgesaugt und das Filtrat wurde getrocknet und dann verdunstet, wobei eine kleine Menge des gebromten Selenophthens gewonnen wurde. Die gesammte Ausbeute war 3.1 g. Sie wurde aus ungefähr 200 c.c. Benzol umkrystallisiert. Farblose Nadeln. Schmp. 247.5° (korr.) ohne Zersetzung. Gefunden: C, 13.28; H, 0.20; Br, 58.62. Berechnet für  $C_6Br_4Se_2$ : C, 13.10; H, 0.00; Br, 58.15%. Die Analyse zeigt, dass alle vier Wasserstoffatome des Selenophthens durch Brom ersetzt sind. Das Tetra-bromselenophthen wird durch alkoholisches Kali nicht verändert; in Alkohol, Schwefelkohlenstoff und kaltem Benzol ist es schwerlöslich.

*Iso-Mononitroselenophthen* (VI). 1 g. Selenophthen wurde in ungefähr 10 c.c. Essigsäureanhydrid suspendiert und in das Gemisch wurde eine Lösung von 0.5 c.c. rauchender Salpetersäure in 8 c.c. Essigsäureanhydrid unter Umschütteln bei ungefähr -18° nach und nach eingetropft, wobei das suspendierte Selenophthen allmählich in Lösung ging. Nachdem das ganze Nitriergemisch eingetragen war, wurde die ganze dunkelbraun gefärbte Lösung in Eiswasser gegossen und zwecks Lösung des Essigsäureanhydrids in der Dunkelkammer einige Zeit stehen gelassen. Das ganze Reaktionsgemisch wurde dann der Wasserdampfdestillation unterworfen, wobei zuerst grösstenteils Essigsäure überdestilliert wurde und dann die Nitroverbindung sich in Form einer gelben Krystallmasse im Kühler ausschied, die sofort abgesaugt wurde. Das Filtrat wurde mit verdünntem Natriumcarbonat neutralisiert, ausgeäthert und dann wurde das Lösungsmittel eingedampft, aus dem noch etwas Nitroverbindung gewonnen wurde. Die gesammte Ausbeute betrug 0.3 g. Umkrystallisiert zweimal aus Alkohol; hell gelbe Säulen. Schmp. 108–9.5°. Gefunden C, 25.60; H, 0.89; N, 4.95. Berechnet für  $C_6H_3O_2NSe_2$ : C, 25.81; H, 1.08; N, 5.02%. Die Analyse zeigt, dass die erhaltene Nitroverbindung ein Mononitroselenophthen ist. Das Mononitroselenophthen ist weit beständiger als  $\alpha$ -Nitroselenophthen<sup>(7)</sup> und kann im gefärbten Exsiccator aufbewahrt werden.

*Bariumsalz der iso-Selenophthen-disulfonsäure* (VII).  $C_6H_2Se_2(SO_3)_2Ba \cdot 3H_2O$ . Ungefähr 250 c.c. Essigsäureanhydrid wurden mit 3 g. Selenophthen bei Zimmertemperatur gesättigt und in die Lösung wurde ein abgekühltes Gemisch von 1.7 c.c. konzentrierter Schwefelsäure und 10 c.c. Essigsäureanhydrid unter Umschütteln bei Zimmertemperatur nach und nach eingetragen. Nachdem die ganze Schwefelsäurelösung eingetragen war, wurde die braun gefärbte Reaktionslösung weiter bis auf 70° erwärmt. Die abgekühlte Reaktionslösung wurde sofort in Eiswasser gegossen und einige Zeit stehen gelassen. Zwecks Beseitigung der Essigsäure wurde die wässrige Lösung der Wasserdampfdestillation unterworfen, was ungefähr sieben Stunden in Anspruch nahm. Die rückständige rohe Selenophthensulfonsäurelösung wurde mit Bariumcarbonat gesättigt, von überschüssigem Bariumcarbonat abfiltriert, mit Tierkohle entfärbt und bis auf ein kleines Volumen im Vakuum eingengt. Zur farblosen Lösung wurde dann das fünffache Volumen Alkohol zugesetzt, wobei sich das Bariumsalz der Selenophthendisulfonsäure, das in wässrigem Alkohol schwer löslich ist, niederschlug. Das Salz wurde abgesaugt, in Wasser aufgelöst und wieder mit Alkohol umgefällt. Abgesaugt, gewaschen mit Alkohol und Äther und getrocknet im Vakuum über Chlorkalzium und Paraffin. Ausbeute 2.8 g. Gefunden:  $H_2O$ , 0.91. Berechnet für  $C_6H_2Se_2(SO_3)_2Ba \cdot 3H_2O$ :  $H_2O$ , 0.92%. Gefunden: Ba, 25.18. Berechnet für  $C_6H_2Se_2(SO_3)_2Ba \cdot 3H_2O$ : Ba, 25.88%.

*Kaliumsalz der iso-Selenophthen-disulfonsäure* (VIII).  $C_6H_2Se_2(SO_3K)_2 \cdot 1\frac{1}{2}H_2O$ . Die wässrige Lösung des selenophthen-disulfonsauren Bariums wurde mit einer äquivalenten Menge Kaliumcarbonatlösung versetzt und vom Bariumcarbonat abfiltriert. Das Filtrat wurde bis auf ein kleines Volumen im Vakuum eingengt und mit Alkohol umgefällt. Abgesaugt, gewaschen mit Alkohol, getrocknet über Chlorkalzium im Vakuum und analysiert. Gefunden:  $H_2O$ , 4.66. Berechnet für  $C_6H_2Se_2(SO_3K)_2 \cdot 1\frac{1}{2}H_2O$ :  $H_2O$ , 4.30%. Gefunden: K, 16.52. Berechnet für  $C_6H_2Se_2(SO_3K)_2$ : K, 16.63%.

*Iso-Selenophthen-disulfochlorid* (IX). 0.7 g. gepulvertes und wohlgetrocknetes Kaliumsalz der Selenophthen-disulfonsäure wurden mit 1 g. Phosphorpentachlorid verrieben und ungefähr bei 90–100° zehn Minuten lang erhitzt. Das schwach braungefärbte Reaktionsgemisch wurde mit Äther und dann Wasser genügend gewaschen. Ausbeute 0.5 g. Umkrystallisiert zweimal aus Benzol unter Zusatz von Tierkohle. Farblose rautenförmige Kryställchen. Zersetzt sich bei 234–6° unter Aufschäumen. Gefunden: Cl, 16.40. Berechnet für  $C_6H_2Se_2(SO_2Cl)_2$ : Cl, 16.45%. Das Selenophthen-disulfochlorid ist schwer löslich in Äther und ziemlich löslich in heissem Benzol.

**cis-Selenophthen (I) und sein Derivat.** *Isolierung des cis-Selenophthens* (I). Die ganze Fraktion (16.5 g.) die, wie oben erwähnt, bei 100–113° unter 14 mm. siedete, wurde im wenig Methanol suspendiert und mit kalt gesättigter alkoholischer Pikrinsäurelösung im Überschuss versetzt. Nach einiger Zeit wurde das ausgeschiedene Pikrat abfiltriert. Beim Verdunsten des Alkohols im Vakuum blieb ein Gemisch von Pikrat, Pikrinsäure und einer ziemlichen Menge des dunkelbraunen öligen Anteils zurück. Dieser ölige Anteil wurde von krystallinischen Körpern abgetrennt, mit verdünntem Ammoniak behandelt, um das so entstandene, labile Pikrat sicher zu zerlegen, und dann ausgeäthert. Getrocknet über Glaubersalz. Nach Eindampfen des Äthers wurde das zurückbleibende Öl mit Wasserdampf destilliert, wobei eine klare schwachgelbe Flüssigkeit überging, die ausgeäthert und getrocknet wurde. Nach Eindampfen des Lösungsmittels wurde das gewonnene Öl der Vakuum-Destillation unterworfen. Die Hauptfraktion wurde nochmals im Vakuum destilliert, wobei fast die ganze Flüssigkeit zwischen 90–93° bei 14 mm. überging. Ausbeute 4.5 g. Die Ergebnisse der Molekulargewichtsbestimmung und der Analyse dieses Öls lassen ein Selenophthen erkennen. Gefunden: C, 30.91; H, 2.12; Se, 66.90. Berechnet für  $C_6H_4Se_2$ : C, 30.77; H, 1.72; Se, 67.52%. 0.257 mg. Subst. in 3.477 mg. Campher:  $\Delta = 13$ –13.5°. Gef. *M*, 222–227. Ber. *M*, 234. Das flüssige Selenophthen ist ein fast farbloses starklichtbrechendes Öl und färbt sich schönviolett beim Zusammenbringen mit Isatin und konzentrierter Schwefelsäure. Beim Schütteln mit wässriger Quecksilberacetatlösung entsteht eine schwachgelbe amorphe Substanz, die für ein Selenophthen-quecksilberacetat gehalten wird. Auch scheidet es sofort beim Schütteln mit alkoholischer wässriger Sublimatlösung einen krystallinischen Körper aus, der wahrscheinlich ein Selenophthenquecksilberchlorid ist. Neben dem chemischen Verhalten lässt auch die optische Untersuchung ein Selenophthen erkennen. Dieses flüssige Selenophthen zeigt folgende Konstanten:  $d_4^{25} = 1.9354$ ;  $n_D^{25} = 1.6586$ . Für das flüssige Selenophthen berechnet sich aus den oben angegebenen Konstanten unter Anwendung der Lorenz-Lorentz'schen Formel die Molekularrefraktion für Natriumlicht, *MR*, zu 44.55. Für die Formel  $C_6H_4Se_2$  des Selenophthens berechnet sich *MR*<sub>D</sub> zu 45.33. Bei dieser Berechnung ist die Differenz (= 10.61) zwischen dem aus Konstanten des Tetrahydroselenophthens ( $n_D^{18} : 1.5510$ ;  $d_4^{18} : 1.4816$ ) abgeleiteten *MR*<sub>D</sub> des Tetrahydroselenophthens<sup>(6)</sup> und dem Wert für  $C_4H_8Se_2$  als eine wahrscheinlichste Atomrefraktion des Selen gebraucht.

*cis-Tetrabromselenophthen* (X). 1 g. flüssiges Selenophthen wurde in wenig Schwefelkohlenstoff mit überschüssigem Brom unter Umschütteln in Eiswasser nach und nach versetzt, wobei sich sehr heftig Bromwasserstoff entwickelt. Lässt man das Reaktionsgemisch einige Tage stehen, so scheidet es krystallinische Körper aus. Aufgearbeitet wie bei der Tetrabromverbindung aus festem Selenophthen. Umkrystallisiert aus viel Benzol unter Zusatz von Tierkohle. Etwas gelb gefärbte kurze Nadeln. Ausbeute 0.6 g. Schmp. 271–272° (korr.) ohne Zersetzung. Die Analyse zeigte, dass alle vier Wasserstoffatome des Selenophthens durch Brom ersetzt sind. Gefunden: C, 13.75; H, 0.19; Br, 58.40. Berechnet für  $C_6Br_4Se_2$ : C, 13.10; H, 0.00; Br, 58.15%. In Alkohol, Schwefelkohlenstoff und kaltem Benzol ist es schwer löslich, aber die Mischschmelzpunkte mit den anderen beiden Isomeren zeigten auffallende Depression.

**trans-Selenophthen (II) und seine Derivate.** *Isolierung des trans-Selenophthens* (II). Braunschwarzes Öl, das von Selenophthen und dann auskrystallisiertem Selenophthen abgetrennt wurde, wurde der Vakuumdestillation unterworfen, wobei eine Hauptfraktion ca. 30 g. bei 93–100° unter 14 mm. überging, die einmal mit Wasserdampf destilliert, über Chlorcalcium getrocknet und mit einer kalt gesättigten alkoholischen Pikrinsäurelösung im Überschuss versetzt wurde, wodurch ein grosser Anteil zu einer eigelben Masse ca. 17 g. erstarrte. Durch fraktionierte Krystallisation



aus Alkohol wurde ein grosser Anteil, der konstant bei 154–155.5° schmolz, erhalten. Analyse: Gefunden: N, 9.47. Berechnet für  $C_6H_4Se_2 \cdot C_6H_5O_7N_3$ : N, 9.07%

*trans-Selenophthen* (II). Das Pikrat wurde mit ziemlich konzentriertem Ammoniak gut verrieben, eine Zeitlang stehen gelassen, und schliesslich bis 50° erwärmt. Ausgeäthert, und über Chlorcalcium getrocknet. Beim Eindampfen des Lösungsmittels wurde eine fast farblose krystallinische Substanz erhalten, noch einmal mit Wasserdampf destilliert, wobei schon *trans*-Selenophthen fast ganz rein erhalten wurde. Umkrystallisiert aus Alkohol. Schmp. 51–51.5°. Gefunden: C, 30.68; H, 1.83. Berechnet für  $C_6H_4Se_2$ : C, 30.77; H, 1.72%. 0.237 mg. Subst. in 2.968 mg. Campher:  $\Delta = 13$ –13.5°. Gef. M, 237–245. Ber. M, 234. Beim Zusammenbringen mit Isatin und Schwefelsäure fand Braun-Färbung und bald darauf schöne Violett-färbung statt. Das *trans*-Selenophthen scheint im allgemeinen in organischen Lösungsmitteln leichter löslich als das Isomer vom Schmelzp. 123–124.5° zu sein. Auch hat das *trans*-Selenophthen einen nicht unangenehmen Geruch, der einigermassen am Naphthalin erinnert.

*trans-Tetrabromselenophthen* (XI). 1 g. *trans*-Selenophthen wurde auf dieselbe Weise wie beim flüssigen Isomer bromiert und aufgearbeitet. Farblose lange Nadeln aus viel Schwefelkohlenstoff. Ausbeute 0.6 g. Schmp. 252.5–253° (korr.) ohne Zersetzung. Die Analyse zeigte, dass alle vier Wasserstoffatome des Selenophthens durch Brom ersetzt sind. Gefunden: C, 13.05; H, 0.00; Br, 58.39. Berechnet für  $C_6Br_4Se_2$ : C, 13.10; H, 0.00; Br, 58.15%. In Alkohol, Schwefelkohlenstoff und Benzol ist es auch schwer löslich. Die Mischschmelzpunkte mit den anderen beiden Isomeren zeigten auffallende Erniedrigung.

**Selenonaphthen.** *Isolierung des Selenonaphthens und seines Pikrats.* Der ölige Anteil, der von auskrystallisiertem, festem Selenophthen abgetrennt wurde, wurde in diesem Zustande der Vakuumdestillation unterworfen, wobei eine Hauptfraktion zwischen ungefähr 123–130° bei 14 mm. übergang. Diese Fraktion gab mit Isatin und konzentrierter Schwefelsäure die Indophenin-Reaktion in ausgezeichneter Weise und der Nachweis des Selens<sup>(14)</sup> in dieser Fraktion war stark positiv. Diese Fraktion wurde nochmals in Vakuum destilliert, aber sie ging bei fast der gleichen Temperatur über. Sie wurde dann der Wasserdampfdestillation und nach Aufarbeiten wieder der Vakuumdestillation unterworfen, wobei der Hauptanteil bei fast der gleichen Temperatur übergang. Diese Fraktion enthielt eine grosse Menge des Selens, die nach quantitativer Selenbestimmung ungefähr 40 Prozent betrug. Alle Wahrscheinlichkeit spricht dafür, dass ein Gemisch von Selenophthen, Selenonaphthen und wenig Naphthalin vorlag. In der Tat wurde das Pikrat des Selenonaphthens rein isoliert: Das Öl wurde im Methylalkohol suspendiert und mit einer kalt gesättigten alkoholischen Pikrinsäurelösung versetzt, wodurch alles zu einer aus feinen Nadelchen bestehenden gelben Masse erstarrte. Nach mehrmaligem Umkrystallisieren aus Methylalkohol schmolz das Pikrat konstant bei 156–157° (korr.). Gefunden: N, 10.25; Se, 18.95. Berechnet für  $C_8H_6Se \cdot C_6H_5(NO_2)_2OH$ : N, 10.25; Se, 19.32%. Das Pikrat ist sehr leicht löslich in Alkohol. Der Rest des Pikrats wurde mit ziemlich konzentriertem Ammoniak zerlegt, dann ausgeäthert und über Glaubersalz getrocknet. Beim Eindampfen des Lösungsmittels wurde eine fast farblose krystallinische Substanz erhalten, die aus Alkohol mehrmals umkrystallisiert wurde. Sie stellt sich als ein sich fettig anführender Körper dar. Schmp. 50–51° (korr.) Gefunden: Se, 42.85. Berechnet für  $C_8H_6Se$ : Se, 43.62%. Das Selenonaphthen ist löslich in heissem Alkohol, leicht löslich in Benzol und Eisessig. Dieses Selenonaphthen ergibt Indophenin-Reaktion mit Isatin und konzentrierter Schwefelsäure.

**Synthese des Selenonaphthens aus o-Nitro-zimtsäure.** *o-Selencyan-zimtsäure*, (XII) 10g. *o*-Amino-zimtsäure, die in bekannter Weise durch Reduktion von synthetischer *o*-Nitrozimtsäure (aus *o*-Nitro-benzaldehyd) erhalten wurden, wurden unter Zusatz von Wasser und 13 c.c. konzentrierter Salzsäure warm gelöst und beim Erkalten das zum Teil auskrystallisierende Hydrochlorid durch Zusatz einer Lösung von 3.7 g. Natriumnitrit in die lösliche und ziemlich beständige Diazoniumverbindung übergeführt. Sofort wurde die überschüssige Mineralsäure durch Zusatz von soviel Natriumacetat neutralisiert, dass die Reaktion auf Kongopapier ausbleibt. Dann wurden 7.8 g.

(14) M. J. Horn, *Ind. Eng. Chem., Anal. Ed.*, **6** (1934), 34.

Selencyankalium in Wasser gelöst, portionsweise zugegeben. Unter kräftiger Stickstoffentwicklung scheidet sich das gelbe Reaktionsprodukt sofort aus. Nach mehrstündigem Stehen wurde es ausgeäthert. Der nachher mit Glaubersalz getrocknete Auszug hinterliess nach dem Eindampfen von Äther eine gelb gefärbte, in Wasser schwer lösliche Substanz, die aus viel Benzol unter Zusatz von etwas Tierkohle umkrystalliert werden konnte. Die Ausbeute betrug etwa 1.5 g. Sie stellte in reinem Zustand fast farblose Büschelchen kurzer Nadeln dar, die bei 171–3° unter Bräunen und Aufschäumen schmolzen. Deren Analyse stimmte wohl auf Selencyanzimtsäure. Gefunden: N, 5.45. Berechnet für  $C_{10}H_7O_2SeN$ : N, 5.56%. Die *o*-Selencyanzimtsäure ist leicht löslich in Alkohol, ziemlich löslich in Äther, schwer in Ligroin.

*Selenonaphthen* (IVa). 2 g. *o*-Selencyanzimtsäure wurden mit Alkohol benetzt und eine Lösung von 2 g. Kaliumhydroxyd hinzugefügt. Das Reaktionsgemisch wurde dann unter Rückfluss etwa zwanzig Minuten gekocht, wobei es eine etwas braun gefärbte klare Lösung bildete. Sobald die Lösung der so entstandenen *o*-Selenohydroxyzimtsäure mit 2.5 g. Ferricyankalium, in Wasser gelöst, nach Erkalten versetzt wurde, trübte sie sich in der Kälte fast momentan und die Bildung von Selenonaphthen war schon bei sehr kleinen Mengen durch einen charakteristischen Geruch zu erkennen. Seine Isolierung gelang leicht durch Destillation mit Wasserdampf, wobei das Selenonaphthen in sehr reinem Zustande als schon im Kühler erstarrendes Öl überging. Die Ausbeute betrug 0.36 g. Zur Analyse wurde es aus wässrigem Alkohol umkrystallisiert. Das Selenonaphthen schmolz bei 50–51° (korr.). Gefunden: C, 52.78; H, 3.45. Berechnet für  $C_8H_6Se$ : C, 53.04; H, 3.32%. In jeder Hinsicht stimmte unser Präparat mit der Beschreibung von Komppa und Nyman<sup>(2)</sup> überein.

Beim Zusammenbringen mit Isatin und konzentrierter Schwefelsäure fand Braunfärbung in schöner Weise statt. Die Identität mit der Substanz, die durch Einwirkung von Acetylen auf Selen erhalten wurde, wurde durch Mischprobe und die charakteristische Pikrinsäureverbindung festgestellt.

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# Chemical Studies in Lake Metabolism.

By Ken SUGAWARA.

(Received June 12, 1939.)

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## I. Introduction.

It will be necessary to begin with a brief explanation of the term "lake metabolism", which the writer believes he first introduced.

After A. Thienemann, the writer regards a lake as a "Lebenseinheit". The word "Lebenseinheit", which is used here in its physiological sense, was primarily understood to represent an individual living thing, animal or plant. After R. Hesse,<sup>(1)</sup> every animal or plant individual is a "Lebenseinheit", because it is "ein abgeschlossener, unabhängig für sich bestehender Organismus, bei dem alle Einzelteile derart zusammenwirken, dass der Fortbestand des Ganzen dadurch gesichert ist; mit anderen Worten, es ist selbsterhaltungsfähig."

What has just been said here concerning an individual organism is also true of what is called biocoenosis, defined as follows by the creator of the idea, Karl Möbius:<sup>(2)</sup> "Die Biocönose ist eine Gesellschaft von lebenden Wesen, eine den durchschnittlichen äusseren Lebensverhältnissen entsprechende Auswahl und Anzahl von Arten und Individuen, welche sich gegenseitig bedingen und durch Fortpflanzung in einem abgemessenen Gebiete dauernd erhalten."

(1) Hesse, "Der Tierkörper als selbständiger Organismus" 33, (1910).

(2) Möbius, *Sitzungsber. d. Ges. naturforsch. Freunde*, Berlin, (1901), 267.

When Hesse's word "Organismus" is substituted by "biocoenosis" and "Einzelteile" by "animals and plants", the "Lebenseinheit" idea is rightly applicable to the case of biocoenosis. Biocoenosis, then, is a "physiologische Lebenseinheit der zweiten Ordnung."

Now, in a lake, there may be distinguished three regions, pelagic, littoral, and abyssal, which are inhabited respectively by a characteristic biocoenosis. Thus plankton and necton inhabit the pelagic region, rooted vegetation and other plants, and the animals depending on them, the littoral region, and the larvae of *Chironomus* and *Corethra*, shellfishes, and Tubificidae worms the abyssal or third region.

Each of these biocoenoses depends on its milieu, that is, the biotope. On the other hand, all these biocoenoses and biotopes of a lake interact and give rise to a cyclic process on a larger scale between the dissolved and the floating or deposited substances, whereby the dynamical equilibrium of these biocoenoses and the permanency of the lake, as a whole, are maintained.

Fig. 1 gives a general scheme of the cyclic process and the correlations between biocoenoses and biotopes, which can be explained briefly by the following three points (1) supply of material, (2) changes in the substance in the lake water, and (3) the circulation of matter in the lake.

(1) The materials necessary for the maintenance of the lake water come from three different sources, namely, influent waters, the atmosphere, and the decomposition products that have been formed in the lake water.

(2) The nutrient materials thus supplied are then assimilated by phytoplankton and transformed into their body substances. Part of the phytoplankton that are suspended in the water are eaten by zooplankton, while the remainder, after death, together with dead zooplankton, sink to the bottom and form the lake deposits, which, filling the lake bottom, gradually make it shallower.

However, not all sediments are destined to remain buried. Not a small part of the deposited substance is given a chance of being returned to the overlying free water.

As a matter of fact, the deposited dead plankton are food for the

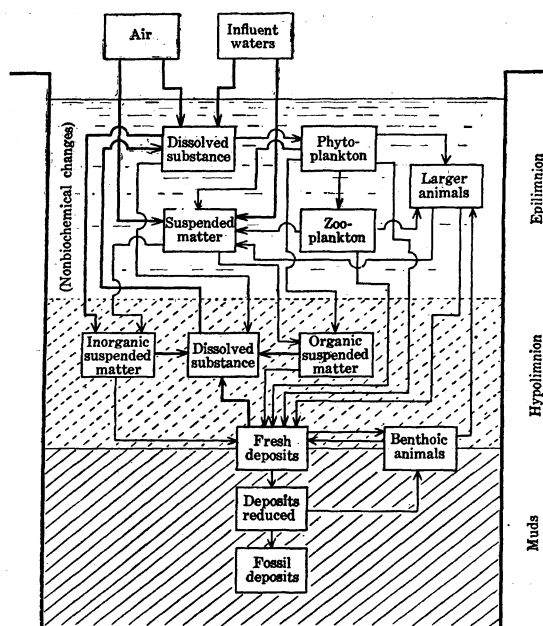


Fig. 1. A general scheme of the cyclic process and the correlation between biocoenoses and biotopes in a lake.

benthic animals which, in their turn, are relished by fish. Another part of the deposit undergoes bacterial action and decomposes into simpler products.

(3) The decomposition products which are fairly soluble, tend to dissolve into the bottom water, where they accumulate in abundance.

These accumulated products are then carried back into the upper water layers by the water current which is caused either by wind or by the lowering of temperature in the night, especially in that season between autumn and winter, thus completing the cycle, to be repeated again and again.

This is the general view (the details being unknown) of the circulation of matter in a lake, by means of which biocoenotic and biotopic equilibrium, that is, the permanency of the lake, is actualized.

Thus G. Werestchagin<sup>(3)</sup> was led to the idea of "limnologische Einheit", as he says: "Der See ist die Einheit der einzig und reel in der Natur vorhandenen Summe von Lebensraum (Biotop) plus Lebensgemeinschaft (Biocönose), eine 'limnologische Einheit'."

Thus the idea of Werestchagin was accepted by Thienemann<sup>(4)</sup> with certain modifications, as follows:

"Das ist richtig, nur sollte man das Wort "Summe" überhaupt lieber vermeiden, denn es handelt sich ja gerade darum, dass der See nicht die Summe, sondern die Einheit von Biotop und Biocönose darstellt. Ja wir glauben, dass hier wohl vielleicht sogar der Drieschsche Begriffe der Ganzheit eine Rolle spielt, noch wissen wir es allerdings nicht."

Thus with lakes, we have come to the idea of "Lebenseinheit der dritten Ordnung."

When, therefore, we regard a lake as a "Lebenseinheit" and investigate from such a point of view the changes that occur in the various substances forming a lake, the system of knowledge thus brought together is called "lake metabolism."

This is the reason why the term "lake metabolism" is introduced into the present study, in which the writer primarily aims to interpret the significance of individual lake factors, their variability, and their relations to one another for the existence of a lake as a "Lebenseinheit," and thus to infer the extent to which the idea "Lebenseinheit" holds for the case of a lake.

Because of lack of available data regarding these lake factors, it was necessary for the writer to begin with the observation of these factors, so that the greater part of the work so far done had to do with the accomplishment of this purpose.

This and other circumstances retarded the writer in the solution of a number of problems, notwithstanding which the writer is glad to be able to report that it was possible to reach a number of results, whereby certain questions were clearly solved, some new questions raised, and new relations discovered, the solutions and interpretations of which latter, it is hoped, will be forthcoming with the aid of further studies.

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(3) Werestchagin, *Verhandl. d. Internat. Vereinigung f. theoret. u. angew. Limnologie*, Stuttgart, **1** (1923), 225.

(4) Thienemann, *Naturwissenschaften*, **13** (1925), 595.

## II. General Descriptions of the Lakes Studied.

### Takasuka-numa.

Takasuka-numa, where the greater part of the writer's investigations were carried out, and which belongs to that peculiar body of water called "Oppori", meaning a swamp formed by flood from a broken river bank, lies about 2.5 km. northe-east of Satte-mati Saitama Prefecture, having an area of about 0.021 km.<sup>2</sup> and a maximum depth of about 6 m. The water is humus brown, and so turbid that Secchi's disc was often invisible at 0.8 m. The lake is protected from north-easterly winds by a bank 7 m. high, running close to the northern shore, and by the village with its old trees, which occupies a part of the eastern beach, while the remaining greater part of the beach stretches directly into extensive corn- and rice-fields.

It is said that the bed of Sima-kawa, a branch of the River Gongendo which formerly was the main stream of the River Tone, was filled with volcanic ashes that were ejected during the severest recorded eruption of Mt. Asama, in 1783, and carried down by the river water, until the river shallowed and caused repeated floods up to the beginning of the Meizi era when the work of river improvement was completed.

The lake is said to owe its origin to the flood of 1786. The earth and sand then loosened seem to have been carried for a considerable distance, their remnants being found to-day as the low sandy hills called "Botti", distributed here and there in the south-western field, each covering from 3000 m.<sup>2</sup> to 4000 m.<sup>2</sup>

Table 1.

|               |                    |       |
|---------------|--------------------|-------|
| Altitude      | (m.)               | 10    |
| Area          | (m <sup>2</sup> .) | 21500 |
| Maximum depth | (m.)               | 6.0   |
| Mean depth    | (m.)               | 3.0   |
| Volume        | (m <sup>3</sup> .) | 65000 |

The morphometrical data of the lake basin are given in Table 1.

The basin is steeper in the east and north than elsewhere, and the littoral is narrow along these sides, while in

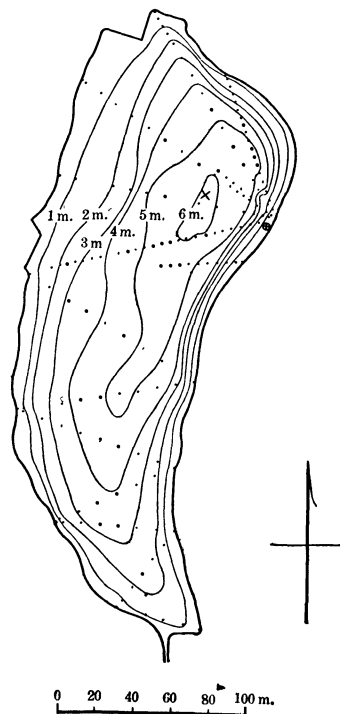


Fig. 2. Bathymetrical map of Takasuka-numa constructed with the data from the latest surveying and sounding in 1939.

- ... Points sounded.
- × ... The point where the water and the mud were sampled.
- ⊗ ... The writer's hut for observation.

the south and west it covers a wider sandy area, with rooted vegetation. The muddy abyssal region is evidently separated from the littoral, with its center near the head, where it occupies about a quarter of the total area of the lake basin.

**The Nisina Lake Group in Nagano Prefecture. Kizaki-ko<sup>(5)</sup>,  
Nakatuna-ko, and Aoki-ko.**

These three lakes are links in a chain in a valley that runs along the northern foot of the North Japan Alps. Their important morphometrical data are given in Table 2.

Table 2.

|                          | Aoki-ko | Kizaki-ko | Nakatuna-ko |
|--------------------------|---------|-----------|-------------|
| Area (km <sup>2</sup> .) | 1.863   | 1.413     | 0.141       |
| Depth (m.)               | 62.0    | 29.5      | 12.0        |
| Altitude (m.)            | 822     | 764       | 815         |

Aoki-ko, the deepest of them, has a transparency of 10 m., the water of the hypolimnion containing abundant oxygen, even late in the period of summer stagnation.

Kizaki-ko, which is the lowest in level and partly surrounded by cultivated land and villages, shows an advanced state of eutrophication. Its transparency does not exceed 8 m., while the hypolimnion water exhibits during the summer stagnation period a marked decrease in its oxygen content.

In Nakatuna-ko, which receives the water from Aoki-ko and sends it into Kizaki-ko, and is the smallest and shallowest of all, the oxygen content in deep water often becomes zero in summer, the transparency being usually less than 5 m.

**The Five Lakes at the Foot of Mt. Huzi. Motosu-ko, Syozi-ko,  
Nisino-umi, Kawaguti-ko, and Yamana-ko.**

These five lakes, which nestle at the foot of Mt. Huzi, owe their origin to damming up at different periods of the valleys between Mt. Huzi, the Misaka or Dosi mountain ranges, and their branches by volcanic ejecta from Mt. Huzi.

Their important morphometrical data are given in Table 3.

Table 3.

|                          | Motosu-ko | Syozi-ko | Nisino-umi | Kawaguti-ko | Yamana-ko |
|--------------------------|-----------|----------|------------|-------------|-----------|
| Area (km <sup>2</sup> .) | 4.87      | 0.87     | 2.30       | 6.13        | 6.46      |
| Depth (m.)               | 119.0     | 16.0     | 73.0       | 15.2        | 13.2      |
| Altitude (m.)            | 908       | 908      | 908        | 830         | 982       |

(5) "ko" is a termination given to all lakes.



Motosu-ko, the most westerly of the five lakes, is surrounded by a branch of the Misaka mountains, except at its eastern shore, which consists of massive accumulations of lava. It is mouthless and has no inflowing streamlet, but there are several reasons supporting the view that the lake is connected with Syozi-ko and Nisino-umi by subterranean communications. The water is a beautiful blue, with a transparency of 16–18 m. According to D. Inaba,<sup>(6)</sup> this lake is the most oligotrophic of the five, the content of protein nitrogen in the winter of 1934, being reported as having been only 23 mg./l.

Syozi-ko, lying east of Motosu-ko, is the smallest of the five, its area being less than 1 km.<sup>2</sup> Except in the south, its shore is surrounded by the Misaka mountains, where a gentle slope of lava-flow from Mt. Huzi projects into the lake in the form of a peninsula.

It is remarkable as has been pointed out by many authors that, throughout the year, below some 10 m., there is a sudden decrease in the oxygen content, and that, as Inaba has reported, in the winter of 1934 the protein nitrogen content was 109 mg./l., which is the highest value of the five lakes. Both of these facts prove that this lake has attained the most eutrophied stage of all the five.

Nisino-umi, called also Sai-ko, lying east of Syozi-ko, is separated from the latter by a gently sloping lava ridge, called "Aokigahara-marubi."

It is said that Nisino-umi and Syozi-ko were a large single lake, called "Seno-umi", until 863, when a lava flow divided this mother lake into two, as we find it to-day.

The lake, which is well aerated to depth, has a transparency of 10 m. Inaba's data of the protein nitrogen content of the water gives 35 mg./l. for the winter of 1934.

Kawaguti-ko, which lies due north of Mt. Huzi, has the lowest water level of the five lakes. The basin is divided into two main parts by a central islet, Uno-sima. According to D. Miyadi,<sup>(7)</sup> the maximum depth was 15.2 m. and the transparency 5.8 m., and according to Inaba's observations, in the winter of 1934, the protein nitrogen content was 34 mg./l.

The depth of Yamanaka-ko, the largest of the five lakes, is small for its area. In the south, it is bordered by a gentle slope of Mt. Huzi, while its northern shore is surrounded by the low Dosi mountains. These facts contribute to the agitation of the lake water by strong winds which are so common in this region, and consequently the water here does not stagnate to the extent that it does in Kawaguti-ko and in Syozi-ko. In the winter of 1934, the transparency was 5.4 m. and the protein nitrogen content 48 mg./l.

### III. Studies of Mud.

Studies of mud are important for the following reasons:

First, they furnish information concerning the roles played by mud in supplying nutrient matter to the lake water.

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(6) Inaba, *Jap. Journ. Limnol.*, **4** (1934), 101–114.

(7) Miyadi, *Japan. J. Zoology*, **4** (2) (1932), 82–100.

Secondly, since the mud consists of organic or inorganic debris that either has been formed in the lake or been carried into it at a certain time and precipitated there, they frequently indicate the condition of the lake in former times.

Thirdly, there is the problem of the changes that occur in mud, which can be answered only by a study of mud itself.

We may mention the names, B. W. Perfiliew,<sup>(8)</sup> Ch. S. Black,<sup>(9)</sup> D. S. Rawson,<sup>(10)</sup> R. T. Allgeier, W. H. Petersen, Ch. Juday and E. A. Birge,<sup>(11)</sup> W. Ohle,<sup>(12)</sup> G. Karsinkin and S. Kusnetzov,<sup>(13)</sup> all of whom have investigated mud along one or another of the lines just mentioned, resulting in the acquisition of much valuable knowledge. But, notwithstanding their importance, we have not yet succeeded in extracting sufficient knowledge from them to help us to solve the main problems, so that further studies are needed.

### Seasonal Variation in the Intensity of the Physical, Chemical, and Biological Factors Affecting Mud Metabolism.

Separate studies of the physical, chemical, and biological factors that may affect metabolism in muds have been carried out repeatedly, but systematic investigation, wherein a number of these factors is treated at the same time in order to secure correct judgement on the correlations between them, has been very rare, as also studies for a protracted period of the variability in the intensity of any of these factors. The following is the result of observations made with the object of filling our present lack of knowledge in these respects, for which purpose, the writer visited Takasuka-numa eleven times in all, from November 1932 to December 1933, and examined the muds from the deepest part of the lake for their temperature, pH, bacteria, and macroscopic benthic animals.

### Methods.

**Sampling and Measurement of Temperature.** For sampling the muds, a Lenz's sampler was used, so devised that, by inserting metallic plates, the muds sampled could be divided horizontally into a few layers. The number of layers, thus divided, varied from six to eight, according to the thickness of the muds dredged.

The sampler has three holes, lying vertically in a line on one of its walls, each with a screwed lid. Immediately after the sampler was hauled up into the boat and its contents were divided into layers by metallic plates, the mud temperature was read in the following manner.

The upper hinged cover of the sampler is opened and the bulb of a thermometer is inserted directly into the mud, and its temperature determined, that is, of the surface mud.

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(8) Perfiliew, *Verhandl. f. Internat. Vereinigung f. theoret. u. angew. Limnologie*, **4** (1929), 107-143.

(9) Black, *Transact. of the Wisconsin Acad. of Sciences, Arts and Letters*, **24** (1929), 127-133.

(10) Rawson, *Univ. of Toronto Studies, Public. of the Ontario Fisheries Research Laboratory*, **40** (1930), 1-183.

(11) Allgeier, Petersen, Juday and Birge, *Internat. Rev. d. gesamt. Hydrobiol. u. Hydrograph.*, **26** (1932), 444-461.

(12) Ohle, *Biochem. Z.*, **258** (1933), 420.

(13) Karsinkin and Kusnetzov, *Arbeiten der Limnologischen Station zu Kossino*, **13-14** (1931), 47-68.

The values of the intermediate layers are determined by merely removing the lids of the holes above mentioned, and inserting the thermometer bulb into the mud through them.

Finally, the temperature of the deepest mud is determined, first, by opening the bottom of the sampler and emptying out the mud of the deepest layer into a receiving vessel, after which the thermometer is introduced.

**Determination of the pH-value.** The sample was carried cold to the laboratory and kept in an ice-chest. 1 c.c. of the thoroughly kneaded mud is mixed well with 2 c.c. of distilled water for one minute, after which a knife-tipful of quinhydrone is added and the mixture stirred cautiously for half a minute. A platinum electrode is then inserted, and the pH determined potentiometrically in three minutes, referring to a saturated calomel cell.

Since it frequently happens that the room temperature, at which the pH-value is determined in the laboratory, differs from that in the mud as it lay in the lake bottom, naturally, the pH-value thus estimated differs from the value in its natural condition. The writer, therefore, studied, as a separate subject, the relation between the pH-value of the muds and the temperature, and constructed a pH-temperature curve, from which the observed values could be corrected into natural values.<sup>(14)</sup> Table 5 gives the values thus corrected.

**Bacteriological Examination.** The muds were transferred into a number of sterilized Petri-dishes and kept cold. The work of counting the number of bacteria by the plate culture method was completed in 24 hours. The method is mainly after E. J. Russel<sup>(15)</sup>. As counting medium, mannitol-agar-asparagine was used, and its pH regulated to 7.6 by caustic soda.

1 c.c. of the mud is shaken with 99 c.c. of sterile salt solution, containing NaCl and MgSO<sub>4</sub>, after which 1 c.c. of what is suspended in the solution is diluted with the same sterile salt solution. 1 c.c. of the latter suspended matter is further diluted with another 99 c.c. of salt solution. From the suspension thus prepared, 1 c.c. is transferred into each of five Petri-dishes, into which the sterile counting medium is poured molten. After ten days incubation at 20°C., the number of colonies developed is counted.

**Examination of Macroscopic Benthic Animals.** Each layer of the sampled mud, divided as already mentioned, was sieved by shaking in water through wire netting with meshes of 1 mm. *Corethra* and *Orthocladinae* larvae, which represent the benthic fauna of this lake, were then picked out from the residue. The number of individuals found in each divided layer and their sum are given in Table 7. The sum, multiplied by 44, is conventionally converted into a value per 1 m.<sup>2</sup>, seeing that the sampler dredges mud (given in the same table) covering a bottom area of 225 cm.<sup>2</sup> at a time.

## Results and Discussions.

**Temperature.** The lowest value observed was 5.3°C, which was found on February 11, 1932, in the 1st layer. The highest value, which was observed on September 17, was 17.2°C in the 3rd layer in the deepest part of the lake, and 19.3°C. in the 1st layer at 4.7 m. depth. Thus the mud temperature, which varies from 5.3°C. to 17.2°C. throughout the year in the deepest part of Takasuka-numa, seems to attain its maximum during the period from the end of September to the middle of October.

It is also noteworthy that, during the period from December 1932 to the following February, the temperature of the muds increased from its surface towards its deeper parts, indicating that heat flows from the muds

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(14) Sugawara, *Bull. Chem. Soc. Japan*, **9** (1934), 446.

(15) Russel, "Soil Condition and Plant Growth," 6th edition, 579, London, (1932).

into the lake water during this season, while during the period from March to the end of September, matters are reversed, the mud temperature increasing from the deeper parts towards the surface.

There are, therefore, two periods in which the flow of heat occurs in mud in opposite directions, between which are two others, where the flow is minimized.

These points will be better understood if we compare the temperature of the muds with that of the bottom water, which is given in the bottom row in the table. But here we meet a difficulty. On March 30 and on April 17, the temperature of the bottom water was lower than that of the muds. Had the temperature relation been reversed, that is, had the temperature of the water been higher than that of the muds, the circumstance could easily be explained. This difficulty should be settled by further studies.

The presence of temperature gradients along the vertical line and its seasonal reversal in sense are of special importance to mud metabolism. They may, on the one hand, affect the migration of benthos either from the surface layer towards the deeper layer or in reverse direction; they may also lead to increase in the vicissitudes of the microflora in different parts of the muds. On the other hand, they may affect the equilibrium, purely physical and chemical, in muds.

For example, they could control the diffusion of dissolved or colloidal dispersed matter through muds by capillary action, which matter could sometimes diffuse into the overlying bottom water, or, contrary to it, they may, another time, be carried back into the deeper muds, and accumulated there to a higher concentration, and thus give rise to unequal distribution of matter in various parts of the mud.

Table 4. Temperature of Muds in °C. (1932-33)

| Depth | Dec.<br>28 | Feb.<br>11 | Mar. 30<br>(a) (b) | Apr.<br>17 | May<br>7 | June<br>11 | Aug.<br>11 | Sept. 17<br>(a) (b) | Oct.<br>22 | Dec.<br>3 |
|-------|------------|------------|--------------------|------------|----------|------------|------------|---------------------|------------|-----------|
| ↓     | 5.5        | 5.3        | 9.1 9.5            | 10.3       | 13.4     | 14.5       | —          | 16.6 19.3           | 17.0       | 9.4       |
|       | 5.6        | 5.4        | 9.1 —              | 9.8        | 12.8     | 13.7       | —          | 16.6 18.1           | 17.1       | 9.7       |
|       | 5.9        | 5.5        | 9.0 9.0            | 9.6        | 12.5     | 13.8       | —          | 17.2 17.8           | 17.0       | 10.3      |
|       | 6.1        |            | 8.3 8.6            | 9.1        | 12.4     | 14.0       | —          | 16.4                |            | 10.9      |
|       | 4.6        | 5.0        | 8.0                | 8.7        | 14.1     | 15.8       | 15.9       | 17.3                | 16.5       | 8.8       |

**The pH-value.** (1) No marked seasonal or vertical fluctuation in pH could be noticed. It varied from 5.70 to 7.54; the former value was recorded on September 17 in the top layer and the latter on February 11 in the 4th layer.

(2) It is notable that the top layer has always a smaller pH than the deeper ones, which is assumed to be due to the following two causes:

First, during the period of circulation, some constituents of the surface muds are oxidized into acidic substances by the oxygen dissolved in the overlying water, whereby the pH of the mud is diminished.

Secondly, decrease in pH can also result secondarily. Very often

the amount of mud in the top layer is not sufficient to fill the Petri-dish, leaving an air space in it, which is never the case with the other layers, where a larger quantity of mud is always available. Thus, while awaiting its turn to be examined, the mud of the top layer, being exposed to atmospheric oxygen, is oxidized, thus resulting in decrease of its  $pH$ . The smaller  $pH$  shown by the top layer mud during the period of stagnation, can be explained by these two reasons.

(3) It is also notable that  $pH$  tended to diminish from winter to summer, where it attains its minimum, and increases towards autumn. On February 11, the  $pH$ -values in almost all the layers were exceptionally small, of which no adequate explanation has yet been made.

(4) In comparing the distribution of benthic animals with the data of  $pH$ , it is remarkable that, in winter and spring, when the density of *Corethra* larva is larger, the variability in  $pH$  in the different layers of mud is larger than in summer, when the larval density is greatly reduced.

Table 5. The  $pH$  of muds (1932-33).

| Depth | Nov.<br>12 | Dec.<br>28 | Feb.<br>11 | Mar.<br>30 | Apr.<br>17 | May<br>7 | June<br>11 | Aug.<br>11 | Sept.<br>17 | Oct.<br>22 | Dec.<br>5 |
|-------|------------|------------|------------|------------|------------|----------|------------|------------|-------------|------------|-----------|
| I     | 6.40       | 7.05       | 6.67       | 6.29       | 6.44       | 6.92     | 6.57       | 6.62       | 5.70        | —          | 6.87      |
| II    | 6.72       | 7.07       | 6.92       | 6.70       | 7.07       | 7.08     | 6.85       | 6.71       | 6.77        | 6.74       | 6.96      |
| III   | 6.73       | 7.03       | 6.77       | 7.07       | 6.92       | 6.94     | 6.85       | 6.73       | 6.87        | 6.92       | 6.97      |
| IV    | 6.54       | 7.23       | 7.54       | 6.96       | 7.13       | 6.92     | 6.82       | 6.75       | 6.90        | 6.89       | 6.97      |
| V     | 6.53       | 7.05       | 6.85       | 7.01       | 6.71       | 6.88     | 6.77       | 6.82       | 6.91        | 6.99       | 6.91      |
| VI    | 6.26       | 7.09       | 6.93       | 7.00       | 7.02       | 6.84     | 6.81       | 6.84       | 6.91        | 7.02       | 6.94      |
| VII   |            | 6.98       | 6.95       | 6.95       | 6.85       |          | 6.79       | 6.81       | 6.92        | 6.98       | 7.00      |
| VIII  |            | 7.03       |            |            |            |          | 6.80       | 6.85       |             |            | 6.85      |

Table 6. Variation in bacterial number (millions per 1 c.c.) (1932-33).

| Depth | Nov.<br>12 | Dec.<br>28 | Feb.<br>11 | Mar.<br>30 | Apr.<br>17 | May<br>7 | June<br>11 | Aug.<br>11 | Sept.<br>17 | Oct.<br>22 | Dec.<br>5 |
|-------|------------|------------|------------|------------|------------|----------|------------|------------|-------------|------------|-----------|
| I     | 0.54       | 1.40       | 1.13       | 1.05       | 0.49       | 0.82     | .          | 0.77       | 0.53        | 0.60       | 0.68      |
| II    |            |            | 1.14       | 1.02       | 1.00       | 1.35     | 1.18       | 0.78       | 0.51        | 0.56       | 0.90      |
| III   | 0.67       | 1.27       | 1.03       | 1.00       | 1.30       | 1.24     | 1.16       | 0.91       | 0.47        | 0.54       | 0.52      |
| IV    |            |            | 0.98       | 0.65       | 0.87       | 1.21     | 1.02       | 1.00       | 0.58        | 0.42       | 0.45      |
| V     | 0.63       | 1.52       | 1.42       | 0.91       | 1.05       | 1.03     | 1.16       | 0.85       | 0.59        | 0.60       | 0.57      |
| VI    | 0.53       |            | 1.35       | 1.08       | 0.79       | 0.86     | 0.85       | 0.17       | 0.36        | 0.58       | 0.58      |
| VII   |            | 1.32       | 1.33       | 0.51       | 0.85       |          | 0.44       | 0.11       |             | 0.64       | 0.50      |
| VIII  |            | 0.98       |            |            | 0.74       |          | 0.60       |            |             |            | 0.57      |

Further, it is worth mentioning that the layer with a considerably larger  $pH$  is always that in which more *Corethra* larvae are counted.

On February 11, contrary to the general relation above, *Corethra* larvae were most abundant in the 3rd layer, while maximum pH was seen in the 4th layer. This discordance, however, can be explained by the fact that, on that day, the determination of benthos and that of pH were carried out on separate samples. In that case, should the thickness of the muds dredged by one operation differ from that of the next, there is the contingency, notwithstanding all precautions, hence remote, that a particular zone of the layers in one dredging may not exactly correspond to that in the layer of another.

**Bacteriological Examination.** (1) The number of bacteria reached maximum on December 28, 1932, in the 5th layer and minimum on August 11, the following year, in the 7th layer. In a year, the number varies between the two extremes of 100,000 and 1,500,000.

(2) On the other hand, there is a tendency for the number to grow somewhat towards winter and spring and diminish towards summer and autumn a variation in the number of bacteria that seems to be intimately related to the distribution of *Corethra* and Orthoclaadiinae larvae. As a matter of fact, on December 28, 1932, when the benthic animals were most abundant, the number of bacteria attained also its maximum. Thence until May 7, the following year, there was only a barely discernible decrease.

Now, in June, especially in the 6th and 7th layers, a marked decrease was seen in the bacterial number, which extended towards the top layer and continued until September 17.

On August 11, when, in the 7th and 8th layers, no individuals of *Corethra* or Orthoclaadiinae larvae could be found, the number of bacteria fell to the order of 100,000.

In September, the bacteria began to increase in number.

(3) On comparing the data for December 3 with those in the previous December, it was found that the former values were much smaller than those in the latter. This difference can easily be explained when we consider that, in the previous December, the observation was made later in the season by practically one month than that in the following year, so that, during that interval of one month, a sudden increase in number of bacteria was quite possible.

**The Examination of Macroscopic Benthic Animals.** From the observation of benthic animals, the following results were obtained.

(1) During the greater part of the year, the muds at all the depths examined were inhabited by a considerable number of *Corethra* or Orthoclaadiinae larvae, by whose movements the muds at different depths can be mixed, affording chances for the products of mud metabolism to be carried into the lake water, and for certain substances in the overlying water to be brought into the deeper parts of the muds.

The greater part of the bacteria mentioned in the previous article may have entered the muds by this latter course. Thus their number greatly declined in August, when the number of *Corethra* larva was also reduced.

(2) The number of *Corethra* larva increased from the end of

December 1932, to the following February, after which there could be found no marked change until May, when the number began to decrease until September 17, when it attained its minimum value and began to increase towards winter.

Thus the number of *Corethra* larva in Takasuka-numa varies between 1190 and 8700 per m.<sup>2</sup>

Table 7. Variation in the distribution of macroscopic benthic animals (1932-33).

| Depth | Dec. 28           |                   | Feb. 11 |       | Mar. 30 |       | Apr. 17 |       | May 7 |       |
|-------|-------------------|-------------------|---------|-------|---------|-------|---------|-------|-------|-------|
|       | (a)<br>Cor. Orth. | (b)<br>Cor. Orth. | Cor.    | Orth. | Cor.    | Orth. | Cor.    | Orth. | Cor.  | Orth. |
| I     | 1 0               | 5 1               | 9       | 0     | 0       | 0     | 4       | 1     | 6     | 2     |
| II    | 8 0               | 13 0              | 35      | 1     | 5       | 0     | 20      | 5     | 8     | 1     |
| III   | 12 0              | 30 0              | 53      | 1     | 44      | 2     | 34      | 6     | 15    | 0     |
| IV    | 35 1              | 31 2              | 35      | 1     | 29      | 4     | 66      | 7     | 19    | 4     |
| V     | 50 8              | 33 1              | 3       | 1     | 23      | 1     | 24      | 1     | 15    | 2     |
| VI    | 8 1               | 9 1               | 5       | 2     | 2       | 5     | 8       | 0     | 6     | 0     |
| VII   | 0 1               |                   |         |       | 1       | 1     | 2       | 0     |       |       |
| VIII  | 5 0               |                   |         |       |         |       |         |       |       |       |
| Sum   | 119 11            | 121 5             | 198     | 6     | 104     | 13    | 158     | 20    | 69    | 7     |
| × 44  | 5240 480          | 5300 220          | 8700    | 260   | 4600    | 570   | 6950    | 880   | 3040  | 310   |

| Depth | June 11 |       | Aug. 11 |       | Sept. 17 |       | Oct. 22 |       | Dec. 3 |       |
|-------|---------|-------|---------|-------|----------|-------|---------|-------|--------|-------|
|       | Cor.    | Orth. | Cor.    | Orth. | Cor.     | Orth. | Cor.    | Orth. | Cor.   | Orth. |
| I     | —       | —     | 3       | 0     | 8        | 0     | 3       | 0     | 2      | 0     |
| II    | 6       | 1     | 7       | 0     | 5        | 0     | 3       | 0     | 4      | 0     |
| III   | 29      | 0     | 13      | 0     | 5        | 1     | 7       | 1     | 5      | 0     |
| IV    | 20      | 0     | 8       | 0     | 7        | 0     | 9       | 0     | 14     | 0     |
| V     | 19      | 1     | 0       | 0     | 1        | 2     | 34      | 0     | 8      | 0     |
| VI    | 2       | 0     | 0       | 0     | 1        | 1     | 17      | 0     | 16     | 1     |
| VII   | 1       | 1     | 0       | 0     |          |       | 6       | 1     | 15     | 0     |
| VIII  |         |       |         |       |          |       |         |       | 1      | 0     |
| Sum   | 77      | 3     | 31      | 0     | 27       | 4     | 79      | 2     | 65     | 1     |
| × 44  | 3390    | 130   | 1370    | 0     | 1190     | 180   | 3480    | 90    | 2860   | 44    |

Cor. = *Corethra* larva. Orth. = Orthoclaadiinae larva.

(3) As to the vertical distribution of the animals, the following points were established. The zone that showed maximum density of animals is in the 5th layer on December 28, 1932, later shifting upwards to the top layer, in September.

The sense of shift thenceforth reversed, and the zone of maximum density suddenly dropped to the 5th layer in October and to the 6th in December.

Thus the zone of maximum density of benthos, **which** shifts upward first, does so downward in the latter half of the **year**, **forming** an annual cycle.

Finally, no individual was found on December 28, 1932, in the 7th layer, and on March 30 in the top layer, and on August 11 in the 6, 7. and 8th layers.

(4) Orthocladiinae larvae were too scanty to offer a clue to any reliable relationship, although they showed that their number increased from December to April, after which it decreased. In August, the animal disappeared completely from all mud depths, after which it began to increase in number again.

### The Chemical Composition of Muds.

Determination of the chemical composition of the muds of a lake is indispensable to systematic study of lake metabolism. On the one hand, it provides knowledge of the transitions the lake has undergone, while, on the other, it gives us some knowledge of the metabolism that has occurred, or is occurring, in the muds themselves.

Many examples of chemical analyses of lake deposits have been reported. In the older examples of such analyses, attention was paid more to the mineral constituents than to the organic ones, the knowledge of which latter, however, is more important to the present problem.

The greater part of recent studies, in which the organic constituents have been treated, are of little help to us, because the objects of their research differ from ours.

Thus, for example, W. Ohle<sup>(12)</sup> determined the organic constituents of the bottom deposits of the "kleines Ukleisee" from the top layer, every 1 m. vertically down to 11 m. This study, the purpose of which was to obtain support for the "lignin theory" of Fr. Fischer, contributed much to the knowledge of the geological transition of the lake itself and of its neighbourhood, but not so much to that of lake metabolism.

The same could be said of many other studies, which were undertaken for the purpose of elucidating the mechanisms of petroleum formation.

The only example of organic analysis of lake muds performed from the view-point of pure limnology, is that of S. Kusnetzov,<sup>(16)</sup> who estimated the sugar, pentosan and hemicellulose, cellulose, lignin and humus, wax and pitch, fatty acids, etc., of samples from two different layers that were 0-5 cm. and 25-40 cm. from the surface of the muds in Lakes Beloje, and 0-5 cm. and 10-15 cm. from the same in Glubokoje, both near Moscow.

The following analysis by the writer was started as an indispensable item in a programme for studying lake metabolism; it brought about some results worth mentioning.

These results, together with those of Kusnetzov, help us in contributing data for geochemistry a long neglected branch of science.

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(16) Kusnetzov, *Verhandl. d. Internat. Vereinigung f. theoret. u. angew. Limnologie*, 7 (1935), 571-582.



### Methods.

The muds that were analysed were dredged on February 11, 1933, from the deepest part of Takasuka-numa. They were 17.5 cm. thick, divided into seven layers, each 2.0 cm. thick, except the bottom layer, which was 5.5 cm. thick. A part of each of the seven kinds of samples thus prepared, was used in determining the bacteria, as shown in the preceding article, while the remainder was used for the chemical analyses, which were made as follows.

First, the density of the sample is determined. Then, by drying at 110°C, the water content of the muds is determined. With the dried sample, the ignition loss and its mineral constituents are determined.

**Determination of the Mineral Constituents.** *Determination of silicon, aluminium, and iron.* For determining the mineral composition, about 0.5 g. of the dried preparation is fused with carbonate mixture, and its silica content determined after the usual method. The filtrate from the silicic acid is made up to 50 c.c., 8 c.c. of which are used for precipitating the aluminium and iron. The precipitated iron and aluminium are dissolved in a small quantity of hydrochloric acid and then diluted to 50 c.c., 20 c.c. of which solution are evaporated to dryness. To the residue, after cooling, are added 5 c.c. of conc. hydrochloric acid. The residue immediately dissolved into a yellow solution, the content of iron in which is determined by the iodometric method of Blackwood-Stirling.<sup>(17)</sup>

From another 8 c.c. of the 50 c.c. filtrate from the silicic acid, iron and aluminium are precipitated as mixtures of their hydroxides, ignited and then weighed as a mixture of ferric oxide and aluminium oxide.

The content of aluminium in the dried preparation is calculated as alumina by reducing the iodometric iron value from the total weight of iron and aluminium oxides.

*Determination of manganese.* 20 c.c. of the filtrate from the silicic acid are used. Hydrochloric acid gas is driven off by evaporation until the residue remains slightly moist. 30 c.c. of water are added, and the residue is dissolved by warming. 0.5 c.c. of colourless concentrated nitric acid and a sufficient quantity of 1% silver nitrate solution are added to precipitate the chlorine ions. 2–3 c.c. in excess of silver nitrate solution are then added and the solution filtered. The precipitate is washed with about 50 c.c. of dilute nitric acid. The filtrate is now evaporated down to about 10 c.c., to which is added 5 c.c. of 10% ammonium persulphate solution. After warming for ten minutes on a water bath, it is diluted with water to 30 c.c. and then compared with standard potassium permanganate solution, 1 c.c. of which contains 0.02 mg. of manganese.

*Determination of calcium.* From the 50 c.c. filtrate from the silicic acid, 20 c.c. are taken, and after separating the iron and the aluminium, the filtrate is neutralized with hydrochloric acid, using methyl red as indicator, and 5 c.c. of ammonium sulphide solution added. After setting aside for 24 hours, the precipitate is filtered off and the filtrate boiled for some time. The precipitate formed during the boiling is filtered off. The filtrate is acidified with hydrochloric acid, evaporated to less than 10 c.c., and neutralized with ammonia and diluted to 30 c.c. To the resulting solution is added, in turns, 5 c.c. of 0.025 N oxalic acid and 0.5 c.c. of 0.1 N hydrochloric acid. The liquid is then neutralized by the addition of 0.2 N ammonia, a drop being added at a time, with 5 minutes' interval after each addition. Neutralisation is continued until the pH of the liquid is 7.8. A further 0.6 c.c. of ammonium oxalate is then added. After two days, the precipitate is filtered off, washed with saturated ammonium oxalate solution, which is regulated to a pH of 7.8, and then ignited in a small platinum crucible.

The ammonium sulphide solution is prepared as follows: Concentrated ammonia is diluted with an equal volume of water, and hydrogen sulphide gas is passed through the solution to saturation. The resulting solution is diluted with the same volume of half-diluted ammonia.

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(17) Blackwood and Stirling, *Biochem. J.*, **26** (1932), 353.

*Determination of phosphorus.*<sup>(18)</sup> 2 c.c. of the 50 c.c. filtrate from the silicic acid, are diluted to 10 c.c. after which 1.2 c.c. of 60% perchloric acid, 1 c.c. of 5% ammonium molybdate solution, and 0.5 c.c. of 1 aminonaphthol-(2)-4-sulphonic acid solution are added, and water to make the whole 15 c.c.

A standard containing 1 mg. of  $P_2O_5$  per 1 c.c. and a quantity of ferric chloride equivalent to the iron content of the sample solution is prepared at the same time and in the same way.

The contents of the flask are gently shaken between each addition, and finally mixed by inverting and shaking. The colours are read after five minutes in a Duboscq colorimeter.

The 0.2% aminonaphtholsulphonic acid is prepared as follows: 0.5 g. of the acid, 40 g. of sodium bisulphite, and 6 g. of crystalline sodium sulphite are dissolved by shaking with enough water to make 250 c.c. If the solution does not filter clear, it should be left overnight and again filtered. A fresh solution should be prepared every two weeks.

**Determination of the Organic Constituents.** Separate portions of the dry preparation are used for determining carbon and hydrogen, total nitrogen, ammoniacal nitrogen, and for the complete organic analysis.

(a) Carbon and hydrogen are determined by microanalysis after Pregl, for which the writer is much indebted to Dr. Shu Furukawa.

(b) For the determination of total nitrogen, 0.1 g. of the material is taken in a small Kjeldahl flask. 1 c.c. of concentrated sulphuric acid, three drops of 5% copper sulphate solution, and 0.05 g. of potassium persulphate are added successively, and the flask is heated for a few hours until the liquid is completely decolourised, when the ammonia content of the liquid is measured in the usual way.

(c) For the determination of ammoniacal nitrogen, 0.5 g. of the dry material is suspended in 30 cc. of distilled water, to which is then added 0.5 c.c. of 1% soda solution, which is sufficient to bring the pH of the liquid to that point where the bromothymol-blue turns blue. Through the suspended matter, air is bubbled for some 40 minutes. The air, here used, is previously freed from traces of ammonia by concentrated sulphuric acid. The ammonia driven off, is absorbed by 10 c.c. of 1/70 N hydrochloric acid solution and estimated by the usual method.

(d) The complete organic analysis is carried out mainly after S. A. Waksman,<sup>(19)</sup> on two or more of 2 g. portions of the dry material.

The procedure is as follows: The material is first extracted with ether in Soxhlet for 20 hours. For this process, 100 c.c. of ether are used, 50 c.c. being added at the start, and the remaining 50 c.c. later. The ether-soluble portion of the material is then determined by evaporating the ether, then drying the residue in a weighing bottle at 90°C. until a constant weight is attained. The residue, left after the ether treatment, is separated from its container, the cylindrical filter paper, by cutting the latter and washing out the contents into a beaker. Water is added to 100 c.c. and the suspended matter is shaken overnight, after which the liquid is filtered and washed with 100 c.c. distilled water for 10 hours. The filtrate from the cold water digestion is condensed into 50 c.c., of which 5 c.c. is used for determining the reducing sugars.

The residue from the cold-water treatment is now digested with 100 c.c. of hot water for two hours in a water bath. The liquid is filtered off and the residue washed with hot water until the filtrate is colourless. The filtrates are combined and evaporated to a small volume, in order to determine the reducing sugar contained. The residue is dried and then extracted with 100 c.c. of boiling alcohol for 5 hours. The filtrates are combined and evaporated, in weighed dishes, to a constant weight at 90°C.

The residue is dried and extracted with 100 c.c. of 2% hydrochloric acid for 5 hours. The hot extract is filtered through filter paper that has been previously dried and weighed, the residue being washed into the filter and treated with distilled water until free from acid. The combined filtrate and washings are analysed for total nitrogen and total reducing sugar (an aliquot portion of the solution having been

(18) King, *Biochem. J.*, **26** (1932), 294.

(19) Waksman and Tenney, *Soil Science*, **24** (1927), 275-283.

neutralised with 40% sodium hydroxide solution). To get the hemicellulose content of the mud, the total reducing sugar is next multiplied by 0.9.

The residue left on the paper after the treatment with dilute acid is dried for 24 hours at 70°C. and weighed. About a 0.3–0.6 g. portion is taken from the dried residue and treated with 5 c.c. of 80% sulphuric acid. The acid is allowed to act in the cold for 2 hours and then 75 c.c. of distilled water are added, and the content is boiled for 5 hours under a reflux condenser. The extract is now filtered through a small dried and weighed quantitative filter paper. The residue is washed thoroughly with distilled water, dried at 70°C., and weighed and finally divided into two portions, one of which is ignited to determine the ash and the other is used to determine the total nitrogen. The weight of the residue after the sulphuric acid treatment, minus the sum of the weight of the ash, and of the total nitrogen which has been multiplied by 6.25, gives the lignin content of the 0.3–0.6 g. portion left after the treatment with dilute hydrochloric acid. From this value, the percentage of lignin in the initial substance is further calculated.

The filtrate from the 80% sulphuric acid solution is analysed for sugar, an aliquot portion having been neutralised previously with 40% caustic soda solution. The reducing sugar multiplied by 0.9 gives the cellulose content in the portion.

The determination of reducing sugar is carried out mostly according to Ch. S. Hanes.<sup>(20)</sup>

### Results and Discussions.

When we compare the data of analysis (Tables 8 and 10) with those of other lakes, whether in Japan or abroad, we easily find a number of facts of special interest, whose description, however, will be here dispensed with, owing to risk of straying from the main object.

**Vertical Variations in Mineral Constituents.** The mineral constituents may be classified into three groups, according to their modes of vertical variation.

Table 8. Vertical variation in the chemical composition of the mud from Takasuka-numa. (A)

| Depth                              | I     | II    | III   | IV    | V     | VI    | VII   |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Density                            | 1.250 | 1.260 |       | 1.260 | 1.263 | 1.280 | 1.285 |
| Weight Decrease(%)<br>(110°C)      | 79.61 | 78.97 |       | 78.50 | 78.08 | 76.08 | 75.60 |
| Loss on ignition (%)               | 18.69 | 18.94 | 18.94 | 19.08 | 18.83 | 18.12 | 17.95 |
| SiO <sub>2</sub> (%)               | 47.48 | 47.79 | 47.73 | 48.03 | 47.93 | 46.88 | 46.29 |
| Fe <sub>2</sub> O <sub>3</sub> (%) | 14.30 | 14.37 | 14.23 | 14.46 | 14.84 | 15.51 | 16.22 |
| Al <sub>2</sub> O <sub>3</sub> (%) | 13.63 | 14.29 | 14.60 | 15.29 | 14.49 | 14.08 | 13.63 |
| MnO (%)                            | 0.64  | 0.60  | 0.61  | 0.61  | 0.66  | 0.74  | 0.76  |
| CaO (%)                            | 2.06  | 1.98  | 1.83  | 1.71  | 1.58  | 1.58  | 1.86  |
| P <sub>2</sub> O <sub>5</sub> (%)  | 0.17  | 0.16  | 0.14  | 0.23  | 0.17  | 0.18  | 0.15  |

*Group. I.* Silica and alumina belong to this group. Their percentages grow from the top layer towards the fourth, where they attain

(20) Hanes, *Biochem. J.*, **23** (1929), 99.

their maxima, after which they diminish with depth. The loss on ignition also varies in parallel with the foregoing.

*Group II.* The iron and manganese oxides belong to this group. Their percentages grow evenly from the top towards the deepest layer, except two anomalous values, which are found for iron in the third layer and for manganese in the top layer. This anomaly in manganese is possible of satisfactory explanation, as will be seen later.

Now, although a part of the iron and manganese may come as components of dead plankton, it is, at any rate, insignificant, while the remaining major part probably comes as ingredients of the clayey substances that are carried into the lake by influent waters.

Notwithstanding this, the mode of vertical variation in the iron and manganese oxides differs entirely from that of alumina and silica—a point on which a satisfactory explanation is desired.

First we shall examine the ratio of ferric oxide to silica (Table 9). It is remarkable that the ratio keeps constant from the top to the fourth

Table 9. The ratios of iron, aluminium and manganese to silicon as their oxides at various depths of the mud of Takasuka-numa.

| Depth                          | I      | II     | III    | IV     | V      | VI     | VII    |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Fe <sub>2</sub> O <sub>3</sub> | 0.301  | 0.301  | 0.298  | 0.301  | 0.310  | 0.331  | 0.350  |
| Al <sub>2</sub> O <sub>3</sub> | 0.286  | 0.298  | 0.300  | 0.318  | 0.302  | 0.300  | 0.294  |
| MnO                            | 0.0134 | 0.0126 | 0.0128 | 0.0127 | 0.0136 | 0.0157 | 0.0164 |

layer, its value lying between 0.301 and 0.298, while the ratio increases further, downwards, to 0.350 in the seventh layer. The same may be said of manganese. The ratio of manganese oxide to silica, except in the top layer, varies between 0.0126 and 0.0127 to the fourth layer, after which it begins to increase downwards until it is 0.0164 in the seventh layer, whence we may conclude that, in muds of about 8 cm. thickness from the surface, the four elements, silicon, aluminium, iron, and manganese are distributed quite uniformly.

Conditions differ, however, at depths below 8 cm. Here the ratios of iron and manganese to silicon are no longer constant; they increase with depth.

In contrast to the foregoing, the ratio of aluminium to silicon seems to decrease at the seventh layer, although the decrease is much smaller in amount compared with the increase in iron or manganese. Moreover, accuracy in analysis in the case of aluminium falls below those of the other elements in question. Thus, when we take these circumstances into consideration, we see that it is better, instead of stressing the matter of decrease, to conclude, as just mentioned, that the ratio of alumina to silica is practically constant through all the depths that were examined.

