

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. V. Die Sorption des Sauerstoffs durch Manganoxyd und die Austauschreaktion der Sauerstoffatome zwischen Sauerstoffgas und Manganoxyd. Teil II. Austauschversuche und Diskussion.⁽¹⁾

Von Noriyoshi MORITA.

(Eingegangen am 10. November 1939.)

Inhaltsübersicht. Anschliessend an den vorhergehenden Sorptionsversuch des Sauerstoffgases durch Manganoxyd wird in der vorliegenden Arbeit die Austauschreaktion der Sauerstoffatome zwischen gasförmigem Sauerstoff und festem Manganoxyd bei verschiedenen Temperaturen unter Verwendung des an schwerem Sauerstoff angereicherten Sauerstoffgases untersucht. Dabei ergibt sich, dass die Austauschreaktion erst oberhalb von etwa 300° bemerkbar wird und bei 400° d.h. der höchsten benutzten Temperatur 4 bis 9% der gesamten O-Atome im benutzten Präparat des Manganoxys gegen die des damit berührenden Sauerstoffgases ausgetauscht werden. Vergleicht man diese Versuchsergebnisse mit denen der vorhergehenden Sorptionsversuche sowie der früher durchgeführten Versuche über die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Manganoxys, so kommt man zu dem Schluss, dass bei der letzt genannten Reaktion die nacheinander folgend verlaufende reversible Oxydation und Zersetzung (bzw. Reduktion) des Manganoxys eine massgebende Rolle spielt.

Einleitung. Wir haben früher bei den Versuchen über die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Kupferoxyds gefunden, dass die Reaktion erst von etwa 650° an mit messbarer Geschwindigkeit stattfindet (vgl. III. Mitteil.). In denselben Versuchen wurde weiter gefunden, dass die O-Atome des Wasserdampfes, der an der Oberfläche des festen Kupferoxyds strömen gelassen wird, ebenfalls von der oben genannten Temperatur (d.h. etwa 650°) an gegen die des damit berührenden festen Kupferoxyds ziemlich leicht ausgetauscht werden. Dagegen konnten wir zwischen gasförmigem Sauerstoff und festem Kupferoxyd auch bei so einer hohen Temperatur wie 900° keine nennenswerte Austauschreaktion der O-Atome ausfindig machen. Aus diesen Befunden wurde deshalb geschlossen, dass bei der katalytischen Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Kupferoxyds die aktivierte Adsorption des Wasserdampfes ein massgebender Prozess sein muss. Bei den späteren Versuchen über die katalytische Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Manganoxys ergab sich nun, dass diese Reaktion erst oberhalb 280° bemerkbar wird

(1) Teil I: dies Bulletin, **14** (1939), 520. Vgl. dazu I. Mitteil.: ebenda., **13** (1938), 357; II. Mitteil.: ebenda., **13** (1938), 601; III. Mitteil.: ebenda., **13** (1938), 656; IV. Mitteil., ebenda **14** (1939), 9.

und bei 500° sehr schnell stattfindet. (vgl. IV. Mitteil.). Daranschliessend haben wir in den vorhergehenden Sorptionsversuchen gefunden, dass die Sorption des Sauerstoffgases durch Manganoxyd erst zwischen 275° und 325° mit messbarer Geschwindigkeit eintritt und bei etwa 400° eine reversible Absorption und Desorption des Sauerstoffgases an demselben Manganoxydpräparat sich untrüglich erkennen lässt. So liegt nun die Vermutung nahe, dass bei der katalytischen Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Manganoxyds, im Gegenteil dieselbe Reaktion an Kupferoxydoberfläche, die aktivierte Adsorption des Sauerstoffgases ein massgebender Prozess sein dürfte. Um diese Vermutung direkt experimentell zu prüfen, wird in den vorliegenden Versuchen die Austauschreaktion der O-Atome zwischen Sauerstoffgas und festem Manganoxyd bei verschiedenen Temperaturen unter Verwendung des an schwerem Sauerstoff angereicherten Sauerstoffgases untersucht. Die dabei benutzte Versuchsanordnung ist genau dieselbe wie in III. Mitteil. Experiment 2 verwendet wurde.

5. Austauschversuche. Das in den vorliegenden Versuchen verwendete Präparat von Manganoxyd wird auf genau demselben Weg wie bei den vorhergehenden Sorptionsversuchen aus Mangan-(II)-Nitrat hergestellt, indem man den daraus durch Versetzung mit Ammoniaklösung gewonnenen Niederschlag von Manganoxydhydrat erst bei 120° trocknet und das so getrocknete Oxydhydrat durch Erhitzung bis auf etwa 400° unter vermindertem Druck vollkommen bis zum Oxyd zersetzt. Etwa 40 g des so hergestellten Manganoxyds wird nun im Mittelteil des Reaktionsrohrs eingeschoben. Aber bevor der eigentliche Austauschversuch mit diesem Manganoxyd stattfindet, wird das Sauerstoffgas aus der Elektrolyse des gewöhnlichen Wassers durch dieses Rohr unter gleichzeitiger Erhitzung des letzteren bis auf etwa 400° mit der Geschwindigkeit von ca. 20 ccm pro Sekunde (bei Zimmertemperatur und unter gewöhnlichem Druck gemessen!) vier Tage lang durchgeleitet. Diese Massnahmeregel ist insofern nötig, weil das Manganoxyd, an dessen Oberfläche wie katalytische Austauschreaktion zwischen Sauerstoffgas und Wasserdampf untersucht wurde, ebenfalls auf demselben Wege wie oben vorbehandelt wurde (vgl. IV. Mitteil.). Das so behandelte Manganoxyd besitzt, wie die chemische Analyse in vorhergehenden Sorptionsversuche ergab, etwa die Zusammensetzung von $\text{MnO}_{1.6}$ bis $\text{MnO}_{1.7}$; es kann als ein Gemisch aus Mangan-(III)-oxyd Mn_2O_3 und Mangandioxyd MnO_2 angesehen werden.⁽²⁾

Das mit dem so vorbehandelten Manganoxyd zu reagierende d.h. O-Atome auszutauschende Sauerstoffgas wird nun dadurch mit schwerem Sauerstoff „etikettiert“, dass man das Gas aus Elektrolyse des an schwerem Sauerstoff angereicherten schweren Wassers entwickeln lässt. Das dabei benutzte an schwerem Sauerstoff angereicherte schwere Wasser

(2) In IV. Mitteil. wurde diesem Oxyd die Formel Mn_3O_4 zugeschrieben. Aber diese Benennung ist nicht ganz richtig. Wenn dieses Oxyd mit einer einzigen Formel ausgedrückt werden soll, kann vielleicht die Formel Mn_2O_3 als die naheliegendste vorgezogen werden.

besitzt bloss wegen der Anreicherung des schweren Sauerstoffs den Dichteüberschuss von 49.6 γ gewöhnlichem Wasser gegenüber. Das so entwickelte schwere aber reine Sauerstoffgas, dessen Volumen insgesamt etwa 7.5 l beträgt, wird dann durch Einmischung von reinem Bombenstickstoffgas bis auf Volumenverhältnis von $O_2:N_2 = 3:1$ verdünnt und in einem Gasbehälter aufbewahrt.

Beim Austauschversuch wird zunächst das Reaktionsrohr, in dem sich das Manganoxyd befindet, bis auf eine bestimmte Temperatur erhitzt und dann das oben angegebene Gasgemisch aus schwerem Sauerstoff und gewöhnlichem Stickstoff durch das Reaktionsrohr langsam durchgeleitet. Das dazu benutzte Reaktionsrohr, das aus Pyrexglas geblasen ist, besitzt 35 mm l.W. und 15 cm Länge, und die Strömungsgeschwindigkeit des Gasgemisches durch dieses Rohr wird immer so kontrolliert, dass sie (bei Zimmertemperatur und unter gewöhnlichem Druck gemessen) möglichst konstant bei etwa 30 cm. pro Minute gehalten wird. Das auf diese Weise aus dem Reaktionsrohr zusammen mit Stickstoffgas ausgeströmte schwere Sauerstoffgas, dessen Dichte wegen des eventuell stattfindenden Austausches seiner schweren O-Atome gegen die leichteren des festen Manganoxys bis zu einem gewissen Grad vermindert worden sein kann, wird nun durch die katalytische Rekombination mit Bombenwasserstoff bis zu Wasser verwandelt und die Dichte und folglich der Gehalt an schwerem Sauerstoff des so rekombinierten Wassers wird nach sorgfältiger Reinigung genau bestimmt. Die dritte Vertikalreihe der Tabelle 1 gibt den Dichteüberschuss Δs des bei jedem Versuch gewonnenen rekombinierten Wassers gewöhnlichem Wasser gegenüber wieder.

Tabelle 1. Austauschreaktion zwischen Sauerstoffgas und festem Manganoxyd bei verschiedenen Temperaturen.

Versuchsnr.	Temperatur °C	Δs in γ	$\Delta s_0 - \Delta s$ in γ	Austauschmass %A	% Mn_2O_3
0*	400	44.7 = Δs_0	0.0	—	—
1	200	44.5	0.2	1	—
2	300	44.2	0.5	2	—
3	400	42.1	2.6	10	4
4	400	39.5	5.2	19	9

* Kontrollversuch, d.h. ohne Manganoxyd.

Unter den fünf in Tabelle 1 angegebenen Versuchen ist der allererste Versuch Nr. 0 ein Kontrollversuch, der ohne Füllung des Reaktionsrohrs mit Manganoxyd ausgeführt wird. Dagegen werden die anderen vier Versuche Nr. 1 bis 4 auf der schon oben erwähnten Weise unter Füllung des Reaktionsrohrs mit Manganoxyd durchgeführt. Dabei wird bei den ersten drei Versuchen Nr. 1 bis 3 ein und dasselbe Manganoxydpräparat wiederholt gebraucht, indem man dies nach der Beendigung eines Versuches mittels elektrolytischen Sauerstoffs auf dem schon oben angegebenen Weg paar Tage lang behandelt und erst dann zum nächsten Versuch verwendet. Diese wiederholte Benutzung eines und desselben Mangan-

oxyds dauert aber nur von Nr. 1 bis 3. Dagegen wird es beim letzten Versuch Nr. 4 durch das frische Präparat ersetzt. Weil nun der Kontrollversuch Nr. 0 ohne Füllung des Reaktionsrohrs mit Manganoxyd durchgeführt wird, kann die dabei gefundene Abnahme des Dichteüberschusses 44.7γ ($= \Delta s_0$) des rekombinierten Wassers dem anfänglichen Dichteüberschuss 49.6γ des verwendeten schweren Wassers gegenüber offensichtlich nicht von der Austauschreaktion der schweren O-Atome zwischen Sauerstoffgas und Manganoxyd herrühren.⁽³⁾ Deshalb können wir den Unterschied des gefundenen Dichteüberschusses des rekombinierten Wassers zwischen Kontrollversuch Nr. 0 (Δs_0) und jedem anderen Versuch (Δs) als ein Mass für die Austauschreaktion der O-Atome zwischen Sauerstoffgas und Manganoxyd bei jedem betreffenden Austauschversuch betrachten. Dieser Unterschied nimmt aber, wie die vierte Spalte der Tabelle 1 zeigt, mit steigender Temperatur ziemlich deutlich zu. Daraus folgt ohne weiteres, dass die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und festem Manganoxyd, wie wir erwartet haben, mindestens bei hohen Temperaturen wirklich stattfindet. Nimmt man deshalb vorläufig an, dass das benutzte Manganoxyd die Zusammensetzung von Mn_2O_3 besitzt⁽⁴⁾ und alle seine O-Atome gleich leicht gegen die des damit berührenden Sauerstoffgases ausgetauscht werden können, dann würde der Dichteüberschuss des rekombinierten Wassers beim vollständigen Austausch im Vergleich mit dem Kontrollversuch um etwa 27γ abnehmen, wie eine einfache Rechnung anzeigt. Das prozentuale Austauschmass $\%A$, das in der zweiten letzten Spalte der Tabelle 1 angegeben ist, wird deshalb mit Hilfe der Gl. (1) berechnet:

$$\%A = \frac{\Delta s_0 - \Delta s}{27} \times 100 \quad (1).$$

Die Temperaturabhängigkeit des so berechneten Austauschmasses $\%A$ ergibt, dass die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und festem Manganoxyd erst bei 300° bemerkbar wird und schon bei 400° mit ziemlich grosser Geschwindigkeit vor sich geht.

Bei der oben angegebenen Ausrechnung des Austauschmasses $\%A$ wird aber vorausgesetzt, dass alle O-Atome im festen Manganoxyd gegen die des damit berührenden Sauerstoffgas gleich leicht austauschbar sind. Diese Voraussetzung entspricht aber insofern der Wirklichkeit nicht, als die an bzw. in der Nähe der Oberfläche des festen Manganoxyds befindlichen O-Atome im Vergleich mit den im Inneren desselben befindlichen viel leichter austauschbar gegen die des damit berührenden Sauerstoffgases angesehen werden müssen. Vielmehr liegt die Annahme

(3) Der Dichteüberschuss 49.6γ des originalen schweren Wassers rührt, wie schon oben bemerkt wurde, ausschliesslich von der Anreicherung des schweren Sauerstoffs her. Dagegen besitzt der Wasserstoff des originalen Wassers fast dieselbe Isotopenzusammensetzung wie gewöhnliches Wasser. Deshalb kann die Verminderung des Dichteüberschusses des rekombinierten Wassers beim Kontrollversuch (44.7γ) dem oben angegebenen anfänglichen gegenüber hauptsächlich auf die Einmischung des leichten Wasserstoffs aus dem Bombenwasserstoffgas beim Rekombinationsprozess zurückgeführt werden.

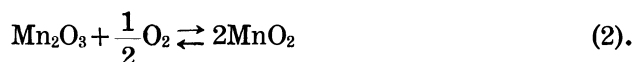
(4) Vgl. Fussnote (2).

nahe, dass unter den benutzten Versuchsbedingungen nur ein Teil der im verwendeten festen Manganoxyd enthaltenen O-Atome gegen die des damit berührenden Sauerstoffgases vollständig ausgetauscht werden, während die sonstigen Teile der O-Atome, die hauptsächlich im Inneren des Manganoxys befänglich sind, unverändert bleiben. Unter dieser Annahme wird deshalb das prozentuale Verhältnis $\% \text{Mn}_2\text{O}_3$ dieser vollständig ausgetauscht angenommenen O-Atome im Manganoxyd gegen die gesamte O-Atome in demselben bei jedem Versuch ausgerechnet⁽⁵⁾ und in der letzten Spalte der Tabelle 1 wiedergegeben. Dieses zeigt aber, dass bei der höchst benutzten Temperatur d.h. bei 400° fast 4 bis 9% der gesamten O-Atome im verwendeten Manganoxyd gegen die des damit berührenden Sauerstoffgases ausgetauscht werden.

6. Diskussion. Bei den vorhergehenden Sorptionsversuchen (Teil I) wird gefunden, dass das frisch aus Oxydhydrat hergestellte Manganoxyd, das etwa die Zusammensetzung von Mn-(III)-oxyd Mn_2O_3 besitzt, anfängt das Sauerstoffgas mit messbarer Geschwindigkeit zu absorbieren, wenn man das Oxyd in $2/3$ atmosphärischem Sauerstoffgas allmählich bis auf etwa 300° erhitzt. Da aber diese Temperatur mit der ziemlich gut übereinstimmt, wo die katalytische Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Manganoxys mit messbarer Geschwindigkeit auftritt (vgl. IV. Mitteil. Abb. 1), so liegt die Annahme nahe, dass diese letzte Reaktion mit der Sorption des Sauerstoffs an der Oberfläche des Manganoxys in engem Zusammenhang steht. Bei dem oben genannten Sorptionsversuche wird weiter gefunden, dass die Sorptionsgeschwindigkeit mit steigender Temperatur ziemlich schnell zunimmt, aber wenn die letztere etwa 530° überschreitet, die Desorption des Sauerstoffs aus dem Manganoxyd ziemlich plötzlich auftritt und ein Teil des im Manganoxyd befindlichen Sauerstoffs verloren geht. Wenn man jedoch die Temperatur des Manganoxys wieder bis auf etwa 400° herabsetzt, wird der Sauerstoff abermals langsam durch das Manganoxyd absorbiert. Dasselbe Verfahren können wir so oft wie man will wiederholen, wenn man nur die Temperatur des Manganoxys abwechselnd ab- und aufsteigen lässt. Diese reversible Absorption und Desorption des Sauerstoffs an ein und demselben Oxydpräparat konnten wir weiter nicht nur mit dem oben angegebenen niedrigeren Oxyd des Mangans Mn_2O_3 sondern auch bei dem Fall ebenso gut ausfindig machen, wo man den Sorptionsversuch mit höherem Oxyd MnO_2 ausführte. Erhitzt man nämlich dieses letztere Oxyd MnO_2 in $2/3$ atmosphärischem Sauerstoff und lässt die Temperatur allmählich ansteigen, so lässt sich die reversible Absorption und Desorption des Sauerstoffs eben bei demselben Temperaturbereich wie beim niedrigerem Oxyd Mn_2O_3 , d.h. zwischen etwa 400° und 500° deutlich erkennen. Aber dieser Temperaturbereich, wo die reversible Absorption und Desorption des Sauerstoffs an Manganoxyd deutlich bemerkbar wird, stimmt genau mit dem überein, wo die katalytische Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Manganoxys lebhaft stattzufinden beginnt (vgl. IV. Mitteil. Abb. 1). Deshalb

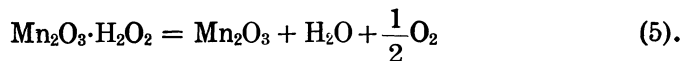
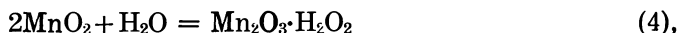
(5) Die dabei benutzte Errechnungsmethode soll später veröffentlicht werden.

liegt weiter die Annahme nahe, dass bei dieser letzten katalytischen Reaktion die reversible Oxydation und Reduktion des Manganoxys, die etwa durch folgendes Schema formuliert werden kann, eine massgebende Rolle spielt:



Diese bzw. die ähnliche Erscheinung ist aber schon der Gegenstand der Untersuchungen von manchen Autoren gewesen.⁽⁶⁾ Honda und Sone⁽⁷⁾ bestätigten z.B. den Übergang $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ bei 530° durch die entsprechende Veränderung der magnetischen Suszeptibilität. Simon und Feher⁽⁸⁾ untersuchten den isobaren Abbau des Mangandioxyds MnO_2 unter dem Druck von etwa 10 mm und fanden dabei, dass der Zersetzungsdruck des Oxyds erst oberhalb 300° bemerkbar wird, bei 337° bis zum Vergleichsdruck (10 mm) wächst und oberhalb 500° ein vollständiger Übergang in Mn_2O_3 stattfindet. Bei diesen letzt genannten Versuchen wurde weiter gefunden, dass der gemessene Zersetzungsdruck bis zu einem gewissen Grad von der Menge des benutzten Oxyds abhängt.

Dass die reversible Oxydation und Reduktion des Manganoxys gemäss Gl. (2) beim Temperaturbereich wirklich nach beiden Seiten genügend schnell stattfindet, wo die katalytische Austauschreaktion zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Manganoxys lebhaft stattzufinden beginnt, wird durch die in der vorliegenden Mitteilung berichteten Austauschversuch bestätigt. Nach diesen Versuchen wird nämlich gefunden, dass beim genannten Temperaturbereich, d.h. in der Nähe von 400° fast 4 bis 9% der gesamten O-Atome im festen Manganoxyd gegen die des damit berührenden Sauerstoffgases vollständig ausgetauscht werden, wenn man das letztere sogar mit ziemlich grosser Geschwindigkeit an der Oberfläche des ersteren strömen lässt. Auf Grund aller dieser Überlegungen erhalten wir als Reaktionsmechanismus für die katalytische Austauschreaktion der O-Atome zwischen gasförmigen Sauerstoff und Wasserdampf an der Oberfläche des Manganoxys das folgende Schema:



Das ganze Reaktionsschema ist deshalb ähnlich wie das früher für dieselbe Austauschreaktion an der Oberfläche des Kupferoxyds ausgesch-

(6) Wie z.B. K. Honda und T. Sone, *Sci. Repts. Tohoku Imp. Univ.*, **3** (1914), 139; A. Simon und F. Feher, *Z. Elektrochem.*, **38** (1932), 137; M. Le Blanc und G. Wehner, *Z. physik. Chem.*, A **168** (1934), 59; A. F. Kapustinskii und K. S. Bayushkina, *J. Phys. Chem. U. R. S. S.* **11** (1938), 77.

(7) Vgl. Fussnote (6).

(8) Vgl. Fussnote (6).

lagene (vgl. III. Mitteil. Gln. (5) bis (7)). Aber es gibt einen wichtigen Unterschied zwischen beiden Reaktionsmechanismen. Beim vorliegenden Fall an der Oberfläche des Manganoxys wird die Geschwindigkeit der ganzen Austauschreaktion durch die der Teilreaktion (3), d.h. der aktivierten Adsorption des Sauerstoffs an der Oberfläche des Manganoxys bestimmt. Dagegen spielt bei der katalytischen Austauschreaktion an der Oberfläche des Kupferoxyds die entsprechende geschwindigkeitsbestimmende Rolle die aktivierte Adsorption des Wasserdampfs an Kupferoxyd (Gl. (5) in III. Mitteil.), d.h. der oben angegebenen Teilreaktion (4) entsprechende Prozess. Diesen Unterschied können wir vielleicht dadurch erklären, dass beim Kupferoxyd der Zersetzungsdruck von CuO mindestens beim Temperaturbereich, wo die katalytische Austauschreaktion schon lebhaft stattfindet, noch sehr gering ist und deshalb dieses Oxyd erst durch die aktivierte Adsorption von H_2O bis zu Cu_2O reduziert werden muss, um das Oxyd Sauerstoff aus der Gasphase absorbieren zu können. Aber weil das Manganoxyd beim Temperaturbereich, wo die Austauschreaktion deutlich auftritt, schon einen messbaren Zersetzungsdruck ausübt und die Dissoziation von MnO_2 in Mn_2O_3 und O_2 spontan verläuft, muss dieses letztere Oxyd Mn_2O_3 zuerst bis zu MnO_2 oxydiert werden, um die Austauschreaktion der O-Atome zwischen dem Oxyd und H_2O gemäss Gln. (4) und (5) stattfinden zu können.

Durch dieselbe Überlegung können wir auch den scheinbaren Widerspruch zwischen dem vorliegenden Versuchsergebnisse und dem über die katalytische Oxydation des Kohlenoxys durch gasförmigen Sauerstoff an der Oberfläche des Manganoxys erklären. Diese letztere Reaktion wurde schon von vielen Autoren untersucht⁽⁹⁾ und dabei kamen sie fast gemeinsam zu dem Schluss, dass bei dieser Reaktion die aktivierte Adsorption des Kohlenoxys ein massgebender Prozess ist. Diese auf den ersten Blick den vorliegenden widersprechend erscheinenden Ergebnisse sind aber keineswegs verwunderlich, weil die bei beiden diesen Versuchen benutzte Versuchstemperatur gegeneinander stark verschieden ist. Die katalytische Oxydation des Kohlenoxys wird nämlich bei viel niedrigerer Temperatur als die Austauschreaktion deutlich erkennbar; die erste Reaktion verläuft schon bei solch einer niedrigen Temperatur mit wohl messbarer Geschwindigkeit, die nur um ein wenig höher als die Zimmertemperatur liegt. Aber bei diesem Temperaturbereich fanden wir in dem vorhergehenden Sorptionsversuche die Sorptionsgeschwindigkeit des Sauerstoffs durch das niedrigere Oxyd des Mangans Mn_2O_3 fast unmessbar so klein. Aus diesem Ergebnis ist deshalb ohne weiteres klar, dass mindestens bei diesem niedrigen Temperaturbereich die so langsam verlaufende aktivierte Adsorption des Sauerstoffs kein geschwindigkeitsbestimmender Prozess für die mit messbarer Geschwindigkeit verlaufende Oxydation des Kohlenoxys sein kann. Roginsky und Zeldowitsch⁽¹⁰⁾ fanden in der Tat bei ihrem Versuche über die katalytische

(9) Wie z.B. J. A. Almquist und W. C. Bray, *J. Am. Chem. Soc.*, **45** (1923), 2305; H. D. Draper, ebenda., **50** (1928), 2637; S. Roginsky und J. Zeldowitsch, *Acta Physicochim. U. R. S. S.*, **1** (1934), 554, 595; S. Elowitz und S. Roginsky, ebenda., **7** (1937), 295; S. Roginsky, ebenda., **9** (1938), 475.

(10) Vgl. Fussnote (9).

Oxydation des Kohlenoxyds an der Oberfläche des Mangan oxyds, dass die Aufnahmegeschwindigkeit des Sauerstoffs durch das mit CO reduzierte MnO_2 bedeutend kleiner als die Verbrauchsgeschwindigkeit des Sauerstoffs ist. Und durch diesen Befund kamen sie zu dem Schluss, dass diese katalytische Reaktion hauptsächlich durch die Reaktion des an der Oberfläche des reduzierten Manganoxys aktiviert adsorbierten CO mit dem Sauerstoff aus der Gasphase bewirkt wird. Dagegen liegt bei der vorliegenden katalytischen Austauschreaktion die Temperatur genügend hoch, wo die Reaktion mit messbarer Geschwindigkeit verläuft und weiter dieser Temperaturbereich eben mit dem gut übereinstimmt, wo die reversible Absorption und Desorption des Sauerstoffs an Manganoxyd deutlich erkennbar wird. Deshalb darf man wohl zu dem Schluss kommen, dass bei der katalytischen Austauschreaktion, wie schon oben hingewiesen, die aktivierte Adsorption des Sauerstoffs an der Oberfläche des reduzierten Manganoxys eine geschwindigkeitsbestimmende Rolle spielt.

Herrn Prof. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Nippon Gakujutsu-Shinkokai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkoku (der Hattori-Stiftung), die durch Gewährung eines Stipendiums die Ausführung dieser Arbeit ermöglicht haben, bin ich auch zu grossem Dank verpflichtet.

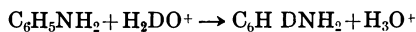
Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyoshitsu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka)

Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in wässrigen Lösungen. II. Die Reaktion in alkalischer Lösung.⁽¹⁾

Von Masao KOIZUMI.

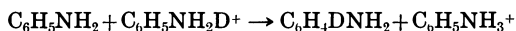
(Eingegangen am 4. Dezember 1939.)

Inhaltsübersicht. Anschliessend an den vorhergehenden Versuch in neutraler und saurer Lösung wird in der vorliegenden Arbeit die Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in alkalischer Lösung untersucht und dadurch kommen wir zu dem Schluss, dass in diesem Fall neben der in saurer Lösung sich als Hauptrolle abspielende Reaktion zwischen neutralen Anilinmolekülen und Hydroxoniumionen:



auch eine solche zwischen Anilinmolekülen und Aniliniumionen:

(1) I. Mittel., dies Bulletin, **14** (1939), 530. Vgl. auch Fussnote (1) in I. Mittel.



als massgebende Reaktion auftritt. Diese Ergebnisse werden durch die Annahme gerechtfertigt, dass in saurer Lösung eine lockere Bindung $\text{C}_6\text{H}_5\text{NH}_2\cdots\text{H}_3\text{O}^+$ zwischen Anilinmolekülen und Hydroxoniumionen entsteht.

Einleitung. Bei den vorhergehenden Versuchen wird gefunden, dass die Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in neutraler bzw. saurer Lösung als eine zwischen neutralen Anilinmolekülen und Hydroxo- bzw. Deuteroxoniumionen verlaufende elektrophile Substitutionsreaktion aufgefasst werden kann (vgl. I. Mitteil.):



Anschliessend daran wird nun in der vorliegenden Arbeit dieselbe Reaktion in alkalischer Lösung untersucht, um zu sehen, ob derselbe Mechanismus (1) wie in saurer Lösung auch in alkalischer Lösung die Hauptrolle spielt. Die Versuche haben aber gezeigt, dass dies nicht immer der Fall ist. Der Reaktionsverlauf in alkalischer Lösung erweist sich nämlich als viel komplizierter als in saurer Lösung und wir müssen neben der oben angegebenen Reaktion (1) auch die Reaktion zwischen neutralen Anilinmolekülen und Aniliniumionen in Betracht ziehen:



um den experimentell gefundenen Reaktionsverlauf in alkalischer Lösung befriedigend zu deuten.

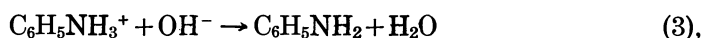
Versuche I. Wenn man zur Lösung des Anilinchlorhydrats in verdünntem schwerem Wasser eine geringe Menge Alkali wie z.B. Kaliumhydroxyd hinzufügt, dann muss die Konzentration der Hydroxoniumionen $[\text{H}_3\text{O}^+]$ — und folglich beim konstant gehaltenen D-Gehalt der Lösung auch die der Deuteroxoniumionen $[\text{H}_2\text{DO}_2^+]$ — mit der zugesetzten Menge des Alkalis umgekehrt proportional ab, dagegen die der neutralen Anilinmoleküle $[\text{C}_6\text{H}_5\text{NH}_2]$ proportional zunehmen. Infolgedessen bleibt das Produkt $[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_2\text{DO}_2^+]$ unabhängig von der zugesetzten Menge des Alkalis fast konstant. Falls deswegen dieselbe Reaktion (1) auch in alkalischer Lösung der wesentlichste Faktor bildete, um etwas abzuwechseln, müsste dann die in alkalischer Lösung gefundene mittlere Geschwindigkeitskonstante $\bar{k}$ unabhängig von der Alkalikonzentration denselben Wert wie in saurer Lösung besitzen, mindestens so lange als die Alkalikonzentration in Lösung nicht sehr gross ist. Um diese Erwartung experimentell zu prüfen, werden die Austauschversuche unter Benutzung des mit verschiedener Menge von KOH versetzten verdünnten schweren Wassers durchgeführt. Die sonstige Versuchsanordnung ist im grossen und ganzen dieselbe wie bei den vorhergehenden Versuchen in neutraler und saurer Lösung. Es wird nämlich bei 100° immer mit etwa 1 g KOH-Lösung in schwerem Wasser und 1.25 g Anilinchlorhydrat gearbeitet. Die dadurch gewonnenen Versuchsergebnisse sind in Tabelle 1 wiedergegeben, wo die Bedeutung der einzelnen Symbole auf I. Mitteil. verwiesen wird.

Tabelle 1. Einfluss der Alkalikonzentration auf die Austauschgeschwindigkeit.

KOH-Normalität im benutzten schweren Wasser	Versuchsdauer in Min.	M_{sc}	M_w	$n\alpha$	$-X \log Y \cdot 10^3$	$(\bar{k}/2.303) \cdot 10^3$
0 N	Vgl. zweite Versuchsreihe in Tabelle 1 der I. Mitteil.					3.5 ~ 3.6
0.25 N	60	0.0174	0.0557	4.57	3.88	3.6 ~ 3.9
	90	0.0174	0.0557	4.92	5.38	
	120	0.0174	0.0559	5.34	7.69	
0.5 N	30	0.0174	0.0541	3.97	1.84	4.4 ~ 4.7
	50	0.0174	0.0543	4.42	3.31	
	55	0.0174	0.0559	4.60	4.02	
	105	0.0174	0.0558	5.43	8.34	
1.03 N	30	0.0174	0.0552	4.23	2.7	5.6 ~ 5.9
	48	0.0174	0.0555	4.78	4.95	
	50	0.0166	0.0544	4.86	5.18	
	70	0.0161	0.0546	5.02	5.92	
	70	0.0174	0.0552	5.09	6.30	
	90	0.0174	0.0551	5.50	8.93	

Aus dieser Tabelle 1 ersieht man ohne weiteres, dass die mittlere Geschwindigkeitskonstante $\bar{k}$ nicht unabhängig von der Alkalikonzentration ist; die Grösse der Konstante $\bar{k}$ nimmt mit der Alkalikonzentration fast linear zu, wie weiter unten gezeigt wird.

Versuche II. Da der direkte Einfluss der Hinzufügung des Alkalis zur Lösung des Anilinchlorhydrats offenbar die Entstehung der freien Anilinmoleküle gemäss der Reaktion (3) verursacht:



können wir vielleicht denselben Einfluss auf die Austauschgeschwindigkeit wie bei dem Alkalizusatz erwarten, wenn man einen Teil des Anilinchlorhydrats in Lösung durch freies Anilin ersetzt, oder mit anderen Worten ausgedrückt, wenn man die Lösung des Anilinchlorhydrats mit einer bestimmten Menge Anilin versetzt. Bezeichnet man mit M_{ac} die Molzahl des von vornherein in der Lösung befindlichen Anilinchlorhydrats und mit M_a die des zugesetzten Anilins, dann können wir das Austauschäquivalent $n\alpha$ für dieses Gemisch von M_{ac} Mol Anilinchlorhydrat und M_a Mol Anilin durch Gl. (4) berechnen (vgl. Gl. (1) und (2) in I. Mitteil.):

$$n\alpha = \frac{2(D_a - D_e)}{D_e} \frac{M_w}{(M_{ac} + M_a)} \quad (4),$$

wo M_w die Molzahl des zum Versuch benutzten verdünnten schweren Wassers und D_a und D_e resp. dessen Gehalt an D vor und nach dem Versuch bedeutet. Die Bestimmung der mittleren Geschwindigkeitskon-

stante $\bar{k}$ aus dem so bei verschiedener Versuchsdauer ermittelten Austauschäquivalent na können wir auch mit Hilfe der Gln. (3) in I. Mitteil. durchführen, wenn man M_{ac} in diesen Gln. durch $(M_{ac} + M_a)$ ersetzt. Dementsprechend müssen wir aber das Austauschäquivalent n_1a_1 für die sehr schnell austauschbaren Wasserstoffatome (d.h. Amidwasserstoffatome) und n_2a_2 für die mit messbarer Geschwindigkeit austauschbaren Wasserstoffatome (d.h. Kernwasserstoffatome) in diesen Gln. (3) in I. Mitteil. resp. durch den effektiven Wert $(n_1a_1)^*$ und $(n_2a_2)^*$ ersetzen. Diese beiden effektiven Werte von n_1a_1 und n_2a_2 lassen sich aus den entsprechenden Werten für reines Anilinchlorhydrat $(n_1a_1)_{ac}$ bzw. $(n_2a_2)_{ac}$ und für reines Anilin $(n_1a_1)_a$ bzw. $(n_2a_2)_a$ sowie der Molzahl der beiden Verbindungen M_{ac} und M_a mittels Gln. (5) berechnen:

$$(n_1a_1)^* = \frac{M_{ac}(n_1a_1)_{ac} + M_a(n_1a_1)_a}{M_{ac} + M_a} \quad (5a),$$

$$(n_2a_2)^* = \frac{M_{ac}(n_2a_2)_{ac} + M_a(n_2a_2)_a}{M_{ac} + M_a} \quad (5b).$$

Da aber das Anilinchlorhydratmolekül drei Stücke, dagegen Anilinmolekül nur zwei Stücke Amidwasserstoffatome enthält, während die Anzahl der mit messbarer Geschwindigkeit austauschbaren Kernwasserstoffatome für die beiden Verbindungen gemeinsam drei ist, können wir für Anilinchlorhydrat $n_1 = n_2 = 3$ und für Anilin $n_1 = 2$ und $n_2 = 3$ setzen. Weiter kann man für die beiden Verbindungen gemeinsam $\alpha_1 = 1.1$ und $\alpha_2 = 0.9$ annehmen (vgl. I. Mitteil.). Setzt man deshalb alle diese Werte in obige Gln. (5) ein, so erhält man die Gln.:

$$(n_1a_1)^* = \frac{3.3M_{ac} + 2.2M_a}{M_{ac} + M_a}$$

$$(n_2a_2)^* = \frac{2.7M_{ac} + 2.7M_a}{M_{ac} + M_a} \quad (6).$$

Bei der praktischen Durchführung der Versuche werden die Molzahl des Anilinchlorhydrats M_{ac} und die des Anilins M_a immer so gewählt, dass deren Summe gleich der des Anilinchlorhydrats wird, die bei den vorhergehenden Versuchen I mit Alkalizusatz benutzt wurde (vgl. Tabelle 1 und 2):

$$M_{ac} + M_a = 0.00174 \text{ Mol.}$$

Durch diese Massnahmeregel können wir nämlich die vorliegenden Versuchsergebnisse, die in Tabelle 2 wiedergegeben sind, direkt mit den der vorhergehenden Versuche I vergleichen.

Durch den Zusatz von Anilin wird die Austauschgeschwindigkeit wie erwartet merklich vergrößert. Aber weil die Summe $(M_{ac} + M_a)$ der Molzahl des Anilinchlorhydrats und des Anilins, die bei den vorliegenden Versuchen II benutzt wurden, wie schon oben erwähnt, möglichst gleich der Gesamtmolzahl des bei den vorhergehenden Versuchen I benutzten

Tabelle 2. Einfluss der Konzentration des Anilins auf die Austauschgeschwindigkeit.

Versuchsdauer in Min.	M_{ac}	M_a	M_w	$n\alpha$	$-X \log Y \cdot 10^3$	$(\bar{k}/2.303) \cdot 10^3$
30	0.0169	0.000646	0.0553	4.04	2.32	3.8 ~ 4.1
30	0.0169	0.000653	0.0557	3.97	2.03	
60	0.0169	0.000574	0.0559	4.38	3.56	
180	0.0169	0.000617	0.0552	6.02	—	
360	0.0169	0.000632	0.0554	6.08	—	
30	0.0163	0.00126	0.0556	4.63	4.46	7.7 ~ 8.4
60	0.0163	0.00124	0.0553	5.23	7.53	
180	0.0163	0.00127	0.0558	6.13	—	
25	0.0162	0.00143	0.0555	4.29	3.17	6.4 ~ 6.9
48	0.0162	0.00142	0.0555	4.89	5.67	
70	0.0162	0.00141	0.0556	5.18	7.25	
30	0.0139	0.00354	0.0554	4.88	6.07	11.3 ~ 11.9
60	0.0139	0.00352	0.0555	5.60	11.4	
180	0.0139	0.00347	0.0561	6.32	—	
360	0.0139	0.00355	0.0558	6.32	—	

Anilinchlorhydrats (M_{ac}) gewählt ist, können wir den Vergrößerungseffekt der Geschwindigkeitskonstante $\bar{k}$ in den beiden Reihen der Versuche ohne weiteres vergleichen, wenn man dies bei derselben Konzentration der überschüssigen Anilinmoleküle ausführt. Die Konzentration des überschüssigen Anilins beim Versuche II lässt sich aus der Menge des zugesetzten Anilins sowie dem Volumen der Lösung ohne Umstände berechnen.⁽²⁾ Dagegen wird diese Konzentration bei Versuch I gleich der des zugesetzten Alakalis angenommen (vgl. Gl. (3)). Die auf diese Weise errechnete Konzentration c_a des überschüssigen Anilins in Lösung wird zusammen mit dem entsprechenden Werte von $\bar{k}$ in Tabelle 3 wiedergegeben.

Tabelle 3. Beziehung zwischen der Konzentration des überschüssigen Anilins c_a und der mittleren Geschwindigkeitskonstante $\bar{k}$.

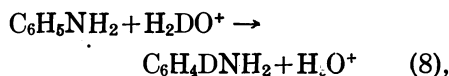
Versuchsreihe I		Versuchsreihe II	
c_a (Mol/Liter)	$(\bar{k}/2.303) \cdot 10^3$	c_a (Mol/Liter)	$(\bar{k}/2.303) \cdot 10^3$
0.09	3.6 ~ 3.9	0.21	3.8 ~ 4.1
0.17	4.4 ~ 4.7	0.43	7.7 ~ 8.4
0.36	5.6 ~ 5.9	0.49	6.4 ~ 6.9
		1.21	11.3 ~ 11.9

(2) Weil für diese Berechnung keine so grosse Genauigkeit verlangt wird, wird das Volumen der Lösung bei Versuchsreihe I durchschnittlich gleich 2.9 ccm und bei Versuchsreihe II 2.8 ccm gesetzt (vgl. Tabelle 1 in I. Mittel).

Die Resultate in Tabelle 3 sind auch in der nebenstehenden Abb. graphisch dargestellt, wo die gefundenen Werte von $\bar{k}$ gegen die Konzentration c_a des überschüssigen Anilins in Lösung aufgetragen. Aus dieser Abb. wird ohne weiteres ersehen, dass die Grösse der direkt gemessenen Konstante $\bar{k}$ mit der Konzentration c_a des überschüssigen Anilins fast linear zunimmt. Die Versuchsergebnisse in Tabelle 3 können deshalb für die beiden Reihen der Versuche gemeinsam durch eine einzige Gl. (7) mit ausreichender Genauigkeit wiedergegeben werden:

$$(\bar{k}/2.303) \cdot 10^3 = 3.3 + 6.9 \times c_a \quad (7).$$

Diskussion. Falls die massgebende Reaktion in alkalischer Lösung ebenso wie in neutraler und saurer Lösung allein die zwischen neutralen Anilinmolekülen und Deuteroxoniumionen nach dem Schema verlaufende wäre:



dann müsste, wie schon oben hingewiesen wurde, die direkt gemessene mittlere Geschwindigkeitskonstante $\bar{k}$ von der Alkalikonzentration unabhängig sein. Aber weil dies in Wirklichkeit nicht der Fall ist, müssen wir eine weitere Reaktion bzw. Reaktionen zwischen anderen Arten der Moleküle und Ionen in Rechnung ziehen. Als solche kommt in erster Linie die Reaktion zwischen Anilinmolekülen und Aniliniumionen in Betracht:



weil unter all den denkbaren Teilreaktionen, die in Gl. (8) in I. Mitteil. angegeben sind, nur diese Reaktion (9) (Teilreaktion (v) in Gl. (8) in I. Mitteil.) mit der gefundenen Tatsache in Einklang steht, dass die direkt gemessene mittlere Geschwindigkeitskonstante $\bar{k}$ sich mit der Menge des zugesetzten Alkalis vergrössert. Die Konzentration der neutralen Anilinmoleküle $[\text{C}_6\text{H}_5\text{NH}_2]$ nimmt nämlich durch den Zusatz von Alkali mit dessen Konzentration proportional zu. Dagegen wird die Konzentration der Aniliniumionen $[\text{C}_6\text{H}_5\text{NH}_3^+]$ durch den Alkalizusatz fast nicht beeinflusst, mindestens so lange als die Menge des zugesetzten Alkalis im Vergleich mit der des Anilinchlorhydrats genügend klein bleibt. Unter diesen Versuchsbedingungen muss deshalb die Geschwindigkeit der Reaktion (9) und folglich auch die Grösse der direkt gemessenen mittleren Geschwindigkeitskonstante $\bar{k}$ mit der zugesetzten Menge des Alkalis proportional zunehmen. Auf diese Weise können wir die vorlie-

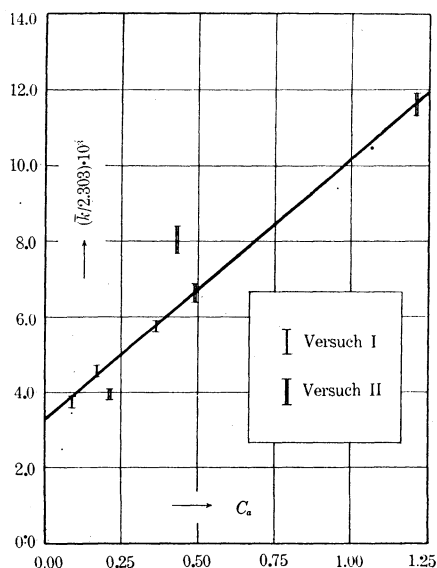


Abb. Beziehung zwischen der Geschwindigkeitskonstante $\bar{k}$ und der Konzentration des überschüssigen Anilins c_a .

genden Versuchsergebnisse in alkalischer Lösung wenigstens qualitativ erklären. Aber weil ein plötzlicher Übergang der massgebenden Reaktion von Reaktion (8) in saurer Lösung zu Reaktion (9) in alkalischer Lösung höchst fraglich erscheint, liegt die Annahme nahe, dass bei der Reaktion in saurer Lösung sich hauptsächlich Reaktion (8) abspielt, dagegen in alkalischer Lösung neben dieser Reaktion (8) auch Reaktion (9) als eine massgebende auftritt.

Dieser auf den ersten Blick schwer begreifliche Übergang des Reaktionsmechanismus von saurer zu alkalischer Lösung können wir vielleicht durch eine Annahme erklären, dass die Anilinmoleküle, die durch die Hydrolyse des Anilinchlorhydrats in neutraler bzw. saurer Lösung entstanden sind, sich in bis zu einem gewissen Grad verschiedenem Zustand befinden als die freien Anilinmoleküle in neutraler bzw. alkalischer Lösung. Beim letzteren Fall befinden sich die Anilinmoleküle $C_6H_5NH_2$ grösstenteils nur als solche in Lösung. Dagegen existieren beim ersten Fall in der Lösung neben den Anilinmolekülen auch eine diesäquivalente (in neutraler Lösung) bzw. diesübertreffende Menge (in saurer Lösung) von Hydroxoniumionen H_3O^+ . Deshalb liegt nahe, dass diese Hydroxoniumionen durch die Aminogruppe des Anilinmoleküls mehr oder weniger herangezogen und unter Umständen eine lockere Bindung zwischen diesen beiden gebildet wird. Diese Annahme erscheint sogar nicht ganz unwahrscheinlich besonders mit Hinsicht auf die moderne Theorie der „Wasserstoffbindung“⁽³⁾ sowie der quasikristallinen Struktur bzw. „Käfig“-Modells von Flüssigkeiten und Lösungen.⁽⁴⁾ Wenn man aus diesem Grunde eine lockere Verbindung zwischen Anilin und Hydroxoniumionen annimmt, die man vielleicht etwa durch die Formel $C_6H_5NH_2 \cdots H_3O^+$ darstellen kann, dann ist naheliegend, dass diese Verbindung wegen ihrer überschüssigen positiven Ladung bzw. infolge Mangels des Benzolkerns an Elektronendichte schwieriger als die freien Anilinmoleküle zu deuterieren ist. Diese Verhältnisse erinnern uns an den Befund der vorhergehenden Versuche in neutraler bzw. saurer Lösung, dass die Aniliniumionen $C_6H_5NH_3^+$ an der Austauschreaktion der Kernwasserstoffatome als die Protonendonatoren fast nicht beteiligt sind. In dieser Hinsicht darf man aber wohl annehmen, dass die Widerstandsfähigkeit der lockeren Verbindung $C_6H_5NH_2 \cdots H_3O^+$ gegen die Deuterierungsreaktion nicht einmal so gross sein kann wie die der Aniliniumionen. Deshalb können diese lockeren Moleküle durch ein so kräftiges Deuterierungsmittel wie Deuteroxoniumionen H_2DO^+ verhältnismässig leicht angegriffen werden, wohl aber nicht durch ein schwächeres Deuterierungsmittel wie z.B. Aniliniumionen $C_6H_5NH_2D^+$. Dies kann gerade die Ursache für den Unterschied sein, dass in saurer bzw. neutraler Lösung hauptsächlich die Reaktion (8) zwischen Anilinmolekülen (streng genommen lockere Verbindung zwischen Anilin und Hydroxoniumionen) und Hydroxoniumionen eine Rolle spielt, während in alkalischer (bzw. mit Anilin versetzter) Lösung daneben auch die Reaktion (9) zwischen Anilinmolekülen und Aniliniumionen als eine massgebende Reaktion auftritt.

(3) Vgl. z.B. K. Kunz, *Angew. Chem.*, **52** (1939), 436.

(4) Vgl. z.B. R. H. Fowler und N. B. Slater, *Trans. Faraday Soc.*, **34** (1938), 81.

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 (Hattori-Stiftung) für ihre finanzielle Unterstützung zu bestem Dank verpflichtet.

Siomi Rikagaku Kenkyu-sho
(*Siomi-Institut für physikalische*
und chemische Forschung)

und

Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyoshitsu
(*Chemisches Institut der wissenschaftlichen*
Fakultät der Kaiserlichen Universität Osaka)

Studies on Cathode-Materials. Part 1. On the Zone-Model of the Oxide-Cathodes.

By Yasuo UEHARA and Masatosi TAKAHASI.

(Received December 7, 1939.)

1. Introduction. The thermionic emission and other behaviours of oxide cathodes have been extensively investigated theoretically as well as technically by many authors. However, a complete picture of the thermionic emission of the oxide cathodes which can explain the many experimental results, has not been given, since the phenomena of the thermionic emission of the oxide cathodes are very complicated.

It appears that metallic atoms are formed in the oxide crystals by the decomposition of the oxides and the system consists of the "impurity semiconductor" whose model has been given by Wilson.⁽¹⁾ Therefore, it may be a reasonable picture that the thermionic emission of the oxide cathodes occurs in the composite system, consisting of the semiconductor and the metallic atoms which are formed on the surface of the semiconductor.

We wish to propose a zone model, based on the quantum mechanical theory of solid state, which can completely explain the mechanism of the thermionic emission and other properties of the oxide cathodes.

2. Résumé of the experimental results. Of the oxide cathodes, especially the alkaline earth metal oxides have been extensively investigated, since they are technically of great importance, but some of the experimental results on the properties of the oxides observed by several authors have not always coincided with each other. The important experimental results which have been supported by most of the authors, are described as follows.

(1) H. A. Wilson: *Proc. Roy. Soc.*, (London), A, **133** (1931), 458; **134** (1932), 277; **136** (1932), 487.

(a) It is believed that the oxide cathodes can emit enough electrons only after the operation of activation, but the oxide itself can scarcely emit electrons. Metallic atoms are formed on the surface of the oxides, and they are responsible for the thermionic emission.^{(2) ~ (12)}

(b) The thermionic emission current varies with the amount of the metallic atoms adsorbed on the surface of the oxides, as in the case of the alkaline metals or alkaline earth metals on the tungsten or other metal filaments. It is believed that the optimum activity is obtained, when the oxide surface is covered with a single layer of the adsorbed metallic atoms, i.e. the fraction of the surface (θ) covered with metallic atoms is equal to unity.^{(2), (3)}

(c) The dependence of the thermionic current of the oxide cathodes on the temperature is given by the so called Richardson's equation,^{(13) ~ (16)} as in the case of pure metals, that is

$$i_s = AT^2 e^{-b_0/kT} \quad (1),$$

with

k = Boltzmann constant,

i_s = saturation thermionic current,

A = constant,

b_0 = thermionic work function,

T = absolute temperature.

(d) By the Huxford's experiment,⁽¹⁷⁾ the photoelectric work function of alkaline earth metal oxide cathodes is equal to the thermionic work function. This experimental result is of great importance, since it can give a direct method to decide the model of the oxide cathodes, as we shall discuss in detail in the following sections.

3. Theory. A. *Energy levels in the oxide crystals.* Alkaline earth oxide crystals are insulators since p -band of O^{2-} ions directly below the conduction band lies in the range of, at least, 10 eV from the conduction band and, therefore, we can practically neglect the number of the electrons

(2) L. R. Koller: *Phys. Rev.*, **22** (1925), 671.

(3) J. A. Becker: *Phys. Rev.*, **34** (1929), 1323; **38** (1931), 2193.

(4) H. Rothe: *Z. f. Physik*, **36** (1926), 737.

(5) W. Espe: *Wiss. Veröff. a. d. Siemens Konz.*, **5** (1927), 5, 46.

(6) F. Detels: *Jahrb. d. drahtl. T.*, **30** (1927), 30, 52.

(7) M. S. Glass: *Phys. Rev.*, **28** (1926), 521.

(8) E. F. Lowry: *Phys. Rev.*, **35** (1930), 1367.

(9) A. Gehrts: *Z. tech. Phys.*, **11** (1930), 246; *Naturwiss.*, **20** (1932), 732.

(10) A. L. Reiman, R. Murgoci: *Phil. Mag.*, **8** (1930), 440.

(11) S. Dushman: *Rev. Mod. Phys.*, **2** (1930), 493.

(12) De Boer: *Elektronenemission und Adsorptionerscheinungen*, Leipzig, (1937).

(13) A. Sommerfeld: *Z. Physik*, **47** (1920), 1.

(14) R. H. Fowler: *Proc. Roy. Soc.*, (London), A, **117** (1928), 549; **122** (1929), 36.

(15) L. Nordheim: *Phys. Z.*, **30** (1929), 177.

(16) W. Howston: *Z. Physik*, **47** (1928), 33.

(17) W. S. Huxford: *Phys. Rev.*, **38** (1931), 379.

$$\eta = \frac{W_2 - W_1}{2} + \frac{kT}{2} \log \left(\frac{|m_1|kT}{2\pi \left(\frac{h}{2\pi}\right)^2 n_a^{2/3}} \right)^{3/2} \quad (2),$$

with

n_a = number of electrons in the B -level per unit volume,

h = Planck's constant,

m_1 = effective mass of the electrons in the B -level,

W_1 = potential energy of the B -level,

W_2 = mean potential energy of the conduction band.

We can obtain the thermionic current emitted from the impurity level by using the same method of calculation for the electric conductivity of semiconductor by Wilson.⁽²²⁾

Let the velocity of the electrons in the conduction band be (u, v, w) , and u the velocity component perpendicular to the potential barrier at the surface, then the distribution function of the electrons in the conduction band is given by^{(21), (22)}

$$n_2(u, v, w) = 2 \left(\frac{m}{h} \right)^3 \cdot B \cdot (kT)^{-3/4} \cdot \exp \left\{ -\frac{1}{2} (W_2 - W_1) - \frac{1}{2} m(u^2 + v^2 + w^2) \right\} / kT \quad (3),$$

with

$$B = \frac{n_a^{1/2}}{2^{5/4}} \left(\frac{h^2}{\pi m} \right)^{3/4} \quad (4).$$

Suppose that the transmission coefficient of the potential barrier at the surface is $D(E)$. Then the thermionic current through the unit area on the surface per unit time is given by

$$i_s = \frac{4\pi m \epsilon}{h^3} \cdot B \cdot (kT)^{1/4} \cdot e^{-\frac{1}{2} \Delta E / kT} \int_0^\infty D(E) \cdot e^{-U/kT} dU \quad (5).$$

with

$$U = \frac{1}{2} m u^2, \quad E = U + \frac{1}{2} m (v^2 + w^2),$$

ϵ = electronic charge.

As the simplest case we put the boundary conditions as follows:

$$\begin{aligned} D(E) &= 1, \text{ if } E \geq W_2 + \chi \\ &= 0, \text{ if } E < W_2 + \chi \end{aligned} \quad (6),$$

(22) H. Wilson: *Proc. Roy. Soc., (London)*, A, **136** (1932), 487.

we can integrate easily above equation

$$i_s = \epsilon n_a^{1/2} \left\{ \frac{2^3 m \pi k^5}{h^6} \right\}^{1/4} \cdot T^{5/4} \cdot e^{-(\frac{1}{2} \Delta E + \chi)/kT} \quad (7).$$

If we compare eq. (7) with eq. (1), we can see that, apart from the constant term, eq. (7) involves term $T^{5/4}$ instead of term T^2 in eq. (1). Since we can not distinguish $T^{5/4}$ and T^2 experimentally, eq. (7) coincides with Richardson's equation formally and the thermionic work function is given by

$$b_0 = \frac{1}{2} \Delta E + \chi \quad (8).$$

The electrical conductivity of the semiconductor is approximately given by

$$\sigma = \sigma_0 e^{-\frac{1}{2} \Delta E/kT} \quad (9)$$

where σ_0 is a constant which is approximately independent of temperature. It is interesting that eq. (8) and eq. (9) involve the factor of $\frac{1}{2} \Delta E$ instead of ΔE as the activation energy.

In the model shown in Fig. 2, the photoelectric work function is given as follows, at least, under the conditions of (6),

$$b' = \Delta E + \chi \quad (10)$$

As we mentioned in (d), the thermionic work function should be equal to the photoelectric work function. However, b_0 is not equal to b' , if we compared eq. (9) with eq. (10). As the results, we can say that the thermionic emission of the oxides is not caused directly from the impurity atoms in the oxides.

In order to interpret correctly the behaviours of the oxide cathodes, we should take into account the metallic atoms adsorbed on the surface of the semiconductor.

As the ideal case, we consider first the case of $\theta = 1$. In the alkaline earth metals with two dimensional regular lattice, s-band of the valency electrons overlaps partially with the empty band directly above it, and the Fermi surface lies about in the middle of the overlapping part, as we see in Fig. 3.

The state which the surface of the semiconductor, shown in Fig. 2, is covered with the monoatomic layer of the metal, whose structure was mentioned above, is shown in Fig. 4.

Electrons in the metal layer and semiconductor exist in the thermal equilibrium. Under this condition, the Fermi surface in the metal lies about in the middle of A and B, i.e.

$$\eta = \frac{1}{2} (W_2 - W_1) - kT \log \{ B(kT)^{-3/4} \},$$

where the energy value of the second term is about 0.16 eV for the value of, for example, $n_a = 10^{18}$ and $T = 1000^\circ\text{K}$. Therefore we can neglect

the second term, compared with the first term, which is about 1 eV, since we do not need the accurate value of η in the following discussion.

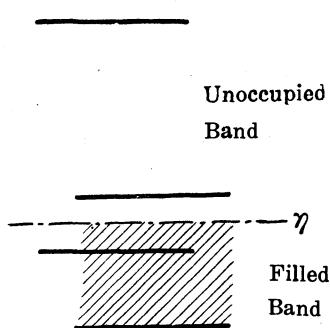


Fig. 3.

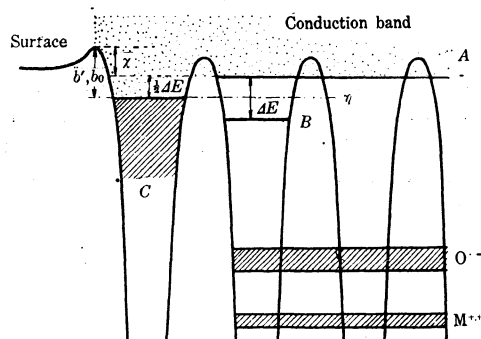


Fig. 4.

In the model shown in Fig. 4, electrons in the C-band are emitted over the potential barrier at the surface after they have absorbed heat energy. The electrons emitted from the C-band are supplied by the electrons which have been thermally raised in the conduction band of the semiconductor from the impurity atoms.

Then the thermionic current is given by eq. (1) and the thermionic work function is given by

$$b_0 = \frac{1}{2} \Delta E + \chi.$$

If we recognize that the photoelectrons are emitted from C-band the photoelectric work function is given by

$$b' = \frac{1}{2} \Delta E + \chi.$$

As the results, the thermionic work function coincides with the photoelectric work function, as we have expected from the experimental result (d).

The behaviours of (a) and (b) in the adsorbed metal layer have been already discussed by many authors. De Boer proposed an atomic picture for the adsorbed atom layer. Therefore, we need not discuss about (a) and (b) in detail here, but only state that we must regard the metal layer as the two dimensional lattice, at least, locally even when θ is less than unity, although De Boer's atomic picture does not need such a condition.

Next we wish to consider the thermionic emission of the solid solution between BaO and SrO. In this solid solution, the lattice constant a becomes linearly larger as the SrO mol percentage increases.⁽²³⁾ Also, one of the authors has confirmed that maxima of the fluorescence bands of the zinc-cadmium sulphide crystalphosphors shift linearly from blue to red with increasing lattice constant. The lattice constant a increases

(23) W. G. Burgers: *Z. Physik*, **80** (1933), 352.

linearly with increasing CdS mol percentage, as we shall report in the next paper.

If we apply zone theory of solid state,⁽²⁴⁾ to these experimental results, we can probably expect that the energy difference between conduction band and impurity level (or that between the excited state and ground state of the impurity atom) becomes linearly smaller with increasing SrO and CdS mol percentage in the individual solid solution.

As the results, the work function of the solid solution between BaO and SrO may become smaller as the SrO mol percentage is increased. And in this solid solution, we suppose that first the impurity level is caused from the Ba atom and later, in the case of large SrO mol percentage, it may be caused mainly from the Sr atom. Then we can expect that the thermionic emission current may become optimum when the SrO mol percentage takes a certain suitable amount. In fact, the optimum value of SrO is from about 50 to 60 percentage.

C. *Fluorescence of the alkaline earth oxides.* J. Ewles⁽²⁵⁾ reported that the alkaline earth oxides which contain no impurities as activator show fluorescence bands in the visible part, that is to say, in CaO at 6200Å and in BaO at 4650Å, 5629Å and 5970Å.

It may be proper to assume that these fluorescence bands are correlated with the alkaline earth metal level in the oxide crystals. As the probable picture, we wish to propose the following mechanism of fluorescence. That is to say, these fluorescence bands are responsible for the transitions of the electron from the excited states $nsnp$ to the ground state ns^2 of the impurity atom, as we see in Fig. 5. Such a impurity atom level lies in the range from about 2 eV to 4 eV below the conduction band, as we have mentioned above. Studies of such a problem of fluorescence are very interesting and important in relation to the problem of the thermionic emission phenomena of the oxides.

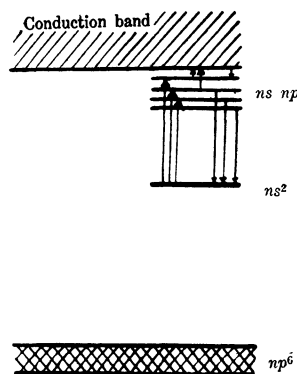


Fig. 5.

After we have written this paper, we received a paper of Blewett.⁽²⁶⁾ In his paper, he also obtained the same equation as eq. (7) in our paper, but as we have already discussed, eq. (7) does not coincide with the experimental results given in (d) of section 2.

In conclusion, we wish to express our sincere thanks to Vice-Director B. Imamura of this institute for his generous help, and also to Prof. S. Mizushima of Tokyo Imperial University for his kind advices and encouragement.

*Laboratory, Tokyo Shibaura Electric Co.
Mazda Division, Kawasaki.*

(24) N. F. Mott, H. Jones: "The Theory of the Properties of Metals and Alloys," Oxford, (1936), 99.

(25) J. Ewles: *Proc. Roy. Soc.*, (London), **167** (1938), 34.

(26) J. P. Blewett: *J. App. Phys.*, **10** (1939), 668.

Veratramine, a New Alkaloid of White Hellebore (*Veratrum grandiflorum* Loes. fil.)^{*}.

By Kojiro SAITO.

(Received December 14, 1939.)

In a previous communication⁽¹⁾ a method of isolating alkaloids from the so-called resinous matters was described. As the chief constituent jervine was obtained with a yield of 37%. Extraction of the resinous matters with ether gave a phenolic substance, melting at 262°. On treatment with dilute alkali the residue was decomposed into bases and acidic substances with angelic acid and an acid melting at 102°. The so-called resinous matters were consequently considered as a mixture of salt-like substances, consisting of alkaloids, acids, and free phenolic substances. A second alkaloid has now been isolated: some experiments on its constitution are hereunder described.

Attempts to isolate a crystalline substance from the material by formation of salts were unsuccessful because the bases are soluble in dilute acids. On the other hand the acidic substances combined with the bases are quite unstable against alkali. Fortunately it has been found that calcium acetate safely decomposes into bases and acids the salt-like compounds dissolved in alcohol, producing soluble acetates and insoluble calcium salts. From the latter substances chelidonic acid was obtained, as was proved by forming oxalic acid by the addition of an alkali. It has now been proved that an acid⁽¹⁾ together with phenolic substances, melting at 102° described before is oxalic acid.

The basic substances thus isolated, however, could not be obtained in crystalline state as they were chemically as well as physically quite similar, forming a solid solution. These were finally separated through sulphates, being soluble with difficulty in water. The salts consisted chiefly of jervine and a new alkaloid for which the name veratramine is proposed. Conversion of the sulphates into hydrochlorides separated jervine, because jervine hydrochloride is less soluble in alcohol than those of the accompanying alkaloids. After being regenerated from the hydrochloride, freed from jervine, the base was again converted into sulphate. After repeated recrystallisation from dilute alcohol, the sulphate was finally converted into acetate, from which veratramine was obtained by dissolving the salt in alcohol, adding ammonia and crystallising the precipitate from alcohol.

Veratramine crystallises from alcohol with one mol. of water in needles, melting at 209.5–210.5°, and having $[\alpha]_D^{19} = -70^\circ$, anhydrous base in methyl alcohol. Analyses of the free base, hydrated as well as anhydrous, and its derivatives, show that it has the formula $C_{26}H_{35}O_2N$.

^{*} On the Alkaloids of White Hellebore IV.

(1) K. Saito and H. Suginome, this Bulletin, **11** (1936), 168.

In dilute acids, such as hydrochloric, sulphuric, nitric, acetic, oxalic, etc. the base is difficultly soluble.

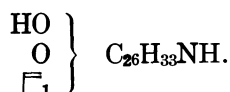
On treatment with hydrogen in the presence of platinum-black an acetic acid solution of veratramine absorbs the equivalent of two atoms of hydrogen, indicating the presence of one double bond in the molecule. This is consistent with the result of determination of double bond according to Wijs.

Veratramine contains no methylimido-group, methoxyl or dioxy-methylene group and behaves as a secondary amine. When veratramine is treated with methyl iodide and sodium carbonate it yields, however, a quaternary ammonium compound, m. p. 268° .

Acetylation of veratramine with acetic anhydride yields a neutral acetate, m. p. 205.5° – 206° . Analyses as well as acetyl determinations show that this substance is the diacetyl derivative, being acetylated at oxygen and nitrogen atom. On heating with alcoholic potassium hydroxide, the acetyl derivative undergoes a remarkable hydrolysis, producing a new compound, m. p. 179 – 180° and having $[\alpha]_D^{19} = +7^{\circ}$. This can be, however, converted into the original diacetylveratramine by acetic anhydride. The acetyl compound may be again hydrolysed by the same reagent to furnish a lowmelting veratramine, m. p. 179 – 180° and having $[\alpha]_D^{19} = +7^{\circ}$. Veratramine treated with alcoholic potassium hydroxide, however, melts at 209.5 – 210.5° and has $[\alpha]_D^{19} = -70^{\circ}$ in methyl alcohol, showing that the base itself undergoes no change by alcoholic potassium hydroxide. As veratramine is not only insoluble in aqueous ammonia, carbonates, and caustic alkali but also is not coloured by ferric chloride, it appears to contain neither phenolic hydroxyl nor carbonyl group. Further evidence of this is afforded by the fact that veratramine does not react with diazomethane. Veratramine is unsaponifiable by alcoholic potassium hydroxide indicating the absence of lactone or ester group. Veratramine is indifferent to carboxyl reagents.

From the above observation one of two oxygen atoms must occur as a member of an alcohol group and the other appears to be indifferent bridged oxygen.

Hence veratramine may be represented by the extended formula:



Experimental.