*Explanation I.* The simplest explanation possible from the foregoing examination is that the ratios of iron and manganese relative to the elements of the first group that were all carried into the lake, varied

gradually in decreasing proportion from the time when the deepest muds deposited until the muds of the fifth layer settled. Then the variation in the ratio stopped; further deposition occurred and continued at the fixed ratio until the present.

Explanation II. There is another possible explanation, in which the variation in the ratios of iron and manganese to silicon and aluminium are assumed to have continued to occur up to the present time, and the uniform distribution of the four elements in question in the upper layers of mud is assumed to have been brought about secondarily by the micro-organisms present. In fact, the upper four layers (8 cm.) are densely inhabited by *Corethra* and Orthocladinae larvae (Table 7), by the movements of which the upper and lower muds are mixed, resulting in uniform distribution of the elements in question, while the layers below 8 cm., which are inhabited by fewer of these insect larvae, are subject to less mixing, hence retaining the previous mean ratios.

Explanation III. In the preceding two explanations, we assumed that the ratios of iron and manganese to silicon and aluminium had varied during deposition of the mud layers in question.

We shall now examine this assumption. As a matter of fact, the time during which the mud layers in question had been deposited, is easily estimated from the result given in page 00 as three years, at least, but not much longer. That during such a short period of time, there should have occurred a considerable change in the ratios of the four elements in question that were carried into the lake by influent waters, is rather improbable. Therefore, in the third explanation, we must try to suppose that the ratio of the iron, manganese and silicon that were carried into the lake water remained constant during the time in question, and further suppose that the apparent change in the ratios occurred secondarily, in the course of settling, or after they had already settled on the bottom.

In order to follow this reasoning, it is necessary to note a certain peculiar property that distinguishes iron and manganese from silicon and aluminium.

The first to be mentioned is the oxidation-reduction property of iron and manganese. These elements are, indeed, deposited in higher oxidized forms, after which, owing to anaerobiosis in the deeper water layers or at the bottom, they are reduced partly into soluble or easily diffusible forms. When this occurs to any considerable extent, and if this occurrence grows more intense year by year, the result is nothing but a vertical decrease in the ratios in question towards the surface, that is, the ratio has a smaller value in the recently precipitated muds than in the older ones, notwithstanding the fact that during the time in question, there was no considerable change in the ratios of these elements that were carried into the lake water.

Now this idea, that the reduction of iron and manganese has been growing more intense during the time in question, seems to be supported by the data of organic analysis. Here the ratios of the various organic constituents of planktonic origin to silicon are also found to increase on the whole towards the surface, which can be explained by saying that the deposited quantity of organic debris has been increasing, that is,

the lake has become more eutrophic and consequently the reductive changes in the lake have grown more intense.

It must be added that, in the present case also, two different ways are conceivable in which the lake became more eutrophic. When we stress the importance of the mixing action of benthic animals, eutrophic action cannot be considered to have continued, not at least, at the same rate until the present, otherwise we have to agree that eutrophication stopped at the time when the fifth layer muds had settled.

Unfortunately, our knowledge at present is still too meagre to enable us to say which of the various explanations suggested above is correct.

*Group III.* Calcium oxide belongs to this group. Although its percentage decreases evenly towards depth, it suddenly begins to grow from the seventh layer.

Calcium differs from other elements in the way in which it is carried to the bottom. In fact, the water of Takasuka-numa, like in many other Japanese lakes, is so poor in calcium that the concentration of this ion is much less than that from which the calcium carbonate is precipitated, so that if calcium be carried to the bottom, it must occur in one of the following two ways.

Table 10. Vertical variation in the chemical composition of the mud from Takasuka-numa. (B)

| Depth                                            | I     | II    | III   | IV    | V     | VI    | VI    |
|--------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Carbon (%)                                       |       | 6.06  |       |       | 6.03  |       | 5.81  |
| Hydrogen (%)                                     |       |       |       |       |       |       | 1.50  |
| Total Nitrogen (%)                               | 0.719 | 0.852 | 0.770 | 0.702 | 0.700 | 0.660 | 0.638 |
| Ammoniacal nitrogen (%)                          | 0.005 | 0.007 | 0.005 | 0.002 | 0.004 | 0.006 | 0.007 |
| C/N                                              |       | 7.11  |       |       | 8.62  |       | 9.10  |
| Ether soluble fraction (%)                       | 0.43  | 0.47  | 0.65  | 0.65  | 0.65  | 0.50  | 0.48  |
| Alcohol soluble fraction (%)                     | 0.59  | 0.59  | 0.61  | 0.62  | 0.51  | 0.56  | 0.50  |
| Reducing sugars soluble in cold water (%)        | 0.24  | 0.24  | 0.19  | 0.24  | 0.23  | 0.21  | 0.18  |
| Reducing sugars soluble in hot water (%)         | 0.23  | 0.24  | 0.24  | 0.21  | 0.25  | 0.21  | 0.20  |
| Reducing sugars soluble in cold or hot water (%) | 0.47  | 0.48  | 0.43  | 0.45  | 0.48  | 0.42  | 0.38  |
| Hemicelluloses (%)                               | 3.37  | 3.44  | 3.65  | 3.09  | 3.68  | 3.54  | 4.16  |
| Cellulose (%)                                    | 0.77  | 0.86  | 0.82  | 0.79  | 0.92  | 0.90  | 1.09  |
| Lignin (%)                                       | 3.60  | 3.86  | 3.65  | 3.54  | 3.82  | 3.40  | 3.74  |
| Ash (%)                                          | 43.8  | 43.8  | 44.1  | 43.3  | 41.7  | 42.3  | 42.9  |

(1) Calcium, which is assimilated first as a body substance of planktonic organisms, is next deposited as a constituent of organic debris.

(2) When certain flocculent precipitates are formed in the lake water, for example, the coagulum of ferric hydroxide or that of planktonic debris, these coagulations tend to adsorb calcium ion from the water and to carry it to the bottom.

Of these two ways here assumed, the former accords with the view of the lake having become more eutrophic. As eutrophication progresses, the deposited amount of planktonic debris increases, with the result that much more calcium is carried down to the bottom, so that the percentage of calcium oxide is larger in the later deposits, namely, in the upper layer. But it is difficult to explain the sudden increase in the percentage in the deepest layer by this assumption, and this point can be interpreted more easily by means of the latter explanation.

These are points on which further researches, it is hoped, will be made.

Finally, the quantity of phosphorus being too small to give precise analytical results, it is not possible to say in what group it should be placed.

**Vertical Variations in Organic Constituents.** The results of organic analysis cannot be regarded as sufficiently accurate, there being many difficulties in the method itself, and not enough samples being at our disposal, but the main features can be seen at a glance.

- (a) The total nitrogen decreases with depth.
- (b) The total carbon seems to decrease in the same way.
- (c) The carbon-nitrogen ratio increases from 7.11 in the 2nd layer to 9.10 in the 7th layer.
- (d) The amount of ether-soluble fraction is large in the middle layers, but smaller in the upper and deeper layers.
- (e) The alcohol-soluble fraction behaves similarly but less evidently.
- (f) The amounts of the sugars soluble in cold and in hot water do not greatly differ. Their totals tend to decrease from the 5th layer with depth.

(g) Hemicelluloses, cellulose, and lignin show no marked variation except in the 7th layer, where their percentages are evidently larger.

In summarising the results, we conclude that nitrogeous and ether- or alcohol-soluble matters are distributed rather densely in the upper layers, and that the celluloses and lignin are in the deeper layers.

As one of the most probable causes that contribute to the development of such distribution of organic substances, we might mention the contingency of the lake becoming more eutrophic during the deposition in question. Thus the composition of muds has varied in such a way that the upper layers, that deposited later, are more planktonic, that is, they are richer in nitrogeous and in ether- or alcohol-soluble substances. Therefore the celluloses and lignin, mainly of littoral or allochthonic origin, became smaller in their relative proportions to these substances.

Another cause, not less important to the question of distribution of matter, is the decomposition of the celluloses or lignin in the lake bottom,

which is believed to become more intense the more the lake becomes eutrophic. Consequently, the proportion of these substances that have been left undecomposed will be reduced to that extent.

The effect also of the distribution of the benthic animals and other microorganisms and that of their excrements cannot be overlooked. And since it is obvious that the substances composing the bodies of these organisms and their excrements are rich in nitrogen, and are often of alcohol- or ether-soluble nature, it is quite conceivable that the distribution of these organisms in the muds affects directly the chemical composition of such muds. But, to what extent do these factors affect them? This is a question that, it is hoped, will be solved by further studies.

### **The Relative Ease with which Iron and Manganese Return to the Lake Water, and its Geochemical Significance.**

It is interesting to find that the ratio of iron to manganese is smaller in the lake water than in the muds, the ratio varying between 21.9 and 24.2 in the muds, as easily calculated from the data given in Table 9, while that in the lake water is, for example, 3.57 at the surface and 4.50 at a depth of 2 m., calculated as follows.

The content of iron is 0.87 mg./l., reckoned as  $\text{Fe}_2\text{O}_3$  at the surface, and 1.19 mg./l. at a depth of 2 m., being each the mean value of the result of six observations made in June 1935–January 1936. The manganese content, also calculated similarly, is 0.23 mg./l. at the surface and 0.25 mg./l. ( $\text{MnO}$ ) at a depth of 2 m. Therefore, the ratio is 3.57 and 4.50 at the two depths. It might be added that this ratio decreases in the deeper water zone (v. Tables 12 and 13).

This larger value of the ratio of iron to manganese in the mud appears to be due merely to the fact that the iron and manganese that were carried into the lake from outside, were already in that larger ratio when they were precipitated to the bottom, without any change in their relative ratio when they entered the lake, so that there is nothing odd in finding a larger ratio in the mud compared with that in the water. However, the actual situation is too complicated to be explained by such a simple cause alone.

The writer will now mention the following two characteristic properties of iron and manganese, one oxido-reductive and the other circulatory, which, no doubt, contribute much to the uneven distribution of iron and manganese, with a ratio in the mud different to that in the hydrosphere.

First, both elements have a circulatory property. As already mentioned, the iron and manganese that have settled on the bottom do not remain there long; a large part of them is transformed into the soluble state by anaerobic decomposition, after which they are returned to the water body.

Now, it is quite conceivable that this "returning" does not occur in a manner equally suitable to both elements; the manganese seems to be better fitted for this process, owing to its oxidation-reduction potential, ( $\text{Mn}^{++} \leftrightarrow \text{Mn}^{+++}$ ), which is higher than that of iron ( $\text{Fe}^{++} \leftrightarrow \text{Fe}^{+++}$ ).



Therefore, when the supply of oxygen to the deeper water is hindered and an anaerobic condition begins to be set up at the bottom, as it does in early spring, the oxidation-reduction potential on the spot is gradually lowered to that point where reduction of manganese is made possible, after which the manganese will be immediately reduced, while the iron oxide remains unaffected, because of its lower reduction potential, so that, of the elements in question, manganese returns first into the hydrosphere.

Further, even when the oxidation-reduction potential on the spot falls to that point where the iron can be reduced to the ferrous state, resulting in the actual reduction of the iron, the ferrous iron thus formed, is immediately reoxidized by the higher oxide of manganese, so long as the latter is present in its vicinity. Thus manganese always precedes iron in returning into the water zone.

The result of these behaviours of the elements consists in nothing more than a larger accumulation of manganese in the water, with simultaneous decrease in the ratio of manganese to iron in the mud.

This view is directly supported by the results of studying deposition. As a matter of fact, as one of the items in the study, which will be given precisely later, the writer determined the iron and manganese contents of the water in a collecting bottle that was kept suspended at depth.

The result, which is given in Table 11, shows that the concentrations of these elements in the examined water were always larger than that in the surrounding water. (v. Tables 12 and 13).

These facts indicate that the larger part of the iron and manganese in the bottle water came, at least, from the deposit that had dropped into the bottle. Moreover, the fact that the ratio of iron to manganese is smaller in the water than in the deposit (Table 15), proves conclusively that redissolution by reduction takes place more readily in manganese than in iron.

Table 11. Iron and manganese contents of the bottle water.

|                                       | Oct. 20<br>(1935) | Nov. 11<br>(1935) | Jan. 19<br>(1936) |
|---------------------------------------|-------------------|-------------------|-------------------|
| Fe <sub>2</sub> O <sub>3</sub> mg./l. | 39.4              | 23.7              | 5.10              |
| MnO mg./l.                            | 12.5              | 22.4              | 0.95              |
| Fe <sub>2</sub> O <sub>3</sub> /MnO   | 3.15              | 1.06              | 5.37              |

Table 12. The iron content of the waters of Takasuka-numa during June 23, 1935—January 19, 1936. (reckoned as Fe<sub>2</sub>O<sub>3</sub> mg./l.)

| Depth (m.) | June 23 | July 24 | Sept. 29 | Oct. 20 | Nov. 11 | Dec. 15 | Jan. 19 |
|------------|---------|---------|----------|---------|---------|---------|---------|
| 0          | 0.75    | 0.44    |          | 0.80    | 1.76    | 0.79    | 0.66    |
| 1          |         | 0.50    | 0.16     | 1.30    | 1.83    |         | 0.53    |
| 2          | 1.11    | 0.83    | 0.86     | 1.20    | 2.60    |         | 0.56    |
| 3          | 0.75    | 0.89    | 3.02     | 0.73    | 1.81    | 2.01    | 0.57    |
| 4          | 1.05    | 5.04    | 6.52     | 1.39    | 1.87    | 0.93    | 0.83    |
| 5          | 4.00    | 14.4    | 17.7     | 21.8    | 2.47    |         |         |
| 5.5        | 6.75    |         | 36.9     | 27.9    | 1.75    | 5.87    |         |

Table 13. The manganese content of the waters of Takasuka-numa during June 23, 1935—January 19, 1936. (reckoned as MnO mg./l.)

| Depth (m.) | June 23 | July 24 | Sept. 29 | Oct. 20 | Nov. 11 | Dec. 15 | Jan. 19 |
|------------|---------|---------|----------|---------|---------|---------|---------|
| 0          | 0.06    | 0.02    |          | 0.40    | 0.37    |         | 0.24    |
| 1          | 0.05    | 0.01    | 0.11     | 0.85    | 0.50    |         | 0.14    |
| 2          | 0.07    | 0.11    | 0.18     | 0.23    | 0.68    |         | 0.16    |
| 3          | 0.07    | 1.11    | 0.45     | 0.70    | 0.45    | 0.18    | 0.20    |
| 4          | 0.86    | 0.82    | 1.05     | 0.95    | 0.69    | 0.24    | 0.13    |
| 5          | 11.2    | 11.2    | 10.3     | 10.6    | 0.84    |         |         |
| 5.5        | 13.8    |         | 18.6     | 12.8    | 0.67    | 0.59    |         |

Going a step further, it is expected that the ratio of iron to manganese in the lake water of Takasuka-numa has decreased to a considerable extent with lapse of time.

As said above, a part of the manganese and iron that had once deposited at the lake bottom returns into the hydrosphere with a ratio richer in manganese. The elements, thus returned to the hydrosphere, are now carried up by the circulation currents toward the upper layers, where they are oxidized and again precipitated to the bottom. The precipitated elements are then subjected to a second fractionation by reductive redissolution, with a much larger proportion of manganese.

Thus the repetition of such a cycle is expected to lead to a yearly decrease in the ratio of iron to manganese in lake water, also that in the deposits, and consequently in mud the ratio may have been gradually increasing from depth upward.

Actually, the vertical variation in the ratio in muds seems to accord generally with this view. Indeed, with the exception of the surface value, whose deviation is comprehensible to a certain extent when we take into consideration the season in which the mud was sampled, the ratio decreases evenly from the deepest layer of the oldest deposition toward the surface that was deposited recently.

It is also of some interest to examine the ratio of iron to manganese in the earth that constitutes the land surrounding the lake, which is regarded as the most important source of the iron and manganese in Takasuka-numa.

Table 14. Chemical composition of the soil surrounding Takasuka-numa

| Sample from the northern bank       |       | Sample from the path along the west beach |
|-------------------------------------|-------|-------------------------------------------|
| SiO <sub>2</sub> (%)                | 56.64 | 60.61                                     |
| Fe <sub>2</sub> O <sub>3</sub> (%)  | 6.55  | 6.31                                      |
| Al <sub>2</sub> O <sub>3</sub> (%)  | 19.92 | 17.40                                     |
| MnO (%)                             | 0.13  | 0.10                                      |
| Fe <sub>2</sub> O <sub>3</sub> /MnO | 50.4  | 63.1                                      |

For this purpose, the writer analyzed two kinds of soil samples, the one from the northern bank and the other from the path that runs along the western beach, the result of which is given in Table 14.

In both samples, the ratio of iron to manganese varied between 50.4–63.1, which is very large compared with that of the lake mud.

From this result, it is also very probable that if iron and manganese were supplied from the surrounding land soils, reductive redissolution played an important part, resulting in the relative concentration of manganese.

Next, it is worth mentioning that the concentration of manganese in the lake water seems to contribute to the geochemical separation of manganese from iron.

In the vadose zone of the earth's crust, iron is always accompanied with manganese. This is comprehensible when we consider the geochemical history of these elements.

Indeed, we have learned that manganese is found in juvenile rocks only in the state of manganous compounds, while the higher oxides of manganese, such as pyrolusite, occur as vadose through the oxidation of manganous compounds by atmospheric oxygen, after the latter have been dissolved in water and brought up to the surface of the earth.

The same may be said of iron. Since, it is then very natural that, in that condition wherein iron is precipitated as its higher oxide, manganese also is precipitated as such, we can easily understand that in the vadose zone of the earth's crust, iron is always accompanied with manganese.

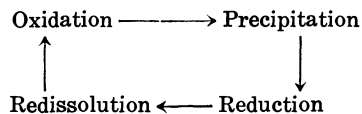
Now, in vadose minerals, there is another relation between manganese and iron which cannot be overlooked.

We usually find vadose minerals to consist mainly of iron with a little manganese, or mainly of manganese with a little iron, it being very seldom that we find minerals in which the ratio of iron to manganese had not such an extreme value.

The geochemical process above mentioned is unsuited for explaining the relationship, because the process, although it brings about the mixing of the two elements, does not cause their separation, so that it is necessary to search for another geochemical process that makes the segregation of manganese and iron possible.

As such a process, there is the returning of the manganese and iron by anaerobic decomposition of the organic detritus in the lake bottom that was fully discussed in the foregoing articles.

Now this process could not have existed until that time when life first appeared on the earth, since when there began a cyclic process for manganese and iron.



It is useless to repeat that, by the repetition of this cyclic process, manganese and iron gradually separated from each other, resulting in increase in the relative concentration of manganese in lake water.

It is not difficult to imagine that, as the destiny of such a lake, segregation of wad would occur, slightly contaminated with iron. On the other hand, it is also not so rare to find limonite contaminated with a slight admixture of manganese.

Thus we are led to the conclusion that the concentration of manganese in lake water, which is caused by the difference in the oxidation-reduction potential between iron and manganese, plays, at any rate, one of the most important parts in the geochemical fractionation of the two elements in question.

### Mud Deposition.

The annual deposition of mud has been estimated repeatedly by a number of investigators. For example, A. Reissinger gave it as 11.8–20.7 mm. in Niedersonthofensee during 1914–32. But no estimate of its annual variation has ever been reported.

In order to obtain some information in this respect, the writer carried out the following observations in Takasuka-numa for twenty months, and established the variation in the amount of deposition and the chemical nature of the deposits.

### Methods.

From four to six wide-mouthed glass bottles were fixed in a wooden frame, and then suspended at a depth of 1 m. above the deepest bottom of the lake. At intervals of about 21–67 days, they were hauled up, and their contents examined.

The sample of the deposits for chemical analysis was prepared as follows: 0.2 g. of the deposit, dried at 110°C., was digested with 2 c.c. of boiling concentrated hydrochloric acid in a small decomposition flask for about two hours: then 0.05 g. of potassium chlorate and 1 c.c. of the hydrochloric acid were added. After digestion for two hours more, 2 c.c. of the acid were again added, and the digestion was continued for another two hours. The liquid was filtered and washed and the filtrate condensed to 50 c.c.

The sample solution, thus prepared, was divided into sufficient portions for the determination of iron, aluminium, and manganese. Further treatment, together with the determinations of loss on ignition and total nitrogen were carried out as already described in a previous paragraph.

### Results and Discussions.

**Seasonal Variations in the Amount of Deposition** (v. Table 15). Owing, unfortunately, to accidental loss of the equipment, for two periods, one between November 11 and December 25, 1935, and the other between June 21 and September 13, 1936, data are unavailable, although there is little doubt that in the former of these two periods there occurred much deposition, as proved by the following facts.

Despite the heavy deposition that occurred during October 20–November 11, not only a large amount of solid matter remained in the lake waters on November 11, but its amount had increased from October to November, as will be seen from the determination of the residue on evaporation (v. Table 17 and Fig. 3).

Table 15. Annual variation in deposition in Takasuka-numa, and in its chemical composition. (1935-37)

| Date<br>(days)                                                   | June 23-<br>July 24<br>(31) | July 24-<br>Sept. 29<br>(67) | Sept. 29-<br>Oct. 20<br>(21) | Oct. 20-<br>Nov. 11<br>(22) | Dec. 25-<br>Jan. 19<br>(24) | Jan. 19-<br>Feb. 28<br>(40) | Feb. 28-<br>Mar. 26<br>(27) | Mar. 26-<br>Apr. 29<br>(34) |
|------------------------------------------------------------------|-----------------------------|------------------------------|------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Deposition during<br>the whole period<br>(mg./cm <sup>2</sup> .) | 131                         | 306                          | 160                          | 230                         | 18.5                        | 39.3                        | 35.5                        | 153                         |
| Deposition per day<br>(mg./cm <sup>2</sup> .)                    | 4.2                         | 4.6                          | 7.6                          | 10.5                        | 0.77                        | 0.98                        | 1.32                        | 4.50                        |
| Loss on Igni-<br>tion (%)                                        | 19.57                       | 19.84                        | 19.61                        | 19.17                       | 17.92                       | 15.30                       | 15.15                       | 14.40                       |
| (mg.)                                                            | 0.828                       | 0.907                        | 1.490                        | 1.970                       | 0.138                       | 0.150                       | 0.200                       | 0.648                       |
| Total nitrogen (%)                                               | 0.782                       | 0.814                        | 0.498                        | 0.736                       | 0.782                       | 0.675                       | 0.661                       | 0.622                       |
| (mg.)                                                            | 0.033                       | 0.037                        | 0.061                        | 0.077                       | 0.006                       | 0.007                       | 0.009                       | 0.028                       |
| Fe <sub>2</sub> O <sub>3</sub> (%)                               | 12.2                        | 11.2                         | 10.9                         | 11.3                        | 12.5                        | 9.96                        | 10.61                       | 8.85                        |
| (mg.)                                                            | 0.52                        | 0.54                         | 0.83                         | 1.17                        | 0.10                        | 0.10                        | 0.14                        | 0.40                        |
| Al <sub>2</sub> O <sub>3</sub> (%)                               |                             |                              |                              |                             |                             | 8.47                        | 9.21                        | 8.82                        |
| (mg.)                                                            |                             |                              |                              |                             |                             | 0.083                       | 0.122                       | 0.397                       |
| MnO (%)                                                          | 0.46                        | 0.63                         | 0.33                         | 0.94                        | 0.70                        | 1.03                        | 0.98                        | 1.12                        |
| (mg.)                                                            | 0.019                       | 0.029                        | 0.025                        | 0.099                       | 0.005                       | 0.010                       | 0.013                       | 0.050                       |

| Date<br>(days)                                                   | Apr. 29-<br>May 25<br>(26) | May 25-<br>June 21<br>(27) | Sept. 13-<br>Oct. 4<br>(21) | Oct. 4-<br>Oct. 25<br>(21) | Oct. 25-<br>Nov. 25<br>(31) | Nov. 25-<br>Dec. 26<br>(31) | Dec. 26-<br>Jan. 31<br>(36) | Jan. 31-<br>Mar. 5<br>(33) |
|------------------------------------------------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|
| Deposition during<br>the whole period<br>(mg./cm <sup>2</sup> .) | 78.0                       | 95.4                       | 258                         | 133                        | 31.1                        | 78.1                        | 43.9                        | 76.9                       |
| Deposition per day<br>(mg./cm <sup>2</sup> .)                    | 3.00                       | 3.09                       | 12.29                       | 6.34                       | 10.05                       | 2.52                        | 1.22                        | 2.33                       |
| Loss on Igni-<br>tion (%)                                        | 14.95                      | 15.47                      | 20.06                       |                            | 16.16                       |                             |                             |                            |
| (mg.)                                                            | 0.449                      | 0.478                      | 2.467                       |                            | 1.625                       |                             |                             |                            |
| Total nitrogen (%)                                               | 0.698                      | 0.718                      | 0.952                       |                            | 0.718                       |                             |                             |                            |
| (mg.)                                                            | 0.021                      | 0.022                      | 0.117                       |                            | 0.072                       |                             |                             |                            |
| Fe <sub>2</sub> O <sub>3</sub> (%)                               | 9.35                       | 9.04                       | 11.54                       |                            | 11.78                       |                             |                             |                            |
| (mg.)                                                            | 0.28                       | 0.28                       | 1.42                        |                            | 1.18                        |                             |                             |                            |
| Al <sub>2</sub> O <sub>3</sub> (%)                               | 8.67                       | 8.05                       | 8.75                        |                            | 13.39                       |                             |                             |                            |
| (mg.)                                                            | 0.260                      | 0.249                      | 1.075                       |                            | 1.345                       |                             |                             |                            |
| MnO (%)                                                          | 0.56                       | 0.54                       | 0.64                        |                            | 1.44                        |                             |                             |                            |
| (mg.)                                                            | 0.017                      | 0.017                      | 0.078                       |                            | 0.145                       |                             |                             |                            |

It is quite natural to suppose from the foregoing that, in the succeeding period, November 11 - December 25, still greater deposition occurred, the amount of which the writer estimated as follows:

First, it was assumed that the whole autumnal deposition did not differ much in amount in the two years 1935 and 1936, so that the amount of deposition for the period September 14 - December 24, 1935, was assumed to have been the same as that for the period September 14 - December 24, 1936. Consequently, 8.1 g. was obtained as the amount of deposition per day during the period, November 11 - December 24, 1935, and the gap in this was filled with a blank rectangle (v. Figs. 3 and 4).

A distinct parallel will now be seen between the variation in deposition and that in the mean values of the residue on evaporation in the

lake water from various layers, ranging from the surface to the bottom, as given in Fig. 3. For the same reason, the second gap between June 21 and September 13 of the following year should have been filled with a moderate quantity of deposits, the deposition curve running similarly to that in the preceding year.

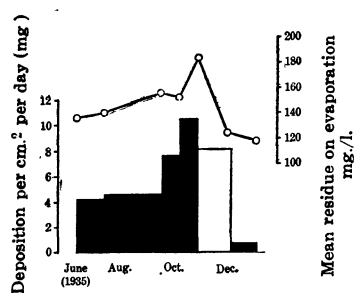


Fig. 3. Seasonal variation in the deposition in Takasukanuma and also in the mean residue on evaporation of the lake water (June 23, 1935—January 19, 1936.)

The deposition throughout the one and a half years actually varied, as follows:

The amount of deposition that began to increase at the beginning of autumn 1935, reached maximum during the period from the middle of November to that of December, after which it suddenly diminished to minimum from the end of December to the middle of January, the following year.

This condition lasted until the beginning of spring, when deposition increased to some extent, after which it again slightly declined during the succeeding time intervals, namely, April 19—May 25 and May 25—June 21.

The last mentioned interval seems to have been followed by moderate deposition that continued till the end of summer.

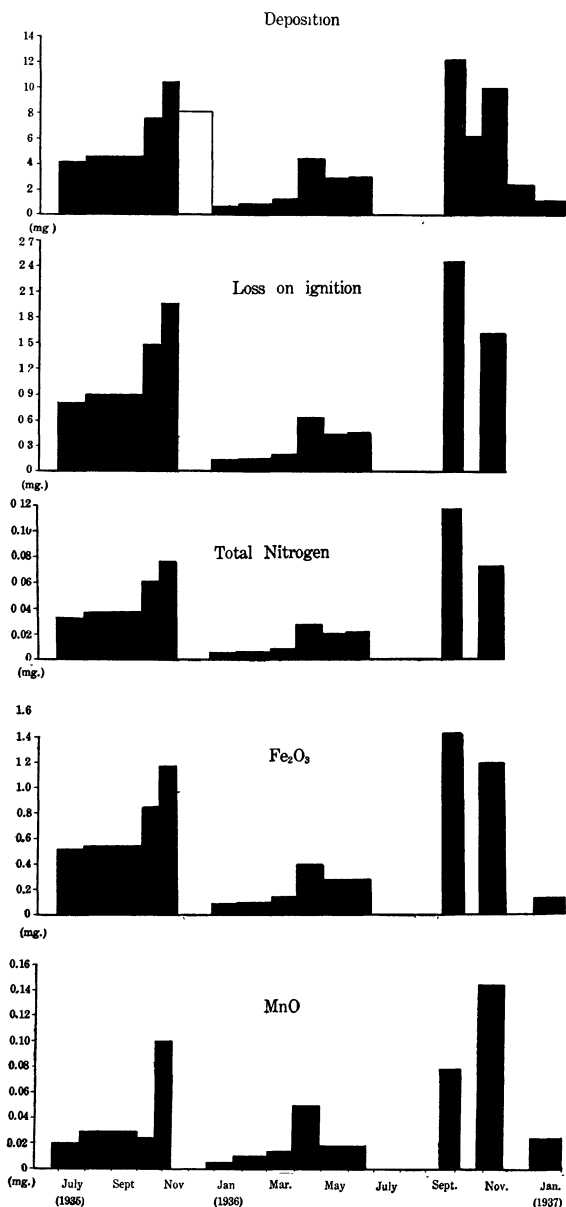


Fig. 4. Annual variation in the deposition in Takasuka-numa, and also in its chemical composition.

Then, as it did in the previous year, a heavy autumnal deposition followed, which continued till the end of November, making it evident that the annual variation in deposition in Takasuka-numa has two maxima, a distinct one in autumn and another one less distinct in spring, with a minimum in winter and a moderate (medium) deposition period ranging from middle spring to the end of summer.

These maximum and minimum will hereafter be called the 'autumnal vernal maximum', and the 'winter minimum', respectively.

In certain years, these maximum and minimum may come earlier and in others, later, as the result of meteorological conditions, etc., whence it is comprehensible that, in 1936, the autumnal maximum seemed to have begun and ended somewhat earlier than in the previous year.

It is also remarkable that the autumnal maximum in 1936 differed from that in the previous year, the development of the two peaks in the graph being supposed to be the effect of meteorological conditions.

At any rate, the diurnal deposition per  $\text{cm}^2$  varied between the two extreme values of 0.77 mg. and 12.29 mg. in dry weight, the deposition for the whole year having amounted to 1.66 g. which would fill the bottom to a thickness of 5.88 cm., assuming that the density and the water content of the deposit were as large as those of the bottom mud.

It is also notable that this amount of deposition for the whole year surpassed all the values hitherto reported for various lakes.

**Chemical Composition of Deposits and its Seasonal Variations.** (a) The loss on ignition was larger in the samples from the end of June to the beginning of November, the value varying between 19.17 and 20.06%, being smaller in the samples from the end of January to the end of June (14.40–15.47%), and medium in the samples from November to the middle of January (16.16–17.92%). It is remarkable that the variation in its values occurred continually in order of magnitude evenly and smoothly.

(b) The percentage of total nitrogen was found to vary between the two extreme values of 0.498 and 0.952%, without any regularity in its seasonal variations.

(c) The percentage of iron reckoned as  $\text{Fe}_2\text{O}_3$  varied between 8.85 and 12.5%. It might be mentioned that the values from the end of January to the middle of June were smaller, while those for the remaining half of the year were generally larger.

(d) With the single exception of a very large value, 13.39%, for the period October 25 – November 25, 1936, the percentage of aluminium, as alumina, did not vary much, lying between 8.47–9.21%.

(e) The percentage of manganese, as manganese oxide, varied between the two extreme values of 0.33 and 1.44%; no regularity was found.

It is also of interest to compare the seasonal variation in the deposited amounts of these chemical components, which are represented graphically in Fig. 4.

At a glance, the graphs for iron, the total nitrogen and the loss on ignition are seen to be shaped similarly to that for the total deposition, while the graph for manganese differs, indicating that the precipitation of manganese in the autumnal maximum was delayed compared with those

of iron and other components; the maximal point consequently appeared later.

This is easily explained by the difference in the oxidation-reduction potential between iron and manganese. As mentioned above, the potential is higher in manganese than in iron. At the end of autumn, when circulation of the water increases considerably, the potential in the deeper water gradually begins to rise, and a condition is reached in which the reduction of manganese proceeds easily, which, however, is difficult for ferric iron. Thus in such a season, in deeper water, the supply and accumulation of manganous salts still continue, and the manganese, thus accumulated, is carried upward by the circulation current, to undergo continuous oxidation and precipitation. Thus, as shown by the present result, complete precipitation of manganese follows that of iron.

**Factors Controlling Deposition.** The following may be mentioned as the factors that control the amount and the character of the deposits.

(a) The circulation of water, which is caused by cooling and by wind. On circulation, the water carries the substances accumulated at depth to the upper water and exposes them to further changes, while it whirls up the deposit that is settled in shallower bottoms, carrying it into depths.

(b) The amount of suspended substances that are carried into the lake by influent waters.

(c) The production of organisms, whose debris are partly deposited as essential constituents of the mud.

(d) The temperature of the deeper waters, which controls the chemical changes that occur in the deposits after they have settled in the suspended bottles.

When the present result of the foregoing studies in the amounts deposited is examined, it is easily found that the effects of the factors (a) and (d) are self-evident, while those of (c) and (e) are not so apparent.

The effects were most obvious in the autumnal maximum. In fact, there is no doubt that the main cause of the heavy deposition was the circulation of water by cooling.

By the circulation of water, a large amount of iron, that was accumulated in the tropholytic zone in the preceding period of stagnation, was carried towards the upper water zones, rich in oxygen. Then there followed the oxidation of ferrous iron to ferric, which, in its turn, formed a flocculent hydroxide and precipitated to the bottom.

It will easily be seen, therefore, that the percentage of iron in the deposit was quite large.

At the same time, the fact cannot be overlooked that, during this interval, deposition of aluminium and total nitrogen increased to a smaller extent than iron, although they were still in fairly large proportions.

Such a circumstance cannot be explained without assuming that the organic debris, as well as the clayey substances that had once settled on the shallower zone of the bottom, were whirled up into the water by the force of the water movement, and after being carried toward



the middle of the lake were deposited there. Such transference of deposits, no doubt, occurs during the period in question to a considerable extent.

The effect of temperature of the bottom water is also evident. As will be seen from the preceding paragraph (Table 4) and also from the following Fig. 12, the temperature attains its maximum in the middle of autumn, so that in this season, the chemical changes that occur in the suspended bottle are expected to be accelerated considerably.

Among the changes that could occur, fermentative decomposition of organic substances may be mentioned as the first, as was clearly proved by studies on the dissolved gases of lake waters, to be given later.

Owing to decomposition, a considerable portion of the organic components of the deposit was consumed before the bottle was hauled up, so that the percentages of these components should be reduced, with consequent increase in those of the other components. Naturally, such a reduction is also conceivable in the case of iron, which would follow the above organic decomposition. But the escape of iron from the deposit, that is, the decrease in percentage of iron will often be insignificant compared with those of the organic components, hence, what follows is nothing but increase in the percentage of iron relative to those of the organic components. It is highly probable that the larger percentage of iron in the autumnal deposits, is due, partly, to just such circumstances.

It must also not be overlooked that, in the development of autumnal deposition, the preceding season of summer stagnation plays an important part.

The large amount of iron and manganese in the tropholytic zone, which forms a storage for the autumnal deposition, had been formed during the period of summer stangantion. Were this period absent, there would be no large precipitation in autumn.

This is the case in the season that embraces the beginning of winter to the beginning of spring, when, despite the continuous circulation of water between the upper and deeper layers, there occurs only a slight deposition, owing to the fact that the greater part of the substances stored were deposited almost completely during the preceding seasons, leaving little to settle.

#### IV. The Density of Lake Water. General Description.

So far as the writer's knowledge goes, examples of density determination, in which the density of the lake water was measured directly, are very rare. The only example available being that of A. Hamberg,<sup>(21)</sup> who measured the density of the water at Lake Walloxen, a small lake near Upsala, in April 1909, when the lake lay covered by ice, and found that the lake water had a density of 1.0003 at a depth of 1 m. and 1.0005 at a depth of 7.5 m.

Little is gained by merely asserting that the density of water plays an important part in problems dealing with the circulation or the

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(21) Hamberg, *Petermanns Mitteilungen*, 57, II (1911).

stability of lake water. It is odd to find that, notwithstanding its importance, our knowledge of the density of lake water is so meagre.

The writer puts it down to the fact that, for directly measuring the density of lake water, special and painstaking care is needed, demanding considerable time.

Heretofore, when investigators desired to compute the density of lake water at a certain depth, they usually chose the easiest way, namely, they first measured the water temperature at a depth, next they resorted to a table for the value of the density of pure water corresponding to the temperature observed, and assumed this value for the actual density at that depth.

A discussion based on a value of density obtained in such a manner can never be hoped to go very far.

At the same time, it is well known that, at present, the method of measuring the temperature of deep water has been improved to such an extent that it is not a difficult task to attain an accuracy of one hundredths of a degree, which is equivalent in the case of density of water to one two-millionths.

When we reflect on the actual situation of our knowledge as just outlined, we are at once confronted with certain problems demanding solution, for example.

(1) What is the difference in density of lake water and that of pure water?

(2) What is the actual variation in the density of lake water with depth?

(3) What is the actual variation in the density of lake water with season?

(4) How does the density of water vary in the various kinds of lakes?

(5) What is the degree of accuracy in the value of density as computed by the customary method just mentioned.

These questions led the writer to undertake the following measurements: (1) Four series of determinations of the water density of Takasuka-numa were made between September and December, 1935, at six to eight different depths. (2) A similar determination was made in Kizaki-ko and Nakatuna-ko, both in Sinano Province, the following summer, the results and discussions of which will now follow.

### Methods.

The bottles containing the sampled waters were tightly stoppered to prevent bubbles and other troublesome gas effects, both from inside and out, that are likely to cause changes in the density of the water.

The determination of density was completed within 24 hours after the water was sampled, although in the case of samples, the density of which was likely to alter, they were determined within a few hours.

For the determination, a Sprengel's pycnometer was used, the temperature of the thermostat being controlled at 20.0°C. in the case of Takasuka-numa, and at 17.9°C. in the cases of Nakatuna-ko and Kizaki-ko the variation in temperature being kept within 0.05°, whereby the error in observation of the water density was kept within 0.00001. But in the observations of September 29 and October 20, these conditions were not yet adequately fulfilled.

From these values at 20.0°C. or at 17.9°C., and from the result of temperature determination, the actual density on the spot was computed on the assumption that the coefficient of cubical expansion of the examined water was the same as that of pure water.

The values at 20.0°C. or at 17.9°C. are given in column (a), while those at the respective temperature on the spot, which were thus computed, are shown in column (b) in Table 16, 19 and 20. The densities of pure water at the corresponding temperatures are also given in (c).

### The Result from Takasuka-numa.

The result of the determination in Takasuka-numa is given in column (a) in Table 16, which when compared with the data of hydrographical observation (Table 17), clearly shows that on September 29, the stratification in water density was parallel with those of a few of the chemical constituents.

Here the value of the water density varied in the different water layers in the order of 1/10,000, and, barring the two exceptions of density decrease, one at a depth of 2 m. and the other at a depth of 5.5 m., the density on the whole increased from the surface towards the bottom.

Although, in appearance, these two exceptions are identical, they are quite different in nature, which may be clearly shown when these values are nevertheless reduced to those at the respective temperatures on the spot, assuming that the coefficient of the cubical expansion of the lake water is identical with that of pure water. In fact, when we examine the reduced values given in column (b), it will readily be seen that the former decrease in density at a depth of 2 m. has disappeared, while the latter, at 5.5 m., is still present.

This point is quite important, because the latter decrease runs counter to the law of stability, whereas the former does not.

It must be added that in the present case the water was not treated previously in any way whatsoever, and that the determination was carried out on it as a whole, including suspended matter, such as planktons, organic debris, etc.

Therefore, it is not certain what part of the difference in density that was observed is owing to the presence of suspended matter, and what part to the water itself?

In order to make this point clear, the writer, on October 20, conducted the determination in two different ways, the one on water not previously treated and the other on water that was filtered.

For filtration, filter paper "Toyo" brand No. 5 was used, and precautions were taken to avoid risk of changes in density of the water during filtration owing to oxidation by atmospheric oxygen, etc.

This time again, waters that were not filtered showed decrease in density at 20.0°C. for two different depths, the one from 1 to 3 m., and the other at a depth of 5.5 m.; and, as in the previous observation, when the observed values of density are reduced to those at temperatures on the spot, decrease at the upper depth disappears, while that at the bottom persists.

Table 16. Densities of the lake waters of Takasuka-numa (1935).

| Date of sampling  | Sept. 29 |                        |         |         | Oct. 20 |                        |         |         |
|-------------------|----------|------------------------|---------|---------|---------|------------------------|---------|---------|
| Date of determin. |          |                        |         |         | Oct. 20 |                        |         |         |
| Depth (m.)        | a        | not filtered<br>b (°C) |         | c       | a       | not filtered<br>b (°C) |         | c       |
| 0                 | 0.9984   | 0.9980                 | (21.9°) | 0.99782 | 0.9983  | 0.9985                 | (18.8°) | 0.99847 |
| 1                 | 0.9985   | 0.9982                 | (21.3°) | 0.99795 | 0.9985  | 0.9988                 | (18.5°) | 0.99852 |
| 2                 | 0.9983   | 0.9985                 | (19.2°) | 0.99839 |         |                        | (18.3°) | 0.99856 |
| 3                 | 0.9985   | 0.9987                 | (18.8°) | 0.99847 | 0.9984  | 0.9988                 | (18.2°) | 0.99858 |
| 4                 | 0.9987   | 0.9990                 | (18.5°) | 0.99852 | 0.9984  | 0.9988                 | (18.1°) | 0.99860 |
| 5                 | 0.9987   | 0.9992                 | (17.3°) | 0.99875 | 0.9985  | 0.9989                 | (17.3°) | 0.99875 |
| 5.5               | 0.9985   | 0.9991                 | (16.6°) | 0.99887 | 0.9982  | 0.9988                 | (16.9°) | 0.99882 |
| 5.7               |          |                        |         |         |         |                        |         |         |

| Date of sampling  | Oct. 20         |        |                 |        | Nov. 11 |                        |          |         |
|-------------------|-----------------|--------|-----------------|--------|---------|------------------------|----------|---------|
| Date of determin. | Oct. 21         |        | Oct. 22         |        | Nov. 13 |                        |          |         |
| Depth (m.)        | filtered<br>a b |        | filtered<br>a b |        | a       | not filtered<br>b (°C) |          | c       |
| 0                 | 0.9983          | 0.9985 | 0.9983          | 0.9985 | 0.99827 | 0.99934                | (13.8°)  | 0.99930 |
| 1                 |                 |        | 0.9983          | 0.9986 | 0.99826 | 0.99931                | (13.9°)  | 0.99928 |
| 2                 |                 |        | 0.9984          | 0.9988 | 0.99828 | 0.99933                | (13.9°)  | 0.99928 |
| 3                 |                 |        | 0.9985          | 0.9988 | 0.99827 | 0.99932                | (13.9°)  | 0.99928 |
| 4                 | 0.9983          | 0.9987 | 0.9985          | 0.9988 | 0.99827 | 0.99933                | (13.85°) | 0.99929 |
| 5                 | 0.9984          | 0.9989 |                 |        | 0.99831 | 0.99937                | (13.85°) | 0.99929 |
| 5.5               | 0.9982          | 0.9988 |                 |        | 0.99827 | 0.99934                | (13.75°) | 0.99930 |
| 5.7               |                 |        |                 |        |         |                        | (13.2°)  | 0.99937 |

| Date of sampling  | Nov. 11         |         |                 |         | Dec. 15  |                    |         |         |
|-------------------|-----------------|---------|-----------------|---------|----------|--------------------|---------|---------|
| Date of determin. | Nov. 11         |         | Nov. 12         |         |          |                    |         |         |
| Depth (m.)        | filtered<br>a b |         | filtered<br>a b |         | a*       | filtered<br>b (°C) |         | c       |
| 0                 |                 |         |                 |         |          |                    |         |         |
| 1                 |                 |         |                 |         |          |                    |         |         |
| 2                 |                 |         |                 |         |          |                    |         |         |
| 3                 |                 |         |                 |         |          |                    |         |         |
| 4                 |                 |         | 0.99829         | 0.99935 |          |                    |         |         |
| 5                 | 0.99828         | 0.99934 | 0.99828         | 0.99934 | 1.00008* | 1.00039            | (6.68°) | 0.99994 |
| 5.5               |                 |         | 0.99826         | 0.99933 | 1.00003* | 1.00034            | (6.67°) | 0.99994 |
| 5.7               | 0.99823         | 0.99937 | 0.99823         | 0.99937 |          |                    |         |         |

a .... densities at 20.0°C.

b .... densities reduced to the temperatures of waters which are given in parenthesis.

c .... densities of pure water at the temperatures of waters.

a\*.... densities at 11.0°C.

Table 17. Residue on evaporation and the potassium permanganate consumption of the lake waters of Takasuka-numa in the autumn 1935.

| Depth<br>(m.) | Sept. 29                       |                                           | Oct. 20            |                               | Nov. 11            |                               | Dec. 15            |                               |
|---------------|--------------------------------|-------------------------------------------|--------------------|-------------------------------|--------------------|-------------------------------|--------------------|-------------------------------|
|               | Resid. on<br>evap.<br>(mg./l.) | Cons. of<br>KMnO <sub>4</sub><br>(mg./l.) | Resid. on<br>evap. | Cons. of<br>KMnO <sub>4</sub> | Resid. on<br>evap. | Cons. of<br>KMnO <sub>4</sub> | Resid. on<br>evap. | Cons. of<br>KMnO <sub>4</sub> |
| 0             | 127                            | 18.8                                      | 120                | 33.4                          | 190                | 19.7                          | 126                | 20.6                          |
| 1             | 127                            | 18.6                                      | 118                | 22.6                          | 180                | 20.3                          | 123                | 20.1                          |
| 2             | 126                            | 17.1                                      | 123                | 19.5                          | 181                | 19.4                          | 117                | 19.6                          |
| 3             | 126                            | 16.1                                      | 119                | 19.1                          | 133                | 18.0                          | 125                | 18.1                          |
| 4             | 121                            | 15.2                                      | 124                | 19.2                          | 173                | 20.5                          | 122                | 21.9                          |
| 5             | 201                            | 23.6                                      | 203                | 44.7                          | 178                | 19.2                          | 124                | 20.7                          |
| 5.2           |                                |                                           |                    |                               |                    |                               | 128                | 16.6                          |
| 5.5           | 262                            | 55.4                                      | 260                | 51.3                          | 247                | 20.7                          |                    |                               |

It is worthy of note that the filtered water usually showed a smaller density than before filtration, the amount of decrease, particularly at a depth of 1 m., was larger, with the result that the irregular stratification of water density found in unfiltered water at the 1–3 m. zone, disappeared in the filtered ones, even at 20.0°C.

It is therefore concluded that of the two kinds of irregular distribution of density, the one found in the upper water zone was caused by unequal distribution of suspended matter in the various layers of this zone. In fact, the consumption of potassium permanganate shows that a smaller amount of reducible substances was always (not only on October 20 but also on September 29) present in the water at a depth of 2 m. than in that at a depth of 1 m., where the amount of decrease in density by filtration was specially larger.

The nature of the decrease in density at the bottom differs also at this point. Since it persisted even after filtration, it was shown that the decrease was not connected, at any rate, with the suspended matter, which can be filtered away by filter paper.

On November 11, although the water had practically circulated completely, as was shown by the smaller content of oxygen and by the larger residue on evaporation, circulation was not yet complete at the bottom, for which reason, the density of the water had become uniform at every depth tested, except in the deepest layers, so far as its value in the order of one ten-thousandths was concerned, although it showed a certain variation in the order of one hundred-thousandths, and notwithstanding which, it is notable that the decrease in density at 5.5 m. was still evident.

Noteworthy also is the fact that, on December 15,<sup>(22)</sup> when the circulation was supposed to have been completed, a faint decrease in density was still evident, so that of these two anomalous stratifications of water density that were found at 20.0°C., that in the upper water

(22) It is necessary to add that the density was measured this time at 11.0 °C.

zone was caused by uneven distribution of the suspended matter, and it disappeared in the actual distribution of water temperature, while that in the bottom still remained, the reason of which will be discussed later as a separate subject.

**Comparison of Results of the Two Different Methods for the  
Determination of Water Density, the Customary Method  
and the Writer's Computation Method.**

A comparison will now be made of the value of the density itself, and of the gradient of the vertical variation in density.

(a) **The Density Value.** This comparison is merely that between the writer's values (a) and those of pure water (c) at corresponding temperatures.

The difference between these two values varied between 0.00000 and 0.0005.

The former value was found at a depth of 5.7 m. on November 11, and the latter 5 m. on September 29.

It is worth mentioning that this difference was somewhat larger during the stagnation period, especially at depths below the thermocline.

At any rate, these results lead to the conclusion that the customary method of determining the density of lake water is followed by an error that is, at least, too small by 0.00000–0.0005.

Now, a difference in density of 0.0005 in pure water through variation in temperature, corresponds to a variation of 2.5°, which means that the customary method of determining the density of lake water often merely yields a result which is equivalent to that given by rough measurement of water temperature with an error of as large as 2.5°.

Consequently, if we continue the customary method in determining the density of lake water, we may frequently disregard, in our measurements of temperature, without hesitation, observation errors up to 2.5°.

(b) **Gradient of Vertical Variation in Water Density.** The gradient of vertical variation in the water density constitutes one of the most important factors that determine the stability, that is, the resistance to the mixing of water. It is expressed by  $\frac{d\rho}{dz}$  where  $\rho$  represents the water density and  $z$  the depth.

In Table 18, its values from the customary density determination are compared with those from the writer's computation method.

During the period of complete circulation, vertical variation in the water density is determined only by water temperature, because both dissolved and suspended matter are distributed uniformly in all the water layers, except the bottom one, where a decrease in density persists, so that during this season, the gradient of vertical variation in water density, as calculated from the values of density by the customary method does not differ much from that of the writer's method.

Table 18. Gradient of vertical variation in the water density in Takasuka-numa (1935).

| Depth<br>(m.) | Sept. 29           |                      | Oct. 20 (filtered) |                      |
|---------------|--------------------|----------------------|--------------------|----------------------|
|               | a                  | b                    | a                  | b                    |
| 0             |                    |                      |                    |                      |
| 1             | $2 \times 10^{-6}$ | $1.3 \times 10^{-6}$ | $1 \times 10^{-6}$ | $0.5 \times 10^{-6}$ |
| 2             | $3 \times "$       | $4.4 \times "$       | $2 \times "$       | $0.4 \times "$       |
| 3             | $2 \times "$       | $0.8 \times "$       | $0 \times "$       | $0.2 \times "$       |
| 4             | $3 \times "$       | $0.5 \times "$       | $0 \times "$       | $0.2 \times "$       |
| 5             | $2 \times "$       | $2.3 \times "$       | $1 \times "$       | $1.5 \times "$       |
| 5.5           | $(-1 \times "$     | $1.2 \times "$       | $(-1 \times "$     | $0.7 \times "$       |

$$\frac{d\rho}{dz} \text{ (c. g. s. units)}$$

a ....  $\frac{d\rho}{dz}$ , from the writer's computation method.

b ....  $\frac{d\rho}{dz}$ , from the customary method.

In contrast to the foregoing, however, when the water stagnates and the distribution of both dissolved and suspended matter is not uniform, the water density is no longer a simple function of temperature, with the result that the two kinds of gradient of vertical variation in water density as calculated by the two methods, differ considerably, the maximum difference being as much as 0.00025.

It is scarcely necessary to add that the value of the change in vertical variation in water density found by the customary method is meaningless at the bottom, where the actual change in density was found to be quite the reverse.

#### Decrease in Density at the Bottom.

The most important result from Takasuka-numa was the discovery of reversed stratification in the density of lake water at the bottom.

Since the water density usually increases with increase in the amount of solid matter dissolved in it, it will easily be understood that the density of lake water increases from the surface towards depth parallel with the increase in the amount of the residue on evaporation. Against this general relation, sudden decrease in density at the bottom is followed by a further increase in the amount of residue after evaporation, which precludes the possibility of the decrease being due to the lighter water with a smaller content of solid matter rising up from the bottom, so that we must look elsewhere for the cause of the decrease.

The question now arises whether there is any substance in sufficient amount in the bottom water that causes a decrease to show in the density of water.

As such a substance we could mention quite a number, namely, diethylamine, trimethylamine, the anilines, and the alkaline soaps of stearic

and palmitic acids, as well as the wellknown examples of alcohol, ammonia etc., although it is difficult to suppose that any of these substances is present in the bottom water in sufficient concentration to cause a decrease in the water density observed.

The effect of dissolved gases is also conceivable. According to the studies of K. Ångström<sup>(23)</sup> and of J. Horiuti,<sup>(24)</sup> the density of a liquid is reduced by the absorption of a gas whose density in the condensed state is smaller than that of the solvent, whence it is quite probable that the density of lake water is lowered by the dissolution of hydrogen and other gases of the hydrocarbon series that have densities less than water when they are condensed. Moreover, these gases are the products of fermentation at the bottom, which are accumulated there especially in large quantities during the stagnation period, when the decrease in density of the bottom water is also large.

As shown in the following paragraphs, it is possible to compute the effects of the various gases dissolved upon the density of the lake water, and to prove that the decrease in question is caused partly by the unequal distribution of these gases in different water layers.

However, as will be shown later, the decrease in density caused by unequal distribution of gases is only one-tenth that of the total, so that search must be made for other causes of the decrease.

From one of the studies begun in this connection, it is probable that the decrease in the density is partly due to changes in the state of aggregation of the dissolved colloidal substances, such as hydroxide of iron, the details of which will be published in a separate paper.

It will also be seen that it is not certain whether the two causes, the unequal distribution of dissolved gases and the variation in the state of aggregation of dissolved substances, are sufficient to explain the phenomena completely. It is hoped to carry out studies in this respect still further.

#### **Significance of the Decrease in Water Density at the Bottom in the Return of the Deposited Matter into the Water Body.**

Although, as just mentioned, the cause of the density decrease in the bottom water of Takasuka-numa is not yet clearly known, it can at any rate, be said to be true, that certain changes are going on incessantly at the bottom or in the bottom water resulting in decrease in the density of water there.

Since a condition in which a heavy body lies upon a lighter one is unstable, granting, for sake of argument, that such a condition did at one time exist, it cannot continue.

Decrease in the density at the bottom is an example of such an unstable state, and if such a distribution of density is once formed, the probability is that it will soon be disturbed by mixing of the upper with the lower water.

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(23) Ångström, *Ann. Physik*, **15** (1882), 297-308.

(24) Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17** (1931-32), 126-256, 257-264.



Nevertheless, we do find such a decrease, which tells nothing beyond the fact that the change which brings about decrease in the density at the bottom water is of a kind that occurs vigorously and constantly, rendering possible the persistence of such an anomalous distribution of density.

Going a step further, the writer thinks it very probable that such a change, which acts in diminishing the water density, is taking place not only in the lake bottom, where its existence is readily found, but also in other places, where it is unnoticed.

At the same time, the writer believes that there is more intense mixing of upper and lower waters in the lastnamed places, by which permanent establishment of density decrease is hindered. He, therefore, concludes that changes that bring about decrease of water density at the bottom, as well as that mixing up of the waters that follow, are of world-wide occurrence.

The mixing of the waters in the bottom, which is accepted as of wide occurrence, has special significance in lake metabolism.

As repeated above, the circulation or mixing of waters in the upper and lower layers plays an important role, giving back the products of anaerobic decompositions at the bottom to the upper water zones.

It has been accepted for a long time that the two main factors, which control the circulation of water are wind and temperature.

Wind gives rise to a current in the lake water, and this leads to mixing of the upper and lower waters. The conditions favourable for this mixing of water by wind are found during such seasons as when the surface water is frequently cooled by cold weather or by fall of temperature in the night. This is the period of circulation that one finds in Takasuka-numa practically through the greater part of the year, from the end of summer to the beginning of the next summer, while the remainder of the year constitutes the period of stagnation.

During the latter season, that is, in summer, the surface water is warmed from day to day, and its cooling, even if it does occur sometimes can scarcely cause the water to circulate, which condition leads to the development of marked stratifications of various kinds chemical, physical, and biological. These are the general features attending the circulation of water in a lake.

Now the changes that are responsible for the decrease in density at the bottom, as found in Takasuka-numa, and which is believed to occur also widely in other lakes, is important, seeing that it forms the third means by which the water is circulated, in addition to two preceding ones, which have to do with the wind and the cooling of the surface water.

As just stated, decrease in water density at the bottom is followed by mixing of water of decreased density with the upper water, whereby a large part of the accumulated matter in the bottom water is enabled to be carried into the upper water zones.

This process of carrying back the bottom substances up into the upper layer is extremely important, since it occurs in the bottom water during periods of stagnation when other means of circulation are virtually unavailable. Moreover it occurs more actively in this season than in others.

### Densities of the Waters of Nakatuna-ko and Kizaki-ko.

The densities of the waters of Nakatuna-ko and Kizaki-ko were determined during the summer of 1936 at the Kizaki Station of the Imperial Fisheries Experimental Institute.

The result is given in Tables 19 and 20. As was the case in the previous table for Takasuka-numa, the values of the water density at

Table 19. Densities of the lake waters of Nakatuna-ko.  
(August 17-19, 1936.)

| Depth<br>(m.) | (a)     | (b)     | Water temp.<br>°C. | (c)     | Residue on<br>evap. mg./l. |
|---------------|---------|---------|--------------------|---------|----------------------------|
| 0             | 0.99862 | 0.99713 | (24.8)             | 0.99713 |                            |
| 1             |         |         |                    |         | 22.6                       |
| 4             |         |         |                    |         | 38.0                       |
| 5             | 0.99863 |         |                    |         | 37.5                       |
| 10            | 0.99863 | 0.99964 | (10.9)             | 0.99964 | 39.3                       |
| 11            | 0.99863 | 0.99976 | (9.6)              | 0.99976 |                            |
| 11.5          | 0.99866 | 0.99981 | (9.4)              | 0.99978 |                            |
| 12.0          | 0.99865 | 0.99982 | (9.1)              | 0.99980 |                            |
| 12.4          | 0.99866 | 0.99983 | (9.1)              | 0.99980 |                            |
| 12.6          | 0.99867 |         |                    |         |                            |
| 12.7          | 0.99867 | 0.99985 | (9.0)              | 0.99981 | 39.3                       |
| 12.8          | 0.99867 | 0.99985 | (9.0)              | 0.99981 | 81.8                       |
| 13.0          | 0.99867 | 0.99985 | (9.0)              | 0.99981 | 94.1                       |
| 13.1          | 0.99869 | 0.99987 | (9.0)              | 0.99981 |                            |

Table 20. Densities of the lake waters of Kizaki-ko.  
(August 7-9, 1936.)

| Depth<br>(m.) | (a)     | (b)     | Water temp.<br>°C. | (c)     |
|---------------|---------|---------|--------------------|---------|
| 24            | 0.99864 | 0.99997 | (6.1)              | 0.99996 |
| 25            | 0.99864 | 0.99998 | (6.0)              | 0.99997 |
| 26            | 0.99864 | 0.99998 | (5.9)              | 0.99997 |
| 28            | 0.99864 | 0.99999 | (5.7)              | 0.99998 |
| 28.3          | 0.99865 | 1.00000 | (5.7)              | 0.99998 |
| 28.6          | 0.99865 | 1.00000 | (5.7)              | 0.99998 |
| 28.7          | 0.99864 | 0.99999 | (5.7)              | 0.99998 |
| 28.8          | 0.99865 | 1.00000 | (5.7)              | 0.99998 |

17.9°C. are given in column (a) and those that were reduced to temperatures on the spot in (b), while the densities of pure water at the respective temperatures are shown in column (c).

The water density of Lake Kizaki-ko exceeded that of pure water only by 0.00002 at the most. It showed a tendency to increase slightly with depth between the 24.0–28.1 m. levels, with an exceptional slight decrease at 28.7 m. But it will be going too far to attribute this decrease of water density to the same causes that were proposed in the case of Takasuka-numa. This point should be carefully investigated.

At layers ranging from the surface to a depth of 11 m., the density of the waters of Lake Nakatuna-ko practically did not differ from those of pure water. The difference, which first appeared at 11.5 m., grew larger with depth, the maximum difference, 0.00006, being found at the bottom, 13.1 m.

The difference between the gradients of vertical changes in the water density by the direct and the computation methods did not exceed 0.000002, one of the lake bottoms on which the matter was tested being that of Nakatuna-ko.

### Effect of Dissolved Gases on the Density of Lake Water.

**The Calculation.** In this chapter, the writer will discuss the effect of dissolved gases on densities of the water of Takasuka-numa, Nakatuna-ko, and Kizaki-ko, using Ångström's dilatation coefficients of water for the absorption of a few of the common gases,<sup>(23)</sup> and Horiuti's formula in referring to the density change in a liquid caused by the dissolution of gas,<sup>(24)</sup> and the writer's own data of analysis in referring to the dissolved gases in the waters of these lakes. (v. Tables 32, 33 and 35)

Horiuti's formula is

$$D - D_0 = g \frac{P_s \gamma}{RT} (d - \delta D_0)$$

where  $D_0$  and  $D$  are respectively the density of the solvent and that of the solution,  $d$  is the normal density, i.e., the density of the solute at N. T. P.  $g$  is its molecular volume;  $P_s$  is the partial pressure of the solute gas,  $\gamma$  is Ostwald's solubility of the solute gas, and  $\delta$  is Ångström's value of the dilatation coefficient of water for the absorption of gas.

The values of  $\delta$ ,  $d$ , and  $d - \delta D_0$  for the five gases that are to be dealt with in the following paragraphs, are given in Table 21.

Table 21.

|                 | $\delta$              | $d$                   | $d - \delta D_0$       |
|-----------------|-----------------------|-----------------------|------------------------|
| O <sub>2</sub>  | $1.13 \times 10^{-3}$ | $1.43 \times 10^{-3}$ | $+0.30 \times 10^{-3}$ |
| N <sub>2</sub>  | $1.44 \times$ „       | $1.26 \times$ „       | $-0.18 \times$ „       |
| CH <sub>4</sub> | $1.23 \times$ „       | $0.566 \times$ „      | $-0.66 \times$ „       |
| H <sub>2</sub>  | $1.06 \times$ „       | $0.071 \times$ „      | $-0.99 \times$ „       |
| CO <sub>2</sub> | $1.27 \times$ „       | $1.96 \times$ „       | $+0.69 \times$ „       |

The values of  $\delta$  for oxygen, nitrogen, hydrogen, and carbon dioxide are quoted from Ångström, while for methane, since its value is lacking, the arithmetical mean of the values of the four gases is adopted as its  $\delta$ .

If it is desired to calculate the change in the density of the lake waters in question, due to the dissolution of the gases,

by means of this formula, and to obtain results with an accuracy of the same order as in the data of the density of the lake waters observed

above, the accuracy of the values that are to be inserted in the formula need not exceed two figures.

The writer adopted  $R = 8.2$ ,  $g = 22400$ ; for  $T$ , 286 was chosen as the middle temperature between 6–20°C., for  $D_0$ , density 1.00 of pure water, free from dissolved gases, was taken. Finally for  $P_{s\gamma}$  was chosen the volume of a gas in one c.c. of water, converted into N. T. P.

**Two Kinds of Gases, the One Decreasing and the Other Increasing the Density of Water by Dissolution.** According to its particular behaviour towards change in density, gases may be divided into two groups.

The one, to which  $d - \delta D_0$  is positive, tends to increase the density of water by dissolution. To this group belong such gases as oxygen and carbon dioxide, whose molecules are rather large. The other, to which belong gases of smaller molecular weights, such as nitrogen, hydrogen, and methane,  $d - \delta D_0$  has a negative sign, and their dissolution brings about a decrease in water density. It is also notable that the smaller the molecule of the gas in question, the larger the decrease in the water density.

Thus the diminishing effect upon the density of water is greatest in methane and hydrogen.

Now, upon comparing the various behaviours of gases towards the density of water with the distribution of these gases in the lake waters, it is interesting to find that, excepting carbon dioxide, the greater part of which is dissolved in the combined or in the partially combined state, all the other gases are distributed in such a way that the deeper lying waters are influenced by these gases to become lighter than the overlying waters.

As already mentioned, oxygen is a gas whose dissolution brings about an increase in the density of water, and the distribution of this gas in lake water is such that it is rich in the upper and middle layers, but poor and often absent, from the deeper layers.

After all, oxygen is so distributed as to make the lake water heavier in the upper zones than in the deeper ones.

In contrast to this, nitrogen, methane, and hydrogen, whose dissolution results in decrease in the density of the water, are distributed in such a way that they are all poor in the upper water zones, getting richer towards the bottom.

Thus the distribution of the latter gases in lake waters is such that the deeper waters tend to become lighter than the upper waters.

Such a general relation in the distribution of dissolved gases in lake waters is not only obtained in Takasuka-numa, but in almost every lake in the temperate zone.

It must be added that such a distribution of the gases helps the mixing of waters between the upper and lower layers, and plays one of the most important roles in the circulation of matter in a lake, a role that is especially important, for during the stagnation period, such a distribution develops to the highest degree when circulation by other means is interrupted, the mixing of the waters being thus made much easier than if distribution were otherwise.

To this general relation, carbon dioxide seems to be an exception.

In effect, this gas, which is distributed abundantly in the deeper layers, but less so in the upper layers, increases the density of the water by dissolution, and seems to make the water density in deeper waters greater, much more so than in the upper waters. However, as stated above, the manner of dissolution of the gas in lake water differs from that in pure water; in the former it is dissolved partly in the combined state and partly in the partially combined one. Therefore it is a question, what proportion of the amount given by analysis acts in increasing the density of lake water, as in the case of pure water. This is a point which, it is hoped, will be elucidated by further studies.

**The Results from Takasuka-numa.** The change in the density of water  $\Delta D = D - D_0$  (in the following descriptions  $\Delta D$  will be used in place of  $D - D_0$ ), which was calculated by means of Horiuti's formula, will be found in Table 22.

On comparing the values for various seasons and depths, we find that

(1)  $\Delta D$  for oxygen varied between  $0.00000 \sim +0.000023$  during the period of observation (September 1935 – October 1936).

The gradient of the change in density due to the dissolved gas with depth,  $\frac{d(\Delta D)}{dz}$  (m. was taken as the unit for the measure of depth) attained its maximum (absolute value), 0.000013, on July 1936 at a depth between 2 and 3 m.

(2)  $\Delta D$  for nitrogen lay between  $-0.000017$  and  $-0.000036$ , and the maximum of its  $\frac{d(\Delta D)}{dz}$ , 0.000006, was found on January 19 at a depth between 3 and 4 m.

(3)  $\Delta D$  for methane varied between 0.00000 and  $-0.000086$ . The maximum of its  $\frac{d(\Delta D)}{dz}$  was found to be 0.000064 and 0.000077 on October 20, 1935, at a depth between 4 and 5 m., and on October 4, the following year, at a depth between 5 and 6 m.

(4)  $\Delta D$  for hydrogen varied between 0.00000 and  $-0.000042$ , and the maximum of its  $\frac{d(\Delta D)}{dz}$  was found to be 0.000008 on July 25, 1936, at a depth between 5 and 5.5 m., and on October 4, the same year, at a depth between 5 and 5.5 m.

Summarizing the result, it may be said that, of the maximum values of the gradient of the change in water density for the four gases, that due to methane was the largest in its absolute value, those for oxygen hydrogen, and nitrogen following in the order named.

For the water depth, where the dissolved gases were completely analysed and the  $\Delta D$  for these gases were all completely calculated, the sum of these  $\Delta D$ , namely, the total change in the water density is also given as  $\Sigma \Delta D$ .

With the exception of the depth of 0 m., in December, where  $\Sigma \Delta D$  had a positive sign, it is remarkable that  $\Sigma \Delta D$  was always negative, that is, the total effect of the dissolved gases was to cause the density to decrease in all seasons and at all depths.

The maximum for the absolute value of  $\Sigma \Delta D$  was found on October 20, 1935, at a depth of 5.5 m. and on October 4, the following year, at a depth of 6 m.

When compared seasonally,  $\Sigma \Delta D$  increased from September until October, when it attained its maximum, after which it began to diminish.

Finally  $\Sigma \Delta D$  had the smallest values below 0.000007 (except the deeper layers) in December, while it showed 0.000004 in November at a depth of 5–5.5 m., and in September 0.000025 at a depth of 4–5.5 m.

Thus it seems that  $\Sigma \Delta D$  had its maximum value in the deepest layer in October 1936, at a depth 5–5.5 m., namely 0.00014.

**The Results from Nakatuna-ko and Kizaki-ko.** (v. Tables 23 and 24). The values of  $\Delta D$  as well as those of  $\Sigma \Delta D$ , for any of the gases in question which we obtained for these lakes, lay always within the range of the two extreme values found in Takasuka-numa.

$\Sigma \Delta D$  was always found to be negative, and its maximum value (in absolute value) was found at a depth of 25 m. in Kizaki-ko, and at a depth of 12.5 m. in Nakatuna-ko.