Decomposition of the so-called resinous matters. The material (120 g.), prepared as before,⁽²⁾ was dissolved in alcohol (500 c.c.) and filtered. To the filtrate 2 N-calcium acetate (200 c.c.) was added; after a while calcium chelidonate separated in crystalline state. After being left at room temperature for two days, the chelidonate was collected, washed, and dried. Yield 19.2 g. The latter was dissolved in 2N-hydrochloric acid (400 c.c.), with boiling, to a yellow solution and was then

(2) This Bulletin, **11** (1936), 168.

treated with charcoal. On being allowed to stand overnight, chelidonic acid separated in needles, yielding 15 g. The acid, after recrystallisation from water, melted either alone or with an authentic specimen at 262° with decomposition (Found: C, 45.55; H, 2.27. Calculated for $C_7H_4O_6$: C, 45.64; H, 2.19 %). The acid was further identified by derivation of the ethyl ester by refluxing a solution of the acid (2.0 g.) thus obtained in absolute alcohol (20 c.c.) in a current of hydrochloric acid, for one hour. Ethyl chelidonate was obtained in prismatic crystals, m. p. $65.5-66.5^{\circ}$ (Found: C, 54.73; H, 4.88. Calculated for $C_{11}H_{12}O_6$: C, 54.98; H, 5.02 %). The ester was identified by the mixed melting point method.

The mother-liquor of calcium chelidonate was acidified with acetic acid and treated with a larger amount of water, whereupon some calcium salts and acetates separated. After filtering off these, ammonium hydroxide was added, a mixture of free bases was separated. This was collected, dried, and worked up applying the following method, yielding pure jervine hydrochloride (8.8 g.), pure veratramine sulphate (4.2 g.), and other free alkaloids (9.0 g.).

Isolation and purification of veratramine. The crude alkaloids (103 g.), isolated from the resinous matters by treating first with dilute acetic acid and subsequently with ether, were dissolved in 0.5 N-acetic acid (800 c.c.). To the filtrate from this was added 2 N-sodium sulphate (300 c.c.), separating sulphates of bases in gelatinous form. After being left overnight these were decanted, treated with a solution of sodium sulphate for its coagulation and was then collected. Yield 71 g. A mixture of the sulphate (71 g.), sodium carbonate (20 g.) and alcohol (700 c.c.) was refluxed. After filtering off the inorganic salts, the filtrate was treated with hydrogen chloride in alcohol, when jervine hydrochloride separated crystalline. After being allowed to stand for two days the hydrochloride was collected, obtaining 36.6 g.

The free base was recovered from the above mother-liquor and was dissolved in 0.5 N-acetic acid. On careful addition of 2 N-sodium sulphate, the sulphate of the base separated gradually as a fine powder, being left overnight. This was collected, washed first with water and next with 50% alcohol. Yield 19.4 g. The sulphate thus obtained was converted into free base and was neutralised by dilute sulphuric acid, yielding 13.8 g. of veratramine sulphate in crystalline state. A mixture of the sulphate (13.5 g.), sodium carbonate (5 g.), and alcohol (100 c.c.) was refluxed and then diluted with water. On cooling, crude veratramine crystallised in slightly brown-coloured needles. Yield 10.3 g. This was dissolved, with rapid heating, in 2 N-acetic acid (50 c.c.), and hot filtered. On being left in the ice-chest overnight veratramine acetate crystallised in prisms whilst the other alkaloids remained in the solution. This was collected, obtaining 7.7 g. From the mother-liquor some more veratramine may be obtained. It was treated with aqueous ammonia, separating free base. On treating with dilute acetic acid the acetate separated crystalline which was collected, to the amount of 1.5 g. Total yield of the acetate is 9.2 g. or 0.1% calculated on the dried roots. The acetate was purified by recrystallisation from dilute alcohol forming prisms, m. p. $201-202^{\circ}$.

Veratramine. The pure base can be obtained from the acetate in alcohol by basifying with aqueous ammonia and crystallising from alcohol. Veratramine forms colourless needles from alcohol and melted at 209.5–210.5° (Found: C, 76.05, 76.06; H, 9.26; N, 3.47; H₂O, 4.04, 4.05. Calculated for C₂₆H₃₅O₂N·H₂O: C, 75.86; H, 9.07; N, 3.41; H₂O, 4.38%. Found: C, 79.25, 79.19; H, 9.14, 9.31; N, 3.65, 3.63. Calculated for C₂₆H₃₅O₂N: C, 79.33; H, 8.97; N, 3.56%).

Veratramine is soluble in methyl and ethyl alcohols, acetic ester, acetone, and toluene but insoluble in light petroleum, water and alkali. The base forms salts with inorganic as well as organic acid and the salts dissolve with difficulty in water. Veratramine reduces neither ammoniacal silver nitrate nor Fehling's solution and Gaebel's test for methylenedioxy-groups was negative. It gave no colour reaction with ferric chloride.

$$[\alpha]_D^{19} = \frac{-1.50^\circ \times 100}{2 \times 1.065} = -70^\circ \text{ in methyl alcohol.}$$

Hydrochloride. It crystallised from alcohol in colourless plates, m. p. 310° (Found: C, 72.73; H, 8.96; N, 3.37. Calculated for C₂₆H₃₅O₂N·HCl: C, 72.60; H, 8.44; N, 3.26%).

Picrate. Crystallised from dilute alcohol in yellow plates, m. p. 217.5–218° (Found: N, 8.85, 8.90. Calculated for C₂₆H₃₅O₂N·C₆H₃O₇N₃: N, 9.00%).

Dihydroveratramine. Veratramine (0.82 g.) was dissolved in glacial acetic acid (5 c.c.) and hydrogenated in the presence of Adam's platinum catalyst (0.1 g.); after one hour 45.5 c.c. or 1.02 mol. of hydrogen was taken up. The catalyst was filtered off, the acetic acid removed under reduced pressure, water added to the residue, and the solution was basified with aqueous ammonia. After collecting, the free base was washed and dried. This was crystallised from benzene and then from dilute alcohol, giving plates, m. p. 197–198° (Found: C, 78.75; H, 9.57. Calculated for C₂₆H₃₇O₂N: C, 78.94; H, 9.43%).

Determinatin of double bond. The double bond in the molecule was determined by the method of Wijs.

0.1081 g. Subst. absorbed 69.78 mg. iodine.

Calculated for C₂₆H₃₅I₂O₂N 79.11 mg. iodine.

The base (0.5 g.) in methyl alcohol (10 c.c.) was refluxed with methyl iodide (1.5 g.) and sodium carbonate (0.6 g.) for 3 hours. After filtering off the inorganic salts, the solvent and the excess of methyl iodide were removed, when the methiodide crystallised in colourless prisms. These were collected, washed, and dried, yielding 0.65 g. Crystallisation from methyl alcohol formed a colourless mass of needles decomp. at 268° (Found: C, 61.47; H, 7.68; CH₃, 5.39. Calculated for C₂₆H₃₄O₂N·CH₃·CH₃I: C, 61.17; H, 7.34; CH₃, 5.47%).

Methylveratramine methochloride. The above methiodide was dissolved in methyl alcohol and then treated with freshly prepared silver

chloride. On filtering off the silver halides, the solvent was removed. The methochloride crystallised from dilute methyl alcohol in colourless needles, m. p. 277° (Found: C, 73.18; H, 8.65. Calculated for $C_{26}H_{34}O_2N \cdot CH_3CH_3Cl$: C, 73.38; H, 8.80%).

Diacetylveratramine. A mixture of the base (0.5 g.) and acetic anhydride (5 g.) was refluxed for 2 hours and then cooled. After removal of most of the acetic anhydride under reduced pressure, the acetate was precipitated by water and was then treated with a solution of sodium carbonate. This was collected, washed, and dried. Yield 0.63 gr. It crystallised from dilute alcohol in colourless needles, m. p. 205–206.5°, containing 1 mol of water and 0.5 mol of alcohol (Found: $H_2O + \frac{1}{2}C_2H_6O$, 7.96, C_2H_5OH , 4.56. Calculated for $C_{26}H_{33}NO_2(C_2H_5O)_2 \cdot H_2O \cdot \frac{1}{2}C_2H_6O$: $H_2O + \frac{1}{2}C_2H_6O$, 7.92; $\frac{1}{2}C_2H_6O$, 4.44%. Found: C, 74.37, 74.32; H, 8.33, 8.06; N, 3.00, 2.97; CH_3-CO , 17.97. Calculated for $C_{26}H_{33}O_2N(CH_3CO)_2$: C, 75.42; H, 8.23; N, 2.94; CH_3CO , 18.03%).

$$[\alpha]_D^{18} = \frac{+0.72^\circ \times 100}{2 \times 0.9172} = +39^\circ \text{ in methyl alcohol.}$$

Alkaline hydrolysis of diacetylveratramine. After treatment of the acetate with 2 N-ethyl-alcoholic potassium hydroxide (25 c.c.) for 4 hours on the boiling water-bath, the solvent was distilled off. The hydrolysed base was obtained as a crystalline mass, recrystallised from 70% alcohol in plates, m. p. 179–180°.

Treatment of veratramine with ethyl-alcoholic potassium hydroxide. After being refluxed for 3 hours with N-ethyl-alcohol potassium hydroxide (10 c.c.), the base (0.5 g) was recovered as a crystalline mass, on distilling off the solvent and treating with water. This was proved to be veratramine, m.p. 209.5°–210.5°, after crystallisation from alcohol.

$$[\alpha]_D^{18} = \frac{-1.40^\circ \times 100}{2 \times 0.9792} = -70^\circ \text{ in methyl alcohol.}$$

The action of diazomethane on veratramine. A solution of the base (0.5 g.) in methyl alcohol (10 c.c.) was treated with diazomethane in ether, prepared from nitroso-N-methylurethane (2 c.c.) and was left overnight; two drops of dilute acetic acid were added. On removing the solvent, unchanged veratramine was recovered as needles, m.p. 209.5–210.5°.

Treatment of Veratramine with Hydroxylamine. (1) *In neutral medium.* A solution of the base (0.25 g.), hydroxylamine hydrochloride (0.5 g.), and sodium acetate (0.75 g.) in 70% ethyl alcohol was refluxed for 3 hours, and then kept for 10 days at room temperature. This was basified by sodium carbonate and diluted with water, when a solid mass was separated. After crystallisation from alcohol it was shown to be veratramine, m. p. 209.5–210.5°, by the mixed melting point method.

(2) *In alkaline medium.* A solution of the base (0.25 g.), hydroxylamine hydrochloride (0.5 g.) and potassium hydroxide (0.5 g.) in 70% alcohol was allowed to stand at room temperature for several days. This

was diluted with water and worked up as above, recovering unchanged veratramine, m. p. 209.5–210.5°.

Treatment of veratramine with semicarbazide. The base was treated under the same conditions as above and also unchanged veratramine, m. p. 200–201.5°, was recovered.

The author acknowledges his indebtedness to Professor H. Suginome for his interest in this work. The cost of this investigation was partly met by a grant from the Foundation for the Promotion of Science and Industrial Research of Japan, hereby gratefully acknowledged.

*Chemical Department,
Imperial University of Hokkaido,
Sapporo.*

On the Formation of Boro-Diol Complexes.

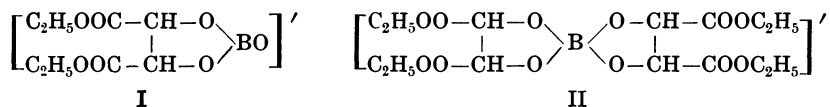
By Yojiro TSUZUKI and Yukio KIMURA.

(Received December 23, 1939.)

We have shown before some time that borate ion BO'_2 comes into union with ethyl tartrate, while free boric acid H_3BO_3 does not seem to give such boro-diol complexes.⁽¹⁾

In the present paper we will show that this conclusion is confirmed by another different method. Experimental results show that H_3BO_3 is without effect on the rotation of ethyl tartrate in aqueous solution, but BO'_2 diminishes its dextro-rotation to a remarkable degree, and indeed, with the increase in the BO'_2 concentration the dextro-rotation decreases, and even changes the sign. Thus potassium borate KBO_2 shows a much more diminishing effect as compared with borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, when we compare their effects in the same molar concentration of B-atom.

This depressing effect may possibly be due to the formation of the following complex ions (I and II) :



The compound II (potassium salt) has been really isolated and shown to have strong laevo-rotation.⁽²⁾

Results of Experiments. The results of the measurements at 20° are shown in Tables 1-4, and those carried out at 25° in Tables 5-8. The symbol *C* denotes the concentration of ethyl *d*-tartrate in mol/24 in the solution.

(1) Y. Tsuzuki, this Bulletin, **13** (1938), 337.

(2) Lowry, Optical Rotatory Power, 290, London (1935).

Table 1. Effect of KBO_2 on the Rotatory Power of Ethyl Tartrate.

M/4- KBO_2 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{20}$
5	10	4	+0.36°	+4.8°
15	15	3	-0.71	-12.5
20	10	2	-0.83	-22.0
25	5	1	-0.45	-23.8

Table 5. Effect of KBO_2 on the Rotatory Power of Ethyl Tartrate.

M/4- KBO_2 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{20}$
10	20	4	+0.57°	+7.5°
15	15	3	-0.59	-10.4
20	10	2	-0.75	-19.9
50	10	1	-0.38	-20.1

Table 2. Effect of Borax on the Rotatory Power of Ethyl Tartrate.

M/16- borax (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{20}$
10	20	4	+1.44°	+19.1°
15	15	3	+0.45	+7.9
20	10	2	-0.26	-6.9
50	10	1	-0.32	-16.3

Table 6. Effect of Borax on the Rotatory Power of Ethyl Tartrate.

M/16 borax (c.c.)	M/4 ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{25}$
5	10	4	+1.43°	+18.9°
15	15	3	+0.43	+7.6
22	10	2	-0.21	-5.0
25	5	1	-0.30	-15.9

Table 3. Rotatory Power of Ethyl Tartrate in Aqueous Solution of Boric Acid.

M/4- H_3BO_3 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{20}$
5	10	4	+2.39°	+31.6°
15	15	3	+1.80	+31.8
20	10	2	+1.23	+31.9
25	5	1	+0.66	+34.9

Table 7. Rotatory Power of Ethyl Tartrate in Aqueous Solution of Boric Acid.

M/4- H_3BO_3 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{25}$
10	20	4	+2.35°	+31.2°
15	15	3	+1.80	+31.7
20	10	2	+1.22	+32.3
25	5	1	+0.64	+33.9

Table 4. Rotatory Power of Ethyl Tartrate in Water.

Water (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{20}$
5	10	4	+2.34°	+31.0°
15	15	3	+1.79	+31.6
20	10	2	+1.17	+31.0
25	5	1	+0.63	+33.4

Table 8. Rotatory Power of Ethyl Tartrate in Water.

Water (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]_{5461}^{25}$
5	10	4	+2.38°	+31.5°
15	15	3	+1.76	+31.1
20	10	2	+1.20	+31.7
25	5	1	+0.62	+32.8

Conditions in common for Tables 1-4:
 $t = 20^\circ\text{C}$, $l = 2.2\text{ dm}$, $\lambda = 5461\text{ Å}$.

Conditions in common for Tables 5-8:
 $t = 25^\circ\text{C}$, $l = 2.2\text{ dm}$, $\lambda = 5461\text{ Å}$.

The above experimental results (at 25°) are graphically shown in Fig. 1.

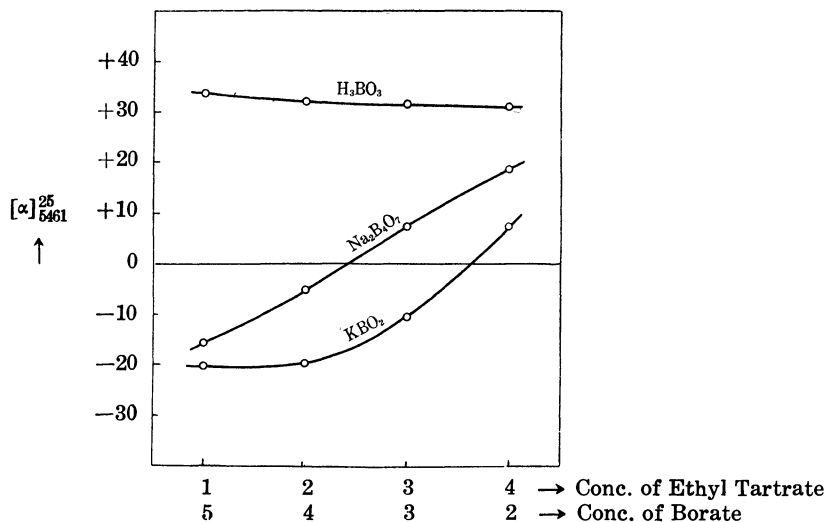
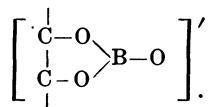


Fig. 1. Effect of Borates on the Rotatory Power of Ethyl *d*-Tartrate at 25°.

Discussion of the Results. The above results indicate that H_3BO_3 exerts only a very little effect on the rotatory power of ethyl tartrate, in sharp contrast to alkali borates. This difference is not due to the change of the acidity of the medium, for the rotation of ethyl tartrate in aqueous solution is not changed by the addition of K_2CO_3 : the solution of 10 c.c. M/4-ethyl tartrate and 20 c.c. N/4- K_2CO_3 shows $[\alpha]_{5461}^{20} = +31.0^\circ$ (compare Tables 3 and 4). This fact leads us to conclude that H_3BO_3 does not practically unite with diol, for the combination of H_3BO_3 must result in changing essentially the rotation of the diol, causing the cyclization of the molecule as follows:⁽³⁾



We are, however, imbued with an idea that free boric acid can form complexes with polyalcohols, the extent being considerable. We have had this impression since Magnanini⁽⁴⁾ concluded from the studies of the effect of mannitol on the electric conductivity of aqueous boric acid that there exists a mannitol-boric acid complex. He thought the composition of this compound to be in the proportions of 3 molecules of acid to 1 of mannitol. This conclusion was confirmed later by K. Matsuno and H. Kojima from the measurements of the hydrogen ion concentration and the viscosity of the mannitol-boric acid solution. Besides, they showed that a complex of acid: mannitol = 1:1 exists.⁽⁵⁾

(3) van't Hoff, *Die Lagerung der Atome in Raume*, Braunschweig, 3 Auflage (1908), 90.

(4) G. Magnanini, *Z. physik. Chem.*, **6** (1890), 58; *Gazz. chim. ital.*, **11** (1891), 8.

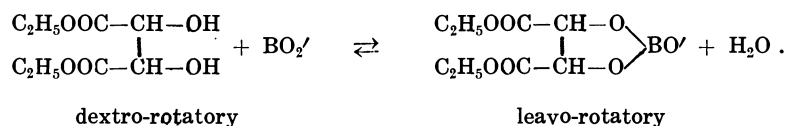
(5) K. Matsuno and H. Kojima, *Bull. Inst. Phys. Chem. Research* (Tokyo), **4** (1925), 45 (in Japanese).

It is, therefore, a somewhat unexpected result that free boric acid gives almost no effect upon the rotatory power of a diol such as ethyl tartrate. This fact can not satisfactorily be explained by the idea of "unfavourable position" of Böeseken,⁽⁶⁾ for this diol forms with BO'_2 a certain complex compound. A similar phenomenon can be observed in the case of mannit; it shows a very feeble laevo-rotation,⁽⁷⁾ which is scarcely changed by the addition of free boric acid, but in the presence of borate, the solution of mannit shows strong dextro-rotation.⁽⁸⁾

These remarkable facts have not yet been given any explanation. But now it seems to us that free boric acid does not come appreciably into union with polyalcohols, in contrast to borate ion.

Recently Murgier and Darmois expressed as the results of the measurement of rotation that boric acid combines with glucose and xylose only to a slight extent, but NaBO_2 gives a well characteristic compound.⁽⁹⁾

The reaction of BO'_2 with ethyl tartrate may be expressed in the following scheme:



Effect of Temperature on the Equilibrium. The author has shown in the distribution experiment⁽¹⁾ that this reaction is exothermic. Thus the equilibrium is shifted to the right when the temperature is lowered, so that the system will be more laevo-rotatory. This supposition has been practically ascertained by experiments. Results are given in Tables 1-4, from which it is evident that the rotation of the system becomes more dextro-rotatory at lower temperature. But in the cases of the solutions containing H_3BO_3 as well as in pure water, where the complex is only scarcely formed, the temperature effect on the totation is negligibly small, as may be seen by comparing the results of the Tables 3 and 4 with Tables 7 and 8 respectively.

As shown above, free boric acid has no effect on the rotatory power of polyvalent alcohols, but exerts a certain remarkable influence on that of hydroxy-acids, such as tartaric acid, gluconic acid, etc. In these cases, the cause may probably be the interaction between the groups COO' and H_3BO_3 . The experimental results and some considerations on this problem will be published in near future.

The authors desire to thank the Department of Education for a grant.

(6) Summary of literature, Hermans, *Z. physik. Chem.*, **113** (1924), 338; J. Böeseken, *Bull. soc. chim. Belg.*, **37** (1928), 385.

(7) $[\alpha]_D^{25} = -0.24^\circ$ (water), J. M. Braham, *J. Am. Chem. Soc.*, **41** (1919), 1707; $[\alpha]_D = -0.303^\circ$ (without solvent), F. B. Marti, *Bull. soc. chim. Belg.*, **39** (1930), 591.

(8) Vignon, *Compt. rend.*, **77** (1873), 1191; *Ann. chim. phys.*, [5], **2** (1874), 440; E. Fischer, *Ber.*, **23** (1890), 385.

(9) M. Murgier and E. Darmois, X International Congress for Chemistry in Rome, May 1938, Ref. *Angew. Chem.*, **51** (1938), 753.

Summary.

It has been found that free boric acid is without effect on the rotation of ethyl *d*-tartrate but alkali borates have a large effect, and it has been shown that boric acid unites with ethyl *d*-tartrate (dextro-rotatory) to an exceedingly small degree, but borate ion combines with the diol, giving laevo-rotatory boro-diol complex, and with increase of the concentration of borate ion and with fall of temperature the complex formation advances. Thus it has been suggested that only borate ion combines with diol (polyvalent alcohol), but undissociable boric acid does not.

*Nezu Chemical Laboratory,
Musashi Higher School, Tokyo-Nakaarai.*

Molecular Structures of Fluorobenzene and *o*-Difluorobenzene by Electron Diffraction.

By Hazime OOSAKA.

(Received December 26, 1939.)

The carbon-fluorine distances in molecules are in many cases shorter than expected from the Pauling and Huggins table of covalent radii.⁽¹⁾ Although no shortening occurs in chloromethanes, the investigation of the structures of fluoro- and fluorochloromethanes has shown the shortening of the C-F distances when the molecule contains two or more fluorine atoms.⁽²⁾ For halogen-substituted benzenes, however, the shortening of the carbon-halogen bond has been found in chlorine, bromine, and iodine derivatives.^{(3) (4)} Keeping these facts in mind the author has investigated the structures of fluorobenzene and *o*-difluorobenzene by the electron diffraction of the vapours.

Experimental. The electron diffraction apparatus of the de Laszlo type⁽³⁾ was used with some modifications. The air supply to the discharge tube controlled by a Leybold valve connected to an air reservoir of the pressure about 10 cm Hg. The electron beam was focussed by a coil placed near the bottom of the discharge tube. The wave length was measured by a resistance voltmeter which was calibrated directly in terms of wave length by taking the gold photographs. All photographs

(1) Pauling and Huggins, *Z. Krist.*, **87** (1934), 205; Pauling and Brockway, *J. Am. Chem. Soc.*, **59** (1937), 1223.

(2) Brockway, *J. Phys. Chem.*, **41** (1937), 185, 747.

(3) de Laszlo, *Proc. Roy. Soc. (London)*, A, **146** (1934) 662.

(4) Brockway and Palmer, *J. Am. Chem. Soc.*, **59** (1937) 2181.

were taken on Ilford X-ray plates. The interpretation of the gas photographs was made by the usual visual method.

Fluorobenzene⁽⁵⁾ was prepared from aniline and *o*-difluorobenzene⁽⁶⁾ from anthranilic ethyl ester by using hydrofluoroboric acid.

Results. Several photographs were made for each substance, the electron wave length used being about 0.065 Å and the camera distance 29.5 cm. The observed values, s_0 , of s given in Tables 1 and 2 are averages of the values found by visual measurement of ring diameters for several plates. The values for inner rings were excluded from the tables because of the strong background intensity. The quantitative comparison and results are also given in Tables 1 and 2. The theoretical scattering curves were calculated by the formula

$$I \sim \sum_{ij} Z_i Z_j (\sin s l_{ij}) / s l_{ij},$$

where $s = 4 \pi (\sin \theta / 2) / \lambda$. In these expressions l_{ij} is the distance between the i th and j th atoms, λ the de Broglie wave length of the electrons, θ the scattering angle, and Z the atomic number. The benzene ring was taken as a regular plane hexagon and all the interference terms except those of hydrogen atoms were included, the distances C-C = 1.39 Å and C-H = 1.06 Å being assumed. The curves for several models of each substance are shown in Figs. 1 and 2, in which the observed values of the measured apparent maxima and minima are given by vertical arrows.

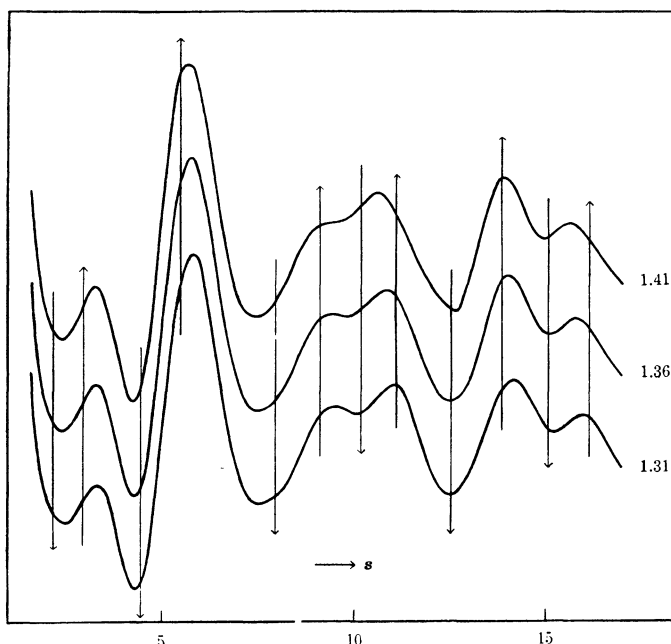


Fig. 1. Theoretical intensity curves for various models of fluorobenzene.

(5) Carothers, "Organic Syntheses", XIII, 48, New York (1933).

(6) Bergmann, Engel and Sándor, *Z. physik. Chem.*, B, **10** (1930), 106.

Table 2. *o*-Difluorobenzene.

Max.	Min.	s_0	s_I	s_I/s_0	s_{II}	s_{II}/s_0	s_{III}	s_{III}/s_0
2	3	5.67	5.55	0.979	5.66	0.998	5.74	1.013
		7.92	7.60	0.960	7.80	0.985	8.00	1.010
3	4	9.09	9.12	1.003	9.28	1.021	9.40	1.034
		10.09	9.73	0.965	9.90	0.982	10.10	1.001
4		11.14	10.71	0.962	10.94	0.982	11.08	0.995
5		13.99	13.95	0.997	14.10	1.008	14.26	1.019
Average				0.978		0.996		1.012
C-F assumed				1.41		1.36		1.31
C-F observed				1.38		1.36		1.33
Final value: C-F = 1.35 ± 0.03 Å.								

Fluorobenzene. The three theoretical curves calculated for fluorobenzene with carbon-fluorine distances of 1.41, 1.36, and 1.31 Å, respectively are shown in Fig. 1. Of these the curve for 1.41 Å is less satisfactory than the other with respect to the fourth minimum and maximum. The other two show qualitative agreement with the observed pattern. The final value, 1.34 ± 0.04 Å, of the C-F distance was taken as intermediate between the results from the latter two models.

***o*-Difluorobenzene.** Theoretical curves were calculated for three undistorted models of *o*-difluorobenzene with C-F distances 1.41, 1.36, and 1.31 Å, respectively. These are shown in Fig. 2. Also in this case the curve for 1.41 Å is less satisfactory for the fourth minimum and maximum. The final value is 1.35 ± 0.03 Å.

In considering the structure of this molecule the angle between the C-F bonds comes in question. In *o*-dichlorobenzene⁽⁴⁾ the bending has been found to be less than 1°. In *o*-difluorobenzene, however, the bending of the C-F bonds would be less than the order of this amount if it existed, because the fluorine atom is smaller than the chlorine atom and the interaction between the fluorine atoms is thus expected to be less significant.

Discussion. The carbon-fluorine distances in fluorobenzene and *o*-difluorobenzene are smaller than 1.41 Å, the sum of the covalent radii of Pauling and Huggins. If we consider the various electronic structures of the molecules as shown in Figs. 3 and 4, the decrease of the C-F distance may be attributed to the contribution of electronic structures which introduce a degree of double bond character in the carbon-fluorine bonds. Although the relation of the amount of double bond character to the interatomic distance is not yet known for the C-F bond, we know the empirical relation for the C-C bond⁽⁷⁾ and are justified to use it for

(7) Pauling and Brockway, *J. Am. Chem. Soc.*, **59** (1937), 1223.

the C-F bond because the ratio between the interatomic distances for single and double bonds does not vary very much for different atoms. Hence the degrees of double bond character of the C-F bonds are calculated as 16% and 13% for fluorobenzene and *o*-difluorobenzene, respectively.

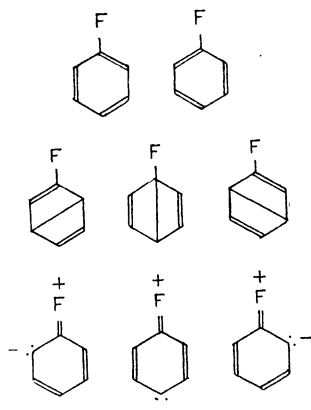
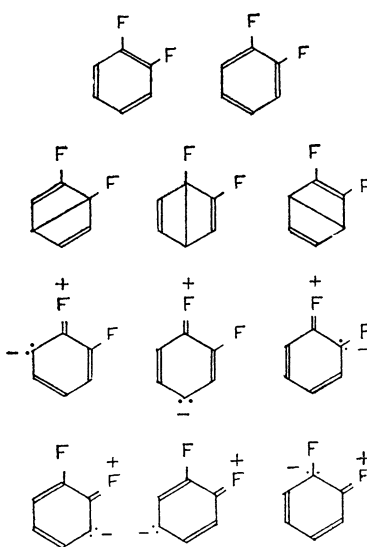


Fig. 3. Fluorobenzene.

Fig. 4. *o*-Difluorobenzene.

Now the dipole moment of halogen-substituted benzenes will be considered in relation to the carbon-halogen distances. These values for monohalogen-substituted benzenes are given in Table 3 together with those of double bond character. While the moment is increasing in the order from iodobenzene to chlorobenzene, the moment of fluorobenzene is smaller than that of chlorobenzene. As the double bond character is

Table 3.

C ₆ H ₅ X	Dipole moment ⁽⁶⁾ (D)	Carbon-halogen distance (Å)	Double bond character (%)
F	1.45	~1.34	16
Cl	1.56	1.70	16
Br	1.49	—	—
I	1.30	—	—

of the same order of magnitude for chloro- and fluorobenzenes, this character seems to be unimportant as the cause of the smaller moment of fluorobenzene. The much shorter C-F bond distance might play an important rôle for the lowering of the moment, the other properties being assumed not much different from each other.

Generally dipole moments of ortho-substituted benzenes show the so-called ortho effect. For these molecules the moment is found to be

smaller than the vector sum of the moments of substituent atoms. In the case of *o*-dihalogen-substituted benzenes the effect is more significant in the order from fluorine to iodine. The actual bond angles measured by electron diffraction are given in Table 4 together with interatomic

Table 4.

<i>o</i> -C ₆ H ₄ X ₂	Carbon-halogen distance (Å)	Double bond character (%)	Bond angle (°)
F	1.35	13	60
Cl ⁽⁴⁾	1.71	11	61.5
I ⁽⁸⁾	2.00	18	80

distances and degrees of double bond character. The bendings of the bonds are increasing in the order from fluorine to iodine and the degrees of double bond character can be said to have the similar tendency as the accuracy of these values is not high. Both tendencies agree with the order in the markedness of the ortho effect.

In conclusion, the author wishes to express his gratitude to Professor C. K. Ingold for his suggestion of the problem and to Mr. H. Terrey for his continued encouragement and helpful suggestions throughout the experimental work. He also wishes to thank Emeritus Professor M. Katayama for his interest in this problem and Professor S. Mizushima for discussing the result. He is indebted to the Ramsay Memorial Fellowships Trust for grants.

Summary.

The molecular structures of fluorobenzene and *o*-difluorobenzene have been investigated by the electron diffraction method. The C-F distances in these molecules have been determined as 1.34 ± 0.04 Å and 1.35 ± 0.03 Å, respectively. These distances are shorter than expected from the covalent radii of Pauling and Huggins. This shortening has been discussed in terms of resonance among several valence-bond structures. The dipole moment of halogen-substituted benzenes has been considered in relation to the carbon-halogen distances and the double bond character of the linkage.

*The Sir William Ramsay and Ralph Forster Laboratories,
University College, London,
and
Chemical Laboratory, Bunrika University, Tokyo.*

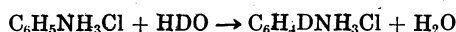
(8) Hendricks, Maxwell, Mosley, and Jefferson, *J. Chem. Phys.*, **1** (1933), 549.

Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in wässrigen Lösungen. III. Die Aktivierungsenergie.⁽¹⁾

Von Masao KOIZUMI.

(Eingegangen am 7. Dezember 1939).