Table 22. The change in the water density in Takasuka-numa due to the dissolved gases ( $\Delta D \times 10^5 = (D - D_0) \times 10^5$ ).

|                  |                               | 0 m. | 1 m. | 2 m. | 3 m. | 4 m. | 4.7 m. | 5 m. | 5.2 m. | 5.5 m. | 6 m. |
|------------------|-------------------------------|------|------|------|------|------|--------|------|--------|--------|------|
| Sept. 29<br>1935 | Oxygen                        | +1.5 |      | +0.6 | +0.5 | 0    |        | 0    | 0      | 0      |      |
|                  | Nitrogen                      | -2.1 |      |      |      | -2.1 |        |      |        |        |      |
|                  | Methane                       | 0    |      |      |      | -0.1 |        |      |        |        |      |
|                  | Hydrogen                      | 0    |      |      |      | -0.1 |        |      |        |        |      |
|                  | $\Sigma \Delta D \times 10^5$ | -0.6 |      |      |      | -2.3 |        |      |        |        |      |
| Oct. 20          | Oxygen                        | +1.5 |      | +0.9 | +0.8 | +0.9 |        | 0    |        | 0      |      |
|                  | Nitrogen                      | -2.2 |      | -2.2 |      |      |        |      |        | -1.8   |      |
|                  | Methane                       | 0    |      | 0    | -0.4 | -0.4 |        | -6.8 |        | -6.3   |      |
|                  | Hydrogen                      | 0    |      | 0    |      |      |        |      |        | -4.2   |      |
|                  | $\Sigma \Delta D \times 10^5$ | -0.7 |      | -1.3 |      |      |        |      |        | -12.3  |      |
| Nov. 11          | Oxygen                        | +1.5 |      | +1.4 | +1.4 | +1.4 |        | +1.4 |        | +1.3   |      |
|                  | Nitrogen                      | -2.2 |      | -2.3 | -2.4 | -2.3 |        | -2.3 |        | -2.3   |      |
|                  | Methane                       | 0    |      | 0    | -0.1 | -0.1 |        | -0.2 |        | -0.2   |      |
|                  | Hydrogen                      | 0    |      | 0    | -0.1 | 0    |        | -0.1 |        | -0.1   |      |
|                  | $\Sigma \Delta D \times 10^5$ | -0.7 |      | -0.9 | -1.1 | -1.1 |        | -1.2 |        | -1.3   |      |
| Dec. 15          | Oxygen                        | +2.3 | +2.2 | +2.1 | +2.2 | +2.1 |        |      | +1.1   |        |      |
|                  | Nitrogen                      | -1.7 |      | -2.8 |      | -2.8 |        | -2.8 | -2.8   |        |      |
|                  | Methane                       | 0    |      | 0    |      | 0    |        | 0    | 0      |        |      |
|                  | Hydrogen                      | 0    |      | 0    |      | 0    |        | 0    | 0      |        |      |
|                  | $\Sigma \Delta D \times 10^5$ | +0.6 |      | -0.7 |      | -0.7 |        |      | -1.7   |        |      |
| Jan. 19<br>1936  | Oxygen                        | +2.3 | +2.3 | +2.2 | +2.3 | +2.2 |        | +2.1 |        |        |      |
|                  | Nitrogen                      | -3.2 | -3.2 | -3.0 | -3.0 | -3.6 |        | -3.2 |        |        |      |
|                  | Methane                       | -0.1 | -0.1 | -0.2 | -0.3 | -0.2 |        | -0.1 |        |        |      |
|                  | Hydrogen                      | 0    | -0.1 | 0    | 0    | 0    |        | -0.1 |        |        |      |
|                  | $\Sigma \Delta D \times 10^5$ | -1.0 | -1.1 | -1.0 | -1.0 | -1.6 |        | -1.3 |        |        |      |

Table 22.—(Continued).

|          |                         | 0 m. | 1 m. | 2 m. | 3 m. | 4 m. | 4.7 m. | 5 m. | 5.2 m. | 5.5 m. | 6 m.  |
|----------|-------------------------|------|------|------|------|------|--------|------|--------|--------|-------|
| Feb. 28  | Oxygen                  | +2.2 |      | +2.2 |      | +2.2 |        | +2.2 |        |        |       |
|          | Nitrogen                | −3.0 |      | −3.0 |      | −3.0 |        | −2.9 |        |        |       |
|          | Methane                 | 0    |      | −0.1 |      | −0.3 |        | −0.1 |        |        |       |
|          | Hydrogen                | −0.2 |      | 0    |      | 0    |        | −0.2 |        |        |       |
|          | $\Sigma AD \times 10^5$ | −1.0 |      | −0.9 |      | −1.1 |        | −1.0 |        |        |       |
| Mar. 28  | Oxygen                  | +1.9 | +1.9 | +1.9 | +1.9 | +1.9 |        |      |        |        |       |
|          | Nitrogen                | −2.6 |      | −2.7 |      | −2.7 | −2.7   |      |        |        |       |
|          | Methane                 | −0.1 |      | −0.1 |      | 0    | −0.1   |      |        |        |       |
|          | Hydrogen                | −0.1 |      | 0    |      | −0.1 | −0.1   |      |        |        |       |
|          | $\Sigma AD \times 10^5$ | −0.9 |      | −0.9 |      | −0.9 |        |      |        |        |       |
| Apr. 29  | Oxygen                  | +2.0 | +2.2 | +1.8 |      | +0.9 |        | +0.3 |        |        |       |
|          | Nitrogen                | −2.3 |      | −2.3 | −2.3 | −2.4 |        | −2.4 |        | −2.6   |       |
|          | Methane                 | −0.1 |      | −0.1 | −0.1 | −0.1 |        | −0.1 |        | −0.1   |       |
|          | Hydrogen                | −0.2 |      | −0.2 | −0.4 | −0.2 |        | −0.2 |        | −0.2   |       |
|          | $\Sigma AD \times 10^5$ | −0.6 |      | −0.8 |      | −1.8 |        | −2.4 |        |        |       |
| May 25   | Oxygen                  | +1.7 | +1.7 | +1.5 | +1.0 | +0.4 |        | 0    |        | 0      |       |
|          | Nitrogen                | −2.0 |      | −2.2 | −2.2 | −2.4 |        | −2.5 |        | −2.5   |       |
|          | Methane                 | 0    |      | −0.1 | −0.1 | 0    |        | −0.1 |        | −0.1   |       |
|          | Hydrogen                | −0.2 |      | −0.1 | −0.1 | −0.1 |        | −0.1 |        | −0.1   |       |
|          | $\Sigma AD \times 10^5$ | −0.5 |      | −0.9 | −1.4 | −2.1 |        | −2.7 |        | −2.7   |       |
| June 21  | Oxygen                  | +1.7 | +1.7 | +1.6 | +1.0 | +0.1 |        | 0    |        | 0      |       |
|          | Nitrogen                | −2.0 | −2.0 | −2.1 | −2.2 | −2.3 |        | −2.4 |        | −2.4   |       |
|          | Methane                 | 0    | −0.1 | 0    | −0.1 | −0.1 |        | −0.5 |        | −0.9   |       |
|          | Hydrogen                | 0    | 0    | −0.1 | 0    | 0    |        | 0    |        | −0.2   |       |
|          | $\Sigma AD \times 10^5$ | −0.3 | −0.4 | −0.6 | −1.3 | −2.3 |        | −2.9 |        | −3.5   |       |
| July 25  | Oxygen                  | +1.8 | +1.8 | +1.4 | +0.1 | +0.1 |        | 0    |        | 0      |       |
|          | Nitrogen                | −1.9 | −1.9 | −1.9 | −2.1 | −2.3 |        | −2.4 |        | −2.6   |       |
|          | Methane                 | −0.1 | −0.1 | −0.1 | −0.2 | −0.8 |        | −2.3 |        | −1.5   |       |
|          | Hydrogen                | 0    | −0.1 | −0.1 | 0    | −0.1 |        | −0.3 |        | −0.7   |       |
|          | $\Sigma AD \times 10^5$ | −0.2 | −0.3 | −0.7 | −2.2 | −3.1 |        | −5.0 |        | −4.8   |       |
| Sept. 13 | Oxygen                  | +1.6 |      | +1.5 | +0.4 | 0    |        | 0    |        | 0      | 0     |
|          | Nitrogen                | −1.9 |      | −1.7 | −1.8 | −2.0 |        | −2.2 |        |        | −2.3  |
|          | Methane                 | −0.1 |      | −0.4 | −0.3 | −2.3 |        | −4.8 |        |        | −5.1  |
|          | Hydrogen                | 0    |      | 0    | −0.1 | −0.1 |        | −0.8 |        |        | −0.8  |
|          | $\Sigma AD \times 10^5$ | −0.4 |      | −0.6 | −1.8 | −4.4 |        | −7.8 |        |        | −8.2  |
| Oct. 4   | Oxygen                  | +1.0 |      | +0.9 | +0.7 | +0.6 |        | +0.6 |        | 0      | 0     |
|          | Nitrogen                | −2.2 |      | −2.0 | −1.8 | −1.9 |        | −2.0 |        | −2.1   | −2.2  |
|          | Methane                 | 0    |      | −0.3 | −1.0 | −0.8 |        | −0.9 |        | −6.8   | −8.6  |
|          | Hydrogen                | 0    |      | −0.1 | −0.2 | −0.1 |        | −0.1 |        | −0.5   | −0.8  |
|          | $\Sigma AD \times 10^5$ | −1.2 |      | −1.5 | −2.3 | −2.2 |        | −2.4 |        | −9.4   | −11.6 |
| Oct. 25  | Oxygen                  | +1.1 | +1.2 | +1.1 | +1.1 | +1.1 |        | +1.0 |        | +0.9   |       |
|          | Nitrogen                | −2.3 | −2.2 | −2.2 | −2.2 | −2.3 |        | −2.2 |        | −2.1   |       |
|          | Methane                 | 0    | 0    | 0    | 0    | −0.1 |        | −0.1 |        | −0.4   |       |
|          | Hydrogen                | 0    | 0    | 0    | 0    | 0    |        | 0    |        | 0      |       |
|          | $\Sigma AD \times 10^5$ | −1.2 | −1.0 | −1.1 | −1.1 | −1.3 |        | −1.3 |        | −1.6   |       |

Table 23. Changes in the water density in Nakatuna-ko due to dissolved gases. (August 17-19, 1936.)  $\Delta D \times 10^5$ .

|                               | 0 m. | 2 m. | 4 m. | 6 m. | 7 m. | 8 m. | 9 m. | 10 m. | 11 m. | 11.5 m. | 12 m. | 12.5 m. |
|-------------------------------|------|------|------|------|------|------|------|-------|-------|---------|-------|---------|
| Oxygen                        | +1.5 | +1.6 | +1.6 | +2.0 | +1.3 | +1.0 | +0.5 | +0.1  | +0.1  |         | +0.1  | 0       |
| Nitrogen                      | -1.8 | -1.8 | -1.8 | -2.0 |      | -2.4 |      | -2.5  | -2.5  | -2.4    | -2.6  | -2.5    |
| Methane                       | -0.1 | -0.1 | -0.1 | -0.1 |      | -0.1 |      | -0.1  | -0.8  | -2.0    | -2.7  | -4.3    |
| Hydrogen                      | 0    | 0    | 0    | 0    |      | 0    |      | 0     | 0     | 0       | -0.4  | -0.6    |
| $\Sigma \Delta D \times 10^5$ | -0.4 | -0.3 | -0.3 | -0.1 |      | -1.5 |      | -2.5  | -3.2  |         | -5.6  | -7.4    |

Table 24. Changes in the water density in Kizaki-ko due to dissolved gases. (August 7-9, 1936.)  $\Delta D \times 10^5$ .

|                               | 0 m. | 1 m. | 2 m. | 5 m. | 10 m. | 15 m. | 20 m. | 25 m. | 28.8 m. | 28.9 m. |
|-------------------------------|------|------|------|------|-------|-------|-------|-------|---------|---------|
| Oxygen                        | +1.5 | +1.6 | +1.6 | +1.8 | +1.9  | +1.8  | +1.4  | +0.8  |         | +0.2    |
| Nitrogen                      | -1.9 |      |      | -2.1 | -2.5  | -2.7  | -2.7  | -2.7  | -2.7    |         |
| Methane                       | 0    |      |      |      |       | 0     | -0.1  | -0.2  | -0.3    |         |
| Hydrogen                      | 0    |      |      |      |       | 0     | 0     | 0     | 0       |         |
| $\Sigma \Delta D \times 10^5$ | -0.4 |      |      |      |       | -0.9  | -1.4  | -2.1  |         |         |

The maximum values of  $\frac{d(\Sigma \Delta D)}{dz}$ , 0.000036 and 0.000010, were found between the depths of 12 to 12.5 m. in the case of Nakatuna-ko, and between 20-25 m. in that of Kizaki-ko respectively.

**Decrease in Density of the Bottom Water of Takasuka-numa, and the Dissolved Gases.** It has been shown that in Takasuka-numa, the four gases, oxygen, nitrogen, hydrogen, and methane, are so distributed that the deeper-lying waters tend to become lighter than those lying above them. Consequently, the total decrease in density due to the dissolved gases, and the gradient of its vertical change, increase with depth, while both attained their maxima in October 20, after which they became smaller with time.

Parallelism is evident when we compare these results with data covering measurements of the densities of the waters of the lake, as already reported. Thus the density decrease in the deepest water reported can be explained partly by the dissolution of gases, but partly, because, as it will be shown in the following, the amount of decrease due to the dissolved gases did not exceed 10 per cent of the total decrease observed. For example, the difference in water density, actually observed between depths of 5 and 5.5 m., was -0.0002 in September and October, and -0.00003 in November and -0.00005 in December, while the corresponding density change by the dissolved gases was merely -0.000001, for example in November. Consequently, the observed difference in the water



density always rises higher by one figure to the density change due to the dissolved gases.

When this point is taken into consideration, we are led to the conclusion that a part of the decrease in the density of the bottom water of Takasuka-numa was naturally caused by the dissolved gases, although this part, presumably did not exceed 10 per cent of the total decrease actually observed.

Moreover, there are, in a lake, various factors, operating to increase the density of water, but more so in deeper water than in the upper, such as the unequal distribution of dissolved solid matter in the upper and deeper waters.

The observed decrease in density at the bottom is then nothing but a balancing of the actual density decrease and the accepted density increase.

We must, therefore, assume an actual decrease in density that is greater in magnitude than the apparent decrease, and we must also assume the presence of a cause that is more conducive to density decrease.

## V. The Dissolved Gases in the Lake Waters, and their Significance in Lake Metabolism.

### General Description.

As an example of an early study of the dissolved gases in lake water, we might mention that of A. Delebecque.<sup>(25)</sup> In the summer of 1894, he determined the content of oxygen by the method of Mohr, at various layers of Lakes Mont-Cenis, Bourget, Genève, and Nantua; and in the following year, he and M. A. Le Royer boiled the sample water of Lake Genève and collected the dissolved gases. The oxygen was absorbed by alkaline pyrogallol solution and the unabsorbed gas reported as nitrogen.

These analyses, done at that time with the utmost care, have to-day only a historical significance.

During 1905-8, following A. Delebecque, E. A. Birge and Ch. Juday<sup>(26)</sup> studied some Wisconsin lakes. The dissolved gases were also collected by boiling, and analyzed after Hempel.

Stimulated by these studies, similar investigations were made repeatedly of the dissolved oxygen in lake waters, for which a simple method of determination, such as that of Winkler, had been devised, the data from numerous lakes all over the world, in which practically all possible types of lake are represented, filling a bulky volume.

In contrast to this, no studies have since been reported on other gases, of which may be mentioned nitrogen, hydrogen, methane, etc. In the circumstances, the old results of Birge and Juday are still the only data available for discussing these gases in lake water.

The strides made by limnology during the past thirty years is so striking that repetitions and extensions of determination of the latter

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(25) Delebecque, "Les Lacs Français," (1898).

(26) Birge and Juday, Wisconsin Geological and Natural History Survey, *Bull.*, **22** (1911), Scientific Series No. 7.

gases have assumed greater importance than before, while more accurate results by improved method of analysis or of procedure are greatly to be desired. It is also desired that continued observations for longer periods than heretofore be done on a particular lake for the purpose of obtaining a right understanding of the seasonal variations in the gases in different water layers, for only then the significance of the gases in "lake metabolism" can be hoped to be elucidated.

Indeed, if we regard a lake as life of a certain kind, as we did in the general introduction to this paper, lake water is nothing but the fluid that circulates through the body which sustains that life in this case, the lake. Therefore, as physiologists study the metabolism that takes place in a particular organ or in the whole body by analyzing the blood gases, analyses of the dissolved gases in lake water will no doubt supply us with the necessary knowledge of the metabolism that is taking place or has taken place in a lake or in a particular part of it.

For this reason, the following studies were made as an indispensable part of the programme of the writer's studies on "lake metabolism".

This study may be divided into three parts.

(1) A study of the five lakes at the foot of Mt. Huzi, the object of which was to compare the distribution of gases (especially in deeper layers) between lakes of different types.

(2) For the purpose of obtaining precise knowledge of the vertical distributions of gases in summer, the three chain-lakes of the Nisina-group in Nagano Prefecture, were examined.

(3) The study of Lake Takasuka-numa, Saitama Prefecture, was for the purpose of obtaining records of the annual variation in the proportions of these gases at different water layers.

In these studies, which were made during 1935-36, parallel with the examinations of the dissolved gases, nitrogen, hydrogen, methane, and total carbonic acid (free, partially, and totally combined), as well as oxygen, the determination of *pH*, temperature, transparency, and the potassium permanganate consumption, and also the iron and manganese contents of the lake water were carried out. The results will be given in the following Tables and Figures.

### Methods.

The water was sampled with either a Kitahara or Eckman's bottle. The latter bottle was found unsuitable for sampling waters at intervals of less than a few score cm., because, in turning the bottle, a considerable amount of the surrounding water is stirred. Therefore in comparing water layers at such small intervals, for example, in the deeper layers of Nakatuna-ko, Kitahara's water bottle was sunk slowly and pulled up very slowly the first 1-2 m., allowing the surrounding waters to remain undisturbed.

The water temperature was read from a reversible thermometer attached to the Eckman bottle.

The *pH* of the waters was determined by the colorimetric method, using phenol-red and bromo-thymol-blue.

Oxygen was determined in two different ways, by Winkler's iodometric method, and by "the carbon dioxide method" to be described later. The values in the following tables are those by the former method.

Nitrogen, methane, and hydrogen were expelled by means of carbon dioxide, and then analysed as usual after Hempel.

The total carbonic acid was determined by the method of Petterson, modified by L. W. Winkler,<sup>(27)</sup> and further improved in certain points by the writer and his co-workers.

**The Carbon Dioxide Method of Winkler, Modified by the Writer.** The usual method for expelling the dissolved gases from water is that by boiling, which, however, has a number of drawbacks, chief among which is the difficulty of transporting the apparatus and the cumbrous work of setting it up and handling it on the field, besides the need for a source of heat.

For these reasons, the writer used the method of expulsion by means of carbon dioxide bubbles, after Winkler, with modification in certain points.

*The procedure.* About 10 g. of crushed marble are placed in a glass bottle, whose capacity (about 500 c.c.) is determined exactly beforehand. The bottle is then filled with the sample water and furnished with a glass funnel (b) to which about 15 c.c. of 25% hydrochloric acid are added. Next, the gas burette (a) is fitted to the funnel with a connecting stop-cock (g), which is previously filled with water and the cock closed after connection.

The burette is filled with 10% caustic soda solution, to which 50 gm. of Rochelle salt have been added per litre. Capillary tube (e) as well as head funnel (c) are also filled with the same solution. While this is being done, a part of the hydrochloric acid in the funnel (b) is made to gradually flow into bottle (A), yet no marked reaction occurs. Stop-cock (g) is then opened. Violent reaction first occurs, and bubbles of the evolved carbon dioxide ascend, carrying along with them other gases from the sample water through the liquid in the burette.

During the passage of the gas bubbles through the caustic soda solution, the carbon dioxide as well as the other gases that are soluble in alkali, are completely absorbed, leaving only insoluble gases in the burette. During this process, to facilitate evolution of gas, the level of the liquid in the reservoir (f) is kept slightly lower than the level in the burette.

For complete absorption, fresh alkali solution is made to flow down from the head funnel along the wall of the burette by opening cock (d). In the cold season, when the evolution of carbon dioxide is frequently very feeble, the bottle (A) is warmed by hot water (k). Expulsion of the dissolved gases is usually completed in 40 minutes. After closing cock (g), the burette is disconnected at (J) and rocked backward and forward several times in order to secure complete dissolution of the soluble gases. The burette is set up again vertically, left standing for a while, and the readings of the volume of the unabsorbed gas, the temperature, and the atmospheric pressure are taken. Pyrogallol solution and fresh caustic soda solution are next made to flow down the burette from the head funnel for the absorption of oxygen. After treatment with alkaline pyrogallol solution, the volume of the unabsorbed gas, as well as that of oxygen, is determined.

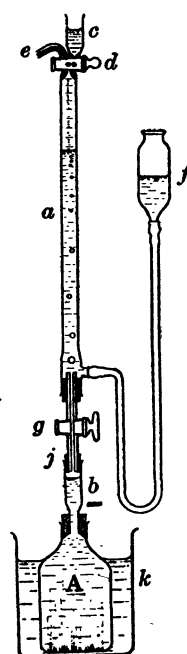


Fig. 5.

**Errors Liable in the Carbon Dioxide Method.** The errors inherent to the present method may be divided into the following two: the error in method, which can occur only through some defect in the method, and the errors in observation, which, for example, may occur in reading the scale, etc., and which may be + or -. The writer examined these two kinds of errors separately.

*Errors in method.* At room temperature, air was continually bubbled through 15 l. of distilled water for a few hours until the water was saturated with air. The water was then transferred into three bottles by a syphon, and the dissolved oxygen in each bottle was determined in the following three different ways.

(27) Winkler, "Trink- und Brauch-wasser in Lung-Berls chemisch-technischen Untersuchungsmethoden", 7. Auflage, Band I, 573.

First, the gas in one of the three bottles was determined by Winkler's carbon dioxide method, that in the second bottle by the usual boiling method as modified by the writer, and that in the remaining bottle by the iodometric method, the results of which are given in Table 25.

When we compare the values of oxygen with one another, it is found at once that the value obtained from the carbon dioxide method is the largest, that from the boiling method the least, and that from the iodometric method intermediate, a result that was expected from the beginning. Of the three, the iodometric method is the most direct and consequently the most reliable. That the value from the boiling method was smaller than that from the iodometric method, is easily explained as being due to the incomplete removal of the dissolved gases from the examined water by the boiling method. On the other hand, that the carbon dioxide method showed a larger value than the iodometric method, is probably due to the fact that the dissolved oxygen in the caustic soda solution, used for the absorption of carbon dioxide, is also partly expelled and is added to the gases from the examined water, leading to the erroneously larger value observed. An error of this kind also occurs with other gases dissolved. Thus the value of the unabsorbed gas that was left over after treatment with alkaline pyrogallol solution, is always smaller with the boiling method than with the carbon dioxide method.

Table 25. Comparison of the three different methods for determining the dissolved gases in water.

|                                                | Oxygen (c.c./l.) |                        | Unabsorbed gas (c.c./l.) |                        |
|------------------------------------------------|------------------|------------------------|--------------------------|------------------------|
|                                                | Result           | Mean observation error | Result                   | Mean observation error |
| a ... The carbon dioxide method                | 7.69             | $\pm 0.03$             | 14.84                    | $\pm 0.06$             |
|                                                | 7.70             |                        | 14.91                    |                        |
|                                                | 7.62             |                        | 14.70                    |                        |
|                                                | 7.68             |                        | 14.84                    |                        |
| b ... The boiling method                       | 7.67             | $\pm 0.04$             | 14.82                    | $\pm 0.09$             |
|                                                | 7.28             |                        | 14.83                    |                        |
|                                                | 7.34             |                        | 14.61                    |                        |
|                                                | 7.24             |                        | 14.63                    |                        |
| c ... The iodometric method                    | 7.29             | $\pm 0.007$            | 14.69                    | 0.13                   |
|                                                | 7.524            |                        |                          |                        |
|                                                | 7.530            |                        |                          |                        |
|                                                | 7.534            |                        |                          |                        |
|                                                | 7.529            |                        |                          |                        |
| The difference between the values from a and b | 0.38             |                        |                          |                        |
| The difference between the values from a and c | 0.14             |                        |                          |                        |
| The difference between the values from b and c | 0.24             |                        |                          |                        |

Table 26. The error in sampling the water and in its transference.

|                                                        | Oxygen (c.c./l.) |      | Unabsorbed gas (c.c./l.) |
|--------------------------------------------------------|------------------|------|--------------------------|
| An example with Kizaki-ko<br>(August 8, 1936.)         | (a)              | 6.10 | 15.40                    |
|                                                        | (b)              | 6.10 | 15.40                    |
| Another example with Nakatuna-ko<br>(August 19, 1936.) | (a)              | 0.20 | 17.29                    |
|                                                        | (b)              | 0.20 | 17.40                    |

Next, quantitatively, the oxygen value from the carbon dioxide method was found to be larger by 0.14 c.c. than that from the iodometric method, which is taken here as the standard, while the value by the boiling method is smaller by 0.24 c.c. than that by standard method. Besides, as referred to the standard, the two values deviate in opposite sense, the magnitude of the deviation by the carbon dioxide method being about half that by the boiling method. Thus it is concluded that the value from the carbon dioxide method is nearer to the right value than that from the boiling method.

It is also remarkable that in both methods, the difference between the values of the unabsorbed gases that were left after the removal of oxygen, does not exceed 0.13 c.c., which is only one-third the difference between the oxygen values, 0.36 c.c., given above.

It would seem more natural if the above values by both of the methods under examination, had differed by double the difference between the oxygen values, when it is considered that the volume of the unabsorbed gases is close to double that of oxygen.

But, as already said, actually this is not the case, the reason for which probably is that the treatment after expulsion of the dissolved gas, such as that with pyrogallol solution, affects the oxygen differently to what it does the unabsorbed gases. At any rate, the small difference in the values of the unabsorbed gases by the two methods, (the true value being assumed to lie between these two values) is better suited to the determination of the gases in question, because there is no simple and accurate method of determining the unabsorbed gases, as the iodometric method does for oxygen.

Next, we must discuss the errors in method to which both methods are subject. As just said, the true value for the unabsorbed gases lies between those given by the two methods, but the question is, at what point between the two does the correct one lie?

Assuming that the true value is the mean of those by the two methods, we get 0.07 c.c., but if we assume that the values by the two methods deviate from the true in the same proportion as they did from the value by the iodometric method in the case of oxygen, the error by the carbon dioxide method works out to 0.05 c.c., and that by the boiling method to 0.09 c.c.

Whichever assumption we may make, the errors from method in both cases, namely, the deviation in the values of the unabsorbed gases from the true value, do not exceed 0.1 c.c. Consequently, should we wish to carry out the determination of these gases where an observation error of 0.1 is of no serious consequence, then the observed values may be taken as true without correction.

Summarising the foregoing, the writer concludes that:

(1) The carbon dioxide method proved to be equal to the boiling method, judged from the point of error in method, in determining the dissolved gases of lake water other than oxygen.

(2) In analysis, where an error of 0.1 is admitted, the value by the carbon dioxide method can be taken as true, without any correction.

*Errors in observation.* Upon comparing, next, the observational errors peculiar to the various methods, it is obvious that the mean error is least in the iodometric method, intermediate in the carbon dioxide method, and largest in the boiling method.

In addition, certain advantages make the carbon dioxide method more appropriate for field work.

(1) By using from five to six sets of apparatus, simultaneous determination can be carried out by a single worker.

(2) The apparatus being simple, in the event of damage, it could be set up again with the aid of readily accessible substitutions and makeshifts, which, however, is fairly difficult with the boiling method.

**An Examination in the Error in Sampling the Water and in Transferring it into the Measuring Bottles.** (Table 26.) This error could be minimized with sufficient care. The two pairs of examples in the table will suffice. Each pair consists of the results of analyses on two different samples obtained from the same depth, at two succeeding samplings. The following results are mostly the mean values of a duplicate analysis.

**Determination of Carbon Monoxide.** The oxygen was absorbed with the alkaline pyrogallol solution from the gas that was expelled by the carbon dioxide method, and the unabsorbed gas charged into a storage tube (Fig. 6) for sending it to the laboratory

for analysis. The analysis was carried out by the usual Hempel method; the procedure, by which the determination of carbon monoxide was made, was found to be worth

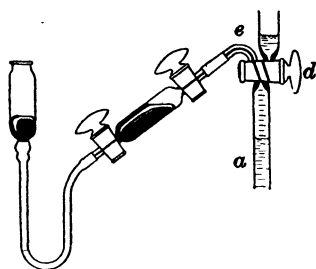


Fig. 6.

discussing. It has been repeatedly reported that the absorption method by ammoniacal cuprous chloride solution gives an unusually large value to this gas. For this reason, even where the presence of carbon monoxide was proved by the cuprous chloride method, the writer tried also the spectroscopical test with the use of diluted blood on the same sample. The test proved that there was no trace of the gas in any of the samples that had been shown to contain considerable amounts of it by the cuprous method. Therefore, in later analyses, the samples were tested first for the gas by the blood method, and if its absence was shown as was usual in the writer's case, the treatment with cuprous chloride solution was omitted.

**The Boiling Method.** The original method of Treadwell<sup>(28)</sup> has two drawbacks.

(1) It was often found difficult to secure air-tight connection between the leading tube (C) and the gas burette (B).

(2) Some errors arise in the reading of the volume of the expelled gas owing to the fact that the dissolved gases are eliminated by a number of expulsions into the measuring burette, which are measured, and the sum of the readings is taken as the volume of the total gas obtained.

S. Sintani, the writer's co-worker, improved these two defects by means of the following modification, and succeeded in securing more accurate results.

First, for remedying the second defect, besides the burette ( $B_1$ ), which corresponds to burette (B) in the original method, a second burette ( $B_2$ ) was installed. The gas, which was driven into burette ( $B_1$ ), in several instalments, was collected into the measuring burette ( $B_2$ ), where the total volume was measured after it was ascertained that no more gas remained in the boiled flask.

In order to improve the first point, (R) was furnished with a side-tube, and the parts (I), (R), (K) and (C) were filled with mercury before the boiling was started.

The procedure is as follows.

A round flask of about 250 c.c. capacity, whose exact volume when level with the etched line at the neck, was previously determined; is filled with the sample water.

Into a rubber stopper, a glass tube (R) is inserted through a hole in it, until a small opening blown near the fused bottom of the tube, appears just below the bottom of the rubber stopper. The stopper is then pushed down into the flask to the etched line. While this is being done, a part of the water in the flask will flow into the tube, which is then raised, so that the side hole is buried in the rubber. In this way, the apparatus is made air-tight, after which the flask is connected with the other parts of the apparatus, as shown in Fig. 7.

By raising (I), and by releasing the screw cock (p), the mercury is made to flow into (R), (K) and (C). The cock (q) is closed so that the connection between (q) and the connecting tube (C) is cut, while the tube ( $B_1$ ) is connected with the exterior by the three-way cock (s). The reservoir ( $N_1$ ) is then raised and the burette ( $B_1$ ), as well as the capillary to the cock (s), are filled with mercury. By giving the cocks (s), (r), and (t) a suitable turn, and by raising the reservoir ( $N_2$ ), the burette as well as the connecting capillaries (rs) and (rt) are filled with water.

The screw-cock (p) is now opened and the reservoir (I) is lowered. The mercury then flows back into the reservoir, when there develops a vacuum in the bulb (K). When the top of the mercury reaches just above the cock (p), the latter is closed, and the reservoir (I) is dipped into boiling water to warm the mercury in it.

The tube (R) is now pushed into the flask until the small opening reaches below

(28) Treadwell, "Lehrbuch der Analytischen Chemie" II (1923), 638.

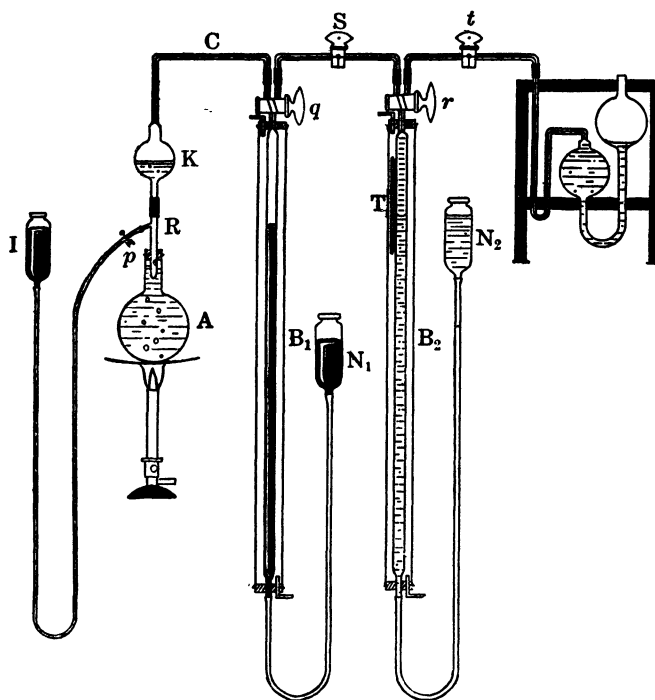


Fig. 7.

the lower surface of the rubber stopper. Evolution of gas begins immediately. The reservoir ( $N_1$ ) is lowered, and the cock is turned so that the bulb (K) and the burette ( $B_1$ ) are in connection. The flask (A) is heated to boiling as soon as possible. Here, it is necessary to regulate the level of the mercury in the reservoir ( $N_1$ ), to prevent the water in the flask from flowing over into the receiving burette ( $B_1$ ). When a sufficient amount of gas has been driven into the burette ( $B_1$ ), the stopcock ( $q$ ) is closed and the gas is transferred into the burette ( $B_2$ ). After this operation is repeated several times, the reservoir (I) is raised and the screw-cock ( $p$ ) opened. Hot mercury is poured into the flask, whereby the level of water in the bulb (K) is elevated and the remaining gas is completely transferred into the receiving burette ( $B_1$ ) and finally into the measuring burette ( $B_2$ ). As soon as the evolved gas is completely transferred into the burette ( $B_2$ ) and brought into equilibrium with the surrounding temperature, its volume is read. The gas is then analyzed.

**Determination of Total Carbon Dioxide.** The apparatus used for this determination is the same as that for the boiling method. In place of mercury, the reservoir (I) is charged with concentrated hydrochloric acid. About 0.01 g. of aluminium wire is placed into the flask, after which the flask is filled with the sample water and stoppered.

The apparatus is set up in the same way as in the "boiling method". The air in the bulb (K), which is drawn out into the burette ( $B_1$ ) by lowering the reservoir ( $N_1$ ), is then expelled through the three-way cock ( $s$ ), whose operation is repeated several times. Then, when the bulb is exhausted of air, the glass tube (R) is pushed into the flask. Evolution of gas immediately begins. The screw-cock ( $p$ ) is now opened, and hydrochloric acid is made to flow into the flask (A). A lively decomposition of carbonates occurs with the evolution of hydrogen gas which, in turn, is caused by the action of the acid upon the aluminium. When the evolution of gas is subdued, the flask is heated to boiling, and the remaining carbon dioxide expelled.

After reading the volume of the gas that has been collected in the burette ( $B_2$ ), the gas is led into the Orsat tube, and the absorbed carbon dioxide determined.

### Study of the Five Lakes at the Foot of Mt. Huzi.

The determination was carried out during August 19–22, 1935. Tables 27–31 show the results of observations, from which the following parallelism could be established.

**Parallelism in the Degree of Eutrophication and that of Nitrogen Saturation.** In the paper previously cited<sup>(6)</sup> D. Inaba pointed out the existence of a parallelism in the amounts of plankton and of protein nitrogen in his observation of the five lakes in the winter of 1934, where the amount of plankton and the degree of eutrophication (the latter, judged from the amount of protein nitrogen), which are the largest in Syozi-ko, decrease in the order of Yamanaka-ko, Kawaguti-ko, Nisino-umi, Motosu-ko.

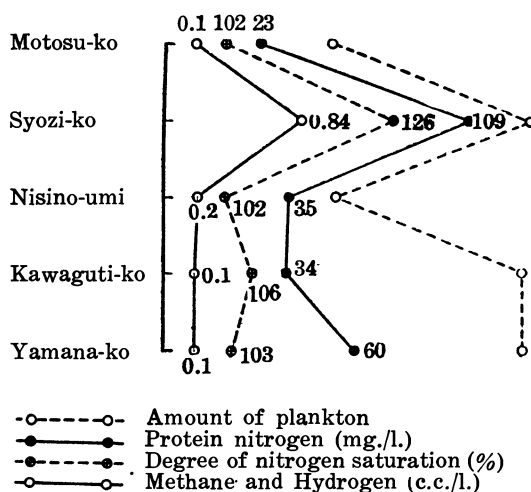


Fig. 8.

Table 27. Motosu-ko.

| August 19, 1935 (1.30-4.00 P.M.), Transparency 12.5 m., Atmospheric pressure 688 mm. |              |     |                   |             |                             |                     |               |                    |                     |
|--------------------------------------------------------------------------------------|--------------|-----|-------------------|-------------|-----------------------------|---------------------|---------------|--------------------|---------------------|
| Depth<br>m.                                                                          | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. |
| 0                                                                                    | 22.8         | 6.9 | 5.63              | 101.8       |                             |                     |               |                    |                     |
| 1                                                                                    | 22.8         |     |                   |             |                             |                     |               |                    |                     |
| 2                                                                                    |              |     |                   |             |                             |                     |               |                    |                     |
| 5                                                                                    | 21.6         | 7.0 | 5.60              | 99.3        |                             |                     |               |                    |                     |
| 10                                                                                   | 21.5         | 7.0 | 5.60              | 99.7        |                             |                     |               |                    |                     |
| 15                                                                                   | 14.3         | 6.9 |                   |             |                             |                     |               |                    |                     |
| 20                                                                                   | 9.8          | 6.8 | 7.79              | 107.8       |                             |                     |               |                    |                     |
| 30                                                                                   | 6.9          |     |                   |             |                             |                     |               |                    |                     |
| 115                                                                                  |              | 6.5 |                   |             | 15.12                       | 15.0                | 102           | 0.03               | 0.11                |
| 120                                                                                  | 6.1          | 6.4 | 6.67              | 84.5        | 15.03                       |                     |               |                    |                     |



Table 28. Syozi-ko.

| August 20, 1935 (5.40-9.00 A.M.), Transparency 5.0 m., Atmospheric pressure 690 mm. |           |     |                |          |                          |                  |            |                 |                  |                                        |
|-------------------------------------------------------------------------------------|-----------|-----|----------------|----------|--------------------------|------------------|------------|-----------------|------------------|----------------------------------------|
| Depth m.                                                                            | Temp. °C. | pH  | Oxygen c.c./l. | Oxygen % | Unabsorbed gases c.c./l. | Nitrogen c.c./l. | Nitrogen % | Methane c.c./l. | Hydrogen c.c./l. | C <sub>n</sub> H <sub>2n</sub> c.c./l. |
| 0                                                                                   | 22.5      | 7.4 | 5.77           | 103.6    |                          |                  |            |                 |                  |                                        |
| 2                                                                                   |           |     | 5.90           |          |                          |                  |            |                 |                  |                                        |
| 5                                                                                   | 22.3      | 7.4 | 6.00           | 107.5    |                          |                  |            |                 |                  |                                        |
| 10                                                                                  | 20.5      | 7.4 | 5.82           | 100.6    |                          |                  |            |                 |                  |                                        |
| 12                                                                                  | 15.4      | 6.4 | 2.98           | 46.5     | 16.17                    | 15.3             | 126        | 0.4             | 0.4              | 0.1                                    |

Table 29. Nisino-umi.

| August 20, 1935 (2.20-5.00 P.M.), Transparency 10.5 m., Atmospheric pressure 690 mm. |           |     |                |          |                          |                  |            |                 |                  |
|--------------------------------------------------------------------------------------|-----------|-----|----------------|----------|--------------------------|------------------|------------|-----------------|------------------|
| Depth m.                                                                             | Temp. °C. | pH  | Oxygen c.c./l. | Oxygen % | Unabsorbed gases c.c./l. | Nitrogen c.c./l. | Nitrogen % | Methane c.c./l. | Hydrogen c.c./l. |
| 0                                                                                    | 23.0      | 7.3 | 5.58           | 101.1    |                          |                  |            |                 |                  |
| 5                                                                                    | 21.7      | 7.4 | 5.72           | 101.2    |                          |                  |            |                 |                  |
| 10                                                                                   | 14.7      |     | 8.18           | 126.6    |                          |                  |            |                 |                  |
| 20                                                                                   | 12.0      | 7.3 | 8.10           | 117.6    |                          |                  |            |                 |                  |
| 30                                                                                   | 5.5       | 7.0 | 7.00           | 88.2     | 15.53                    |                  |            |                 |                  |
| 40                                                                                   | 5.2       | 6.8 | 6.50           | 80.3     |                          | 15.4             | 102        | 0               | 0.2              |
| 52                                                                                   | 5.2       | 6.8 | 6.44           | 79.6     |                          |                  |            |                 |                  |
| 70                                                                                   | 5.2       | 6.5 |                |          | 15.53                    |                  |            |                 |                  |

Table 30. Kawaguti-ko.

| August 21, 1935 (9.55 A.M.-1.50 P.M.), Transparency 5.0 m., Atmospheric pressure 696 mm. |           |     |                |          |                          |                  |            |                 |                  |
|------------------------------------------------------------------------------------------|-----------|-----|----------------|----------|--------------------------|------------------|------------|-----------------|------------------|
| Depth m.                                                                                 | Temp. °C. | pH  | Oxygen c.c./l. | Oxygen % | Unabsorbed gases c.c./l. | Nitrogen c.c./l. | Nitrogen % | Methane c.c./l. | Hydrogen c.c./l. |
| 0                                                                                        | 23.1      | 7.9 | 5.86           | 105.6    |                          |                  |            |                 |                  |
| 2                                                                                        | 23.1      | 7.9 | 5.92           | 106.6    |                          |                  |            |                 |                  |
| 5                                                                                        | 22.8      | 7.9 | 5.89           | 105.3    |                          |                  |            |                 |                  |
| 8                                                                                        | 20.8      | 6.7 | 4.01           | 69.2     |                          |                  |            |                 |                  |
| 9                                                                                        | 17.2      | 6.4 | 0.20           | 3.2      |                          |                  |            |                 |                  |
| 10                                                                                       | 16.4      | 6.4 | 0.10           | 1.9      |                          |                  |            |                 |                  |
| 11                                                                                       | 15.0      | 6.4 | 0.11           | 1.7      |                          |                  |            |                 |                  |
| 11.5                                                                                     | 15.0      |     |                |          | 13.26                    | 13.1             | 106        | 0               | 0.1              |

Table 31. Yamanaka-ko.

| August 22, 1935 (8-10 A.M.), Transparency 5.5 m., Atmospheric pressure 686 mm. |             |     |                   |             |                             |                     |               |                    |                     |
|--------------------------------------------------------------------------------|-------------|-----|-------------------|-------------|-----------------------------|---------------------|---------------|--------------------|---------------------|
| Depth<br>m.                                                                    | Temp.<br>C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. |
| 0                                                                              | 23.7        | 7.9 | 5.63              | 104.0       |                             |                     |               |                    |                     |
| 2                                                                              | 23.3        | 7.9 | 5.72              | 104.8       |                             |                     |               |                    |                     |
| 5                                                                              | 21.7        | 7.9 | 5.60              | 99.8        |                             |                     |               |                    |                     |
| 6                                                                              | 21.5        | 7.7 |                   |             |                             |                     |               |                    |                     |
| 7                                                                              | 21.2        | 7.1 |                   |             |                             |                     |               |                    |                     |
| 8                                                                              | 20.9        | 6.9 |                   |             |                             |                     |               |                    |                     |
| 9                                                                              | 20.4        | 6.7 | 1.09              | 19.0        |                             |                     |               |                    |                     |
| 10                                                                             | 20.1        | 6.5 | 1.21              | 20.6        |                             |                     |               |                    |                     |
| 10.5                                                                           | 20.0        | 6.5 | 0.89              | 15.3        | 11.53                       | 11.5                | 103           | 0.1                | 0                   |

It was also seen from the writer's observation that the distribution of nitrogen and other gases in the deep waters varies in a similar order. In fact, the degree of nitrogen saturation in the deepest waters was always more than 100% in all the five lakes, and its maximum value, 126%, was found in Syozi-ko, which is the most eutrophic, while in the other lakes, the degree of saturation of this gas decreased in the above order of eutrophication. Thus it was 106% and 103% in Kawaguti-ko and Yamanaka-ko, both moderately eutrophic, and 102% in Nisino-umi and Motosu-ko, the least eutrophic.

The conclusion is that the degree of eutrophication of a lake runs parallel with that of saturation of nitrogen gas in the deepest water in summer.

Such a conclusion indicates that, although the greater part of the nitrogen in the deepest water might have come from the atmosphere, a considerable part was no doubt supplied by the denitrifying decomposition going on in the bottom water or in the bottom deposits.

Since, in an eutrophic lake, the quantity of organic debris deposited is large, much more decomposition is expected to occur, whence it is quite natural to find there a large production of free nitrogen as was found above. This point will be referred to again.

**Methane and Hydrogen.** The two other members of the unabsorbed gas family after treatment with alkaline pyrogallol solution, were methane and hydrogen. The sum of the volumes of these gases per 1 litre of water was 0.1 c.c. in Motosu-ko, 0.2 c.c. in Nisino-umi, 0.1 c.c. in Yamanaka-ko, 0.1 c.c. in Kawaguti-ko, and 0.9 c.c. in Syozi-ko. We find here, as in the case of nitrogen, the largest methane and hydrogen content in the most eutrophic lake, the cause of which can also be ascribed to the intense decomposition in the bottom.

Since the values approximate the observational error, precise comparison and discussion of the values in the remaining four lakes are omitted.

### Study of the Nisina Lake Group in Nagano Prefecture.

A study was carried out during August 7-19, 1936, for the purpose of establishing precise vertical distributions of the gases that are not absorbed by alkaline pyrogallol solution.

In Lake Kizaki, 11 different water layers were examined with intervals of 1-5 m. in the upper layers and with that of 0.3-0.5 m. in the deeper layers. The samples from the surface and from depths below 20 m. were completely analyzed, the results of which showed that the samples from the intermediate layers must have had oxygen and nitrogen up to 99%. In the case of these intermediate layers, therefore, the collected gas was merely treated with alkaline pyrogallol solution, the unabsorbed gas being treated as nitrogen.<sup>(29)</sup>

In Nakatuna-ko, 14 different layers were examined with an interval of 1-2 m., except in the deeper layers, where the interval was reduced to 0.5-0.2 m.

Owing to weather conditions and to difficulties in obtaining various articles necessary in prosecuting these studies, determinations in Aoki-ko were not so reliable as in the case of the other two lakes.

#### The Vertical Variation in the Degree of Saturation of Nitrogen Gas.

(1) The amount of the dissolved nitrogen gas, which increased evenly with depth, suddenly decreased, although slightly, at the bottom. (The data from Aoki-ko does not follow this general tendency, to which, however, little importance can be attached, because of less accuracy in the observation of this lake.)

(2) The degree of nitrogen saturation was always above 100%, except in Nakatuna-ko at depths of 0, 2 and 4 m., where the degree was either 100% or just below it.

(3) Maximum saturation lay always slightly below thermocline. In the case of Nakatuna-ko, a second maximum was found at a depth of 12 m.

Such vertical distribution of nitrogen may be very common in many lakes during the period of summer stagnation, and the way in which such a distribution develops, is easily conceivable. As is usually the case with oxygen, from autumn to winter, abundant nitrogen is absorbed from the air and supplied to the water in all the layers during this period of circulation, while from the following spring to summer, the waters are daily warmed from the surface. This warming occurs in two different ways: (a) by the direct absorption of radiation and (b) by the mixing of the warmed water with the underlying cooler water.

In the latter way, the deepest water, which lies beyond the effective limit of heat radiation, can also be gradually warmed.

At any rate, from the rise in temperature of the water, decrease in solubility of nitrogen gas as well as those of other gases in water, results. Consequently, the degree of gas saturation in water grows larger, often exceeding 100%.

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(29) Here and in the following descriptions, the term "dissolved nitrogen" means dissolved nitrogen and argon.

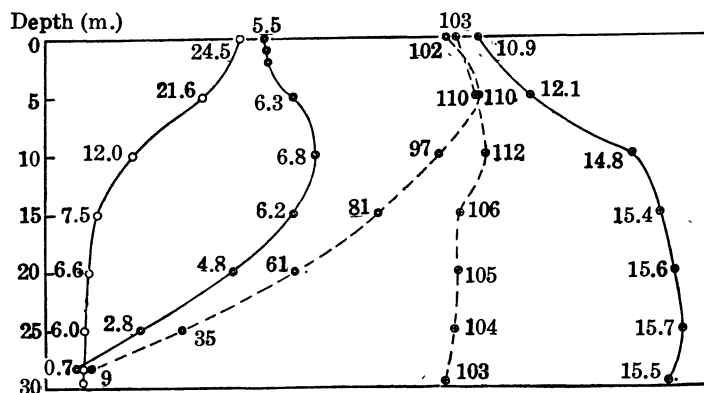


Fig. 9. Kizaki-ko (August 7-9, 1936.)

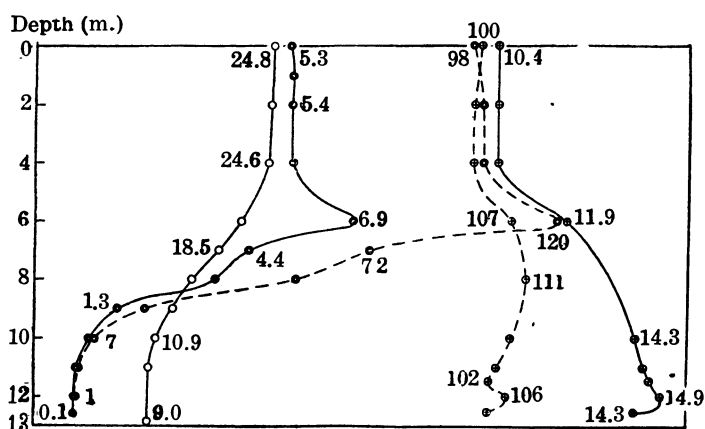


Fig. 10. Nakatuna-ko (August 17-19, 1936.)

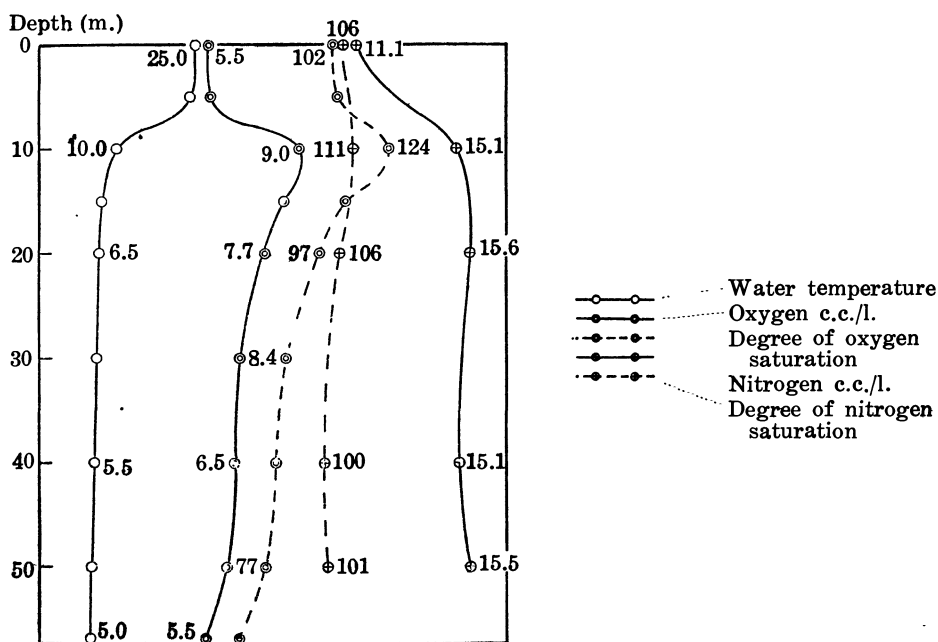


Fig. 11. Aoki-ko (August 18, 1936.)

Table 32. Kizaki-ko.

| August 7-9, 1936. |              |     |                   |             |                             |                     |               |                    |                     |
|-------------------|--------------|-----|-------------------|-------------|-----------------------------|---------------------|---------------|--------------------|---------------------|
| Depth<br>m.       | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. |
| 0                 | 24.5         | 6.9 | 5.51              | 101.6       | 10.94                       | 10.9                | 103           | 0                  | 0                   |
| 1                 |              | 6.9 | 5.49              |             | 11.20                       |                     |               |                    |                     |
| 2                 |              | 6.9 | 5.70              |             | 11.13                       |                     |               |                    |                     |
| 5                 | 21.6         | 6.8 | 6.29              | 110.1       | 12.12                       | (12.1)              | 110           |                    |                     |
| 10                | 12.0         | 6.5 | 6.76              | 97.4        | 14.80                       | (14.8)              | 112           |                    |                     |
| 15                | 7.5          | 6.3 | 6.22              | 80.5        | 15.40                       | 15.4                | 106           | 0                  | 0                   |
| 20                | 6.6          | 6.2 | 4.81              | 61.0        | 15.80                       | 15.6                | 105           | 0.2                | 0                   |
| 25                | 6.0          | 6.0 | 2.81              | 35.1        | 15.97                       | 15.7                | 104           | 0.3                | 0                   |
| 28                | 5.7          |     |                   |             | 16.01                       |                     | 103           |                    |                     |
| 28.8              | 5.7          |     |                   |             | 16.03                       | 15.5                |               | 0.5                | 0                   |
| 28.9              | 5.7          | 6.0 | 0.74              | 9.2         | 15.82                       |                     |               |                    |                     |

Table 33. Nakatuna-ko.

| August 17-19, 1936. |              |     |                   |             |                             |                     |               |                    |                     |
|---------------------|--------------|-----|-------------------|-------------|-----------------------------|---------------------|---------------|--------------------|---------------------|
| Depth<br>m.         | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. |
| 0                   | 24.8         | 6.8 | 5.29              | 98.1        | 10.62                       | 10.4                | 100           | 0.2                | 0                   |
| 2                   | 24.7         | 6.8 | 5.40              | 100.2       | 10.55                       | 10.3                | 99            | 0.2                | 0                   |
| 4                   | 24.6         | 6.8 | 5.41              | 100.2       | 10.37                       | 10.3                | 98            | 0.1                | 0                   |
| 6                   | 20.9         | 7.0 | 6.91              | 119.5       | 12.08                       | 11.9                | 107           | 0.1                | 0                   |
| 7                   | 18.5         | 6.4 | 4.35              | 71.8        |                             |                     |               |                    |                     |
| 8                   | 14.9         | 6.1 | 3.60              | 55.2        | 13.81                       | 13.7                | 111           | 0.1                | 0                   |
| 9                   | 12.4         | 6.1 | 1.27              | 18.5        |                             |                     |               |                    |                     |
| 10                  | 10.9         | 6.0 | 0.49              | 6.9         | 14.37                       | 14.3                | 107           | 0.1                | 0                   |
| 11                  | 9.6          | 6.1 | 0.22              | 3.0         | 15.59                       | 14.3                | 104           | 1.3                | 0                   |
| 11.5                | 9.4          |     |                   |             | 17.35                       | 14.2                | 102           | 3.1                | 0                   |
| 12.0                | 9.1          | 6.3 | 0.21              | 2.9         | 19.73                       | 14.9                | 106           | 4.2                | 0.4                 |
| 12.5                | 9.1          | 6.4 | 0.11              | 1.4         | 21.47                       | 14.3                | 101           | 6.8                | 0.6                 |
| 12.7                | 9.0          |     |                   |             | 20.83                       | 13.9                | 100           | 6.1                | 0.8                 |
| 12.8                | 9.0          | 6.4 | 0.10              | 1.3         |                             |                     |               |                    |                     |

Table 34. Aoki-ko.

| August 18, 1936. |              |     |                   |             |                             |                     |               |
|------------------|--------------|-----|-------------------|-------------|-----------------------------|---------------------|---------------|
| Depth<br>m.      | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% |
| 0                | 25.0         | 6.8 | 5.47              | 102.1       | 11.12                       | (11.1)              | 106           |
| 5                | 24.0         | 7.0 | 5.63              | 102.9       |                             |                     |               |
| 10               | 10.0         | 7.4 | 8.99              | 123.8       | 15.10                       | (15.1)              | 111           |
| 15               | 7.2          | 7.0 | 8.37              | 107.8       |                             |                     |               |
| 20               | 6.5          | 6.6 | 7.70              | 97.3        | 15.64                       | (15.6)              | 106           |
| 30               | 5.9          | 6.4 | 6.73              | 83.9        |                             |                     |               |
| 40               | 5.5          | 6.3 | 6.54              | 80.6        | 15.12                       | (15.1)              | 100           |
| 50               | 5.0          | 6.2 | 6.30              | 76.7        | 15.51                       | (15.5)              | 101           |
| 57               | 5.0          | 6.2 | 5.48              | 66.7        |                             |                     |               |

This is the case with the metalimnion where, although the warming effect from the above two causes is still sufficiently strong, escape of the nitrogen, in excess, is greatly hindered. In the surface layers, however, the nitrogen excess has a better chance of escaping from the water into the atmosphere, so that the degree of saturation is kept at 100% or near it, notwithstanding that the warming effect is greatest in these layers.

On the other hand, in the deeper layers, where the temperature elevation of the water is small, no marked supersaturation was found.

Thus in summer, the degree of nitrogen saturation that starts from the surface value of 100% or near it, increases towards the bottom and attains maximum at a layer slightly below thermocline, from which it decreases towards the bottom, as established.

A brief discussion is also necessary regarding the origin of the second increase in the degree of nitrogen saturation at the bottom, such as was found in a layer near the bottom of Nakatuna-ko.

This increase, no doubt, has no relation to the factors above considered, but owes its origin to the denitrifying decomposition that occurs at the bottom, as was suspected to be the case in Syozi-ko, and was proved conclusively in Takasuka-numa, as will be referred to later.

**Methane and Hydrogen.** These two gases, besides oxygen and nitrogen, represent the two other dissolved gases from these lakes, which were abundant in water layers below 20 m. in Kizaki-ko and in those below 11 m. in Nakatuna-ko. The content of these gases in water layers less deep, never exceeded 0.2 c.c. per litre.

The parallelism that was pointed out as existing between the content of these gases at the bottom water and the eutrophication of lakes in the case of the five lakes at the foot of Mt. Huzi, was here also found true; the content of these gases in the bottom water greatly exceeded that in Nakatuna-ko, which is more eutrophic than Kizaki-ko.

**Comparison of Oxygen with Nitrogen.** The difference in form of the curves of oxygen and nitrogen is worth mentioning.

Oxygen starts also from the surface value of its degree of saturation, 100% or near it, and increases with depth, as was found in the case of nitrogen. But, in contrast to nitrogen, it attains maximum at a less deep layer, lying slightly above the thermocline. Oxygen also differs from nitrogen in that the degree of saturation, as well as the absolute amount, begins to decrease suddenly and evenly from the maximum layer towards the bottom.

No doubt, this difference in the distribution of these gases is due solely to differences in the chemical nature of these gases, seeing that, physically, the two are similar.

Chemically, however, the two differ distinctly from each other. Owing to its activity, oxygen is easily consumed in the decompositions that go on in the water, while it is produced in the assimilation process by phytoplankton in sufficiently illuminated water layers, so that the oxygen content of the water is controlled by these two kinds of chemical changes as well as by its exchange, namely, the supply from the air and its

escape from the water, which occurs at the surface of the water. Nitrogen, on the contrary, is practically inert, the content of this gas in the water being virtually determined solely by the gaseous exchange that takes place at the surface. It is true, of course, as said above, that in many lakes nitrogen evolves in the bottom layer, and that the fixation of this gas in the water is also possible. However, the effect of these two changes is insignificant on the content of this gas in the waters of the upper and middle layers of a lake of medium size or larger.

Then, by accurately tracing the distribution of nitrogen, it may be possible to obtain some knowledge of the physical factors that control the distribution of the dissolved gases in the water. On the other hand, we may find in the oxygen curve the total effect of these factors, physical as well as chemical, that is, assimilative production and consumption in decomposition. Therefore, by comparing the distribution of oxygen with that of nitrogen, we may obtain the most reliable knowledge of the net effect of assimilation and dissimilation upon the oxygen in lake waters. Further discussion in these respects will be reserved until sufficient data are obtained.

### The Study of Takasuka-numa.

Observations were begun in September 1935, and continued to the end of October the following year. (v. Table 35)

**Water Temperature.** (v. Fig. 12) The circulation of water, which began towards the end of summer in 1935, proceeded to such an extent that, on October 20, the water layers, ranging from the surface to the depth of 4 m., had practically the same temperature, while on November 11, the temperature difference between the surface and the bottom layers was only  $0.6^{\circ}$ .

On January 14, the water began to freeze, and continued till January 19, when the lake was covered almost completely by ice, leaving uncovered only a small area in the south-eastern corner of the lake. The ice, which was 33 mm. thick on the east coast, and 45 mm. at a point 50 m. distant, melted away on February 23. From this time onward, the water was gradually warmed, but had not yet been sufficiently stabilized, the isothermal, therefore, still running vertically.

Toward May, the temperature gradient grew quite steep, the temperature difference between the surface and the bottom layers being more than  $15^{\circ}\text{C}$ , the deeper waters having completely stagnated. This stagnation continued till the beginning of autumn, when a sudden mixing of waters occurred and a distribution of temperature, similar to that in the previous year, again set in.

**Nitrogen.** (v. Figs. 13 and 14) *Degree of saturation.* The nitrogen in the water was found to have increased in all the water layers at every observation from September 1935 to the following January.

This increase, needless to say, was brought about by supply of the gas from the atmosphere in order to satisfy the increased solubility of this gas in the waters caused by lowering of the temperature.