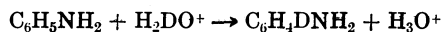
Inhaltsübersicht. Die Austauschreaktion der Kernwasserstoffatome des Anilinchlorhydrats in wässrigen Lösungen wird ohne jeden anderen Zusatz bei verschiedenen Temperaturen zwischen 79° und 100° quantitativ untersucht. Die dabei gefundene Geschwindigkeitskonstante $\bar{k}$ für die stöchiometrische Reaktion:



kann durch die Formel gut wiedergegeben werden:

$$\log \bar{k} = 11.6 \pm 0.4 - \frac{29,500 \pm 500}{4.574T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1}.$$

Nimmt man aber an, dass die wirklichen Reaktionsteilnehmer die durch die Hydrolyse des Anilinchlorhydrats entstehenden neutralen Anilinmoleküle und Hydroxo- bzw. Deuteroxoniumionen sind, dann wird die Geschwindigkeitskonstante $\bar{k}_0$ für diese grundlegende Reaktion:



durch die Formel wiedergegeben:

$$\bar{k}_0 = 10^{9.7} e^{-\frac{20,800}{RT}}.$$

Zum Schluss werden die in dieser Reihe der Versuche bisher gewonnenen Ergebnisse zusammengestellt und diskutiert.

Einleitung. Bei den vorhergehenden Versuchen (I. und II. Mitteil.) wird die Austauschreaktion des Anilinchlorhydrats in wässrigen Lösungen kinetisch verfolgt:



Dadurch wird gefunden, dass die Reaktion in neutraler und saurer Lösung hauptsächlich zwischen neutralen Anilinmolekülen und Hydroxo- bzw. Deuteroxoniumionen stattfindet:



und in alkalischer Lösung neben dieser auch die Reaktion zwischen Anilinmolekülen und Aniliniumionen als eine massgebende auftritt:



Deshalb liegt nun nahe, die Aktivierungsenergie für diese Reaktion bzw.

(1) I. Mitteil., dies Bulletin, **14** (1939), 530; II. Mitteil., *ibid.*, **15** (1940), 8.

Reaktionen zu bestimmen. Zu diesem Zweck wird zunächst die Geschwindigkeitskonstante $\bar{k}$ für die stöchiometrische Reaktion (1) bei verschiedenen Temperaturen ermittelt und daraus die Aktivierungsenergie für diese Reaktion (1) gefunden. Dann wird aus der so ermittelten „scheinbaren“ Aktivierungsenergie für Reaktion (1) die „wahre“ Aktivierungsenergie für die grundlegende Reaktion (2) unter Benutzung der Hydrolysenwärme des Anilinchlorhydrats berechnet.

Versuche und Resultate. Einfachheitshalber wird nur die Reaktion in neutraler Lösung d.h. ohne jeden anderen Zusatz untersucht und als Versuchstemperatur werden vier Temperaturen 79°, 90°, 95° und 100° gewählt, weil die Austauschgeschwindigkeit bei niedrigeren Temperaturen viel zu klein ist, um sie mit ausreichender Genauigkeit zu bestimmen. Die dabei erhaltenen Resultate sind in Tabelle 1 zusammengestellt, wo die Bedeutung der einzelnen Symbole auf I. Mittel. hin verweisen.

Tabelle 1. Austauschgeschwindigkeit in neutraler Lösung bei verschiedenen Temperaturen.

Versuchs-temp. °C	Versuchsdauer in Stdn.	M_{ac}	M_w	$n\alpha$	$(-X \log Y) \cdot 10^3$	$(\bar{k}/2.303) \cdot 10^3$
79°	2	0.0174	0.0562	3.59	0.75	0.335
	5	0.0174	0.0557	3.92	1.67	
	9.5	0.0175	0.0557	4.35	3.09	
	15	0.0194	0.0649	4.65	4.13	
	20	0.0174	0.0559	5.12	6.68	
	50	0.0174	0.0557	6.16	—	
90°	1	0.0174	0.0556	3.62	0.84	1.04 ~ 1.07
	3	0.0174	0.0554	4.31	2.96	
	6	0.0174	0.0558	5.16	6.62	
	9	0.0174	0.0556	5.56	9.32	
95°	1	0.0174	0.0557	3.08	1.59	1.80 ~ 2.00
	2	0.0174	0.0557	4.31	2.97	
	3.5	0.0174	0.0558	5.08	7.26	
100°	0.5	0.0174	0.0555	3.89	1.63	3.50
	0.5	0.0174	0.0563	3.98	1.92	
	1	0.0174	0.0558	4.27	2.36	
	1	0.0174	0.0559	4.50	3.64	
	2	0.0174	0.0554	5.16	6.63	
	3	0.0174	0.0557	5.35	7.8	
	3	0.0174	0.0554	5.69	10.6	
	6	0.0174	0.0558	6.18	—	
	6	0.0174	0.0558	6.18	—	
	10	0.0174	0.0562	6.37	—	
	25	0.0174	0.0554	6.41	—	

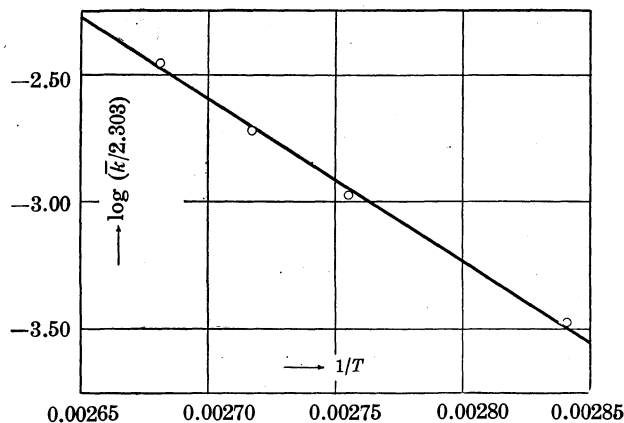


Abb. Abhängigkeit der Geschwindigkeitskonstante $\bar{k}$ von der absoluten Temperatur T .

Die in Tabelle 1 angegebenen Resultate können, wie aus der obestehenden Abb. ersichtlich ist, durch die Formel gut wiedergegeben werden:

$$\log(\bar{k}/2.303) = (14.8 \pm 0.4) - \frac{29,500 \pm 500}{4.574T} \quad (\text{Mol/Liter})^{-1}(\text{Stunde})^{-1} \quad (4).$$

Oder wenn man die Zeiteinheit von Stunde zu Sekunde umrechnet, ergibt sich die Formel:

$$\log \bar{k} = (11.6 \pm 0.4) - \frac{29,500 \pm 500}{4.574T} \quad (\text{Mol/Liter})^{-1}(\text{Sekunde})^{-1} \quad (5).$$

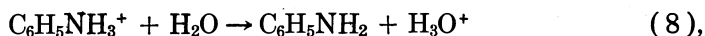
Diese Konstante $\bar{k}$ entspricht aber der stöchiometrischen Reaktion (1) und wird deshalb durch Gl. (6) definiert:

$$\begin{aligned} (\text{Austauschgeschwindigkeit}) &= \bar{k}[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}][\text{HDO}] \\ &= \bar{k}[\text{C}_6\text{H}_5\text{NH}_3^+][\text{HDO}] \end{aligned} \quad (6),$$

wo die Formel in den Klammern die Konzentration der betreffenden Substanz ausdrückt und im letzten Ausdruck in erster Annäherung $[\text{C}_6\text{H}_5\text{NH}_3\text{Cl}] = [\text{C}_6\text{H}_5\text{NH}_3^+]$ angenommen wird. Dagegen verläuft die wirkliche Reaktion, wie schon oben in Einleitung mit Gl. (2) gezeigt wird, zwischen neutralen Anilinmolekülen und Hydroxoniumionen. Deshalb wird die wahre Geschwindigkeitskonstante $\bar{k}_0$ für Reaktion (2) durch Gl. (7) definiert:

$$(\text{Austauschgeschwindigkeit}) = \bar{k}_0[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_2\text{DO}^+] \quad (7).$$

Da aber neutrale Anilinmoleküle und Hydroxoniumionen durch die Hydrolyse der Aniliniumionen gemäß Gl. (8) erzeugt werden:



muss zwischen den Konzentration der einzelnen Reaktionsteilnehmer folgende Beziehung (9) bestehen:

$$K = \frac{[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{H}_2\text{O}]} = \frac{[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_2\text{DO}^+]_2^{(2)}}{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{HDO}]_3} \quad (9),$$

wo die Konstante K die Gleichgewichts- bzw. Hydrolysenkonstante für Reaktion (8) darstellt. Wenn man deshalb beide Gln. (6) und (7) gleichsetzt und weiter Beziehung (9) in Rechnung zieht, dann ergibt sich ohne weiteres die Gl.:

$$\log \bar{k} = \log \bar{k}_0 + \log \left(K \times \frac{3}{2} \right) \quad (10).$$

Die Hydrolysenkonstante K des Anilinchlorhydrats wurde bisher nur bei verhältnismässig niedrigen Temperaturen und kleineren Konzentrationen gemessen. Denison und Steele⁽³⁾ haben z.B. bei 18° $K = 1.62 \times 10^{-5}$ und bei 25° $K = 2.29 \times 10^{-5}$ gefunden. Diese beiden Daten können aber durch die Formel gut wiedergegeben werden:

$$\log K = \frac{-8,700}{4.574T} + 1.7 \quad (11).$$

Nimmt man deshalb an, dass diese Formel auch bei höheren Temperaturen und grösseren Konzentrationen Gültigkeit findet, dann erhält man aus Gln. (5) und (10) ohne weiteres die Formel für die wahre Geschwindigkeitskonstante $\bar{k}_0$ der grundlegenden Reaktion (2):

$$\log \bar{k}_0 = 9.7 - \frac{20,800}{4.574T} \quad \text{bzw.} \quad \bar{k}_0 = 10^{9.7} e^{-\frac{20,800}{RT}} \quad (12).$$

Die Aktivierungsenergie für Reaktion (2) beträgt nämlich etwa 21 Kcal. und nach der Grössenordnung des Stossfaktors ($10^{9.7}$) zu urteilen, darf diese Reaktion ebenso wie die bisher untersuchten anderen Arten der Austauschreaktion der Kernwasserstoffatome der Benzolderivate als eine normal verlaufende bimolekulare Reaktion in Lösung aufgefasst werden.

Diskussion. In dieser Reihe der Versuche sind schon die Austauschreaktion der Kernwasserstoffatome verschiedener Arten der substituierten Benzole in wässrigen Lösungen kinetisch untersucht worden und bei den meisten Fällen wurde auch die Aktivierungsenergie sowie der Stossfaktor der bei jedem Fall grundlegenden Reaktion bestimmt. Deshalb liegt nun nahe, diese Versuchsergebnisse untereinander zu vergleichen und daraus irgendeinen Schluss zu ziehen. Die folgende Tabelle 2 ist nämlich die Zusammenstellung der in dieser Reihe der Versuch bisher gewonnen Ergebnisse.

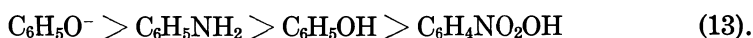
(2) Bezeichnet man die D-Konzentration in H_3O^+ bzw. H_2O mit x , dann ist offenbar $3x[\text{H}_3\text{O}^+] = [\text{H}_2\text{DO}^+]$ und $2x[\text{H}_2\text{O}] = [\text{HDO}]$. Daraus folgt der Koeffizient $2/3$ in dieser letzten Formel.

(3) R. B. Denison und B. D. Steele, *J. Chem. Soc.*, **89** (1906), 999.

Tabelle 2. Zusammenstellung der Versuchsergebnisse über die Austauschreaktion der Kernwasserstoffatome verschiedener Arten der substituierten Benzole.

Nr.	Reaktion	Protonacceptor bzw. zu deuterie- rende Substanz	Protondonator bzw. Deuterierungs- mittel	Stoss- faktor	Aktivie- rungsenergie in Kcal.
1	Phenol in saurer Lösung ⁽⁴⁾	C ₆ H ₅ OH	H ₂ DO ⁺	10 ^{12,5}	27.3
2	Phenol in alkalischer Lösung ⁽⁵⁾	C ₆ H ₅ O ⁻	C ₆ H ₅ OD	10 ^{9,9}	24.8
3	<i>o</i> -Nitrophenol in alkalischer Lösung ⁽⁶⁾	<i>o</i> -C ₆ H ₅ O ⁻ ?	<i>o</i> -C ₆ H ₄ NO ₂ OD ?	—	—
4	<i>m</i> -Nitrophenol in alkalischer Lösung ⁽⁶⁾	<i>m</i> -C ₆ H ₅ O ⁻	<i>m</i> -C ₆ H ₄ NO ₂ OD	10 ^{11,3}	29.0
5	<i>p</i> -Nitrophenol in alkalischer Lösung ⁽⁶⁾	<i>p</i> -C ₆ H ₅ O ⁻	<i>p</i> -C ₆ H ₄ NO ₂ OD	10 ^{10,9}	28.4
6	Anilinchlorhydrat in neutraler und saurer Lösung ⁽⁷⁾	C ₆ H ₅ NH ₂	H ₂ DO ⁺	10 ^{11,0}	20.8
7	Anilinchlorhydrat in alkalischer Lösung ⁽⁸⁾	C ₆ H ₅ NH ₂	{ H ₂ DO ⁺ C ₆ H ₅ NH ₂ D ⁺	—	—

Nach der empirisch gefundenen Regel für die elektrophile bzw. kationische Substitutionsreaktion der aromatischen Verbindungen können wir die in Tabelle 2 angegebenen Verbindungen ihrer Reaktionsfähigkeit der Kernwasserstoffatome etwa in folgender Reihe anordnen:⁽⁹⁾



Falls nun die Austauschreaktion der Kernwasserstoffatome als eine Art elektrophile Substitutionsreaktion aufgefasst werden kann, wie darauf schon von Ingold und seinen Mitarbeitern⁽¹⁰⁾ hingewiesen und auch in dieser Reihe der Versuche wiederholt angenommen wurde, dann können

(4) M. Koizumi, dies Bulletin, **14** (1939), 353.

(5) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 681. Der damals angegebene Stossfaktor 10^{10,8} in Formel (14) ist wegen des Rechnungsfehlers falsch. Er soll richtig 10^{9,9} heissen. Dementsprechend müssen die damals angegebenen Formeln (8) und (14) durch die folgenden ersetzt werden:

$$\bar{k} = 10^{7.8 \pm 0.5} e^{-\frac{24,800 \pm 800}{RT}} \quad (\text{Mol/Liter})^{-1}(\text{Sekunde})^{-1} \quad (8),$$

$$\bar{k}_o = 10^{9.9} e^{-\frac{24,800}{RT}} \quad (14).$$

(6) M. Koizumi und T. Titani, dies Bulletin, **14** (1939), 40; vgl. auch M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 318, 595 und 631.

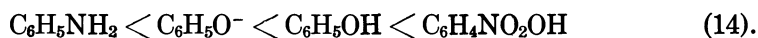
(7) Vorliegende Arbeit.

(8) M. Koizumi, dies Bulletin, **15** (1940), 8.

(9) Vgl. z.B. C. K. Ingold, *Chem. Rev.*, **15** (1934), 225.

(10) C. K. Ingold, C. G. Raisin und C. L. Wilson, *J. Chem. Soc.*, **1936**, 1637.

wir erwarten, dass diese Reihenfolge (13) gerade mit der übereinstimmen wird, die wir bei der wirklichen Austauschreaktion experimentell gefunden haben. Die Leichtigkeit, mit der eine Reihe ähnlicher Reaktionen stattfindet, können wir nun im allgemeinen und am zweckmässigsten durch die Aktivierungsenergie vergleichen. Da aber die in Tabelle 2 zusammengestellten Arten der Austauschreaktionen alle unter den ähnlichen Versuchsbedingungen (das molekulare Verhältnis von organischer Verbindung und Wasser ist immer fast gleich 1:3 und die Versuchstemperatur liegt zwischen 70° und 140°) untersucht worden sind, darf man diese Ergebnisse ohne weiteres miteinander vergleichen.⁽¹¹⁾ Wenn man aus diesem Grunde die in Tabelle 2 angegebenen Verbindungen, oder streng genommen die zu deuterierenden Substanzen, in der Reihenfolge der zunehmenden Aktivierungsenergie anordnet, erhält man die Reihe:



Diese Reihe stimmt mit der oben angegebenen aus der Substitutionsregel zu erwartende (13) fast gut überein, ausgenommen die ersten zwei Glieder $\text{C}_6\text{H}_5\text{NH}_2$ und $\text{C}_6\text{H}_5\text{O}^-$, deren Stellungen in Reihe (14) im Vergleich mit den in (13) gerade umgekehrt sind. Nach der empirischen Substitutionsregel muss nämlich $\text{C}_6\text{H}_5\text{O}^-$ leichter als $\text{C}_6\text{H}_5\text{NH}_2$ in Reaktion eintreten. Dagegen wird bei der wirklichen Austauschreaktion die Aktivierungsenergie für $\text{C}_6\text{H}_5\text{NH}_2$ deutlich kleiner als für $\text{C}_6\text{H}_5\text{O}^-$ gefunden. Als eine plausible Deutung für diese Diskrepanz kommt zuerst das Wesen der Aktivierungsenergie selbst in Betracht. Diese Energie wird nämlich nicht für einen bestimmten Reaktionsteilnehmer sondern für die angegebene Reaktion als ganzes bestimmt. Deshalb muss die Grösse der Aktivierungsenergie für eine angegebene Deuterierungsreaktion nicht nur von der Art der zu deuterierenden Substanz sondern auch (mindestens bis zu einem gewissen Grad) von der Natur des Deuterierungsmittels abhängen. Aber wie aus Tabelle 2 ersichtlich ist, wirken gegen $\text{C}_6\text{H}_5\text{NH}_2$ in neutraler bzw. saurer Lösung H_2DO^+ -Ionen als das Deuterierungsmittel. Dagegen wirken als solches gegen $\text{C}_6\text{H}_5\text{O}^-$ in alkalischer Lösung $\text{C}_6\text{H}_5\text{OD}$ -Moleküle. Da aber Hydroxoniumionen im allgemeinen als ein viel kräftigerer Protonendonator als neutrale Phenolmoleküle angesehen werden, trägt die Annahme wohl nicht, dass H_2DO^+ -Ionen geringere Aktivierungsenergie als $\text{C}_6\text{H}_5\text{OH}$ -Moleküle in Anspruch nehmen, mindestens so lange als die zu deuterierende Substanz in beiden Fällen dieselbe ist. Es scheint deshalb auf den ersten Blick, als ob gerade dieser Unterschied der Deuterierungsfähigkeit zwischen H_2DO^+ und $\text{C}_6\text{H}_5\text{OH}$ die Umkehrung der Stellung von $\text{C}_6\text{H}_5\text{NH}_2$ und $\text{C}_6\text{H}_5\text{O}^-$ in Reihe (14) verursacht hätte. Diese Deutung ist jedoch in sofern nicht ganz richtig, als wir dabei die Reaktionsfähigkeit der zu deuterierenden Substanz

(11) Dabei muss man die Tatsache in Rechnung ziehen, dass die in Tabelle 2 angegebene Aktivierungsenergie keine wahre sondern eine mittlere Aktivierungsenergie aller austauschbaren Arten der Kernwasserstoffatome in einem in Rede kommenden organischen Molekül darstellt, weil die zur Ausrechnung dieser Aktivierungsenergie benutzte Austauschgeschwindigkeitskonstante $\bar{k}$ keine wahre sondern eine mittlere Geschwindigkeitskonstante aller oben genannten Arten der H-Atome ausdrückt.

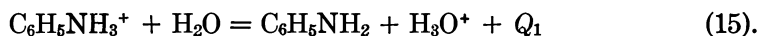
nicht in Rechnung gezogen haben. Aber in Wirklichkeit müssen wir vielmehr gerade diese letztere als einen massgebenden Faktor für die Aktivierungsenergie ansehen, wie weiter unten gezeigt wird.

Nach der modernen Theorie der elektrophilen bzw. kationischen Substitutionsreaktion⁽¹²⁾ wird im allgemeinen angenommen, dass unter den drei bei dieser Art der Reaktionen dirigierenden Effekt ausübenden Erscheinungen, nämlich Induktion, Polarisierung und Mesomerie, die letztere für den Verlauf der Reaktion massgebend ist. Wenn dies wirklich der Fall ist, dann muss die Aktivierungsenergie für eine angegebene Deuterierungsreaktion grösstenteils zur Valenzänderung bzw. Elektronenverschiebung innerhalb der Moleküle der zu deuterierenden Substanz verbraucht werden. Dagegen kann die Art des Deuterierungsmittels auf die Grösse der Aktivierungsenergie keinen grossen Effekt ausüben, weil die erstere bloss mit der Polarisierung der zu deuterierenden Moleküle in Zusammenhang steht. Die mit dieser Ansicht in Einklang stehenden Tatsachen können wir auch in den in Tabelle 2 angegebenen Versuchsergebnissen finden. Die Aktivierungsenergie für die Deuterierungsreaktion von C_6H_5OH in saurer Lösung (Nr. 1) beträgt 27.3 Kcal. Da aber das Deuterierungsmittel bei dieser Reaktion die Hydroxoniumionen H_2DO^+ sind, müsste die Aktivierungsenergie für dieselbe Reaktion in alkalischer Lösung (Nr. 2), wo die neutralen Phenolmoleküle C_6H_5OD als Deuterierungsmittel wirken, mindestens 30 Kcal. betragen, falls die Ersetzung des kräftigen Deuterierungsmittels H_2DO^+ in saurer Lösung durch das schwache C_6H_5OD in alkalischer Lösung die Vergrösserung der Aktivierungsenergie zur Folge hätte. Dadurch würde aber die in Formel (13) angegebene Reihenfolge wiederum umgestürzt, weil dann die Aktivierungsenergie für unsubstituiertes Phenol in alkalischer Lösung (Nr. 2) die für Nitrophenole in alkalischer Lösung (Nr. 3 bis 5) d.h. 28 bis 29 Kcal. weit übertreffen müsste. In Wirklichkeit haben wir jedoch die Aktivierungsenergie (= 24.8 Kcal) für diese erstere Reaktion Nr. 2 gut übereinstimmend mit Reihenfolge (13) deutlich kleiner als die für die letzteren Nr. 3 bis 5 gefunden. Aus all diesen Gründen liegt nahe, die Deutung für die Umkehrung der Stellungen von $C_6H_5NH_2$ und $C_6H_5O^-$ in Formel (14) vielmehr in der Bestimmungsmethode der Aktivierungsenergie bei dem Austauschversuche zu suchen. Wir sind bei der Bestimmung der Aktivierungsenergie der Deuterierungsreaktion von $C_6H_5NH_2$ in neutraler bzw. saurer Lösung zu dem Schluss gekommen, dass die experimentell (aus $\log k - 1/T$ -Kurve) gefundene Aktivierungsenergie um den Betrag der Hydrolysenwärme des Anilinchlorhydrats (bzw. Aniliniumions $C_6H_5NH_3^+$) grösser als die wahre Aktivierungsenergie für neutrale Anilinmoleküle $C_6H_5NH_2$ sein muss. Und aus diesem Grunde haben wir im vorliegenden Versuch von dem direkt gefundenen Wert der Aktivierungsenergie d.h. 29.5 Kcal. die Hydrolysenwärme des Anilinchlorhydrats 8.7 Kcal. abgezogen und dadurch den in Tabelle 2 angegebenen Wert 20.8 Kcal. gewonnen. Die dabei benutzte Hydrolysenwärme wird nun, wie schon oben erwähnt, von Denison und Steele bei Zimmertemperatur unter Verwendung verdünnter Lösung von

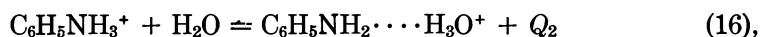
(12) Vgl. z.B. L. Pauling, Seite 1888 von „Organic Chemistry“ herausgegeben von H. Gilman, 1938, Vgl. weiter B. Eistert, „Tautomerie und Mesomerie“, 1938.

Anilinchlorhydrat bestimmt. Aber der so gefundene Wert der Hydrolysenwärme ist zum vorliegenden Zweck insofern nicht ganz geeignet, als wir bei dem Austauschversuche immer konzentrierte Lösung verwendet haben.

Wir sind in den vorhergehenden Versuchen (vgl. II. Mitteil.) zu dem Ergebnis gekommen, dass in konzentrierter Lösung von Anilinchlorhydrate in neutralem Wasser bzw. mit HCl versetzter Lösung die beiden Moleküle $C_6H_5NH_2$ und H_3O^+ untereinander nicht ganz unabhängig sein können. Vielmehr liegt die Annahme nahe, dass eine lockere Bindung zwischen H_3O^+ und dem Aminoradikal von $C_6H_5NH_2$ gebildet ist und dadurch die letzteren Moleküle immer in ihrer Umgebung die ersteren Ionen begleiten. Diese Erscheinung muss offensichtlich immer weiter zurücktreten, je kleiner die Konzentration der Lösung wird, und zum Schluss bei genügend grosser Verdünnung können die beiden Moleküle untereinander ganz unabhängig werden. Die von Denison und Steele bestimmte Hydrolysenwärme Q_1 entspricht gerade diesem letzten Grenzfall, wo $C_6H_5NH_2$ und H_3O^+ voneinander vollkommen abgetrennt angesehen werden können:



Dagegen muss die Hydrolysenwärme Q_2 , die für die Ausrechnung der Aktivierungsenergie der Austauschreaktion in konzentrierter Lösung benutzt werden soll, der Reaktion entsprechen:



weil in diesem Fall wegen der grossen Konzentration die durch Hydrolyse gebildeten $C_6H_5NH_2$ und H_3O^+ untereinander nicht ganz unabhängig sind. Vergleicht man beide Gln. (15) und (16), so überzeugt man sich leicht, dass die Wärmetönung Q_2 kleiner als die von Denison und Steele bestimmte Q_1 sein muss. Daraus folgt ohne weiteres, dass bei der oben angegebenen Ausrechnung der Aktivierungsenergie zu grosse Hydrolysenwärme von dem direkt gefundenen Wert abgezogen wurde und deshalb die so gefundene Aktivierungsenergie zu klein sein muss. Die wahre Aktivierungsenergie der Deuterierungsreaktion von $C_6H_5NH_2$ in neutraler bzw. saurer Lösung muss somit um einen gewissen Betrag grösser als der in Tabelle 1 angegebene Wert (= 20.8 Kcal.) sein. Über die absolute Grösse der dabei anzubringenden Korrektur wissen wir noch kaum etwas. Aber falls die oben angegebene Ansicht der Wirklichkeit entspricht, so ist die Möglichkeit vorhanden, dass die Aktivierungsenergie für $C_6H_5NH_2$ in neutraler bzw. saurer Lösung (Nr. 6) durch diese Verbesserung mindestens bis zu derselben Grösse wie die für $C_6H_5O^-$ in alkalischer Lösung (Nr. 2) oder diese übertreffend vergrössert werden kann. Beim letzteren Fall stimmen offensichtlich die Ergebnisse der Austauschversuche mit den aus der gewöhnlichen Substitutionsregel erwarteten überein.

Was den Stossfaktor der Reaktion anbetrifft, so ist er, wie aus Tabelle 2 ohne weiteres ersichtlich wird, für alle untersuchten Reaktionen von fast derselben Grössenordnung und liegt im Bereich zwischen 10^{10}

bis 10^{12} . Deshalb dürfen diese Reaktionen alle als normal verlaufende bimolekulare Reaktion in Lösung aufgefasst werden⁽¹³⁾ Die Grösse des Stossfaktors der Reaktion in Lösungen hängt hauptsächlich von zwei Faktoren ab, ohne Unterschied ob man Flüssigkeiten klassisch als einen Grenzfall der verdichteten Gase auffasst oder ihnen die quasikristalline Struktur zuschreibt. Der eine dieser beiden Faktoren ist offensichtlich die Stosszahl der Moleküle und der andere der sogenannte Orientierungs- bzw. sterische Faktor. Bei diesem letzteren handelt es sich um die Wahrscheinlichkeit der geeigneten Anordnung der gegeneinander zu reagierenden Moleküle beim Zusammentreffen. Deshalb muss die Grösse des sterischen Faktors um so kleiner werden je grösser und komplizierter das zu reagierende Molekül wird, weil die Wahrscheinlichkeit, mit der ein bestimmter reaktionsfähiger Teil der Moleküle in einer geeigneten Anordnung gefunden wird, mit der zunehmenden Komplikation des Molekülbaus abnehmen muss. Dagegen wird die Stosszahl der Moleküle von der Molekülgrösse und -struktur nicht viel beeinflusst.⁽¹⁴⁾ Deshalb darf wohl angenommen werden, dass die Grösse des Stossfaktors durch den Molekülbau beeinflusst wird und zwar derart, dass die erstere mit zunehmender Komplikation des letzteren verringert wird. Wenn man diese Überlegung auf den Fall der Kernaustauschreaktion anwendet, kommt man ohne weiteres zu dem Ergebnis, dass mindestens gegen dieselben bzw. ähnlich gebauten zu deuterierenden Moleküle H_2DO^+ -Ionen im Vergleich mit den anderen kompliziert gebauten Deuterierungsmitteln wie z.B. $\text{C}_6\text{H}_5\text{OD}$ den grössten sterischen Faktor besitzen muss, weil H_2DO^+ -Ionen unter den benutzten Deuterierungsmitteln am einfachsten gebaut sind. Dieser Schluss stimmt in der Tat mit den Ergebnissen überein, die wir mit $\text{C}_6\text{H}_5\text{OH}$ in saurer und in alkalischer Lösung gewonnen haben (vgl. Nr. 1 und 2 in Tabelle 2). Bei der Austauschreaktion von $\text{C}_6\text{H}_5\text{OH}$ in saurer Lösung, wo H_2DO^+ -Ionen gegen $\text{C}_6\text{H}_5\text{OH}$ -Moleküle als Deuterierungsmittel wirkt, fanden wir als Stossfaktor den Wert $10^{12.5}$ (vgl. Nr. 1). Dagegen erhielten wir bei der Reaktion in alkalischer Lösung, wo $\text{C}_6\text{H}_5\text{OD}$ -Molekül als Deuterierungsmittel gegen $\text{C}_6\text{H}_5\text{O}^-$ -Ionen wirkt, den viel kleineren Wert nämlich $10^{9.9}$ (vgl. Nr. 2). Dieser Stossfaktor wird jedoch bei der Reaktion von Nitrophenol in alkalischer Lösung um ein wenig aber untrüglich vergrössert (vgl. Nr. 4 und 5). Die Deutung für diese Zunahme des Stossfaktors beim Übergang von unsubstituiertem Phenol zu Nitrophenole kann vielleicht darin gefunden werden, dass die durch die Nitrogruppe hervorgerufene intermolekulare Dipolanziehung die Wahrscheinlichkeit der geeigneten Molekularanordnung beim Zusammentreffen im Vergleich mit dem Fall des unsubstituierten Phenols bis zu einem gewissen Grad vermehren dürfte.

Bei der Austauschreaktion von $\text{C}_6\text{H}_5\text{NH}_2$ in saurer bzw. neutraler Lösung (Nr. 6) wirken offensichtlich H_2DO^+ -Ionen als das Deuterierungsmittel. Deshalb können wir als den Stossfaktor dieser Reaktion

(13) Vgl. K. H. Geib, *Z. physik. Chem.*, A **180** (1937), 211.

(14) Die Stosszahl der Moleküle hängt offensichtlich vom Stossdurchmesser der Moleküle ab. Aber dieses letztere wird durch die Molekülgrösse und insbesondere durch die Molekülstruktur nicht so sehr beeinflusst.

(abgesehen von der Verschiedenheit der zu deuterierenden Moleküle)⁽¹⁵⁾ fast dieselbe Grösse wie bei der Austauschreaktion von C_6H_5OH in saurer Lösung (Nr. 1) nämlich 10^{12} bis 10^{13} erwarten. Aber in Wirklichkeit fanden wir den viel kleineren Wert nämlich $10^{9.7}$. Wenn auch ein Teil dieses Unterschiedes auf dem ungeeigneten Wert der bei der Ausrechnung der Aktivierungsenergie benutzten Hydrolysenwärme zurückgeführt werden kann (vgl. oben), können wir doch die abnehmende Neigung des Stossfaktors bei dieser Reaktion nicht übersehen. Die Deutung für diese abnehmende Neigung des Stossfaktors bei der Austauschreaktion von $C_6H_5NH_2$ in saurer bzw. neutraler Lösung können wir aber auch vielleicht aus demselben Grunde finden, wie wir daraus die zu kleine (gefundene) Aktivierungsenergie derselben Reaktion erklärt haben, was nämlich auf der Annahme beruht, dass H_3O^+ -Ionen in konzentrierter Lösung des Anilinchlorhydrats nicht ganz frei angesehen werden und zwischen ihnen und neutralen $C_6H_5NH_2$ -Molekülen vielmehr eine lockere Bindung etwa nach dem Schema $C_6H_5NH_2 \dots H_3O^+$ geschaffen werden muss. Wenn dies der Fall ist, so kann das Deuterierungsmittel bei der Austauschreaktion von $C_6H_5NH_2$ in neutraler bzw. saurer Lösung keine einfachen H_2DO^+ -Ionen sein, sondern es muss vielmehr als kompliziert gebaute, grosse Ionen aufgefasst werden, die durch etwa die Formel $C_6H_5NH_2 \dots H_2DO^+$ ausgedrückt werden dürften. Dann ist aus dem schon oben angegebenen Grund ohne weiteres klar, dass diese Vergrösserung der Molekülgrösse des Deuterierungsmittels die Verminderung des Stossfaktors zur Folge hat.