Table 35. Takasuka-numa.

|                                                                                              | Depth<br>m. | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsor-<br>bed gases<br>c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. | Total<br>carbon<br>dioxide<br>c.c./l. |
|----------------------------------------------------------------------------------------------|-------------|--------------|-----|-------------------|-------------|----------------------------------|---------------------|---------------|--------------------|---------------------|---------------------------------------|
| September 29, 1935.<br>Weather fine<br>Air temp. 23.0°C. (9.20 A.M.)<br>Transparency 1.70 m. | 0           | 21.9         | 6.7 | 5.23              | 85.6        | 12.35                            | 12.4                | 106           | 0                  | 0                   | 13.2                                  |
|                                                                                              | 1           | 21.3         | 6.7 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                              | 2           | 19.2         | 6.4 | 3.34              | 34.6        |                                  |                     |               |                    |                     |                                       |
|                                                                                              | 3           | 18.8         | 6.4 | 1.58              | 24.3        |                                  |                     |               |                    |                     |                                       |
|                                                                                              | 4           | 18.5         | 6.4 | 0.19              | 2.9         | 12.82                            | 12.4                | 98            | 0.2                | 0.2                 | 50.4                                  |
|                                                                                              | 5           | 17.3         | 6.4 | 0                 | 0           |                                  |                     |               |                    |                     | 81.8                                  |
| October 20<br>Weather fine<br>Air temp. 16.7°C. (9.30 A.M.)<br>Transparency 0.80 m.          | 0           | 18.8         | 6.7 | 5.20              | 80.0        | 12.82                            | 12.8                | 102           | 0                  | 0                   | 23.8                                  |
|                                                                                              | 1           | 18.5         | 6.7 |                   |             |                                  |                     |               |                    |                     | 24.2                                  |
|                                                                                              | 2           | 18.3         | 6.6 | 3.34              | 50.8        | 12.61                            | 12.6                | 99            | 0                  | 0                   | 25.8                                  |
|                                                                                              | 3           | 18.2         | 6.6 | 2.98              | 45.3        | 13.13                            |                     |               | 0.6                |                     | 23.8                                  |
|                                                                                              | 4           | 18.1         | 6.6 | 3.10              | 44.7        | 13.40                            |                     |               | 0.6                | 0                   |                                       |
|                                                                                              | 5           | 17.3         | 6.6 | 0                 | 0           | 13.70                            | 10.5                | 80            | 11.2               | 4.5                 | 20.0                                  |
| November 11<br>Weather fine<br>Air temp. 12.0°C. (9.40 A.M.)<br>Transparency 1.10 m.         | 0           | 13.8         | 6.7 | 5.27              | 73.0        |                                  | 12.7                | 92            | 0                  | 0                   | 23.4                                  |
|                                                                                              | 1           | 13.9         | 6.7 | 5.73              | 79.6        |                                  |                     |               |                    |                     | 24.2                                  |
|                                                                                              | 2           | 13.9         | 6.7 | 5.00              | 69.5        | 13.27                            | 13.3                | 96            | 0                  | 0                   | 24.7                                  |
|                                                                                              | 3           | 13.9         | 6.7 | 4.97              | 68.9        | 13.60                            | 13.4                | 97            | 0.1                | 0.1                 | 25.1                                  |
|                                                                                              | 4           | 13.85        | 6.7 | 5.14              | 71.3        |                                  |                     |               |                    |                     |                                       |
|                                                                                              | 5           | 13.85        | 6.7 | 5.15              | 71.5        | 13.67                            | 13.3                | 96            | 0.3                | 0.1                 | 20.2                                  |
| December 15<br>Weather fine<br>Air temp. 4.4°C. (9.30 A.M.)                                  | 0           | 6.8          | 7.3 | 5.40              | 63.5        |                                  |                     |               |                    |                     | 21.9                                  |
|                                                                                              | 1           | 6.8          | 7.2 | 4.93              | 58.0        |                                  |                     |               |                    |                     |                                       |
|                                                                                              | 2           | 6.7          | 7.2 | 5.37              | 62.9        | 16.17                            | 16.2                | 100           | 0                  | 0                   | 20.3                                  |
|                                                                                              | 3           | 6.7          | 7.2 | 4.96              | 58.2        |                                  |                     |               |                    |                     | 18.0                                  |
|                                                                                              | 4           | 6.7          | 7.2 | 4.82              | 56.5        | 16.20                            | 16.2                | 101           | 0                  | 0                   | 18.1                                  |
|                                                                                              | 5           | 6.7          | 7.2 |                   |             | 16.13                            | 16.1                | 100           | 0                  | 0                   | 20.3                                  |
|                                                                                              | 5.5         | 6.7          | 7.2 |                   |             | 16.26                            | 16.3                | 101           | 0                  | 0                   | 22.3                                  |
|                                                                                              |             |              |     |                   |             |                                  |                     |               |                    |                     | 27.8                                  |



Table 35.—(Continued)

|                                                                                            | Depth<br>m. | Temp.<br>°C. | pH. | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsor-<br>bed gases<br>c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. | Total<br>carbon<br>dioxide<br>c.c./l. |
|--------------------------------------------------------------------------------------------|-------------|--------------|-----|-------------------|-------------|----------------------------------|---------------------|---------------|--------------------|---------------------|---------------------------------------|
| December 26<br>Weather fine<br>Air temp. 7.7°C. (11.30 A.M.)<br>Transparency 1.90 m.       | 0           | 5.1          | 7.1 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 1           | 4.95         | 7.1 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 2           | 4.95         | 7.1 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 3           | 4.9          | 7.1 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 4           | 4.9          | 7.1 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 5           | 4.9          | 7.1 |                   |             |                                  |                     |               |                    |                     |                                       |
| January 19, 1936.<br>Weather fine<br>Air temp. 0.35°C. (9.30 A.M.)<br>Transparency 2.03 m. | 0           | 0.85         | 7.2 | 8.04              | 80.7        | 17.81                            | 17.6                | 95            | 0.2                | 0                   | 20.0                                  |
|                                                                                            | 1           | 3.4          | 7.1 | 7.90              | 85.2        | 17.80                            | 17.6                | 101           | 0.1                | 0.1                 | 28.5                                  |
|                                                                                            | 2           | 3.4          | 7.1 | 7.66              | 82.6        | 17.70                            | 17.4                | 100           | 0.3                | 0                   | 30.0                                  |
|                                                                                            | 3           | 3.5          | 7.2 | 7.88              | 85.3        | 17.80                            | 17.4                | 100           | 0.4                | 0                   | 27.3                                  |
|                                                                                            | 4           | 3.6          | 7.1 | 7.75              | 84.2        | 18.13                            | 17.8                | 103           | 0.3                | 0                   | 32.3                                  |
|                                                                                            | 4.5         | 3.7          |     |                   |             |                                  |                     |               |                    |                     |                                       |
| February 28<br>Weather fine<br>Air temp. 2.7°C. (9.30 A.M.)<br>Transparency 2.48 m.        | 5           | 3.7          | 7.0 | 7.37              | 80.1        | 17.81                            | 17.6                | 102           | 0.1                | 0.1                 | 18.3                                  |
|                                                                                            | 0           | 4.0          | 7.0 | 7.71              | 84.4        | 17.31                            | 17.1                | 99            | 0                  | 0.2                 | 14.6                                  |
|                                                                                            | 1           |              |     |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 2           | 4.0          | 7.0 | 7.63              | 83.5        | 17.32                            | 17.1                | 100           | 0.2                | 0                   | 14.4                                  |
|                                                                                            | 3           | 4.0          | 7.0 |                   |             |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 4           | 4.0          | 7.0 | 7.65              | 83.8        | 17.54                            | 17.1                | 100           | 0.4                | 0                   | 15.8                                  |
| March 28<br>Weather fine<br>Transparency 2.00 m.                                           | 5           | 4.0          | 7.0 | 7.55              | 82.7        | 17.03                            | 16.6                | 97            | 0.2                | 0.2                 | 17.0                                  |
|                                                                                            | 0           | 8.7          | 7.0 | 6.78              | 83.6        | 15.72                            | 15.4                | 100           | 0.2                | 0.1                 | 16.3                                  |
|                                                                                            | 1           | 8.6          | 7.0 | 6.72              | 82.8        |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 2           | 8.6          | 7.0 | 6.73              | 82.9        | 15.61                            | 15.5                | 101           | 0.1                | 0                   | 15.9                                  |
|                                                                                            | 3           | 8.6          | 7.0 | 6.76              | 83.1        |                                  |                     |               |                    |                     |                                       |
|                                                                                            | 4           | 8.7          | 7.0 | 6.53              | 80.3        | 15.80                            | 15.7                | 102           | 0                  | 0.1                 | 15.4                                  |
|                                                                                            | 4.7         | 8.7          | 7.0 |                   |             | 15.88                            | 15.7                | 102           | 0.1                | 0.1                 | 15.5                                  |

Table 35.—(Continued)

|                                                                                     | Depth<br>m. | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases<br>c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. | Total<br>carbon<br>dioxide<br>c.c./l. |
|-------------------------------------------------------------------------------------|-------------|--------------|-----|-------------------|-------------|--------------------------------|---------------------|---------------|--------------------|---------------------|---------------------------------------|
| April 29<br>Weather cloudy<br>Air temp. 13.2°C. (9.30 A.M.)<br>Transparency 1.40 m. | 0           | 16.4         | 7.3 | 6.90              | 101.0       | 13.61                          | 13.2                | 100           | 0.2                | 0.2                 | 32.1                                  |
|                                                                                     | 1           | 16.4         | 7.3 | 7.54              | 110.4       |                                |                     |               |                    |                     | 18.6                                  |
|                                                                                     | 2           | 16.35        | 7.3 | 6.42              | 93.9        | 13.60                          | 13.2                | 100           | 0.2                | 0.2                 | 17.4                                  |
|                                                                                     | 3           | 16.35        | 7.3 |                   |             | 13.78                          | 13.3                | 101           | 0.2                | 0.4                 | 18.4                                  |
|                                                                                     | 4           | 15.65        | 6.7 | 3.29              | 47.3        | 14.24                          | 13.9                | 104           | 0.1                | 0.2                 |                                       |
|                                                                                     | 5           | 15.6         | 6.6 | 1.01              | 14.5        | 14.44                          | 14.2                | 107           | 0.1                | 0.2                 |                                       |
|                                                                                     | 5.5         | 15.6         | 6.6 |                   |             | 14.57                          | 14.3                | 107           | 0.1                | 0.2                 | 25.2                                  |
| May 25<br>Weather fine<br>Air temp. 17.3°C (9.20 A.M.)<br>Transparency 1.26 m.      | 0           | 19.9         | 7.1 | 5.92              | 89.6        | 11.91                          | 11.7                | 95            | 0                  | 0.2                 | 13.5                                  |
|                                                                                     | 1           | 19.3         | 7.1 | 5.96              | 92.3        |                                |                     |               |                    |                     | 13.5                                  |
|                                                                                     | 2           | 19.2         | 7.1 | 5.09              | 78.8        | 12.79                          | 12.6                | 101           | 0.1                | 0.1                 | 15.3                                  |
|                                                                                     | 3           | 17.8         | 6.7 | 3.44              | 51.7        | 13.20                          | 13.0                | 101           | 0.1                | 0.1                 | 20.5                                  |
|                                                                                     | 3.5         | 15.8         | 6.4 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                     | 4           | 14.7         | 6.6 | 0.13              | 1.7         | 14.03                          | 13.9                | 102           | 0                  | 0.1                 | 24.2                                  |
| June 21<br>Weather fine<br>Air temp. 27.5°C. (9.20 A.M.)<br>Transparency 2.55 m.    | 5           | 13.3         | 6.8 | 0.09              | 1.2         | 14.24                          | 14.5                | 104           | 0.2                | 0.1                 |                                       |
|                                                                                     | 5.5         | 13.0         | 6.9 | 0                 | 0           | 14.87                          | 14.7                | 104           | 0.1                | 0.1                 | 28.3                                  |
|                                                                                     | 0           | 25.4         | 7.7 | 5.89              | 103.0       | 11.74                          | 11.7                | 105           | 0                  | 0                   | 12.8                                  |
|                                                                                     | 1           | 25.2         | 7.7 | 5.93              | 103.0       | 11.93                          | 11.8                | 105           | 0.1                | 0                   | 13.7                                  |
|                                                                                     | 2           | 24.7         | 7.5 | 5.71              | 98.1        | 12.61                          | 12.5                | 110           | 0                  | 0.1                 | 18.3                                  |
|                                                                                     | 3           | 20.2         | 6.6 | 3.62              | 57.0        | 13.00                          | 12.9                | 105           | 0.1                | 0                   | 17.4                                  |
| June 21<br>Weather fine<br>Air temp. 27.5°C. (9.20 A.M.)<br>Transparency 2.55 m.    | 3.5         | 16.55        | 6.5 | 0.18              | 2.7         | 13.68                          | 13.6                | 104           | 0.1                | 0                   | 23.2                                  |
|                                                                                     | 4           |              | 6.6 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                     | 4.5         |              | 6.6 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                     | 5           | 14.1         | 6.9 | 0                 | 0           | 14.73                          | 13.9                | 101           | 0.8                | 0                   | 42.2                                  |
|                                                                                     | 5.5         | 13.7         | 7.1 | 0                 | 0           | 15.78                          | 14.1                | 102           | 1.5                | 0.2                 | 57.8                                  |
|                                                                                     | 5.8         |              | 7.1 |                   |             |                                |                     |               |                    |                     |                                       |
| July 25<br>Weather fine<br>Air temp. 32.0°C (9.30 A.M.)<br>Transparency 1.35 m.     | 0           | 23.7         | 7.5 | 6.25              | 115.7       | 11.24                          | 11.1                | 105           | 0.1                | 0                   | 13.4                                  |
|                                                                                     | 1           | 23.2         | 7.5 | 6.45              | 118.6       | 11.29                          | 11.1                | 104           | 0.1                | 0.1                 | 13.9                                  |
|                                                                                     | 2           | 23.9         | 6.7 | 4.86              | 86.5        | 11.28                          | 11.1                | 100           | 0.2                | 0.1                 | 16.1                                  |
|                                                                                     | 2.5         | 22.9         | 6.3 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                     | 3           | 20.7         | 6.3 | 0.22              | 3.8         | 13.27                          | 12.4                | 102           | 0.3                | 0                   | 22.4                                  |
|                                                                                     | 4           | 16.85        | 6.5 | 0.20              | 3.0         | 14.62                          | 13.3                | 102           | 1.3                | 0.1                 | 36.1                                  |
|                                                                                     | 5           | 15.0         | 6.9 | 0                 | 0           | 17.56                          | 13.8                | 102           | 3.6                | 0.3                 | 53.0                                  |
|                                                                                     | 5.5         | 14.6         | 6.9 | 0                 | 0           | 18.43                          | 15.4                | 113           | 2.3                | 0.7                 | 57.9                                  |

Table 35.—(Continued)

|                                                                                         | Depth<br>m. | Temp.<br>°C. | pH  | Oxygen<br>c.c./l. | Oxygen<br>% | Unabsorbed<br>gases<br>c.c./l. | Nitrogen<br>c.c./l. | Nitrogen<br>% | Methane<br>c.c./l. | Hydrogen<br>c.c./l. | Total<br>carbon<br>dioxide<br>c.c./l. |
|-----------------------------------------------------------------------------------------|-------------|--------------|-----|-------------------|-------------|--------------------------------|---------------------|---------------|--------------------|---------------------|---------------------------------------|
| September 13<br>Weather cloudy<br>Air temp. 29.6°C. (1.30 P.M.)<br>Transparency 1.68 m. | 0           | 31.0         | 7.6 | 5.41              | 104.6       | 10.98                          | 10.8                | 105           | 0.2                | 0                   | 17.0                                  |
|                                                                                         | 1           | 28.95        | 7.5 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                         | 2           | 28.5         | 7.5 | 5.09              | 93.9        | 10.49                          | 9.8                 | 96            | 0.7                | 0                   | 20.7                                  |
|                                                                                         | 2.25        |              | 7.1 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                         | 2.35        |              | 6.6 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                         | 2.5         |              | 6.5 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                         | 3           | 26.2         | 6.4 | 1.36              | 24.1        | 11.21                          | 10.7                | 101           | 0.4                | 0.1                 | 26.9                                  |
|                                                                                         | 3.5         | 23.35        | 6.2 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                         | 4           | 20.2         | 6.4 | 0                 | 0           | 15.41                          | 11.7                | 95            | 3.6                | 0.1                 | 61.2                                  |
|                                                                                         | 5           | 16.8         | 6.5 | 0                 | 0           | 21.65                          | 12.8                | 98            | 7.6                | 0.8                 | 76.7                                  |
|                                                                                         | 5.5         | 15.75        | 6.5 | 0                 | 0           |                                |                     |               |                    |                     | 96.5                                  |
|                                                                                         | 6           | 15.6         | 6.5 |                   |             | 25.59                          | 13.1                | 98            | 8.1                | 0.8                 |                                       |
|                                                                                         | 6.1         | 15.6         | 6.5 |                   |             |                                |                     |               |                    |                     |                                       |
| October 4<br>Weather fine<br>Air temp. 19.6°C. (9.00 A.M.)<br>Transparency 1.55 m.      | 0           | 20.2         | 6.6 | 3.47              | 54.8        | 12.60                          | 12.6                | 102           | 0                  |                     | 26.1                                  |
|                                                                                         | 1           | 20.1         | 6.6 |                   |             |                                |                     |               |                    |                     |                                       |
|                                                                                         | 2           | 19.9         | 6.6 | 3.28              | 51.5        | 11.96                          | 11.4                | 92            | 0.5                | 0.1                 |                                       |
|                                                                                         | 3           | 19.7         | 6.6 | 2.56              | 40.1        | 12.20                          | 10.4                | 83            | 1.6                | 0.2                 | 28.2                                  |
|                                                                                         | 4           | 19.5         | 6.6 | 2.17              | 33.7        | 12.37                          | 11.1                | 89            | 1.2                | 0.1                 | 27.2                                  |
|                                                                                         | 5           | 18.7         | 6.6 | 2.04              | 31.3        | 16.83                          | 11.4                | 90            | 1.4                | 0.1                 | 55.7                                  |
|                                                                                         | 5.5         | 16.6         | 6.6 | 0                 | 0           | 23.33                          | 12.0                | 92            | 10.8               | 0.5                 | 113.7                                 |
|                                                                                         | 6           | 15.85        | 6.6 | 0                 | 0           | 27.01                          | 12.7                |               | 13.6               | 0.8                 | 117.8                                 |
| October 25<br>Weather cloudy<br>Air temp. 12.5°C. (9.20 A.M.)<br>Transparency 1.26 m.   | 0           | 14.9         | 6.7 | 3.92              | 55.7        | 13.24                          | 13.2                | 98            | 0                  | 0                   | 25.7                                  |
|                                                                                         | 1           | 14.85        | 6.7 | 4.03              | 57.1        | 13.02                          | 13.0                | 96            | 0                  | 0                   | 25.7                                  |
|                                                                                         | 2           | 14.8         | 6.7 | 3.80              | 53.8        | 12.96                          | 13.0                | 96            | 0                  | 0                   | 25.5                                  |
|                                                                                         | 3           |              | 6.7 | 3.71              | 52.6        | 12.95                          | 13.0                | 96            | 0                  | 0                   | 26.6                                  |
|                                                                                         | 4           |              |     | 3.69              | 52.3        | 13.27                          | 13.2                | 98            | 0.1                | 0                   | 26.6                                  |
|                                                                                         | 5           | 14.8         | 6.6 | 3.50              | 49.6        | 13.01                          | 12.9                | 95            | 0.1                | 0                   | 27.7                                  |
|                                                                                         | 5.5         | 14.75        | 6.6 | 3.17              | 44.9        | 12.97                          | 12.3                | 91            | 0.7                | 0                   |                                       |

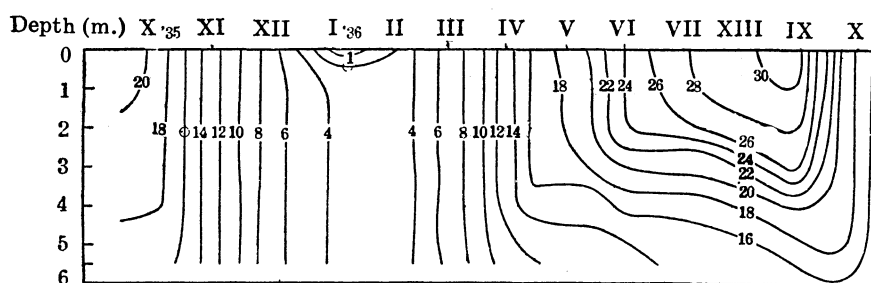


Fig. 12. Annual variation in the isothermals in Takasuka-numa.

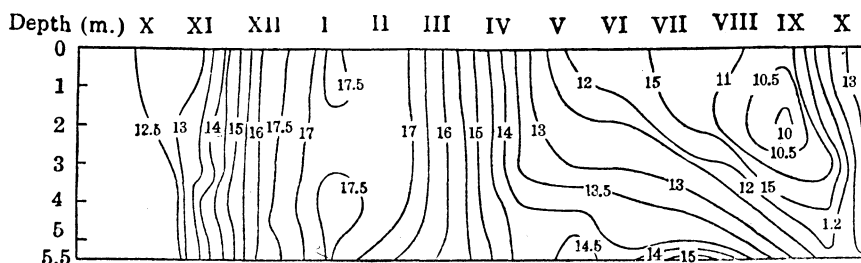


Fig. 13. Annual variation in the nitrogen content of the lake waters of Takasuka-numa (c.c./l.).

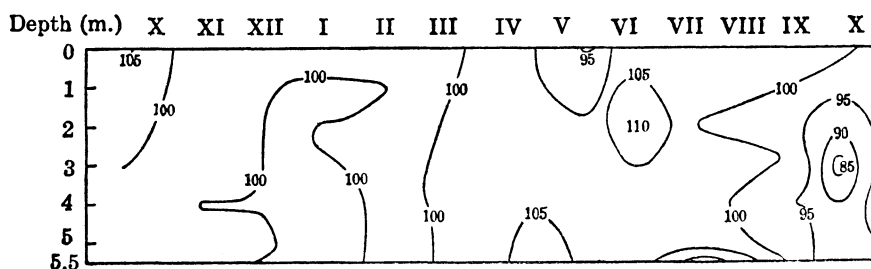


Fig. 14. Annual variation in the degree of saturation of nitrogen in the lake waters of Takasuka-numa.

What is noteworthy is that, this supply of nitrogen from the air was satisfied very quickly, as is evident from the fact that degree of nitrogen saturation lay always between 96 and 100% with two exceptions, one at a depth of 5.5 m. on October 20 and the other at the surface on November 11.

At any rate, the above period which covers the season from the end of summer to the middle of the following January, is a period when the waters are more or less in a state of undersaturation with respect to nitrogen, this gas being continually absorbed by the water from the atmosphere. For this reason, this period may be called the "period of nitrogen absorption", which completes the annual cycle with the "period of nitrogen escape" that follows. In the latter period, owing to the warming of the water, the excess of nitrogen is expelled from the water into the atmosphere.

From the foregoing observations in the Nisina Lake Group, it was ascertained that this escape of nitrogen into the atmosphere is hindered considerably, and that in every one of the cases examined, a maximum value of more than 110% in the degree of saturation of nitrogen gas was observed. Now in the case of Takasuka-numa, owing to the smallness of the lake, the water is easily mixed, as a consequence of which the escape of nitrogen from the surface is greatly facilitated. In this lake, therefore, it is very rare to find a value of more than 105% for the degree of saturation of nitrogen gas.

The value of 110%, found at a depth of 2 m. on June 21, and 113%, at a depth of 5.5 m. on July 25, represent the only two exceptions. The latter was, no doubt, due to the evolution of nitrogen caused by anaerobic decomposition of organic debris at the bottom, which will be discussed later, while the former was due to too rapid temperature rise in a particular layer that did not allow an immediate effect on the nitrogen percentage.

At all events, the general conclusion is that, in a shallow lake, as in the case of Takasuka-numa, ingress or egress of nitrogen to or from the hydrosphere takes place so soon that the nitrogen contents of the waters are always suited to the temperature variation of the waters.

This point will be found to be far more important when we consider that that is the case also for other gaseous constituents of the lake water, for example, oxygen, which is similar to nitrogen in nature, as will be discussed later.

*Nitrogen gas evolution at the bottom, and its effect on the gas content of the waters.* Along with the study of the dissolved gases in lake water, direct measurements of the gas evolution at the bottom were made and an analytical study of them was carried out in the following way.

A glass bell-jar was suspended at about 50 cm. above the bottom in the deepest part of the lake, which, after a certain period, was hauled up, and the volume of the gas accumulated in it measured and its chemical composition examined, with results as given in Table 36.

The gas, which had accumulated during the period from May 25 to June 21, 1936, and which amounted to 221 c.c. per day/m.<sup>2</sup>, was shown to be composed mainly of nitrogen, its percentage being 95.77%.

There are many reasons for supposing that this proportion of the gas is not what it was at the time the gas was evolved.

First, it is very likely that a certain chemical change occurs in some of the constituents of the evolved gas mixture while in the bell-jar. Second, when the evolved gas bubbles rise up toward the jar, it is also likely that gaseous exchanges occur between the gas bubbles and the water. Thus, both these causes might bring about a measurable change in the composition of the evolved gas.

It is also conceivable that the change in the gaseous composition cannot be so large as to make it difficult to surmise the chemical composition of the gas at its beginning from that of the gas after storage in the bell-jar.

Then, as shown by the composition of the stored gas during the period from May 25 to June 21, it is highly probable that considerable

Table 36. Volume of the gas, accumulated in the suspended glass bell-jar and its composition.

|                                | May 25 - June 21 |                                                  | September 13 - October 4 |                                                  |
|--------------------------------|------------------|--------------------------------------------------|--------------------------|--------------------------------------------------|
|                                | Composition %    | Accumulated amount c.c. per day/m <sup>2</sup> . | Composition %            | Accumulated amount c.c. per day/m <sup>2</sup> . |
| Nitrogen                       | 95.77            | 211.7                                            | 10.34                    | 144                                              |
| Methane                        | 2.60             | 5.7                                              | 80.83                    | 1129                                             |
| Hydrogen                       | 0.05             | 0.1                                              | 6.44                     | 90                                               |
| Carbon dioxide                 | 0.24             | 0.5                                              | 1.12                     | 16                                               |
| Oxygen                         | 1.36             | 3.0                                              | 0.80                     | 11                                               |
| C <sub>n</sub> H <sub>2n</sub> | 0                | 0                                                | 0.47                     | 7                                                |
|                                |                  | — (+                                             |                          | — (+                                             |
|                                |                  | 221.0                                            |                          | 1397                                             |

|                                | October 4 - October 25 |                                                  | October 25 - November 25 |                                                  |
|--------------------------------|------------------------|--------------------------------------------------|--------------------------|--------------------------------------------------|
|                                | Composition %          | Accumulated amount c.c. per day/m <sup>2</sup> . | Composition %            | Accumulated amount c.c. per day/m <sup>2</sup> . |
| Nitrogen                       | 20.27                  | 112                                              | 32.69                    | 14.4                                             |
| Methane                        | 73.66                  | 408                                              | 61.30                    | 27.1                                             |
| Hydrogen                       | 4.31                   | 24                                               | 3.82                     | 1.7                                              |
| Carbon dioxide                 | 0.88                   | 5                                                | 0.23                     | 0.1                                              |
| Oxygen                         | 0.34                   | 2                                                | 1.02                     | 0.5                                              |
| C <sub>n</sub> H <sub>2n</sub> | 0.54                   | 3                                                | 0.95                     | 0.5                                              |
|                                |                        | — (+                                             |                          | — (+                                             |
|                                |                        | 554                                              |                          | 44.3                                             |

evolution of nitrogen occurred with the slightest evolution of other gases at the bottom, a result that agree well with the foregoing results of observation on the dissolved gases at the bottom water during the time in question, that is, early summer.

Indeed, the amount of nitrogen in deeper waters was found to increase during two periods, namely, the one just preceding and the other succeeding the period in which the above measurement of gas evolution was made. Thus, in the former period, from April 29 to May 25, the nitrogen value increased from 14.2 c.c. at 5 m. and 14.3 c.c. at 5.5 m. to 14.5 c.c. and 14.7 c.c. at corresponding depths, while in the latter period from June 21 to July 25, it also increased from 14.1 c.c. at 5.5 m. to 15.4 c.c. at the same depth.

Such an increase in nitrogen value in the deeper water layers can be explained only by evolution of this gas in the bottom water or in the mud, because the season now in question is that in which nitrogen escapes, hence one would naturally expect to find a decrease of this gas in the deeper waters, which, however, is contrary to the present case.

These circumstances indicate that the formation of nitrogen at the bottom began as early as the end of April and continued to the end of July, at least, with considerable intensity.

The fact also that no increase in nitrogen was found during May 25 to June 21, does not contradict the above direct observation of nitrogen evolution, it being easily understood if we assume that, during this period, there were circumstances owing to which a more rapid escape of the gas took place.

The conclusion, therefore, is that, in Takasuka-numa, evolution of nitrogen occurs to such an extent that its content in deeper waters often increases notwithstanding its tendency to decrease, owing to rise of temperature in the water layers in question.

*Evolution of nitrogen and the bottom temperature.* As shown in the foregoing paragraphs, the temperature of the bottom water is minimum in January, whence it begins to increase towards autumn, attaining maximum at the end of September or in the beginning of October.

Now, if the denitrification at the bottom is accelerated by rise in temperature, which is usually the case in ordinary chemical changes, the amount of gas evolved should increase from spring towards autumn, and attain maximum between September to October.

The writer's result is contrary to this expectation. The amount of evolved nitrogen decreased from 212 c.c. per day/m.<sup>2</sup> (May – June, when the bottom water was still cold) to 144 c.c. (September 13 – October 4), and further to 112 c.c. (October 4 – 25), when the bottom water was quite warm.

The evolution of nitrogen by denitrification at the bottom is thus apparently independent of the temperature of the bottom water.

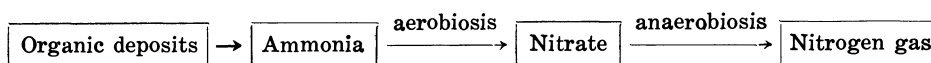
As the causes of such behaviour in denitrification at the lake bottom, the following three are conceivable:

- (1) Smallness of the temperature coefficient of the reaction velocity of denitrification.
- (2) The optimal temperature of denitrification is comparatively low.
- (3) The existence of a certain factor that acts against rise of temperature upon denitrification.

As to (1) and (2), the writer lacks sufficient information to enable him to deal further with the problem, while (3) may be claimed to represent, at least, one of the most important causes of the observed phenomenon, and which the writer attributes to diminution in the nitrate reserve in the water.

As is well known, pre-existence of nitrate or nitrite is an indispensable condition for the evolution of nitrogen gas. Besides these, ammonium salts also part with their nitrogen when they come in contact with one of the intermediate products of nitrate reduction, nitrite, under favourable conditions.

Now, since in the case of the deeper waters of a lake, the main or often unique source of these salts, is organic deposits, evolution of nitrogen in the lake occurs in the following stages:



Of these three steps in the process, nitrate production occurs more in aerobiosis, while for reduction of nitrate, which in turn leads to the final evolution of nitrogen, an anaerobic condition is required.

Thus for the evolution of nitrogen gas, two different conditions, namely, aerobic and anaerobic, are necessary. In the former condition, much nitrate is formed and stored in deeper waters, and when the condition turns to anaerobic, then reduction of the nitrate begins, resulting in the formation of nitrogen.

That such a change from aerobiosis into anaerobiosis did occur during the period between April 29 and May 25, has been conclusively shown by the oxygen value of the deeper waters. In fact, on April 29, there was still sufficient oxygen, even in the deepest water, whereas on May 25, the water at a depth of 5.5 m. was already completely deprived of its oxygen, this depletion of oxygen extending thereafter into less deeper water zones.

It is, therefore, only natural that we found a heavy production of nitrogen, as much as 214 c.c. per day/m.<sup>2</sup> in May-June, following the turning period.

When such an anaerobiosis had continued for a certain period, it is also natural that the stored nitrate should be gradually consumed and the production of nitrogen eventually checked, which will thus be admitted as the most probable reason for the nitrogen evolution being checked towards autumn, despite the rise in temperature of the bottom water.

To the writer's regret, there is no result of a simultaneous determination of ammonia and nitrate contents of lake waters that should support his views, although it is fortunate that his views are supported by Yoshimura's observation in 1930, provided it can be admitted that the bottom metabolism took place that year in the same order that it did in 1936.

The following quotations are from Yoshimura's paper<sup>(29)</sup> (in Japanese) that relates to the present discussion.

"In May, the water began to stagnate and, at a depth of 5 m., a sudden increase in ammonia was observed. This increase in ammonia lasted to the end of August, when the accumulated ammonia suddenly vanished....."

"With the beginning of the period of stagnation, the nitrate content of the waters increased actively for a while, but this did not last long, and the nitrate content began to decrease. The decrease was more evident in autumn, the reason for which is not yet certain....."

"Also, the organic nitrogen in the deeper waters increased slightly at the beginning of the period of stagnation, but it decreased to that value, that is customary in the period of stagnation."

When these observations of Yoshimura are compared with the writer's views, we find many points in agreement, so that the former are regarded as supporting the latter view.

It is also worth while comparing the writer's result with that of the

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(29) Yoshimura, *The Geographical Review of Japan*, 6 (1931), 733-736.



laboratory experiment that was carried out by R. J. Allgeier, W. H. Peterson, Ch. Juday, and E. A. Birge.<sup>(30)</sup>

These authors filled a number of glass bottles with samples of the bottom deposits of Lake Mendota, Wisconsin, to which was added a sufficient amount of water. The bottles were left to ferment at different temperatures, and the evolved gases examined after a lapse of about 100 and 200 days.

Of the results of this experiment, the most important to the present problem is that the percentage of nitrogen in the fermented gas in the bottle at lower temperature exceeded that of higher temperature.

Such a result can no doubt be understood only by assuming that denitrification itself is suited to a lower temperature, or that it is interfered with by a certain external force, for example, by the effect of methane or hydrogen fermentations, which are greatly accelerated by rise in temperature owing to their larger temperature coefficients.

Another result, also worth mentioning here, is that within the range of temperature examined (7°–55°C), the percentage of nitrogen in the fermented gas was smaller on the 200–210th day than on the 112th day. This observation agrees with the writer's view, according to which at least one of the limiting factors of nitrogen production is attributed to diminution in the nitrate supply.

To conclude, the reason that in Takasuka-numa, the evolution of nitrogen declines towards autumn, despite temperature elevation in the deeper waters, is explained partly by interruption in the nitrate supply and partly by assuming that denitrification had adapted itself to a lower temperature, the exact cause being yet obscure.

**Methane and Hydrogen.** (v. Fig. 15) *Methane and hydrogen accumulation.* Contrary to the case of nitrogen evolution, in a bell-jar suspended at the bottom, fermentations of methane and hydrogen are accelerated by rise in temperature.

The amounts of both these gases, accumulated in the suspended bell-jar, increased from their small values in early summer (2.6 c.c. per day/m.<sup>2</sup> of methane and 0.1 c.c. of hydrogen) to the enormous values in the period, September 13–October 4, of 1129 c.c. of the former gas and 90 c.c. of the latter, while fermentation had declined, the amount of the evolved methane and hydrogen having dropped to 408 c.c. and 24 c.c. between October 4–25, and further to 27 c.c. and 1.7 c.c. in the succeeding period until November 25.

The contents of methane and hydrogen in the lake waters varied similarly. In all the waters, neither of these two gases were found to any measureable extent until May 25. On June 21, small amounts of these gases were found first at depths of 5 and 5.5 m., with the simultaneous disappearance of oxygen. Thereafter, their contents in deeper waters increased evenly towards autumn, and on October 4 they reached the maximum values of 10.8 c.c. of methane and 0.5 c.c. of hydrogen at a depth of 5.5 m. and 13.6 c.c. and 0.8 c.c. at 6 m. Then, owing to circulation of the water, the stored gases in deeper waters were dispersed and,

(30) Allgeier, Peterson, Juday, Birge, *Internat. Rev. d. gesamten Hydrobiologie und Hydrographie*, **26** (1932), 444–461.

due to the accompanying temperature drop and to the supply of oxygen to the deepest water, bottom fermentation was greatly hindered. From this time onwards, no considerable amount of these gases was found in any of the water layers. This was the same as in the previous autumn.

*Methane and hydrogen fermentations and temperature.* One of the outstanding features in the present study of methane and hydrogen is that the daily amount of methane evolution reached in autumn to nearly 500-fold of that in early summer.

Such a huge increase in gas production cannot easily be explained merely by rise in temperature in the bottom water.

Three factors that are supposed also to contribute more or less to the huge acceleration of methane and hydrogen production towards autumn will now be discussed.

(1) Anaerobiotic condition in the deeper waters. The fermentation of the two gases in question being anaerobic, it is inhibited by the presence of oxygen, so that it is rather natural to find both these changes greatly inhibited when the supply of oxygen to the bottom is still sufficient, as in the period of circulation and at the beginning of the stagnation period. It is also natural to find gas evolution suddenly accelerated as soon as the water stagnates for a certain period and the bottom oxygen is completely consumed.

(2) Bacteria that oxidize methane and hydrogen. Next, the role played by bacteria that oxidize methane and hydrogen, will be considered.

Recently, Kuznetsov<sup>(31)</sup> and his co-workers proved the existence of such bacteria in the water of Lake Beloje, near Moscow, and tried to explain the limnological characteristics of that lake.

It is very likely that such bacteria are not restricted to any particular lake, such as Beloje, but are widely distributed in all lakes where the evolution of these gases occurs.

In the water layers of a lake, where the evolved methane or hydrogen easily comes in contact with the dissolved oxygen, we find the most appropriate breeding ground for these bacteria. In such a layer of water, the oxygen, owing to the action of bacteria, acts on the gases in question as soon as they are evolved, so long as the supply of oxygen continues there.

This will exactly be the case with the bottom water in the period of circulation or at the beginning of the period of stagnation, so that in these periods, no marked storage of dissolved methane or hydrogen in the bottom water can be expected, even if these gases were produced in considerable quantities.

In contrast to this, when the stagnation of water continues for some time and the oxygen in the deeper waters is completely consumed, bacterial decomposition of the evolved gases is hindered and the gases are dissolved (unaltered) in the water or are accumulated in the collecting jar as they are evolved.

For these reasons, the apparent evolution of these gases, as computed from the amounts accumulated in the collecting jar, is very much larger in the advanced season, compared with that in early summer.

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(31) Kuznetsov, *Verhandl. d. Internat. Vereinigung f. theoret. und angew. Limnologie*, 7 (1935), 562-582.

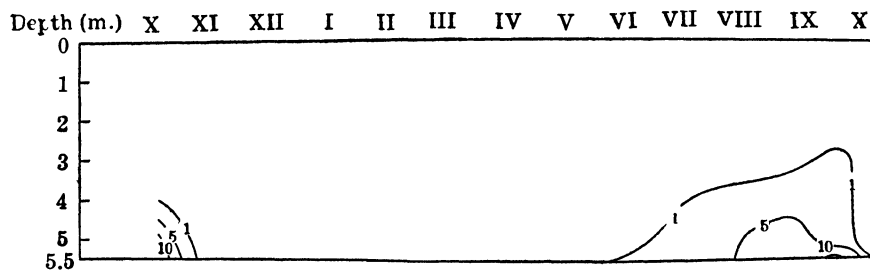


Fig. 15. Annual variation in the content of methane of the lake waters of Takasuka-numa (c.c./l.)

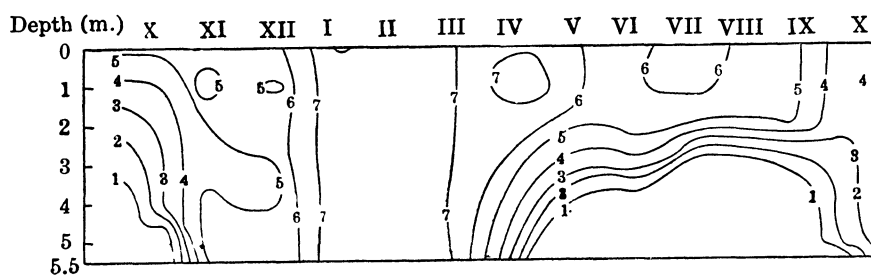


Fig. 16. Annual variation in the oxygen content of the lake waters of Takasuka-numa. (c.c./l.)

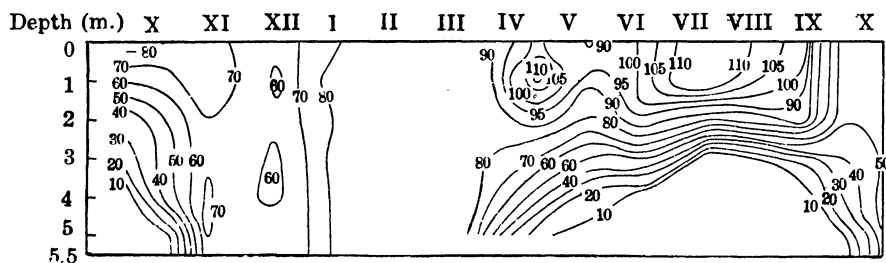


Fig. 17. Annual variation in the degree of oxygen saturation in the lake waters of Takasuka-numa (c.c./l.)

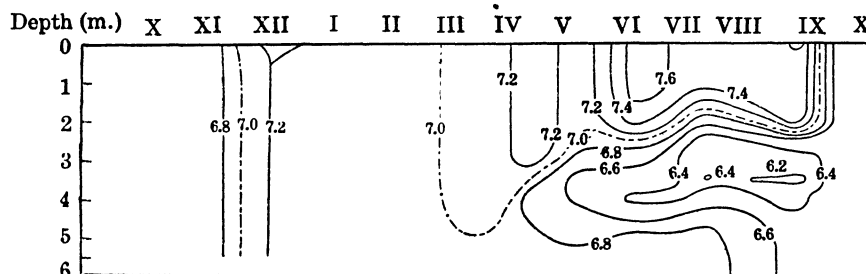


Fig. 18. Annual variation in the pH value of the lake waters of Takasuka-numa

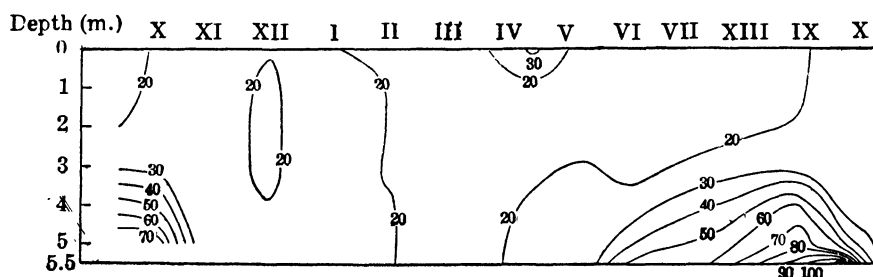


Fig. 19. Annual variation in the content of total carbon dioxide in the lake waters of Takasuka-numa (c.c./l.)

(3) Direct and indirect effects of rising bubbles. When the bottom fermentation has advanced to a certain extent, and the evolved gases have dissolved sufficiently into the waters in the neighbourhood, the gases begin to escape in the form of bubbles rising towards the upper water surface. In this case, oxygen as well as other gases, that are dissolved in the waters lying in the way of the rising bubbles, are very likely to be driven out by them.

On the one hand, such a process seems to secure directly a sooner establishment of anaerobic conditions in deeper waters, while, on the other, it hinders the ingress of oxygen from the upper water zones into the deeper ones, as the result of which, anaerobiosis, once established at the bottom, is indirectly extended quickly in range and increased in intensity.

The author therefore holds that the huge increase in the accumulation of methane and hydrogen towards autumn was owing to the following three causes:

- (1) Rise in temperature of the bottom water.
- (2) Decomposition oxidation of the evolved methane and hydrogen by bacteria in the earlier period, and its cessation in the later period.
- (3) Setting up of anaerobic conditions in the deeper waters, which in their turn, are maintained by the stagnation of water as well as by the rising bubbles of the evolved gases.

**Oxygen.** (v. Figs. 16 and 17) *Degree of oxygen saturation.* Although the saturation of oxygen varied between 0 and 118.6%, generally speaking, the value was usually below 100%, except those in the upper water layers during the four or five months from early summer to early autumn. Then throughout the year, excepting these months, oxygen must have been continually absorbed from the air into the hydrosphere in order to make up for its lack in the waters. Seeing that the surface water was markedly undersaturated, this absorption must have been intense, whence the bulk of the oxygen that is absorbed into the lake water per annum per unit surface must reach an enormous value in Takasuka-numa, thus differing from many other lakes, where the degree of oxygen saturation never drops to any great extent.

*The roles of iron and manganese as oxygen carriers.* This large quantity of absorbed oxygen is at the end consumed for the oxidative

decomposition of organic matter that was either formed in the lake or had been carried into it.

But we cannot overlook the fact that, in the course of the oxidative consumption of oxygen, this gas, at any rate, does not directly act upon organic matter in general, but is frequently first combined with ferrous iron or with manganous manganese, after which the oxygen is transferred to less oxidizable organic substances. In this case, it is worth mentioning that the oxidation-reduction property of these elements in question plays an important role in facilitating such oxygen-transference.

Such is also the case with the flocculation and precipitation of oxidized iron and manganese, by which the deeper lying organic matter are made accessible to oxygen, resulting in oxidation.

Such relation between the absorbed oxygen and the amount of iron and manganese in the lake water, is very evident in the autumnal observations.

In the autumn of 1935, the oxygen content in the waters was found to have increased in harmony with increase in solubility due to lowering of the water temperature, but saturation was found to have decreased every time it was observed from September to December.

Thus the latter value dropped gradually, for example, at the surface layer, from 85.6% on September 29 to a minimum of 63.5% on December 15.

When we compare these data with those of nitrogen, and are reminded of the above conclusion that the absorption velocity of oxygen by water can never differ much from that of nitrogen, and that, in the case of nitrogen, absorption occurs so easily that it adapts itself to the autumnal lowering of temperature of the lake waters, we know that the small autumnal value of oxygen saturation does not arise from any interruption in the supply of this gas, but from its heavy consumption by a huge quantity of oxygen-consuming substances present in the water.

The amount of these oxygen-consuming substances in the waters was greatly reduced towards the end of December, as shown by a sudden increase in oxygen saturation in the observation of January 19, despite the still continued lowering of the temperature of the lake water.

From the variation in the iron and manganese contents in the waters that ran parallel with that of the degree of oxygen saturation, the writer concludes that these two elements are nothing but substances that play, at least, one of the main roles in the consumption of oxygen by the autumnal waters.

In fact, as shown in Tables 12 and 13, the contents of iron and manganese in the upper waters increased continually from September to November, corresponding to the decreasing variation in oxygen saturation, after which the iron and manganese contents began to decrease to their minimum values on January 19, also corresponding to the sudden increase in oxygen saturation as well as in its absolute content in the water. It might be scarcely worth repeating that the direct determination of iron and manganese by the suspending bottle method (Table 15) also gave a result that pointed to a similar variation in iron and manganese deposition. The circulatory property of iron and manganese is also significant in the matter of oxygen supply to the deeper waters.

As shown in the foregoing paragraphs, these elements precipitate upon combining with oxygen, and when they part with this oxygen to combine with other oxidizable substances at depths, they change into the soluble state, whence they are carried back by the circulation current into the upper water zone.

In this way, owing to this circulatory property of these elements, the transport of oxygen from the upper aerated zone to the deeper oxygen deficient zone is effected by these carriers, so long as there remain substances to receive the oxygen in the deeper waters.

Thus the role of iron and manganese as oxygen carriers is accomplished by their circulatory property.

It will also be of some interest to compute the amount of oxygen that is carried downwards by the elements in question per annum, per unit area, and to estimate roughly the percentage of the organic deposits that are likely to be oxidized completely by this computed amount of oxygen.

In the previous determination of deposition, what was lacking in observation was made up as shown in Fig. 4, the percentages of iron and manganese in the deposit for this period being assumed equal to 10.78% and 0.74% respectively, the mean values of 12 observations during the whole period. Then the deposited iron during a period of one year, June 24, 1935 – June 24, 1936, was computed to be 0.179 g. (as  $\text{Fe}_2\text{O}_3$ ), and the corresponding manganese to be 0.0122 g. (as  $\text{MnO}$ ). The loss in oxygen that occurred in the reductions of  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$  and of  $\text{MnO}_2$  to  $\text{MnO}$ , are respectively 10.02% and 18.45%, referred to the mother oxides, whence the amount of oxygen that was freed by the above deposited iron and manganese, must amount to 17.9 mg. and 2.6 mg. respectively, and to a total of 20.5 mg. per annum/cm.<sup>2</sup>.

On the other hand, the annual deposition of organic matter is roughly estimated as follows. The total deposition per annum is computed to be 1.66 g. as given in the foregoing paragraph. The mean percentage of carbon in this deposit is assumed to be 6.00% and the mean composition of the organic deposit is taken to be practically the same as that of cellulose. These assumptions are admissible from the result of analysis of the mud, given above. The annual deposition of organic matters is then equivalent to about 99.6 mg. of cellulose, which requires 124 mg. of oxygen for its complete combustion, so that the oxygen transported by manganese and iron amounts to 16.5% of this cellulose requirement.

But since the actual supply of oxygen is not restricted to that by iron and manganese, the actual amount of organic deposits that are destined to oxidative decomposition would considerably exceed this estimate.

At any rate, it is noteworthy that more than 16.5% of the deposited organic matter is decomposed into carbon dioxide, again to be assimilated.

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Mention should be made here that the expenses of the present studies were partly defrayed by grants from the Imperial Academy and from the Ministry of Education, and that this publication was accomplished through financial aid from the Sakamoto-hôkôkai.

Also the writer is deeply indebted to Professor Y. Shibata for the ardent encouragement he gave in the present studies, and for his kind advice in the publication of the results.

Thanks are also due to Dr. K. Kikuchi of the Tokyo Teachers College for Women, Dr. S. Yoshimura of the Tokyo Bunrika University, Messrs. M. Kawajiri and K. Hata of the Kizaki Station of the Imperial Fisheries Experimental Institute, and to the co-workers in the writer's laboratory for the kind help and facilities rendered him.

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# Über den Austausch der Wasserstoffatome zwischen Pyrrol, Indol sowie ihren Methylderivaten und Wasser. VI. Austausch der Wasserstoffatome zwischen $\alpha$ -Methyl-, $\beta$ -Methyl- sowie $\alpha,\beta$ -Dimethylindol und Wasser.<sup>(1)</sup>

Von Masao KOIZUMI.

(Eingegangen am 31. August 1939.)

**Inhaltsübersicht.** Die Austauschreaktion der H-Atome zwischen  $\alpha$ -Methyl-,  $\beta$ -Methyl- sowie  $\alpha,\beta$ -Dimethylindol und Wasser wird bei verschiedenen H-Ionenkonzentrationen (von  $pH = 7$  bis auf  $pH = -0.5$ ) unter Benutzung verdünnten schweren Wassers untersucht. Die dabei gefundenen Tatsachen können wie folgend zusammengefasst werden.

(1)  $\alpha$ -Methylindol tauscht zwei seiner H-Atome bei allen untersuchten  $pH$ -Gebieten gegen die des Wassers aus. Das eine von diesen beiden leicht austauschbaren H-Atomen ist offensichtlich das an N gebundene Imidwasserstoffatom, während das andere höchstwahrscheinlich das in  $\beta$ -Stellung des Pyrrolkerns an C gebundene H-Atom sein kann.

(2) Dagegen erwiesen sich die Wasserstoffatome des  $\beta$ -Methylindols, bis auf das eine an N gebundene, sehr schwer austauschbar, auch wenn man es mit ziemlich stark angesäuertem Wasser schüttelt.

(3)  $\alpha,\beta$ -Dimethylindol, das keine an C gebundenen H-Atome im Pyrrolkern enthält, tauscht nur das eine an N gebundene H-Atom gegen die des Wassers aus. Dagegen findet keine weitere Austauschreaktion der H-Atome statt, auch wenn man es mit 3 normaligen HCl-Lösungen bei  $60^\circ C$ . zwanzig Stunden lang schüttelt.

Alle diese Versuchsergebnisse werden im Zusammenhang mit den vom unsubstituierten Indol erhaltenen Tatsachen diskutiert und zugleich wird die Zusammenfassung der bisher in dieser Reihe der Versuche gewonnenen Ergebnisse angegeben.

**Einleitung.** Titani und ich haben in den vorhergehenden fünf Mitteilungen berichtet, dass Pyrrol, Indol, *N*-Methylpyrrol sowie *N*-Methylindol einige ihrer H-Atome stufenweise gegen die des Wassers austauschen, wenn man diese Verbindungen resp. im geschmolzenen Zustand zusammen mit durch HCl immer stärker angesäuertem verdünntem schwerem Wasser schüttelt. Behandelt man z.B. das geschmolzene Indol auf diese Weise und vermehrt die H-Ionenkonzentration der damit geschüttelten Lösung allmählich von  $pH = 7$  bis auf  $pH = -0.5$ , so werden drei H-Atome in dieser Verbindung entsprechend der zunehmenden H-Ionenkonzentration eins nach dem andern austauschbar; das erste (d.h. am leichtesten austauschbare) H-Atom wird schon bei neutraler Lösung, dagegen das zweite von  $pH = 2.5$  ab und das dritte (am schwersten austauschbare) erst von  $pH = 0.5$  ab austauschbar (vgl. IV. Mitteil.). Bezüglich der Art und Lage dieses ersten H-Atoms besteht kein Zweifel, dass es sich um das an N gebundene Imidwasserstoffatom handelt. Aber was die anderen beiden verhältnismässig schwer austauschbaren H-Atome anbetrifft, äusserten wir damals aus chemischen Gründen die Vermutung,

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(1) I. Mitteil., dies Bulletin, **13** (1938), 85; II. Mitteil., *ibid.*, **13** (1938), 95; III. Mitteil., *ibid.*, **13** (1938), 298; IV. Mitteil., *ibid.*, **13** (1938), 307; V. Mitteil., **13** (1938), 643.



dass das zweite austauschbare H-Atom höchstwahrscheinlich das in  $\beta$ -Stellung des Pyrrolkerns an C gebundene und das dritte (am schwersten austauschbare) das in  $\alpha$ -Stellung des Pyrrolkerns befindliche H-Atom sein kann. Für diese Vermutung hatten wir jedoch keinen sicheren experimentellen Beweis. Der Zweck der vorliegenden Versuche, die wir mit  $\alpha$ -Methyl-,  $\beta$ -Methyl- und  $\alpha,\beta$ -Dimethylindol ausgeführt haben, liegt deshalb darin, dadurch über die Art und Lage dieser letzteren beiden austauschbaren H-Atome nähere Kenntnis zu gewinnen.

**Darstellung der Präparate.** Unter den drei zum vorliegenden Versuche verwendeten Arten von Indolderivaten, wurde das  $\alpha$ -Methylindol teils von Prof. Kotake und teils von Dr. Masayama mir freundlich zur Verfügung gestellt und das  $\beta$ -Methylindol (Skatol) von Kahlbaum chemisch rein bezogen. Dagegen wurde das  $\alpha,\beta$ -Dimethylindol teils von Prof. Akabori und teils von Dr. Yoshida nach den Angaben von E. Fischer<sup>(2)</sup> durch die Einwirkung von Phenylhydrazin auf Methyläthylketon und die darauffolgende Behandlung mit getrocknetem Chlorwasserstoffgas hergestellt. Bei dieser Gelegenheit möchte ich allen diesen Herren meinen herzlichsten Dank aussprechen.

**Versuche mit  $\alpha$ -Methylindol (Methylketol).** Man schüttelt etwa 0.6 g. (aber wohl abgewogene Menge)  $\alpha$ -Methylindol zusammen mit etwa 0.2 g. (aber ebenfalls wohl abgewogene Menge) verdünnten, schweren und durch den Zusatz von Salzsäure verschieden stark angesäuerten Wassers in einem zugeschmolzenen Glasrohr (unter Luftabschluss!) bei einer bestimmten Temperatur während einer bestimmten Zeitlänge. Als Versuchstemperatur benutzen wir stets 60°C. und die Schüttelungsdauer beträgt immer etwa fünf Stunden. Nach der Zusammenschüttelung wird das Wasser durch zweimalige Destillation im Vakuum vom  $\alpha$ -Methylindol abgetrennt und der D-Gehalt des so abgetrennten Wassers, nachdem es auf die übliche Weise gereinigt worden ist, durch die Dichtebestimmung ermittelt. Das Austauschäquivalent  $nk$  des  $\alpha$ -Methylindols unter den benutzten Versuchsbedingungen wird dann wie üblich durch die folgende Gl. (1) errechnet:

$$nk = \frac{M_w}{M_j} \frac{D_a - D_e}{D_e} \quad (1).$$

In dieser Gl. bedeutet  $M_w$  und  $M_j$  je die Molzahl des zum Versuch benutzten schweren Wassers und  $\alpha$ -Methylindols und  $D_a$  und  $D_e$  resp. den D-Gehalt des Wassers vor und nach dem Versuch. Die so gewonnenen Versuchsergebnisse sind in der folgenden Tabelle 1 zusammengestellt, wo die Versuchsnr. die zeitliche Reihenfolge der einzelnen Versuche angibt.

Aus dieser Tabelle wird ersichtlich, dass das Austauschäquivalent  $nk$  des  $\alpha$ -Methylindols mindestens innerhalb des untersuchten pH-Bereichs praktisch konstant bleibt. Errechnet man aus diesem Grunde den Mittelwert der gefundenen  $nk$ -Werte, so ergibt sich einer von etwa 1.88. Da aber diese Verbindung ein freies Imidwasserstoffatom enthält, können wir ohne weiteres erwarten, dass mindestens eins ihrer H-Atome schon bei neutraler Lösung leicht austauschbar sein muss. Wenn man deshalb diesem Imidwasserstoff denselben Verteilungsquotienten (V.Q.) 1.07 wie beim unsubstituierten Indol zuschreibt (vgl. IV. Mitteil.) und vom ge-

(2) E. Fischer, *Ann.*, **236** (1886), 126.

Tabelle 1. Austauschäquivalent  $nk$  von  $\alpha$ -Methylindol (Methylketol) bei verschiedenen H-Ionenkonzentrationen.

| Versuchs-nr. | Normalität der benutzten Lösung | pH    | $M_w$  | $M_j$  | $nk$ |
|--------------|---------------------------------|-------|--------|--------|------|
| 1            | neutral                         | 7.00  | 0.0124 | 0.0052 | 1.86 |
| 5            | 0.00001 N HCl                   | 5.00  | 0.0101 | 0.0053 | 1.74 |
| 7            | 0.0001 „                        | 4.00  | 0.0076 | 0.0050 | 1.75 |
| 4            | 0.01 „                          | 2.00  | 0.0122 | 0.0060 | 1.93 |
| 2            | 0.8 „                           | 0.10  | 0.0123 | 0.0041 | 2.12 |
| 3            | 3.0 „                           | -0.48 | 0.0129 | 0.0047 | 1.90 |

fundenen Totalaustauschäquivalent 1.88 des  $\alpha$ -Methylindols diesen Wert abzieht, dann bleibt nur noch 0.81 übrig. Dieser Wert kommt aber sehr nahe dem V.Q. 0.69, den wir beim Versuch mit unsubstituiertem Indol dem in  $\beta$ -Stellung des Pyrrolkerns befindlichen H-Atom zuschrieben. Aus diesem sowie anderen Gründen und insbesondere daraus, dass das gefundene Austauschäquivalent des  $\alpha$ -Methylindols bis auf eine ziemlich grosse H-Ionenkonzentration konstant bleibt, liegt die Annahme nahe, dass das zweite austauschbare H-Atom des unsubstituierten sowie  $\alpha$ -Methylindols nichts anders als das in  $\beta$ -Stellung des Pyrrolkerns an C gebundene H-Atom ist. Aber in jedem Fall erscheint uns hoch interessant, dass dieses zweite und offensichtlich an C gebundene H-Atom ebenso leicht wie das an N bzw. O gebundene H-Atom austauschbar ist. Diese ausserordentlich grosse Reaktionsfähigkeit des zweiten austauschbaren H-Atoms, wenn es sich dabei wirklich um das in  $\beta$ -Stellung des Pyrrolkerns befindliche H-Atom handelt, müssen wir auf den lockernden Effekt der in  $\alpha$ -Stellung eingeführten Methylgruppe zurückführen.

Für die Annahme, dass sich unter den benutzten Versuchsbedingungen tatsächlich zwei H-Atome in einem Molekül gleichzeitig an der Austauschreaktion beteiligen; gewinnt man einen direkten experimentellen Beweis, indem die Anzahl der austauschbaren H-Atome unter Benutzung des fast reinen schweren Wassers bestimmt wird. Dabei wird nämlich eine kleine Menge  $\alpha$ -Methylindol gegen eine überschüssige aber wohl abgewogene Menge fast reinen schweren Wassers  $D_2O$  ausgetauscht. Zeichnet man nun mit  $H_a$  und  $H_e$  resp. den H-Gehalt des benutzten schweren Wassers vor und nach dem Versuch, dann lässt sich die Anzahl  $n$  der austauschbaren H-Atome in einem  $\alpha$ -Methylindolmolekül mittels Gl. (2) ohne weiteres errechnen:<sup>(3)</sup>

$$n \approx (H_e - H_a) \frac{2M_w}{M_j} \quad (2).$$

In dieser Gl. bedeutet  $M_w$  und  $M_j$  je die Molzahl des zum Versuch benutzten schweren Wassers und  $\alpha$ -Methylindols. In Praxis schüttelten wir bei 60°C. 0.00108 Mol  $\alpha$ -Methylindol zusammen mit 0.0521 Mol 99.4-prozenti-

(3) Vgl. dazu M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 90.

gen schweren Wassers etwa fünf Stunden lang. Nach der Schüttelung wird das Wasser durch die Destillation im Vakuum von  $\alpha$ -Methylindol abgetrennt und die durch die Austauschreaktion hervorgerufene Dichteabnahme des schweren Wassers mittels eines zu diesem Zweck besonders konstruierten Glasschwimmers genau bestimmt. Diese ergibt aber 0.00268. Deshalb beträgt die nach Gl. (2) berechnete Anzahl  $n$  der austauschbaren H-Atome in einem  $\alpha$ -Methylindolmolekül 2.5. Zieht man die Schwierigkeit dieser Art von Versuchen in Betracht, dann darf wohl geschlossen werden, dass es sich dabei wirklich um die Austauschreaktion von zwei H-Atomen handelt.

**Versuche mit  $\beta$ -Methylindol (Skatol).** Die Versuchsanordnung ist im grossen und ganzen dieselbe wie bei dem vorstehenden Versuche mit  $\alpha$ -Methylindol bis auf die Versuchstemperatur. Bei diesem letzten Versuche arbeiteten wir, wie schon oben erwähnt, immer bei 60°C., weil der Schmelzpunkt des  $\alpha$ -Methylindols bei 59°C. liegt. Dagegen müssten wir im vorliegenden Versuche mit  $\beta$ -Methylindol, dessen Schmelzpunkt bei 95°C. liegt, die Versuchstemperatur erhöhen, um die Verbindung während der Versuche vollkommen flüssig zu halten. In der Praxis arbeiteten wir bei 105°C. Etwa 1 g. schweren Wassers von verschiedener H-Ionenkonzentration wird zusammen mit etwa 2.5 g.  $\beta$ -Methylindol in einem zugeschmolzenen Rohr bei der oben genannten Temperatur immer etwa fünf Stunden lang geschüttelt und aus der Abnahme des D-Gehaltes des benutzten schweren Wassers wird das Austauschäquivalent  $nk$  des  $\beta$ -Methylindols unter allen benutzten Versuchsbedingungen bestimmt. Die Versuchsergebnisse sind in Tabelle 2 zusammengestellt.

Tabelle 2. Austauschäquivalent  $nk$  von  $\beta$ -Methylindol (Skatol) bei verschiedenen H-Ionenkonzentrationen.

| Versuchs-nr. | Normalität der benutzten Lösung | pH    | $M_j$  | $M_w$  | $nk$ | $nk-1.07$ |
|--------------|---------------------------------|-------|--------|--------|------|-----------|
| 1            | neutral                         | 7.00  | 0.0204 | 0.0531 | 1.07 | 0.00      |
| 3            | 0.03 N HCl                      | 1.52  | 0.0159 | 0.0470 | 1.23 | 0.16      |
| 4            | 0.1 „                           | 1.00  | 0.0134 | 0.0397 | 1.91 | 0.84      |
| 5            | 0.3 „                           | 0.52  | 0.0214 | 0.0539 | 2.23 | 1.16      |
| 6            | 0.8 „                           | 0.10  | 0.0204 | 0.0533 | 3.18 | 2.11      |
| 2            | 3.0 „                           | -0.48 | 0.0174 | 0.0496 | 4.98 | 3.91      |

In diesem Fall nimmt also das gefundene Austauschäquivalent  $nk$  des  $\beta$ -Methylindols mit zunehmender H-Ionenkonzentration der damit geschüttelten Lösung allmählich zu. Da aber diese Verbindung ebenso wie das  $\alpha$ -Methylindol ein an N gebundenes freies Imidwasserstoffatom enthält, muss das kleinste gefundene Austauschäquivalent 1.07 bei neutraler Lösung diesem H-Atom entsprechen. Wenn man aus diesem Grunde von den gefundenen Werten von  $nk$  diesen Wert (1.07) abzieht, so erhält man die Werte, die in der letzten Spalte der Tabelle 2 angegeben

sind. Die Grösse dieser Differenz ( $nk - 1.07$ ) legt uns nun die Vermutung nahe, dass ausserhalb des Imidwasserstoffatoms mindestens noch ein und offensichtlich an C gebundenes H-Atom an der Austauschreaktion teilnimmt. Als solch ein austauschbares H-Atom kommt erstens das in  $\alpha$ -Stellung des Pyrrolkerns befindliche und zweitens irgendein Kernwasserstoffatom im Benzolkern in Betracht. Aber allem Anschein nach, besonders aus dem Grunde, weil die Kernwasserstoffatome im Benzolkern, wie weiter unten bei dem Versuche mit  $\alpha,\beta$ -Dimethylindol gezeigt wird, viel schwieriger als die im Pyrrolkern austauschbar sind, liegt die Annahme nahe, dass das bei nicht zu grosser H-Ionenkonzentration (neben dem Imidwasserstoffatom) austauschbar werdende H-Atom das in  $\alpha$ -Stellung des Pyrrolkerns befindliche Kernwasserstoffatom ist. Aber auch wenn dies wirklich der Fall ist, muss die Austauschbarkeit dieses  $\alpha$ -H-Atoms des  $\beta$ -Methylindols im Vergleich mit der des  $\beta$ -H-Atoms des  $\alpha$ -Methylindols viel kleiner sein, weil die oben angegebenen Differenz ( $nk - 1.07$ ) erst von  $pH = 1$  ab (und zwar bei  $105^\circ C.$ !) merklich zunimmt. Bei noch grösserer H-Ionenkonzentration nimmt das gefundene Austauschäquivalent, wie die Tabelle zeigt, weiter zu. Aber ob es sich bei dieser Zunahme wirklich um die weitere Austauschreaktion von z.B. im Benzolkern befindlichen H-Atome handelt oder ob irgendeine andere Nebenreaktion dabei eine Rolle spielt, das können wir noch nicht so ohne weiteres entscheiden. Aus den weiter unten zu erwähnenden Versuchen mit  $\alpha,\beta$ -Dimethylindol zu urteilen, erscheint uns die zweite Möglichkeit näher als die erste: es dürfte sich dabei höchstwahrscheinlich um die durch die hohe H-Ionenkonzentration und Versuchstemperatur hervorgerufene Zersetzung oder dergleichen Nebenreaktion der untersuchten Substanz, nämlich des  $\beta$ -Methylindols, handeln.

**Versuche mit  $\alpha,\beta$ -Dimethylindol.** Diese Versuche werden ausgeführt, um über die Austauschbarkeit der im Benzolkern der Indolverbindungen befindlichen H-Atome eingehendere Kenntnis zu gewinnen. Aber weil in diesem Fall der Schmelzpunkt ( $104^\circ C.$ ) des  $\alpha,\beta$ -Dimethylindols viel höher als bei den bisher untersuchten Verbindungen liegt, mussten wir die Versuchsanordnung so abändern, dass wir statt des reinen geschmolzenen  $\alpha,\beta$ -Dimethylindols seine Lösung in Benzol zusammen mit schwerem Wasser schüttelten; etwa 1 g. (aber gut abgewogene Menge)  $\alpha,\beta$ -Dimethylindol wird in etwa 2 c.c. im voraus gut getrocknetem Benzol aufgelöst und die so hergestellte Lösung zusammen mit etwa 0.25 g. (aber gut abgewogene Menge) verdünnten schweren Wassers geschüttelt. Das dazu benutzte schwere Wasser besitzt wie üblich unter Zusatz von Salzsäure eine bestimmte H-Ionenkonzentration und die Schüttelung dauert bei  $60^\circ C.$  etwa fünf Stunden. Nach der Schüttelung wird das Wasser, nachdem es zusammen mit dem Benzol vom  $\alpha,\beta$ -Dimethylindol durch die Destillation im Vakuum abgetrennt worden ist, von der Benzolschicht abpipettiert. Da das so abgeschiedene Wasser eine noch ziemlich beträchtliche Menge Benzol enthält, wird das Wasser, bevor es auf die übliche Weise gereinigt wird, durch eine der folgenden beiden Methoden behandelt:

**Methode a.** Das Wasser wird zunächst zusammen mit gut getrocknetem Äther kräftig geschüttelt und der dabei im Wasser wenig gelöste

Äther durch die Behandlung mit Pumpenöl beseitigt.<sup>(4)</sup>

Methode b. Das vom Benzol abgeschiedene Wasser wird zuerst auf eine Menge gut entwässertem Chlorcalcium abdestilliert und das dabei entstandene Hydrat, nachdem es im Vakuum etwa zwei Stunden lang gut abgesaugt worden war, ebenfalls im Vakuum stark erhitzt, um das Wasser aus dem Hydrat wieder frei zu machen.

Der D-Gehalt des auf diese Weise vom Benzol befreiten und dann vollständig gereinigten Wassers wird zum Schluss mittels eines Quarzschwimmers bestimmt. Aber weil der D-Gehalt des verwendeten schweren Wassers wegen des oben geschilderten etwas umständlichen Versuchs- und Reinigungsverfahrens nicht nur durch die Austauschreaktion sondern auch durch die Aufnahme der atmosphärischen Feuchtigkeit u.s.w. mehr oder weniger extra verdünnt worden ist, wird der direkt gemessene D-Gehalt nach dem Versuch für diese Extraverdünnung korrigiert. Zu diesem Zweck wird ein Kontrollversuch durchgeführt, indem man zunächst dasselbe schwere Wasser wie beim Hauptversuch benutzt, es zusammen mit etwa 2 c.c. Benzol schüttelt und nachdem das Wasser ebenfalls auf dieselbe Weise wie beim Hauptversuch vom Benzol getrennt und gereinigt worden ist, der D-Gehalt des Wassers bestimmt. Dies ergibt aber, wie erwartet, immer einen D-Gehalt, der um ein wenig kleiner ist als der Anfangs-D-Gehalt des verwendeten schweren Wassers. Deshalb wird diese Differenz zu dem beim Hauptversuch (nach dem Versuch!) direkt gefundenen D-Gehalt des Wassers addiert und unter Benutzung des so korrigierten D-Gehaltes des Wassers wird das Austauschäquivalent  $nk$  des  $\alpha,\beta$ -Dimethylindols auf die übliche Weise berechnet. Die dadurch gewonnenen Versuchsergebnisse sind in Tabelle 3 zusammengestellt.

Tabelle 3. Austauschäquivalent  $nk$  von  $\alpha,\beta$ -Dimethylindol bei verschiedenen H-Ionenkonzentrationen.

| Versuchs-<br>nr. | Normalität<br>der benutzten<br>Lösung | pH    | Schüttelungs-<br>dauer<br>in Stdn. | $nk$ | Reinigungs-<br>methode |
|------------------|---------------------------------------|-------|------------------------------------|------|------------------------|
| 1                | neutral                               | 7.00  | 5                                  | 0.85 | a                      |
| 8                | "                                     | "     | 5                                  | 1.01 | b                      |
| 9                | 0.001 N HCl                           | 3.00  | 5                                  | 1.01 | b                      |
| 4                | 0.01 N HCl                            | 2.00  | 5                                  | 0.96 | a                      |
| 2                | 0.1 N HCl                             | 1.00  | 5                                  | 1.03 | a                      |
| 5                | "                                     | "     | 10                                 | 0.84 | a                      |
| 7                | 1.0 N HCl                             | 0.00  | 21                                 | 1.32 | a                      |
| 10               | "                                     | "     | 5                                  | 0.93 | b                      |
| 11               | 2.0 N HCl                             | -0.30 | 5                                  | 1.07 | b                      |
| 12               | "                                     | "     | 11                                 | 1.02 | b                      |
| 13               | "                                     | "     | 12                                 | 1.07 | b                      |
| 14               | 3.0 N HCl                             | -0.48 | 5                                  | 1.03 | b                      |
| 3                | "                                     | "     | 20                                 | 1.29 | a                      |

(4) Vgl. dazu M. Harada und T. Titani, dies Bulletin, **11** (1936), 468.

Die in der letzten Spalte der Tabelle angegebenen Symbole a und b zeigen die Methode, die bei der Befreiung des Benzols aus dem Wasser benutzt wurde.

Aus diesen Versuchsergebnissen darf wohl geschlossen werden, dass das  $\alpha,\beta$ -Dimethylindol mindestens unter den benutzten Versuchsbedingungen nur eins und zwar das an N gebundene H-Atom gegen die des Wassers auszutauschbare besitzt. Dafür spricht u.a., dass der Mittelwert des gefundenen Austauschäquivalents, der etwa 1.03 beträgt, mit dem beim unsubstituierten Indol gefundenen ( $nk = 1.07$ , vgl. dazu Tabelle 4, IV. Mitteil.) sowie beim  $\beta$ -Methylindol gefundenen ( $nk = 1.07$ , vgl. oben Tabelle 2) sehr gut übereinstimmt. Ferner wird gefunden, wie die obige Tabelle 3 zeigt, dass das Austauschäquivalent des  $\alpha,\beta$ -Dimethylindols fast konstant bleibt, auch wenn man es zusammen mit ziemlich konzentrierter HCl-Lösung verhältnismässig lange Zeit schüttelt. Dies weist aber ohne weiteres darauf hin, dass die Kernwasserstoffatome im Benzolkern des Indols nicht so leicht wie die im Pyrrolkern austauschbar sind, weil das  $\alpha,\beta$ -Dimethylindol offensichtlich keine an C gebundenen Kernwasserstoffatome im Pyrrolkern enthält. Es liegt deshalb nahe anzunehmen, dass es sich bei dem im vorhergehenden Versuch mit  $\beta$ -Methylindol gefundenen Zuwachs des Austauschäquivalents sowie um die dritte Stufe der Austauschreaktion, die beim unsubstituierten Indol gefunden wurde, (vgl. dazu IV. Mitteil.) höchstwahrscheinlich um die Austauschreaktion des in  $\alpha$ -Stellung des Pyrrolkerns befindlichen Kernwasserstoffatoms handelt, wie wir das aus rein chemischen Gründen vermuteten.

**Zusammenfassung und Diskussion.** Die in dem vorliegenden Versuche gewonnenen Ergebnisse sind in der nebenstehenden Abb. graphisch zusammengestellt, wo das gefundene Austauschäquivalent  $nk$  der untersuchten Substanzen gegen den  $pH$  der damit geschüttelten Lösung aufgetragen ist. Die Nummer bei jedem kleinen Kreis zeigt die Schütteldauer.

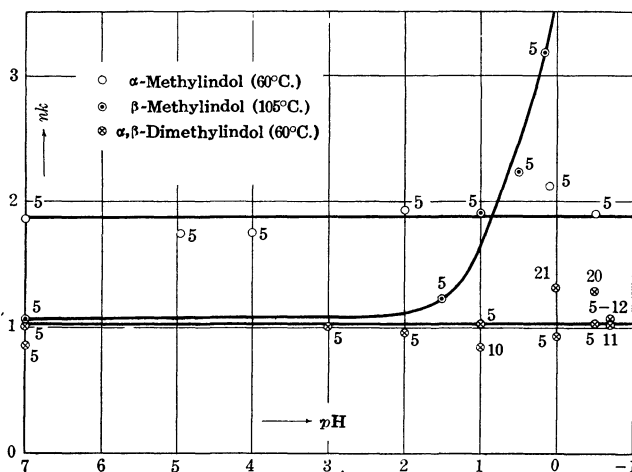


Abb. Abhängigkeit des Austauschäquivalents  $nk$  des  $\alpha$ -Methyl-,  $\beta$ -Methyl- und  $\alpha,\beta$ -Dimethylindols auf den  $pH$  des damit geschüttelten Wassers und der Schütteldauer.



Worten, dass das H-Atom dieses Radikals bei der angegebenen H-Ionenkonzentration erst beweglich bzw. austauschbar wird. Die Formel  $\leftarrow\text{NH}\rightarrow$  unter  $\text{pH} = 7$  bedeutet z.B., dass das Imidwasserstoffatom schon bei dieser H-Ionenkonzentration austauschbar ist. Dagegen zeigt die Formel  $4\text{CH}\rightarrow$  unter  $\text{pH} = 1.5$  bei unsubstituiertem Pyrrol, dass alle vier Kernwasserstoffatome des Pyrrols erst von dieser H-Ionenkonzentration ab gleichzeitig austauschbar werden. Der in der letzten Spalte der Tabelle 4 angegebene V.Q.  $k$  gibt offenbar den des bei jeder Stufe der Reaktion austauschbar werdenden H-Atoms an.

Zum Schluss ist es mir eine angenehme Pflicht Herrn Prof. T. Titani für seine stetigen Ratschläge und freundliche Unterstützung meinen herzlichsten Dank auszusprechen. Zugleich spreche ich der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Durchführung dieser Arbeit meinen besten Dank aus.

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**Chemical Studies of the Western Pacific Ocean. V.  
The Vertical Variation of Minor Constituents  
in the "Kuroshio" Region. Part 1.**

By Yasuo MIYAKE.

(Received September 5, 1939.)

**Introduction.** In the previous papers,<sup>(1)</sup> the present author reported the results of the chemical analyses of the major constituents of the oceanic salt collected from the western part of the North Pacific Ocean. These major constituents of the oceanic salt vary scarcely in their relative concentrations in sea water, while it cannot be over-looked that there are many minor constituents which, in spite of their smaller concentrations, have biological significances for the marine lives and vary widely in their concentrations according to depth and locality.

In the present report, the writer studied the vertical distributions of some minor elements in the region of the "Kuroshio" (the Japan-Current), one of the largest oceanic current in the North Pacific Ocean

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(1) This Bulletin, **14** (1939), 29, 55.

which runs north-eastwardly along the south-western coast of Japan, and obtained the some knowledge of the vertical structure of this current.

The samples of water for analyses were collected by M.S. "Ryôhûmaru".\* The dates and the positions of sampling are as follows:

For the sampling of water Nansen's water-bottles were used and the measurement of water temperature, done at each position, down to the depth of 1,000 m., was carried out with Richter's reversing thermometers. Of each sample, determinations of hydrogen ion concentration and that of the amount of dissolved oxygen were made on board immediately after the collection, while the chlorinity determination and the chemical analyses of other elements were made later on land.

Table 1. The Dates and the Positions.

| Date       | Position |         | Date       | Position |         |
|------------|----------|---------|------------|----------|---------|
| Jan. 1939. | Lat. N   | Long. E | Jan. 1939. | Lat. N   | Long. E |
| 16         | 33°24'   | 137°59' | 23         | 32°30'   | 137°32' |
| 20         | 32°35'   | 135°13' | 24         | 31°37'   | 136°14' |
| 21         | 31°35'   | 134°32' | 24         | 31°22'   | 137°01' |
| 21         | 30°49'   | 135°40' | 24         | 32°00'   | 136°55' |
| 21         | 30°37'   | 136°53' | 25         | 32°08'   | 135°46' |
| 21         | 31°00'   | 138°37' | 25         | 32°29'   | 136°37' |
| 22         | 32°06'   | 139°25' | 25         | 32°33'   | 137°00' |
| 23         | 31°48'   | 137°55' | 25         | 32°21'   | 136°47' |
| 23         | 32°35'   | 138°40' |            |          |         |

**The Water Temperature.** The average values of the water temperature at various depths are given in Table 2 and Fig. 1.

Table 2. The Water Temperature at Various Depths.

| Depth (m.) | t°C. | Depth (m.) | t°C. |
|------------|------|------------|------|
| 0          | 17.9 | 300—400    | 8.9  |
| 25         | 18.0 | 400—500    | 8.1  |
| 50         | 17.8 | 500—600    | 7.6  |
| 100        | 17.6 | 600—700    | 5.8  |
| 100—150    | 15.2 | 700—800    | 4.6  |
| 150—200    | 14.6 | 800—900    | 4.3  |
| 200—250    | 13.9 | 900—1000   | 3.2  |
| 250—300    | 11.0 |            |      |

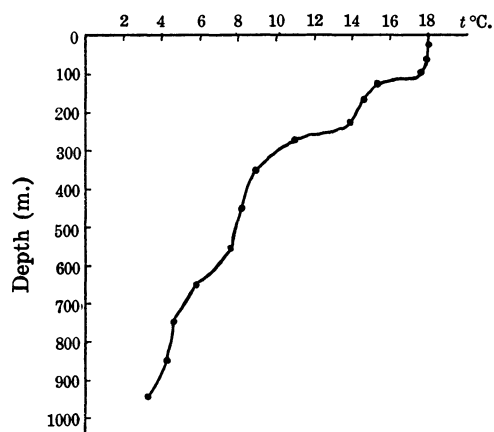


Fig. 1. The Vertical Variation of the Water Temperature.

\* An observation ship of the Central Meteorological Observatory of Japan.

As seen in Table 2 and Fig. 1, the water temperature of the upper layer ranging from 0 to 100 m. is almost constant, and it suddenly falls in the next 50 m. Then it begins to decrease gradually down to the depth of 900–1000 m., where about 3°C. was recorded. It is notable that there is found the existence of a second layer of sudden decrease in temperature at the depth of 600–700 m.

**The Chlorinity.** The chlorinity was determined in the usual way. Table 3 and Fig. 2 give the mean vertical variation of the chlorinity, on whose relation to the vertical structure of the "Kuroshio" will be briefly discussed in the following.

Table 3. The Chlorinity at Various Depths.

| Depth (m.) | Cl ‰  | Depth (m.) | Cl ‰  |
|------------|-------|------------|-------|
| 0          | 19.24 | 300–400    | 19.03 |
| 25         | 19.23 | 400–500    | 19.03 |
| 50         | 19.23 | 500–600    | 19.01 |
| 100        | 19.22 | 600–700    | 18.98 |
| 100–150    | 19.15 | 700–800    | 19.01 |
| 150–200    | 19.14 | 800–900    | 19.02 |
| 200–250    | 19.13 | 900–1000   | 19.06 |
| 250–300    | 19.07 |            |       |

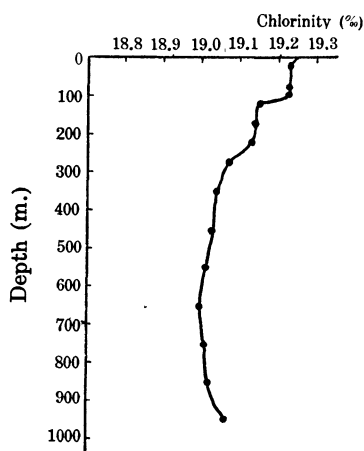


Fig. 2. The Vertical Variation of the Chlorinity.

**The Temperature Salinity Diagram. The Vertical Structure of the "Kuroshio".** Needless to say, the vertical variation of elements in sea water is governed to a great degree by the vertical structure of the ocean, therefore it is necessary to draw a T-S diagram (Fig. 3) in order to investigate the vertical structure of the "Kuroshio".

In the first place, we can see from this diagram that there is a thick surface water layer which is almost homogeneous and extends down to a depth of about 100 m. A marked discontinuity is noticeable between 100 and 150 m., followed by a layer down to about 600–700 m. with the gradual decrease in temperature and in salinity. The 100–150 m. layer, having a relatively higher chlorinity and temperature seems to form the center of the "Kuroshio"; on the other hand, the 600–700 m. layer with relatively low salinity seems to consist of the subarctic intermediate water. Then it is very

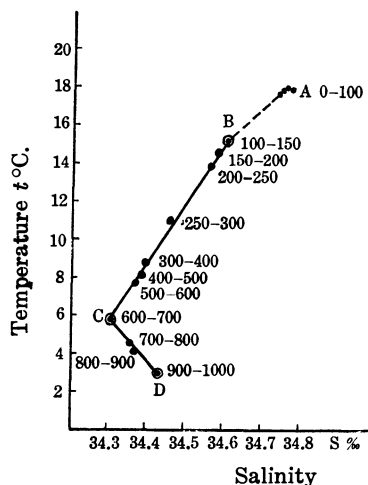


Fig. 3. The T-S Diagram.

likely that there occurs mixing of the two water masses of different character.

Below the 600–700 m. layer, the salinity gradually increases again; this increase is perhaps due to the mixing of two kinds of water masses, the subarctic intermediate water and the deep water.

Thus from the T-S diagram, we can distinguish four different water layers or strata in the vertical structure of the “Kuro시오”, namely, (A) the surface water, having both a higher temperature and a higher chlorinity, and its thickness being about 100 m.; (B) the main part of the “Kuro시오” at about 100–150 m. below the surface and having a moderately high temperature and chlorinity ( $Cl\%$  19.15,  $t^{\circ}C$ . 15.2); (C) the subarctic intermediate water, found at a depth of 600–700 m. and having a lower chlorinity ( $Cl\%$  18.98); and finally (D) the deep water.

The above result of the vertical structure of the “Kuro시오” agrees on the whole with those obtained formerly by other oceanographers, however, it will be noteworthy that the existence of some characteristic features were made out in the author’s present result.

**The Density *in situ*.** As the rate of the vertical stability mainly depends upon the density of water *in situ*, it is of interest to see the vertical change of the density in the “Kuro시오” region.

In Table 4 and Fig. 4, the average values of  $\sigma_t$  at various depths are given, where  $\sigma_t$  is the  $(\text{density} - 1) \times 1,000$  at temperature,  $t^{\circ}C$ .

Table 4. The Vertical Variation of the Density.

| Depth (m.) | $\sigma_t$ | Depth (m.) | $\sigma_t$ |
|------------|------------|------------|------------|
| 0          | 25.13      | 300–400    | 26.68      |
| 25         | 25.09      | 400–500    | 26.78      |
| 50         | 25.13      | 500–600    | 26.82      |
| 100        | 25.17      | 600–700    | 27.05      |
| 100–150    | 25.65      | 700–800    | 27.22      |
| 150–200    | 25.77      | 800–900    | 27.27      |
| 200–250    | 25.90      | 900–1000   | 27.43      |
| 250–300    | 26.37      |            |            |

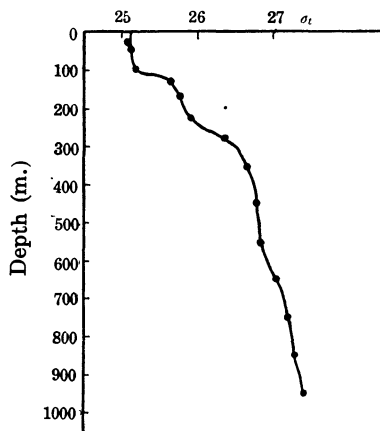


Fig. 4. The Vertical Variation of the Density *in situ*.

As seen in Table 4 and Fig. 4, we can recognize that the vertical stability of the “Kuro시오” below 100 m. is so large that it hinders the vertical convection, while, the densities of the surface water down to 100 m. are practically the same, therefore the mixing of water allowed to take place easily.

**Oxygen.** The dissolved oxygen was determined by the Winkler’s method by Dr. T. Yanagisawa immediately after the collection of the

sample. Table 5 and Fig. 5 give the result, which confirms the existence of a similar vertical structure of the "Kuroshio" as mentioned in the foregoing paragraph.

Table 5. The Dissolved Oxygen in Sea Water.

| Depth (m.) | Dissolved Oxygen (c.c./l.) | Saturation Percentage (%) | Depth (m.) | Dissolved Oxygen (c.c./l.) | Saturation Percentage (%) |
|------------|----------------------------|---------------------------|------------|----------------------------|---------------------------|
| 0          | 5.17                       | 93.2                      | 300—400    | 2.86                       | 45.5                      |
| 25         | 5.09                       | 91.5                      | 400—500    | 2.75                       | 43.4                      |
| 50         | 5.06                       | 91.1                      | 500—600    | 2.46                       | 39.0                      |
| 100        | 4.93                       | 88.3                      | 600—700    | 2.07                       | 28.5                      |
| 100—150    | 4.34                       | 74.8                      | 700—800    | 1.73                       | 23.9                      |
| 150—200    | 3.99                       | 68.2                      | 800—900    | 1.65                       | 22.6                      |
| 200—250    | 3.80                       | 58.8                      | 900—1000   | 1.61                       | 20.3                      |
| 250—300    | 3.40                       | 54.9                      |            |                            |                           |

It is a well known fact that there is found a peculiar intermediate minimum in the vertical variation of oxygen in the open sea. Thus in the Atlantic, it often occurs at the depth of several hundred metres, while in the eastern part of the Pacific, as has been reported by E. G. Moberg,<sup>(2)</sup> the amount of oxygen decreases from the surface with a nearly complete saturation towards the depth of 700 m., where it attains its minimum of less than about 1 ml./l.

H. Wattenberg<sup>(3)</sup> ascribes recently the actual cause of this intermediate oxygen minimum to the biological actions, considering that the biological consumption of oxygen decreases rapidly with increasing depth. He pointed also an intimate relation between the maximum of phosphate and the minimum of oxygen in which he states that the maximum of phosphate is usually found in the water layer below the intermediate oxygen minimum.

It is also well known that besides this intermediate minimum, there often occurs a maximum in oxygen content near the surface. In the present case, down to 1,000 m., so far as the range explored is concerned, neither minimum nor maximum in the amount of dissolved oxygen could be found. According to E. G. Moberg, the eastern Pacific-water contains

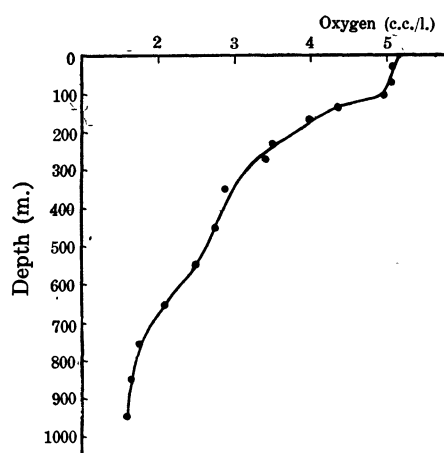


Fig. 5. The Vertical Variation of Oxygen (c.c./l.)

(2) E. G. Moberg, *Bull. Nat. Research Council*, **85** (1932), 95.

(3) H. Wattenberg, *Ann. Hydrographie*, **67** (1939), 257.

less oxygen than the Atlantic water. It is interesting to compare the content of oxygen in the western Pacific with other oceans. It appears that the oxygen content in the "Kuroshio" is even less than in the eastern part of the Pacific. Further quantitative study will be done in future.

**The Hydrogen Ion Concentration.** The hydrogen ion concentration of the sea water determined on board colorimetrically using cresol red and thymol blue as indicators. As in the cases of other oceans, the  $pH$  is about 8.2<sub>5</sub> at the surface and decreases gradually with the depth (Table 6 and Fig. 6).

Table 6. The Vertical Variation of  $pH$ .

| Depth (m.) | $pH$ | Depth (m.) | $pH$ |
|------------|------|------------|------|
| 0          | 8.25 | 300—400    | 8.00 |
| 25         | 8.25 | 400—500    | 7.95 |
| 50         | 8.25 | 500—600    | 7.90 |
| 100        | 8.25 | 600—700    | 7.81 |
| 100—150    | 8.20 | 700—800    | 7.80 |
| 150—200    | 8.19 | 800—900    | 7.74 |
| 200—250    | 8.14 | 900—1000   | 7.78 |
| 250—300    | 8.12 |            |      |

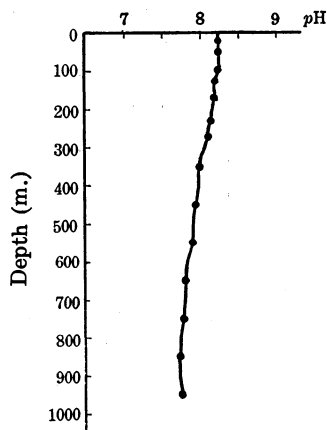


Fig. 6. The Vertical Variation of  $pH$ .

The constancy of  $pH$  values from the surface down to about 100 m. indicates the complete mixing of the upper water, which brings the sea water in equilibrium with carbon dioxide in the air.

### Summary.

(1) The vertical variations of chlorinity, temperature, the oxygen content and the hydrogen ion concentration in the region of the "Kuroshio" (the Japan-Current) were investigated.

(2) From the result above, the vertical structure of the "Kuroshio" was discussed.

In conclusion, the author wishes to express his hearty thanks to Professor T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for the assistance of the work.

*The Central Meteorological Observatory  
of Japan, Tokyo.*

## Chemical Studies of the Western Pacific Ocean. VI. The Vertical Variation of Minor Constituents of the "Kuroshio" Region. Part 2.

By Yasuo MIYAKE.

(Received September 5, 1939.)

**Silicate.** Silicon is assimilated by diatoms in the upper water layer in the ocean; therefore, its concentration in such layers is smaller and it increases gradually with depth. Thus in the Atlantic water, H. W. Harvey<sup>(1)</sup> gave 0.05–0.1 mg. Si per litre at the surface, 0.17 mg. at 1,000 m. and 0.50 mg. at 3,000 m. According to H. Wattenberg,<sup>(2)</sup> deep sea water less affected by diatoms contains 0.8–1.2 mg. Si per litre. It is of interest to note that the waters of the east side of the Pacific Ocean contain a larger quantity of silicon than the Atlantic; thus the content of silicon in the former waters often attains the value as high as 0.3–0.9 mg. Si per litre even at the surface.

The author determined the vertical variation of silicate in the "Kuroshio". The analytical results by the Diénert-Wandenburg's method show that the silicate content in the region of this ocean current is much smaller than that of the Californian-Current, flowing along the eastern coast of the Pacific.

Such difference can be easily explained when we consider that the Californian-Current is a cold one with an upwelling turbulent motion, while the "Kuroshio" is a warm current with a large vertical stability.

In Table 1 and Fig. 1, the average values of milligram Silicon per litre at various depths are given.

Table 1. The Vertical Variation  
of Silicate.

| Depth<br>(m.) | Si<br>(mg./l.) | Depth<br>(m.) | Si<br>(mg./l.) |
|---------------|----------------|---------------|----------------|
| 0             | 0.13           | 300–400       | 0.93           |
| 25            | 0.21           | 400–500       | 1.21           |
| 50            | 0.15           | 500–600       | 1.26           |
| 100           | 0.20           | 600–700       | 1.77           |
| 100–150       | 0.46           | 700–800       | 2.01           |
| 150–200       | 0.52           | 800–900       | 2.05           |
| 200–250       | 0.68           | 900–1000      | 2.28           |
| 250–300       | 0.74           |               |                |

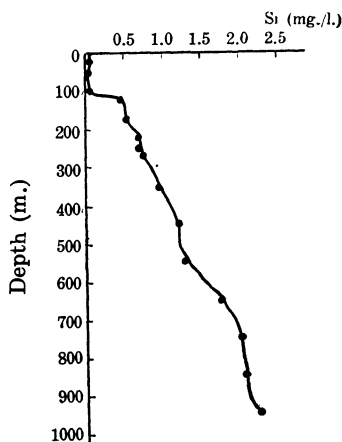


Fig. 1. The Vertical Variation  
of Silicate.

(1) H. W. Harvey, "Biological Chemistry and Physics of Sea Water", 50, Cambridge (1928).

(2) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

A similar vertical variation of silicate was seen in the "Tusima-Current" in the Japan Sea. This similarity is easily understood when we consider that the "Tusima-Current" is one of the branches of the "Kurosio".

**Phosphate.** As it is the case with silicate and nitrogen compounds, phosphate is essential to marine organisms, and as the concentration of this compound in sea water is small, it often acts as an important limiting factor to the growth of plankton.

Thus the content of phosphate varies very much with the depth and the location, and it shows a marked annual variation.

The average amount of phosphate in sea water has been found about 1–60  $\gamma$  P per litre, and in general, deeper water contains more phosphate than the shallower. According to H. Wattenberg,<sup>(3)</sup> in the open sea, the maximum of phosphate occurs just below the intermediate oxygen minimum. Now, as stated in the foregoing paper, there was no intermediate oxygen minimum in the "Kurosio" in the range of 1,000 m. from the surface, no wonder if we did not find any distinct maximum of phosphate.

Table 2 and Fig. 2 give the result of the phosphate analyses by the Denigés-Atkins' method which were carried out in the "Korosio" region.

Table 2. The Vertical Variation of Phosphate.

| Depth (m.) | P ( $\gamma$ /l.) | Depth (m.) | P ( $\gamma$ /l.) |
|------------|-------------------|------------|-------------------|
| 0          | 2.0               | 300–400    | 10.0              |
| 25         | 0.8               | 400–500    | 12.5              |
| 50         | 1.6               | 500–600    | 11.8              |
| 100        | 1.3               | 600–700    | 15.7              |
| 100–150    | 4.2               | 700–800    | 13.0              |
| 150–200    | 3.5               | 800–900    | 17.8              |
| 200–250    | 6.3               | 900–1000   | 11.7              |
| 250–300    | 8.0               |            |                   |

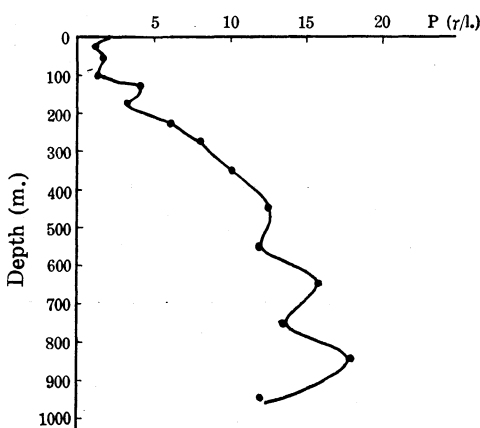


Fig. 2. The Vertical Variation of Phosphate.

As shown in Table 2 and Fig. 2, the surface water contains almost a negligible amount of phosphate. The concentration increases with the depth in a rather complicated manner; however, as a whole the phosphate content of the "Kurosio" water seems to be somewhat lower than that of other oceanic waters. The maximum value was only 25  $\gamma$  P per litre.

**Boron.** In a previous paper,<sup>(4)</sup> the present author determined volumetrically the borate content of the surface water from the western

(3) H. Wattenberg, *Ann. Hydr.*, **65** (1937) September Beiheft.

(4) This Bulletin, **14** (1939), 55.



part of the North Pacific Ocean. In that paper, the author calculated the chlorinity ratio of boron without taking into account the density of water; therefore the obtained values were slightly higher than actual ones. If a proper attention is paid in regards to the density of water, as it was done in some later determination by the author, the value of the chlorinity ratio is in quite a good agreement with Th. G. Thompson's analysis. (0.0222 and 0.0228 instead of 0.0228 and 0.0234)

The vertical variation of boron in sea water was recently studied by Th. G. Thompson and his collaborators<sup>(5)</sup> in the eastern coast of the North Pacific Ocean. According to their results, the curve of the boron chlorinity ratio did not show any remarkable vertical change, except a minimum at a depth of about 25 m. and a peculiar maximum at a depth of about 800 m.

The present study was started in order to prepare the data of analyses of the samples from the western coast of the Pacific for the comparison with the eastern ones. The analytical procedure was the same as was reported in the previous paper. Seventy-seven selected samples from various depths were analyzed. In Table 3, the average concentration of boron expressed in number of milligrams of boron per kilogram of sea water is given.

Table 3. The Vertical Variation of Boron.

| Depth (m.) | B (mg./kg.) | Depth (m.) | B (mg./kg.) |
|------------|-------------|------------|-------------|
| 0          | 4.61        | 400 - 500  | 5.24        |
| 25         | 4.33        | 500 - 600  | 4.86        |
| 50         | 4.67        | 600 - 700  | 5.28        |
| 100        | 4.83        | 700 - 800  | 5.56        |
| 200        | 5.00        | 800 - 900  | 5.32        |
| 300-400    | 5.07        | 900-1000   | 5.44        |

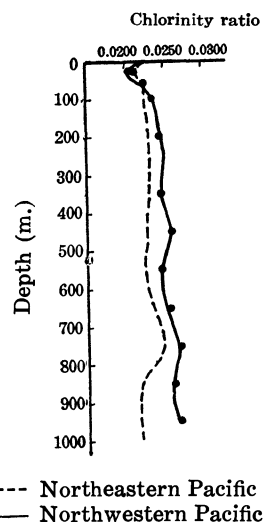


Fig. 3. The Vertical Variation of Boron.

As shown in Table 3, in spite of the gradual diminution in chlorinity with increasing depth, the concentration of boron increases slightly. In Fig. 3 the vertical variation of the chlorinity ratio of boron (the value milligram atom boron divided by the chlorinity) in the "Kurosio" is compared with the results by Th. G. Thompson and his collaborators. The difference between the two curves is probably due to some difference in the nature of the two oceanic currents which were dealt with in the foregoing paragraph.

(5) Th. G. Thompson, I. Igelsrud and B. M. G. Zwicker, *Am. J. Sci.*, [5], **35** (1938), 47.

**Copper.** The biochemistry of copper is one of the most interesting problem at present,<sup>(6)</sup> inasmuch as it has been known that various marine animals, for instance oysters, contain much copper in their shells and flesh. It is also notable that copper is an essential constituent of haemocyanin, the blood pigment of many marine invertebrates.

The copper content of the sea water, however, is not yet clearly determined, because of the lack of a reliable process for its micro-analysis.

Recently, H. Meyer<sup>(7)</sup> determined the copper content of a sample of sea water with Pulfrich's stufen-photometer using sodium-diethyl-dithiocarbamate as a reagent, and found that the sea water contains 6 to 26  $\gamma$  Cu per litre. After H. Meyer, K. Kalle and H. Wattenberg<sup>(8)</sup> using the same method reported 3 to 12  $\gamma$  Cu per litre in surface waters collected by the observation ship "Meteor" during the German North Atlantic Expedition (1938).

Since all of these estimations have been done only with the surface water, it will be of interest to investigate the vertical variation of copper in the open sea.

**Results of the Analyses.** Diethyl-dithiocarbamate method was adopted. 0.5 c.c. of the reagent solution (0.1%) was added to each 30 c.c. of a sample, and the colour thus developed was compared with the standard copper solution in an artificial sea water.

Seventy-seven samples collected from various depths in the "Kuroshio" region were analyzed. From the analytical results obtained, we can see that the copper content of the surface water from the "Kuroshio" region is from trace to 30  $\gamma$  Cu per litre which is in a good agreement with the results of the above mentioned authors.

It is noteworthy that the concentration of copper increases evidently with the depth and the highest values attained was as high as a hundred times that of the surface water. But, lately it became clear that there is a fear of contamination in so far as Nansen's water-bottles are used for sampling of water below the surface. Then, in the first place, it seems to be necessary to collect the samples of water with bottles completely free from copper. Further study will be done in near future.

**Fluoride.** Of the halogens in sea water, fluorine is the third in abundance. In 1850, Forchhammer first called attention to the presence of this element and reported that the sea water contains 0.7 mg. fluorine per litre. The results of Forchhammer and his successors are all incredible because of the inherent difficulty in the methods of determining minute quantities of fluoride in the presence of other salts.

Recently Th. G. Thompson and H. J. Taylor<sup>(9)</sup> determined the

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(6) Dittmar, "Challenger" Reports. "Physics and Chemistry". Vol. 1. (1884); Phillips, *Marine Biol. Pap. Carnegie Inst.*, **9** (1917), 9; Hiltner and Wichmann, *J. Biol. Chem.*, **38** (1919), 205; Rose and Bodansky, *ibid.*, **44** (1920), 99; Phillips, *Papers Marine Biology*, **18** (1922), 97; Orton, *Fish. Invest. London* (2), No. 3, (1924), *ibid.*, No. 4; Gaarder, *Bergens Museums Arbok*, (1932), *Naturvidenskapelig rekke*, Nr. 3; Atkins, *Marine Biol. Ass. Journ.*, N.S., **18** (1932), 193; Plytherch, *Ecol. Monogr.*, **4** (1934), 47; Riley, *J. Marine Research*, **1** (1937), 60; Webb, *Sci. Proc. Royal Dublin Soc.*, **21** (1937), 505.

(7) H. Meyer, *Ann. Hydr.*, **66** (1938), 325.

(8) K. Kalle and H. Wattenberg, *Naturwiss.*, **26** (1938), 1.

(9) Th. G. Thompson and H. J. Taylor, *Bull. Nat. Research Council*, **85** (1932), 136.

fluorine content of sea water colorimetrically using alizarine-sulphonate and zirconium nitrate, and found that 1.4 mg. of fluorine is present per litre when the chlorinity is 35‰. This is at the present, the most reliable value for the concentration of fluoride in sea water.

The author tried to investigate the vertical variation of fluorine in sea water by this recent analytical method. The analytical result shows that the average value of the fluorine is 1.3 mg. F per litre when the salinity is about 34.6‰, which is in a good agreement with the value of Th. G. Thompson and H. J. Taylor.

In Table 5, the average values of fluorine corresponding to each depth are given.

Table 4. The Vertical Variation of Fluorine.

| Depth<br>(m.) | F<br>(mg./l.) | Depth<br>(m.) | F<br>(mg./l.) |
|---------------|---------------|---------------|---------------|
| 0             | 1.31          | 400— 500      | 1.36          |
| 25            | 1.32          | 500— 600      | 1.33          |
| 50            | 1.34          | 600— 700      | 1.28          |
| 100           | 1.20          | 700— 800      | 1.31          |
| 200           | 1.30          | 800— 900      | 1.30          |
| 300 — 400     | 1.38          | 900—1000      | 1.28          |

Differing from other minor elements, fluorine shows no appreciable vertical variation in its concentration. Then, fluorine, a scanty element in sea water, seems to be quite indifferent to biological action.

### Summary.

The vertical variation of silicate, phosphate, borate, copper and fluoride in the region of the "Kurosio" were studied.

In conclusion, the author wishes to express his hearty thanks to Professor T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and permission of publishing this report. He is also indebted to Mr. H. Matui, for his earnest assistance throughout this work.

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## On the Metallo-organic Compounds: Alkyltin Compounds and their Derivatives.\*

By Taichi HARADA.

(Received September 8, 1939.)

Tetralkyltin may be prepared in various ways. The two most important methods heretofore known are those of Grignard and Löwig. The method used by Löwig<sup>(1)</sup> i.e. treating an Sn-Na alloy with an alkyl iodide, is preferred from the economic point of view if the high cost of the iodide could be replaced by some cheap alkyl halide. A critical study on the preparation of tetraethyltin has been made by treating various Sn-Na alloys containing various percentage of Zn with ethyl bromide under ordinary conditions. The results of the study show that the alloy consisting of 14% Na, 12–22% of Zn and the least amount of Sn gives the highest yield (97%) of tetraethyltin. The compounds represented by  $R_4Sn$  ( $R = Me$  or  $Et$ ) are colourless, volatile liquids, and may be distilled without being decomposed. They combine with one molecule of halogen directly giving one molecule of  $R_3SnX$  and one molecule of alkyl halide, white with two molecules of halogen they give  $R_2SnX_2$  and two molecules of alkyl halide. With two atoms of sodium they form under certain conditions  $NaSnB_3$  and  $NaR$ . The compounds of the type  $R_3Sn$  exist in free state<sup>(2)(3)</sup>. These free radicals are readily obtained by reducing the compounds of the type  $R_3SnX$  with an alkali metal in liquid ammonia.  $(CH_3)_3Sn$  and  $(C_2H_5)_3Sn$  may be given as examples of this type of products. The reaction is explained by the following equation, where  $X$  represents halogen, an electronegative element:



The radicals are also obtained by either of the following reactions in liquid ammonia:



The group are slowly oxidized to the oxide in air. The oxides are readily decomposed by water into the hydroxides:  $[(C_2H_5)_3Sn]_2O$  is representative of the oxides. The interesting properties of the groups are that they combine with the strong electropositive element Na in liquid ammonia, and form the salts of the type represented by the formula  $R_3SnNa$ . The sodium compounds of the group  $R_3Sn$  are electrolytes for the reason that they ionize into  $R_3Sn^-$  and  $Na^+$  in the solution.

\* This paper is an abstract of the paper published in the Scientific Papers of the Institute of Physical and Chemical Research, **35** (1939), 290–329.

(1) Löwig, *Ann.*, **84** (1852), 309, 313.

(2) Rügheimer, *ibid.*, **364** (1909), 53.

(3) Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2629.

The halides of the group  $(\text{CH}_3)_3\text{Sn}$  are non-electrolytes.<sup>(4)</sup> For example, trimethyltin chloride in pure state or in a medium having a relatively high dielectric constant, such as in nitrobenzene or nitromethane, it does not conduct electric current. However, the solutions of the halides in alcohol and pyridine exhibit marked electrolytic properties. It is, therefore worthy of notice that in these solutions the compounds combine with the solvents, alcohol and pyridine, and form the oxonium and ammonium salts respectively. Trimethyltin chloride (m.p.  $37^\circ\text{C}$ ; b.p.  $150\text{--}153^\circ\text{C}$ ) combines with one molecule of ammonia<sup>(5)</sup> like hydrogen chloride. The ammonium chloride sublimes without melting when it is heated. In view of these facts the properties of  $(\text{CH}_3)_3\text{SnCl}$  very closely resemble those of  $\text{HCl}$ .

The groups of the type  $\text{R}_2\text{Sn}$ —e.g.,  $(\text{C}_2\text{H}_5)_2\text{Sn}$ , orange yellow amorphous powder and ignites in air—also are set free, when the compounds  $\text{R}_2\text{SnX}_2$  are reduced with sodium in liquid ammonia under proper condition. The properties of these groups resemble in many respects those of the groups of the type  $\text{R}_3\text{Sn}$ , i.e., the groups combine directly with electronegative elements, oxygen and halogens, producing the oxide and dihalides, respectively. The groups combine not only with a strong electronegative element halogen, but also with a strong electropositive metal. For example the group  $(\text{C}_2\text{H}_5)_2\text{Sn}$  combines with one and two atoms of sodium to form the salts,  $\text{Na}(\text{C}_2\text{H}_5)_2\text{SnSn}(\text{C}_2\text{H}_5)_2\text{Na}$  and  $\text{Na}_2(\text{C}_2\text{H}_5)_2\text{Sn}$  respectively.

When the halogens in the molecule of  $\text{R}_3\text{SnX}$  and  $\text{R}_2\text{SnX}_2$  are replaced by the same number of hydroxyl groups, the corresponding basic compounds of the hydroxide,  $\text{R}_3\text{SnOH}$ , and the oxide,  $\text{R}_2\text{SnO}$ , are formed respectively.

The  $\text{R}_3\text{Sn}$  groups in the hydroxide series show an electropositive character, and this was proved by the fact that the hydrogen in the hydroxyl group can not be replaced by sodium in liquid ammonia. In other words, the sodium compounds  $\text{R}_3\text{SnONa}$  cannot be obtained by the method, but the trialkyltin radical can be obtained. For example, trimethyltin hydroxide reacts readily with one atomic proportion of metallic sodium in liquid ammonia according to the following equation<sup>(6)</sup>:



Further addition of sodium results in the formation of the sodium stannide by the following reaction:



Therefore, the hydroxides are not comparable to alcohols and phenol. The latter substances react with metallic sodium in liquid ammonia according to the following equation, and form the compounds of the type  $\text{NaOR}$ :

(4) Kraus and Callis, *J. Am. Chem. Soc.*, **45** (1923), 2624; Kraus and Greer, *ibid.*, **45** (1923), 2446.

(5) Kraus and Greer, *ibid.*, **45** (1923), 3078.

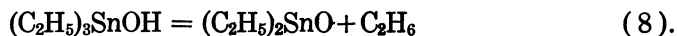
(6) T. Harada, *Bull. Chem. Soc. Japan*, **4** (1929), 266; Kraus and Bullard, *J. Am. Chem. Soc.*, **52** (1930), 4057.



The hydroxides of the group  $\text{R}_3\text{Sn}$  are, therefore, comparable to  $\text{NaOH}$  and  $\text{KOH}$ . Trialkyltin hydroxides are decomposed easily under certain conditions into the corresponding oxides and water according to the following equation:



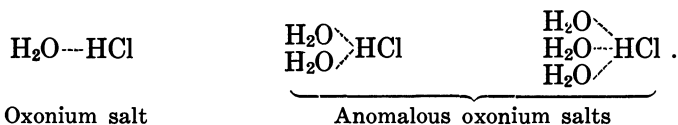
For example, triethyltin hydroxide, heated in the neighbourhood of its boiling point or dried over  $\text{CaCl}_2$ , gives triethyltin oxide and water. However, by prolonged heating at a high temperature, it decomposes into diethyltin oxide and ethane with the following equation:<sup>(7)</sup>



One of the most interesting properties of the compounds of the types  $\text{R}_3\text{SnX}$ <sup>(8)</sup> and  $\text{R}_2\text{SnX}_2$  is their characteristic affinity for  $\text{R}_3\text{SnOH}$  and  $\text{R}_3\text{SnO}$  respectively with the formation of various complex crystalline compounds in various proportions. Trialkyltin halides combine with one or two molecules of the corresponding hydroxides to form the complex salts having the following formulae:



These compounds resemble the crystalline compounds<sup>(9)</sup> formed between hydrogen chloride and water. According to Werner the structural formulae for the hydrates of hydrogen chloride are represented as follows:



Dialkyltin dihalides and the diacetates also combine with various molecular proportions of the corresponding oxides and produce various complex compounds, such as  $\text{R}_2\text{SnOSnR}_2\text{X}_2$ ,  $[\text{R}_2\text{SnO}]_2\text{SnR}_2\text{X}_2$  and  $\text{H}[\text{R}_2\text{SnO}]_3\text{OH} \cdot \text{SnR}_2\text{X}_2$ , for the former, and  $\text{R}_2\text{SnOSnR}_2(\text{OAc})_2$  and  $[\text{R}_2\text{SnO}]_3\text{SnR}_2(\text{OAc})_2$  for the latter under controlled conditions.

Recently Smith and Kipping<sup>(10)</sup> reported that the formation of di-anhydro-tris-di-benzyl-tin di-hydroxide  $\text{HOSnBz}_2\text{OSnBz}_2\text{OSnBz}_2\text{OH}$  (di-anhydro-tris-di-benzyl-stannane-diol) takes place by the condensation of three molecules of dibenzyltin dihydroxide  $\text{Bz}_2\text{Sn}(\text{OH})_2$  (di-benzyl-stannane-diol). They also reported that when  $\text{HOSnBz}_2\text{OSnBz}_2\text{OSnBz}_2\text{OH}$  is heated above  $150^\circ\text{C}$  it loses water and gives off  $\text{Bz}_2\text{SnO}$  or a six-membered ring  $[\text{Bz}_2\text{SnO}]_3$  (tri-anhydro-tris-di-benzyl-stannane-diol). Therefore, it may be assumed that the compound of the type  $[\text{R}_2\text{SnO}]_3$ .

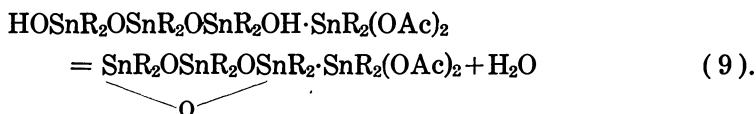
(7) T. Harada, unpublished observations.

(8) Kraus and T. Harada, *J. Am. Chem. Soc.*, **47** (1925), 2568; T. Harada, *Bull. Chem. Soc. Japan*, **6** (1931), 240.

(9) Rupert, *J. Am. Chem. Soc.*, **31** (1909), 851.

(10) Smith and Kipping, *J. Chem. Soc.*, **103** (1913), 2042.

$\text{SnR}_2(\text{OAc})_2$  in which  $[\text{R}_2\text{SnO}]_3$  group occurs, should have the following ring formation by splitting off water as follows:



Two attempts have been made by the present author on the preparation of di-ethyl-stannane-diol or its condensation product of the type  $\text{HOSnR}_2\text{OSnR}_2\text{OSnR}_2\text{OH}$  according to the method described by Smith and Kipping for the preparation of di-anhydro-tris-di-benzyl-stannane-diol. However, in the results, di-ethyltin oxide was obtained contrary to the expectation.

The evidence for the formation-tendency of the compound of the type  $\text{HOSnR}_2\text{OSnR}_2\text{OSnR}_2\text{OH}$  was obtained when dimethyltin oxide was dissolved in phenol and its molecular weight was determined. That is, the value was found to increase parallel with the increase in the concentration. This finding of the increase in values is apparently due to a characteristic phenomenon for the presence of the OH or the  $\text{OC}_6\text{H}_5$  group, or both in the molecule of the compound. Therefore, the formula for the compounds formed by the combination of three molecules of dialkyltin oxide and one molecule of the corresponding dihalides in the medium of water or alcohol will be represented by  $\text{R}'[\text{SnR}_2\text{O}]_3\text{OR}'\text{SnR}_2\text{X}_2$ <sup>(11)</sup> where  $\text{R}'$  represents hydrogen or alkyl radical of the respective solvents.  $\text{R}'$  representing an alkyl group can be replaced by hydrogen by means of hydrolysis; hence di-anhydro-tris-diethyltin-di-alkoxy-diethyltin dihalide is hydrolysed or decomposed into the corresponding hydroxy-compound by water that may be present as moisture in benzene or in air. The formation of the hydroxy-compound is explained by the following reaction:

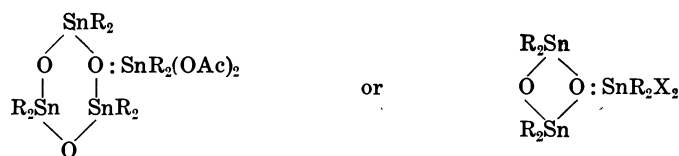


The compound of the type  $\text{R}'[\text{SnR}_2\text{O}]_3\text{OR}'\text{SnR}_2\text{X}_2$  is now conveniently called di-anhydro-tris-dialkyltin-dihydroxy-dialkyltin dihalide.

It is evident, therefore, that the dialkyltin dihalides do not link to any other elements of the molecule except to the oxygen by either principal, or auxiliary valencies of the tin. It is consequently conceivable to have various forms, and among which the linkage  $\text{>O}:::\text{SnR}_2\text{X}_2$  will be highly probable in view of the existence of the compounds of the type  $\text{R}_2\text{SnOSnR}_2\text{X}_2$  and  $(\text{NH}_3)_2\text{SnR}_2\text{X}_2$ .<sup>(12)</sup> The other type of compounds formed between dialkyltin oxides and dialkyltin diacetates or the halides may, therefore, be represented by the following formulae:

(11) Kraus and T. Harada, *J. Am. Chem. Soc.*, **47** (1925), 2568:— The bromide and the iodide of the type  $\text{C}_2\text{H}_5[\text{Sn}(\text{CH}_3)_2\text{O}]_3\text{OC}_2\text{H}_5 \cdot \text{Sn}(\text{CH}_3)_2\text{X}_2$  were actually obtained by Kraus and T. Harada in a small quantity by heating trimethyltin hydroxide with trimethyltin bromide and trimethyltin iodide respectively and were recrystallized from alcohol. However they misconcluded and misrepresented the compounds by the formulae  $(\text{CH}_3)_3\text{SnOHSn}(\text{CH}_3)_3\text{Br} \cdot \text{H}_2\text{O}$  and  $(\text{CH}_3)_3\text{SnOHSn}(\text{CH}_3)_3\text{I} \cdot \text{H}_2\text{O}$ .

(12) Werner and Pfeiffer, *Z. anorg. Chem.*, **17** (1898), 82.



Similarly in the constitution of the compounds  $\text{R}_3\text{SnOH}\cdot\text{SnR}_3\text{XH}_2\text{O}$ ,  $[\text{R}_3\text{SnOH}]_2\text{SnR}_3\text{X}$ , and  $[\text{R}_3\text{SnOH}]_2\text{SnR}_3\text{XH}_2\text{O}$  formed between trialkyltin hydroxides and the corresponding halides in the presence of moisture it is conceivable that the oxygen compounds, viz., the hydroxides and water in the compounds, are linked to the metallic atoms in trialkyltin halides by the auxiliary valencies. The linkages are explained by the

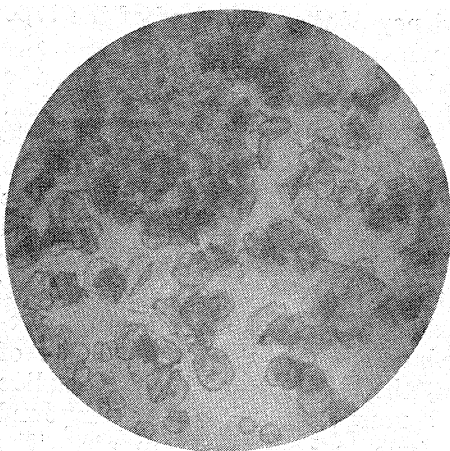


Fig. 1.  $[(\text{C}_2\text{H}_5)_3\text{SnOH}]_2\text{Sn}(\text{C}_2\text{H}_5)_3\text{ClH}_2\text{O}$   
Crystals.

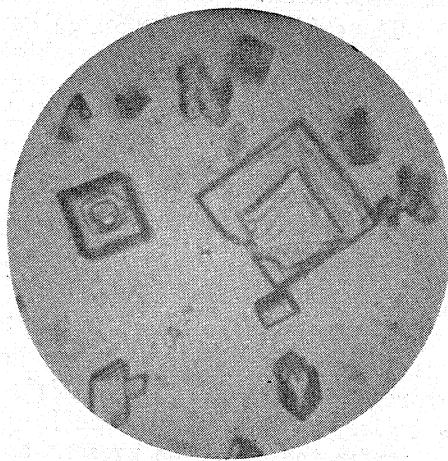


Fig. 2.  $\text{H}[\text{Sn}(\text{C}_2\text{H}_5)_2\text{O}]_3\text{OHSn}(\text{C}_2\text{H}_5)_2\text{I}_2$   
Crystals.

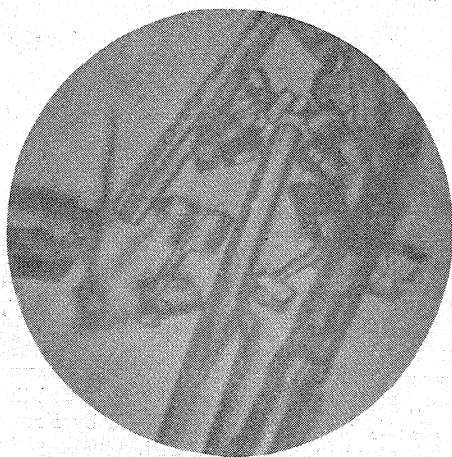


Fig. 3.  $\text{C}_2\text{H}_5[\text{Sn}(\text{CH}_3)_2\text{O}]_3\text{OC}_2\text{H}_5\cdot\text{Sn}(\text{CH}_3)_2\text{I}_2$   
Crystals.

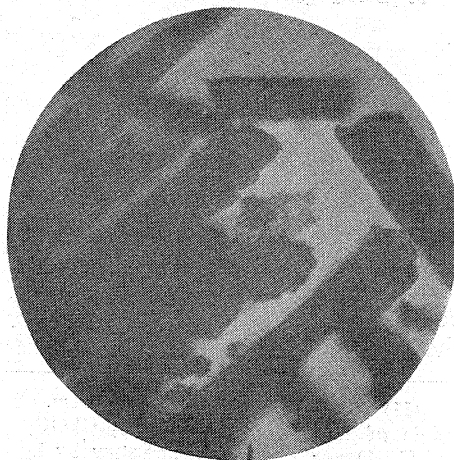


Fig. 4.  $\text{H}[\text{Sn}(\text{CH}_3)_2\text{O}]_3\text{OHSn}(\text{CH}_3)_2\text{I}_2$   
obtained by exposing of  
 $\text{C}_2\text{H}_5[\text{Sn}(\text{CH}_3)_2\text{O}]_3\text{OC}_2\text{H}_5\cdot\text{Sn}(\text{CH}_3)_2\text{I}_2$   
to moisture.





Fig. 5.  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{OSn}(\text{C}_2\text{H}_5)_2\text{Br}_2$   
Crystals.

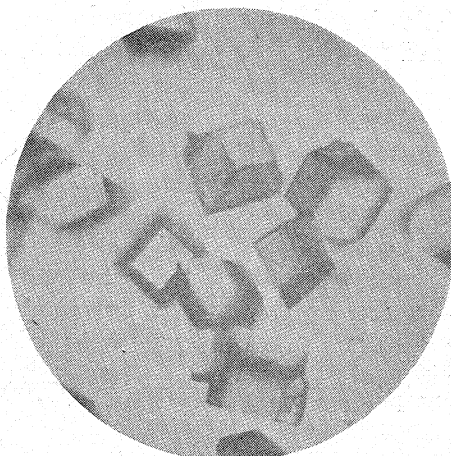


Fig. 6.  $[\text{Sn}(\text{C}_2\text{H}_5)_2\text{O}]_3\text{Sn}(\text{C}_2\text{H}_5)_2(\text{OAc})_2$   
Crystals.

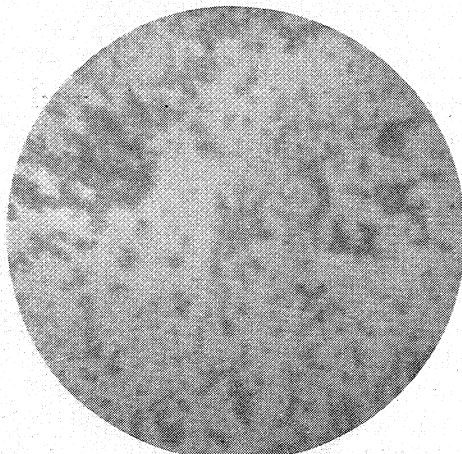


Fig. 7.  $[(\text{CH}_3)_2\text{SnO}]_2\text{Sn}(\text{CH}_3)_2\text{Cl}_2$   
precipitate-like crystals.

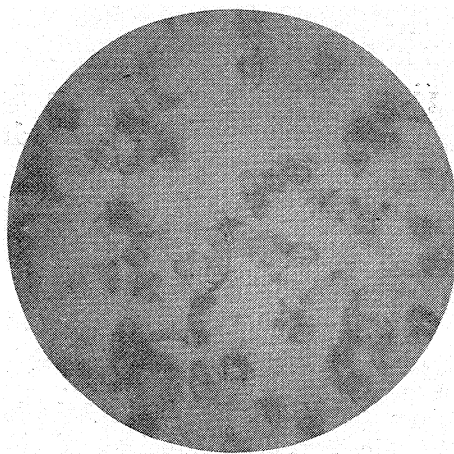


Fig. 8.  $(\text{CH}_3)_2\text{SnOSn}(\text{CH}_3)_2(\text{OAc})_2$   
Crystals.

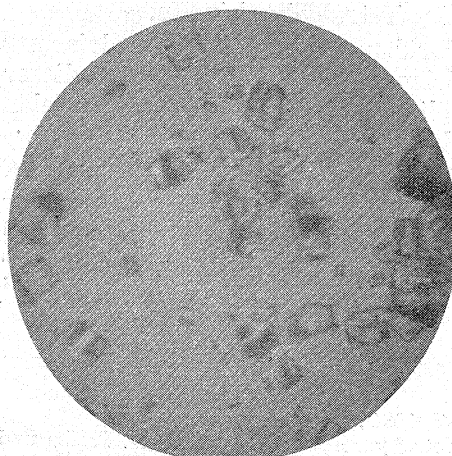


Fig. 9.  $(\text{CH}_3)_3\text{SnOHSn}(\text{CH}_3)_3\text{ClH}_2\text{O}$   
Crystals.

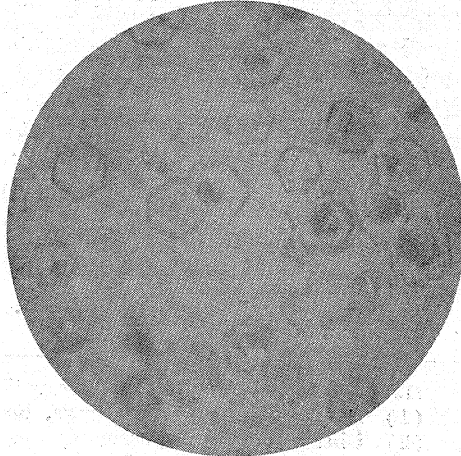
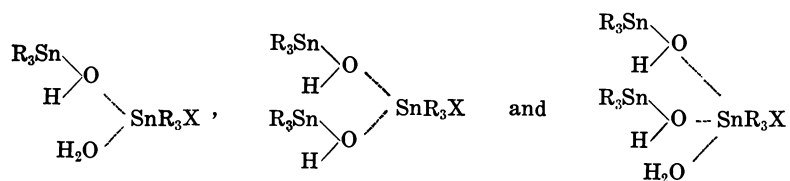


Fig. 10.  $[(\text{CH}_3)_3\text{SnOH}]_2\text{Sn}(\text{CH}_3)_3\text{Cl}$   
Crystals.

following formulae (anomalous oxonium salts) in a similar manner as used for the expression of the hydrates of hydrogen chloride:



The water in the compounds can be demonstrated without difficulty. For example when  $(\text{CH}_3)_3\text{SnOH}\text{Sn}(\text{CH}_3)_3\text{Cl}\cdot\text{H}_2\text{O}$  (m.p.  $81-95^\circ\text{C}$ ) is heated with  $\text{HCCl}_3$  the water separates floating on the top while the compound  $[(\text{CH}_3)_3\text{SnOH}]\text{Sn}(\text{CH}_3)_3\text{Cl}$  (m.p.  $85-91^\circ\text{C}$ )<sup>(13)</sup> does not.

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(13) T. Harada, unpublished observations.

## Über die Einwirkung von Selen auf Indolen, Chinolin und seine perhydrierten Derivate.

Von Shin-ichiro FUJISE und Kozo TIBA.

(Eingegangen am 16. September 1939.)

Zur Ermittlung der Konstitution hydrierter cyclischer organischer Substanzen sind die katalytische Dehydrierungsmethode und die mit Selen von grosser Bedeutung. M. Ehrenstein und W. Bunge<sup>(1)</sup> haben schon über die katalytische Dehydrierung von *cis*- bzw. *trans*-Dekahydrochinolin berichtet, wobei sie als Dehydrierungsprodukt Chinolin und Bz-Tetrahydrochinolin erhielten. Sie verläuft also in ihrer Stufenfolge über eine andere Zwischenstufe als die Hydrierung des Chinolins, die letztere führt in jedem Falle über das Py-Tetrahydrochinolin.

Es fehlte noch eine Untersuchung darüber, ob die Selen-Dehydrierung von perhydrierten Chinolinen und Indolen<sup>(2)</sup> ausführbar ist. In dieser Mitteilung möchten wir über die Resultate der Einwirkung von Selen auf Octahydro- $\alpha$ -methylindol, Dekahydro-6-methylchinolin, Indol,  $\alpha$ -methylindol, Chinolin und 6-Methylchinolin berichten. Durch die Erhitzung des *trans*-Dekahydro-6-methylchinolin mit Selen erhielten wir 6-Methylchinolin und Bz-Tetrahydro-6-methylchinolin. Zur Trennung der beiden Dehydrierungsprodukte wurden sie zuerst in Gold-doppelsalze umgewandelt. Die Doppelsalze wurden durch mechanisches Auslösen in zwei verschiedene Kristallarten getrennt.

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(1) M. Ehrenstein und W. Bunge, *Ber.*, **67** (1934), 1715.

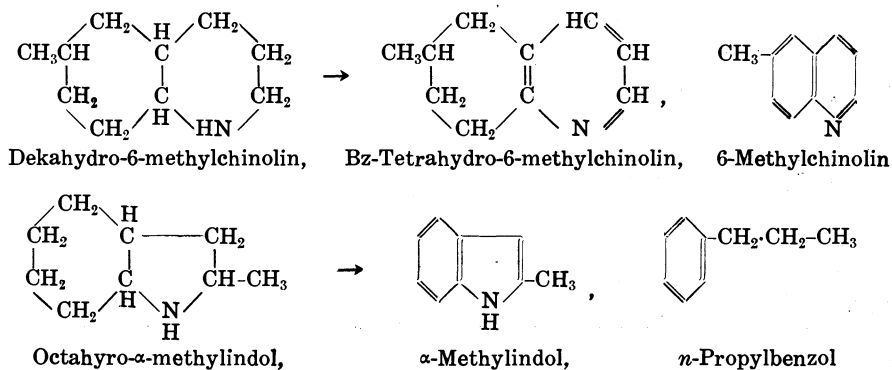
(2) Über die Selen-Dehydrierung von Bz-Tetrahydroindol-derivat, vgl. A. Treibs und D. Dineth, *Ann.*, **517** (1935), 152.

Octahydro- $\alpha$ -methylindol-bromwasserstoffsalze wurden mit Selen erhitzt, dabei entstand als Reaktionsprodukt  $\alpha$ -Methylindol, *n*-Propylbenzol und Ammoniak. Die Ausbeute des *n*-Propylbenzols betrug etwa 23% des Ausgangsmaterials, doch die des  $\alpha$ -Methylindols war schlecht. In diesem Fall tritt nicht nur Dehydrierung des hydrierten Ringes, sondern auch die Ringsprengung ein. Dies scheint ein interessanter Gegenstand über die Nickel-Hydrierung von  $\alpha$ -Methylindol<sup>(3)</sup> bei hoher Temperatur zu sein; nämlich bei 200° trat nur vollständige Hydrierung von  $\alpha$ -Methylindol auf, doch bei 240° wurde der Hetero-ring abgespalten und es entstand Hexahydro-*o*-propyl-anilin.

Bei unseren Versuchen war die Ausbeute der Dehydrierungsprodukte (d.h. 6-Methylchinolin und  $\alpha$ -Methylindol) nicht günstig, daher vermuteten wir, dass die schlechte Ausbeute durch weitere Zersetzung von 6-Methylchinolin, bzw.  $\alpha$ -Methylindol verursacht worden sei, aber dies war nicht der Fall. 6-Methylchinolin, Chinolin und  $\alpha$ -Methylindol wurden mit Selen auf 310–330° erhitzt, wobei wir wieder 80–90% der Ausgangsmaterialien zurückgewinnen konnten. Die Stabilität des Indols war ganz anderes als die der oben beschriebenen drei Substanzen. Indol reagiert unter starker Selenwasserstoffentwicklung auf Selen, darauf verharzen die grossen Teile, und aus dem Reaktionsprodukt erhielten wir eine sehr geringe Menge Indols und einige Kristalle vom Schmelzpunkt 192–195°: die Kristalle sind noch nicht weiter untersucht worden; doch stimmt der Schmelzpunkt nicht mit dem des Di- oder Tri-indols<sup>(4)</sup> überein. Die Resultte werden tabellarisch wiedergegeben.

Tabelle

| Substanz              | Temperatur | Stunden | Unveränderte Base (%) |
|-----------------------|------------|---------|-----------------------|
| Chinolin              | 310–320°   | 12      | 90                    |
| 6-Methylchinolin      | „          | 7       | 81                    |
| $\alpha$ -Methylindol | „          | 1       | 80                    |
| Indol                 | „          | 1       | 50                    |
| „                     | „          | 12      | 0.7                   |



(3) R. Willstätter und J. v. Braun, *Ber.*, **58** (1925), 385; J. v. Braun und O. Bayer, *Ber.*, **58** (1925), 387.

(4) O. Schmitz-Dumont und B. Nicolajannis, *Ber.*, **63** (1930), 323; O. Schmitz-Dumont und K. Hamann, *Ber.*, **66** (1933), 71; O. Schmitz-Dumont und J. ter Horst, *Ann.*, **583** (1939), 261.

Zum Schluss möchten wir zusammenfassend sagen, dass die Selen-Dehydrierung von *trans*-Dekahydro-6-methylchinolin normalerweise verläuft; Chinolin und 6-Methylchinolin sind bei hoher Temperatur gegen Selen sehr beständig und wir vermuten, dass bei Selen-dehydrierung, ähnlich wie bei Acetanilid<sup>(5)</sup>, auch Chinolin als Lösungsmittel verwendet werden kann. Die Selen-dehydrierung von Octahydro- $\alpha$ -methylindol verläuft wie die normale Dehydrierung und Ringsprengung; weiter weist die Unbeständigkeit des Indols gegen Selen darauf hin, dass man eine Substanz, deren Moleküle einen perhydrierten Indol-ring besitzen, sehr vorsichtig mit Selen erhitzen müsse.

### Beschreibung der Versuche.

**Dehydrierungsversuche.** (a) 4 g. *trans*-Dekahydro-6-methylchinolin<sup>(6)</sup> (Sdp. 212° Schmp. 68–69°), und 6 g. Selen wurden in elektrisch geheiztem Luftbad erhitzt. Wegen des niedrigen Siedepunktes der Base, wurde die Temperatur langsam gesteigert; erst 5 Stdn. auf 205–215°, dann 7 Stdn. auf 280–290° und darauf wurde die Erhitzung unterbrochen. Die unveränderte Base, die oben am Rohr als Kristall geblieben war, wurde mittels Flamme erwärmt und in den Kolben zurückgeflossen. Nochmals wurde die Dehydrierung fortgesetzt; diesmal 10 Stdn. auf 160–190°, weitere 5 Stdn. auf 280–290° erhitzt. Das Reaktionsprodukt wurde mit Äther extrahiert und der Äther wurde mit verd. Salzsäure geschüttelt. Die ätherische Lösung wurde auf dem Wasserbad eingedunstet, wobei nur wenig harzige Masse zurückblieb.

Die wässrige Salzsäurelösung wurde mit konz. Kalilauge bis stark alkalisch versetzt, mit Äther gut extrahiert und mit festem Kaliumhydroxyd getrocknet. Nach Abdampfung des Äthers wurde der Rückstand rektifiziert. Das Destillat wurde in drei Fraktionen getrennt. (1) Sdp. bis 240°; 0.07 g. (2) Sdp. 242–256°; 0.77 g. (3) Sdp. 256–262°; 0.48 g.

Die Fraktionen (2) und (3) wurden in verd. Salzsäure gelöst, dann wurden mit Goldchloridlösung versetzt wobei die Ausscheidung des metallischen Goldes erfolgte. (Die Wirkung von Py-Tetrahydro-6-methylchinolin?). Wenn die Lösung keine Reduzierungswirkung mehr zeigte, wurde sie filtriert und das Filtrat mit genügender Menge Goldchlorid versetzt. Das ausgeschiedene Gold-doppelsalz wurde filtriert und aus verd. Salzsäure umkristallisiert. Die Kristalle schmolzen bei 126–156°. Die rohen Kristalle wurden wieder im salzsäurehaltigen Wasser gelöst und die Lösung langsam erkalten lassen; dabei schieden sich hellgelbe Nadeln und tiefgelbe Prismen aus. Nach Filtrieren und Trocknen wurden diese zwei Kristallarten mechanische unter der Lupe auseinander getrennt. Jede Kristallart wurde nochmals aus demselben Lösungsmittel umkristallisiert.

Die hellgelben Nadeln schmolzen bei 181–182° und die Mischprobe mit dem 6-Methylchinolin-golddoppelsalz gab keine Depression.

Gefunden: Au 40.70, 40.73 Berechnet für C<sub>10</sub>H<sub>9</sub>N.HAuCl<sub>4</sub> 40.81

(5) O. Diels, *Ann.*, **527** (1937), 279.

(6) S. Fujise und M. Iwakiri, *Bull. Chem. Soc. Japan*, **11** (1936), 293.

Der Schmelzpunkt der tief gelben Kristalle zeigte 134–135° und das Analysenresultat stimmte mit Bz-Tetrahydro-6-methylchinolin überein.

Gefunden: Au 40.32, 40.22 Berechnet für  $C_{10}H_{13}N.HAuCl_4$  40.38

(b) 3.6 g. Octahydro- $\alpha$ -methyldiol-bromwasserstoffsalt<sup>(7)</sup> und 6 g. Selen wurden 15 Stdn. auf 310–335° erhitzt. Das Reaktionsprodukt wurde zerkleinert und mit Äther extrahiert. Der Äther wurde nach dem Trocknen mit Kaliumhydroxyd eingedampft; der Rückstand wurde unter gewöhnlichem Druck bis auf den Siedepunkt von 160° abdestilliert, das Destillat wurde über metallischem Natrium rektifiziert. Die Hauptfraktion siedete bei 154° (Ausbeute 0.46 g.) und roch nach *n*-Propylbenzol. Diese Fraktion wurde nach der Vorschrift von Ipatieff und Schmerling<sup>(8)</sup> zu Diacetamidderivat über geführt (Schmpt. 208°). Der Schmelzpunkt und Mischschmelzpunkt waren mit dem *n*-Propylbenzoldiacetamid identisch. Der ölige Rückstand, der bis auf 160° nicht abdestilliert war, und das Reaktionsprodukt, das schon mit Äther behandelt war, wurden nach Zusatz von Kalilauge mit Wasserdampf destilliert. Zuerst wurde mit Wasser noch eine kleine Menge *n*-Propylbenzol destilliert, die beseitigt wurde. Aus dem nächsten Destillat schieden sich nach dem Erkalten schöne Kristalle aus; die Mischprobe mit  $\alpha$ -Methyldiol zeigte keine Depression. Das Filtrat der Kristalle ist stark alkalisch, es wurde mit Salzsäure neutralisiert und abgedampft; aus dem Rückstande gewannen wir Ammoniumchlorid.

**Einwirkung von Selen auf Chinolinen und Indolen.** (a) *Chinolin*. 4 g. Chinolin und 4 g. Selen wurden 6 Stdn. auf 310–330° erhitzt; dabei entwickelte sich kein Selenwasserstoff. Das Ätherextrakt des Kolbeninhaltes wurde nach Verdampfung des Äthers destilliert. Die Ausbeute des Chinolins betrug 3.2 g. (80% des angewandten Chinolins).

20 g. Chinolin und 20 g. Selen wurden 12 Stdn. auf 310–320° erhitzt. Die Ausbeute des Chinolins betrug 18.3 g.

(b) *6-Methylchinolin*. 1.3 g. 6-Methylchinolin und 1.4 g. Selen wurden 2 Stdn. auf 240–320°, dann 7 Stdn. auf 320–330° erhitzt (kein Selenwasserstoff entwickelt). Nach dem Erkalten wurde der Kolbeninhalt wie oben beschrieben behandelt.

Wir gewannen 1.05 g. 6-Methylchinolin (Sdp. 256°), das in Alkohol selöst und mit alkoholischer Pikrinsäure versetzt wurde. Das Pikrat war identisch mit dem 6-Methylchinolin-pikrat (Mischprobe).

(c)  *$\alpha$ -Methyldiol*.  $\alpha$ Methyldiol und Selen wurden zu gleichen Teilen 1 Stde. auf 310–320° erhitzt (kein Selenwasserstoff entstanden); in diesem Fall konnten wir etwa 80%  $\alpha$ -Methyldiol wiedergewinnen.

(d) *Indol*. 20 g. Indol und 20 g. Selen wurden 12 Stdn. auf 310–320° erhitzt, dabei entwickelte sich Selenwasserstoff. Nach Einengen des ätherischen Extraktes des Reaktionsproduktes, wurde der Rückstand im Vakuum rektifiziert; durch Kühlung der ersten Fraktion und anschließendes Umkristallisieren erhielten wir 1.58 g. reines Indol (0.7%).

(7) S. Fujise, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **9** (1928), [157], 91.

(8) V. N. Ipatieff und L. Schmerling, *J. Am. Chem. Soc.*, **59** (1937), 1056.

Die zweite Fraktion (Sdp.  $250^{\circ}/2\text{ mm}$ ) wurde zweimal aus Benzol umkristallisiert und schmolz bei  $192\text{--}195^{\circ}$ . Ausbeute 0.43 g. Die Kristalle sind noch nicht weiter untersucht worden. 2 g. Indol und 2 g. Selen wurden 1 Stde. auf  $310\text{--}320^{\circ}$  erhitzt; dabei wurden 0.98 g. Indol wiedergewonnen (ca. 50%).

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## A Note on the Constitution of Dehydroergopinacone.

By Toshio ANDO.

(Received September 28, 1939.)

Since ergosterol (Ia) was found to be transformed into a dimolecular dehydrogenation product  $C_{56}H_{86}O_2$ , the so-called ergopinacone, on exposing it to sunlight with eosin in alcoholic solution in the absence of oxygen<sup>(1)</sup>, some analogously constructed sterol derivatives, e.g. 22-dihydro-ergosterol (Ib)<sup>(2)</sup>, 7-dehydrocholesterol (Ic)<sup>(3)(4)</sup>, and 7-dehydrositosterol (Id)<sup>(5)</sup>, have been shown to undergo similar dehydrogenation. The location of the conjugate double bonds at the same positions as in ergosterol seems however neither necessary nor sufficient for the pinacone formation, because, on the one hand, Windaus and Zühlsdorff<sup>(6)</sup> obtained the same product from  $\Delta^{6,8}$ -cholestadienol (II) and from  $\Delta^{6,8}$ -coprostadienol (III) as from 7-dehydrocholesterol (Ic), and, on the other, of the four stereoisomerides, ergosterol, lumisterol, pyrocalciferol, and isopyrocalciferol, represented by formula Ia, in which the stereovariants are the carbon atoms 9 and 10<sup>(7)</sup>, ergosterol and pyrocalciferol (acetate)<sup>(7)</sup> yield "pinacones", while lumisterol<sup>(8)</sup> and isopyrocalciferol (acetate)<sup>(7)</sup> do not. An additional double bond between the carbon atoms 9 and 11 facilitates the pinacone formation. Thus dehydroergosterol (IV)<sup>(9)</sup> derived from ergosterol or isopyrocalciferol, and dehydrolumisterol (V) (acetate)<sup>(8)</sup> from lumisterol and pyrocalciferol, are both able to form "pinacones" more easily than ergosterol. Thus Kennedy and Spring<sup>(7)</sup> inferred that the pinacone formation depends on the absence of the steric effect of

(1) A. Windaus and P. Borgeaud, *Ann.*, **460** (1928), 235.

(2) A. Windaus and R. Langer, *ibid.*, **508** (1933), 105.

(3) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802; **12** (1937), 495; T. Ando, *ibid.*, **14** (1939), 285.

(4) F. Schenck, K. Buchholz, and O. Wiese, *Ber.*, **69** (1936), 2696.

(5) W. Wunderlich, *Z. physiol. Chem.*, **241** (1936), 116.

(6) A. Windaus and G. Zühlsdorff, *Ann.*, **536** (1938), 204.

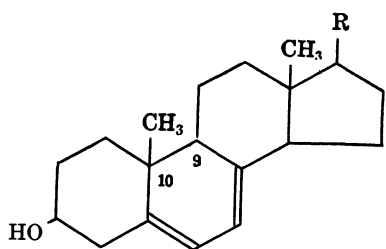
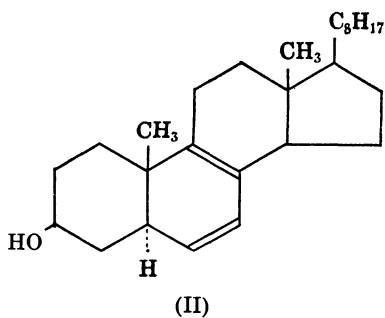
(7) T. Kennedy and F. S. Spring, *J. Chem. Soc.*, **1939**, 250.

(8) K. Dimroth, *Ber.*, **69** (1936), 1123.

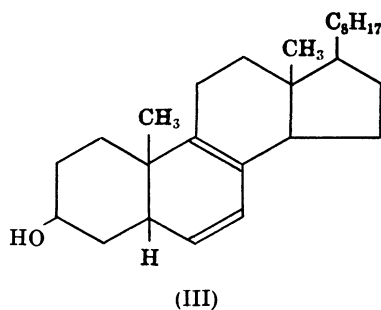
(9) A. Windaus and O. Linsert, *Ann.*, **465** (1928), 148.