Kurz zusammengefasst können wir sagen, dass bei den hier untersuchten Arten der Kernaustauschreaktion die Molekülstruktur der zu deuterierenden Substanz für die Aktivierungsenergie und die des Deuterierungsmittels für den Stossfaktor massgebend ist. Ich hoffe, diese halbqualitative Ansicht später noch nach quantitativer Seite hin erweitern zu können. Ich glaube weiter, dass es sehr nützlich und fruchtbar sein wird, wenn man solche Vergleichsversuche noch mit vielen anderen Arten der Austauschreaktionen ausführt und das Deuterierungsvermögen der einzelnen Deuterierungsmittel einerseits und die Austauschbarkeit der Kernwasserstoffatome der einzelnen Verbindungen anderseits separat vergleichen könnte.

Zum Schluss ist es mir eine angenehme Pflicht, Herrn Prof. T. Titani für seine wertvollen Ratschläge und stetige Unterstützung bei der Durchführung der vorliegenden Arbeit meinen herzlichsten Dank auszusprechen. Der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der Wissenschaftlichen Forschung) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) möchte ich auch für ihre finanzielle Unterstützung meinen besten Dank aussprechen.

*Siomi-Institut für physikalische
und chemische Forschung
und
Physikalisch-chemisches Laboratorium
der Kaiserlichen Universität Osaka*

(15) Der Effekt auf den Stossfaktor bezüglich der Verschiedenheit der zu deuterierenden Moleküle muss in diesem Fall sehr klein sein, weil die beiden in Frage kommenden Moleküle $C_6H_5NH_2$ und $C_6H_5OH_2$ miteinander ähnlich gebaut sind.

Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. VI. Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche der Oxyde von zweiter, vierter und sechster Gruppe des periodischen Systems.

1. Experimenteller Teil.⁽¹⁾

Von Noriyoshi MORITA.

(Eingegangen am 27. Dezember 1939)

Inhaltsübersicht. Die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche der Oxyde, die zur II., IV. und VI. Gruppe des periodischen Systems gehören, nämlich der Oxyde von Magnesium, Calcium, Strontium, Barium; Zink, Cadmium; Titan, Zirkonium, Thorium; Silicium, Zinn; und Chrom, Molybdän, Wolfram, wird bei verschiedenen Temperaturen untersucht und die dabei gewonnenen Versuchsergebnisse sind tabellarisch angegeben.

Einleitung. Während der Versuche über die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche der verschiedenen Arten von Oxyden, fanden wir, dass es eine gewisse regelmässige Beziehung zwischen der katalytischen Wirksamkeit des Oxyds und dem Platz gibt, den das betreffende Oxyd im periodischen System einnimmt. So z.B. kamen wir in den letzten Versuchen (vgl. IV. Mitteil.), wo die katalytische Wirksamkeit der zur IV. Hauptreihe gehörenden Oxyde nämlich CaO , (Al_2O_3) , TiO_2 , V_2O_5 , Cr_2O_3 , Mn_2O_3 , Fe_2O_3 und NiO miteinander verglichen wurde, zu dem Ergebnis, dass Mn_2O_3 die grösste und TiO_2 die kleinste Wirksamkeit besitzt, während die anderen Oxyde ihrer katalytischen Wirksamkeit gemäss sich zwischen diesen beiden Extremen regelmässig anordnen (vgl. Tabelle 8 und Abb. 2 in IV. Mitteil.). Da aber seitdem ähnliche Austauschversuche noch mit vielen anderen Arten von Oxyden ausgeführt wurden und folglich das Versuchsmaterial sich ziemlich akkumuliert hat, wollen wir hier die Ergebnisse der Versuche mitteilen, die mit den Oxyden der II., IV. und VI. Gruppe des periodischen Systems durchgeführt wurden. Die dabei untersuchten Oxyde sind nämlich MgO , CaO , SrO , BaO ; ZnO , CdO ; TiO_2 , ZrO_2 , ThO_2 ; SiO_2 , SnO_2 ; und Cr_2O_3 , MoO_3 , WO_3 . Da unter diesen vierzehn Arten der Oxyde CaO , TiO_2 , SiO_2 und Cr_2O_3 schon in den früheren Versuchen bearbeitet und über die dabei gewonnenen Ergebnisse in II. (SiO_2) und IV. (CaO , TiO_2 und Cr_2O_3) Mitteil. berichtet wurden, werden die ausführlichen Beschreibungen der Versuche mit diesen Oxyden auf dort verwiesen. Unter den übrigen zehn Arten der Oxyde wurden die Ergebnisse mit CdO und SnO_2 -I (vgl. weiter unten) von den in hiesigem Institut von Dr. H. Tanaka durchgeführten unveröffentlichten Versuche entnommen. Bei dieser

(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: ebenda, **13** (1938), 601; III. Mitteil.: ebenda, **13** (1938), 656; IV. Mitteil.: ebenda, **14** (1939), 9; V. Mitteil.: ebenda, 520; **15** (1940), 1.

Gelegenheit möchte ich Herrn Dr. Tanaka für seine freundliche Genehmigung zur Veröffentlichung seiner Arbeit in dieser Mitteilung herzlichst danken.

Die in der vorliegenden Arbeit benutzte Versuchsmethode ist im grossen und ganzen dieselbe wie die in I. Mitteil. beschriebene.⁽²⁾ Deshalb werden alle Einzelheiten der Arbeitsmethode auf dort verwiesen und hier sollen nur die Herstellungsmethode jedes verwendeten Oxyds und die unter Verwendung dieser Oxyde gewonnenen Versuchsergebnisse ausführlich mitgeteilt werden.

1. Versuchsreihe. Austauschreaktion an der Oberfläche der Oxyde von II. Gruppe. Die in dieser Reihe der Versuche verwendeten Oxyde werden auf folgende Weise hergestellt.

Magnesiumoxyd MgO —Der Niederschlag von Magnesiumhydroxyd, der sich beim Versetzen der wässrigen Lösung von reinem Magnesiumnitrat mit fast äquivalenten Mengen verdünnter Ammoniaklösung abgeschieden hat, wird zunächst mit heissem Wasser gründlich gewaschen, dann im Trockenschrank gut getrocknet und zum Schluss durch Erhitzung in einem Porzellantiegel bis auf dunkler Rotglut vollständig bis zum Oxyd zersetzt.

Calciumoxyd CaO —Vgl. S. 9, IV. Mitteil.

Strontiumoxyd SrO —Strontiumnitrat aus dem Handel wird zunächst durch zweimalige Umkristallisation aus destilliertem Wasser gereinigt und dann im Vakuumexsikator gut getrocknet. Das Oxyd wird nun aus dem so gereinigten Nitrat auf folgende Weise hergestellt. Das Nitrat wird nämlich zuerst in einem Porzellantiegel langsam erhitzt und möglichst vollständig bis zum Oxyd zersetzt. Dann wird der innere Teil des so entstandenen Oxyds, das mit der Tiegelwand nicht direkt in Berührung kommt, sorgfältig herausgenommen und in einem neuen Porzellantiegel abermals bis auf etwa 900° einige Stunden lang erhitzt.

Bariumoxyd BaO —Dieses Oxyd wird auf genau dieselbe Weise wie bei dem oben erwähnten Strontiumoxyd aus dem käuflichen Bariumnitrat bereitet.

Zinkoxyd ZnO —Der Niederschlag von Zinkhydroxyd, der sich bei der Versetzung der wässrigen Lösung des reinen Zinksulfats mit fast äquivalenten Mengen der Ammoniaklösung abgeschieden hat, wird mit heissem destilliertem Wasser solange gewaschen, bis keine Sulfationen im Filtrat sich mehr nachweisen lassen. Dann wird er im Trockenschrank gut getrocknet und aus dem so getrockneten Hydroxyd wird das Oxyd dadurch gewonnen, dass das erstere in einem Porzellantiegel bis auf etwa 700° einige Stunden lang erhitzt wird.

Cadmiumoxyd CdO —Die wässrige Lösung von reinem Cadmiumnitrat wird mit der Lösung von Ammoniumcarbonat versetzt und der dabei abgeschiedene Niederschlag von Cadmiumcarbonat, nachdem er mit heissem destilliertem Wasser gründlich gewaschen und dann im Trockenschrank gut getrocknet worden ist, in einem Porzellantiegel so lange erhitzt bis das Carbonat vollkommen in Oxyd verwandelt wird.

(2) Vgl. dazu III. und IV. Mitteil.

Jedes Oxyd behandelt man aber direkt vor Beginn des Austauschversuches immer mit reinem Sauerstoffgas, indem das letztere durch das mit dem Oxyd beschickte Katalysatorrohr unter zugleichiger Erhitzung des Rohres bis auf 600° bis 800° einige Stunden lang durchgeleitet wird und erst dann wird das Reaktionsgasgemisch durch das Rohr geleitet. Das dabei verwendete Reaktionsgasgemisch, das aus gewöhnlichem (leichtem) elektrolytischem Sauerstoffgas und an schwerem Sauerstoff angereichertem schwerem Wasserdampf besteht, besitzt ebenso wie bei den früheren Versuchen in I. bis IV. Mitteil. die Zusammensetzung von $O_2:H_2O = 2:1$, und die Strömungsgeschwindigkeit dieses Gasgemisches durch das Katalysatorrohr beträgt (bei Zimmertemperatur und unter gewöhnlichem Druck gemessen!) 60 ccm pro Minute. Die dadurch gewonnenen Versuchsergebnisse mit den Oxyden der II. Gruppe sind in Tabelle 1 bis 5 zusammengestellt, wo die einzelnen Buchstaben bzw. Abkürzungen folgende Bedeutungen besitzen (vgl. IV. Mitteil.):

Δs_a und Δs_e : der gewöhnlichem Wasser gegenüber gemessene Dichteüberschuss des zum Versuch benutzten an schweren Sauerstoff angereicherten schweren Wassers vor (Δs_a) und nach (Δs_e) dem Versuch.

$\Delta s_a(O)$: solch ein Teil des gesamten anfänglichen Dichteüberschusses Δs_a des verwendeten schweren Wassers, der lediglich auf der Anreicherung der schweren Sauerstoffisotope zurückgeführt werden kann.

%A: das prozentuale Austauschmass, d.h. das prozentuale Verhältnis der wirklich gefundenen Abnahme der Dichte des verwendeten schweren Wassers nach dem Versuch, nämlich $(\Delta s_a - \Delta s_e)$, gegen den theoretischen Wert, der sich beim vollständigen Austausch ergeben würde. Dieser letztere Wert lässt sich aber mit Hilfe des Mengenverhältnisses des zum Versuch verwendeten gasförmigen Sauerstoffs und des Wasserdampfs sowie von Δs_a und $\Delta s_a(O)$ leicht errechnen (vgl. I. Mitteil.).

M: Gewichtsmenge des zum Versuch verwendeten Oxyds.

Die in der ersten Spalte der Tabelle angegebene Versuchsnr. zeigt die zeitliche Reihenfolge der einzelnen Versuche an, die bei verschiedenen Temperaturen ausgeführt wurden und zwischen, d.h. vor und nach, jedem dieser einzelnen Versuche wird reines Sauerstoffgas immer durch das Katalysatorrohr einige Stunden lang durchgeleitet.

Tabelle 1. Magnesiumoxyd MgO. $\Delta s_a = 36.8 \gamma$, $\Delta s_a(O) = 22.8 \gamma$, $M = 6 g$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
5	370	36.5	0.3	2
3	480	36.8	0.0	0
4	530	27.3	9.5	49
1	570	17.7	19.1	98
2	670	17.8	19.0	93

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

Über die Versuchsergebnisse, die mit Calciumoxyd CaO gewonnen werden, vgl. Tabelle 1 in IV. Mitteil.

Tabelle 2. Strontiumoxyd SrO. $\Delta s_a = 36.9 \gamma$, $\Delta s_a(O) = 23.5 \gamma$, $M = 15 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
4	350	35.3 ?	1.6	8 ?
2	410	33.3	3.6	18
1	500	19.1	17.8	89
3	610	15.7	21.2	105

$$\%A = \frac{\Delta s_a - \Delta s_e}{20.1} \times 100.$$

Tabelle 3. Bariumoxyd BaO. $\Delta s_a = 36.9 \gamma$, $\Delta s_a(O) = 23.5 \gamma$, $M = 6 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
4	340	34.1 ?	2.8	14 ?
2	380	31.4	5.5	27
1	430	20.2	16.7	83
3	530	16.4	20.5	102
5	590	16.4	20.5	102

$$\%A = \frac{\Delta s_a - \Delta s_e}{20.1} \times 100.$$

Tabelle 4. Zinkoxyd ZnO. $\Delta s_a = 41.6 \gamma$, $\Delta s_a(O) = 26.1 \gamma$, $M = 6 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
3	510	41.6	0.0	0
2	700	37.8	3.8	17
1	750	34.1	7.5	34
4	800	25.1	16.5	74

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

Tabelle 5. Cadmiumoxyd, CdO .⁽³⁾ $\Delta s_a = 35.5 \gamma$, $\Delta s_a(\text{O}) = 23.1 \gamma$, $M = 15 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
3	510	35.3	0.2	1
6	580	34.5	1.0	5
1	630	33.6	1.9	10
4	690	26.1	9.4	48
2	750	21.0	14.5	73
5	810	16.4	19.1	96

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

2. Versuchsreihe. Austauschreaktion an der Oberfläche der Oxyde von IV. Gruppe. Die in dieser Reihe der Versuche verwendeten Oxyde werden auf folgende Weise hergestellt.

Titanoxyd TiO_2 —Vgl. S. 9, IV. Mitteil.

Zirkoniumoxyd ZrO_2 —Die konzentrierte wässrige Lösung von Zirkoniumnitrat, die durch Auflösen von etwa 3 g Zirkoniumnitrat von Kahlbaum in möglichst wenige Mengen von Wasser bereitet wird, wird mit etwa 1 g sorgfältig gereinigten feinen Asbestfasern vermischt und die so gewonnene breiartige Masse wird zunächst auf dem Wasserbad unter guter Durchmischung und zum Schluss in einem Trockenschrank bis zum Trockenwerden verdampft. Der Zirkoniumoxyd-tragende Asbestfaserkatalysator wird nun aus der so bereiteten getrockneten Masse dadurch gewonnen, dass man das letztere in einem Porzellantiegel bis auf etwa 400° einige Stunden lang erhitzt.⁽⁴⁾

Thoriumoxyd, ThO_2 —Der Thoriumoxyd-tragende Asbestfaserkatalysator wird auf genau demselben Wege wie beim oben erwähnten Zirkoniumoxyd unter Verwendung von 3.9 g reinen Thoriumnitrats von Fränkel und Landau sowie 1 g gereinigten Asbestfasern dargestellt.

Siliciumoxyd SiO_2 —Vgl. Experiment 1 auf S. 602 in II. Mitteil.

Zinnoxid SnO_2 —Zwei Arten der Präparate werden unter Benutzung zweier verschiedener Methoden hergestellt und mit diesen beiden Arten der Präparate zwei Reihen der Versuche separat durchgeführt. Das eine Präparat, das weiter unten Zinnoxid-I (SnO_2 -I) genannt werden soll, wird aus käuflichem Zinnoxid bloss durch starke Erhitzung im Porzellantiegel gewonnen. Dagegen wird das andere Präparat, Zinnoxid-II (SnO_2 -II), aus Zinn-(IV)-chlorid auf folgendem Wege hergestellt. Die durch Auflösen von Zinnchlorid in salzsaurem Wasser hergestellte Lösung wird mit Natronlauge so lange versetzt, bis sich der zuerst aufgetretene Niederschlag von Zinnoxihydrat gerade wieder auflöst. Die

(3) Dieser Versuch wurde von Dr. Tanaka durchgeführt.

(4) Der so bereitete Katalysator besteht offensichtlich aus Metalloxyd und Asbestfasern. Aber dass der Asbest keine nennenswerte katalytische Wirksamkeit besitzt, wurde schon in II. Mitteil. bestätigt.

Lösung filtriert man dann ab (von minimal zurückgebliebenem Niederschlag!) und das gewonnene Filtrat wird mit gereinigtem Kohlendioxyd aus Marmor und Salzsäure so lange durchgeleitet, bis kein Niederschlag mehr abgeschieden wird. Der Niederschlag wird dann von der Mutterlauge abfiltriert, mit destilliertem Wasser gründlich gewaschen und im Trockenschrank bei 120° getrocknet. Das Oxyd wird aus dem so bereiteten Carbonat dadurch gewonnen, dass man das letztere in einem Porzellantiegel bis auf etwa 600° zwei Stunden lang erhitzt.

Die Ergebnisse der katalytischen Austauschreaktion, die unter Verwendung der oben bereiteten Oxyde der IV. Gruppe durchgeführt wurden, sind in Tabellen 6 bis 10 zusammengestellt, wo die einzelnen Buchstaben und Abkürzungen dieselben Bedeutungen wie in den vorhergehenden Tabellen besitzen.

Über die Versuchsergebnisse, die mit Titanoxyd TiO_2 gewonnen werden, vgl. Tabelle 2 in IV. Mitteil.

Tabelle 6. Zirkoniumoxyd ZrO_2 . $\Delta s_a = 36.9 \gamma$, $\Delta s_a(\text{O}) = 23.5 \gamma$,
 $M = 0.8 \text{ g (+1 g Asbest)}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	520	36.6	0.3	1
1	590	36.0	0.4	4
4	700	35.0	1.9	9
3	780	29.6	7.3	36
5	840	26.4	10.5	52

$$\%A = \frac{\Delta s_a - \Delta s_e}{20.1} \times 100.$$

Tabelle 7. Thoriumoxyd ThO_2 . $\Delta s_a = 36.9 \gamma$, $\Delta s_a(\text{O}) = 23.5 \gamma$,
 $M = 1.8 \text{ g (+1 g Asbest)}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	500	36.2	0.7	3
1	610	34.2	2.7	13
6	680	33.9	3.0	15
3	710	30.5	6.4	32
4	760	29.0	7.9	39
5	830	20.0	16.9	83

$$\%A = \frac{\Delta s_a - \Delta s_e}{20.1} \times 100.$$

Über die Versuchsergebnisse, die mit Siliciumoxyd SiO_2 gewonnen wurden, vgl. Tabelle 1 in II. Mitteil.

Tabelle 8. Zinnoxid-I, $\text{SnO}_2\text{-I.}^{(5)}$ $\Delta s_a = 35.5 \gamma$, $\Delta s_a(\text{O}) = 23.1 \gamma$, $M = 15 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
5	380	25.3	0.2	1
4	430	29.1	6.4	32
3	480	21.0	14.5	73
6	530	15.7	19.8	100
2	580	15.3	20.2	102
1	680	15.7	19.8	100

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

Tabelle 9. Zinnoxid-II $\text{SnO}_2\text{-II.}$ $\Delta s_a = 41.6 \gamma$, $\Delta s_a(\text{O}) = 26.1 \gamma$, $M = 6 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
3	510	41.6	0.0	0
1	610	41.2	0.4	2
2	700	37.8	3.8	17
4	800	25.1	16.5	74

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

3. Versuchsreihe. Austauschreaktion an der Oberfläche der Oxyde von VI. Gruppe. Die in dieser Reihe der Versuche verwendeten Oxyde werden auf folgende Weise hergestellt.

Chromoxyd Cr_2O_3 —In diesem Fall werden ebenso wie beim Zinnoxid zwei verschiedene Arten der Präparate auf zwei verschiedene Wege hergestellt und damit zwei Reihen der Versuche durchgeführt. Chromoxyd-I ($\text{Cr}_2\text{O}_3\text{-I}$) ist dasselbe Oxyd, das wir bei dem Versuch in IV. Mitteil. verwendet haben. Dagegen wird Chromoxyd-II, das erst im vorliegenden Versuche benutzt wurde, aus Ammoniumchromat durch thermische Zersetzung gewonnen. Zu diesem Zweck wird reines Ammoniumchromat aus Merck in einem Porzellantiegel langsam bis auf 400° erhitzt und die dadurch gewonnene voluminöse Masse von Chromoxyd wird in einem erneuten Tiegel nochmals bis auf ca. 500° eine Stunde lang erhitzt.

(5) Dieser Versuch wurde von Dr. Tanaka durchgeführt.

Molybdänoxyd MoO_3 —Dieses Oxyd wird aus Ammoniummolybdat von Merck auf genau demselben Weg wie beim vorhergehenden Chromoxyd-II hergestellt.

Wolframoxyd WO_3 —Dieses Oxyd wird ebenfalls aus Ammoniumwolframat von Merck auf genau dieselbe Weise wie beim Chromoxyd-II hergestellt.

Die Ergebnisse der unter Verwendung aller dieser Oxyde von VI. Gruppe durchgeführten Versuche sind in Tabelle 10 bis 12 wiedergegeben.

Über die Versuchsergebnisse, die mit Chromoxyd-I gewonnen werden vgl. Tabelle 4 in IV. Mitteil.

Tabelle 10. Chromoxyd-II Cr_2O_3 -II. $\Delta s_a = 36.9 \gamma$, $\Delta s_a(\text{O}) = 23.5 \gamma$, $M = 2.5 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	300	36.5	0.4	2
4	350	36.9	0.0	0
1	400	36.6	0.3	1
3	450	26.5	10.4	52
6	500	17.6	19.3	96
5	550	16.6	20.3	101

$$\%A = \frac{\Delta s_a - \Delta s_e}{20.1} \times 100.$$

Tabelle 11. Molybdänoxyd MoO_3 . $\Delta s_a = 61.3 \gamma$, $\Delta s_a(\text{O}) = 34.4 \gamma$, $M = 15 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	430	60.6	0.7	2
3	490	61.3	0.0	0
6	570	59.1	2.2	8
1	580	55.4	5.9	20
5	650	44.3	17.0	59
4	690	32.5	28.8	100

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.8} \times 100.$$

Tabelle 12. Wolframoxyd WO_3 . $\Delta s_a = 36.9 \gamma$, $\Delta s_a(\text{O}) = 23.5 \gamma$, $M = 15 \text{ g}$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
4	500	36.8	0.1	0
2	600	36.5	0.4	2
5	700	36.2	0.7	3
1	750	29.1	7.8	38
3	800	28.4	8.5	42

$$\%A = \frac{\Delta s_a - \Delta s_e}{20.1} \times 100.$$

Die Zusammenfassung der vorliegenden Versuchsergebnisse sowie die damit ausgeführte theoretische Überlegung soll später im 2. Teil ausführlich berichtet werden.

Herrn Prof. Dr. 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-Hohkohkai (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung der vorliegenden Arbeit ermöglicht haben, bin ich auch zu bestem Dank verpflichtet.

Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyositu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka).

Optical Activity and Chemical Structure in Tartaric Acid. X.* Influence of Substituent and Solvent Effect.

By Yojiro TSUZUKI.

(Received December 26, 1939).

In a previous paper⁽¹⁾ it was shown that in a number of bridged derivatives of tartaric acid, $\begin{array}{c} R_1 \diagdown \\ C \\ R_2 \diagup \end{array} \begin{array}{l} \diagup O-CH-COOR \\ | \\ \diagdown O-CH-COOR \end{array}$ the laevo-rotation

of the compound falls off with increasing bulk of R_1 and R_2 . And it was discussed that this effect should be expected from the deduction of the molecular theory of optical activity⁽²⁾ and the author's view⁽³⁾ that hydroxyl oxygen of tartaric acid contributes the positive partial rotation.

It was also pointed out that among these bridged derivatives, obtained by condensing carbonyl compounds with alkyl *d*-tartrates, aldehyde condensation products have always a larger molecular rotation than those from ketone of the same molecular weight.

The compounds furnished for discussion were, however, mostly ketone derivatives, and those of aldehyde were only from form aldehyde and acetaldehydes.

In the present investigation, the author has prepared some new derivatives from ethyl *d*-tartrate and higher homologues of acetaldehyde,

whose constitution is: $\begin{array}{c} R \diagdown \\ C \\ H \diagup \end{array} \begin{array}{l} \diagup O-CH-COOC_2H_5 \\ | \\ \diagdown O-CH-COOC_2H_5 \end{array}$ and determined their

rotatory power and observed the solvent effect on it. The results are all in good agreement with the expectation.

* Part IX, *Scient. Pap. Inst. Phys. Chem. Res.*, Tokyo **36** (1939), 31.

(1) Y. Tsuzuki, *Scient. Pap. Inst. Phys. Chem. Res.*, Tokyo **35** (1939), 466.

(2) R. de Malleman, *Trans. Farad. Soc.*, **26** (1930), 281; F. S. Boys, *Proc. Roy. Soc.*, (London), A, **144** (1934), 655.

(3) Y. Tsuzuki, *Scient. Pap. Inst. Phys. Chem. Res.*, Tokyo **35** (1939), 425.

Influence of the Radical R on the Rotation. In Table 1 are given the values of the molecular rotation in the homogeneous state of the bridged derivatives of ethyl *d*-tartrate. We see clearly a definite relation between the rotation and the bulk of R, which can be expressed as parachor, a quantity equivalent to the molecular volume, that is, the laevo-rotation decreases progressively in magnitude, as the bulk of the left-hand side of the molecule increases. This fact is in complete harmony with the conclusion expressed in the previous paper.

Table 1. Molecular rotation of $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \diagup \\ \text{O-CH-COOC}_2\text{H}_5 \\ | \\ \text{O-CH-COOC}_2\text{H}_5 \end{array}$ and
parachor of R.

Compound	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \diagup \\ \text{O-CH-COOC}_2\text{H}_5 \\ \\ \text{O-CH-COOC}_2\text{H}_5 \end{array}$	$[\text{M}]_D^{50}$ (no solvent)	$[\text{M}]_D^{20}$ (in cyclohexane)	Parachor of R
R = H		-171.1	-160.3	17.1
R = CH ₃		-173.3	-159.9 ⁽⁴⁾	56.1
R = <i>n</i> -C ₃ H ₇		-144.8	-133.5	134.1
R = <i>i</i> -C ₃ H ₇		-134.9	-126.0	134.1
R = C ₆ H ₁₃		-126.2	-115.6	251.1

It should be noted that in Table 1 we see the effect of isopropyl radical is stronger than *n*-propyl radical. This is possibly due to the vicinal effect of isopropyl group.⁽⁵⁾ Since this radical furnishes the dextro-rotatory contribution, as already shown by the present author,⁽³⁾

Table 2. Molecular rotation of isomers of $\begin{array}{c} \text{R}_1 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_2 \end{array} \begin{array}{c} \diagup \\ \text{O-CH-COOC}_2\text{H}_5 \\ | \\ \text{O-CH-COOC}_2\text{H}_5 \end{array}$.

Compound	$\begin{array}{c} \text{R}_1 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_2 \end{array} \begin{array}{c} \diagup \\ \text{O-CH-COOC}_2\text{H}_5 \\ \\ \text{O-CH-COOC}_2\text{H}_5 \end{array}$	$[\text{M}]_D^{20}$ (no solvent)	$[\text{M}]_D^{20}$ (in cyclohexane)
R ₁ = <i>n</i> -C ₃ H ₇ R ₂ = H		-144.8	-133.5
R ₁ = C ₂ H ₅ R ₂ = CH ₃		- 91.10 ⁽⁶⁾	- 82.25
R ₁ = C ₆ H ₁₃ R ₂ = H		-134.9	-126.0
R ₁ = C ₃ H ₇ R ₂ = C ₃ H ₇		- 59.74 ⁽⁶⁾	- 54.91

(4) Y. Tsuzuki, this Bulletin, **11** (1936), 363.

(5) P. A. Levene and A. Rothen, *J. Org. Chem.*, **1** (1936), 76.

(6) Y. Tsuzuki, this Bulletin, **14** (1939), 19.

it is conceivable that this vicinal effect depresses the laevo-rotation of the derivatives of tartaric acid.

It was already noticed in the previous paper⁽¹⁾ that the compounds, in which R_1 is different from R_2 (Formula in Table 2), have a larger molecular rotation than those isomers in which R_1 and R_2 are equal. This difference is more remarkable when $R_2 = H$, i.e. in the case of aldehyde condensation products the molecular rotation is far greater than that of the isomeric ketone condensation product. This is evident from Table 2.

Influence of Solvent. As may be seen in Table 3 to the sequence of solvents arranged in order of their effect on the molecular rotation of the newly synthesized bridged derivatives of ethyl *d*-tartrate is:

Benzene > Alcohol > Cyclohexane.

This series is just the same found in the previous investigation,⁽¹⁾ which was observed about ketone condensation products of the analogous structure. The result can be satisfactorily explained by taking into consideration the refractive index and the associable character of the liquid, as in the case of the previous paper.

It is to be noticed that the molecular rotation in the homogeneous state is nearly the same as in alcohol. This fact is easily explained by considering that the hydroxyl and carboxyl groups in tartaric acid have partial rotations which are in direction opposite to each other.

Table 3. Molecular rotation of $\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ H \end{array} \begin{array}{c} \diagup O-CH-COOC_2H_5 \\ | \\ \diagdown O-CH-COOC_2H_5 \end{array}$

Compound	$\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ H \end{array} \begin{array}{c} \diagup O-CH-COOC_2H_5 \\ \\ \diagdown O-CH-COOC_2H_5 \end{array}$	[M] _D ²⁰ in			
		no solvent	benzene	alcohol	cyclohexane
R = <i>n</i> -C ₃ H ₇		-144.8	-157.0	-142.9	-133.5
R = <i>i</i> -C ₃ H ₇		-134.9	-154.3	-134.9	-126.0
R = C ₆ H ₁₃		-126.2	-148.3	-123.1	-115.6

Experimental.

Ethyl n-butylal-d-tartrate C₁₂H₂₀O₆ (260.16)
 $\begin{array}{c} n-C_3H_7 \\ \diagdown \\ C \\ \diagup \\ H \end{array} \begin{array}{c} \diagup O-CH-COOC_2H_5 \\ | \\ \diagdown O-CH-COOC_2H_5 \end{array}$ To a mixture of 9 g. ethyl *d*-tartrate and 7 g. *n*-butylaldehyde (Takeda, b.p. 67–74°) was added 10 g. phosphorus pentoxide in portions at room temperature during a period of 40 minutes. The liquid coloured brownish red. The reaction product was extracted with ether. The ethereal solution was washed three 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. This process of purification was repeated three times. Colourless liquid. Yield 4.5 g. Boiling point 160° (15 mm), $n_D^{20} = 1.4376$, $d_4^{20} = 1.0942$, $M_D = 62.36$ (62.01), $[\alpha]_D^{20} = -55.80^{\circ}$, $[M]_D^{20} = -144.8^{\circ}$. $[\alpha]_D^{20} = -54.94^{\circ}$ (in ethyl alcohol, 4.874%), $[M]_D^{20} = -142.9^{\circ}$ (in ethyl alcohol). $[\alpha]_D^{20} = -60.37^{\circ}$ (in benzene, 2.956%), $[M]_D^{20} = -157.0^{\circ}$ (in benzene). $[\alpha]_D^{20} = -51.32^{\circ}$ (in cyclohexane, 2.533%), $[M]_D^{20} = -133.5^{\circ}$ (in cyclohexane).

Ethyl isobutyral-d-tartrate. $C_{12}H_{20}O_6$ (260.16)

$i-C_3H_7 \setminus \begin{matrix} O-CH-COOC_2H_5 \\ | \\ H \end{matrix} \begin{matrix} C \\ / \end{matrix} \begin{matrix} O-CH-COOC_2H_5 \\ | \\ H \end{matrix}$. To a mixture of 12 g. ethyl *d*-tartrate

and 10 g. isobutyraldehyde (Kahlbaum) was added 12 g. phosphorus pentoxide in portions at 70° during a period of 40 minutes, and heating was continued for 40 minutes at $80-90^{\circ}$. Almost colourless liquid. Yield 5 g. Boiling point 160° (20 mm), $n_D^{20} = 1.4375$, $d_4^{20} = 1.0847$, $M_D = 62.89$ (62.01). $[\alpha]_D^{20} = -54.17^{\circ}$, $[M]_D^{20} = -141.0^{\circ}$. $[\alpha]_D^{20} = -51.86^{\circ}$ (in ethyl alcohol, 4.830%), $[M]_D^{20} = -134.9^{\circ}$ (in ethyl alcohol). $[\alpha]_D^{20} = -59.29^{\circ}$ (in benzene, 2.941%), $[M]_D^{20} = -154.3^{\circ}$ (in benzene). $[\alpha]_D^{20} = -48.43^{\circ}$ (in cyclohexane, 2.503%), $[M]_D^{20} = -126.0^{\circ}$ (in cyclohexane).

Ethyl oenanthal-d-tartrate $C_{15}H_{26}O_6$ (302.21).

$C_6H_{13} \setminus \begin{matrix} O-CH-COOC_2H_5 \\ | \\ H \end{matrix} \begin{matrix} C \\ / \end{matrix} \begin{matrix} O-CH-COOC_2H_5 \\ | \\ H \end{matrix}$. The condensation of 10 g. ethyl *d*-tartrate

with 10 g. oenanthol (Takeda, b.p. $154-6^{\circ}$) by means of 10 g. P_2O_5 at $50-60^{\circ}$, gave 6 g. colourless liquid boiling at 190° (16 mm). $n_D^{20} = 1.4414$, $d_4^{20} = 1.0451$, $M_D^{20} = 76.42$ (75.87). $[\alpha]_D^{20} = -41.76^{\circ}$, $[M]_D^{20} = -126.2^{\circ}$. $[\alpha]_D^{20} = -40.72^{\circ}$ (in ethyl alcohol, 2.469%), $[M]_D^{20} = -123.1^{\circ}$ (in ethyl alcohol). $[\alpha]_D^{20} = -49.08^{\circ}$ (in benzene, 2.217%), $[M]_D^{20} = -148.3^{\circ}$ (in benzene). $[\alpha]_D^{20} = -38.25^{\circ}$ (in cyclohexane, 2.504%), $[M]_D^{20} = -115.6^{\circ}$ (in cyclohexane).