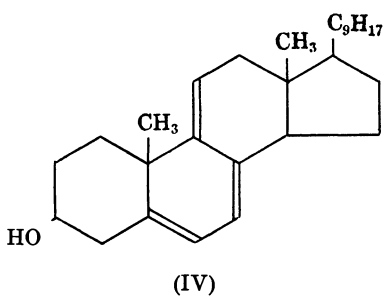
the C<sub>9</sub>-hydrogen on the C<sub>10</sub>-methyl group and concluded that the C<sub>10</sub>-methyl group and the C<sub>9</sub>-hydrogen atom are cis-oriented in lumisterol and isopyrocalciferol and trans-oriented in ergosterol and pyrocalciferol. Such structural characteristics of steroids capable of pinacone formation seem to afford little bases for the consideration of the constitution of "pinacones".

(Ia)  $R = C_9H_{17}$ (Ib)  $R = C_9H_{19}$ (Ic)  $R = C_8H_{17}$ (Id)  $R = C_{10}H_{21}$ 

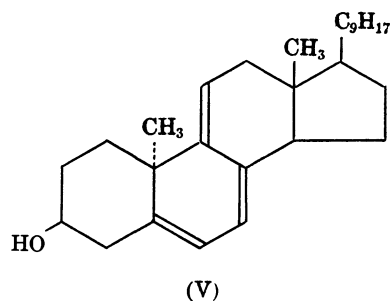
(II)



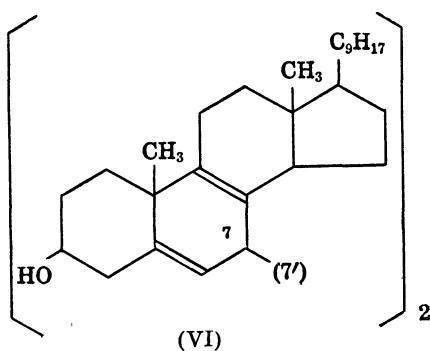
(III)



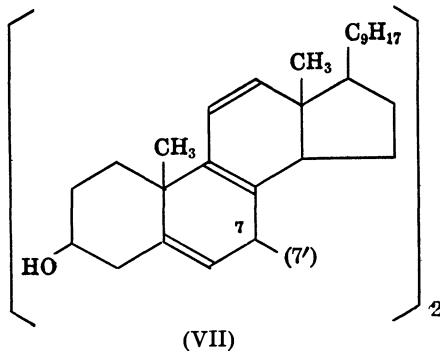
(IV)



(V)



(VI)



(VII)

It has already been shown from various sides that the so-called pinacones are by no means real pinacones, but di-secondary dihydric alcohols, and thus it is very probable that the carbon atom 3 or the hydroxyl group there does not take part in the pinacone formation. The preparation of a similar dehydrogenation product from 7-dehydrocholestene in this laboratory<sup>(10)</sup> confirms this view conclusively.

Inhoffen<sup>(11)</sup> presented a tentative formula (VI) for ergopinacone. The isolation by the present author<sup>(12)</sup> of iso-dehydroergosterol  $C_{28}H_{42}O$  besides neoergosterol<sup>(1) (13)</sup> from the pyrolysis of ergopinacone has substantiated Inhoffen's hypothetical formulation<sup>(11)</sup> for the decomposition of ergopinacone. Inhoffen's formula is well consistent also with the fact that "pinacones" show no longer the absorption spectrum of ergosterol<sup>(14) (15)</sup>.

In an attempted dehydrogenation of ergopinacone diacetate with mercuric acetate according to the method of preparation of dehydroergosterol from ergosterol, the starting material was recovered unchanged. This finding may be regarded as another indication that the original conjugate double bonds in ergosterol are not retained in ergopinacone.

The author has examined the absorption spectra of dehydroergopinacone to see if there remain any conjugate double bonds in this "pinacone". On account of the small solubility of dehydroergopinacone, its diacetate was derived from the former in the usual way. Dehydroergopinacone diacetate thus prepared forms needles melting at 195–196.5° (corr.) to an opaque yellow mass and clearing with decomposition at 200.5° (corr.), gives a specific rotation  $[\alpha]_D^{20} = -242^\circ$  in chloroform solution, and shows a characteristic colour change with trichloroacetic acid as described in the experimental part. In hexane solution it shows a distinct absorption band in ultraviolet region with a maximum at 275  $m\mu$  ( $\log \epsilon_{\max} = 3.8$ ). Dehydroergopinacone diacetate was prepared also by the photochemical dehydrogenation of dehydroergosteryl acetate. This specimen gave just the same melting point, the same specific rotation, and an identical absorption spectrum as the specimen described above.

Dehydroergosterol shows an absorption maximum at 320  $m\mu$  in accordance with the three conjugate double bonds in the molecule. This maximum is no longer present in the absorption spectrum of dehydroergopinacone, but the appearance of a maximum at 275  $m\mu$  indicates that two double bonds are conjugated in a ring. If Inhoffen's formula for ergopinacone is followed, formula VII can be given to dehydroergopinacone.

### Experimental.

**Dehydroergosterol.** Prepared from ergosterol (3.00 g.) and mercuric acetate (6.90 g.) in alcoholic solution according to the directions of Windaus and Linsert<sup>(9)</sup>. On

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(10) A. Tominaga, this Bulletin, **14** (1939), 486.

(11) H. H. Inhoffen, *Naturwissenschaften*, **25** (1937), 125.

(12) T. Ando, this Bulletin, **14** (1939), 169.

(13) K. Bonstedt, *Z. physiol. Chem.*, **185** (1929), 165; H. H. Inhoffen, *Ann.*, **497** (1932), 130; H. Honigmann, *ibid.*, **511** (1934), 292.

(14) T. Ando, this Bulletin, **14** (1939), 285.

(15) K. Buchholz, Inaugural Dissertation, Göttingen, 1937.

recrystallizing repeatedly from chloroform-methanol and then from 80% alcohol dehydroergosterol formed colourless small plates (1.05 g.), m.p. 146–147° (corr.).

*Acetate.* Prepared from dehydroergosterol (365 mg.), acetic anhydride (5.6 g.), and pyridine (3 c.c.). Recrystallization from chloroform-methanol gave colourless plates (337 mg.), m.p. 147.5–148.5° (corr.).

**Dehydroergopinacone.** Prepared from dehydroergosterol substantially according to the directions of Windaus and Linsert<sup>(9)</sup>. To remove air, carbon dioxide was passed for thirty minutes through an alcoholic solution (250 c.c. of 95% alcohol) of dehydroergosterol (1.04 g.) and eosin (1.04 g.). After a week's exposure of the solution to sunlight the needles which separated out were collected, washed (ca. 600 mg.), and recrystallized three times from pyridine–95% alcohol. Colourless extremely fine needles (217 mg.), m.p. 198.5–200.5° (corr.).

*Acetate.* The above dehydroergopinacone (130 mg.) was dissolved in pyridine (20 c.c.) and acetic anhydride (2.0 g.) was added. After standing at room temperature for two days, the orange-red mixture was poured into ice water, and the separating slightly yellowish crystals (130 mg.) were collected after standing overnight, washed with water, with dilute acetic acid, and again with water, recrystallized three times from benzene–95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (71 mg.), melting at 191–192.5° (uncorr.) or 195–196.5° (corr.) to an opaque yellowish mass and clearing with decomposition at 196.5° (uncorr.) or 200.5° (corr.) to a brownish orange liquid (Found: C, 82.96, 83.10; H, 10.21, 10.02. Calculated for  $C_{30}H_{46}O_4$ : C, 82.69; H, 9.96 %).  $[\alpha]_D^{25} = -242^\circ$  (11.9 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{25} = -2.88^\circ$ ). Ultraviolet absorption maximum in 0.048% hexane solution 275  $m\mu$  (distinct),  $\log \epsilon_{\max} = 3.8$ . In the Rosenheim test the diacetate gives pink, light green, green, and finally dark green colouration.

**Dehydroergopinacone Diacetate from Dehydroergosteryl Acetate.** A solution of dehydroergosteryl acetate (337 mg.) and eosin (337 mg.) in 95% alcohol (100 c.c.) was exposed to sunlight after removing air by passing carbon dioxide. The precipitation appeared to occur sooner in this case. After a week's irradiation the deposit (ca. 140 mg.) was collected, washed, recrystallized four times from benzene–95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (85 mg.), melting at 191–192.5° (uncorr.) or 195–196.5° (corr.) to an opaque yellowish mass and clearing with decomposition at 197.5° (uncorr.) or 201.5° (corr.) to a brownish orange liquid (Found: C, 82.83; H, 9.98. Calculated for  $C_{30}H_{46}O_4$ : C, 82.69; H, 9.96 %). No depression of the melting point was observed in admixture with the specimen of dehydroergopinacone diacetate prepared from dehydroergopinacone.  $[\alpha]_D^{25} = -242^\circ$  (9.35 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{25} = -2.26^\circ$ ). Ultraviolet absorption maximum in 0.045% hexane solution 275  $m\mu$  (distinct),  $\log \epsilon_{\max} = 3.8$ .

**Attempted Dehydrogenation of Ergopinacone Diacetate with Mercuric Acetate.** A mixture of a solution of ergopinacone diacetate<sup>(14)</sup> (200 mg., m.p. 206.5–207°,  $[\alpha]_D^{16} = -202^\circ$ ) in benzene (15 c.c.) and a solution of mercuric acetate (480 mg.) in alcohol (10 c.c.) containing a few drops of glacial acetic acid was boiled for two and a half hours. The filtered yellowish solution was evaporated up under diminished pressure, and the residual crystals were dissolved in chloroform. The chloroform solution was filtered to remove insoluble matters, and was again evaporated up. The residue was recrystallized four times from benzene–95% alcohol, and dried in vacuum at 110° over phosphorus pentoxide. Colourless fine needles (135 mg.), m.p. 201.5–202° (uncorr.) or 206–206.5° (corr.) with decomposition. No depression of the melting point was observed in admixture with the specimen of original ergopinacone diacetate, while the melting point was lowered when mixed with dehydroergopinacone diacetate (mixed m.p. 189.5–193.5°, uncorr.). The substance gave an identical specific rotation with ergopinacone diacetate:  $[\alpha]_D^{25} = -202^\circ$  (11.3 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{25} = -2.28^\circ$ ).

### Summary.

Dehydroergopinacone diacetate was prepared and its absorption spectrum in ultraviolet region was studied. Ergopinacone diacetate was shown not to be dehydrogenated with mercuric acetate. From the results a probable constitution (VII) was assigned to dehydroergopinacone, following Inhoffen's ergopinacone formula.

The author wishes to express his sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement. He expresses his gratitude also to Dr. K. Yamasaki for his kindness in taking absorption spectra, and to Mr. Yasohachi Yamaguchi and to Ozi Seisi Co. for generous help to this work.

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## The Photochemical Dehydrogenation of 7-Dehydrocholestene.

By Akira TOMINAGA.

(Received September 28, 1939.)

Ergopinacone,  $C_{56}H_{86}O_2$ , which is formed on exposing ergosterol,  $C_{28}H_{44}O$ , to sunlight with eosin in alcoholic solution in the absence of oxygen, was at first considered to be a pinacone and to be produced by the condensation of ergosterol and a ketone formed intermediately by the dehydrogenation of ergosterol.<sup>(1)</sup> Subsequently it has been shown from various sides that ergopinacone is not really a pinacone and is not produced by the intermediate formation of a ketone: Ergopinacone yields easily a diacetate,<sup>(2)</sup> which is also obtained by exposing ergosteryl acetate to sunlight with eosin.<sup>(3)</sup> The methyl ether of ergosterol gives similarly ergopinacone dimethyl ether.<sup>(3)</sup> Ergopinacone can be converted into a diketone after hydrogenation.<sup>(3)</sup> Thus it can be regarded as established that ergopinacone is a di-secondary dihydric alcohol. Then it is very probable that the carbon atom 3 or the hydroxyl group there does not take part in the formation of ergopinacone.

Besides ergosterol, many analogously constructed steroids, viz., dehydroergosterol,<sup>(4)</sup> 22-dihydroergosterol,<sup>(5)</sup> 7-dehydrocholesterol<sup>(6)</sup>, 7-de-

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(1) A. Windaus and P. Borgeaud, *Ann.*, **460** (1928), 235.

(2) A. Windaus, H. H. Inhoffen, and K. Buchholz, "Über Sterine, Gallensäuren und verwandte Naturstoffe" by H. Lettré and H. H. Inhoffen, 135, Stuttgart (1936).

(3) K. Buchholz, "Über einige Versuche in der Reihe der Sterine", Inaugural Dissertation, Göttingen, 1937.

(4) A. Windaus and O. Linsert, *Ann.*, **465** (1928), 148.

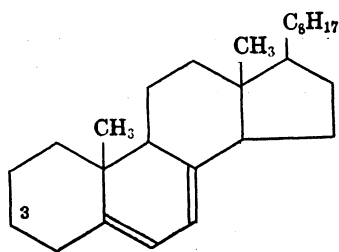
(5) A. Windaus and R. Langer, *Ann.*, **508** (1933), 105.

(6) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 802; **12** (1937), 495; F. Schenck, K. Buchholz, and O. Wiese, *Ber.*, **69** (1936), 2696.

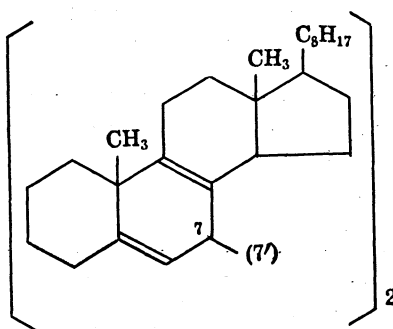
hydrositosterol,<sup>(7)</sup> dehydrolumisterol,<sup>(8)</sup> pyrocalciferol,<sup>(9)</sup> 7-dehydrostigmasterol and 3-hydroxy- $\Delta^{5,7}$ -choladienic acid,<sup>(10)</sup> have been shown to be dehydrogenated to similar dimolecular compounds. All these steroids possess hydroxyl groups at carbon atoms 3. Since it seemed desirable to see whether or not a  $C_3$ -hydroxyl group (or equivalents) was necessary for the formation of an ergopinacone analogue, the author prepared 7-dehydrocholestene (I) according to the method of Dimroth and Trautmann<sup>(11)</sup> and subjected it to the photochemical dehydrogenation.

In spite of every effort in adjusting the experimental conditions, the pyrolysis of 7-hydroxycholestene benzoate gave specimens of 7-dehydrocholestene contaminated with more or less isomeric cholestadiene, as revealed by the ultraviolet absorption spectra of the products. Since it was however expected that the isomeride would remain unaffected by insolation, the mixture was used in the photochemical dehydrogenation.

The alcohol-benzene solution of the material with eosin was exposed to sunlight after removing air by passing carbon dioxide. In the course of a week's irradiation, micaceous crystals separated out gradually, which were collected and recrystallized from chloroform-methanol. The substance thus obtained forms glittering micaceous plates, melts at  $269-270^\circ$  (corr.) with decomposition, is soluble in benzene and chloroform but insoluble in ether and alcohol, shows a specific rotation  $[\alpha]_D^{30} = +260^\circ$  in chloroform, and gives the colour reactions of steroids. The analysis and the molecular weight determination by Rast's method indicate that the substance possesses the expected formula  $C_{54}H_{86}$ . Thus it has been shown that the hydroxyl-free 7-dehydrocholestene undergoes a similar dehydrogenation to yield a dimolecular product analogous to ergopinacone. The dehydrogenation product from 7-dehydrocholestene may be called "7-dehydrocholestene-pinacone" for lack of an appropriate nomenclature for the substances of this type, and Inhoffen's ergopinacone formula<sup>(12)</sup> requires formula II for this new "pinacone".



(I)



(II)

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- (7) W. Wunderlich, *Z. physiol. Chem.*, **241** (1936), 116.  
 (8) K. Dimroth, *Ber.*, **69** (1936), 1123.  
 (9) T. Kennedy and F. S. Spring, *J. Chem. Soc.*, **1939**, 250.  
 (10) G. A. D. Haslewood, *Biochem. J.*, **33** (1939), 454.  
 (11) K. Dimroth and G. Trautmann, *Ber.*, **69** (1936), 669.  
 (12) H. H. Inhoffen, *Naturwissenschaften*, **25** (1937), 125.

The formation of 7-dehydrocholestene-pinacone affords a more reliable evidence that the carbon atom 3 or any group attached there does not take part in the formation of "pinacones", and that the seat of change must be sought at the other reactive group, the conjugate double bonds, thus favouring Inhoffen's ergopinacone formula.

### Experimental.

**Preparation of 7-Dehydrocholestene.** 7-Dehydrocholestene was prepared according to the directions of Dimroth and Trautmann<sup>(13)</sup> from cholesterol through the following intermediates.

*Cholesteryl chloride.*<sup>(13)</sup> Colourless needles, m.p. 97° (corr.).

*Cholestene.*<sup>(14)</sup> Colourless needles from alcohol, m.p. 93–94° (corr.). Mauthner and Suida gave m.p. 89–90°.

*7-Ketocholestene.*<sup>(15)</sup> Cholestene (31 g.) was oxidized with chromic anhydride (39 g.) in glacial acetic acid at 75–80°. After two hours an excess of alcohol was added to decompose chromic anhydride. The neutral fraction from the reaction mixture was recrystallized several times from acetone, m.p. 130–130.5° (corr.) (Found: C, 84.84, 84.12; H, 11.84, 11.85. Calculated for  $C_{27}H_{44}O$ : C, 84.30; H, 11.54%).  $[\alpha]_D^{25} = -138^\circ$  (13.4 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{25} = -1.85^\circ$ ). M.p. 145°<sup>(15)</sup> and 125°<sup>(16)</sup> are recorded in the literature. Oxime, needles from alcohol, m.p. 179–180° (corr.) (Found: N, 3.80, 3.84. Calculated for  $C_{27}H_{45}ON$ : N, 3.50%).

*7-Hydroxycholestene.*<sup>(13)</sup> Thick plates from acetone, m.p. 87–94° (corr.). It gave the Rosenheim reaction.

*7-Hydroxycholestene benzoate.*<sup>(11)</sup> Fine needles from acetone-methanol, m.p. 106–108° (corr.).

*7-Dehydrocholestene.*<sup>(11)</sup> (a) The above benzoate was decomposed and distilled at 120–125° under a pressure of  $3-7 \times 10^{-4}$  mm. in the course of about thirty hours. The distillate was taken in ether and the ethereal solution was washed with dilute alkali and with water. The residue from the ethereal solution was recrystallized from ether-methanol. Needles, m.p. 89–91° (corr.),  $[\alpha]_D = \pm 0^\circ$  (in chloroform).

(b) The benzoate was decomposed and distilled at 110–113° in the vacuum of a mercury diffusion pump ( $3-7 \times 10^{-5}$  mm.) in the course of about eighteen hours. The distillate was treated with alkali as described above and recrystallized from ether-methanol, m.p. 90–91° (corr.),  $[\alpha]_D^{17} = -22^\circ$  (in chloroform). The substance dissolved in hexane showed ultraviolet absorption maxima at 295, 282, and 273  $m\mu$  due to 7-dehydrocholestene and another at about 240  $m\mu$  probably due to isomeric cholestadiene.

(c) The distillation was carried out as (b), but the distillate was cooled with water to keep it from heat during distillation. The solidified distillate melted at 80–86° (corr.) and recrystallization gave a substance melting at 91° (corr.).

The specimens obtained in (a), (b) and (c), showed no melting point depression when mixed with one another.

**Photochemical Dehydrogenation of 7-Dehydrocholestene.** 7-Dehydrocholestene prepared as described above was treated according to the directions of Inhoffen<sup>(17)</sup> for the preparation of ergopinacone from ergosterol. 7-Dehydrocholestene (300 mg.) and eosin (300 mg.) were dissolved in a mixture of 95% alcohol (190 c.c.) and a small amount (5 c.c.) of benzene and carbon dioxide was passed through the solution to remove air. The solution was exposed to sunlight for a week. In the course of irradiation the colour of eosin was faded and micaceous plates separated out. The

(13) O. Diels and D. Blumberg, *Ber.*, **44** (1911) 2837.

(14) J. Mauthner and W. Suida, *Monatsh.*, **15** (1894), 86.

(15) A. Windaus and A. Kirchner, *Ber.*, **53** (1920), 488.

(16) A. Windaus and A. von Staden, *Ber.*, **53** (1920), 614.

(17) H. H. Inhoffen, *Ann.*, **497** (1932), 130.

precipitate was collected (40 mg.), washed with alcohol and with water, and recrystallized from chloroform-methanol. The product thus obtained forms glittering micaceous plates melting at 269–270° (corr.) with decomposition (Found: C, 88.51, 88.28; H, 11.77, 11.73. Calculated for  $C_{64}H_{86}$ : C, 88.21; H, 11.79%).  $[\alpha]_D^{30} = +260^\circ$  (3.3 mg. in 1 c.c. chloroform solution,  $l = 1$  dm.,  $\alpha_D^{30} = +0.87^\circ$ ). Molecular weight by Rast's method 750 (0.413 mg. in 4.000 mg. camphor, depression of m.p. 5.5°). Calculated for  $C_{64}H_{86}$ : 735. The substance is soluble in benzene and chloroform but insoluble in ether and alcohol. In the Liebermann-Burchard test it gives rose, red, violet, and finally dark blue colours, while in the Rosenheim test light pink, wine red, and blue colours.

### Summary.

7-Dehydrocholestene was exposed to sunlight with eosin in alcohol-benzene solution in the absence of oxygen. A product analogous to ergopinacone from ergosterol was obtained. Thus it was demonstrated that the carbon atom 3 or any group attached there does not take part in the photochemical dehydrogenation of ergosterol and its analogues.

The author expresses his hearty thanks to Prof. Y. Urushibara for his kind guidance and encouragement, to Dr. K. Yamasaki for taking absorption spectra and to Dr. T. Ando for analyses. Thanks are also due to Ozi Seisi Co. and to Yasohachi Yamaguchi for grants.

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# Über den Austausch der Wasserstoffatome zwischen Pyrrol, Indol sowie ihren Methylderivaten und Wasser. VII. Austausch der Wasserstoffatome zwischen Indol sowie Inden und Wasser in alkalischer Lösung.<sup>(1)</sup>

Von Masao KOIZUMI.

(Eingegangen am 18. September 1939.)

**Inhaltsübersicht.** Die Austauschreaktion der H-Atome zwischen Indol sowie Inden und Wasser wird in alkalischer Lösung unter Benutzung verdünnten schweren Wassers untersucht. Dabei ergibt sich, dass das Indol nicht nur das an N gebundene Imidwasserstoffatom sondern auch seine an C gebundenen Kernwasserstoffatome im Pyrrolring gegen die des Wassers austauscht. Aber die Geschwindigkeit dieser Austauschreaktion der Kernwasserstoffatome ist auch bei ziemlich konzentrierter alkalischer Lösung sehr gering und der Reaktionsverlauf ist ganz anders als bei der früher untersuchten Reaktion in saurer Lösung (vgl. IV. Mitteil.); das Austauschäquivalent des Indols nimmt mit zunehmender Alkalikonzentration und Versuchsdauer nur allmählich zu, und es gibt im Gegensatz zur Reaktion in saurer Lösung keine Anzeichen für eine stufenweise Austauschreaktion. Ähnlich verhält sich auch das Inden, wenn man dies mit alkalischem schwerem Wasser schüttelt; das Austauschäquivalent des Indens nimmt mit zunehmender Alkalikonzentration und Versuchsdauer allmählich zu, aber es sind keine Anzeichen für eine stufenweise Austauschreaktion vorhanden. Aus diesen Versuchsergebnissen wird geschlossen, dass der Austauschmechanismus in alkalischer Lösung ganz anders als in saurer Lösung sein müsse: es handelt sich in alkalischer Lösung vielmehr um eine einfache säurebasekatalytische Reaktion.

**Einleitung.** Nach den vorhergehenden Versuchen von Titani und dem Verfasser wird gefunden, dass Pyrrol, Indol sowie ihre verschiedenen Arten der Methylderivate einige ihrer H-Atome und zwar die im Pyrrolring befindlichen Kernwasserstoffatome stufenweise gegen die des Wassers austauschen, wenn man diese Verbindungen im geschmolzenen Zustand bzw. als eine Lösung in mit Wasser nicht mischbarem Lösungsmittel zusammen mit immer stärker angesäuertem schwerem Wasser schüttelt. Diese Versuchsergebnisse werden dadurch gedeutet, dass die Reaktionsfähigkeit der H-Atome der betreffenden Verbindung mit zunehmender H-Ionenkonzentration in damit geschütteltem Wasser nicht kontinuierlich sondern stufenweise zunimmt; von einer bestimmten H-Ionenkonzentration an wird ein bestimmtes H-Atom in der Verbindung ziemlich plötzlich austauschbar. Es liegt deshalb nahe, die ähnlichen Austauschversuche auch in alkalischer Lösung auszuführen und deren Ergebnisse mit den in saurer Lösung zu vergleichen. Als Versuchsmaterial benutzten wir erstens das Indol, weil diese Verbindung ihre H-Atome gegen die des angesäuerten Wassers sogar drei stufig austauscht (vgl. IV. Mitteil.). Die zugleich untersuchte Substanz, Inden, ist für uns insofern von Interesse, als ihr Molekül ähnlich wie das Indol gebaut

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(1) I. Mitteil., dies Bulletin, **13** (1933), 85; II. Mitteil., *ibid.*, **13** (1933), 95; III. Mitteil., *ibid.*, **13** (1933), 298; IV. Mitteil., *ibid.*, **13** (1933), 307; V. Mitteil., *ibid.*, **13** (1933), 643; VI. Mitteil., *ibid.*, **14** (1939), 453.

ist aber in Gegensatz zu dem letzteren der Fünfring dieser Verbindung homozyklisch ist, d.h. er keine direkt an N gebundenen ionisierbaren H-Atome enthält.

**Versuche mit Indol.** Die Versuche werden unter den ähnlichen Anordnungen wie bei den früheren Versuchen in saurer Lösung ausgeführt. Verdünntes schweres Wasser wird unter Zusatz von KOH auf eine bestimmte Alkalikonzentration gebracht. Etwa 1 g. dieser Lösung wird dann zusammen mit etwa 1 g. Indol in einem gut evakuierten und zugeschmolzenen Glasrohr verschiedener Zeitlänge aber immer bei 100°C. kräftig geschüttelt. Das dazu benutzte Indol wird von Laire chemisch rein bezogen. Nach der Schüttelung wird das Wasser wie üblich durch die Destillation im Vakuum vom Indol abgetrennt und gründlich gereinigt. Die Dichte und folglich der D-Gehalt des so gereinigten Wassers wird mit Hilfe eines Quarzschwimmers bestimmt. Das Austauschäquivalent  $nk$  des Indols unter der benutzten Versuchsbedingung lässt sich dann unter Benutzung des so bestimmten D-Gehaltes des schweren Wassers nach dem Versuch ( $D_s$ ) sowie vor dem Versuch ( $D_a$ ) mittels Gl. (1) errechnen:

$$nk = \frac{M_w}{M_j} \frac{D_a - D_e}{D_e} \quad (1),$$

wo die Symbole  $M_w$  und  $M_j$  resp. die Molzahl des zum Versuch verwendeten schweren Wassers und Indols bedeutet. Die auf diese Weise unter verschiedenen Versuchsbedingungen, d.h. bei verschiedener Alkalikonzentration sowie Versuchsdauer, gefundenen Austauschäquivalente des Indols sind in Tabelle 1 zusammengestellt, wo die Versuchsnr. in der ersten Spalte die zeitliche Reihenfolge der einzelnen Versuche anzeigt.

Tabelle 1. Austauschäquivalent  $nk$  des Indols bei verschiedener Alkalikonzentration und Versuchsdauer (100°C.).

| Versuchs-nr. | Normalität der benutzten Lösung | Schüttelungs-dauer in Stdn. | $M_w$  | $M_j$  | $nk$  |
|--------------|---------------------------------|-----------------------------|--------|--------|-------|
| 13           | 0.03 N KOH                      | 2                           | 0.0472 | 0.0247 | 1.07  |
| 14           | „ „                             | 15                          | 0.0446 | 0.0236 | 1.05  |
| 17           | „ „                             | 57                          | 0.0464 | 0.0225 | 1.14  |
| 9            | 0.3 N KOH                       | 5                           | 0.0549 | 0.0232 | 1.26  |
| 8            | „ „                             | 20                          | 0.0432 | 0.0231 | 1.61  |
| 10           | „ „                             | 40                          | 0.0441 | 0.0226 | 1.72* |
| 18           | „ „                             | 60                          | 0.0463 | 0.0223 | 1.78* |
| 19           | „ „                             | 85                          | 0.0463 | 0.0238 | 1.72* |
| 3            | 3 N KOH                         | 3                           | 0.0489 | 0.0249 | 1.53  |
| 11           | „ „                             | 3                           | 0.0437 | 0.0231 | 1.40  |
| 6            | „ „                             | 5                           | 0.0448 | 0.0233 | 1.73* |
| 1            | „ „                             | 6                           | 0.0544 | 0.0249 | 1.89* |
| 5            | „ „                             | 7                           | 0.0437 | 0.0237 | 1.69* |
| 2            | „ „                             | 15                          | 0.0493 | 0.0259 | 1.79* |
| 7            | „ „                             | 15                          | 0.0446 | 0.0236 | 1.70* |
| 5            | „ „                             | 30                          | 0.0458 | 0.0238 | 1.89* |
| 12           | „ „                             | 40                          | 0.0470 | 0.0233 | 1.87* |

Dieselben Ergebnisse sind auch in Abb. 1 graphisch dargestellt, indem das bei einer bestimmten Alkalikonzentration gefundene Austauschäquivalent  $nk$  gegen die Versuchsdauer aufgetragen wird. In derselben Abb. sind auch einige Ergebnisse aus den früheren Versuchen in saurer Lösung zum Vergleich eingezeichnet.

Aus dieser Abb. 1 wird ohne weiteres ersichtlich, dass das Austauschäquivalent des Indols bei einer bestimmten Alkalikonzentration mit zunehmender Versuchsdauer allmählich anwächst und zum Schluss ein Gleichgewicht erreicht wird. Der Wert von  $nk$  bei diesem Gleichgewicht ergibt sich als der Mittelwert der in Tabelle 1 mit \* versehenen Werte

$1.79 \pm 0.1$ . Wenn man von diesem Wert den anfänglichen Wert von  $nk$ , der, wie aus Tabelle 1 ersichtlich ist, 1.06 beträgt<sup>(2)</sup> und offensichtlich den Verteilungsquotienten (V. Q.) der Imidgruppe ausdrückt, abzieht, dann bleibt nur noch  $1.77 - 1.06 = 0.71$  übrig. Dieser Wert von  $nk$  stimmt aber mit dem V. Q. des bei der zweiten Stufe der Austauschreaktion des Indols in saurer Lösung austauschbar werdenden H-Atoms nämlich  $k_{H_2} = 0.69$ <sup>(3)</sup> sehr gut überein. Da aber dieses zweite austauschbare H-Atom des Indols nichts anderes als das in  $\beta$ -Stellung des Pyrrolkerns des Indolmoleküls befindliche H-Atom ist, so liegt die Annahme nahe, dass bei der Austauschreaktion in alkalischer Lösung neben dem Imidwasserstoffatom auch ein an C und zwar in  $\beta$ -Stellung des Pyrrolkerns verbundene H-Atom der Reaktion sich beteiligt.

Ähnliche Versuche werden auch mit Pyrrol unter Benutzung 3 N KOH-Lösung in schwerem Wasser bei 100°C. ausgeführt. Aber in diesem Fall konnte man überhaupt (bis auf das Imidwasserstoffatom) keine Austauschreaktion ausfindig machen. Daher darf wohl vermutet werden, dass die Kernwasserstoffatome im Pyrrolmolekül viel stärker als die im Pyrrolring des Indolmoleküls an C gebunden sind.

**Versuche mit Inden.** Die Versuche werden nicht nur in alkalischer Lösung sondern auch in saurer Lösung ausgeführt, um deren Ergebnisse mit denen des mit dieser Verbindung zum Teil isoelektronischen Pyrrols,

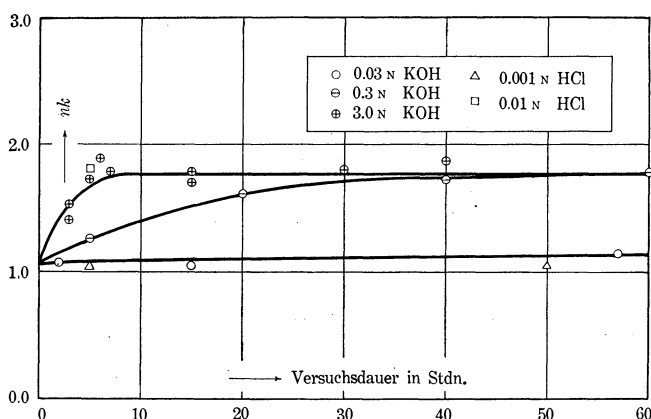


Abb. 1. Abhängigkeit des Austauschäquivalents  $nk$  des Indols von der Alkalikonzentration der damit geschüttelten Lösung und der Schütteldauer.

(2) Dieser Wert stimmt sehr gut mit dem bei den Versuchen in saurer Lösung gefundenen nämlich  $k = 1.07$  überein (vgl. Tabelle 4, IV. Mittel).

(3) Vgl. Tabelle 4 in IV. Mittel.

Thiophens und Furans zu vergleichen. Die dabei benutzte Versuchsanordnung ist im grossen und ganzen dieselbe wie bei dem vorhergehenden Versuche mit Indol. Nachdem eine bestimmte Menge mit HCl bzw. mit KOH versetzten verdünnten schweren Wassers zusammen mit ebenfalls gut abgewogener Menge Inden bei einer bestimmten Temperatur (meistens 100°C.) eine bestimmte Zeitlänge geschüttelt worden ist, wird das Wasser vom Inden sorgfältig abpipettiert. Da aber das so abgesonderte Wasser noch von einer ziemlich beträchtlichen Menge Inden verunreinigt ist, wird das Wasser zusammen mit gut getrocknetem Äther kräftig geschüttelt, um das Wasser vom Inden vollständig zu befreien. Der dabei im Wasser um ein wenig aufgelöste Äther wird durch die Behandlung des Wassers mit Pumpenöl beseitigt.<sup>(4)</sup> Das auf diese Weise von Inden und von Äther vollständig befreite Wasser wird zum Schluss wie üblich gereinigt und dessen Dichte und folglich Gehalt an D mittels eines Glasschwimmers bestimmt. Die Auswertung des Austauschäquivalents  $nk$  aus dem so bestimmten D-Gehalt des Wassers vor und nach dem Versuch sowie der Molzahl des benutzten schweren Wassers ( $M_w$ ) und Indens ( $M_j$ ) wird ebenfalls wie üblich ausgeführt (vgl. die vorhergehenden Versuche mit Indol). Die dadurch gewonnenen Ergebnisse sind in Tabelle 2 zusammengestellt.

Tabelle 2. Austauschäquivalent  $nk$  des Indens bei verschiedener Säure- und Alkalikonzentration sowie Versuchsdauer (100°C.).

| Versuchs-<br>nr. | Normalität<br>der benutzten<br>Lösung | Schüttelungs-<br>dauer<br>in Stdn. | $M_w$  | $M_j$  | $nk$   |
|------------------|---------------------------------------|------------------------------------|--------|--------|--------|
| 2**              | 2.97 N HCl                            | 5                                  | 0.0561 | 0.0268 | -0.006 |
| 3                | „ „                                   | 5                                  | 0.0563 | 0.0254 | 0.1    |
| 1**              | neutral                               | 5                                  | 0.0550 | 0.0276 | 0.01   |
| 6**              | 0.091 N KOH                           | 5                                  | 0.0608 | 0.0291 | 0.07   |
| 8                | „ „                                   | 5                                  | 0.0550 | 0.0256 | 0.28   |
| 10               | „ „                                   | 24                                 | 0.0586 | 0.0261 | 1.10   |
| 18               | „ „                                   | 29                                 | 0.0561 | 0.0268 | 1.27   |
| 14               | „ „                                   | 50                                 | 0.0566 | 0.0266 | 1.14   |
| 13               | „ „                                   | 80                                 | 0.0556 | 0.0259 | 1.43   |
| 19               | 0.3 N KOH                             | 5                                  | 0.0545 | 0.0263 | 0.94   |
| 20               | „ „                                   | 15                                 | 0.0555 | 0.0262 | 1.88   |
| 21               | „ „                                   | 28                                 | 0.0551 | 0.0261 | 2.42   |
| 25               | „ „                                   | 40                                 | 0.0555 | 0.0259 | 2.44*  |
| 33               | „ „                                   | 40                                 | 0.0562 | 0.0272 | 2.44*  |
| 22               | „ „                                   | 49                                 | 0.0552 | 0.0260 | 2.57*  |

(4) Vgl. M. Harada und T. Titani, dies Bulletin, **11** (1936), 468.

Tabelle 2.—(Fortsetzung)

| Versuchs-nr. | Normalität der benutzten Lösung | Schüttelungs-dauer in Stdn. | $M_w$  | $M_j$  | $nk$  |
|--------------|---------------------------------|-----------------------------|--------|--------|-------|
| 5**          | 1 N KOH                         | 5                           | 0.0544 | 0.0256 | 0.06  |
| 7            | „ „                             | 5                           | 0.0532 | 0.0261 | 1.80  |
| 9            | „ „                             | 16                          | 0.0558 | 0.0259 | 2.38  |
| 11           | „ „                             | 24                          | 0.0556 | 0.0262 | 2.49* |
| 29           | „ „                             | 25                          | 0.0548 | 0.0261 | 2.57* |
| 31           | „ „                             | 30                          | 0.0551 | 0.0268 | 2.58* |
| 26           | „ „                             | 40                          | 0.0551 | 0.0260 | 2.56* |
| 16           | „ „                             | 45                          | 0.0551 | 0.0265 | 2.58* |
| 15           | 3 N KOH                         | 1                           | 0.0550 | 0.0259 | 1.72  |
| 4            | „ „                             | 5                           | 0.0541 | 0.0264 | 2.54  |
| 28           | „ „                             | 5                           | 0.0549 | 0.0259 | 2.21  |
| 32           | „ „                             | 10                          | 0.0552 | 0.0275 | 2.42* |
| 27           | „ „                             | 14                          | 0.0550 | 0.0261 | 2.39* |
| 17           | „ „                             | 20                          | 0.0549 | 0.0263 | 2.50* |
| 24           | „ „                             | 25                          | 0.0546 | 0.0276 | 2.32* |
| 28           | „ „                             | 35                          | 0.0556 | 0.0258 | 2.47* |

\*\* Diese Versuche werden bei 60°C. ausgeführt.

Aus den ersten drei Versuchen (Versuchsnr. 2, 3 und 1) wird ersehen, dass das Inden in saurer und neutraler Lösung eine Austauschreaktion äusserst schwer ausführt. In diesem Punkt erinnert uns diese Verbindung an das Verhalten von Thiophen und Furan (vgl. II. Mitteil.) aber nicht von Indol bzw. Pyrrol in saurer Lösung. Was die Reaktion in alkalischer Lösung anbetrifft, so ähnelt das Verhalten des Indens dem des oben gezeigten Indols, wie aus der nebenstehenden Abb. 2 ohne weiteres ersichtlich ist. In dieser Abb. wird ebenso wie in Abb. 1 das bei einer bestimmten Alkalikonzentration gefundene Austauschäquivalent  $nk$  gegen die Versuchsdauer aufgetragen. Die Abb.

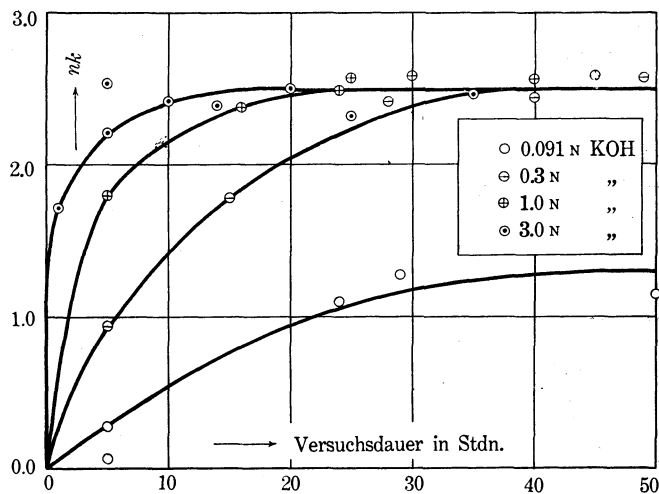


Abb. 2. Abhängigkeit des Austauschäquivalents  $nk$  des Indens von der Alkalikonzentration der damit geschüttelten Lösung und der Schüttelungsdauer.

zeigt, dass das Austauschäquivalent  $nk$  des Indens bei einer bestimmten Alkalikonzentration mit zunehmender Versuchsdauer allmählich zunimmt und zum Schluss ein Gleichgewichtswert erreicht wird. Wenn man diesen Gleichgewichtswert von  $nk$  als den Mittelwert der in Tabelle 2 mit \* versehenen Werte berechnet, so erweist er sich als  $2.50 \pm 0.1$ . Nimmt man an, dass alle vier H-Atome im Pentadienring des Indenmoleküls sich gleichzeitig an der Austauschreaktion beteiligen, dann muss der V. Q. jedes dieser H-Atome gerade ein Viertel des oben angegebenen Gleichgewichtswerts von  $nk$  sein, was offenbar  $(2.50 \pm 0.1)/4 = 0.63 \pm 0.02$  beträgt. Dieser Wert von  $k(\text{CH}/\text{H}_2\text{O})$  ist aber nun um ein wenig kleiner als der des  $\beta$ -H-Atoms des Pyrrols (d.h.  $k(\beta\text{CH}/\text{H}_2\text{O}) = 0.70$ ) sowie der des Indols (d.h.  $k(\beta\text{CH}/\text{H}_2\text{O}) = 0.69$ ).

**Diskussion.** Die in dem vorliegenden Versuche gefundenen Ergebnisse können wir zusammen mit einem Teil der früher in dieser Reihe der Versuche gewonnenen kurz wie folgt zusammenfassen:

(1) Indol tauscht seine im Pyrrolring befindlichen H-Atome stufenweise gegen die des damit geschüttelten Wassers aus, wenn man die Säurekonzentration im letzteren allmählich verstärkt. Schüttelt man dagegen dieselbe Verbindung mit alkalischer Lösung, so werden die H-Atome des Indols, und zwar die im Pyrrolring befindlichen, mit zunehmender Alkalikonzentration und Versuchsdauer nur allmählich ausgetauscht, und es gibt keine Anzeichen für die stufenweise Austauschreaktion.

(2) Das Pyrrol, das in saurer Lösung die stufenweise Austauschreaktion so leicht ausführt, zeigt einen äusserst grossen Widerstand gegen die Austauschreaktion in alkalischer Lösung.

(3) Inden führt ebenso wie Thiophen und Furan zu keiner nennenswerten Austauschreaktion in saurer Lösung wohl aber in alkalischer Lösung. Dabei erfährt die Austauschgeschwindigkeit ebenso wie beim Indol in alkalischer Lösung mit zunehmender Alkalikonzentration allmählich eine Zunahme bis schliesslich ein Gleichgewicht erreicht wird. Höchstwahrscheinlich werden hierbei alle vier H-Atome im Pentadienring gegen die des Wassers ausgetauscht.

Dass die Austauschreaktion des Indens in alkalischer Lösung keine stufenartige Natur besitzt, ist aus der oben angegebenen Abb. 2 ohne weiteres klar. Aber weil die entsprechende Abb. 1 von Indol den gewünschten Schluss nicht so klar wie Abb. 2 zeigen dürfte, möchte ich dafür noch einige zusätzliche Beweise anführen. Die unten in Tabelle 3 angegebenen Daten sind die ausgewählte Wiedergabe der in Tabelle 1 der I. Mitteil., der in Tabelle 1 der IV. Mitteil. sowie der in Tabelle 1 der vorliegenden Mitteil. angegebenen Versuchsergebnisse mit Pyrrol in saurer Lösung, Indol in saurer Lösung sowie Indol in alkalischer Lösung.

Aus dieser Tabelle 3 lässt sich ersehen, dass bei den Versuchen mit Pyrrol und Indol in saurer Lösung das gefundene Austauschäquivalent  $nk$  sich ausserordentlich vergrössert, wenn man die Normalität der benutzten Lösung zehnmal vergrössert und statt dessen die Versuchsdauer zehnmal verkürzt (vgl. z.B. Nr. 6 und 11 bei den Versuchen mit Pyrrol

Tabelle 3. Ausgewählte Wiedergabe der Versuchsergebnisse mit Pyrrol und Indol in saurer sowie alkalischer Lösung.

| Versuche                    | Versuchs-nr. | Normalität der benutzten Lösung | pH   | Versuchsdauer in Stdn. | nk        |
|-----------------------------|--------------|---------------------------------|------|------------------------|-----------|
| Pyrrol in saurer Lösung     | 4            | 0.01 N HCl                      | 2.00 | 1                      | 0.90      |
|                             | 6            | " "                             | 2.00 | 10                     | 0.90      |
|                             | 11           | 0.1 N HCl                       | 1.00 | 1                      | 3.64      |
|                             | 13           | " "                             | 1.00 | 9                      | 3.70      |
| Indol in saurer Lösung      | 10           | 0.001 N HCl                     | 3.00 | 5                      | 1.04      |
|                             | 11           | " "                             | 3.00 | 50                     | 1.05      |
|                             | 6            | 0.01 N HCl                      | 2.00 | 5                      | 1.81      |
|                             | 3            | 0.3 N HCl                       | 0.52 | 5                      | 1.77      |
| Indol in alkalischer Lösung | 13           | 0.03 N KOH                      | —    | 2                      | 1.07      |
|                             | 17           | " "                             |      | 57                     | 1.14      |
|                             | 9            | 0.3 N KOH                       |      | 5                      | 1.26      |
|                             | 8            | " "                             |      | 20                     | 1.61      |
|                             | 10           | " "                             |      | 40                     | 1.72      |
|                             | 3, 11        | 3 N KOH                         |      | 3                      | 1.53~1.40 |
|                             | 6            | " "                             |      | 5                      | 1.73      |
|                             | 12           | " "                             |      | 40                     | 1.87      |

in saurer Lösung und Nr. 11 und 6 bei den Versuchen mit Indol in saurer Lösung). Dagegen bei den Versuchen mit Indol in alkalischer Lösung erhält man fast einen gleich grossen Wert des Austauschäquivalents  $nk$ , wenn man die Normalität der benutzten alkalischen Lösung zehnmal vergrössert und statt dessen die Versuchsdauer etwa zehnmal verkürzt (vgl. z.B. Nr. 8 und 3, 11 in Tabelle 3). Aber die Austauschgeschwindigkeitskonstante  $\bar{k}$ , die Versuchsdauer  $t$  und das Austauschäquivalent  $nk$  sind, wie weiter unten gezeigt wird (vgl. Gl. (3), im allgemeinen durch die Gleichung der folgenden Form miteinander verknüpft:

$$\bar{k} = \frac{1}{t} F(nk) \quad (2),$$

wo  $F(nk)$  eine bestimmte Funktion von  $nk$  ausdrückt. Deshalb darf man aus den oben angegebenen Versuchsergebnissen wohl schliessen, dass die Austauschgeschwindigkeitskonstante  $\bar{k}$  des Indols in alkalischer Lösung mit der Alkalikonzentration fast proportional zunimmt. Dagegen besteht bei der Austauschreaktion des Pyrrols und Indols in saurer Lösung keine einfache Beziehung zwischen der Austauschgeschwindigkeit und der Säurekonzentration.

Aus den oben in Tabelle 3 angegebenen Versuchsergebnissen folgt weiter, dass bei den Versuchen mit Pyrrol in 0.01 N HCl-Lösung das gefundene Austauschäquivalent  $nk$  sogar nach 10 stündiger Schüttelung fast konstant bleibt (vgl. Nr. 6). Wenn man dagegen mit derselben Substanz die HCl-Konzentration zehnmals vergrößert d.h. 0.1 N HCl-Lösung benutzt, wird das Gleichgewicht schon innerhalb einer Stunde erreicht (vgl. Nr. 11). Ebenso verhält sich auch das Indol in saurer Lösung: in 0.001 N HCl-Lösung zeigt das gefundene Austauschäquivalent  $nk$  des Indols sogar nach 50 Stunden keine zunehmende Neigung (vgl. Nr. 11), wohl aber in zehnmals konzentrierter Lösung d.h. in 0.01 N HCl-Lösung, wo der Gleichgewichtswert von  $nk$  mindestens innerhalb fünf Stunden erreicht wird. Im Gegensatz zu diesem Verhalten des Pyrrols und Indols in saurer Lösung zeigt das gefundene Austauschäquivalent  $nk$  des Indols in alkalischer Lösung von bestimmter Konzentration immer eine zunehmende Neigung mit zunehmender Versuchsdauer: das in 0.03 N KOH-Lösung nach 57 Stunden bestimmte  $nk$  (Nr. 17) erweist sich z.B. untrüglich grösser als das in derselben Lösung nach 2 Stunden bestimmte (Nr. 13). Weiter wird ersichtlich, dass das in 0.3 N KOH-Lösung nach 5 Stunden bestimmte  $nk$  (Nr. 9) noch viel kleiner als der Gleichgewichtswert ( $= 1.79$ ) ist. Alle diese Ergebnisse legen uns die Annahme nahe, dass die Austauschreaktion des Indols in alkalischer Lösung im Gegensatz zu der in saurer Lösung als eine einfache säurebasekatalytische Reaktion aufzufassen ist.

Die Versuchsergebnisse, dass Inden ebenso wie Thiophen und Furan keine nennenswerte Austauschreaktion in saurer Lösung ausführt, weisen nun darauf hin, dass die stufenweise Austauschreaktion von Pyrrol, Indol und ihren Derivaten in saurer Lösung hauptsächlich auf dem basischen Charakter der in diesen Molekülen befindlichen Imidgruppe zurückgeführt werden kann. Weiter liegt die Annahme nahe, dass die katalytische Austauschreaktion von Inden und Indol in alkalischer Lösung mit der Existenz des dem Sechsring zugeschmolzenen Fünfring der C-Atome in engem Zusammenhang steht. Obwohl oben ziemlich klar gezeigt worden ist, dass diese Austauschreaktion des Indens (und Indols) in alkalischer Lösung als eine einfache säurebasekatalytische Reaktion aufgefasst werden kann, möchte ich dazu noch einen weiteren direkten Beweis geben. Dieser beruht nämlich darauf, dass die Austauschgeschwindigkeitskonstante wirklich mit der Alkalikonzentration proportional zunimmt. Bei den Versuchen der Austauschreaktion der Kernwasserstoffatome einiger Benzolderivate wurde gezeigt,<sup>(5)</sup> dass die mittlere Austauschgeschwindigkeitskonstante  $k$  im allgemeinen mit Hilfe folgender Gln. gefunden werden kann:

$$-X \log Y = \frac{\bar{k}}{2.303} t \quad (3),$$

(5) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 595. Vgl. die dortigen Gln. (15) und (16). Dort haben wir für den Verteilungsquotienten statt des Buchstaben  $k$  den Buchstaben  $\alpha$  benutzt.



wo

$$X = \frac{V}{\left(n_2 M_o + \frac{k_1}{k_2} n_1 M_o + \frac{2}{k_2} M_w\right)} \quad \text{und}$$

$$Y = \frac{1 - \frac{nk - n_1 k_1}{n_2 k_2}}{1 + \frac{nk - n_1 k_1}{\frac{2M_w}{M_o} + n_1 k_1}} \quad (4) \text{ ist.}$$

In diesen Gln. bedeutet  $t$  die Versuchsdauer,  $V$  das Volumen der Lösung,  $n_1$  die Anzahl der H-Atome in einem organischen Molekül, die sehr schnell ausgetauscht werden, wie z.B. Imidwasserstoffatom,  $n_2$  die der H-Atome, die mit messbarer Geschwindigkeit ausgetauscht werden, wie z.B. die Kernwasserstoffatome,  $k_1$  und  $k_2$  resp. den Verteilungsquotienten der D-Atome für die beiden Arten der H-Atome,  $nk$  das beobachtete Austauschäquivalent bei einer bestimmten Versuchsdauer  $t$  und  $M_o$  und  $M_w$  die Molzahl der zum Versuch benutzten organischen Verbindung und des verdünnten schweren Wassers. Da aber bei der Austauschreaktion des Indens in alkalischer Lösung angenommen werden darf, dass die Reaktion hauptsächlich in der Wasserphase stattfindet, können obige Gln. (3) und (4) auch für diese Reaktion ohne weiters angewendet werden, wenn man als  $V$  das Volumen der Wasserphase benutzt und  $n_1 = 0$  setzt, weil das Indenmolekül keine direkt ionisierbaren H-Atome enthält. Setzt man weiter die entsprechenden Werte von  $n_2$  ( $= 4$ ),  $k_2$  ( $= 0.63$ ) und  $n_2 k_2$  ( $= 2.50$ ) in Gln. (4) ein, so erhält man die Formeln:

$$X = \frac{V}{4M_o + 3.2M_w} \quad \text{und} \quad Y = \frac{1 - \frac{nk}{2.50}}{1 + \frac{nk}{2M_w/M_o}} \quad (5).$$

Wenn man gemäss dieser Gln. und unter Benutzung der in Tabelle 2 angegebenen Daten die Quantität ( $-X$ log  $Y$ ) bei verschiedenen Versuchsdauern und Alkalikonzentrationen ausrechnet und dann mit Hilfe der so gefundenen Werte von ( $-X$ log  $Y$ ) bei verschiedenen Versuchsdauern aber bei einer bestimmten Alkalikonzentration die Geschwindigkeitskonstante  $\bar{k}$  bei jeder bestimmten Alkalikonzentration nach Gl. (3) graphisch ermittelt,<sup>(6)</sup> dann erhält man die Werte, die in Tabelle 4 wiedergegeben sind. Die Einheit für die in dieser Tabelle 4 angegebene  $\bar{k}$  ist (Mol/Liter)<sup>-1</sup> (Stunde)<sup>-1</sup>.

Zieht man die verhältnismässig grobe Natur dieser Art der Ermittlung von  $\bar{k}$  in Rechnung, dann darf wohl geschlossen werden, dass die Geschwindigkeitskonstante  $\bar{k}$  mit der Alkalikonzentration fast proportional zunimmt. Bei den Versuchen von Indol in alkalischer Lösung

(6) Vgl. z. B. M. Koizumi und T. Titani, dies Bulletin, 13 (1938), 631.

Tabelle 4. Austauschgeschwindigkeitskonstante  $\bar{k}$  des Indens bei verschiedener Alkalikonzentration (100°C.).

| Alkalikonzentration<br>der benutzten Lösung | $\bar{k} / 2.303$   |
|---------------------------------------------|---------------------|
| 0.091 N                                     | 0.000035 ~ 0.000050 |
| 0.3 N                                       | 0.00018 ~ 0.00020   |
| 1 N                                         | 0.0003 ~ 0.0005     |
| 3 N                                         | 0.001 ~ 0.002       |

reichen die in Tabelle 1 angegebenen Daten nicht immer aus, um daraus die Geschwindigkeitskonstante bei jeder benutzten Alkalikonzentration auszurechnen. Aber falls man diese bei 0.3 N auf ähnliche Weise wie oben errechnet, wo verhältnismässig eine reichliche Menge von Daten vorliegt, so erhält man die Formel:

$$\bar{k} / 2.303 = 0.00015 \quad (\text{Mol/Liter})^{-1} (\text{Stunde})^{-1}.$$

Dieser Wert steht aber sehr nahe dem für Inden bei derselben Alkalikonzentration gefundenen (vgl. Tabelle 4 bei 0.3 N). Diese Übereinstimmung von  $\bar{k}$ -Wert des Indols mit dem des Indens bei derselben Alkalikonzentration darf man vielleicht als eine Stütze für die Annahme ansehen, dass Indol in alkalischer Lösung nach ähnlichem Mechanismus wie beim Inden verläuft.

Zum Schluss möchte ich Herrn Prof. T. Titani für seine stetige Unterstützung und wertvollen Ratschläge bei der Durchführung der vorliegenden Versuche meinen wärmsten Dank aussprechen. Der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkoku (der Hattori-Stiftung) bin ich auch für ihre finanzielle Unterstützung zu grösstem Dank verpflichtet.

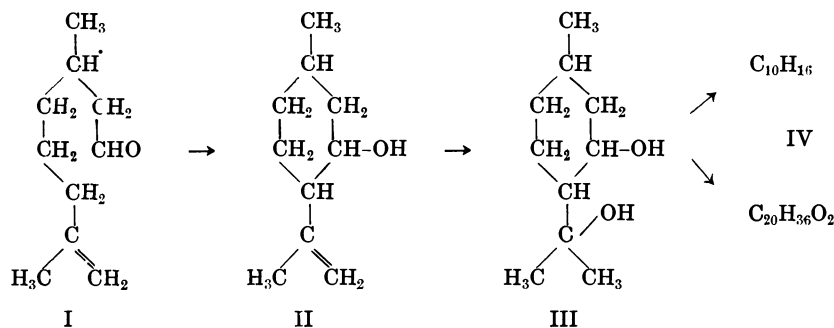
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der Kaiserlichen Universität zu Osaka.*

## Constitution of Two New Terpenes, Menogene and Menogerene ( $C_{10}H_{16}$ and $C_{10}H_{14}$ ).—The Mechanism of Cyclisation of Citronellal and Citral.

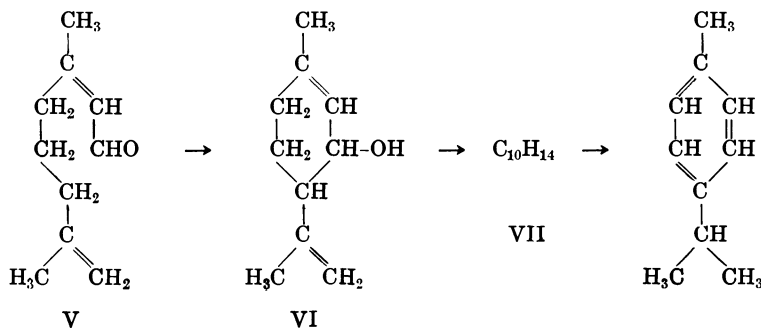
By Riki HORIUCHI, Hiroshi OTSUKI, and Osamu OKUDA,

(Received September 28, 1939.)

One of the writers<sup>(1)</sup> has studied the cyclisation-mechanism of olefinic terpenes, citral,  $C_{10}H_{16}O$ , and citronellal,  $C_{10}H_{18}O$ , into isomeric monoterpenes, and proved the formation of menthoglycol (III) from citronellal (I) through isopulegol (II), opposing to the theories of P. Barbier and G. Leser,<sup>(2)</sup> F. W. Semmler<sup>(3)</sup> and F. Tiemann.<sup>(4)</sup> A new terpene,  $C_{10}H_{16}$  (IV), has been isolated in the reaction and named as citronellat-terpene, the scheme being as follows:



Although the cyclisation-mechanism of citral has not been proved, *p*-cymene and a new terpene,  $C_{10}H_{14}$ , which is named citral-terpene (VII), corresponding to citronellat-terpene, are formed in the cyclisation reaction, the mechanism is, therefore, supposed to be as follows:



(1) Horiuchi, *Mem. Col. Sci. Kyoto*, **11** (1928), 171.

(2) P. Barbier and G. Leser, *Compt rend.*, **124** (1897), 1308.

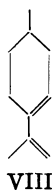
(3) F. W. Semmler, *Ber.*, **42** (1909), 2015.

(4) F. Tiemann, *ibid.*, **32** (1899), 107.

When the constitutions of these terpenes have been elucidated, we may have a deeper insight into the proposed cyclisation-mechanisms of citral and citronellal and an explanation may be afforded of the biosynthesis and isomerisation *in vivo* of olefinic terpenes.

**Menogene,  $C_{10}H_{16}$ .** J. Dœuvre<sup>(5)</sup> obtained a mixture of unknown terpenes by the dehydration of menthoglycol, supposing to be a mixture of  $\Delta^{2:4(8)}$ -menthadiene and  $\Delta^{3:8(9)}$ -menthadiene. Then W. J. Grubb and J. Read<sup>(6)</sup> isolated a terpene by dehydrating and reducing pulegone and supposed it to be  $\Delta^{3:8(9)}$ -menthadiene identical with citronellal-terpene obtained by Horiuchi. J. Dœuvre and H. Perret<sup>(7)</sup> repeated the experiment of Grubb and Read, without obtaining any concrete conclusion.

All terpenes produced by the direct dehydration of isopulegol and menthoglycol will be represented by the following three formulas:



VIII and IX are to be produced from both isopulegol and menthoglycol, but X from only menthoglycol. VIII has been synthesised by W. H. Perkin<sup>(8)</sup> and his coworkers and IX has been discovered by Henry and Paget;<sup>(9)</sup> the properties of these compounds are therefore known. Among these three, IX has no rotatory power.

Citronellal is treated with 50% sulphuric acid according to Horiuchi's<sup>(1)</sup> method, a terpene part is separated from the product and fractionated by repeated distillation, physical properties of the main part being as follows:

| B. p. (764.5 mm. Hg) | $d_4^{20}$ | $n_D^{20}$ | $[\alpha]_D^{17}$ | $[\text{RL}]_D$ | Ex.  |
|----------------------|------------|------------|-------------------|-----------------|------|
| 184–186°             | 0.8624     | 1.5026     | +49.11°           | 46.59*          | 1.35 |

\* Calculated for  $C_{10}H_{16}F_2$ :  $[\text{RL}]_D$ , 45.24.

#### Analysis

Found: C, 87.82; H, 12.16. Calculated for  $C_{10}H_{16}$ : C, 88.2; H, 11.8%.

The analytical result shows that the formula of the compound is  $C_{10}H_{16}$ , but the specific gravity and the refractive index are extremely high

(5) J. Dœuvre, *Bull. soc. chim.* [4], **53** (1933), 27.

(6) W. J. Grubb and J. Read, *J. Chem. Soc.*, **1934**, 242.

(7) J. Dœuvre and H. Perret, *Bull. soc. chim.* [5], **55** (1935), 2985.

(8) W. H. Perkin, *J. Chem. Soc.*, **1906**, 848; **1911**, 537.

(9) Henry and Paget, *J. Chem. Soc.*, **1921**, 1714.

compared with those of the formerly known terpenes. When  $C_{10}H_{16}\overline{F}_2$  is adopted, the exaltation is 1.35 and the presence of conjugated double bonds is supposed, favouring the adoption of formula X.

The terpene was dissolved in petroleum ether and shaken with an aqueous solution of sodium nitrite and crystals were obtained, which were recrystallised out as colourless scales from a mixture of methanol and chloroform, melting at  $154.5 - 155^\circ$ . The melting point of a mixture of the nitrosite and  $\alpha$ -terpinene nitrosite was lower by about  $30^\circ$ . The terpene is therefore not identical with any known terpene, but is a new one.

The nitrosite has large specific rotation:  $[\alpha]_D^{20}, -174.06^\circ$ ; and the elementary analysis gives the following data:

Found: C, 56.41; H, 7.70; N, 13.29. Calculated for  $C_{10}H_{16}N_2O_3$ :

C, 56.58; H, 7.61; N, 13.20%.

When reduced with hydrogen, using palladium oxide as a catalyst in an alcoholic solution, the terpene absorbs two moles of hydrogen. The main fraction of the reduced product absorbs no bromine and has the following constants, which show good agreement with those of *p*-menthane; the terpene is therefore identical with *p*-menthadiene.

| B. p. (756.5 mm. Hg) | $d_4^{20}$ | $n_D^{20}$ | $[\alpha]_D^{25}$ |
|----------------------|------------|------------|-------------------|
| 168–171°             | 0.8102     | 1.4490     | $\pm 0$           |

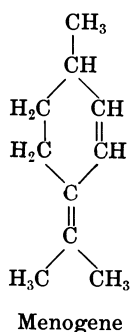
The terpene absorbs one mole of bromine in its amyl alcohol ether or glacial acetic acid solution, but white fume is evolved by further addition of bromine to the solution. So the terpene should have conjugate double bonds in it. To prove this, the writers utilised the diene synthesis:<sup>(10)</sup> a solid is obtained by warming a benzene or ether solution of the terpene and an equivalent amount of maleic anhydride, its melting point being  $205 - 208^\circ$  and  $[\alpha]_D^{25} - 18.76^\circ$  in an acetone solution. By neutralising the compound with 30% potassium hydroxide solution, white crystalline powder is produced, its melting point being  $228 - 230^\circ$ . This powder absorbs bromine equivalent to one double bond; the bromide melts at  $282 - 285^\circ$ . Thus combining with maleic anhydride the terpene in question gave a dibasic acid anhydride having one double bond. It is therefore concluded that the terpene has conjugated double bonds.

A cooled glacial acetic acid solution of the terpene is mixed with ethyl nitrite, to which hydrochloric acid is added drop by drop. No nitroso-chloride is obtained but the product remains in a liquid state. At low temperature, the product is of deep blue colour, and the colour changes gradually to green, yellow, deep red, reddish brown, and deep brown, according to the elevation of temperature of the liquid. The

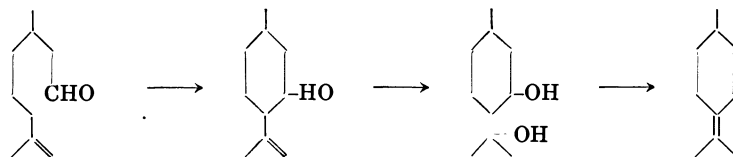
(10) Diels and Alder, *Ann.*, **460** (1928), 98; **478** (1930), 139.

same phenomena had been observed by A. Baeyer<sup>(11)</sup> as a characteristic property of tertiary-tertiary ethylene bond,  $>C = C <$ . From these facts the terpene is assumed to have a semicyclic structure.

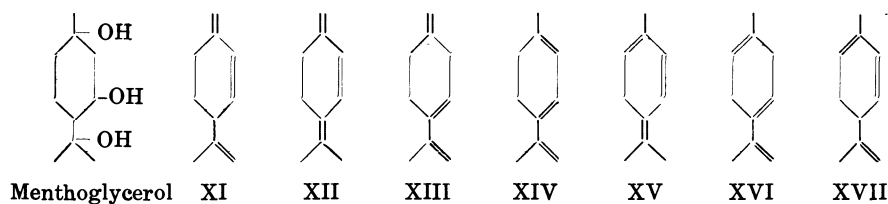
A mixture of the terpene and metallic sodium becomes orange yellow and the colour changes to deep red by heating. When distilled, small amounts of liquid are obtained at 55–75° and at 100–130° and then the main fraction of the terpene follows. The former has an odour of acetone and gives feathery crystals of golden colour, melting at 148–148.5°, by reacting with *p*-nitrophenyl-hydrazine. A mixture of the obtained hydrazone and acetone-*p*-nitrophenyl-hydrazone shows no depression of the melting point. The acetone should be the product of the split of the semicyclic part of the terpene. Wallach<sup>(12)</sup> obtained acetone by the decomposition of pulegone and A. Pfau<sup>(13)</sup> from atlantone. The terpene should therefore have double bonds between 4- and 8-carbon atoms and 2- and 3- or 5- and 6-carbon atoms; and the structure of the so-called citronellal-terpene is as shown below.



Among fourteen isomers of  $C_{10}H_{16}$  terpenes, two of them have not yet been reported, and now one of the two has been clearly and definitely identified. It is not a derivative of isopulegol, but that of menthoglycol, it is therefore named menogene. The cyclisation mechanism of citronellal proposed by one of the writers<sup>(1)</sup> has been proved by the above facts as follows, contrary to the theories proposed by Barbier<sup>(2)</sup> Semmler<sup>(3)</sup> Tiemann<sup>(4)</sup> and Dœuvre<sup>(5)</sup>:



**Menogerene,  $C_{10}H_{14}$ .** As one of the writers<sup>(1)</sup> has reported, citral-terpene has the formula  $C_{10}H_{14}$  and is an isomer of *p*-cymene, if it has the skeleton of *p*-menthane; but none of supposed twelve isomers has not yet been definitely identified. As discussed above, menogene derived from citronellal is produced by dehydration of menthoglycol, citral-terpene should therefore be derived by dehydration of menthoglycerol and their isomers may be represented by the following seven formulas:



(11) A. Baeyer, *Ber.*, **27** (1894), 436.

(12) Wallach, *Ann.*, **365** (1909), 243.

(13) A. Pfau, *Helv. Chim. Acta*, **17** (1934), 129.

Pearl and Dehn<sup>(14)</sup> obtained a terpene,  $C_{10}H_{14}$ , by treating camphor with phosphoric acid, which is presumed to be  $\Delta^{3:5:8(9)}$ -*p*-menthatriene, from its rotatory property, and moreover to be identical with the citral-terpene obtained by Horiuchi.<sup>(1)</sup>

By repeating fractional distillation of citral-terpene obtained by treating citral with 20% sulphuric acid as reported by Horiuchi,<sup>(1)</sup> the following four fractions were obtained, none of them having rotatory power:

| Fraction | B. p. (769 mm. Hg) | Weight (g.) | $d_4^{20}$ | $n_D^{20}$ | $\alpha_D$ | [RL] <sub>D</sub> |
|----------|--------------------|-------------|------------|------------|------------|-------------------|
| A        | 80–82°             | 5.5         | 0.8209     | 1.4095     | ± 0        |                   |
| B        | 110–111°           | 9.6         | 0.8451     | 1.4783     | ± 0        |                   |
| C        | 175–176°           | 27.5        | 0.8595     | 1.4916     | ± 0        |                   |
| D        | 180–181°           | 50.5        | 0.8672     | 1.5005     | ± 0        | 45.66*            |

\* Calculated for  $C_{10}H_{14}F_3$ : [RL]<sub>D</sub>, 44.78.

Below 80° a small fraction was obtained, which was proved to be acetone by the identification of *p*-nitrophenylhydrazone, m.p. 148–148.5°. Fraction A may be isopropyl alcohol as its phenylurethane melts at 88–89°.

Fraction B has toluene-like odour and is unstable in air quickly producing a syrup and explosively decomposes by distillation. From the easy polymerisation of  $\Delta^{1:3}$ -*L*-methylcyclohexadiene and easy formation of peroxide of cyclohexene and of general methylcyclohexenes, some peroxide should be produced also in this case. By oxidising with potassium permanganate as usual, it gives succinic acid, m.p. 180–182°. When hydrogenated on palladium oxide, it absorbs two moles of hydrogen exactly. Fraction B is therefore a new compound, 1-methyl- $\Delta^{1:5}$ -cyclohexadiene, i.e., 3,4-dihydrotoluene. The analytical results are as follows and the other constants are described above:

Found: C, 89.06; H, 10.31. Calculated for  $C_7H_{10}$ : C, 89.14; H, 10.71%.

Fraction C is *p*-cymene, as it gives *p*-hydroxyisopropyl benzoic acid, m.p. 157–158°, by oxidising with potassium permanganate as usual.

Fraction D is the so-called citral-terpene and has the constants described above. The elementary analysis of the compound gives the following results:

Found: C, 89.96; H, 10.90. Calculated for  $C_{10}H_{14}$ : C, 89.48; H, 10.52%.

In a glacial acetic acid solution, the terpene absorbs one mole of bromine, producing a dibromide, m.p. 114.5–115°; a mixture of the dibromide and terpinolene tetrabromide melts lower by about 10°.

The terpene is unstable. By distillation after long standing, one part of the terpene changes into *p*-cymene. By treating with 20% sul-

(14) Pearl and Dehn, this Bulletin, **12** (1937), 493.

phuric acid, it changes also into *p*-cymene; it contains, therefore, *p*-cymene skeleton in it. The terpene is therefore the intermediate compound in the changing course of citral into *p*-cymene by treatment with sulphuric acid.

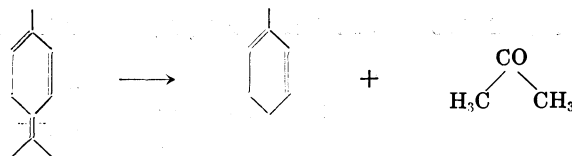
A nitroso-chloride of the terpene is not isolated as crystals and gives special colour reaction as in the case of menogene. The terpene has a semicyclic structure having a tertiary-tertiary ethylene bond. When distilled with metallic sodium the terpene gives acetone. The structure of the terpene should therefore be XII or XV among seven isomers given above.

In a pure methanol solution, the terpene absorbs one mole of hydrogen in the presence of palladium oxide and then the absorption-velocity of hydrogen is extremely small. The product gives the following two main fractions, (a) and (b) by fractional distillation.

| Fraction | B. p.    | Weight (g.) | $d_4^{20}$ | $n_D^{20}$ | $\alpha_D$ |
|----------|----------|-------------|------------|------------|------------|
| a        | 168–170° | 0.3         | 0.8109     | 1.4495     | $\pm 0$    |
| b        | 172–174° | 5.2         | 0.8440     | 1.4795     | $\pm 0$    |

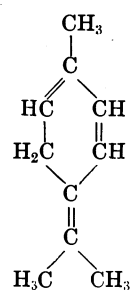
As fraction (a) does not absorb bromine and is not oxidised with potassium permanganate, it should be *p*-menthane from its physical constants. By treating with maleic acid anhydride, fraction (b) gives a crystalline substance, melting at 126–127°; melting point of a mixture of (b)-addition product and *dl*- $\alpha$ -phellandrene addition product does not fall. From these results, the terpene gives, by the hydrogenation, *p*-menthane on one side by saturating all double bonds and *dl*- $\alpha$ -phellandrene on the other by saturating semicyclic structure. So the positions of the ethylene bonds other than the tertiary-tertiary ethylene bond are between carbon atoms 2 and 3 and carbon atoms 6 and 1.

The terpene is, as stated above, very unstable. Not only it reacts with acids or alkalis, but also it changes during keeping. That acetone and 1-methyl- $\Delta^{1:5}$ -cyclohexadiene were produced in the course of fractional distillation of the terpene obtained from citral is due to the breakage of a double bond between carbon atoms 4 and 8. And the production of isopropyl alcohol is due to the reduction of acetone in the course of distillation with metallic sodium.



From the above stated facts the terpene should have the following structure. As just like menogene is produced from menthoglycol, the terpene should be produced from the corresponding menthoglycerol, so

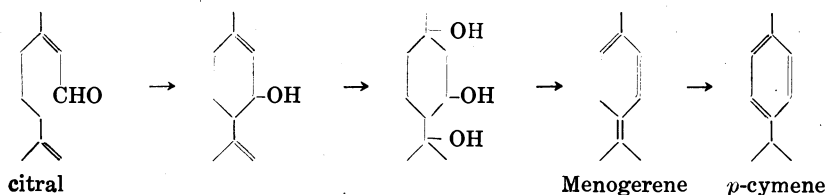




Menogerene

the terpene is named menogerene. A terpene, C<sub>10</sub>H<sub>14</sub>, an isomer of *p*-cymene is here now definitely identified.

The mechanism of the formation of the new compound by the action of sulphuric acid upon citral should be as follows, as proposed by Horiuchi,<sup>(1)</sup> presuming the formation of dehydro-isopulegol and menthoglycerol as intermediates. The intermediate between menthoglycerol and *p*-cymene is, however, menogerene contrary to the presumption by Horiuchi.<sup>(1)</sup>



This explanation of the mechanism is further substantiated by the formation of menogene from citronellal, and the formation-mechanism proposed by A. Verley<sup>(15)</sup> was proved to be only a supposition.

### Summary.

One of the writers (Horiuchi)<sup>(1)</sup> has proposed a mechanism of the cyclisation which occurs in treatment of citronellal and citral with sulphuric acid. The constitutions of two new terpenes, C<sub>10</sub>H<sub>16</sub> and C<sub>10</sub>H<sub>14</sub>, produced by the reaction, are cleared up and they are named menogene and menogerene respectively.

The mechanism of cyclisation of citronellal and citral or generally of olefinic terpene aldehydes is largely cleared up. The intermediate state of these compounds in organisms is assumed. Not only the ring formation, but also the formation process of the terpenes is suggested. It is also shown that the semicyclic double bond is unstable and changes its position into the ring, taking the form of *p*-cymene.

Especially these two olefinic terpene aldehydes show the same behavior; that is, water is not needed for the ring formation; the terpenes are formed by dehydration of the hydrate; and the forms and positions of the double bonds are completely corresponding.

Their derivatives, menogene nitrosite and menogerene bromides, and 1-methyl- $\Delta^{1:5}$ -cyclohexadiene are formed and their natures are described.

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Tokyo.

(15) A. Verley, *Bull. soc. chim.*, [3], **21** (1899), 408.

## Boiling Points of the System of Formic Acid and Water.

By Sotozi TAKAGI.

(Received October 2, 1939.)

Papers related to the vapour pressure of pure formic acid are published by Richardson,<sup>(1)</sup> Kahlbaum,<sup>(2)</sup> Schmidt<sup>(3)</sup> and Coolidge,<sup>(4)</sup> and those related to the constant boiling point in the system of formic acid and water by Roscoe<sup>(5)</sup> and Jones.<sup>(6)</sup>

As these papers, however, give only descriptions of the azeotropic mixtures, they do not fit for the purpose of reference to obtain the concentrated acid.

Thus, the author repeated the measurements on the head article to fill up the lacking data of this system and to establish facts for practical use.

**Experimental.** Sample used was purified by repeated redistillation and the measurement of boiling point was carried out by ordinary dynamical method. About 500 c.c. of the original solution was taken for distillation and by using a short condenser, about 2 c.c. of the distillate of required constant boiling point was collected.

Accuracy of the data is 0.5 mm. Hg in pressure and 0.1°C. in temperature. The composition of the distillate is not of high accuracy as the distillate can not be seized completely.

As the data of azeotropic mixture, however, were obtained by carrying out the experiments to the coincidence of constant boiling points starting from samples of higher and lower concentrations than the azeotropic mixture, the data are of considerable precision, i.e. the error is within  $\pm 0.1^\circ\text{C}$ . in temperature, and within  $\pm 0.1\%$  in composition.

**Result.** Boiling points of liquid and the compositions of liquid and the vapour phase in equilibrium are shown in the following table and figure.

The data of Jones, Roscoe and International Critical Tables are approximate to the results of the author with the exception of the last ones which are perhaps due to error in transcribing the Roscoe's data.

From above table, the equation of vapour pressure of azeotropic point is obtained as follows:

$$p = 25 + 1.87715(t - 31.4) + 0.017706(t - 31.4)^2 + 0.00102904(t - 31.4)^3$$

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(1) Richardson, *J. Chem. Soc.*, **1886**, 761.

(2) Kahlbaum, *Ber.*, **16** (1883), 2480; *Ber.*, **27** (1894), R 459; *Z. physik. Chem.*, **26** (1898), 591.

(3) Schmidt, *Z. physik. Chem.*, **7** (1891), 433.

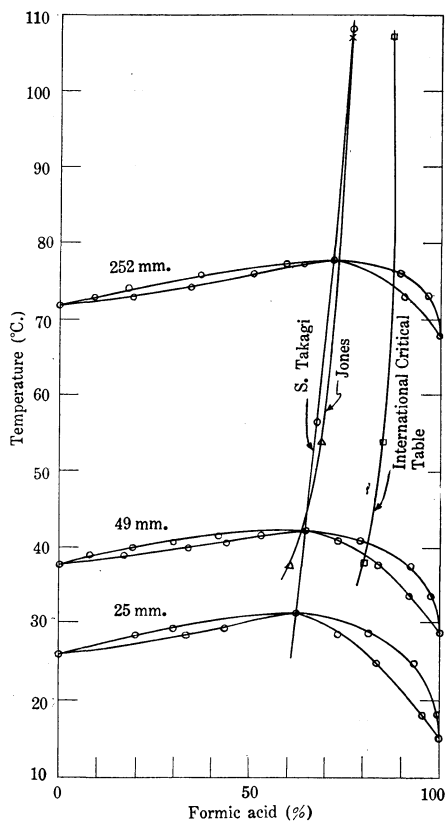
(4) Coolidge, *J. Am. Chem. Soc.*, **52** (1930), 1877.

(5) Roscoe, *J. Chem. Soc.*, **1862**, 270.

(6) Jones, *J. Soc. Chem. Ind.*, **1919**, 363.

| No. | Pressure<br>(mm. Hg) | HCOOH (%) |        | Temperature<br>(°C.) |
|-----|----------------------|-----------|--------|----------------------|
|     |                      | Liquid    | Vapour |                      |
| 1   | 25                   | 95.6      | 99.4   | 18.0                 |
| 2   | "                    | 83.5      | 93.6   | 24.3                 |
| 3   | "                    | 73.2      | 81.3   | 29.0                 |
| * 4 | "                    | 62.3      | 62.3   | 31.4                 |
| 5   | "                    | 43.6      | 30.1   | 29.2                 |
| 6   | "                    | 33.6      | 20.1   | 28.3                 |
| 7   | 49                   | 91.8      | 97.4   | 33.7                 |
| 8   | "                    | 83.4      | 92.4   | 37.7                 |
| 9   | "                    | 73.0      | 79.0   | 41.0                 |
| *10 | "                    | 64.7      | 64.7   | 42.3                 |
| 11  | "                    | 58.0      | 52.9   | 41.5                 |
| 12  | "                    | 43.9      | 30.0   | 40.7                 |
| 13  | "                    | 33.7      | 19.1   | 40.1                 |
| 14  | "                    | 16.9      | 7.3    | 39.0                 |
| *15 | 100                  | 67.4      | 67.4   | 56.6                 |
| 16  | 252                  | 90.7      | 96.8   | 73.0                 |
| 17  | "                    | 83.2      | 89.6   | 75.8                 |
| *18 | "                    | 72.1      | 72.1   | 77.7                 |
| 19  | "                    | 64.5      | 59.5   | 77.2                 |
| 20  | "                    | 51.0      | 37.2   | 75.8                 |
| 21  | "                    | 34.3      | 18.0   | 74.0                 |
| 22  | "                    | 19.1      | 8.9    | 72.8                 |
| *23 | 774                  | 76.8      | 76.8   | 108.1                |

\* are azeotropic mixtures. Boiling points of pure formic acid are calculated from Coolidge's equation  $\log p = 7.8584 - 1860/T$ .



$\Delta$ ,  $\times$  and  $\square$  are data by Jones, Roscoe and International Critical Tables (Vol. III, p. 364) respectively.

### Summary.

Boiling points of liquid and the compositions of the liquid and the vapour phase in equilibrium in the system of formic acid and water were determined in wide range of composition and temperature, and from above data the equation of vapour pressure of azeotropic point was determined.

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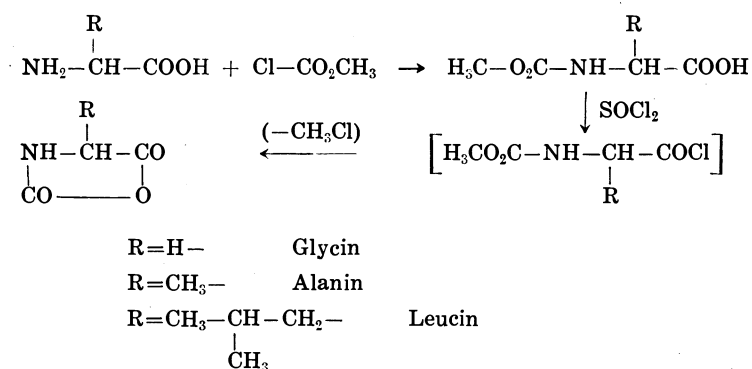
## Über die hochkondensierten Produkte aus einigen Aminosäuren.

Von Yukichi GO und Hisaya TANI.

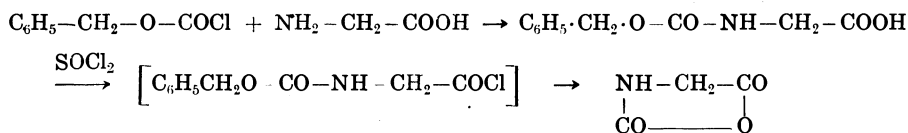
(Eingegangen am 12. October 1939.)

Früher untersuchte einer von uns<sup>(1)</sup> das hochkondensierte Produkt von Glycin und stellte fest, dass die Debye-Scherrer-Aufnahme dieser Substanz praktisch identisch mit der des nur aus Glycin aufgebauten Polypeptids war, dessen Kettenlänge grösser ist als die von Hexaglycylglycin. Wir haben jetzt die Untersuchung auf die hochkondensierten Produkte von *l*-Alanin und von *l*-Leucin erweitert und studierten einige Eigenschaften dieser Körperklasse.

Die hochkondensierten Produkte sind nach H. Leuchs<sup>(2)</sup> aus dem *N*-Carbonsäureanhydrid der Aminosäuren dargestellt worden.



Nach dieser Methode wird reines *N*-Carbonsäureanhydrid aus Leucin leicht gewonnen, aber im Falle von Alanin und Glycin ist die Reinigung verhältnismässig schwer. Deshalb gewannen wir zuerst Carbobenzoxyglycin<sup>(3)</sup> und dann reines Glycin-*N*-carbonsäureanhydrid einfach durch die Einwirkung von Thionylchlorid darauf.



Alle nach solcher Methode hergestellten krystallisierten *N*-Carbonsäureanhydride gehen, unter Verlust von Kohlenstoffdioxid, in pulverig hochmolekulare Verbindungen über, wenn sie in Wasserdampf stehen gelassen, oder in Pyridin gelöst und dann auf 100° erhitzt werden. Die

(1) K. H. Meyer und Y. Go, *Helv. Chim. Acta*, **17** (1934), 1488.

(2) H. Leuchs, *Ber.*, **39** (1906), 857; **40** (1907), 3243; **41** (1908), 1721.

(3) M. Bergmann und L. Zervas, *Ber.*, **65** (1932), 1192.

Elementaranalyse dieser hochkondensierten Produkte ergibt Übereinstimmung mit den aus den obigen Formeln berechneten Werten.

Die Molekulargewichtsbestimmung solcher Substanzen ist nach üblicher Methode unmöglich. Da Polyglycin<sup>(4)</sup> aber löslich in wässriger Lithiumbromidlösung ist, bestimmten wir Amino-Stickstoff in solcher Lösung nach der van Slykeschen Methode. Wenn solches Polyglycin natürlich auch keine einheitliche Substanz ist, so können wir, unter der Annahme, dass es sich um ein Polypeptid handelt, doch für die mittlere Kettenlänge Werte von 18 bis 101 und für das mittlere Molekulargewicht Werte von 1044 bis 5775 erhalten. Diese Werte verändern sich natürlich je nach den Kondensationsbedingungen. Da Polyalanin und Poly-leucin aber nicht in Lösungszustand gebracht werden können, war bei ihnen die Bestimmung von Amino-Stickstoff nicht möglich.

Die Seide enthält grössere Mengen von Glycin, aber die Wolle grössere Mengen von Leucin, und die erstere ist löslich in Lithiumbromidlösung, dagegen die letztere unlöslich. Vergleicht man dieses Verhalten mit den Löslichkeitsunterschieden unserer synthetischen Polypeptiden, so beruhen diese Löslichkeitsunterschiede nicht auf der Bindungsart von Aminosäuren in Eiweisskörpern, sondern auf den Eigenschaften der in Eiweisskörpern enthaltenen Aminosäuren. Die mit Pirkrinsäure und Natriumcarbonat gemachte Diketopiperazin-Reaktion über Polyaminosäuren ist negativ.

**Enzymatische Untersuchung.** Wir studierten, welches Verhalten solche Verbindungen gegen Enzym zeigen. Die Kettenlänge des angewandten Polyglycin wird als etwa 26 angenommen.<sup>(5)</sup> Diese Substanz wird nicht mit allen benutzten proteolytischen Enzymen verdaut, wie im experimentellen Teil gezeigt wird.

Abderhalden<sup>(6)</sup> untersuchte die Wirkung von Erepsin auf die nur aus Glycin aufgebauten Peptide bis zum Dekapeptid. Er zeigte, dass diese Polypeptide bis zum Hexaglycin mit Erepsin verdaut, aber dass die höheren Peptide nicht verdaut werden. Hieraus kann man schliessen, dass unsere Substanz zum mindesten kein kleineres Peptid als Hexaglycin enthält. Trypsin kann alle niederen bereits synthetisch gewonnenen Peptide bis zum Eikosapeptid nicht verdauen. Doch ist es bisher nicht bekannt, ob Trypsin die höheren Peptide als Eikosapeptid verdaut. Es ist aber jetzt durch unsere Untersuchung festgestellt, dass Polypeptide von grösserer Kettenlänge als Eikosapeptid nicht verdaut werden, da wir gefunden haben dass unser Polyglycin und Poly-(glycin+leucin)<sup>(7)</sup> nicht verdaut werden.

**Ergebnisse der Röntgenuntersuchung.** Die nur aus Glycin aufgebauten Peptide bis zum Hexaglycin geben voneinander verschiedene Röntgenodiagramme. Doch geben die höheren Peptide als Hexaglycin praktisch identische Diagramme. Da unsere Polyglycine das gleiche

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(4) Die Hochkondensationsprodukte aus Aminosäuren werden später kurz als Polyglycin u. s. w. bezeichnet.

(5) Siehe: Experimenteller Teil, Verbindung (VIII).

(6) E. Abderhalden, *Fermentforschung*, 12 (1931), 42.

(7) Poly-(glycin+leucin) wird durch Erhitzung eines äquimolekularen Gemisches von *N*-Carbonsäureanhydride des Glycins und Leucins in Pyridin dargestellt.

Diagramm wie die Peptide von grösserer Kettenlänge als Heptaglycin geben, kann man für unser Polyglycin mindestens eine grössere Kettenlänge als Heptaglycin annehmen. Ausserordentlich grosse Ringe (z. B. hochgliedrige Ringe) geben auch die gleichen Diagramme wie zwei parallele Ketten. Daher können wir nicht erkennen, ob diese Substanzen Ringe oder Ketten enthalten.

Die Aufnahmen des Polyleucin und Polyalanin können nicht mit denen der nur aus Alanin oder Leucin stufenweise synthetisch aufgebauten Peptide verglichen werden, da Aufnahmen der letzteren noch unbekannt sind. Man kann aber wohl ähnliche Zusammenhänge wie im Falle von Glycin annehmen. Im Falle von Leucin entsprechen die Werte (11 Å und 4.8 Å) den der gewöhnlichen wasserlöslichen kugelförmigen Eiweisskörper.<sup>(8)</sup>

Weil die Werte der grössten Gitterdimensionen um so höher werden, je länger die Seitenketten der Aminosäureresidue sind, schliessen wir, dass diese Werte auf der Seitenkettenlänge beruhen.

Die Aufnahme des aus Glycin und Alanin gleichzeitig hergestellten Hochkondensationsproduktes zeigt die Einzeldiagramme von Polyglycin und Polyalanin; jedoch ist die Aufnahme so unscharf, dass sie schon beinahe ein amorphes Diagramm ist. Wir schliessen daher, dass die Substanz neben dem reinen Polyglycin und Polyalanin auch noch ein aus Glycin- und Alaninresiduen unregelmässig aufgebautes Kondensationsprodukt enthält.

Die im Wasserdampf dargestellten Substanzen geben stets stärkere und deutlichere Aufnahmen als die in Pyridin dargestellten.

Diese Ergebnisse zusammen mit den oben erwähnten enzymatischen Verhältnissen sprechen dafür, dass diese Substanzen kleinere Kettenlängen als Hexapeptid nicht enthalten. Ob diese Substanzen nur grössere Ketten oder Gemische von Ketten und Ringen enthalten, können wir nach den obigen beiden Methoden nicht entscheiden.

### Experimenteller Teil.

A. Darstellung von *N*-Carbonsäureanhydrid aus einigen Aminosäuren. 1. *Glycin-N*-Carbonsäureanhydrid. (I). Eine Mischung von 35g. (1 Mol) Carbobenzoxyglycin<sup>(9)</sup> und 100g. (5 Mol) Thionylchlorid werden, unter Abschluss von Luftfeuchtigkeit, etwa eine Stunde auf dem Wasserbad auf 40° erwärmt. Im Laufe der Zeit wird die Krystallmasse aus der klaren Lösung abgeschieden. Nach dem Abdestillieren des überschüssigen Thionylchlorids unter vermindertem Druck wird der Rückstand mit wasserfreiem Benzol gut gewaschen. Schwach gelbliche Krystalle (15.3g.) werden erhalten. Ausbeute 92% d. Theor. Umkrystallisiert aus Äthylacetat. Farblose Krystalle. Schmp. 100°.

2. *Carbomethoxy-l-alanin*. (II). Zu der Lösung von *l*-Alanin (1 Mol) in *N*-Natronlauge (1 Mol), wird bei 0° unter dauerndem Umrühren Chlorkohlensäuremethylester (1.1 Mol) tropfenweise zugesetzt. Nach Zusatz von wässriger Natriumcarbonatlösung (0.5 Mol) wird das Umrühren einige Stunden fortgesetzt. Nach beendeter Reaktion wird die Lösung mit *N*-Salzsäure versetzt und unter vermindertem Druck zur Trockne verdampft. Der Rückstand wird mit Äther extrahiert und dieser mit Natriumsulfat getrocknet und eingedampft, so erhielt man farblosen Sirup. Ausbeute etwa 85% d. Theor.

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(8) Für gewöhnliche wasserlösliche kugelförmige Eiweisskörper ergeben sich zwei Halos: 4.5 Å und 10-11 Å.

3. *l-Alanin-N-Carbonsäureanhydrid*. (III). 2.8 g. des oben erwähnten Sirups werden mit 4c.c. Thionylchlorid auf dem Wasserbad bei 40° etwa eine halbe Stunde erwärmt. Nach dem Abdestillieren von überschüssigem Thionylchlorid unter vermindertem Druck bei 40°, erhitzt man weiter bis auf 65° und lässt bei dieser Temperatur stehen. Die sirupöse Masse erstarrt nach etwa einer halben Stunde und wird dann mit wenig abs. Äther gewaschen. Ausbeute 1.6 g. oder 70% d. Theor. Umkrystallisiert aus abs. Äther, farblose lange Nadeln. Schmp. 92° (u. Zersetz.). (Gefunden: N, 12.73. Berechnet für  $C_3H_5O_3N$ : N, 12.18%).

4. *Carbomethoxy-l-leucin*. (IV). Die Reaktion wird unter ähnlichen Bedingungen wie im Falle des oben erwähnten Carbomethoxy-l-alanin (II) durchgeführt. Durch Zusatz von N-Salzsäure werden die Krystalle abgeschieden und abfiltriert. Ausbeute 80% d. Theor. Umkrystallisiert aus abs. Äther und wasserfreiem Petroläther. Schmp. 52°. (Gefunden: C, 48.67; H, 8.10. Berechnet für  $C_8H_{16}O_4N \cdot \frac{1}{2}H_2O$ : C, 48.46; H, 8.14%).

5. *l-Leucin-N-Carbonsäureanhydrid*. (V). 9.05g. der oben erwähnten Krystalle (IV) werden unter vermindertem Druck getrocknet. Der erhaltene Sirup wird mit 12c.c. Thionylchlorid etwa eine halbe Stunde auf dem Wasserbad auf 40° erwärmt. Das überschüssige Thionylchlorid wird unter vermindertem Druck bei 40° abdestilliert. Im Laufe von etwa 40 Minuten erstarrt die sirupöse Masse. Ausbeute 6.9g. oder 90% d. Theor. Umkrystallisiert aus abs. Äther und wasserfreiem Petroläther. Schmp. 77–78° (u. Zersetz.). (Gefunden: N, 9.05. Berechnet für  $C_7H_{11}O_3N$ : N, 8.92%).

## B. Kondensation von Aminosäure-N-carbonsäureanhydriden.

I. **Unter Wasserdampf.** Im geschlossenen Gefässe werden die Krystalle von N-Carbonsäureanhydrid fünf bis sieben Tage über Wasser stehen gelassen. Die erhaltene pulverige hochkondensierte Masse wird, nach dem Trocknen im Exsiccator über Phosphorpentoxyd, gewogen, und die Gewichtsabnahme bei der Kondensation wird mit der Menge verglichen, die sich für befreites Kohlendioxyd berechnen lässt.

1. *Polyglycin*. (a) N-Carbonsäureanhydrid dargestellt nach der Leuchsschen Methode. (VI). N-Carbonsäureanhydrid: 1.5705g. Gewichtsabnahme: 0.6663g. daher  $CO_2$ -Abspaltung: 97.41% d. Theor.

Gesamt-Stickstoff nach mikro-Kjeldahl. (Gefunden: N, 24.95, 27.71. Berechnet für  $C_2H_5ON$ : N, 24.57%).

Bestimmung des Amino-Stickstoffs: 0.4370g. der Substanz werden mit 50%iger wässriger Lithiumbromidlösung versetzt und auf 10c.c. aufgefüllt. Zur Bestimmung werden je 2c.c. dieser Lösung benutzt und nach der mikro-van Slyke Methode bestimmt. (Gefunden: N, 0.405, 0.402%).

$$100 \times \frac{14}{n \times 57 + 18} = 0.40 \quad \text{daher } n \approx 61$$

$$\frac{\text{Amino-N}}{\text{Gesamt-N}} \approx \frac{1}{61} \quad \text{Molekulargewicht} \approx 3095$$

(b) N-Carbonsäureanhydrid dargestellt nach der Bergmannschen Methode. (VII).

N-Carbonsäureanhydrid: 11.1646g. Gewichtsabnahme: 4.5735g. daher  $CO_2$ -Abspaltung: 94.09% d. Theor.

Bestimmung des Amino-Stickstoffs: Die Ausführung der Bestimmung schliesst sich ganz an die im Falle (a) beschriebene Methodik an. (Gefunden: N, 1.373%).

$$\text{daher } \frac{\text{Amino-N}}{\text{Gesamt-N}} \approx \frac{1}{18} \quad \text{Molekulargewicht} \approx 1044$$

(c) Umgefälltes Polyglycin (VIII).

Die oben beschriebene Substanz (VII) wird in gesättigter Lithiumbromidlösung gelöst und mit der zehnfachen Menge Wasser umgefällt.

Amino-Stickstoff: N, 0.919%.

$$\frac{\text{Amino-N}}{\text{Gesamt-N}} \approx \frac{1}{26} \quad \text{Molekulargewicht} \approx 1492$$

2. *Polyalanin* (IX) *N*-Carbonsäureanhydrid: 0.5556g. Gewichtsabnahme: 0.2005g. daher CO<sub>2</sub>-Abspaltung: 94.31% d. Theor.

Gesamt-Stickstoff nach mikro-Kjeldahl: Gefunden: N, 19.90. 19.89. Berechnet für C<sub>5</sub>H<sub>5</sub>ON: N, 19.72%.

3. *Polyleucin*. (X). *N*-Carbonsäureanhydrid: 1.8561g. Gewichtsabnahme: 0.4761g. daher CO<sub>2</sub>-Abspaltung: 91.58% d. Theor.

Gesamt-Stickstoff nach mikro-Dumas: Gefunden: N, 12.04. Berechnet für C<sub>6</sub>H<sub>11</sub>ON: N, 12.39%.

II. Unter Erhitzung mit wasserfreiem Pyridin. Wasserfreie Pyridinlösungen der *N*-Carbonsäureanhydride werden etwa 15 Minuten auf dem Wasserbad auf 100° erhitzt und die dabei abgeschiedenen Substanzen filtriert.

1. *Polyglycin*. (XI). 0.73g. des *N*-Carbonsäureanhydrids dargestellt nach der Leuchsschen Methode werden in 15c.c. wasserfreiem Pyridin gelöst. Die erhaltene Substanz wird abfiltriert und mit Alkohol gewaschen. Farbloses Pulver. Ausbeute 0.15g.

Amino-Stickstoff Bestimmung: 81.1 mg. Substanz werden mit 50% iger Lithiumbromidlösung versetzt und auf 2c.c. aufgefüllt. Gefunden: N, 0.243%.

$$\text{daher } \frac{\text{Amino-N}}{\text{Gesamt-N}} = \frac{1}{101} \quad \text{Molekulargewicht} = 5775$$

2. *Polyalanin*. (XII) 0.50g. *N*-Carbonsäureanhydrid werden in 15c.c. wasserfreiem Pyridin gelöst.

Gesamt-Stickstoff Bestimmung: Gefunden: N, 19.01. Berechnet für C<sub>5</sub>H<sub>5</sub>ON: N, 19.72%.

3. *Polyleucin*. (XIII) 2.0g. *N*-Carbonsäureanhydrid werden in 10c.c. wasserfreiem Pyridin gelöst. Nach beendeter Reaktion wird mit *n*-Hexan versetzt, die dabei ausgefällte Substanz abfiltriert und mit *n*-Hexan gewaschen. Farblose Pulver. Ausbeute 1.1g.

Gesamt-Stickstoff Bestimmung: Gefunden: N, 12.40. Berechnet für C<sub>6</sub>H<sub>11</sub>ON: N, 12.39%

### C. Enzymatische Versuche mit Polyglycin und Poly-(glycin+leucin).

1. *Herstellung der Substratlösungen*. Da die beiden Substrate in Wasser nicht löslich sind, benutzen wir ihre Suspensionen.

a). *Polyglycin*. Zu der Lösung von 1.5g. Polyglycin (VII) in wässriger gesättigter Lithiumbromidlösung werden 130c.c. Wasser zugesetzt, die dabei ausgefällte Substanz abzentrifugiert und wiederholt mit Wasser gewaschen bis sie von Lithiumbromid befreit ist. Diese Substanz wird mit M/15 sekundäres Natriumphosphat (pH 8.4) oder mit M/5 Acetat-Puffer (pH 5.0) versetzt und auf 100c.c. aufgefüllt.

b) *Poly-(glycin + leucin)*. 1.7g. *Poly-(glycin + leucin)* werden mit M/15 sekundärem Natriumphosphat (pH 8.4) versetzt und auf 50c.c. aufgefüllt.

2. *Verdauungs-Versuche*. a). Mit Papain. Papainlösung: 10% iger wässrige Lösung von Papain (E. Merck) wurden nach den Angaben von A. Purr<sup>(9)</sup> mit Cystein aktiviert.

Ansatz A: 4% Gelatinlösung 5c.c. + Acetat (pH 5.0) 2c.c. + Papainlösung 1c.c. Ansatz B: P-G. 5c.c. + Papainlösung 1c.c. Ansatz C: M/5 Acetat (pH 5.0) 5c.c. + Papainlösung 1c.c.

Verdauungsversuche bei 30°.

| Std. | COOH-Zuwachs (c.c. N/5 KOH) |      |      |
|------|-----------------------------|------|------|
|      | A                           | B    | C    |
| 1/3  | 0.64                        | —    | —    |
| 1    | 1.01                        | —    | —    |
| 24   | —                           | 0.01 | 0.00 |
| 48   | —                           | 0.04 | 0.00 |

(9) A. Purr, *Biochem. J.*, **29** (1935), 5.



b). Mit Erepsin. Erepsinlösung ist aus dem Glycerinextrakt der frischen Schleimhaut von Schweinedärmen hergestellt worden. Dieses Präparat enthält Aminopolypeptidase und wenig Dipeptidase, aber nicht Trypsin.

Ansatz A: Leucylglycin 5c.c. + Erepsinlösung 1c.c. Ansatz B: *dl*-Leucylglycylglycin 5c.c. + Erepsinlösung 1c.c. Ansatz C: P-G, 5c.c. + Erepsinlösung 1c.c. Ansatz D: M/15 Phosphat (pH 8.4) 5c.c. + Erepsinlösung 1c.c.

Verdauungsversuche bei 30°.

| Stdn. | COOH-Zuwachs (c.c. N/5 KOH) |      |       |      |
|-------|-----------------------------|------|-------|------|
|       | A                           | B    | C     | D    |
| 1/3   | —                           | 1.64 | —     | —    |
| 1     | 0.75                        | 2.53 | —     | —    |
| 5     | —                           | —    | 0.00  | 0.00 |
| 24    | —                           | —    | 0.03  | 0.01 |
| 48    | —                           | —    | —0.03 | 0.03 |

Ansatz A: *dl*-Leucylglycylglycin 5c.c. + Erepsinlösung 1c.c. Ansatz B: P-G-L, 5c.c. + Erepsinlösung 1c.c. Ansatz C: Phosphat (pH 8.4) 5c.c. + Erepsinlösung 1c.c.

Verdauungsversuche bei 30°.

| Stdn. | COOH-Zuwachs (c.c. N/5 KOH) |      |      |
|-------|-----------------------------|------|------|
|       | A                           | B    | C    |
| 1     | 1.80                        | —    | —    |
| 24    | —                           | 0.02 | 0.01 |
| 48    | —                           | 0.18 | 0.11 |

c. Mit Trypsin. Chymotrypsinfreie Trypsinlösung ist nach Angaben von Northrop<sup>(10)</sup> hergestellt worden.

Ansatz A: 6% Caseinlösung 5c.c. + Phosphat (pH 8.4) 2c.c. + Trypsinlösung 1c.c. Ansatz C: M/15 Phosphat (pH 8.4) 5c.c. + Trypsinlösung 1c.c.

Verdauungsversuche bei 30°.

| Stdn. | COOH-Zuwachs (c.c. N/5 KOH) |       |       |
|-------|-----------------------------|-------|-------|
|       | A                           | B     | C     |
| 1/3   | 0.64                        | —     | —     |
| 1     | 0.77                        | —     | —     |
| 16    | —                           | 0.02  | —0.01 |
| 48    | —                           | —0.09 | 0.00  |

d). Mit Trypsin-Kinase. Trypsin-Kinase-Lösung ist nach Waldschmidt-Leitz<sup>(11)</sup> hergestellt worden.

(10) J. H. Northrop und M. Kunitz, *J. Gen. Physiol.*, **16** (1933), 267.

(11) E. Waldschmidt-Leitz und K. Linderström-Lang, *Z. physiol. Chem.*, **166** (1927), 241.

Ansatz A: 0.04 Mol Chloracetyl-L-Tyrosin 5c.c. + Trypsin-Kinase 1c.c. Ansatz B: P-G. 5c.c. + Trypsin-Kinase 1c.c. Ansatz C: P-G-L. 5c.c. + Trypsin-Kinase 1c.c. Ansatz D: Phosphat (pH 8.4) 5c.c. + Trypsin-Kinase 1c.c.

Verdauungsversuche bei 30°.

| Stdn. | NH <sub>2</sub> -Zuwachs<br>(c.c.) | COOH-Zuwachs (c c. N/5 KOH) |      |      |  |
|-------|------------------------------------|-----------------------------|------|------|--|
|       | A                                  | B                           | C    | D    |  |
| 1/3   | 0.351                              | —                           | —    | —    |  |
| 1     | 0.720                              | —                           | —    | —    |  |
| 5     | —                                  | 0.03                        | 0.01 | 0.04 |  |
| 24    | —                                  | 0.13                        | 0.17 | 0.14 |  |
| 48    | —                                  | 0.22                        | 0.36 | 0.27 |  |

D. Röntgenographische Untersuchung.

Cu K<sub>α</sub> 57 KV. 6 mA. 7 Stdn.

| Substanz                  | Herstellungs<br>Methode | Netzebenenabstände in Å |               |                 |          |
|---------------------------|-------------------------|-------------------------|---------------|-----------------|----------|
| Polyleucin                | H <sub>2</sub> O        | 11.9 (s.s.st.)          | 4.8 (m.)      |                 |          |
| „                         | Pyridin                 | 11.5 (s.s.st.)          | 5.1 (m.)      |                 |          |
| Polyalanin                | H <sub>2</sub> O        | 5.3 (s.st.)             | 4.4 (st.)     | 3.7 (m.)        |          |
| „                         | Pyridin                 | 5.4 (m.)                | 4.3 (m.)      | 3.8 (schw.)     |          |
| Polyglycin                | H <sub>2</sub> O        |                         | 4.2 (s.s.st.) | 3.9 (schw.)     | 3.1 (m.) |
| „                         | Pyridin                 |                         | 4.4 (m.)      | 3.9 (schw.)     | 3.5 (m.) |
| Poly-(glycin<br>+ alanin) | Pyridin                 | 5.1 (s.s.schw.)         | 4.4 (m.)      | 3.7 (s.s.schw.) |          |

An dieser Stelle möchten wir Herrn. Prof. Dr. Shiro Akabori für seine freundliche Unterstützung unseren besten Dank aussprechen.

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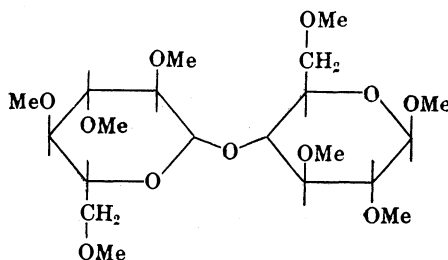
# The Unit Cell and Space-Group of $\beta$ -Octamethylcellobiose and $\beta$ -Hendecamethylcellotriose.

By Tatuó OHASI.

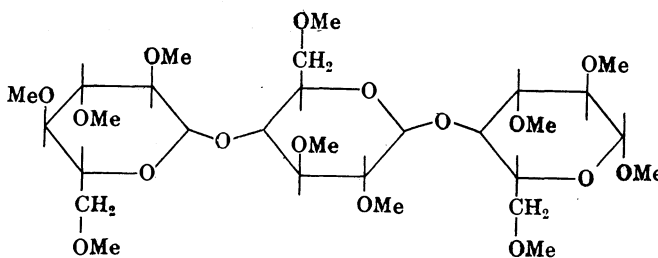
(Received October 30, 1939).

By means of X-rays the dimensions of the rhombic unit cell have been determined to be  $a = 12.0 \text{ \AA}$ ,  $b = 43.7 \text{ \AA}$ ,  $c = 4.50 \text{ \AA}$  for  $\beta$ -octamethylcellobiose and  $a = 21.3 \text{ \AA}$ ,  $b = 34.5 \text{ \AA}$ ,  $c = 4.50 \text{ \AA}$  for  $\beta$ -hendecamethylcellotriose. These substances possess the same corresponding space group  $D_{2h}^4 - P2_12_12_1$ , the number of molecules in the unit being four. The results are completely different from that reported by Trogus and Hess.

**Introduction.** An X-ray investigation on the crystals of  $\beta$ -octamethylcellobiose and  $\beta$ -hendecamethylcellotriose had already been made by Trogus<sup>(1)</sup> in 1932 and by Trogus and Hess<sup>(2)</sup> in 1935, who determined the identity period along the needle axis of the former crystal to be  $4.3 \text{ \AA}$



$\beta$ -Octamethylcellobiose



$\beta$ -Hendecamethylcellotriose

and the unit cell of the latter to be monoclinic having the dimensions  $a = 20.4 \text{ \AA}$ ,  $b = 4.8 \text{ \AA}$  (along the needle axis),  $c = 21.0 \text{ \AA}$ , with  $\beta = 75^\circ$ . From these constants and the density  $\rho = 1.25$ , the number of the methylcellotriose molecules in the unit was calculated to be 2-3, and, according to their choice, the two molecule unit is more probable. The substances

(1) C. Trogus, *Naturwissenschaften*, **20** (1932), 317.

(2) C. Trogus and K. Hess, *Ber.*, **68** (1935), 1605.

used in these investigations were bundles of fine long crystals paralleled along the needle axis and so the photographs taken corresponded to the complete rotation or fiber diagrams. Thus not quite free from doubt is the correctness in indexing the reflexions from these photographs and it seems also strange that the number of molecules in the unit calculated by us to be 2.3 is so much deviated from the whole number 2.

Accordingly, it seems very desirable to make re-examination more precisely by the single crystal methods. Fortunately comparatively large single crystals of  $\beta$ -methylcellobiose and  $\beta$ -methylcellotriase were obtained from aqueous solutions in our laboratory and the present investigation has been carried out with these substances.<sup>(3)</sup>

**The Unit Cell and Space-Group.** The crystals used were long thin rhombic prisms, the diameters being about 0.3 mm. for octamethylcellobiose and about 0.1 mm. for hendecamethylcellotriase.

In each case, the needle axis was taken as the  $c$ -axis which corresponds to the  $b$ -axis chosen by Trogus and Hess. There is a perfect cleavage parallel to a plane along the needle axis, and the axis perpendicular to this cleavage plane was chosen as the  $a$ -axis.

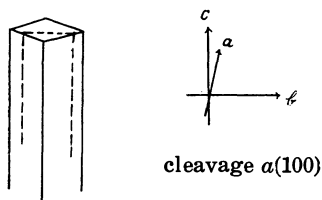


Fig. 1.

The apparent densities, which were measured by the floatation method in aqueous solution of  $K_2CO_3$ , are about 1.23 and 1.26 respectively. The true values should perhaps be somewhat larger than the above, because of the adsorbed air on the surface of the crystals which could not be removed completely.

The symmetry of Laue photographs taken with X-ray beams normal to the  $a$ -plane (100) and  $b$ -plane (010) was  $D_{2h}$ . Oscillation photographs about the  $c$ -axis and Weissenberg photographs of  $(hk0)$ ,  $(hkl)$  with  $l = 1$  to 3, and  $(0kl)$  were taken with  $Cu K_\alpha$ -radiation. The results of the analyses of these photographs are as follows:

|                                  | $a$    | $b$  | $c$  | Number of mols.<br>in the unit. |
|----------------------------------|--------|------|------|---------------------------------|
| Octamethylcellobiose . . . .     | 12.0 Å | 43.7 | 4.50 | 3.88 $\approx$ 4                |
| Hendecamethylcellotriase . . . . | 21.3 Å | 34.5 | 4.50 | 3.87 $\approx$ 4                |

Assuming the number of molecules in the unit to be four, the densities are calculated to be 1.27 and 1.30 respectively. Taking the accuracy of the measurements into account, these values seem very reasonable.

As mentioned above Laue photographs show  $D_{2h}$  symmetry. Weissenberg photographs show that the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between three axes are all  $90^\circ$  and, moreover, the intensities of the reflexions of  $(hk1)$ ,  $(\bar{h}k1)$ ,  $(h\bar{k}1)$  and  $(\bar{h}\bar{k}1)$  are all completely equal to each other and those of  $(hk2)$ , and  $(\bar{h}k2)$ , and  $(h\bar{k}2)$ , and  $(\bar{h}\bar{k}2)$  are all equal, and so on. Thus there is

(3) These substances were prepared by means of acetolysis followed by methylation of cellulose.

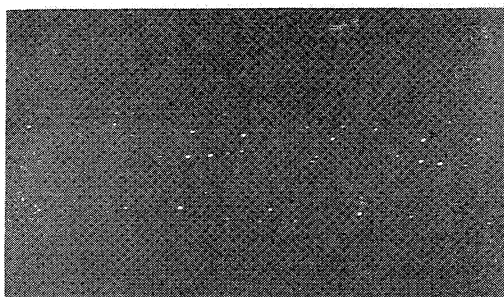


Plate 1. ( $hk0$ ) Weissenberg photograph of  $\beta$ -octamethylcellobiose.

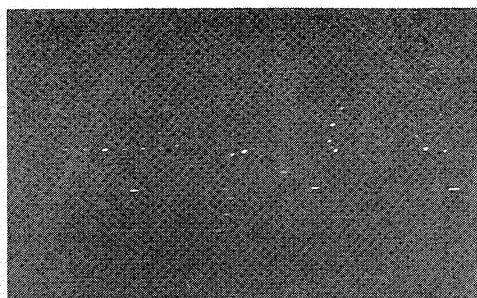


Plate 2. ( $hkl$ ) Weissenberg photograph of  $\beta$ -octamethylcellobiose.

no doubt that the crystals belong to the rhombic system instead of monoclinic. Powder photographs of these substances agree with those of Trogus and Hess completely, so that the substances used by them and by the present author must be identical, possibility of polymorphism being thus eliminated. Perhaps the results of Trogus and Hess would be incorrect.

It is characteristic that reflections ( $h00$ ), ( $0k0$ ) and ( $00l$ ) are not present when  $h = 2n + 1$ ,  $k = 2n + 1$  and  $l = 2n + 1$ . Accordingly, the space groups of these substances are  $D_2^4 - P2_12_12_1$ .

**Some Discussion about Molecular Arrangement in the Crystals.** The value  $4.50\text{\AA}$  of the identity periods along the  $c$ -axis for both substances and the present chemical view of the pyranose unit lead to the arrangement that the molecular plane containing the pyranose rings, or at least the longest axis of these molecules, lies perpendicular, or almost perpendicular, to the needle axis. Although this was suggested by Trogus and Hess, the present equality of the value  $4.50\text{\AA}$  for both crystals seems to account for the analogous structure in a more natural manner.

The acetyl derivatives of these substances were investigated in 1934 by Leuck and Mark,<sup>(4)</sup> and they also concluded that the molecular chains lie perpendicular to the needle axis from the fact that their identity periods of these acetyl-compounds are always  $5.7\text{\AA}$  corresponding to the above value  $4.50\text{\AA}$ .

In this respect, molecular arrangement in crystals of acetyl derivatives suggested by Leuck and Mark is quite analogous to that of methyl derivatives given by Trogus and Hess and by the present author.

Furthermore, Leuck and Mark speculated that the identity period  $15\text{\AA}$  along the  $b$ -axis is common to all these substances and that along the  $a$ -axis increases steadily with the number of glucose residues in the molecule: viz.  $\frac{1}{2} \times 24.3\text{\AA}$ ,  $21\text{\AA}$  and  $29\text{--}30\text{\AA}$  for acetyl derivatives of glucose, cellobiose, and cellotriase. According to this view, the molecular chains of these substances are to be parallel, or almost parallel, to the  $a$ -axis in the crystals.

In the present investigation of the methyl derivatives, however, such a relation is not found between the dimensions of the two unit cells. There

(4) G. J. Leuck and H. Mark, *J. Am. Chem. Soc.*, **56** (1934), 1959.

are no common values except along the needle axis. The period along the  $a$ -axis of methylcellobiose ( $12.0\text{\AA}$ ) is smaller than that of methylcellotriase ( $21.3\text{\AA}$ ), and the  $b$ -axis of the former ( $43.7\text{\AA}$ ) is larger than that of the latter ( $34.5\text{\AA}$ ). These facts suggests that the molecular chains are not parallel but have some inclination to each other, accordingly to the  $a$ -axis, and have such a tendency that the angle of this inclination decreases with the increasing number of glucose residues in the molecule, in other words the molecular chains of methylcellotriase are more parallel to each other (or to the  $a$ -axis) than methylcellobiose.

In such a way the molecules of  $\beta$ -octamethylcellobiose or  $\beta$ -hendecamethylcellotriase are presumably arranged in the rhombic crystal lattice, fulfilling at the same time the condition of the space group symmetry  $D_2^4$ .

In conclusion, the author wishes to express his best thanks to Professor I. Nitta, Professor Y. Go, and Dr. T. Watanabe for their kind interest during the work, and also to Mr. H. Tani for supplying the crystals which were used in this investigation.

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**Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs.  
V. Die Sorption des Sauerstoffs durch Manganoxyd und die  
Austauschreaktion der Sauerstoffatome zwischen Sauerstoffgas  
und Manganoxyd. Teil I. Sorptionsversuche.<sup>(1)</sup>**

Von Noriyoshi MORITA.

(Eingegangen am 10. November 1939.)

**Inhaltsübersicht.** Die Sorption des Sauerstoffgases durch Manganoxyd bei verschiedenen Temperaturen wird unter konstantem Druck (2/3 atmosphärischem Druck) kinetisch verfolgt. Dabei wird gefunden, dass die Sorptionsgeschwindigkeit bei Zimmertemperatur fast unmessbar klein und auch bei 275°C. sehr gering ist. Wenn man dagegen die Temperatur des Manganoxyds bis auf 325°C. steigen lässt, tritt ziemlich plötzlich eine lebhafte Sorption ein und die Sorptionsgeschwindigkeit bei dieser letzt genannten Temperatur ist etwa fünfzehnmal so gross wie bei 275°C. Dieser Zuwachs der absorbierten Menge des Gases mit der Temperatur dauert bis auf etwa 530°C. Aber wenn man das auf diese Weise mit Sauerstoff reichlich absorbierte Manganoxyd weiter oberhalb 530°C. erhitzt, tritt eine lebhafte Desorption des Sauerstoffgases ein und ein Teil des im Oxyd enthaltenen Sauerstoffs geht verloren. Bringt man aber die Temperatur des auf diese Weise einen Teil des Sauerstoffs verlorenen Manganoxyds wieder auf ein niedrigeres Niveau zurück, dann nimmt es wieder Sauerstoff auf und dasselbe Verfahren können wir, so oft wie man will, wiederholen.

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(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: *ibid.*, **13** (1938), 601; III. Mitteil.: *ibid.*, **13** (1938), 656; IV. Mitteil.: *ibid.*, **14** (1939), 9.

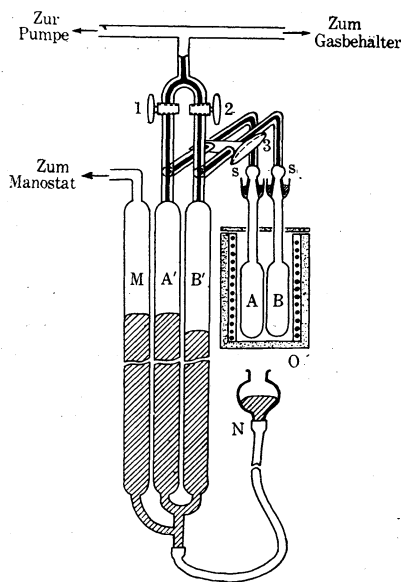
**Einleitung.** Beim vorhergehenden Versuch (IV. Mitteil.), wo die katalytische Wirksamkeit der Oxyde der zur vierten Hauptreihe des periodischen Systems gehörigen Elemente für die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf verglichen wurde, ergab sich, dass das Manganoxyd unter den dabei untersuchten Oxyden, nämlich den Oxyden von Ca, Al, Ti, V, Cr, Mn, Fe und Ni, die grösste Wirksamkeit besitzt. An der Oberfläche des Manganoxyds wird nämlich die Austauschreaktion schon bei 280°C. bemerkbar und oberhalb 400°C. die Reaktionsgeschwindigkeit so gross, dass das Austauschgleichgewicht sehr schnell erreicht wird. Über den Mechanismus dieser katalytischen Reaktion äusserten wir damals die Vermutung, dass die aktivierte Adsorption des Sauerstoffs an der Oberfläche des Manganoxyds eine massgebende Rolle spielen dürfte. Der Zweck der vorliegenden Versuche liegt deshalb darin, dass durch Sorptions- und Austauschversuche direkte experimentelle Beweise für diese Vermutung gesucht werden.

Über die Sorption des Sauerstoffgases durch Manganoxyd bei der Erhitzung des letzteren im Sauerstoffgas fehlte es bisher nicht an eingehenden Versuchen. Da aber bei manchen dieser Versuche das Experiment unter verhältnismässig kleinem Partialdruck von Sauerstoff (wie z.B. in verdünntem Sauerstoffgas bzw. in atmosphärischer Luft) durchgeführt wurde, so können wir deren Ergebnisse nicht ohne weiteres mit den der früher von uns ausgeführten Austauschversuche vergleichen. Die letzteren Versuche wurden nämlich immer unter dem etwa  $\frac{2}{3}$  atmosphärischen Partialdruck von Sauerstoff durchgeführt (vgl. IV. Mitteil.). Bei dem vorliegenden Versuche kommt deshalb zunächst (Teil I) die Sorption des Sauerstoffs durch Manganoxyd bei verschiedenen Temperaturen unter  $\frac{2}{3}$  atmosphärischem Druck zur Untersuchung. Anschliessend an diesen Sorptionsversuch wird dann die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und festem Manganoxyd unter den ähnlichen Versuchsbedingungen wie beim Sorptionsversuche untersucht (Teil II) und zum Schluss werden die beiden Versuchsergebnisse verglichen und diskutiert.

**1. Apparatur und Versuchsanordnung.** Um die Menge des Sauerstoffs, der durch eine bestimmte Menge von Manganoxyd unter verhältnismässig hohem Druck und bei hohen Temperaturen absorbiert wird, in Abhängigkeit von Zeit und Temperatur möglichst genau zu messen, wird eine Differentialmethode verwendet. Die dabei benutzte Apparatur wird in Abb. 1 schematisch erläutert. Das Sorptionsgefäss A, das das Manganoxyd enthält, und das leere Vergleichsgefäss B sind beide aus Quarz, während die sonstigen Teile der Apparatur aus Glas bestehen. Die beiden Gefässe A und B befinden sich in einem elektrisch erhitzten Thermostat O und können durch Schliff s,s mit Quecksilberdichtung sowie die mit drei Hähnen 1, 2 und 3 versehenen Glaskappillaren separat zu der mit Quecksilber gefüllten Gasbürette A' und B' bzw. zusammen zum (nicht in der Abb. gezeigten) Gasbehälter oder zur Vakuumpumpe geführt werden. Das Vergleichsmanometer M, das an seinem unteren Ende zusammen mit Gasbüretten A' und B' durch einen Gummischlauch zu einem gemeinsamen Quecksilberniveaugefäss N verbunden ist, führt an seinem oberen Ende zu einem (nicht in Abb. gezeigten) Manostat.



Da aber der Gasdruck in diesem Manostat auf einem gewünschten Druck konstant gehalten werden kann,<sup>(2)</sup> bleibt der Druck im Vergleichsmanometer M auch immer konstant. Die Höhe der Quecksilberniveaus in beiden Gasbüretten A' und B', die offensichtlich durch passende Handhabung des Niveaugefäßes N gleichzeitig mit dem in Vergleichsmanometer M



- A : Sorptionsgefäß.
- B : Vergleichsgefäß.
- A' : Zum Sorptionsgefäß gehörende Gasbürette.
- B' : Zum Vergleichsgefäß gehörende Gasbürette.
- M : Zum (nicht in Abb. gezeigten) Manostat führender Vergleichsmanometer.
- N : Quecksilberniveaugefäß.
- O : Elektrischer Ofen.
- 1. u. 2 : Einfache Hähne.
- 3 : Doppeldurchgebohrter Hahn.
- s, s : Schliffe mit Quecksilberdichtung.

Abb. 1. Sorptionsapparat.

ab- und aufgehoben werden können, werden auf einem für alle diese drei Rohre gemeinsamen Spiegelmasstab abgelesen, der dicht hinter den Rohren befestigt ist. Die Temperatur um diese Gasbüretten, die immer bei Zimmertemperatur gehalten ist, wird mit einem Quecksilberthermometer und die des elektrischen Ofens O, die während des Versuches allmählich gesteigert wird, mit einem Quecksilberthermometer bzw. mittels eines Platin/Platin-Rhodium-Thermoelements gemessen.

Um mit Hilfe dieser Apparatur die Menge des durch Manganoxyd absorbierten Sauerstoffs in Abhängigkeit von Zeit und Temperatur zu messen, wird zunächst eine bestimmte Menge Manganoxyd, das auf dem weiter unten zu erwähnenden Wege bereitet worden ist, in Sorptionsgefäß A eingewogen und dann die ganze Apparatur so weit wie möglich evakuiert, indem man sie durch Hähne 1, 2 und 3 mit der Vakuumpumpe verbindet. Während dieser Evakuierung wird aber der elektrische Ofen O bis auf 800°C. erhitzt, um dadurch die im benutzten Manganoxyd von vorn herein absorbiert enthaltenen Gase so weit wie möglich auszuschalten. Danach werden beide Hähne 1 und 2 (aber nicht Hahn 3!) aufgeschlossen und die Temperatur des Ofens wieder bis auf Zimmertemperatur gebracht. Wenn in dieser Weise die ganze Apparatur bis auf Zimmertemperatur abgekühlt worden ist, wird die Apparatur mit dem Behälter

(2) C.C. Coffin, *J. Am. Chem. Soc.*, **55** (1933), 3645; N. Morita, *J. Chem. Soc. Japan*, **56** (1935), 325.

des Sauerstoffgases verbunden, und man lässt das Gas durch Hähne 1, 2 und 3 in die ganze Apparatur d.h. in Gefässe A und B sowie in Gasbürette A' und B' einströmen. Aber so bald als die Quecksilberniveaus in beiden Gasbüretten A' und B' bis zu derselben Höhe wie im Vergleichsmanometer M herabgedrückt worden sind, werden beide Hähne 1 und 2 (aber nicht Hahn 3!) geschlossen und von diesem Zeitpunkt an beginnt nun der Versuch. Dieser wird nun derart ausgeführt, dass man die Temperatur des elektrischen Ofens O stufenweise bzw. möglichst langsam zum Steigen bringt (vgl. weiter unten Abb. 2 und 3) und zugleich die von Manganoxyd absorbierte Menge des Sauerstoffgases mit Hilfe der Gasbüretten A' und B' misst.

Das Sauerstoffgas fängt schon an bei dem Moment, wo es in die Apparatur eingeführt wird, durch das Manganoxyd absorbiert zu werden, weil Hahn 3 immer offen bleibt.<sup>(3)</sup> Dementsprechend steigt das Quecksilberniveau in Gasbürette A', die mit Sorptionsgefässe A verbunden ist, allmählich und unter den sonst gleich bleibenden Versuchsanordnungen müsste der Gasdruck in Bürette A' und folglich in Sorptionsgefäss A nach und nach abnehmen. Deshalb wird im wirklichen Fall Niveaugefäss N während des Versuches allmählich aufgehoben, so dass das Quecksilberniveau in Bürette A' immer gleich hoch wie das in Vergleichsmanometer M gehalten ist. Da aber dieses letztere Rohr M, wie schon oben erwähnt, mit einem Manostat verbunden ist und folglich der Gasdruck in diesem Manometer immer konstant bleibt, können wir auf diese Weise die Sorptionsgeschwindigkeit unter konstantem Druck bestimmen. In der Praxis halten wir den Druck im Manostat immer konstant bei 2/3 atmosphärischem Druck. Vergleichsgefäss B und die dazu gehörende Gasbürette B' werden mit dem Zweck eingeführt, um aus dem Unterschied zwischen den Ablesungen an Bürette A' und B' das Volumen des wirklich von Manganoxyd absorbierten Gases zu bestimmen (Differentialmethode!).<sup>(4)</sup> Deshalb wird die Niveauhöhe in Bürette B' auch möglichst

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(3) Bei dieser Versuchsanordnung wird deshalb immer eine kleine aber unbestimmte Menge des Gases zwischen dem Augenblick der Einführung des Gases in die Apparatur und dem Beginn des Sorptionsversuches durch Manganoxyd absorbiert. Aber diese Menge des Gases braucht man bei dem vorliegenden Versuche nicht in Rechnung bringen, weil es sich hier nicht um die Bestimmung einer absoluten Menge des absorbierten Gases sondern um ihrer Abhängigkeit von der Temperatur handelt. Wenn dagegen die erstere, d.h. die absolute Menge des bei einer bestimmten Temperatur durch Manganoxyd absorbierten Gases gemessen werden soll, kann die Versuchsanordnung wie folgt abgeändert werden, indem Doppelhahn 3 benutzt wird. Dieser wird nämlich nach der Evakuierung der ganzen Apparatur geschlossen und auf diese Weise nur Gasbüretten A' und B' (nicht aber Sorptionsgefäss A und Vergleichsgefäss B) resp. bis zu Hahn 1 und 2 mit dem betreffenden Gas ausgefüllt. Dann wird Hahn 3, nachdem Sorptionsgefäss A und Vergleichsgefäss B bis auf eine gewünschte Temperatur erhitzt worden ist, schnell geöffnet und das Volumen des Gases, das durch das in A befindliche Absorptionsmittel (wie z.B. Manganoxyd) absorbiert wird, genau so wie bei dem vorliegenden Versuche differentialmethodisch bestimmt.

(4) Selbstverständlich braucht man diese Differentialmethode nicht zu verwenden, wenn die absolute Menge des absorbierten Gases sehr gross ist, wie z.B. bei höheren Temperaturen in vorliegendem Versuche. Bei solch einem Fall kann man nämlich die absorbierte Menge des Gases allein mit Hilfe des Sorptionsgefässes A und die zugehöriger Gasbürette A' (aber nicht unter Benutzung des Vergleichsgefässes B und der Gasbürette B') ohne weiteres bestimmen. Über die dabei benutzte Rechnungsmethode vgl. z.B. J. Sameshima, *Bull. Chem. Soc. Japan*, **2** (1927), 2.

gleichzeitig wie Bürette A' abgelesen. Da aber das Quecksilberniveau in Bürette B', ausgenommen den ersten Augenblick beim Anfang des Versuches, sich offensichtlich nicht in derselben Höhe wie in Bürette A' bzw. Vergleichsmanometer M befindet, wird der Quecksilberkopf in Bürette B' bei seiner Ablesung augenblicklich in dieselbe Höhe wie Vergleichsmanometer M gebracht und nach der Ablesung wieder gesenkt. Auf diese Weise wird die Niveauhöhe in beiden Gasbüretten A' und B' von Zeit zu Zeit aber bei genau gemessenen Zeitpunkten verglichen, während die Temperatur des elektrischen Ofens O, in dem sich Sorptionsgefäß A und Vergleichsgefäß B befinden, stufenweise bzw. möglichst langsam von Zimmertemperatur bis auf die höchste benutzte Temperatur erhöht wird. Die Temperatur um Gasbüretten A' und B' sowie Vergleichsmanometer M wird dabei immer bei Zimmertemperatur gehalten.

**2. Ausrechnung der Sorptionsmenge.** Um aus den direkt abgelesenen Skalentellen an beiden Gasbüretten A' und B', die wir mit  $S_A$  und  $S_B$  bezeichnen wollen, das wirkliche Volumen  $V_A$  und  $V_B$  des in diesen beiden Büretten befindlichen Gases auszurechnen, wird angenommen, dass die letzteren als eine Funktion zweiter Ordnung der ersteren ausgedrückt werden können:

$$V_A = a_A S_A + b_A S_A^2 \quad \text{und} \quad V_B = a_B S_B + b_B S_B^2 \quad (1).$$

In diesen Gln. drücken  $a_A$ ,  $b_A$ ,  $a_B$  und  $b_B$  die auf beiden Büretten beziehenden Konstanten aus und können experimentell bestimmt werden. Wenn so das Volumen in beiden Gasbüretten A' und B' beim Anfang des Versuches<sup>(5)</sup> sowie bei einem anderen gewissen Zeitpunkt bestimmt wird, dann lässt sich das Volumen des Gases  $V_s$ , das zwischen diesen beiden Zeitpunkten durch Manganoxyd absorbiert wird, in erster Annäherung durch Gl. (2) angeben, wenn man dieses Volumen auf Normaltemperatur (0°C) bezieht:

$$V_s = (V'_B - V'_A) \frac{273}{273 + t'} - (V_B - V_A) \frac{273}{273 + t} \quad (2).$$

In dieser Gl. drückt  $V_A$ ,  $V_B$  und  $t$  resp. das Volumen in Bürette A' und B' sowie die Temperatur um Gasbüretten (Zimmertemperatur!) beim Anfang des Versuches und  $V'_A$ ,  $V'_B$  und  $t'$  (ebenfalls Zimmertemperatur!) die entsprechenden Werte bei einem bestimmten Zeitpunkt während des Versuches aus. Diese Gl. (2) ist aber, wie oben erwähnt, nur in erster Annäherung richtig, weil wir bei ihrer Ableitung den kleinen Unterschied des Volumens zwischen beiden Gefässen A und B sowie das Volumen des in Gefäß A befindlichen Manganoxys ausser Acht liessen. Die Korrektur gegen diese beiden Vernachlässigungen wird nun auf folgende Weise in Rechnung gebracht.

Erstens wird die Korrektur gegen den Unterschied des Volumens zwischen beiden Gefässen A und B experimentell bestimmt. Zu diesem Zweck wird das Manganoxyd im Sorptionsgefäß A abgeleert und dann

(5) D.h. beim Augenblick, wo beide Hähne 1 und 2 geschlossen werden.

dieses Gefäss A sowie Vergleichsgefäss B beide gleich mit  $2/3$  atmosphärischem Sauerstoffgas bei Zimmertemperatur  $T$  ausgefüllt. Wird nun die Temperatur des elektrischen Ofens O mit offen bleibendem Hahn 3 von Zimmertemperatur  $T$  bis auf eine bestimmte Temperatur  $T'$  erhöht, so wird ein Teil des in beiden Gefässen A und B befindlichen Gases wegen der Wärmeausdehnung aus diesen Gefässen A und B in beide Gasbüretten A' und B' ausgetrieben. Da aber die Volumen beider Gefässe A und B sowie ihrer Temperaturen miteinander nicht streng gleich sind, können die Volumen des Gases, das in beide Büretten A' und B' ausgetrieben worden ist, auch nicht immer miteinander gleich sein. Nimmt man deshalb an, dass das Volumen des Gases, das aus Sorptionsgefäss A in Bürette A' ausgetrieben wird, um  $\Delta V_1$  grösser als das des aus Vergleichsgefäss B in Bürette B' ausgetriebenen Gases ist, dann müssen wir diesen Unterschied  $\Delta V_1$  zu dem aus Gl. (2). ausgerechneten Volumen des absorbierten Gases  $V_s$  addieren:

$$V_s(\text{korr.}) = V_s + \Delta V_1 \quad (3).$$

In der Praxis haben wir in einem Vorversuch den Volumenunterschied  $\Delta V_1$  bei verschiedenen Ofentemperaturen  $T'$  gemessen und den ersteren gegen den Unterschied zwischen der betreffenden Temperatur  $T'$  und Zimmertemperatur  $T$  graphisch aufgetragen. Deshalb können wir beim Haupt- d.h. Sorptionsversuch die nötige Korrektur  $\Delta V_1$  bei einer bestimmten Ofentemperatur  $T'$  aus dieser Kurve ohne weiteres finden.<sup>(6)</sup>

Die zweite Korrektur  $\Delta V_2$ , die von dem durch Manganoxyd besetzten Volumen in Gefäss A herrührt, wird rechnerisch ermittelt.<sup>(7)</sup> Bezeichnet man nämlich mit  $V_m$  das Volumen des zum Versuch benutzten Manganoxys, so wird das gleiche Volumen des Gases in Gefäss A durch dieses feste Adsorptionsmittel ausgesperrt. Deshalb wird eine grössere Menge Sauerstoffgas in Vergleichsgefäss B als in Sorptionsgefäss A angesammelt und dementsprechend müssen grössere Mengen Sauerstoffgas aus dem ersteren in Bürette B' als aus dem letzteren in Bürette A' ausgetrieben werden, wenn die Temperatur des Ofens von Zimmertemperatur  $T$  bis auf eine bestimmte Temperatur  $T'$  erhöht wird. Dieser Volumenunterschied  $\Delta V_2$  beträgt aber offensichtlich:

$$\Delta V_2 = V_m \left( \frac{273 + T'}{273 + T} - 1 \right) \frac{273}{273 + T} \quad (4),$$

wenn man ihn auf Normaltemperatur ( $0^\circ\text{C}$ ) bezieht und weiterhin die geringe Wärmeausdehnung des festen Adsorptionsmittels d.h. Manganoxys ausser Acht lässt. Da diese zweite Korrektur  $\Delta V_2$  offensichtlich

(6) In Wirklichkeit erweist sich diese Korrektur  $\Delta V_1$  wegen des fast gleich grossen Inhalts beider Gefässe A und B im allgemeinen als sehr gering.

(7) Bei der vorliegenden Versuchsanordnung erweist sich diese zweite Korrektur  $\Delta V_2$  viel grösser als die oben angegebene erste Korrektur  $\Delta V_1$ . Eventuell kann man auch die Apparatur von vorn herein so konstruieren, dass beide Korrekturen  $\Delta V_1$  und  $\Delta V_2$  sich gegeneinander möglichst vollständig kompensieren. Zu diesem Zweck muss offensichtlich Sorptionsgefäss A bis zu einem gewissen Grad grösser als Vergleichsgefäss B geblasen werden.

von  $V_s$  aus Gl. (2) abgezogen werden soll, ergibt sich als die endgültige Formel für das korrigierte Volumen  $V_2$  (korr.) des absorbierten Gases die Gl.:

$$V_s(\text{korr.}) = V_s + \Delta V_1 - \Delta V_2 = \left\{ (V'_B - V'_A) \frac{273}{273 + t'} - (V_B - V_A) \frac{273}{273 + t} \right\} + \Delta V_{T'-T} - V_m \left( \frac{273 + T'}{273 + T} - 1 \right) \frac{273}{273 + T} \quad (5),$$

wo das Volumen  $\Delta V_{T'-T}$  die graphisch ermittelte erste Korrektur  $\Delta V_1$  bei Ofentemperatur  $T'$  bedeutet (vgl. oben). Bei dieser Ausrechnung von  $V_s$  wird die Wärmeausdehnung des Gases, das in dem Kapillarenteile der Apparatur enthalten ist, wenig berücksichtigt, weil erstens die beiden Kapillarenteile zwischen A und A' sowie B und B' gegeneinander möglichst ähnlich konstruiert sind und zweitens die Temperatur um diese Teile (Zimmertemperatur!) während des Versuches fast konstant bleibt.