The author is indebted to the Department of Education for a grant.

Summary.

By comparing the molecular rotation of some bridged derivatives of tartaric acid, $R \setminus \begin{matrix} O-CH-COOC_2H_5 \\ | \\ H \end{matrix} \begin{matrix} C \\ / \end{matrix} \begin{matrix} O-CH-COOC_2H_5 \\ | \\ H \end{matrix}$ obtained by condensing aliphatic aldehydes with ethyl *d*-tartrate, it has been found that the laevo-rotation of the compounds diminishes with increasing bulk (parachor) of R, that is, R affects the positive partial rotation.

It has been shown that the molecular rotation of these compounds is greater than the isomer, $R_1 \setminus \begin{matrix} O-CH-COOC_2H_5 \\ | \\ R_2 \end{matrix} \begin{matrix} C \\ / \end{matrix} \begin{matrix} O-CH-COOC_2H_5 \\ | \\ R_2 \end{matrix}$ obtained by the condensation of ketone with ethyl *d*-tartrate. This phenomenon is to be explained by the idea of vicinal effect of the radicals R_1 and R_2 .

It has been shown that the sequence of solvents arranged in order of the effect on the rotation of these compounds is

Benzene > alcohol > cyclohexane.

and that it is related with the refractive index together with the association of the liquid.

*Musashi Higher School,
Tokyo-Nakaarai.*

Properties of Bismuth Oxide as an Active Material of Negative Electrode in Alkaline Storage Cell.

By Kyôji KINOSHITA.

(Received January 16, 1940.)

It is a difficult matter to construct, in a laboratory, an electrode of the ordinary alkaline storage cell reproducibly under same condition, owing to its very complicated mechanical structure. This fact may be a principal cause of the difficulty to study the properties of the cell.

The present author has succeeded previously in constructing positive electrode of the alkaline storage cell in pasted form,⁽¹⁾ using silver oxide as its active material. By the use of this pasting method, it becomes comparatively easy to study the electrochemical properties of various metallic oxide as an active material of the alkaline storage cell.

Bismuth oxide is very difficultly soluble in acid, excepting nitric acid, and in alkalies, so it has a possibility to be used as an active material for the storage cell. In this connection, the author studied some electrochemical properties of the oxide by using above cited pasting method.

Experimental. (1) *Results from the electrodes in the pasted form.* Ordinary yellow bismuth oxide, Bi_2O_3 , has been used in the experiment. Take necessary amount of the oxide, and add suitable electrolyte solution from a burette, drop by drop, with constant stirring, and make up into paste. Then the paste is applied to a grid which was prepared by plating silver on the ordinary grid of lead antimony alloy in the same manner as the ordinary pasted type electrodes of the lead acid storage cells. The size of the grid used was about 6.0 cm. $\times$ 1.5 cm. $\times$ 0.3 cm. .

The electrolyte solutions, for preparing the paste, were chosen to be 20% KOH, 5N NH_4OH , and 5N NH_4Cl . Three different kinds of electrodes were prepared, the details of which are given in Table 1.

(1) K. Kinoshita, this Bulletin, **12** (1937), 164-172.

K. Kinoshita, this Bulletin, **12** (1937), 366-376.

Table 1.

Plate	Amounts of oxide pasted in the plates w in grams	Pasting liquid
A	4.95	20% KOH
B	3.83	5N NH_4OH
C	4.52	5N NH_4Cl

The values of w in Table 1 were calculated as the difference of the weight of the pasted grid after drying and the weight of the grid used. So that the values of w may be considered to be the weight of Bi_2O_3 , which was pasted in the grid. Then the pasted plates were dipped into 20% KOH solution, and negatively electrolyzed (technically called as "formation") by the current of 100 milliamperes for 47 hours. During the process of "formation" changes in colour of the paste (from yellow to brownish black) was discernible.

The plate B, the paste of which being prepared by mixing 5N NH_4OH solution, could not be formed into the negative, for its paste fell to the bottom of the vessel as soon as the formation has begun.

After the "formation" the plates A and C were subjected to charge and discharge for four cycles, the results of these discharges are tabulated in Table 2.

Table 2.

Number of discharge	Discharge current i (in milliamperes)	Plate A		Plate C	
		Discharge hour t (in hours)	Discharge capacity C (in ampere hours)	Discharge hour t (in hours)	Discharge capacity C (in ampere hours)
1	100~200	9.250	1.030	9.033	1.006
2	150	6.116	0.917	3.500	0.525
3	150	5.550	0.832	3.100	0.465
4	150	4.833	0.725	3.000	0.450

At the first cycle of discharge, the discharge current was taken, at first, to be 100 milliamperes for 6 hours, but the capacity of the plates were found to be unexpectedly large, so that the discharge current was increased to 200 milliamperes. From the second cycle of discharge, thenceforth, the discharge current was taken to be 150 milliamperes.

As can be seen from Table 2, the capacities of the plates decreased cycle by cycle, and this tendency is especially remarkable in plate C. Some discharge characteristic curves of the plate A are shown in Fig. 1.

The numbers I, II, etc. in the figures correspond to the number of cycle of discharge. From the above figures, it can be noticed that the form

of the discharge characteristic curve changes its form with the progress of the number of cycle. Thus (1) the fall of the terminal voltage for about 1 hour from the beginning of discharge, becomes gradual and (2) discharge characteristic curve changes its nature abruptly at a point denoted by the letter a in Fig. 1.

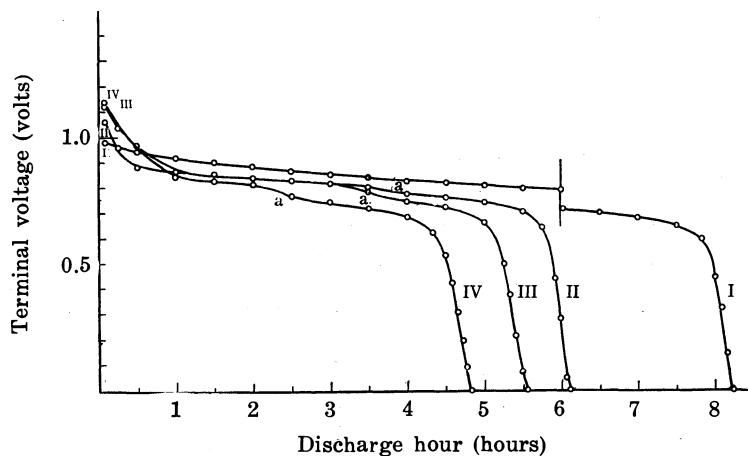


Fig. 1.

In Table 3 the discharge capacities per one gram of Bi_2O_3 are tabulated.

Table 3.

Number of discharge n	Discharge current i (in milliamperes)	Plate A	Plate B
		C/w (in $\frac{\text{milliampere hour}}{\text{gram}}$)	C/w (in $\frac{\text{milliampere hour}}{\text{gram}}$)
1	100 ~ 200	208	223
2	150	185	116
3	150	168	103
4	150	147	100

(2) *Results from the electrode in the pocketed form.* As the results of experiment (1), it was found that the bismuth oxide can be used as an active material for the alkaline storage cell, but it seemed to be wanting in sticking property to adhere to the ribs of grid. Thus in the case of electrode B, the active material fell to the bottom of the electrolyte vessel during the "formation."

Thereupon, the electrode in a pocketed form was prepared. A positive tube (pocket) of the Nife's alkaline storage cell was taken out, and the active material in a tube was thoroughly pushed out and rinsed well.

Then powdered bismuth oxide was packed into the empty tube thus obtained and formed into the negative electrode of an alkaline storage cell. The weight (w) of bismuth oxide packed in a pocket was found to be 12.65 grams.

"Formation" of the plate was undertaken in 20% KOH solution, by the current of 150 milliamperes for 6 hours and thereafter by the current of 200 milliamperes for 17 hours. After the "formation" it was combined with well charged Nife's positives and was subjected to 13 cycles of charges and discharges.

The discharge capacities (C) thus observed, and the capacities per one gram of bismuth oxide (C/w) are tabulated in Table 4.

Table 4.

Number of discharge n	Discharge current i (in milliamperes)	Discharge hour (in hours)	Discharge capacity C (in ampere hours)	C/w (in $\frac{\text{milliampere hour}}{\text{gram}}$)
1	250	5.500	1.375	109
2	250	4.000	1.000	79
3	150	6.716	1.007	80
4	150	5.933	0.899	71
5	150	5.433	0.815	64
6	150	5.166	0.775	61
7	100	5.450	0.545	43
8	150	3.000	0.450	36
9	150	3.333	0.500	40
10	150	3.250	0.488	39
11	150	3.366	0.505	40
12	150	3.016	0.453	36
13	150	2.500	0.375	30

We know from these tables that the values of C/w in Table 4 are very small in comparison with those in Table 3. These facts may be considered to be due to the effects of separation of the active material

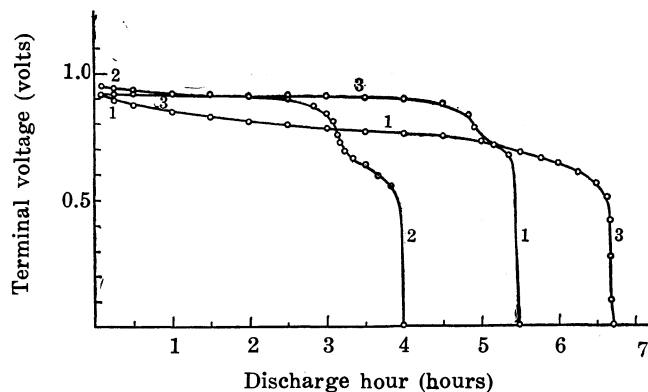


Fig. 2.

and the electrolyte solution with the metallic diaphragm, which composes the metallic pocket, and the results of the poor electrical conductivity of bismuth oxide.

The discharge characteristic curves of the first three cycles can be seen in Fig. 2.

The curve for the first cycle indicates the monotonous fall of terminal voltage, while the curves of the 2nd and the 3rd cycles proceeded in two stages.

(3) *Experiments with the active material mixed with graphite powder.* It was pointed out in the preceeding paragraph that the low

Table 5.

Number of discharge n	Discharge current i (in milliamperes)	Discharge hour t (in hours)	Discharge capacity C (in ampere hours)	C/w ($\frac{\text{milliampere hours}}{\text{gram}}$)
1	150 ~ 300	19.600	3.215	261
2	400	6.016	2.405	196
3	300	8.666	2.600	211
4	400	5.183	2.074	169
5	400	4.750	1.900	155
6	400	4.500	1.800	146
7	400	4.400	1.760	143
8	300	6.650	1.995	162
9	300	6.483	1.945	158
10	300	6.433	1.940	158
11	300	6.316	1.895	154
12	300	6.033	1.810	147
13	300	6.233	1.880	153

values of C/w in experiment (2) may be attributed to the poor electrical conductivity of bismuth oxide. So that, bismuth oxide mixed with 20% of graphite powder was used as an active material, in order to increase the electrical conductivity. The construction of the electrode was the same with that in the case of experiment (2). The amount of the active material packed in a tube was found to be 15.37 grams, accordingly the amount of bismuth oxide (w) contained in it was 12.30 grams. "Formation" was undertaken in 20% KOH solution by the current of 100 to 150 milliamperes for 38 hours. The results of 13 cycles of discharges are tabulated in Table 5.

As can be seen in Table 5 the values of C/w are 261–143 milliamperehour/gram and show remarkable increase in value compared with the results of experiment (2), and are comparable to the values tabulated in Table 3. In Fig. 3 the values of C/w in experiment (2) and

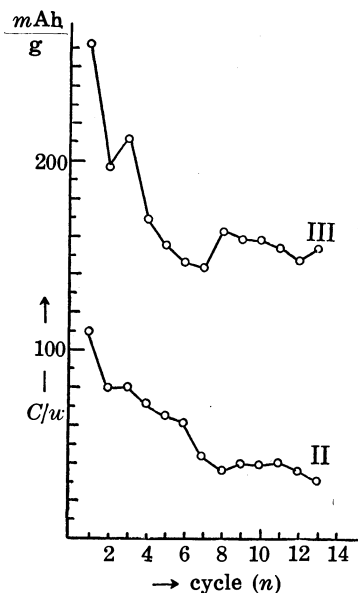


Fig. 3.

(3) were plotted against the number of cycle of discharge (n), the curves denoted by the letter II and III are the results of experiments (2) and (3) respectively.

It may be considered, from the result of Fig. 3 that the low values of C/w observed in the case of experiment (2) are the effects of the poor electrical conductivity of bismuth oxide, and the effect of adsorbed electrolyte around the carbon particles, and the increase of porosity of the active material by the mixing of carbon particles must be taken into considerations.

Some of the discharge characteristic curves obtained in experiment (3) are shown in Fig. 4.

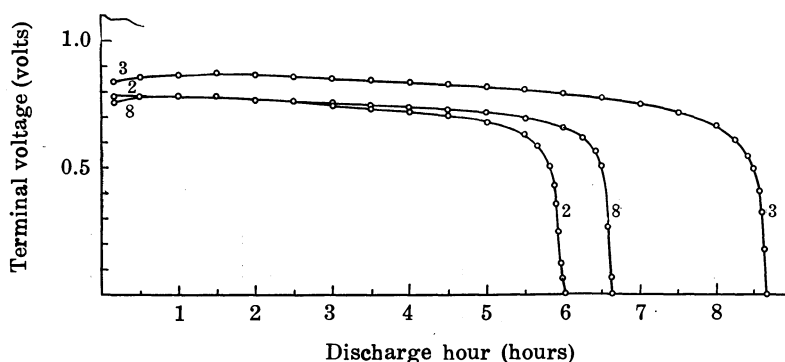


Fig. 4.

It is noteworthy, that in the case of experiment (3) the terminal voltage of the cell does not change in two stages as was seen in the case of experiments (1) and (2).

Conclusions. As the results of the experiments above described it is evident that the bismuth oxide can be used as an active material for the negative electrode in the alkaline storage cell, in pocketed or in pasted forms. But the output of the bismuth oxide alkaline cell seems to be limited by the poor electrical conductivity of bismuth oxide for some extent. It is very curious that the discharge characteristic curve changes its form in two staged type or in monotonous one staged type according to the conditions of the electrodes. These facts may have some connection with the above described electrically resistant nature of the bismuth oxide.

Summary.

(1) Negative electrode of the alkaline storage cell can be prepared using bismuth oxide as an active material, in pasted form or in pocketed form.

(2) The capacity of the electrode is improved greatly by mixing graphite powder to the active material, amounting the value 261 milliamperehour at highest per one gram of the oxide.

(3) It is thought to be probable, therefore, that the electrochemical properties of the electrode prepared from bismuth oxide, seems to have close connection with electrically resistant nature of the oxide.

In conclusion the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University, for his valuable advices throughout this experiments.

*Toyoda Research Laboratory,
Imperial Invention Society, Shimomeguro,
Tokyo.*

Radium, Vanadium, Chromium and Molybdenum Contents of the Hot Springs of Yunohanazawa, and their Seasonal Variations.

By Kazuo KURODA.

(Received January 18, 1940.)

It has recently been discovered spectroscopically by K. Kimura that the minute traces of vanadium, chromium and molybdenum are widely distributed in the mineral waters of Japan.⁽¹⁾ The author published on the vanadium, chromium and molybdenum contents of a number of hot springs of Japan, in the previous paper.⁽²⁾

In the present work, the author attempted the quantitative estimation of the amounts of these elements in the hot springs of Yunohanazawa, Hakone and the observation of their seasonal variations depending upon external conditions, such as abundant rain or drought. The radium content and its seasonal variation was also studied.

Methods of analysis. The analytical procedures are quite the same as those which were described already.⁽²⁾ For the determinations of vanadium, chromium and molybdenum, Sandell's colorimetric method⁽³⁾ was adopted. For the determination of radium, a 6000 c.c. portion of the mineral water was taken each time.

Results. A. *Temperature, pH and Total Residue.* The result of observation of the seasonal variations of temperature, pH and total residue is given in Table 1.

(1) Not yet published.

(2) This Bulletin, **14** (1939), 307.

(3) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8** (1936), 336.

Table 1. Temperature, pH and Total Residue of the "Gongen-yu" Spring.

No.	Date	Temperature (°C.)	pH	Total Residue (g./l.)
1	Aug. 20, 1938	42.0	2.6	0.85
2	Dec. 11, 1938	35.3	2.9	0.72
3	Mar. 16, 1939	48.0	2.8	0.82
4	Aug. 2, 1939	48.6	2.75	1.24
5	Aug. 22, 1939	50.3	2.6	1.41
6	Sept. 1, 1939	51.6	2.6	1.23
7	Sept. 9, 1939	51.6	2.6	1.22

B. Vanadium, Chromium and Molybdenum Contents of the Hot Springs of Yunohanazawa and their Seasonal Variations.

The variations of the amounts of vanadium, chromium and molybdenum in the "Gongen-yu" spring are shown in Table 2 and Fig. 1. The seasonal variations were found to be unexpectedly marked. The amount of vanadium fluctuated in the period of experiments between 28×10^{-6} and 98×10^{-6} g. per litre. The maximum amount (98×10^{-6} g.) occurred in the summer of 1939 after a heavy rain, and the minimum (28×10^{-6} g.) in the autumn of 1938 after a long drought. The amount of chromium fluctuated in the same period between 16×10^{-7} and 39×10^{-7} g. per litre, and the amount of molybdenum between 7×10^{-7} and 16×10^{-7} g. per litre. The relations between water temperature, pH and vanadium content are shown in Fig. 2 and Fig. 3.

Table 2.

A. Seasonal Variations of the Vanadium, Chromium and Molybdenum Contents of the Hot Springs of Yunohanazawa.

No.	Date	Temperature (°C.)	pH	V (g./l.)	Cr (g./l.)	Mo (g./l.)
1	Aug. 20, 1938	42.0	2.6	$*98 \times 10^{-6}$	$*25 \times 10^{-7}$	$*7 \times 10^{-7}$
2	Dec. 11, 1938	35.3	2.9	28 "	23 "	8 "
3	Mar. 16, 1939	48.0	2.8	51 "	39 "	14 "
4	Aug. 2, 1939	48.6	2.75	72 "	16 "	10 "
5	Aug. 22, 1939	50.3	2.6	82 "	20 "	10 "
6	Sept. 1, 1939	51.6	2.6	84 "	23 "	16 "
7	Sept. 9, 1939	51.6	2.6	94 "	16 "	10 "

B. Seasonal Variations of the Vanadium, Chromium and Molybdenum Contents Expressed in Percentages to the Total Residue.

No.	Date	V	Cr	Mo
1	Aug. 20, 1938	0.0116	0.00029	0.00008
2	Dec. 11, 1938	0.0039	0.00032	0.00011
3	Mar. 16, 1939	0.0062	0.00048	0.00018
4	Aug. 2, 1939	0.0051	0.00012	0.00007
5	Aug. 22, 1939	0.0058	0.00014	0.00007
6	Sept. 1, 1939	0.0068	0.00019	0.00013
7	Sept. 9, 1939	0.0077	0.00013	0.00007

*) Quantitatively estimated by S. Oana.

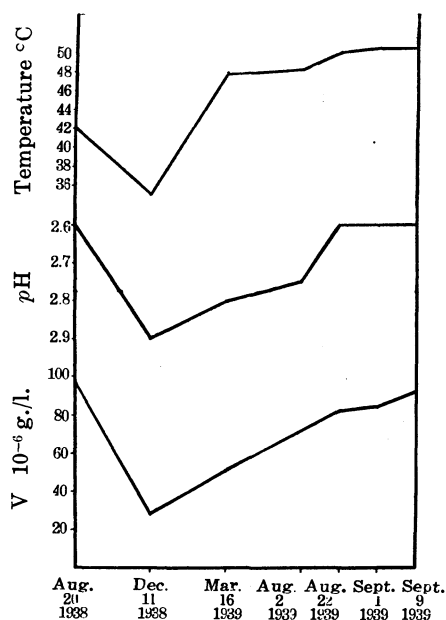


Fig. 1. Seasonal Variation of Temperature, pH and Vanadium Content.

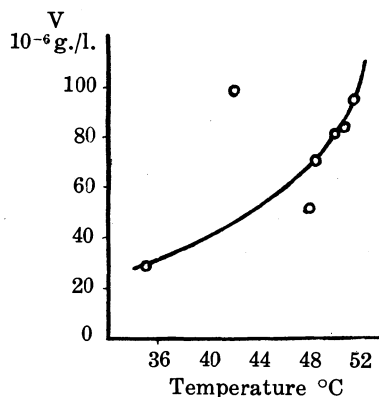


Fig. 2. Temperature and Vanadium Content.

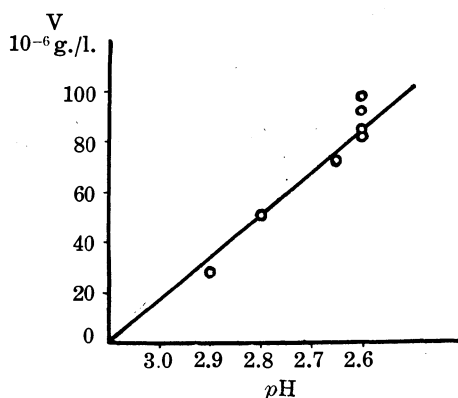


Fig. 3. pH and Vanadium Content.

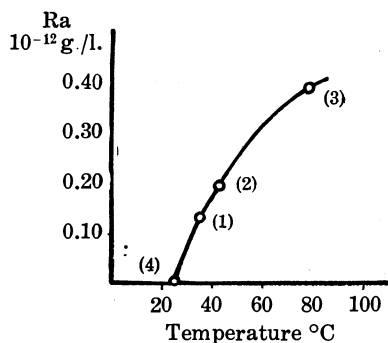
C. *Radium Content and its seasonal variation.* The results from the quantitative estimation of the amount of radium and the observation of its seasonal variation are shown in Table 3 and Table 4. The seasonal variation was also found. The relations between pH, temperature and radium content are shown in Fig. 4 and Fig. 5. The seasonal variation of the amount of radium seems to be quite the same as that of vanadium, as is shown in Fig. 6.

Table 3. Radium Content of the Hot Springs of Yunohanazawa. (Dec. 11, 1938).

No.	Springs	Temperature (°C)	pH	Ra (g./l.)	Ra (g. per g. of dry residue)
1	Gongen-yu	35.3	2.9	0.13×10^{-12}	0.18×10^{-12}
2	Kōbō-yu	41.0	2.8	0.19 "	0.19 "
3	Yoemon-yu	78.0	2.3	0.39 "	0.22 "
4	Fuezuka-yu	25.0	3.5	0.00 "	0.00 "

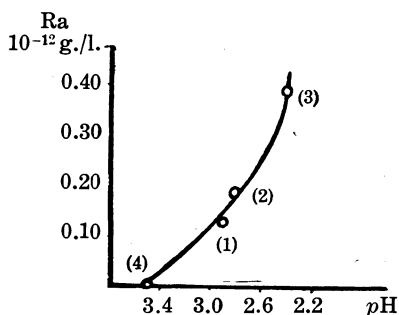
Table 4. Seasonal Variation of the Radium Content of the "Gongen-yu" Spring.

No..	Date	Temperature (°C.)	pH	Ra (g./l.)	Ra (g. per g. of dry residue)
1	Aug. 20, 1938	42.0	2.6	0.60×10^{-12}	0.71×10^{-12}
2	Dec. 11, 1938	35.3	2.9	0.13 ,,	0.18 ,,
3	Mar. 16, 1939	43.0	2.8	0.31 ,,	0.38 ,,



(1) Gongen-yu (2) Kōbō-yu
(3) Yoemon-yu (4) Huezuka-yu

Fig. 4. Temperature and Radium Content of the Hot Springs of Yunohanazawa.



(1) Gongen-yu (2) Kōbō-yu
(3) Yoemon-yu (4) Huezuka-yu

Fig. 5. pH and Radium Content of the Hot Springs of Yunohanazawa.

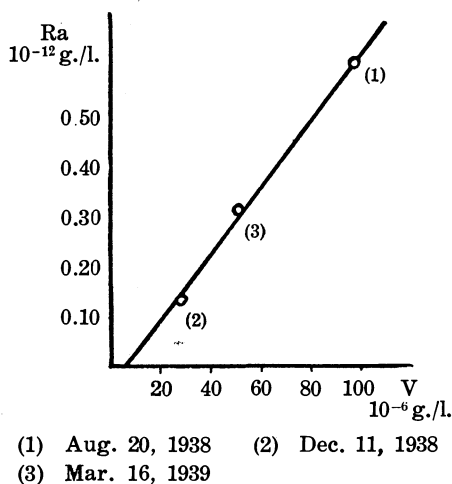


Fig. 6. Vanadium and Radium in the "Gongen-yu" Spring.

D. Seasonal Variation of Iron Content and its Relation to that of Vanadium, Chromium and Molybdenum Content.

The seasonal variation of iron in the same period is shown in Table 5. The amount of iron fluctuated between 21.7 and 0.2 mg. per litre. The maximum amount (21.7 mg.) occurred in the summer of 1938 after a heavy rain, and the minimum (0.2 mg) in the autumn of 1938 after a long drought. In Table 6, the seasonal change of the ratio of the amount of vanadium, chromium and molybdenum to that of iron is given.

Table 5. Seasonal Variation of the Iron Content of the Hot Springs of Yunohanazawa.

No.	Date	Fe (g./l.)	Fe (g. per g. of dry residue)
1	Aug. 20, 1938	0.0217	0.0258
2	Dec. 11, 1938	0.0002	0.0003
3	Mar. 16, 1939	0.0053	0.0065
4	Aug. 2, 1939	0.0011	0.0008
5	Aug. 22, 1939	0.0097	0.0068
6	Sept. 1, 1939	0.0034	0.0028
7	Sept. 9, 1939	0.0023	0.0019

Table 6. Seasonal Variation of the Ratios of Vanadium, Chromium and Molybdenum to Iron.

No.	Date	V/Fe	Cr/Fe	Mo/Fe
1	Aug. 20, 1938	45×10^{-4}	11×10^{-5}	3×10^{-5}
2	Dec. 11, 1938	1400×10^{-4}	1150×10^{-5}	400×10^{-5}
3	Mar. 16, 1939	962×10^{-4}	74×10^{-5}	26×10^{-5}
4	Aug. 2, 1939	655×10^{-4}	150×10^{-5}	91×10^{-5}
5	Aug. 22, 1939	85×10^{-4}	21×10^{-5}	10×10^{-5}
6	Sept. 1, 1939	247×10^{-4}	68×10^{-5}	47×10^{-5}
7	Sept. 9, 1939	408×10^{-4}	70×10^{-5}	44×10^{-5}

The ratios increased in the winter after a long drought, and decreased in the summer as a result of abundant rain.

The abundance of iron in the earth's crust is 4.7%. Vanadium constitutes 0.016% of the ten-mile crust, while chromium constitutes 0.033% and molybdenum 0.00075%. From these values, we can calculate the ratio of vanadium, chromium and molybdenum to the amount of iron in the earth's crust as shown in Table 7.

Table 7. Vanadium, Chromium, Molybdenum and Iron in the Earth's Crust.

V/Fe	Cr/Fe	Mo/Fe
34×10^{-4}	70×10^{-4}	16×10^{-5}

The ratio of vanadium to iron in the hot springs of Yunohanazawa is considerably greater than that of the earth's crust. The ratio of chromium to iron is (with one exception) always smaller than that of the earth's crust, while the ratio of molybdenum to iron is (with one

exception) greater than that of the earth's crust. Heavy metals, such as vanadium, chromium and molybdenum are supposed to be present abundantly in deep within the earth and, according to A. Gautier,⁽⁴⁾ they are the essential constituents of juvenile waters. The author is of the opinion that the changes of the relative abundance of these metals are dependent upon the variations of the proportion of juvenile water in the mineral water, and it is expected that we can estimate the proportion from the results of the quantitative determination of these heavy metals in the mineral waters.

Summary.

(1) The radium, vanadium, chromium and molybdenum contents of the hot springs of Yunohanazawa, Hakone were determined.

(2) The seasonal variations of the amount of these elements were studied.

In conclusion, the author wishes to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. It is also the author's pleasant duty to acknowledge the valuable advice offered by Dr. S. Oana. The expence 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

(4) *Compt. Rend.*, **150** (1910), 436.

Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. VI. Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche der Oxyde von zweiter, vierter und sechster Gruppe des periodischen Systems.

2. Theoretischer Teil.⁽¹⁾

Von Noriyoshi MORITA.

(Eingegangen am 27. Dezember 1939).

Inhaltsübersicht. Die katalytische Wirksamkeit der Oxyde, die zu II. IV. und VI. Gruppe des periodischen Systems gehören, nämlich der Oxyde von Magnesium, Calcium, Strontium, Barium; Zink, Cadmium; Titan, Zirkonium, Thorium; und Chrom, Molybdän, Wolfram, für die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des resp. Oxyds wird unter Verwendung der im 1. Teil der vorliegenden Versuche gewonnenen Ergebnisse miteinander verglichen. Daraus ergibt sich, dass die Oxyde, die zu IV. Gruppe gehören, innerhalb einer bestimmten Reihe bzw. Periode die geringste Wirksamkeit besitzen. Was die Reihenfolge der Katalytischen Wirksamkeit innerhalb einer bestimmten Gruppe anbetrifft, so liegt die Sache noch nicht so ganz klar wie oben. Aber in einigen Fällen können wir doch eine gewisse Beziehung zwischen der katalytischen Wirksamkeit und Reihennr. der einzelnen Oxyde ausfindig machen. So. z.B. nimmt die Wirksamkeit der Oxyde der Erdalkalimetalle mit zunehmender Reihennr. allmählich zu. Dagegen nimmt die Wirksamkeit der zu VI. Gruppe angehörigen Oxyde nämlich Cr_2O_3 , MoO_3 und WO_3 mit wachsender Reihennr. ziemlich erheblich zu. Plausible Deutung für die so gefundene regelmässige Änderung der katalytischen Wirksamkeit mit der Gruppen- bzw. Reihennr. findet sich am Schluss.

Ermittlung von Temperatur t (10%). In vorhergehender Mitteil. (Teil 1) werden die Versuchsergebnisse berichtet, die wir bei den Austauschversuchen zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche verschiedener Arten der Oxyde von II. IV. und VI. Gruppe des periodischen Systems gewonnen haben. Deshalb sind wir jetzt in der Lage mit Hilfe des so gewonnenen Versuchsmaterials die katalytische Wirksamkeit der in Rede kommenden Oxyde miteinander zu vergleichen. Zu diesem Zweck werden zunächst die in Teil 1 (in Tabelle 1 bis 12) angegebenen Versuchsergebnisse in nebenstehenden Abb. 1 bis 3 graphisch wiedergegeben, wo das gefundene Austauschmaß %A gegen die Versuchstemperatur eingezeichnet sind. Dabei entspricht Abb. 1 der in Tabelle 1 bis 5 von 1. Teil angegebenen Versuchsreihe 1 mit den Oxyden von II. Gruppe des periodischen Systems, Abb. 2 der in Tabelle 6 bis 9 angegebenen Versuchsreihe 2 mit den Oxyden von IV. Gruppe und Abb. 3 der in Tabellen 10 bis 12 angegebenen Versuchsreihe 3 mit den Oxyden von VI. Gruppe. Weiter wird die Kurve von CaO in Abb. 1, die von $\text{SnO}_2\text{-I}$ in Abb. 2, die von $\text{Cr}_2\text{O}_3\text{-I}$ in Abb. 3 werden aus Abb. 1 in IV. Mitteil. und Kurve von SiO_2 aus Tabelle 1 in II. Mitteil. entnommen.

(1) 1. Teil: dies Bulletin, **15** (1940), 47. Vgl. dazu I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: ebenda, **13** (1938), 601; III. Mitteil.: ebenda, **13** (1938), 656; IV. Mitteil.: ebenda, **14** (1939), 9; V. Mitteil.: ebenda, **14** (1939), 520; **15** (1940), 1.

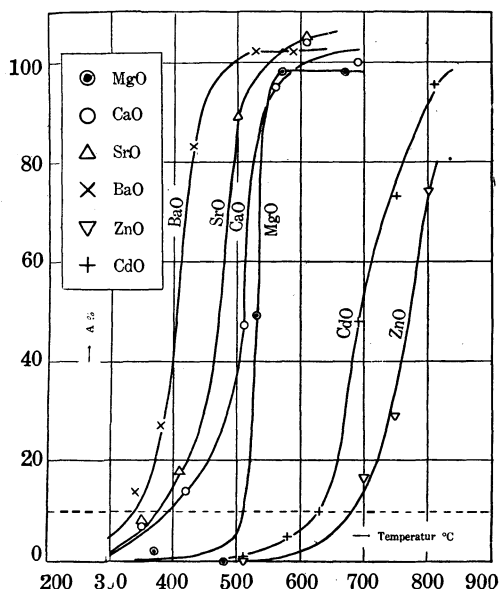


Abb. 1. Die Abhängigkeit des Austauschmasses %A von der Versuchstemperatur bei den Oxyden von II. Gruppe.