**3. Sorptionsversuch I mit niedrigerem Oxyd des Mangans.** Das in diesem Versuch verwendete Manganoxyd wird auf folgendem Weg hergestellt. Die wässrige Lösung von reinem Mangan-(II)-nitrat wird zunächst mit Ammoniaklösung versetzt und der dabei entstandene Niederschlag von Manganoxhydroxyhydrat, nachdem er mit heissem destilliertem Wasser wiederholt gewaschen worden ist, im Trockenschrank bei 120°C möglichst vollständig getrocknet. Reines Manganoxyd wird dann aus diesem getrockneten Niederschlag dadurch gewonnen, dass man ihn in einem Quarzrohr unter vermindertem Druck etwa fünf Stunden lang bis auf etwa 500°C erhitzt. Aus dem so hergestellten Oxyd wird nun 11.2 g in Sorptionsgefäß A eingewogen und die ganze Apparatur möglichst vollständig evakuiert. Während dieser Evakuierung wird die Temperatur des elektrischen Ofens O, in dem sich Sorptionsgefäß A befindet, zunächst bis auf etwa 800°C erhöht. Da aber bei dieser Temperatur eine minimale Entwicklung des Gases (höchstwahrscheinlich wegen der thermischen Dissoziation des Manganoxys) noch nach fünf Stunden bemerkbar ist, wird die Temperatur des Ofens bald bis hinunter auf 500°C herabgesetzt. Durch diese Herabsetzung der Ofentemperatur hört jetzt die Gasentwicklung vollkommen auf und so wird ein sehr kleiner Druck (kleiner als ein tausendstel mm Hg!) in der Apparatur erreicht. Hierauf wird nun der elektrische Ofen O sofort bis hinunter auf Zimmertemperatur abgekühlt und nachdem die ganze Apparatur mit Sauerstoffgas bis 2/3 atmosphärischem Druck ausgefüllt worden ist, wird mit dem Sorptionsversuch begonnen, indem man die Temperatur des elektrischen Ofens O stufenweise steigen lässt und bei jeder stationär bleibenden Temperatur das Volumen des absorbierten Gases bestimmt. Die dabei gewonnenen Versuchsergebnisse sind in der nebenstehenden Abb. 2 graphisch angegeben. In dieser Abb. wird nämlich das Volumen des Gases, das vom Anfang bis zu einem gewissen Zeitpunkt während des Versuches durch ein Gramm Manganoxyd absorbiert worden ist, sowie die Temperatur des elektrischen Ofens bei jedem Zeitpunkt gegen die Versuchsdauer eingezeichnet. Dabei gibt Kurve I und II die Abhängigkeit des Volumens des

absorbierten Gases und Kurve III die der Ofentemperatur von der Versuchsdauer wieder.<sup>(8)</sup>

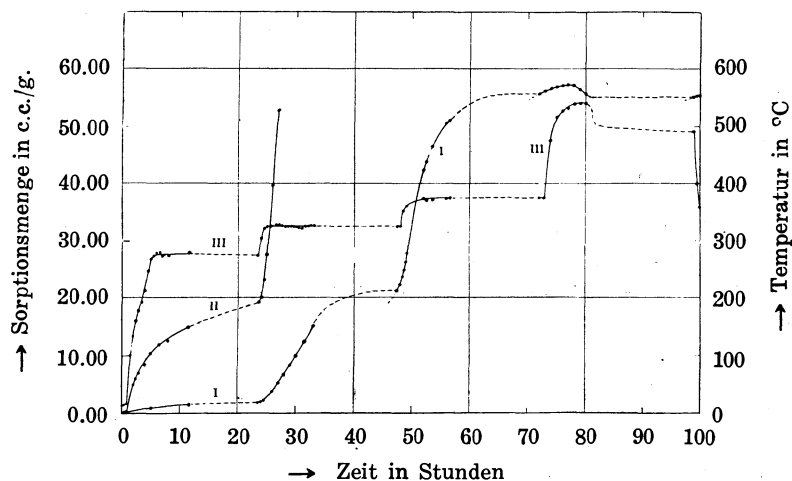


Abb. 2. Sörption des Sauerstoffgases durch niedrigeres Oxyd des Mangans.

- Kurve I. Zeitabhängigkeit der Sorptionsmenge.
- Kurve II. Zehnfache Vergrößerung von Kurve I.
- Kurve III. Zeitabhängigkeit der Ofentemperatur.

Wenn man die Form beider Kurven I (bzw. II) und III bei jedem entsprechenden Zeitpunkt auf der Abszisse vergleicht, wird ersichtlich, dass die Sorptionsgeschwindigkeit des Sauerstoffs bei Zimmertemperatur fast unmessbar klein und auch bei 275°C. noch sehr gering ist. Sie beträgt nämlich bei Zimmertemperatur (unter 2/3 atmosphärischem Druck und bei gewöhnlicher Temperatur gemessen) nur 0.04 c.c. pro Stunde pro g. Manganoxyd und bei 275°C. in derselben Einheit gemessen nur noch 0.1 c.c. pro Stunde. Wenn aber die Temperatur des Manganoxys bis auf 325°C. erhöht wird, nimmt die Sorptionsgeschwindigkeit ziemlich plötzlich zu. Sie beträgt z.B. bei dieser letzten Temperatur in derselben Einheit wie bei den oben genannten beiden Temperaturen gemessen ca. 1.5 c.c. pro Stunde pro g. Manganoxyd, d.h. sogar fünfzehnmal so gross wie bei 275°C. Deshalb darf wohl geschlossen werden, dass die merkliche Sorption des Sauerstoffgases durch Manganoxyd erst zwischen diesen beiden Temperaturen d.h. zwischen 275°C. und 325°C. eintritt. Von diesem Temperaturbereich an nimmt die Sorptionsgeschwindigkeit mit steigender Temperatur im steigenden Grade zu. Sie ist z.B. bei 360°C., wo der Gehalt des benutzten Manganoxys an Sauerstoff schon sehr gross sein muss, noch so gross wie 5 c.c. pro Stunde pro g. Manganoxyd. Diese Zunahme der absorbierten Menge des Gases mit

(8) Die punktierten Teile auf jeder Kurve in vorliegender Abb. 2 sowie in weiter unten gezeigter Abb. 3 entsprechen solchen Zeiten während der Versuche, wo die ganze Apparatur ohne Druckregulierung (aber bei fast konstant bleibender Temperatur) über Nacht stehen gelassen wurde.

steigender Temperatur dauert bis auf etwa 530°C. Aber wenn die Temperatur des Manganoxys diese letzte Temperatur überschreitet, tritt ziemlich plötzlich die Desorption des Sauerstoffs auf und ein Teil des bisher von Manganoxyd aufgenommenen Sauerstoffgases wird daraus abgeben, wie man dies aus der absteigenden Form der Kurve I in Abb. 2 bei diesem Temperaturbereich ersieht. Das so desorbierte Sauerstoffgas kann aber doch wieder vom Manganoxyd langsam aber untrüglich absorbiert werden, wenn die Temperatur des letzteren bis zu etwa 400°C. herabgesetzt wird. Weiter findet man, dass diese Abgabe und Aufnahme des Sauerstoffgases an demselben Manganoxyd beliebig oft wiederholt beobachtet werden kann, lässt man die Temperatur des letzteren nur abwechselnd ab- und aufsteigen.

Aus diesen Versuchsergebnissen wird ohne weiteres ersichtlich, dass die maximale Menge des Sauerstoffs, der unter den benutzten Versuchsbedingungen durch das Manganoxyd absorbiert wird, aus dem Volumen des Sauerstoffs sich leicht errechnen lässt, der vom Beginn des Versuches d.h. von Zimmertemperatur bis zur oben angegebenen maximalen Temperatur d.h. bis zu 530°C. von der benutzten Menge des Manganoxys aufgenommen wird. Dies entspricht etwa einem O-Atom pro vier Mn-Atom. Andererseits wird durch die chemische Analyse gefunden, dass dieses den Sauerstoff bis zur maximalen Grenze absorbierte Manganoxyd etwa die Zusammensetzung von  $\text{MnO}_{1.6}$  bis  $\text{MnO}_{1.7}$  besitzt. Aus diesen beiden Ergebnissen folgt deshalb, dass die Zusammensetzung des Präparats von Manganoxyd, das noch kein Sauerstoff absorbiert, d.h. direkt nach der Herstellung aus Manganoxxyhydrat, der Formel  $\text{MnO}_{1.4}$  nahe steht, d.h. Mangan-(III)-oxyd entsprechen muss. Da aber zur Herstellung dieses Oxyds, wie schon oben erwähnt, Mangan-(II)-nitrat verwendet wurde, muss geschlossen werden, dass  $\text{Mn}^{\text{II}}$  während des Prozesses zur Bereitung des Oxyds grösstenteils bis zu  $\text{Mn}^{\text{III}}$  oxydiert wird.

**4. Sorptionsversuch II mit höherem Oxyd des Mangans.** Aus vorhergehendem Versuch I wird gefunden, dass Mangan-(III)-oxyd  $\text{Mn}_2\text{O}_3$  unter den benutzten Versuchsbedingungen durch die Sorption des Sauerstoffs mindestens bis zu  $\text{MnO}_{1.6}$  bis  $\text{MnO}_{1.7}$  d.h. nahe bis zu Mangandioxyd  $\text{MnO}_2$  oxydiert wird. In vorliegendem Versuch II wird deshalb dieses höchste oxydierte Manganoxyd von vorn herein im Sorptionsgefäss bereitet und das Verhalten dieses Oxyds in 2/3 atmosphärischem Sauerstoffgas bei allmählich steigender Temperatur beobachtet. Zu diesem Zweck wird zunächst 5.7 g. Manganoxyd, das frisch aus Oxyhydrat bereitet worden ist, in Sorptionsgefäss A eingewogen und unter gleichzeitiger Ausfüllung der Apparatur mit 2/3 atmosphärischem Sauerstoff bei 400°C. so lange erhitzt, bis kein Sauerstoffgas mehr von dem Manganoxyd aufgenommen wird. Danach wird der Sorptionsversuch, nachdem die ganze Apparatur einmal wieder bis zu Zimmertemperatur abgekühlt worden ist, auf ganz ähnliche Weise wie bei Versuch I angefangen, indem die Sorptions- bzw. Desorptionsgeschwindigkeit des Sauerstoffgases unter konstantem 2/3 atmosphärischem Druck aber bei möglichst langsam steigender Temperatur gemessen wird. Die dabei gewonnenen Ergebnisse werden ebenfalls graphisch in Abb. 3 angegeben, wo Kurve I die Ab-

hängigkeit der adsorbierten Menge des Sauerstoffs und Kurve II die der Ofentemperatur von der Versuchsdauer wiedergibt.

Wenn man die Form beider Kurve I und II in Abb. 3 auf gleiche Weise wie in Abb. 2 bei jedem entsprechenden Zeitpunkt untereinander vergleicht, wird gefunden, dass das benutzte höhere Oxyd des Mangans ebenso wie das in vorhergehendem Versuch I benutzte niedrigere Oxyd eine kleine Menge Sauerstoff aufnimmt, lässt man die Temperatur des elektrischen Ofens allmählich steigen. Aber diese Sorption des Sauerstoffgases dauert dieses Mal nicht so lang. Wird nämlich die Ofentemperatur auf oberhalb von etwa 350°C. gesteigert, so tritt ziemlich plötzlich die Desorption des Sauerstoffs auf und ihre Geschwindigkeit nimmt mit steigender Temperatur heftig zu. Sie beträgt z.B. bei 500°C. sogar 0.4 c.c. pro Stunde pro g. Manganoxyd. Wenn man jedoch die Temperatur des Manganoxys wieder bis zu etwa 400°C. herabsinken lässt, dann tritt abermals eine geringe Absorption des Sauerstoffs auf, wie die aufsteigende Form des rechten Endes der Kurve I zeigt. Wir können deshalb auch in vorliegendem Versuch II mit höherem Oxyd des Mangans ebenso wie in vorhergehendem Versuch I mit niedrigerem Oxyd die reversible Absorption und Desorption des Sauerstoff an einem und demselben Manganoxyd bei höheren Temperaturen beobachten.

Über die Bedeutung dieser Erscheinung für die katalytische Austauschreaktion der O-Atome an der Oberfläche des Manganoxys soll in folgendem II. Teil gesprochen werden.

Herrn Prof. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkaih (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung dieser Arbeit ermöglicht haben, bin ich auch zu grossem Dank verpflichtet.

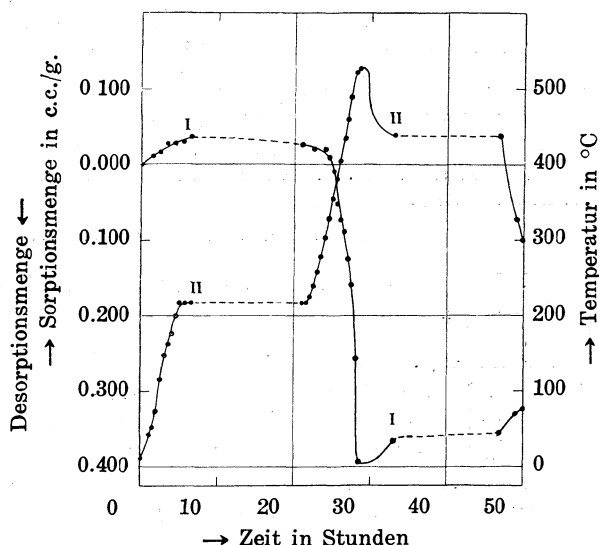


Abb. 3. Sorption des Sauerstoffgases durch höheres Oxyd des Mangans.

Kurve I. Zeitabhängigkeit der Sorptionsmenge.

Kurve II. Zeitabhängigkeit der Ofentemperatur.

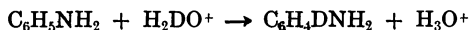


## Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in wässrigen Lösungen. I. Die Reaktion in neutraler und saurer Lösung.<sup>(1)</sup>

Von Masao KOIZUMI.

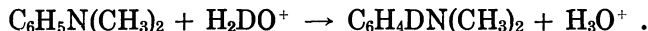
(Eingegangen am 15. November 1939.)

**Inhaltsübersicht.** Die Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in neutralen sowie sauren schwer-wässrigen Lösungen wird mit Hilfe der früher von Titani und dem Verfasser entwickelten Methode kinetisch verfolgt, indem man die Austauschgeschwindigkeitskonstante  $\bar{k}$  unter verschiedenen Versuchsbedingungen bestimmt. Dabei ergibt sich, dass die Geschwindigkeitskonstante  $k$ , die unter der Annahme berechnet wird, dass die Reaktion als die bimolekulare Reaktion zwischen Anilinchlorhydrat und Wasser verläuft, fast unverändert bleibt, wenn man der Konzentration des Anilinchlorhydrats sowie der Säure in Lösung einen ziemlich weiten Spielraum lässt. Daraus wird geschlossen, dass die grundlegende Reaktion nach dem Schema:



d.h. zwischen neutralen Anilinmolekülen und Hydroxo- bzw. Deuterioxoniumionen stattfindet.

**Einleitung.** Titani und der Verfasser<sup>(1)</sup> haben früher mitgeteilt, dass das Anilinchlorhydrat drei seiner – in *o*-, *o'*- und *p*-Stellung befindlichen<sup>(3)</sup> – Kernwasserstoffatome mit messbarer Geschwindigkeit gegen die des Wassers austauscht, wenn man dies in verdünntem schwerem Wasser auflöst und die so hergestellte Lösung etwa bei 80°C. einige Stunden lang stehen lässt. Später haben Ingold und seine Mitarbeiter<sup>(4)</sup> die relative Geschwindigkeit der Deuterierungsreaktion von verschiedenen Arten der monosubstituierten Benzolderivate durch ebenfalls verschiedene Arten der Deuterierungsmittel von saurem Charakter, wie z.B.  $\text{DHSO}_4$ ,  $\text{DH}_2\text{O}^+$  u.s.w., verglichen und kamen dadurch zu dem Schluss, dass alle diese Arten der Deuterierungsreaktion ihrer Charakteristik nach als eine Art elektrophile Substitutionsreaktion aufgefasst werden können. Die genannten Autoren nahmen z.B. an, dass die Austauschreaktion des Dimethylanilins in wässriger HCl-Lösung zwischen den freien Dimethylanilinmolekülen und Hydroxo- bzw. Deuterioxoniumionen verläuft:



Diese Annahme erscheint auch sehr plausibel. Doch weil die von diesen Autoren ausgeführten Versuche vielmehr noch von qualitativer

(1) In dieser sowie in den folgenden Mitteilungen wird die Lösung, die mit Säure bzw. Alkali versetzt wird, und die ohne jeden Zusatz einfachheitshalber als resp. saure, alkalische und neutrale Lösung bezeichnet, ohne Rücksicht darauf, ob die Lösung wirklich sauer, alkalisch bzw. neutral reagiert.

(2) M. Harada und T. Titani, dies Bulletin, **11** (1936), 554.

(3) Vgl. A.P. Best und C.L. Wilson, *J. Chem. Soc.*, **1938**, 28.

(4) C.K. Ingold, C.G. Raisin und C.L. Wilson, *J. Chem. Soc.*, **1936**, 1637.

Natur waren, ist es wünschenswert dieselben Versuche weiter nach der quantitativen Seite hin durchzuführen. Aus diesem Grunde wird in der vorliegenden Arbeit die Austauschreaktion des Anilinchlorhydrats in wässrigen Lösungen mit Hilfe der von Titani und dem Verfasser früher entwickelten Methode<sup>(5)</sup> kinetisch verfolgt, indem man die Austauschgeschwindigkeit unter verschiedenen Versuchsbedingungen quantitativ bestimmt.

**Versuchsanordnung.** Da die in der vorliegenden Arbeit benutzte Methode im grossen und ganzen dieselbe ist wie bei den früheren Versuchen mit Nitrophenol<sup>(6)</sup> und Phenol<sup>(7)</sup> berichtet wurde, wird die nähere Erklärung der benutzten Gln. u.s.w. auf dort verwiesen. Bei den Versuchen in neutralen Lösungen wird etwa 2 bis 3 g. (aber wohl abgewogene Menge) getrocknetes Anilinchlorhydrat in etwa 1 g. (ebenfalls wohl abgewogene Menge) verdünnten schweren Wassers aufgelöst und die so hergestellte Lösung wird in einem zugeschmolzenen und gut evakuierten Glassrohr bei verschiedener Temperatur verschiedener Zeitlänge stehen gelassen. Danach wird das Wasser durch die Destillation im Vakuum vom Anilinchlorhydrat abgetrennt und dann gereinigt. Dagegen bei den Versuchen in saurer Lösung, die man unter Benutzung des mit Salzsäure zugesetzten schweren Wassers auf ähnliche Weise wie bei der neutralen Lösung ausführt, wird das aus der Lösung im Vakuum abdestillierte Wasser zunächst unter Zusatz von gut entwässertem festem Kaliumcarbonat sorgfältig neutralisiert und erst dann auf übliche Weise gereinigt. In jedem Fall wird der D-Gehalt des verwendeten schweren Wassers vor ( $D_a$ ) und nach ( $D_e$ ) dem Versuch mittels eines Quarzschwimmers genau bestimmt und das Austauschäquivalent  $na$  des Anilinchlorhydrats wie üblich mittels Gl. (1) errechnet:

$$na = \frac{2(D_a - D_e)}{D_e} \frac{M_w}{M_{ac}} \quad (1).$$

In dieser Gl. bedeutet  $M_w$  und  $M_{ac}$  resp. die Molzahl des zum Versuch benutzten schweren Wassers und Anilinchlorhydrats und das Austauschäquivalent  $na$  wird durch Gl. (2) definiert:

$$na = \sum n_i a_i \quad (2),$$

wo  $n_i$  und  $a_i$  resp. die Anzahl und den Verteilungsquotient (V.Q.) der unter den angegebenen Versuchsbedingungen wirklich ausgetauschten Arten der H-Atome in einem organischen Molekül bedeutet und die Summation für alle austauschbaren Arten H-Atome in einem Molekül ausgeführt werden muss.

Wenn auf diese Weise das Austauschäquivalent  $na$  des Anilinchlorhydrats bei verschiedener Versuchsdauer  $t$  bestimmt wird, dann lässt sich die mittlere Geschwindigkeitskonstante  $\bar{k}$  für die Austauschreaktion der

(5) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 595.

(6) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 595, 631.

(7) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 681.

Kernwasserstoffatome mit Hilfe der folgenden drei Gln. (3) graphisch ermitteln:<sup>(8)</sup>

$$-X \log Y = \frac{\bar{k}}{2.303} t \quad (3a),$$

$$X = \frac{V}{\left( n_2 M_{ac} + \frac{\alpha_1}{\alpha_2} n_1 M_{ac} + \frac{2}{\alpha_2} M_w \right)} \quad (3b),$$

$$Y = \frac{1 - \frac{n\alpha - n_1\alpha_1}{n_2\alpha_2}}{1 + \frac{n\alpha - n_1\alpha_1}{\frac{2M_w}{M_{ac}} + n_1\alpha_1}} \quad (3c).$$

In diesen Gln. bedeutet  $n_1$  und  $\alpha_1$  resp. die Anzahl und den V.Q. der sehr schnell (fast momentan) austauschbaren H-Atome im betreffenden Molekül, dagegen  $n_2$  und  $\alpha_2$  die für die mit messbarer Geschwindigkeit austauschbaren H-Atome in demselben Molekül. Beim vorliegenden Fall mit Anilinchlorhydrat gehören zu den erstenen Arten der H-Atome offensichtlich drei an N gebundene Amidwasserstoffatome und zu den letzteren drei (in *o*-, *o'*- und *p*-Stellung befindlichen) Kernwasserstoffatome. Deshalb kann man  $n_1 = 3$ ,  $\alpha_1 = 1.1$  und  $n_2 = 3$ ,  $\alpha_2 = 0.9$  setzen.<sup>(9)</sup> Das im Zähler der Formel (3b) befindliche Volumen  $V$  der Lösung wird mit Hilfe der in Tabelle 1 angegebenen Daten über das spezifische Volumen einiger ausgewählter Lösungen von bekannter Zusammensetzung (eventuell unter Extra- bzw. Interpolation) rechnerisch gefunden.

Tabelle 1. Spezifisches Volumen der Lösung des Anilinchlorhydrats in Wasser bzw. in Salzsäure.

| Zusammensetzung der Lösung                                                                                                                                      | Gewichtsverhältnis des Anilinchlorhydrats zu Wasser | Temp. °C. | sp. Volumen |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|-----------|-------------|
| 2.25 g. C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> Cl + 1.00 g. H <sub>2</sub> O                                                                             | 2.25                                                | 79.5      | 0.9019      |
| „ „ „                                                                                                                                                           | „                                                   | 90.0      | 0.9069      |
| „ „ „                                                                                                                                                           | „                                                   | 100.0     | 0.9121      |
| 3.00 g. C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> Cl + 1.00 g. H <sub>2</sub> O                                                                             | 3.00                                                | 100.0     | 0.9028      |
| 2.25 g. C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> Cl + 1.00 g. 3N-HCl                                                                                       | 2.25                                                | 100.0     | 0.9012      |
| 1.79 g. C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> Cl + 1.00 g. H <sub>2</sub> O<br>+ 0.325 g. C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> <sup>(10)</sup> | —                                                   | 100.0     | 0.9070      |

(8) Vgl. Gl. (15) und (16) in der in Fussnote (5) referierten Mitteilung.

(9) Für diese Werte von V.Q.,  $\alpha_1$  und  $\alpha_2$  vgl. die in Fussnote (2) und (6) referierten Arbeiten.

(10) Dieses letzte Datum ist für die später zu veröffentlichen Versuche in alkalischer Lösung nötig.

Die mittlere Geschwindigkeitskonstante  $\bar{k}$ , die mit Hilfe der Gln. (3) ermittelt wird, entspricht aber, wie man dies aus der Ableitung dieser Gln. ohne weiteres ersieht, der einfachen stöchiometrischen Gl.:



Man nimmt nämlich vorläufig an, dass die Reaktion zwischen neutralen Anilinchlorhydratmolekülen und Wassermolekülen verläuft. Diese Annahme entspricht jedoch nicht immer (und zwar höchstwahrscheinlich nicht) der Wirklichkeit und dementsprechend kann die so ermittelte Konstante  $\bar{k}$  nicht immer von der Konzentration des Anilinchlorhydrats und (bei der Reaktion in saurer Lösung) der Säure unabhängig sein. Wir können deshalb unter Umständen über den Mechanismus der Reaktion Näheres kennen lernen, wenn man den Einfluss der Konzentration des Anilinchlorhydrats und der Säure auf die Konstante  $\bar{k}$  näher untersucht.

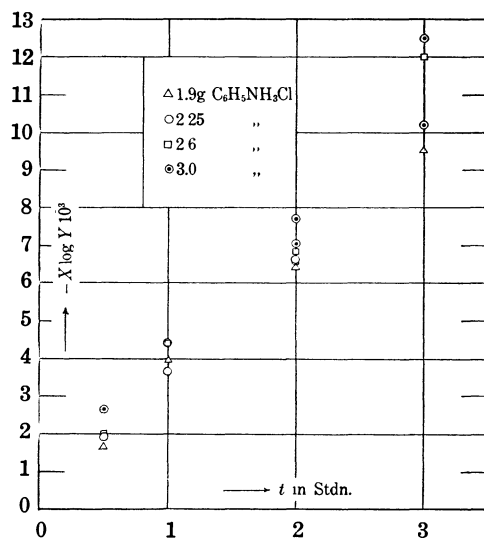
**Einfluss der Konzentration des Anilinchlorhydrats auf die Austauschgeschwindigkeit.** Um uns zunächst über den Einfluss der Konzentration des Anilinchlorhydrats auf die Austauschgeschwindigkeit Kenntnis zu verschaffen, werden die Versuche unter sonst möglichst konstant bleibenden Bedingungen (bei 100°C. und mit 1g. schweres Wasser) mit wechselnder Menge Anilinchlorhydrat durchgeführt. Die in der ersten Vertikalreihe der Tabelle 2 angegebenen Werte drücken die durchschnittliche Menge des Anilinchlorhydrats aus, die bei jeder Reihe der Versuche in 1g. schweres Wasser aufgelöst und damit ausgetauscht wird.

**Tabelle 2. Einfluss der Konzentration des Anilinchlorhydrats auf die Austauschgeschwindigkeit.**

| Gewichtsmenge<br>des benutzten<br>Anilin-<br>chlorhydrats | Versuchs-<br>dauer<br>in Stdn. | $M_{ac}$ | $M_w$  | $n\alpha$ | $-X \log Y \cdot 10^3$ | $(\bar{k}/2.303) \cdot 10^3$ |
|-----------------------------------------------------------|--------------------------------|----------|--------|-----------|------------------------|------------------------------|
| 1.9 g.                                                    | 0.5                            | 0.0146   | 0.0559 | 3.92      | 1.66                   | 3.3 ~ 3.4                    |
|                                                           | 1                              | 0.0147   | 0.0555 | 4.61      | 3.94                   |                              |
|                                                           | 2                              | 0.0147   | 0.0556 | 5.16      | 6.40                   |                              |
|                                                           | 3                              | 0.0147   | 0.0554 | 5.62      | 9.46                   |                              |
|                                                           | 6                              | 0.0147   | 0.0556 | 6.06      | —                      |                              |
| 2.25 g.                                                   | 0                              | 0.0174   | 0.0556 | 3.43      | —                      | 3.5 ~ 3.6                    |
|                                                           | 0.5                            | 0.0174   | 0.0563 | 3.98      | 1.92                   |                              |
|                                                           | 1                              | 0.0174   | 0.0559 | 4.50      | 3.64                   |                              |
|                                                           | 2                              | 0.0174   | 0.0554 | 5.16      | 6.63                   |                              |
|                                                           | 3                              | 0.0174   | 0.0554 | 5.69      | 10.6                   |                              |
|                                                           | 6                              | 0.0174   | 0.0558 | 6.18      | —                      |                              |
|                                                           | 6                              | 0.0174   | 0.0558 | 6.28      | —                      |                              |
|                                                           | 10                             | 0.0174   | 0.0562 | 6.37      | —                      |                              |
|                                                           | 25                             | 0.0174   | 0.0562 | 6.43      | —                      |                              |

Tabelle 2. (Fortsetzung)

| Gewichtsmenge<br>des benutzten<br>Anilin-<br>chlorhydrats | Versuchs-<br>dauer<br>in Stdn. | $M_{ac}$ | $M_w$  | $n^a$ | $-X \log Y \cdot 10^3$ | $(\bar{k}/2.303) \cdot 10^3$ |
|-----------------------------------------------------------|--------------------------------|----------|--------|-------|------------------------|------------------------------|
| 2.6 g.                                                    | 0.5                            | 0.0201   | 0.0556 | 4.00  | 2.00                   | 3.5 ~ 3.9                    |
|                                                           | 1                              | 0.0201   | 0.0556 | 4.66  | 4.40                   |                              |
|                                                           | 2                              | 0.0201   | 0.0555 | 5.16  | 6.85                   |                              |
|                                                           | 2                              | 0.0201   | 0.0560 | 5.20  | 6.60                   |                              |
|                                                           | 3                              | 0.0202   | 0.0552 | 5.78  | 12.0                   |                              |
|                                                           | 6                              | 0.0201   | 0.0552 | 6.26  | —                      |                              |
| 3.0 g.                                                    | 0                              | 0.0232   | 0.0556 | 3.43  | —                      | 3.6 ~ 4.0                    |
|                                                           | 0.5                            | 0.0232   | 0.0556 | 4.14  | 2.64                   |                              |
|                                                           | 1                              | 0.0232   | 0.0555 | 4.61  | 4.41                   |                              |
|                                                           | 1                              | 0.0232   | 0.0553 | 4.62  | 4.45                   |                              |
|                                                           | 2                              | 0.0232   | 0.0556 | 5.25  | 7.70                   |                              |
|                                                           | 2                              | 0.0232   | 0.0560 | 5.15  | 7.03                   |                              |
|                                                           | 3                              | 0.0232   | 0.0554 | 5.80  | 12.5                   |                              |
|                                                           | 3                              | 0.0232   | 0.0555 | 5.58  | 10.2                   |                              |
|                                                           | 3                              | 0.0232   | 0.0558 | 5.58  | 10.2                   |                              |
|                                                           | 6                              | 0.0232   | 0.0552 | 6.20  | —                      |                              |
|                                                           | 6                              | 0.0232   | 0.0560 | 6.18  | —                      |                              |

Abb. 1. Beziehung zwischen der Quantität  $(-X \log Y)$  und Versuchsdauer ( $t$ ) bei verschiedenen Konzentrationen des Anilinchlorhydrats.

Die in der letzten Spalte der Tabelle angegebene mittlere Geschwindigkeitskonstante  $\bar{k}$  wird unter Benutzung der nebenstehenden Abb. 1 graphisch bestimmt, da die Neigung der  $(X \log Y) - t$  Kurve, wie aus der Form der Gl. (3a) offensichtlich ist, ohne weiteres die Konstante  $\bar{k}$  angibt. Die so bestimmte Konstante  $\bar{k}$  ergibt sich aber fast unabhängig von der Konzentration des Anilinchlorhydrats.<sup>(11)</sup> Oder wenn man die verhältnismässig grobe Natur dieser Art der Bestimmung von  $\bar{k}$  in Rechnung zieht, darf wohl geschlossen werden, dass die Konstante  $\bar{k}$  von der Konzentration des Anilinchlorhydrats praktisch unabhängig ist.

#### Einfluss der Säurekonzentration auf die Austauschgeschwindigkeit

(11) Wir können in Wirklichkeit eine kleine anwachsende Neigung von  $\bar{k}$  mit zunehmender Konzentration des Anilinchlorhydrats bemerken. Aber diese Neigung ist viel zu unbedeutend, um daraus ohne weiteres irgendeinen Schluss zu ziehen.

igkeit. Bei diesen Versuchen benutzt man statt neutralen schweren Wassers das durch den Zusatz von Salzsäure verschieden stark (1N, 2N und 3N) angesäuerte schwere Wasser. Etwa 1 g. (aber wohl abgewogene

Tabelle 3. Einfluss der Säurekonzentration auf die Austauschgeschwindigkeit.

| HCl-Normalität<br>im benutzten<br>schweren Wasser | Versuchs-<br>dauer<br>in Stdn.          | $M_{ac}$ | $M_w$  | $n\alpha$ | $-X \log Y \cdot 10^3$ | $(\bar{k}/2.303) \cdot 10^3$ |
|---------------------------------------------------|-----------------------------------------|----------|--------|-----------|------------------------|------------------------------|
| 0 N                                               | Vgl. dritte Versuchsreihe in Tabelle 2. |          |        |           |                        | 3.5 ~ 3.6                    |
| 1 N                                               | 1                                       | 0.0174   | 0.0544 | 4.43      | 3.46                   | 3.0 ~ 3.5                    |
|                                                   | 2.25                                    | 0.0174   | 0.0542 | 5.20      | 6.88                   |                              |
|                                                   | 3                                       | 0.0174   | 0.0545 | 5.43      | 8.45                   |                              |
|                                                   | 6                                       | 0.0174   | 0.0553 | 6.20      | —                      |                              |
| 2 N                                               | 1                                       | 0.0174   | 0.0542 | 4.40      | 3.4                    | 3.1 ~ 3.2                    |
|                                                   | 2                                       | 0.0174   | 0.0537 | 4.99      | 5.85                   |                              |
|                                                   | 3                                       | 0.0174   | 0.0538 | 5.52      | 9.26                   |                              |
|                                                   | 5                                       | 0.0174   | 0.0536 | 6.07      | —                      |                              |
| 3 N                                               | 0.5                                     | 0.0174   | 0.0537 | 3.94      | 1.79                   | 3.3 ~ 3.5                    |
|                                                   | 1                                       | 0.0174   | 0.0537 | 4.34      | 3.18                   |                              |
|                                                   | 1                                       | 0.0174   | 0.0534 | 4.45      | 3.52                   |                              |
|                                                   | 1.5                                     | 0.0174   | 0.0534 | 4.78      | 4.88                   |                              |
|                                                   | 2.5                                     | 0.0174   | 0.0537 | 5.32      | 7.73                   |                              |
|                                                   | 3                                       | 0.0174   | 0.0537 | 5.68      | 10.6                   |                              |
|                                                   | 6                                       | 0.0175   | 0.0535 | 6.02      | —                      |                              |

Menge) dieser Lösung wird bei 100°C. immer gegen 2.25 g. Anilinchlorhydrat ausgetauscht. Die sonstige Arbeitsweise ist genau dieselbe wie bei den vorhergehenden Versuchen in neutraler Lösung. Die bei der vorliegenden Versuchen erhaltenen Ergebnisse sind in Tabelle 3 zusammengestellt, wo die erste Vertikalreihe die Konzentration der Salzsäure in bei allen Reihen der Versuche verwendetem schwerem Wasser angibt und die in der letzten Spalte der Tabelle angegebene Geschwindigkeitskonstante  $\bar{k}$  unter Benutzung der nebenstehenden Abb. 2 graphisch ermittelt wird.

Aus diesen Ergebnissen darf wohl geschlossen werden, dass die Geschwindigkeitskonstante  $k$  ebenso wenig wie durch die Veränderung der Konzentration des Anilinchlorhydrats auch durch die der Säurekonzentration beeinflusst wird.

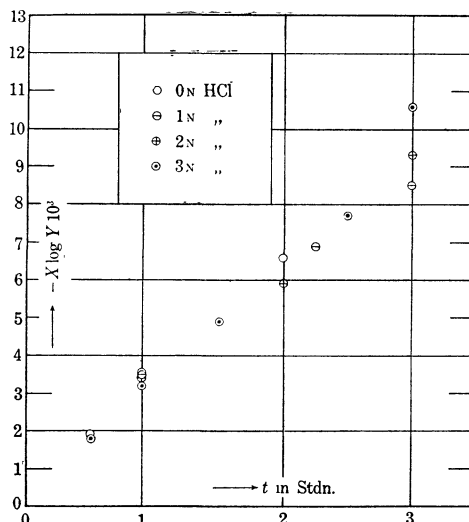


Abb. 2. Beziehungen zwischen der Quantität ( $-X \log Y$ ) und Versuchsdauer ( $t$ ) bei verschiedenen Säurekonzentrationen.

**Diskussion.**<sup>(12)</sup> Wir haben oben gefunden, dass die mittlere Austauschgeschwindigkeitskonstante  $\bar{k}$  fast unabhängig von der Konzentration des Anilinchlorhydrats und der Säure konstant bleibt. Diese Konstante  $\bar{k}$  ist aber, wie schon oben darauf hingewiesen, nur für die stöchiometrische Gl. (4) gültig und dementsprechend wird diese  $\bar{k}$  durch Gl. (5) definiert:<sup>(13)</sup>

$$-\frac{d[[\text{HDO}]]}{dt} = \bar{k}n_2 [[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]] [[\text{HDO}]] - (\text{Gegenreaktion}) \quad (5),$$

wo die Formel in den doppelten Klammern  $[[ \quad ]]$  die zum Austausch effektive analytische Konzentration der betreffenden Substanz ausdrückt und  $n_2$  die Anzahl der austauschbaren Kernwasserstoffatome in einem organischen Molekül bedeutet (deshalb  $n_2 = 3$ ). Weil aber die wirkliche Austauschreaktion als eine Art zwischen Protonacceptoren und -donatoren verlaufende elektrophile Substitutionsreaktion aufgefasst werden darf, können wir im vorliegenden Fall folgende fünf Arten der Moleküle und Ionen als die Reaktionsteilnehmer in Betracht ziehen:

Protonacceptor:  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_3^+$ ,

Protodonator:  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_5\text{NH}_3^+$ .

Unter diesen Molekül- und Ionenarten werden die neutralen Anilinmoleküle  $\text{C}_6\text{H}_5\text{NH}_2$  und die Hydroxoniumionen  $\text{H}_3\text{O}^+$  durch die Hydrolyse der Aniliniumionen  $\text{C}_6\text{H}_5\text{NH}_3^+$  erzeugt:



Deshalb muss zwischen den Konzentrationen dieser vier Arten der Moleküle und Ionen die Beziehung bestehen:

$$\frac{[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{H}_2\text{O}]} = \text{Konst.}$$

Besonders wenn es sich um die reine Lösung des Anilinchlorhydrats in (schwerem) Wasser handelt, d.h. es keinen weiteren Zusatz gibt, muss deshalb die Beziehung bestehen:

$$[\text{H}_3\text{O}^+] = \text{Konst} \sqrt{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{H}_2\text{O}]} \quad (7),$$

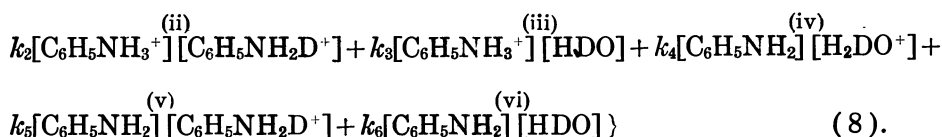
da in diesem Fall offensichtlich  $[\text{C}_6\text{H}_5\text{NH}_2] = [\text{H}_3\text{O}^+]$  ist.

Unter dieser Annahme können wir nun die durch Gl. (5) definierte mittlere Geschwindigkeitskonstante  $\bar{k}$  im allgemeinen wie folgt setzen:

$$\bar{k} = \frac{1}{[[\text{HDO}]] [[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]]} \{ k_1 [\text{C}_6\text{H}_5\text{NH}_3^+]^{(i)} [\text{H}_2\text{DO}^+] +$$

(12) Über die weiter unten zu erwähnende Diskussion vgl. auch die in Fussnote (6) und (7) referierten Arbeiten.

(13) Aus dieser Gl. (5) wird ersehen, dass die Konstante  $k$  die *mittlere* Austauschgeschwindigkeitskonstante der  $n_2$  Stücke Kernwasserstoffatome ausdrückt.



In dieser Gl. drückt die Formel in den doppelten Klammern  $[[ \quad ]]$  die zum Austausch effektive analytische Konzentration und die in den einfachen Klammern  $[ \quad ]$  die wirklich in der Lösung bestehende Konzentration aller Molekül- bzw. Ionenarten aus. Unter diesen sechs Teilreaktionen (i) bis (vi) können wir aber die letzte Reaktion (vi) ohne weiteres ausser Acht lassen, weil zwischen Anilin und Wasser in Wirklichkeit keine merkliche Austauschreaktion der Kernwasserstoffatome stattfindet.<sup>(14)</sup> Deshalb haben wir nur noch fünf Teilreaktionen übrig, um zu entscheiden, welche Reaktion beim wirklichen Austausch eine Hauptrolle spielt. Wäre es nun die erste Reaktion (i), dann müsste die direkt gemessene mittlere Geschwindigkeitskonstante  $\bar{k}$  durch die Veränderung der Konzentration der Reaktionsteilnehmer gemäss Gl. (9) beeinflusst werden, wie aus der oben angegebenen Gl. (8) ohne weiteres ersichtlich ist:

$$\bar{k}(i) = k_1 \frac{[\text{C}_6\text{H}_5\text{NH}_3^{+}][\text{H}_2\text{DO}^{+}]}{[[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]] [[\text{HDO}]]} \quad (9).$$

In dieser Gl. (9) bedeutet  $\bar{k}(i)$  die mittlere Geschwindigkeitskonstante  $\bar{k}$ , die sich ergeben würde, wenn die Teilreaktion (i) die Hauptreaktion wäre. Setzt man nun in diese Gl. (9) in erster Annäherung  $[\text{C}_6\text{H}_5\text{NH}_3^{+}] = [[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]]$  und zieht weiter die Beziehung (7) in Rechnung, so folgt, dass

$$\bar{k}(i) \approx k_1 \frac{[\text{H}_2\text{DO}^{+}]}{[[\text{HDO}]]} \infty \frac{[\text{H}_3\text{O}^{+}]}{[[\text{H}_2\text{O}]]} \infty \sqrt{\frac{[\text{C}_6\text{H}_5\text{NH}_3^{+}]}{[[\text{H}_2\text{O}]]}} \infty \sqrt{\frac{[[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]]}{[[\text{H}_2\text{O}]]}} \quad (10a) \text{ ist,}$$

wenn die D-Konzentration in der Lösung immer konstant gehalten wird. Auf ähnliche Weise kommt man zu dem Schluss, dass eine der folgenden Beziehungen bestehen müsste, je nachdem ob die zweite, dritte, vierte bzw. fünfte Teilreaktion in Gl. (8) beim wirklichen Austausch die Hauptrolle spielt:

$$\bar{k}(\text{ii}) \infty \frac{[[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]]}{[[\text{H}_2\text{O}]]}, \quad (10b),$$

$$\bar{k}(\text{iii}) \text{ und } \bar{k}(\text{iv}) \approx \text{Konst.}, \quad (10c),$$

$$\bar{k}(\text{v}) \infty \sqrt{\frac{[[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}]]}{[[\text{H}_2\text{O}]]}} \quad (10d).$$

Wenn man deshalb unter sonst konstant gehaltenen Versuchsbedingungen (konstante Wassermenge!) die Menge des Anilinchlorhydrats von 1.9 g. bis auf 3.0 g. vermehrt, müsste die mittlere Geschwindigkeits-

(14) M. Harada und T. Titani, dies Bulletin, **11** (1936), 470.



konstante  $\bar{k}$  oder  $\bar{k}(i)$ ,  $\bar{k}(ii)$ ,  $\bar{k}(iii)$ ,  $\bar{k}(iv)$  und  $\bar{k}(v)$  resp. sich um 1.25, 1.57, 1.00, 1.00 und 1.25-fach vergrössern, je nachdem ob die Teilreaktion (i), (ii), (iii), (iv) oder (v) die Hauptreaktion wäre.

Bei den oben in Tabelle 2 angegebenen Versuchen haben wir unter den sonst möglichst konstant gehaltenen Versuchsbedingungen die benutzte Menge des Anilinchlorhydrats von 2 g. in 1 g. Wasser bis auf 3 g. in derselben Menge Wasser erhöht und fanden dadurch, dass die Geschwindigkeitskonstante  $\bar{k}$  fast unverändert bleibt. Wenn man deshalb diese Versuchsergebnisse mit den eben erwähnten Schlüssen vergleicht, dann können wir die Teilreaktion (ii) sicher ausschliessen, weil, falls diese die Hauptreaktion wäre, die mittlere Geschwindigkeitskonstante  $\bar{k}$  unter den benutzten Versuchsbedingungen sogar um 1.57-fach zunehmen müsste.

Es bleiben auf diese Weise nur noch vier Reaktionen (i), (iii), (iv) und (v) zu betrachten übrig. Um zwischen diesen vier Möglichkeiten zu unterscheiden, müssen wir aber weiter die Versuchsergebnisse in Rechnung ziehen, die wir unter Benutzung verschieden starker HCl-Lösung gewonnen haben (vgl. Tabelle 3). Unter diesen Versuchsbedingungen wurde ebenfalls gefunden, dass die mittlere Geschwindigkeitskonstante  $\bar{k}$  von der Säurekonzentration fast unabhängig ist. Durch den Zusatz von Salzsäure wird die Konzentration der Aniliniumionen  $[C_6H_5NH_3^+]$  sowie die des Wassers  $[H_2O]$  wohl nicht beeinflusst. Dagegen muss die Konzentration der Hydroxoniumionen  $[H_3O^+]$  mit der zugesetzten Menge der Säure proportional zunehmen und die der neutralen Anilinmoleküle  $[C_6H_5NH_2]$  umgekehrt proportional abnehmen. Daraus folgt, dass das Produkt  $[C_6H_5NH_3^+][H_2DO^+]$  in Teilreaktion (i) in Gl. (8) durch den Zusatz der Salzsäure in seiner Konzentration proportional zunimmt, das Produkt  $[C_6H_5NH_3^+][HDO]$  in (iii) sowie  $[C_6H_5NH_2][H_2DO^+]$  in (iv) fast unverändert bleibt und zum Schluss das Produkt  $[C_6H_5NH_2][C_6H_5NH_2D^+]$  in (v) umgekehrt proportional abnehmen muss. Da aber in Wirklichkeit die gefundene Konstante  $\bar{k}$  fast unabhängig von der Säurekonzentration konstant bleibt, kommt man ohne weiteres zu dem Schluss, dass Teilreaktion (iii) bzw. (iv) die Hauptrolle spielen muss. Zwischen diesen beiden Reaktionen können wir aber auf rein experimentellem Weg noch zu keiner endgültigen Unterscheidung kommen, weil die Reaktionsteilnehmer in den beiden Reaktionen durch das Gleichgewicht (6) miteinander verknüpft sind und folglich das Produkt  $[C_6H_5NH_3^+][HDO]$  gegen  $[C_6H_5NH_2][H_2DO^+]$  immer in konstantem Verhältnis steht. Wenn man jedoch die Tatsache in Rechnung zieht, dass Hydroxoniumionen viel kräftigere Protonendonatoren als neutrale Wassermoleküle sind, bleibt nur Teilreaktion (iv) als die Hauptreaktion übrig; die Austauschreaktion der Kernwasserstoffatome zwischen Anilinchlorhydrat und Wasser kann als die zwischen neutralen Anilinmolekülen und Deuteroxoniumionen verlaufende bimolekulare Reaktion aufgefasst werden:



In dieser Hinsicht stimmen nämlich die vorliegenden Versuchsergebnisse mit der vorläufigen Annahme von Ingold und seinen Mitarbei-

tern<sup>(3)</sup> sehr gut überein, die sie durch die halbquantitativen Versuche mit Dimethylanilin gewonnen haben. Aber über die Annahme, ob derselbe Mechanismus sich auch in alkalischer Lösung abspielt, lässt sich ohne weiteres nichts Bestimmtes sagen, bis eingehendere Versuche in alkalischer Lösung ausgeführt werden. Über diese Versuche soll später in II. Mitteil. berichtet werden.

Zum Schluss möchte ich Herrn Prof. T. Titani für seine wertvollen Ratschläge und stetige Unterstützung bei der Durchführung der vorliegenden Arbeit meinen herzlichsten Dank aussprechen. Zugleich bin ich der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der Wissenschaft) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung zu bestem Dank verpflichtet.

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## Studies on Luminescent Materials. Part 1. Theory of Zinc Sulphide-copper Crystal Phosphor.

By Yasuo UEHARA.

(Received November 15, 1939.)

**Introduction.** Crystals which can emit all kinds of excitation energy which they absorbed as the light energy, are called crystal phosphors. Of such phosphors, especially zinc sulphide phosphors have been extensively investigated, since they are theoretically important as well as technically. Most of the studies on the zinc sulphide phosphors, however, were restricted in the description of the properties of the phosphors and they have not been able to give a fairly complete picture of the mechanism of fluorescence and photoconductivity, and of many other behaviours of the phosphors.

In the present paper, the author wish to propose a picture of the zinc sulphide-copper crystal phosphor, based on the quantum mechanical theory of solid state, which can explain the mechanism of fluorescence and phosphorescence, the distribution of fluorescence- and excitation-bands, photoconductivity, and many other behaviours of the phosphors.

The treatment is similar in some way to that of F. Seitz<sup>(1)</sup> which was reported while this paper was written, but the mechanism of fluorescence and the interpretation of the properties of the phosphors,

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(1) F. Seitz: *J. Chem. Phys.*, **6** (1938), 454; **6** (1938), 150.

proposed by the author, are different from that of F. Seitz, as we shall see in the following sections.

**Theory.** (a) Energy levels in the zinc sulphide-copper crystal phosphor. Let us consider electrons moving in the self-consistent field  $V(\mathbf{r})$  in the crystal which has the same periodicity and symmetry with the crystal lattice. If we assume that  $V(\mathbf{r})$  is large near the lattice point (and falls rapidly with distance, we can solve the Schrödinger equation) by the Wilson-Bloch's method.<sup>(2)</sup>

We shall first deal with the state whose wave function of atom  $\phi(\mathbf{r})$  is spherically symmetrical. For the energy value, we can obtain the following results.

In a simple cubic lattice

$$E = E_0 - \alpha - 2\gamma(\cos \bar{f}_x a + \cos \bar{f}_y a + \cos \bar{f}_z a),$$

in a body-centred cubic lattice

$$E = E_0 - \alpha - 8\gamma \left( \cos \frac{1}{2} \bar{f}_x a + \cos \frac{1}{2} \bar{f}_y a + \cos \frac{1}{2} \bar{f}_z a \right),$$

in a face-centred cubic lattice

$$E = E_0 - \alpha - 4\gamma \left( \cos \frac{1}{2} \bar{f}_x a \cos \frac{1}{2} \bar{f}_y a + \cos \frac{1}{2} \bar{f}_x a \cos \frac{1}{2} \bar{f}_z a + \right. \\ \left. \cos \frac{1}{2} \bar{f}_y a \cos \frac{1}{2} \bar{f}_z a \right)$$

$$\text{with } -\alpha = \int \phi_g^*(\mathbf{r}) \{ V(\mathbf{r}) - U_g(\mathbf{r}-\mathbf{g}) \} \phi_g d\tau,$$

$$-\gamma = \int \phi_g^*(\mathbf{r}) \{ V(\mathbf{r}) - U_g(\mathbf{r}-\mathbf{g}) \} \phi_g d\tau,$$

$\bar{f}$  = wave number,  $\mathbf{g}, \mathbf{h}$  = lattice vector,

$a$  = lattice constant,

$\phi$  = eigenfunction of the isolated atom,

$U_g$  = potential function of the isolated atom.

By the same method, we can obtain the energy value in the crystal for the wave function of  $p$ - or  $d$ -state.

As the results, we can say that the energy of an electron in the crystal consists of a constant term  $E_0 - \alpha$ , together with a term which depends on the wave number.  $E_0$  is the electronic energy of an isolated atom.  $\alpha$  is the mean value of the potential energy which is due to all the neighbouring atoms, and it is approximately given by the Madelung energy, in the ionic crystals, if we neglect the polarisation energy.  $\gamma$  which is represented by the exchange integral, defines the breadth of

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(2) Hand. d. Physik, 24/2 (1933), 394.

the energy band and it will be greater the more the wave functions overlap.

Thus we see that, if we consider the forces due to the neighbouring atoms, each energy level of the electron splits into a number of levels forming a band in the crystal.

Let us obtain the energy value of  $E_0 - a$  in the zinc sulphide crystal phosphors and of the impurity level arising from the copper which is added to the phosphors as an activator, by the following considerations.

There are two crystal forms in the zinc sulphide crystal phosphors,

(1) Zinc blende, cubic system, it is formed above the temperature of  $1015^\circ - 1024^\circ\text{C}.$ <sup>(3)</sup>

(2) Wurzite, hexagonal system, it is formed below the temperature of  $1015^\circ - 1024^\circ\text{C}.$ <sup>(3)</sup>

These two crystal forms of the zinc sulphide phosphors show the same properties as the luminescent materials,<sup>(4)</sup> and in fact, we can obtain the same results for the two crystal forms, in the zero order approximation, by the following calculations. Therefore we shall deal only with the zinc blende crystal.

We can consider the zinc sulphide crystals as the nearly ionic crystal, since it has "Reststrahlen" at  $31\mu$ <sup>(5)</sup> and trigonal polar axis of symmetry.<sup>(6)</sup>

In the ionic crystals, Madelung energy is given by the theory of Hund<sup>(7)</sup> as follows:

$$W = \frac{ZAe^2}{r} \quad (4),$$

where  $Z$  is valence of ions in the lattice point,  $r$  is the shortest distance between the nearest unlike ions, and  $e$  is electronic charge.

Putting into (4)  $r = 2.35\text{\AA}$ ,  $Z = 2$  and  $A = 1.6831$  for the zinc blende, we obtain  $W = 19.9\text{ eV}$ .

As the results, the energy of electrons on positive ions is increased by the amount of 19.9 eV and that on negative ions is decreased by the same amount in the zinc blende crystal.

If we assume that the electron affinity of ions in the crystal is approximately equal to the ionization energy of the free ions,<sup>(1),(8),(9)</sup> we can obtain the energy levels of the ions in the crystal by the algebraic sum of the electron affinity and Madelung energy, i.e. by  $E - a$ .

The energy levels in the crystal broaden into bands by the zone-theory and we can estimate the broadening roughly. The energy levels in the zinc sulphide-copper crystal phosphors are shown in Fig. 1.

In Fig. 1 the lowest energy band is  $3d^{10}$ -band of  $\text{Zn}^{++}$  ions which is completely occupied by ten electrons. The energy immediately above the  $d$ -band of  $\text{Zn}^{++}$  ions is  $4p^6$ -band of  $\text{S}^-$  ions which is completely occupied by six electrons. These two bands are narrow compared with the conduction band.

(3) E. T. Allen, J. L. Creshaw: *Z. anorg. Chem.*, **79** (1920), 186.

(4) E. Tiede, A. Schleede: *Ber.*, **53** (1920), 1721.

(5) K. Forsterling: *Z. Physik*, **8** (1922), 251.

(6) P. P. Ewald: "Kristalle u. Röntgenstrahlen," Berlin, (1923), 186.

(7) F. Hund: *Z. Physik*, **34** (1925), 833.

(8) J. H. De Boer, E. J. W. Verwey: *Proc. Phys. Soc. (London)*, **49** (1937), 59.

(9) N. F. Mott: *Trans. Faraday Soc.*, **34** (1938), 500.

Levels about 9 and 13 eV above the  $S^{--}$ -band are respectively 1st and 2nd excited levels of  $Zn^{++}$  ions. The uppermost band is  $4s$ -band of  $Zn^+$  ions and its broadening can be estimated a few eV. This band corresponds to the conduction band.

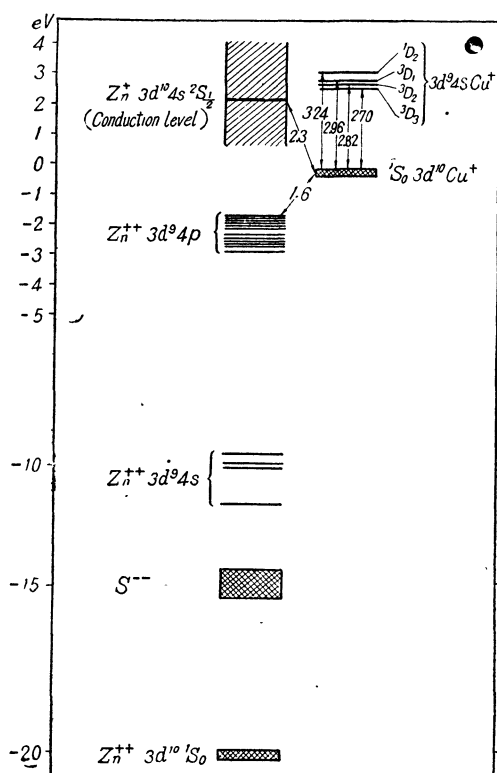


Fig. 1. Energy levels in ZnS/Cu.

forbidden region, the broadening of the level is very narrow. The excited levels of  $Cu^+$  ion, that is to say,  $^1D_2$ ,  $^3D_1$ ,  $^3D_2$  and  $^3D_3$  levels lie immediately below the conduction band or on the position overlapping each other in the real crystal.

(b) Excitation bands of fluorescence. If the zinc sulphide crystal absorbs the excitation energy such as light, an electron of the  $Cu^+$  ion in the activation centre makes transitions from the ground state  $S^{--}$  into the excited states of  $^1D_2$ ,  $^3D_1$ ,  $^3D_2$  and  $^3D_3$ . As the results, we can expect the four excitation bands of fluorescence whose maxima lie about at following wave length:

$$a_1 = 3.24 \text{ eV}, \quad a_2 = 2.96 \text{ eV}, \quad a_3 = 2.82 \text{ eV}, \quad a_4 = 2.70 \text{ eV}.$$

In fact, Tomascheck<sup>(11)</sup> observed following excitation bands of fluorescence in the zinc sulphide-copper crystal phosphor,

(10) B. Gudden, R. Pohl: *Z. Physik*, **2** (1920), 181.

(11) R. Tomascheck. "Handb. d. exp. Phys.", Tell I, (1928), 392.

|                                     |                                                   |                                                    |
|-------------------------------------|---------------------------------------------------|----------------------------------------------------|
| for $\alpha$ -fluorescence-band     | $d_1^\alpha = 430 \text{ m}\mu = 2.87 \text{ eV}$ | $d_2^\alpha = 360 \text{ m}\mu = 3.43 \text{ eV},$ |
|                                     | $d_3^\alpha = 260 \text{ m}\mu = 4.11 \text{ eV}$ | $d_4^\alpha = 235 \text{ m}\mu = 7.22 \text{ eV},$ |
| for $\beta$ -       ,,       ,,     | $d_1^\beta = 365 \text{ m}\mu = 3.37 \text{ eV}$  | $d_2^\beta = 270 \text{ m}\mu = 4.57 \text{ eV},$  |
| (for $\gamma$ -       ,,       ,, ) | $d_1^\gamma = 470 \text{ m}\mu = 2.62 \text{ eV}$ | $d_2^\gamma = 380 \text{ m}\mu = 3.25 \text{ eV},$ |
| for $\delta$ -       ,,       ,,    | $d_1^\delta = 425 \text{ m}\mu = 2.90 \text{ eV}$ | $d_2^\delta = 370 \text{ m}\mu = 3.37 \text{ eV}.$ |

The author interprets these results of the observations on the excitation bands of fluorescence as follows:

$^1S_0 \rightarrow ^1D_2$   $a_1 = 3.24 \text{ eV}$  corresponds to the observed excitation bands

$$d_2^\alpha = 3.43 \text{ eV} \quad d_1^\beta = 3.37 \text{ eV}$$

$$(d_2^\delta = 3.37 \text{ eV}) \quad (d_2^\gamma = 3.25 \text{ eV}),$$

$^1S_0 \rightarrow ^3D_1$   $a_2 = 2.96 \text{ eV}$  corresponds to the observed excitation bands

$$d_1^\delta = 2.90 \text{ eV},$$

$^1S_0 \rightarrow ^3D_2$   $a_3 = 2.82 \text{ eV}$  corresponds to the observed excitation bands

$$d_1^\alpha = 2.87 \text{ eV},$$

$^1S_0 \rightarrow ^3D_3$   $a_4 = 2.70 \text{ eV}$  corresponds to the observed excitation bands

$$d_1^\gamma = 2.62 \text{ eV}).$$

We must, however, notice the following facts: We could confirm that the fluorescence spectra of zinc sulphide-copper crystal phosphors consisted of  $\alpha$ - and  $\beta$ -band (and probably  $\delta$ -band), and  $\gamma$ -band was not correlated to the  $\text{Cu}^+$  ion, but to the Zn atom diffused in the phosphors.

The excitation bands of fluorescence above quoted have a wide broadening due to molecular and lattice vibrations in the crystal as a whole, as we see in the following sections.

(c) Fluorescence band. Since  $\text{Cu}^+$  ion in the activation centre is surrounded by  $\text{Zn}^{++}$  and  $\text{S}^{--}$  ions in the crystal, the normal and excited states of the electron of  $\text{Cu}^+$  ion can be represented as functions of a parameter ( $u$ ) describing the positions of the ions.

After an electron in the equilibrium position of the normal state has absorbed the excitation energy, it makes a transition to the excited state and then it moves into a new equilibrium position of the excited state, the excess energy is taken up by the vibrations of the surrounding ions.

Fig. 2 shows the energy curve of  $\text{Cu}^+$  ion in the activation centre. A represents an equilibrium position of the normal state of  $\text{Cu}^+$  ion in the activation centre. After an electron in this position has absorbed light quanta, it makes a transition into one of the excited states of  $\text{Cu}^+$  ions, for example, to C of the energy curve  $^3D_2$ . Then it moves into a new equilibrium position  $f$  of  $^3D_2$  curve in about  $10^{-13}$  second, mean-

while giving up the excess energy as the lattice vibrations. From *f* the electron makes a transition either to *h* of  $^3D_3$  curve or to *g* of the ground state, in accordance with Franck-Condon principle.

The transition  $f \rightarrow h$  occurs with radiation of infra-red waves or elastic vibration waves, and the latter case is more probable when the coupling between the electron and lattice vibrations is strong.

The transition  $f \rightarrow g$  gives the fluorescence. The electron in *h* moves into the equilibrium position of  $^3D_3$  and then it makes a transition to *j* of the ground state with the radiation of the fluorescence. By such a picture, these fluorescence bands will show a wide breadth by the molecular vibrations coupled with the elastic vibrations of the lattice. In fact, the author could observe the molecular vibration structure of the fluorescence bands which will be reported in the following paper.

On the other hand, the electron which moved into the equilibrium position *c* from *D* of  $^3D_1$  curve, will make a transition into *d* and the transition from *c* to the ground state will scarcely occur when the interaction between the electron and lattice vibrations is very strong. The same process is possible for the electron which has made a transition to *E* of the energy curve  $^1D_2$ .

As it can be seen in Fig. 3 and Fig. 4, the author observed two fluorescence bands at about 5250 Å and 4550 Å arising from the copper activator in the zinc sulphide phosphor. They are considered to correspond to  $\alpha$ - and  $\beta$ -band respectively. The author assigns  $\alpha$ -band to the electronic transition of  $^3D_3 \rightarrow ^1S_0$  ( $i \rightarrow j$ ) and  $\beta$ -band to that of  $^3D_2 \rightarrow ^1S_0$  ( $f \rightarrow g$ ) of the  $\text{Cu}^+$  ion in the activation centre.

On the other hand, F. Seitz<sup>(1)</sup> reported that the activation centre of the zinc sulphide-copper phosphor consisted of the copper atom which diffused into the crystal. And he concluded that the direct transition of the electron (which is raised in the conduction band from the ground state) from the conduction band

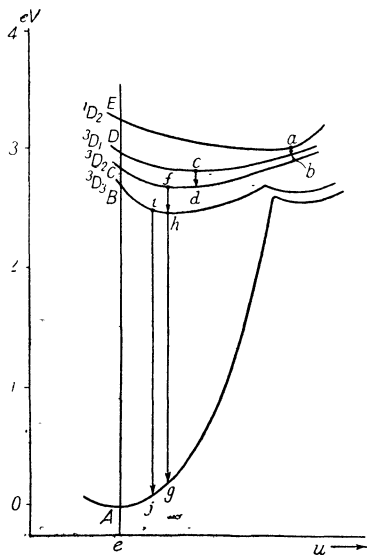


Fig. 2. Potential curves in the activation centre.

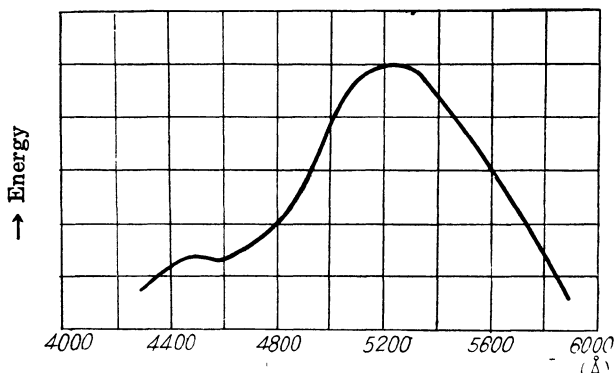


Fig. 3. Fluorescence spectrum of  $\text{ZnS/Cu}$   
 $\text{Cu} = 1 \times 10^{-5}$  mol fraction, 25°C.



to the ground state is responsible for the fluorescence band. If it is the case, the fluorescence spectra of zinc sulphide-copper phosphor should show a simple wide band.

But it is well known that the fluorescence spectra of zinc sulphide-copper phosphor consist of a few bands.<sup>(11)</sup> In fact, the author could confirm that the fluorescence spectrum of zinc sulphide phosphor consists of two fluorescence bands of  $\alpha$  and  $\beta$  and each fluorescence band shows the molecular vibration structure.

Therefore we can not adopt the Seitz's model of the zinc sulphide-copper phosphor. And it will be a reasonable picture that the electronic transition from the excited states to ground state of  $\text{Cu}^+$  ion

is responsible for the fluorescence. In other words, the resonance radiation, in the wide meaning, in the activation centre is responsible for the fluorescence of the zinc sulphide crystal phosphor.

The same picture will be possible in the case of the excitation bands of fluorescence and photoconductivity.

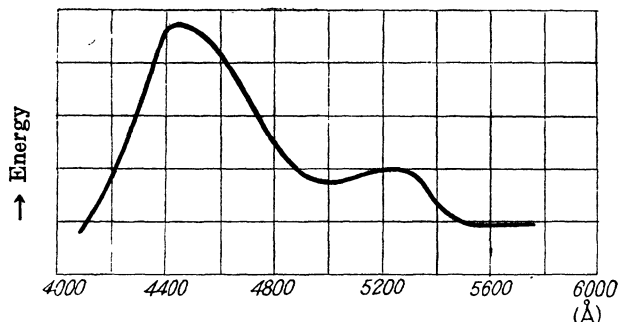


Fig. 4. Fluorescence spectrum of ZnS/Cu  
Cu =  $1 \times 10^{-4}$  mol fraction, 25°C.

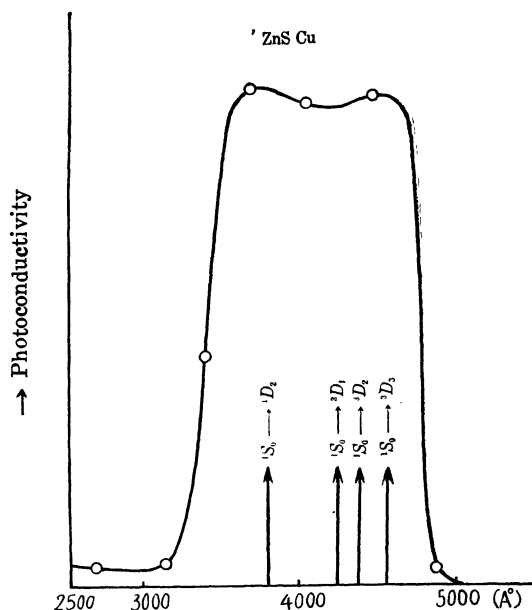


Fig. 5. Photoconductivity of ZnS/Cu

If the electron in the excited states of  $\text{Cu}^+$  ion in the activation centre, absorbs the heat energy, it can make a transition to the conduction band and be free to move in the crystal phosphor.

Therefore we can expect that the zinc sulphide-copper crystal phosphor has photoconductivity at room temperature or at enough high temperature, if it absorbs the light corresponding to the excitation bands of fluorescence.

Fig. 5 shows excitation band of the photoconductivity observed by Gudden and Pohl<sup>(10)</sup> and in this figure the arrows show the maxima of the excitation bands obtained theoretically by the author.

In the above quoted picture, the photoconductivity will decrease with decreasing temperature. In fact, it is the case by the observation of the photoconductivity of zinc sulphide crystal by Lentz.<sup>(12)</sup> And the author could calculate theoretically the temperature dependence of the photoconductivity of zinc sulphide phosphor by using the above quoted mechanism of the photoconduction, and the results coincide with the experiment of Lentz<sup>(12)</sup> very good, as we shall see in the following paper.

### Summary.

In this paper, the author has attempted to interpret the properties of the zinc sulphide-copper crystal phosphor from the view point of zone-theory.

(1) It was pointed out that the activation centre of zinc sulphide-copper phosphor consists of Cu ion surrounded by the ions of Zn and S.

(2) The transition of electron of Cu<sup>+</sup> ion from the ground state  $^1S_0$  to the conduction band is responsible for the excitation bands of fluorescence.

(3) The two fluorescence bands with maxima at 5250 Å and 4550 Å in this phosphor may be correlated with the electronic transitions

$$^3D_3 \rightarrow ^1S_0 \text{ (}\alpha\text{-band)},$$

$$^3D_2 \rightarrow ^1S_0 \text{ (}\beta\text{-band)}.$$

(4) If the electron in the excited states of Cu<sup>+</sup> ion absorbs heat energy, it makes a transition to the conduction band and be free to move in the phosphor, then the phosphor will show a phenomenon of the photoconduction.

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(12) H. Lentz: *Ann. Physik*, **77** (1925), 449.