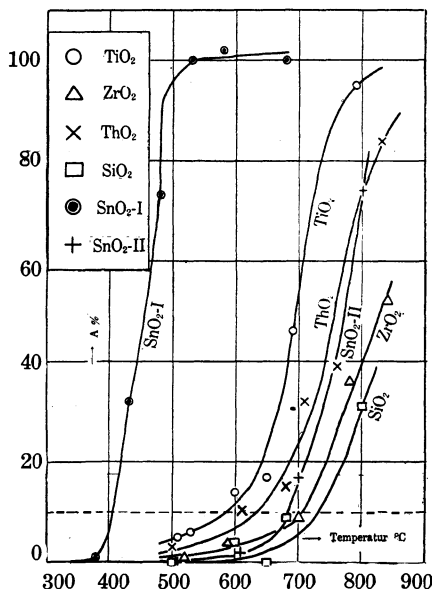


Abb. 2. Die Abhängigkeit des Austauschmasses %A von der Versuchstemperatur bei den Oxyden von IV. Gruppe.

Wenn man aus jeder dieser Kurven in Abb. 1 bis 3 solch eine Temperatur $t(10\%)$ entnimmt, wo das gefundene Austauschmass %A sich

zuerst auf 10% beläuft, erhält man die Zahlenwerte, die in Tabelle 1 unterhalb jeder chemischen Formel der betreffenden Oxyde angegeben sind. Da aber diese Temperatur $t(10\%)$ um so niedriger liegen muss je grösser die katalytische Wirksamkeit des betreffenden Oxyds ist und weiter die Höhe von $t(10\%)$, wie darauf schon in IV. Mitteil. hingewiesen wurde, nicht sehr von den benutzten Versuchsbedingungen beeinflusst wird, darf man wohl mit dieser Temperatur $t(10\%)$ bzw. ihrem reziproken Wert die katalytische Wirksamkeit der Oxyde miteinander vergleichen. Dass diese Temperatur $t(10\%)$ für ein bestimmtes Oxyd durch seine Herstellungsmethode nicht stark beeinflusst wird, können wir bei Cr_2O_3 wohl ersehen. In diesem Fall ergeben nämlich die zwei verschiedenen Arten der Präparate, Cr_2O_3 -I und Cr_2O_3 -II, miteinander

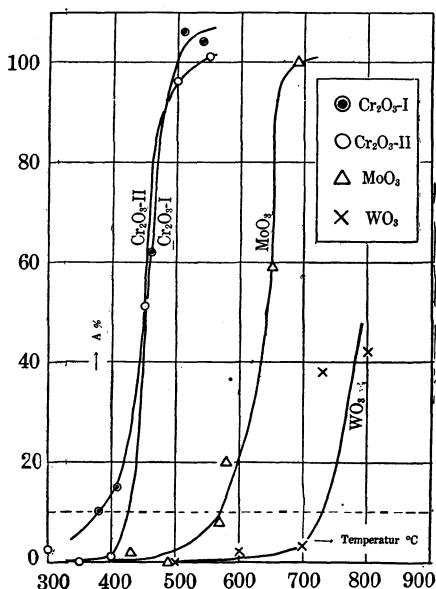


Abb. 3. Die Abhängigkeit des Austauschmasses %A von der Versuchstemperatur bei den Oxyden von VI. Gruppe.

Tabelle 1. Vergleich der katalytischen Wirksamkeit der verschiedenen Oxyde für die Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf: $t(10\%)$.

Reihe \ Gruppe	II		IV		VI	
	a	b	a	b	a	b
3	MgO 500			SiO ₂ 700		
4	CaO 390		TiO ₂ 590		Cr ₂ O ₃ I, 380 II, 420	
5		ZnO 680		GeO ₂ —		
6	SrO 380		ZrO ₂ 700		MoO ₃ 570	
7		CdO 630		SnO ₂ I, 400 II, 670		
8	BaO 350		CeO ₂ —			
10					WO ₃ 710	
11			ThO ₂ 640			

eine fast gleich hohe Temperatur $t(10\%)$, obgleich das aus Ammoniumchromat hergestellte Cr₂O₃-II viel voluminöser als das aus Chromhydroxyd gewonnene Cr₂O₃-I aussieht. Nur beim Fall von Zinnoxid haben wir einen ziemlich grossen Unterschied von $t(10\%)$ zwischen SnO-I und SnO₂-II gefunden. Solch ein grosser Unterschied der katalytischen Wirksamkeit zwischen verschiedenen Arten der Präparate von einem und demselben Oxyd wird aber oft bei solchem Oxyd gefunden, das verhältnismässig kleine katalytische Wirksamkeit besitzt und besonders wenn, wie es vorkommen kann, das Präparat unflüchtige Verunreinigungen wie z.B. unflüchtige Alkali enthält. Deshalb liegt die Annahme sehr nahe, dass es sich dabei meistens um die Promotorwirkung bzw. Mischkatalysatorwirkung der unbewusst eingetretenen Verunreinigungen handelt, worüber später in einer anderen Mitteilung ausführlich berichtet werden soll. Zieht man diese Tatsache in Rechnung, dann darf wohl vermutet werden, dass die viel niedrigere Temperatur $t(10\%)$ und folglich grössere Wirksamkeit des einen Präparats SnO₂-I als das andere SnO₂-II von der Promotorwirkung irgendwelcher Verunreinigungen herrühren dürfte, die im ersteren Präparat unbewusst hineingeraten sind. Diese Vermutung liegt aber um so näher, als das erste Präparat SnO₂-I bloss nach starker Erhitzung käuflichen Zinnoxids direkt zum Versuch verwendet wurde. Aus diesem Grund möchten wir lieber die höhere Temperatur $t(10\%)$

des zweiten Präparats $\text{SnO}_2\text{-II}$ d.h. 670° als den richtigen Wert für Zinnoxid vorziehen.

Beziehung zwischen $t(10\%)$ bzw. katalytischer Wirksamkeit und Gruppennummer. Wenn man auf diese Weise jedem Oxyd in Tabelle 1 den ihm eigentlichen Wert von $t(10\%)$ zuschreibt, können wir zwischen der Höhe von $t(10\%)$ und der Stellung des betreffenden Oxyds im periodischen System eine gewisse Beziehung finden. Vergleicht man zunächst den Wert von $t(10\%)$ innerhalb einer bestimmten Reihe (bzw. Periode), so finden wir ebenso wie in IV. Mitteil., dass das Oxyd von IV. Gruppe den grössten Wert von $t(10\%)$ zeigt. Dies weist aber ohne weiteres darauf hin, dass die katalytische Wirksamkeit der Oxyde für die Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf bei den Oxyden der IV. Gruppe am geringsten ist und nach beiden Seiten d.h. nach II. und VI. Gruppe allmählich zunimmt. Wir kamen in III. Mitteil. zu dem Ergebnis, dass bei der katalytischen Austauschreaktion an der Oberfläche des Kupferoxyds CuO die aktivierte Adsorption des Wasserdampfes der massgebende Prozess ist. Dagegen berichteten wir in letzter V. Mitteil., dass bei derselben Reaktion an der Oberfläche des Manganoxyds Mn_2O_3 die aktivierte Adsorption des Sauerstoffgases massgebend ist und weiter, dass diese aktivierte Adsorption des Sauerstoffs an Manganoxyd mit dem verhältnismässig hohen Zersetzungsdruck des betreffenden Oxyds bei Versuchstemperaturen in engem Zusammenhang steht. Deshalb liegt nahe im allgemeinen anzunehmen, dass bei den Oxyden, die mindestens bei benutzten Versuchstemperaturen einen kleinen Zersetzungsdruck ausüben aber dementsprechend verhältnismässig grosse Hydratisierbarkeit zeigen, wie z.B. CuO , CaO und Al_2O_3 , die aktivierte Adsorption des Wasserdampfes, während bei den Oxyden, die verhältnismässig grossen Zersetzungsdruck aber kleine Hydratisierbarkeit zeigen, wie z.B. Mn_2O_3 , Cr_2O_3 , und MoO_3 , die aktivierte Adsorption des Sauerstoffs eine massgebende Rolle spielt. Mithin darf wohl geschlossen werden, dass bei bei solchen Oxyden, an deren Oberfläche infolge kleiner Hydratisierbarkeit und kleinen Zersetzungsdruckes weder die aktivierte Adsorption des Wasserdampfes noch die des Sauerstoffs leicht stattfinden kann, die katalytische Wirksamkeit den Minimumwert zeigen muss. Dies kann gerade der Fall mit den Oxyden der IV. Gruppe sein, weil die zu dieser Gruppe gehörigen Oxyde im allgemeinen schwer hydratisierbar sind, aber zugleich ihr Zersetzungsdruck auch bei ziemlich hohen Temperaturen gewöhnlich sehr klein ist. Auf diese Weise können wir vielleicht das Auftreten des Minimums der katalytischen Wirksamkeit für die in Rede kommende Austauschreaktion bei den Oxyden in IV. Gruppe verständlich machen.

Beziehung zwischen $t(10\%)$ bzw. katalytischer Wirksamkeit und Reihenummer. Was die Reihenfolge der katalytischen Wirksamkeit in einer bestimmten Gruppe anbetrifft, so liegt die Sache nicht so einfach wie oben. Aber wir können doch in einigen Fällen eine ziemlich ausgeprägte Beziehung zwischen der katalytischen Wirksamkeit der Oxyde und ihrer Reihennr. ausfindig machen. So wird z.B. die deutlichste Regelmässigkeit bei den Oxyden der II. Gruppe a d.h. bei den Oxyden der Erdalkalimetalle sowie in VI. Gruppe a d.h. bei den Oxyden von Cr, Mo

und W gefunden. Beim ersten Fall lässt sich leicht ersehen, dass MgO die höchste $t(10\%)$ und folglich die kleinste Wirksamkeit besitzt und die letztere mit zunehmender Reihennr. d.h. von CaO bis BaO allmählich zunimmt. Diese regelmässige Zunahme der katalytischen Wirksamkeit der Erdalkalimetalloxyde mit zunehmender Reihennr. lässt sich vielleicht dadurch deuten, dass die Hydratisierbarkeit dieser Oxyde gerade in dieser Reihenfolge allmählich zunimmt. Das Oxyd von Beryllium BeO, das erste Glied dieser Gruppe, bildet bekanntlich ein Kristallgitter von Wurzittypus und die innerhalb dieses Gitters zwischen einzelnen Atomen herrschende Bindung wird bis zum grössten Teil als Atombindung angenommen. Dementsprechend ist dieses Oxyd sehr schwer hydratisierbar. In diesem Punkt ähnelt das Verhalten des Oxyds des zweiten Gliedes dieser Gruppe, nämlich das von MgO mehr dem ersten Glied BeO als dem darunter liegenden dritten Glied CaO. Obwohl das Kristallgitter von MgO ebenso wie das von CaO und das der Oxyde der anderen höheren Homologe der Gruppe als ein Ionengitter aufgefasst wird, wurde doch von Nakagawa in unserem Laboratorium in einem noch nicht veröffentlichten Versuch gefunden, dass MgO viel schwerer hydratisierbar als CaO ist. Dieser Befund legt uns deshalb die Annahme nahe, dass die kleine katalytische Wirksamkeit von MgO mit dieser geringen Fähigkeit dieses Oxyds zur Hydratbildung in engem Zusammenhang steht. Die ähnliche Neigung der abnehmenden $t(10\%)$ d.h. der zunehmenden katalytischen Wirksamkeit mit der wachsenden Versuchsnr. lässt sich auch in II. Gruppe b, d.h. bei ZnO und CdO erkennen. Aber weil in diesem Fall erstens das Versuchsmaterial noch ziemlich wenig und zweitens der Unterschied von $t(10\%)$ zwischen beiden untersuchten Oxyden nicht so ausgeprägt ist, können wir noch nichts so Bestimmtes sagen. Aber in jedem Fall liegt die Vermutung nahe, dass der Unterschied der katalytischen Wirksamkeit zwischen einzelnen Oxyden in Subgruppe b, d.h. zwischen den zur Nebenreihe gehörigen Oxyden, im allgemeinen nicht so ausgeprägt sein dürfte als bei den Oxyden, die zu Subgruppe a bzw. Hauptreihe des periodischen Systems gehören.

Die zweite verhältnismässig deutliche Reihenfolge der katalytischen Wirksamkeit lässt sich bei den Oxyden in VI. Gruppe a nämlich bei Cr_2O_3 , MoO_3 und WO_3 finden. In diesem Fall nimmt aber die katalytische Wirksamkeit der Oxyde, gerade im Gegenteil als bei den oben beschriebenen Alkalierdmetallen, mit zunehmender Reihennr. ziemlich stark ab, wie man dies aus der zunehmenden $t(10\%)$ der Oxyde mit der Reihennr. ersieht (vgl. Tabelle 1.) Nimmt man nun an, wie darauf schon oben hingewiesen wurde, dass der massgebende Prozess bei der katalytischen Austauschreaktion an der Oberfläche dieser Arten der Oxyde ebenso wie bei Mn_2O_3 die aktivierte Adsorption des Sauerstoffs ist, so stimmt die oben gefundene Reihenfolge der katalytischen Wirksamkeit gerade mit der der Reduzierbarkeit der Oxyde der in Rede kommenden Metalle gut überein. Denn nach der chemischen Erfahrung ist wohl bekannt, dass die unter den gewöhnlichen Versuchsbedingungen stabilste Form des Oxyds jedes in Rede kommenden Metalls resp. Cr_2O_3 , MoO_3 und WO_3 ist und weiter, dass unter den letzteren zwei Arten der Oxyde MoO_3 und WO_3 das letztere eine grössere Bildungswärme besitzt als das erstere.

Die Reihenfolge der katalytischen Wirksamkeit der Oxyde von IV. Gruppe ist nicht so einfach und klar wie bei den erwähnten beiden Gruppen II und VI. Obwohl auch in dieser Gruppe IV ein viel geringerer Unterschied der katalytischen Wirksamkeit innerhalb der Subgruppe b d.h. zwischen SiO_2 und $\text{SnO}_2^{(2)}$ als bei den Oxyden der Subgruppe a d.h. zwischen TiO_2 , ZrO_2 und ThO_2 gefunden wird, ist die Reihenfolge der katalytischen Wirksamkeit zwischen den letzt genannten drei Oxyden in Subgruppe a ganz unregelmässig; das erste Glied TiO_2 besitzt die grösste katalytische Wirksamkeit, dann folgt das letzte Glied ThO_2 und das zweite Glied ZrO_2 zeigt die geringste Wirksamkeit. Aber über diese gefundene Unregelmässigkeit in IV. Gruppe a können wir ohne weiteres nichts Bestimmtes sagen, bis weitere Versuche ausgeführt werden, erstens weil der gefundene Unterschied der katalytischen Wirksamkeit bzw. der Temperatur t (10%) nicht so deutlich ist und zweitens weil die katalytische Wirksamkeit eines gegebenen Oxyds, wie darauf schon oben hingewiesen wurde, manchmal durch die Beimengung verhältnismässig geringer Mengen Verunreinigungen ziemlich stark beeinflusst wird.

Herrn Prof. Dr. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit bestens danken. Der Nippon-Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung der vorliegenden Arbeit ermöglicht haben, bin ich auch zu grösstem Dank verpflichtet.

Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyositu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka).

(2) Bei diesem Vergleich wird t (10%) von SnO_2 -II d.h. 670°C aus dem schon oben angegebenen Grunde verwendet.

Vergleichung der Dichte des Wassers aus verschiedenen Orten auf der Erde.⁽¹⁾

Von Kokiti GOTO und Kenzo OKABE.

(Eingegangen am 29. Januar 1940).

Inhaltsübersicht. Die Dichte des Wassers aus verschiedenen Orten auf der Erde innerhalb und ausserhalb Japans wird nach gründlicher Reinigung untereinander schwebemetrisch verglichen. Dabei kommt man zu der Feststellung, dass sie innerhalb des geschätzten Messfehlersbereiches ($\pm 0.5\gamma$) untereinander gut übereinstimmt. Aus diesem Grunde darf wohl geschlossen werden, dass alle diese untersuchten Arten von Wasser fast dieselbe Isotopenzusammensetzung besitzen. Die Orte, wo die Probewasser

(1) Abgekürzte Übersetzung der japanischen Mitteilungen *J. Chem. Soc. Japan*, **60** (1939), 705, 707.

gesammelt werden, sind folgende 28: (innerhalb von Japan) Osaka, Muroran, Niigata, Tokuyama, Moji, Kagosima, Kiirun (Keelung), Takao, (ausserhalb von Japan) Hongkong, Cebu in Philippine, Manila, Singapore, Bangkok, Colombo, Bombay, Monbassa in Africa, New York, Cambridge in Ma. U.S.A., Hopewell in Va. U.S.A., Galveston in Tex. U.S.A., Houston in Tex. U.S.A., Panamakanal, Los Angeles in Calif. U.S.A., San Pedro in Calif. U.S.A. und Tacoma in Wash. U.S.A.

Einleitung. Bei den Versuchen mit schwerem Wasser und besonders bei den Untersuchungen über die Isotopenzusammensetzung des Wassers aus verschiedenen natürlichen Ursprüngen nimmt man gewöhnlich die Dichte bzw. die Isotopenzusammensetzung des Leitungswassers bei jedem betreffenden Ort als den Eichpunkt. Aus diesem Grunde ist es höchst wünschenswert die Dichte des Leitungswassers von verschiedenen Orten auf der Erde direkt bzw. indirekt miteinander zu vergleichen. Über die mittelbare Vergleichung der Dichte des Wassers aus verschiedenen Orten fehlen bisher auch keine Versuche. So wird z.B. durch die Versuche einiger Autoren festgestellt, dass das Kristallisationswasser von ein- und demselben natürlichen Mineral dem Leitungswassers aus verschiedenen Orten auf der Erde gegenüber immer fast denselben Dichteüberschuss ergibt.⁽²⁾ Diese Ergebnisse weisen aber offensichtlich darauf hin, dass die in Rede kommenden Arten Leitungswasser miteinander fast dieselbe Dichte bzw. Isotopenzusammensetzung besitzen. Aber was den unmittelbaren Vergleich der Dichte des Leitungswassers aus verschiedenen Orten auf der Erde anbetrifft, so sind bis jetzt, wenigstens so weit unsere Kenntnisse reichen, keine ausführlichen Versuche veröffentlicht worden.⁽³⁾ Von diesem Gesichtspunkt aus hat Dr. K. Yamasaki vom chemischen Institut der Kaiserlichen Universität Tokio mit Unterstützung der Frachtabteilung der Mitsui Bussan Kaisha (Mitsui Handelsgesellschaft) verschiedene Arten von Leitungswasser gesammelt und die so gesammelten Wasserarten uns alle zur Verfügung gestellt. Die vorliegenden Versuche wurden deshalb unter Verwendung dieser Arten von Leitungswasser durchgeführt. Die dabei benutzte Versuchsmethode ist prinzipiell ganz einfach; das betreffende Wasser wird zunächst möglichst gründlich gereinigt und dann die Dichte des so gereinigten Wassers mittels eines gut bewährten Quarzschwimmers mit der des ebenfalls sorgfältig gereinigten Osaka-Leitungswassers verglichen. Da bei dieser

(2) Das Kristallisationswasser von Tincal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) aus Californien zeigt dem Leitungswasser von Osaka, Washington und London gegenüber einen Dichteüberschuss von 2 γ , 3 γ und 0 γ . Auf ähnliche Weise besitzt das Kristallisationswasser von Rasorit ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) desselben Ursprungs dem Osaka-, Washington- und London-Leitungswasser gegenüber einen Dichteüberschuss von 4 γ , 7 γ und 6 γ und das von Carnalit aus Stassfurt dem Osaka- und London-Leitungswasser gegenüber einen Dichteüberschuss von 2 γ und 3 γ . Vgl. E. W. Washburn und E. R. Smith, *Bur. Standard J. Research*, **12** (1934), 305; H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207, 1948. Die Daten über den Vergleich mit dem Osaka-Leitungswasser wird aus dem nicht veröffentlichten Versuch von T. Titani und M. Koizumi entnommen.

(3) T. Titani und N. Morita sowie C. H. Greene und R. J. Voskuyl haben gefunden, dass das Osaka-Leitungswasser nur um 0.2 γ bzw. 0.07 γ dichter als das Cambridge-Leitungswasser ist. Vgl. T. Titani und N. Morita, *J. Chem. Soc. Japan*, **58** (1937), 1151 und dies Bulletin, **13** (1938), 409. Die umfangreiche Mitteilung von Greene und Voskuyl ist erst nach der Veröffentlichung der japanischen Mitteilung der vorliegenden Arbeit in unsere Hände gelangt. Vgl. den Nachtrag am Ende der vorliegenden Mitteilung.

Art der Versuche die Reinheit des zu untersuchenden Wassers der wesentlichste Faktor bildet, so haben wir darauf die grösste Sorgfalt verwendet.

Reinigung des Wassers. Die uns zur Verfügung gestellten Wasserproben sind alle in Glasflaschen mit Gummi- bzw. Korkstöpsel aufbewahrt worden. Aus diesen Flaschen werden nun bei den Versuchen mit dem Wasser japanischen Ursprungs immer 200 ccm dagegen bei den anderen Arten von Wasser 50 ccm herausgegossen und dem Reinigungsprozess unterworfen. Dieser besteht aber aus folgenden vier Prozessen, die mit ein- und demselben Probewasser nacheinander durchgeführt werden.

(1) Das Wasser wird zunächst in Dampfform über erhitztes Kupferoxyd bis auf etwa 450° geleitet, um dadurch schwer angreifbare Verunreinigungen vollständig oxydiert zu zersetzen. Das dabei benutzte Kupferoxyd wird aber aus reduzierten Kupferdrähtchen und dem Sauerstoffgas aus der Elektrolyse des Osaka-Leitungswassers hergestellt. Diese letztere Massnahme wird deshalb vorgenommen, um dadurch die Veränderung der Isotopenzusammensetzung des behandelten Wassers wegen der eventuell aufzutretenden Austauschreaktion der O-Atome zwischen Wasserdampf und festem Kupferoxyd möglichst zu vermeiden.⁽⁴⁾ Diese bis zu einem gewissen Grad derbe Methode der Reinigung wird aber nur für verhältnismässig stark verunreinigte Wasserproben verwendet (Nr. 15, 20, 21, 22, 24, 27 und 28 in unterstehender Tabelle 3).⁽⁵⁾ Die sonstigen nicht so stark verunreinigten Wasserproben werden dagegen ohne weiteres dem nächsten Reinigungsprozess (2) unterworfen.

(2) Bei diesem Prozess wird das Wasser aus dem oben angegebenen Prozess (1) bzw. die frische Wasserprobe aus der Flasche (vgl. oben) unter Zusatz von möglichst wenigen Mengen KOH und KMnO_4 in einem mit Rückflusskühler versehenen Kolben so lange sieden gelassen, bis die oxydierbaren Verunreinigungen im Wasser als restlos zersetzt angesehen werden können. So dauerte Prozess (2) mit den Proben Nr. 1 8 bis 12 Stunden, mit Nr. 9 bis 26 und Nr. 28 3 bis 6 Stunden, dagegen mit der Probe Nr. 27, die verhältnismässig stark verunreinigt war, sogar 100 Stunden lang.

(3) Das Destillat aus dem Prozess (2) wird unter Zusatz von wenigen Mengen P_2O_5 und KMnO_4 abdestilliert.

(4) Das Destillat aus dem Prozess (3) wird unter Zusatz von möglichst wenigen Mengen $\text{Ba}(\text{OH})_2$ in einem Kohlensäure-, Feuchtigkeit- und staubfreien Luftstrom abdestilliert.

(5) Das aus dem Prozess (4) erhaltene Destillat wird schliesslich ohne jeden Zusatz aber ebenfalls in einem gereinigten Luftstrom durch den Quarzkühler abdestilliert.

Bei jeder dieser Stufe der Destillationen wird immer 0.5 ccm aus dem Anfangsdestillat entfernt und nach der Beendigung der Destillation wird dieselbe Menge (0.5 ccm) Wasser im Kolben zurückgelassen. Diese Massnahmeregel ist offensichtlich insofern nötig, um die Veränderung der Dichte des Wassers wegen der isotopischen Fraktionierung bei der

(4) Vgl. N. Morita, dies Bulletin, 13 (1938), 656.

(5) Der grösste Teil dieser Verunreinigungen dürfte während der Aufbewahrung des Wassers in Flaschen hauptsächlich durch Gummi- bzw. Korkstöpsel verursacht worden sein.

Destillation für alle untersuchten Arten von Wasser möglichst gleich zu halten.⁽⁶⁾

Bestimmung der Dichte des Wassers. Die Dichte des so gereinigten Wassers wird unter Benutzung eines Quarzschwimmers mit der des auf genau dieselbe Weise gereinigten Osaka-Leitungswassers verglichen. Der dabei benutzte Quarzschwimmer ist im hiesigen Laboratorium schon paar Jahre lang in Gebrauch und deshalb gut geartet.⁽⁷⁾ Die Dichtebestimmung mittels dieses Quarzschwimmers führt man nach der von Koizumi⁽⁸⁾ entwickelten Methode bei 9.5° durch, indem man den Unterschied ΔT der Gleichgewichtstemperatur zwischen der betreffenden Wasserprobe und dem Standardwasser (Osaka-Leitungswasser) mittels eines Beckmannthermometers abliest und aus dem so gefundenen Temperaturunterschied ΔT den Dichteunterschied Δs nach Gl. (1) berechnet:

$$\Delta s = -79\Delta T \quad (1).$$

Zu dieser Dichtebestimmung wird aber das Wasser aus dem oben erwähnten Reinigungsprozess (4) ohne weiteres d.h. ohne Entfernung der gelösten Luft verwendet. Deshalb wird das Wasser immer mit Luft gesättigt. Der Fehler wegen der Schwankungen des Sättigungsgrades der Luft in den einzelnen untersuchten Wasserproben darf wohl unberücksichtigt bleiben, weil jedes Wasser, wie schon oben erwähnt wurde, unter möglichst gleichen Versuchsbedingungen gereinigt wird. Nach den Versuchen von Titani und Morita über die Vergleichung der Dichte des Osaka- und Cambridge-Leitungswassers wird der Fehler wegen dieser Schwankung des Sättigungsgrades der Luft in untersuchtem Wasser kleiner als $\pm 0.2 \gamma$ geschätzt.⁽⁶⁾ Diese Grösse liegt aber schon innerhalb des eben zu erwähnenden gesamten Messfehlerbereiches der vorliegenden Versuche.

Die Dichtebestimmung eines angegebenen Probewassers wird jedesmal zwei bis fünfmal wiederholt, indem man untereinander ganz unabhängig gereinigte frische Proportionen des Wassers verwendet. Die dabei gefundenen einzelnen Werte von Δs ein- und desselben Probewassers schienen aber höchstens innerhalb $\pm 0.5 \gamma$ untereinander gut übereinzustimmen, wie man dies aus den in Tabelle 1 angegebenen Musterversuchen mit Kagosima-Leitungswasser ersieht.

Tabelle 1. Versuchsergebnisse mit Kagosima-Leitungswasser.

Versuchsnr.	ΔT	Δs in γ	Mittel
1	-0.005	+0.40	+0.40
2	-0.003	+0.24	
3	-0.006	+0.48	
4	-0.007	+0.56	
5	-0.004	+0.32	

(6) N. Morita, *J. Chem. Soc. Japan*, **58** (1937), 1151. Vgl. dazu T. Titani und N. Morita, dies Bulletin, **13** (1938), 409.

(7) Derselbe Schwimmer, den Titani und Morita zur Vergleichung der Dichte des Leitungswassers von Osaka und Cambridge benutzt haben. Vgl. Fussnote (6).

(8) M. Koizumi, *J. Chem. Soc. Japan*, **56** (1935), 811. Vgl. auch Y. Shibata, K. Noguchi und O. Kaneko, dies Bulletin, **14** (1939), 275.

Aus diesen Ergebnissen darf man wohl zu dem Schluss kommen, dass der Messfehlerbereich der vorliegenden Versuche höchstens innerhalb $\pm 0.5 \gamma$ liegt. Dabei wird offensichtlich auch der Fehler wegen der unvollständigen Reinigung (isotopische Fraktionierung u.s.w.!) mitberechnet.⁽⁹⁾ Weil die einzelnen Werte von Δs ein- und desselben Probewassers untereinander so gut übereinstimmen, geben wir in weiter unten angegebenen Tabellen 2 und 3 nur den Mittelwert von Δs für jedes Probewasser wieder.

Versuchsergebnisse. Die in den vorliegenden Versuchen gewonnenen Ergebnisse sind in Tabelle 2 und 3 zusammengestellt, wo das Datum in der letzten Spalte die Zeit angibt, als die betreffende Wasserprobe ange-

Tabelle 2. Dichteüberschuss Δs des Leitungswassers aus verschiedenen Orten in Japan dem Osaka-Leitungswasser gegenüber.

Nr.	Leitungswasser	ΔT	Δs in γ	Datum
0	Osaka	± 0.000	± 0.0	—
1	Tokio	—	+0.4	—
2	Muroran	-0.003	+0.2	1936. 3. 29.
3	Niigata	-0.005	+0.4	„ 5. 11.
4	Tokuyama	-0.004	+0.3	„ 4. 11.
5	Moji	-0.003	+0.2	„ 4. 20.
6	Kagosima	-0.005	+0.4	„ 2. 17.
7	Kiirun (Keelung)	-0.003	+0.2	„ 6. 8.
8	Takao	+0.001	-0.1	„ 2. 1.

Tabelle 3. Dichteüberschuss Δs des Leitungs-,Quellen- bzw. Kanalwassers aus verschiedenen Orten auf der Erde dem Osaka-Leitungswasser gegenüber.

Nr.	Ort	Art des Wassers	ΔT	Δs in γ	Datum
0	Osaka	Leitungswasser	± 0.000	± 0.0	—
9	Hongkong	„	—	± 0.0	1936. 4. 13.
10	Manila	„	—	+0.1	„ 4. 28.
11	Cebu in Philippinen	„	—	+0.1	„ 4. 30.
12	Singapore	„	—	+0.4	„ 3. 3.
13	Bangkok	„	—	+0.6	„ 5. 10.
14	Colombo	„	—	± 0.0	„ 4. 4.
15	Bombay	„	+0.006	-0.5	„ 5. 20.
16	Mombassa in Africa	„	—	± 0.0	„ 3. 24.
17	New York	„	—	-0.6	„ 2. 26.
18	Cambridge in Ma. U. S. A.	„	—	+0.2	„ 12. 22.
19	Hopewell in Va. U. S. A.	„	—	-0.2	„ 2. 29.
20	Norfolk in Va. U. S. A.	Quellenwasser	-0.006	+0.5	„ 1. 2.
21	Jacksonville in Flor. U. S. A.	Leitungswasser	-0.007	+0.6	„ 3. 6.
22	Corpus Christi in Tex. U. S. A.	„	-0.007	+0.6	„ 1. 7.
23	Galveston in Tex. U. S. A.	„	—	+0.6	„ 1. 6.
24	Houston in Tex. U. S. A.	„	-0.008	+0.6	„ 1. 14.
25	Panamakanal	Kanalwasser	—	+0.4	„ 3. 11.
26	Los Angeles in Calf. U. S. A.	Leitungswasser	-0.007	+0.6	„ 3. 20.
27	San Pedro in Calf. U. S. A.	„	+0.009	-0.7	„ 3. 30.
28	Tacoma in Wash. U. S. A.	„	—	+0.4	„ 5. 11.

(9) Der Fehlerbereich der Schwimmermethode an sich selbst ist selbstverständlich viel kleiner als dies.

sammelt wurde. Weiter wird das Ergebnis mit Tokio-Leitungswasser aus dem unveröffentlichten Versuch von Dr. Koizumi und das von Cambridge-Leitungswasser aus dem Versuch von Titani und Morita⁽⁶⁾ entnommen.

Zusammenfassung und Diskussion. Aus den oben in Tabelle 2 und 3 angegebenen Versuchsergebnissen zu urteilen, erscheint das Wasser amerikanischen Ursprungs im allgemeinen um ein wenig dichter als das von japanischem Ursprungs zu sein. Aber auch wenn dieser Dichteunterschied wirklich vorhanden wäre, hätten wir es damit hauptsächlich mit dem Unterschied des Gehaltes des betreffenden Wassers an schwerem Sauerstoff zu tun, weil der Gehalt des natürlichen Wassers an schwerem Sauerstoff viel grösser ist als der an schwerem Wasserstoff und infolgedessen die minimale Schwankung des ersteren viel grösseren Effekt auf die Dichte des Wassers ausübt als die des letzteren. Aber weil in jedem Fall der gefundene Dichteunterschied bei dem vorliegenden Versuche kaum ausserhalb des geschätzten Messfehlerbereiches ($\pm 0.5 \gamma$) liegt, möchten wir lieber annehmen, dass die untersuchten Arten von Wasser mindestens mit der Genauigkeit von $\pm 0.5 \gamma$ alle fast dieselbe Dichte und folglich dieselbe Isotopenzusammensetzung besitzen.

Nachtrag zur Übersetzung. Gleich nach der Veröffentlichung der originalen japanischen Mitteilungen der vorliegenden Versuche ist die ausgezeichnete Arbeit von Greene und Voskuyl⁽¹⁰⁾ eingetroffen. Verfasser fanden in diesen Versuchen gut übereinstimmend mit den vorliegenden Versuchsergebnissen, dass das sorgfältig gereinigte Leitungswasser von Cambridge, Osaka, London, Columbus und Washington jedes mit der Genauigkeit von 0.1γ dieselbe Dichte besitzt.

Zum Schluss sprechen wir Herrn Dr. K. Yamasaki und der Frachtabteilung der Mitsui Bussan Kaisha für ihre freundliche Überlassung der in den vorliegenden Versuchen benutzten Probewasser unseren verbindlichsten Dank aus. Der Nippon Gakujutsu-Shinkokai (der Japanischen Gesellschaft zur Förderung der Wissenschaftlichen Forschungen) sowie der Hattori-Hokokai (der Hattori-Stiftung) für ihre finanzielle Unterstützung und Herrn Prof. T. Titani für seine Anregung zu dieser Arbeit sind wir auch zu bestem Dank verpflichtet.

*Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyositu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka)
und Kobe Jogakuin (Kobe Women's College).*

(10) G. N. Greene und R. J. Voskuyl, *J. Am. Chem. Soc.*, **61** (1939), 1342.

Properties of Mercury Oxide as an Active Material of Positive Electrode in Alkaline Storage Cell.

By Kyôji KINOSHITA.

(Received January 18, 1940).

(1) *Experiments with red mercury oxide.* The author has reported that the positive and the negative electrode plates of the alkaline storage cell can be prepared with silver oxide⁽¹⁾ and bismuth oxide⁽²⁾ respectively in pasted form. In the present paper, the results of similar experiments with mercury oxide will be reported.

When red mercury oxide is mixed with 5N NH_4OH solution, a paste-like material will be obtained such as we get in kneading lead oxide with dilute sulphuric acid. We shall call this material "paste" throughout the present report. The electrode plate was prepared by applying this paste to the grids made of nickel plated lead antimony alloy (the size of the grid being about 6.0 cm. $\times$ 1.5 cm. $\times$ 0.3 cm.) which can also be used for preparing the lead accumulator plate. When the plate thus prepared was dipped into 20% KOH solution a small amount of the active material fell off from the surface. This seemed to happen owing to the poor cohesive power of the active material made of mercury oxide. Similar experiments were undertaken therefore, with the electrode plate which was made by the paste produced by mixing silver oxide and red mercury oxide.

Table 1 shows the properties of the plate used for the experiments.

Table 1.

Number of electrode plate	Amount of active material <i>w</i> (in gram)	Composition of Paste		Weight of grid (in gram)
		Amount of Ag_2O mixed (in gram)	Amount of HgO mixed (in gram)	
6	9.63	—	10.00	15.26
8	5.22	4.00	2.00	15.98
9	6.20	3.75	3.75	13.04
10	6.98	2.00	6.00	16.66

After the paste was applied to the grids, they were left to dry for about 72 hours, then they were dipped into 20% KOH solution. There was no falling off of the active material in any electrode plate.

Electrolytical "formation" of the pasted plate thus obtained were undertaken in 20% KOH solution by the current of 80 milliamperes for

(1) K. Kinoshita, this Bulletin, **12** (1937), 164, 366.

(2) K. Kinoshita, this Bulletin, **15** (1940), 59.

about 90 hours. With the completion of the formation, the positives were combined with the negative electrode of the Nife's accumulator which had already been fully charged, and were subjected to four cycles of charges and discharges by the current of 250 milliamperes. Table 2 shows the results of the experiments.

Table 2.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	Discharge hour (in hour)	Capacity C . (in ampere-hours)	Discharge hour (in hour)	Capacity C . (in ampere-hours)	Discharge hour (in hour)	Capacity C . (in ampere-hours)
1	7.266	1.817	7.833	1.958	8.216	2.054
2	5.500	1.375	6.333	1.583	6.166	1.542
3	5.183	1.296	6.466	1.617	5.633	1.408
4	5.166	1.292	6.500	1.625	5.916	1.479
mean		1.445		1.696		1.621

The voltage of the accumulator No. 6 has fallen to zero at fifteen minutes after the starting of the discharge, so that it was left out from discharging afterwards.

As shown in Table 2, the discharge capacity is comparatively large for each accumulator in the first discharge, but falls remarkably in the second discharge, then it tends to fall continuously.

Fig. 1 shows the discharge characteristic curve in the first discharge.

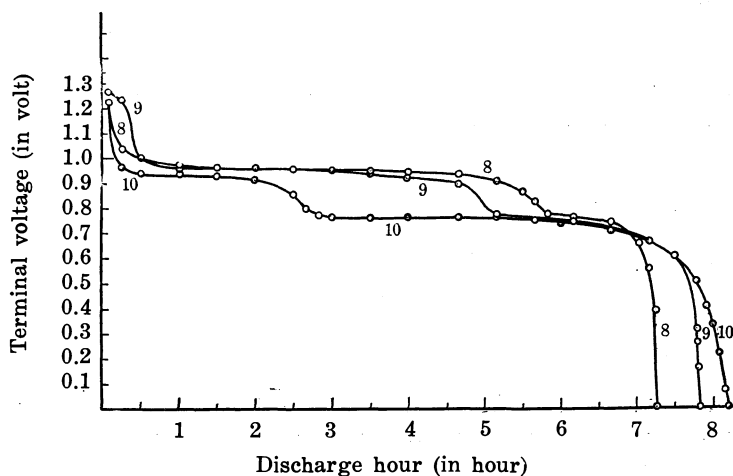


Fig. 1.

As shown in the figure, the voltage falls in two stages the first stage being about 0.95 volt and the second about 0.75 volt. The cell No. 9 gives at the beginning of discharge, the value of over 1.2 volts. Now,

the whole discharge capacity C , is divided into two parts C_1 and C_2 , at the inflexion points of the voltage curve between these two stages. The results are given in Table 3.

Table 3.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)	capacity C_1 (in ampere-hours)	capacity C_2 (in ampere-hours)
1	1.417	0.400	1.242	0.717	0.667	1.388
2	0.983	0.392	0.875	0.708	0.317	1.225
3	1.000	0.296	0.908	0.708	0.292	1.117
4	0.863	0.429	1.008	0.617	0.333	1.146
mean	1.066	0.379	1.008	0.688	0.402	1.219

By examining more closely the discharge characteristic curve of Fig. 1, we know, that the variation in the terminal voltage is much like that of silver oxide positives in the pasted form, which the author has previously noticed.⁽¹⁾ When the silver oxide plate combined with the negative electrode of the Nife accumulator was discharged in 20% KOH solution with the same rate of the discharge current, the terminal voltage of about 0.95–0.99 volt was obtained.

Moreover, the terminal voltage of about 1.2 volts at the beginning of the discharge for the cell No. 9 in this experiments was also observed in the case of the silver oxide electrode. This is understood as the discharge capacity obtained by the chemical changes of silver peroxide into silver oxide. The discharge capacity shown in Fig. 1, C_1 , therefore, may be resulted from the discharge of the silver oxide which has been mixed in the active material of the electrode.

The following shows the amount of the silver oxide and the mercury oxide in the active material of the electrode, which has been calculated from Table 1.

Number of the electrode plate...	No. 8	No. 9	No. 10
Amount of silver oxide (g.) $\dots W_s$	3.48	3.10	1.74
Amount of mercury oxide (g.) W_m	1.74	3.10	5.24
Total $\dots w$	5.22	6.20	6.98

The values of C_1/W_s have been calculated assuming that the discharge of the first stage is resulted from the discharge of silver oxide, and are shown in Table 4. In this table the values of C_2/W_m are also shown for comparison.

This table shows that the value of C_1/W_s is the same as, or a bit smaller than, that of the alkaline storage cell in the pasted form consisting of silver oxide alone, which was determined previously by the author.⁽¹⁾

Table 4.

Number of discharge n	Number of electrode plate					
	No. 8		No. 9		No. 10	
	C_1/W_s in ma. h./g.	C_2/W_m in ma. h./g.	C_1/W_s in ma. h./g.	C_2/W_m in ma. h./g.	C_1/W_s in ma. h./g.	C_2/W_m in ma. h./g.
1	414	230	401	231	383	265
2	284	225	282	228	182	234
3	287	170	294	228	168	213
4	248	246	325	199	191	219
mean	311	218	326	222	231	233

The value of C_1/W_s decreases as the amount of HgO increases, while the value of C_2/W_m does not change so much with the variation of the content of Ag_2O .

Now, plotting C_1 or C_2 in ordinate (in amperehour) and W_s or W_m in abscissa (in gram) we obtain Fig. 2 and Fig. 3.

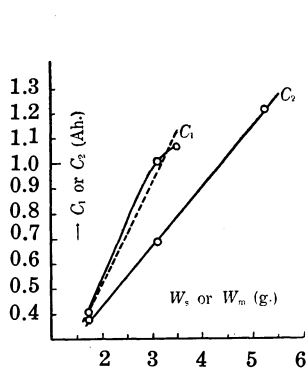


Fig. 2.

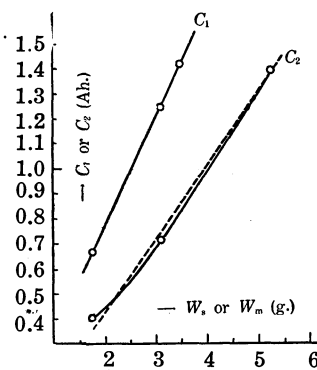


Fig. 3.

In Fig. 2 the average value of the four discharges is used for each of C_1 and C_2 , and in Fig. 3 the result of the first discharge is used for each of C_1 and C_2 . As can be seen from Fig. 2, there is a linear relation between C_2 and W_m , while no such relation between C_1 and W_s . From Fig. 3, both C_1 and C_2 may be presumed as linear. However, all these have only three measuring points and the relation cannot accurately be brought out.

In calculating the value of C_1 , in the case of such electrode as No. 9 which shows the characteristic curve that seems to result owing to the reaction $Ag_2O_2 \rightarrow Ag_2O$, should be left out from the calculation.

(2) *Experiments with yellow mercury oxide.* Similar experiments as above were undertaken on the yellow mercury oxide. The grid used for the experiments were made of lead antimony alloy plated with nickel as in the previous case. Four electrode plates were prepared having different constitution of the paste, which are shown in table 5.

Table 5.

Number of electrode plate	Amount of active material <i>w</i> (in gram)	Composition of paste		Weight of grid (in gram)
		Amount of Ag ₂ O mixed (in gram)	Amount of HgO mixed (in gram)	
1	5.26	4.50	1.50	16.95
2	5.00	4.00	4.00	15.37
3	4.81	2.00	6.00	15.10
4	5.68	—	10.00	15.70

When the paste was applied to the grids, each plate showed considerable stiffness, and seemed to give a satisfactory result. But in dipping in 20% KOH solution, the active materials of No. 3 and No. 4 have dropped off readily. The active material in No. 1 and No. 2 did not fall

Table 6.

Number of discharge <i>n</i>	Number of electrode plate			
	No. 1		No. 2	
	Discharge hour (in hours)	Discharge capacity <i>C</i> (in ampere hours)	Discharge hour (in hours)	Discharge capacity <i>C</i> (in ampere hours)
1	4.333	1.083	4.333	1.083
2	3.333	0.833	4.000	1.000
mean	3.833	0.954	4.167	1.042

off so much and could be formed into the positive electrode plate by the current of 100 milliamperes for about 96 hours. Immediately after the "formation," they were charged and discharged for two times.

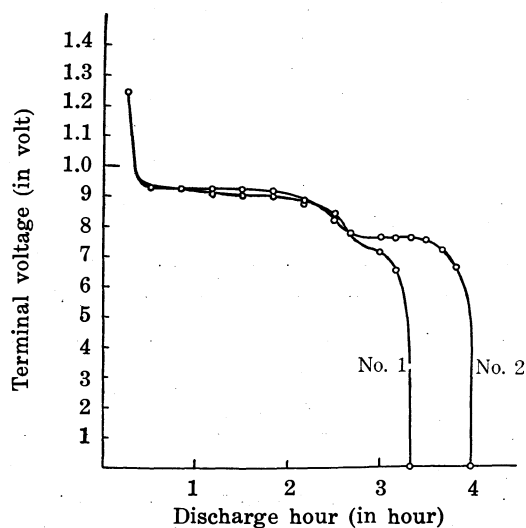


Fig. 4.

The colour of the plate of No. 1 was brown, when the paste was applied in the grids, and that of No. 4 yellow, and No. 2 and No. 3 showed medium colours between brown and yellow according to their constitution. The discharge current was taken to be 250 milliamperes and the charge was undertaken by the current of 200 milliamperes for about 10 hours. Table 6 shows the discharge capacity.

Fig. 4 shows the discharge characteristic curves.

Both No. 1 and No. 2 show the first stage of about 0.92 volt and the second stage of about 0.75 volt. This is just the same as obtained in the experiments with red mercury oxide. The fact that No. 2 which contains more mercury oxide than No. 1 has larger discharge capacity in the second stage, is the same tendency as seen in the red mercury oxide experiment.

(3) *Conclusion.* The positive plate of an accumulator in pasted form can be made by the mercury oxide (both red and yellow) provided that it is given some cohesive power as the active material by mixing with silver oxide.

The discharge characteristic curve has two steps in general, so that the whole discharge capacity can be divided into the two parts C_1 and C_2 . The discharge characteristic curve of the first stage resembles much with the curve of the silver oxide positive plate, moreover, C_1 and C_2 stand in proportional relations with W_s and W_m , the quantities of silver oxide and mercury oxide in the active material respectively. This fact proves that C_1 is the result of the activity of silver oxide and C_2 the result of that of mercury oxide.

The appearance of the terminal voltage of about 1.2 volts at the beginning of the discharge, may be accounted for by the formation of silver peroxide. At present, the author will not discuss fully on the discharge characteristics of mercury oxide, but will insist the fact that if we can keep up mercury oxide as the active material of the electrode plate by some proper means, it can be used as the alkaline accumulator positive.

It was not possible to get an electrode plate made of yellow mercury oxide alone and the author can say nothing about it. In the case of red mercury oxide, however, the plate No. 6 which was made of red mercury oxide alone showed a small discharge capacity. This is a notable fact.

All these and the fact that the increasing of mercury oxide decreases the value of C_1/W_s seem to show the poor electrical conductivity of mercury oxide as the active material of electrode plate. It is thought to be probable from the result of experiments that the silver oxide mixed with the mercury oxide gives not only cohesive power but also better electrical conductivity of the active material, for it leaves powdered metallic silver as the result of the discharge.

Summary.

(1) Mercury oxide (both red and yellow) can be used into the electrode plate of the alkaline accumulator in the pasted form by mixing silver oxide.

(2) Its discharge characteristic curve varies in two stages, the first stage being caused by the discharge of silver oxide and the terminal voltage of about 0.95 volt, and the second stage being caused by mercury oxide.

(3) Mercury oxide seems to be a considerably poor substance in the electrical conductivity and the mixing of silver oxide raises its electrical conductivity.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his valuable advice.

*Toyoda Research Laboratory,
Imperial Invention Society,
Shimomeguro Tokyo.*

Zinc Content of the Hot Springs of Japan.

By Kazuo KURODA.

(Received January 18, 1940.)

Recently, considerable interest has been attached to the determination of the minute traces of rarer elements in natural waters and the observations have revealed the apparently universal distribution of heavy metals throughout the hydrosphere. A number of reports on the occurrence of zinc in sea water and in the mineral waters have already been published. The polarographic method for the determination of heavy metals such as copper, lead, nickel and zinc in the mineral waters has recently been quite well established by K. Heller, G. Kuhla and F. Machek.⁽¹⁾ P. R. Stout and his collaborators⁽²⁾ have reported that the polarographic method is quite satisfactory for the determination of the minute traces of zinc in plant and animal tissues. The present author tested these methods and found that the following modified procedure was satisfactory for the determination of zinc in natural waters.

Method of Analysis. The method and apparatus used for the determination of zinc will be described in the following paragraphs.

(a) *Purification of the Diphenylthiocarbazone Carbon Tetrachloride Solution.* The solution of diphenylthiocarbazone in carbon tetrachloride was purified before use in the following manner:—Dissolve 0.1 g. of diphenylthiocarbazone in 100 ml. of carbon tetrachloride and wash the solution repeatedly with 6N hydrochloric acid in a separating funnel. Reject the aqueous layers, add 100 ml. of ammonia (5:95), shake, allow the layers to separate, reject the carbon tetrachloride layer. Add 100 ml. of carbon tetrachloride, acidify the aqueous layer with hydrochloric acid, draw off the carbon tetrachloride solution, and wash it with distilled water. This washed carbon tetrachloride solution constitutes the purified diphenylthiocarbazone reagent.

The amount of zinc derived from the glass bottle in which the mineral water was collected was found to be less than 10 γ per litre. The presence of zinc in water kept in the bottle for a long time was detected colori-

(1) *Mikrochemie*, **23** (1937), 78.

(2) *Collection Czechoslov. Chem. Commun.* **10** (1938), 129.

metrically, but it was difficult to estimate the amount by the polarographic method. The glass vessels was always washed with diphenylthiocarbazone solution before use to remove the traces of zinc and other heavy metals.

(b) *Extraction of Zinc with Diphenylthiocarbazone.* Add 10 ml. of N ammonium citrate solution to a suitable quantity (100 ml. to 500 ml.) of the mineral water, adjust to pH 8.5 with ammonia using phenol red as indicator, and shake with successive 10 ml. portions of the purified carbon tetrachloride solution of diphenylthiocarbazone. Continue the extraction until the carbon tetrachloride layer remains green. Wash the combined extracts with dil. ammonia (1:1000), run the carbon tetrachloride solution into a separating funnel, and shake with three separate 10 ml. portions of 6N hydrochloric acid. Combine the acid layers and wash them by pouring small quantities of carbon tetrachloride through the aqueous liquid without shaking. Add 10 mg. of sodium chloride to the acid solution, and evaporate to complete dryness.

(c) *Determination of Zinc by the Polarographic Method.* Dissolve the residue in water, add 1 ml. of N ammonium acetate solution and 1 ml. of 0.25N potassium thiocyanate solution, and make up the volume of the solution to 10 ml. with water. A part of the solution is brought to a small electrolysis vessel, freed from the air by a current of hydrogen and then polarographically examined. The amount of zinc present is obtained from the height of the polarographic wave at -1.0 V. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amounts of zinc salt in a solution which is 0.1N with respect to ammonium acetate and 0.025N to potassium thiocyanate, freed from atmospheric oxygen.

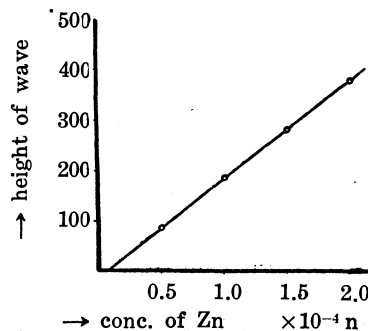


Fig. 1. The calibration curve for the wave due to zinc in a solution which is 0.1N with respect to ammonium acetate and 0.025N to potassium thiocyanate.

Results. The efficacy of the method was first tested by adding known amounts of standard zinc sulphate solution to 50 ml. of water and submitting the solutions to the complete process of extraction and polarographic examination; the results obtained are shown in Table 1.

Table 1.

Zinc added (γ)	Zinc found (γ)	Error (γ)
32.7	31.6	-1.1
65.3	67.1	+1.8
98.0	93.3	-4.7
130.6	136.9	+6.3

Further experiments were made in which known quantities of zinc were added to 1000 ml. of the mineral water, and submitted to the complete process of extraction. The results are given in Table 2,

Table 2.

No.	Mineral Waters	Zinc added to 1000 ml. of the mineral water (γ)	Zinc found (γ)	Difference (Zinc Content) (γ)
1	Monkawa, Kanagawa Prefecture	0	113	113
		65	176	111
2	Huezuka-Yu, Yunohanazawa, Kanagawa Prefecture.	0	20	20
		130	154	24
3	Drinking water of Yunohanazawa	0	46	46
		130	178	48

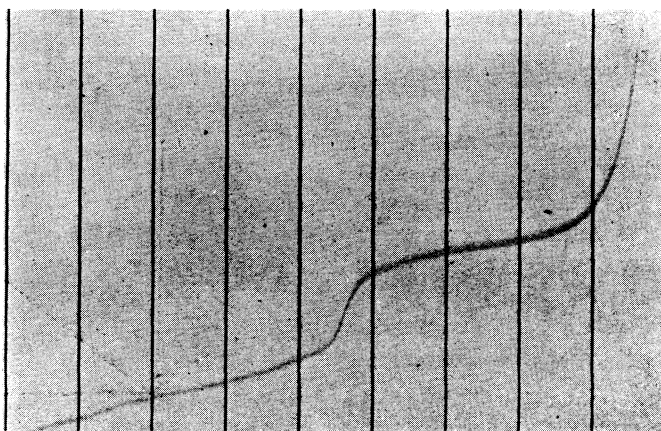


Fig. 2. Wave due to 68 γ of zinc extracted from the mineral water. (Military Sanatorium at the Misasa hot spring.) 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate. Sensitivity $\frac{1}{10}$. Curve starts from zero E.M.F. 4 V. accumulator.

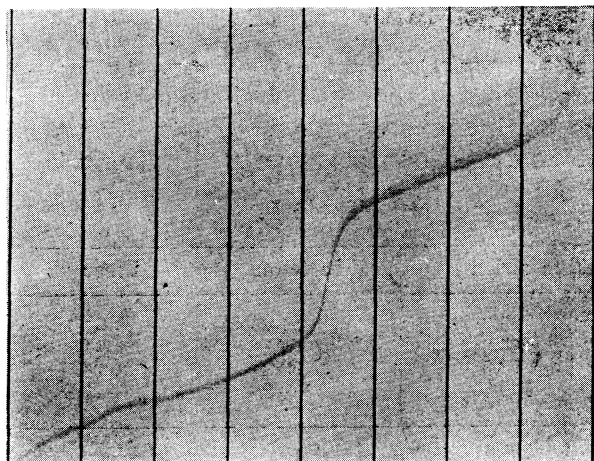


Fig. 3. Wave due to 112 γ of zinc extracted from the "Yuzawa No. 1" spring. 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate. Sensitivity $\frac{1}{10}$. Curve starts from zero E.M.F. 4 V. accumulator.

The results of the determinations of the zinc contents, mainly of the hot springs of Japan, are collected in Table. 3.

Table 3.
Zinc Content of the Hot Springs of Japan.

No.	Hot Springs	Zinc Content.	
		(γ /l.)	% (total residue.)
(1)	Katakosi-Yu, Arima.	2010	0.0085
(2)	Yuzawa No. 10, Masutomi	284	0.019
(3)	Misasa Hotel, Misasa.	235	0.033
(4)	Yuzawa No. 1, Masutomi.	224	0.102
(5)	Kuridaira No. 1, Masutomi.	215	0.0060
(6)	Yuzawa No. 3, Masutomi.	164	0.082
(7)	Hana-no-Yu, Arima.	160	0.0009
(8)	Ikaho No. 1.	156	0.0014
(9)	Sanatorium at Misasa.	140	0.0045
(10)	Hon-Onsen. Arima.	140	0.0008
(11)	Military Sanatorium at Misasa.	136	0.0112
(12)	Yoemon-Yu, Yunohanazawa, Hakone.	132	0.0066
(13)	Yuzawa No. 5, Masutomi.	126	0.115
(14)	Daruma-Zigoku, Yunohanazawa.	120	0.0060
(15)	Wadamatuba, Masutomi.	113	0.0008
(16)	Monkawa.	113	0.0004
(17)	Yuzawa No. 4, Masutomi.	102	0.051
(18)	Yuzawa No. 7, Masutomi.	102	0.0065
(19)	Yagendo, Arima.	96	0.0009
(20)	Yuzawa No. 2, Masutomi.	88	0.0151
(21)	Sanatorium of the Medical College of Okayama at Misasa.	81	0.0053
(22)	Yuzawa No. 6, Masutomi.	80	0.022
(23)	Kinsentō, Masutomi.	80	0.0011
(24)	Ginsentō, (Huru-Yu), Masutomi.	80	0.0078
(25)	Ginsentō (Naka-no-Yu), Masutomi.	78	0.0080
(26)	Nanasigure.	73	0.0006
(27)	Bansuiro, Misasa.	66	0.0042
(28)	Yuzawa No. 9, Masutomi.	64	0.0042
(29)	Wadegawara (Simo-no-Yu), Masutomi.	64	0.0009
(30)	Yuzawa No. 8, Masutomi.	60	0.0036
(31)	Azuro.	46	0.0004
(32)	Higasiobi, Masutomi.	39	0.0004
(33)	Gantōhunsen, Masutomi.	35	0.0012
(34)	Kōbō-Yu, Yunohanazawa.	34	0.0034
(35)	Tuganerō, Masutomi.	26	0.0003
(36)	Umamitizawa, Masutomi.	26	0.0007
(37)	Gongen-Yu, Yunohanazawa.	25	0.0039
(38)	Huezuka-Yu, Yunohanazawa.	20	0.0033
(39)	Hii-no-Yu, Matunoyama.	less than 10	0.000
(40)	Tamagono-Yu, Matunoyama.	less than 10	0.000
(41)	Iriyamabe.	less than 10	0.000
(42)	Simokurohira.	less than 10	0.000
(43)	Hiukemizu, Masutomi.	less than 10	0.000
(44)	River water, Yunohanazawa.	less than 10	0.000
(45)	Sea water, Yoshihama.	less than 10	0.000
(46)	Drinking water of Yunohanazawa.	46	0.0170
(47)	Tap water of Tokyo, Oct. 26, 1939.	116	
(48)	Tap water of Tokyo, Oct. 27, 1939.	133	
(49)	Tap water of New York.	124	
(50)	Distilled water.	less than 10	

Table 3. shows that the traces of zinc are widely distributed in the mineral waters in Japan. The mineral springs of Arima had the highest

zinc content. The average zinc content of forty-three samples was 0.013% (of the total residue), or 136 γ per litre. The presence of zinc in sea water was detected colorimetrically, but the author could not estimate the amount polarographically. The zinc content of sea water is considered to be less than 10 γ per litre.

Summary.

(1) The polarographic method was tested and found to be satisfactory for the determination of zinc in natural waters.

(2) The zinc content of a number of hot springs of Japan was polarographically estimated.

(3) The amount of zinc in sea water is considered to be less than 10 γ per litre.

The author wishes to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. It is author's pleasant duty to acknowledge the valuable advice offered by Dr. H. Hamaguti. 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

Studies on the Organic Molecular Compounds. Part I. The Influence of Nitro Radicals and Second Substitution Radicals on the Formation of the Aromatic-Nitroaromatic Molecular Compounds. I.

By **Chiro SHINOMIYA.**

(Received February 5, 1940).

Graduation of Molecular Compound Formation. Organic "molecular compound formation" is discussed in this paper, with the binary solid—liquid phase equilibrium diagram as basis. The aromatic—nitroaromatic molecular compound formation studied by the writer is summarised schematically in Fig. 1.

Curve $A_1C_1B_1$ indicates a stable compound type with a congruent melting point C_1 . Curves A_1DB_2 , A_2UB_1 , and $A_2E_6B_2$ in the diagrams illustrate the successive changes that occur with the decrease of the tendency of compound formation.⁽¹⁾ A_1DB_2 is a dissociation type,

(1) For simplicity, only a single compound of the type AB (1:1) is considered. The argument, however, can readily be extended to other types.

A_2UB_1 an incongruent type, and $A_2E_6B_2$ a simple eutectic type, for which last named no compound is found in the diagram.

The Existence Range of Molecular Compounds. In the ideal case, the crystallisation curve A_2E_6 represents the ideal solution equation, namely

$$\ln x = -\frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right),$$

where x is the mol fraction of A_2 in the saturated solution at temperature T , Q the differential mol heat of solution of A_2 , T_0 the melting point of pure A_2 , and R the gas constant. Curve B_2E_6 is also of a similar nature. E_6 , the intersection of the two curves, is the eutectic point of this system.

Kendall and his co-workers,⁽²⁾ who studied the various factors that induce deviations from the ideal solubility curve in polar systems, concluded that the predominant disturbing factor is the "addition compound formation" between the components of the systems. The essential point to be noted is the depression of the crystallisation curve (AE or BE) from its ideal position, which is made necessary by compound formation in the solution.⁽³⁾

"If only a part of the total A in solution exists as uncombined A, then the total mol fraction of A in the saturated solution must exceed the ideal value by an amount depending on the stability of the compound AB in the liquid state, since the solution will not become saturated with respect to A until the mol fraction of uncombined A reaches this ideal value." Consequently, in Fig. 1, at any fixed temperature T under the melting point of A_2 , the solubility of A_2 in the system A_2UB_1 is larger than that in $A_2E_6B_2$, as also the solubility of A_1 in the system $A_1C_1B_1$ is larger than that in A_1DB_2 .

Increasing solubility and increasing tendency of compound formation, therefore, for one fixed component (A_1) in a series of different others (B_1 or B_2 , etc.), proceed in parallel. Since it is the same when we take B in place of A, the increased solubility necessitates an enlarged range of existence of compounds ($E_1E_2 = \omega$ in the system $A_1C_1B_1$) in the solid—liquid equilibrium state.

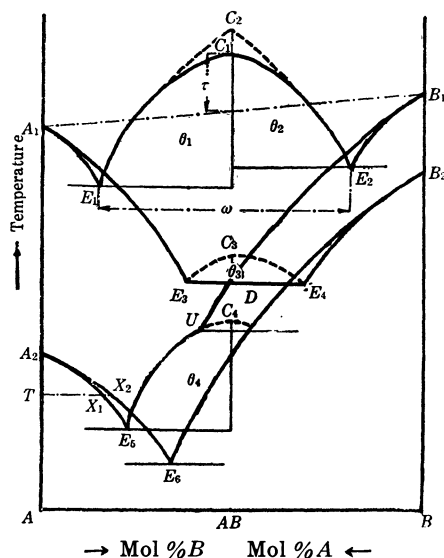
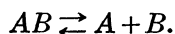


Fig. 1.

(2) J. Kendall, A. W. Davidson, H. Adler, *J. Am. Chem. Soc.* **43** (1921), 1481.

(3) Curve A_2E_6 is asymptotic to the ordinate at B ($x = 0$), and curve A_1E_1 is asymptotic to the ordinate at AB ($x = 0.5$). In the remaining case, AE assumes an intermediate position between the two.

The Melting Point of Molecular Compounds⁽⁴⁾. Increasing stability of the compound and elevation of its melting point also proceeded in parallel. In the system $A_1C_1B_1$, the virtual point C_2 indicates the melting point of the compound, not dissociated into its components in the fused state, the system consisting, indeed, of two simple eutectic systems of type $A_2E_6B_2$ compressed into one composition range. Point C_1 is the dystectic point of an actual compound in which some degree of dissociation is realized on fusion,



In the less stable A_1DB_2 system, further dissociation takes place, the crystallisation curve $E_3C_3E_4$ becomes flatter, and, finally, in the case of complete dissociation, it coincides with the straight line E_3DE_4 .

Generallization is used here in order to compare the compound formation in systems of various types. It has been shown that—

- (a) Compound formation and its stability decreases in the order,⁽⁵⁾ congruent type $>$ dissociation type, incongruent type $>$ simple eutectic type.
- (b) In the first three types, where compound crystals are perceived, the order of compound formation is generally parallel to the solubility of the mutual components, which spreads the existence range of the compound: ω .⁽⁶⁾
- (c) In the congruent melting type, stability is related to the curvature of the crystallisation curve near the dystectic point.

In the non-dissociation type, the dystectic point C_2 , which designates the melting point of a pure solid compound, is on the apex of $E_1C_2E_2$, although usually in the case of organic molecular compounds in the fused state, dissociation takes place to a certain extent, so that, the crystallisation curve becomes progressively flat with the depression of the melting point, whence the greater the dissociation, the lower the melting point.

Regardless of this consideration, actually, the melting point of the molecular compound is higher or lower than that of the component, depending on other intermolecular factors. At present, these factors are so complicated that no satisfactory resolution has yet been accomplished. However, if we take the following value τ from a large number of congruent systems, consisting of analogously constituted components, we can conveniently compare the sequence of compound formation, namely,

$$\tau = t_c - \frac{mt_A + nt_B}{m + n},$$

where t_A , t_B , and t_C are respectively the melting points of the binary components and their compound, $m:n$ is the compound mol ratio ($A:B = m:n$), and τ is provisionally called the "melting point elevation."

(4) R. Kremann, *Monatsh.*, **25** (1904), 1215; *Z. Elektrochem.*, **12** (1906), 259.

(5) Crystallisation velocity is greatly diminished in viscous liquids.

(6) Area θ in Fig. 1 may be taken for this comparison.

The Molecular Compounds between Naphthalene, Naphthols, and Aromatic Nitrobenzenes⁽⁷⁾. In recent crystal chemistry, the crystal lattices of typical organic compounds have gradually been found to belong to the molecular lattice type. Benzene,⁽⁸⁾ naphthalene,⁽⁹⁾ anthracene,⁽⁹⁾ and the series of the aromatic condensed ring compounds with simple substitution radical⁽¹⁰⁾ have been determined as having the flat molecular structure. Fixation of the lattices by intermolecular force is generally weakened by melting. At the melting point, the crystal lattice structure being disturbed, a freer molecular state follows, in which the molecular compounds usually dissociate into their components. In this sense, it is possible to discuss the formation and stability of molecular compounds in fusion together with the structure of their components. Tables 1 and 2⁽⁷⁾ give the essential data of molecular compounds between naphthalene, naphthols, and aromatic nitrobenzenes.

Table 1. Binary Systems of Trinitro and Tetranitro Compounds.

Mol ratio A : B (τ) B	A	α -Naphthol	β -Naphthol	Naphthalene
<i>sym</i> -Trinitrobenzene	90.6	1 : 1 (84.0)	1 : 1 (36.0)	1 : 1 (51.0)*
Picric acid	92.8	1 : 1 (81.5)	1 : 1 (34.3)**	1 : 1 (50.5)*
Picramide	71.3	1 : 1 (52.3)	1 : 1 (7.3)	1 : 1 (34.8)*
2, 4, 6-Trinitrotoluene	73.2	1 : 1 (37.8) or (3 : 2)	1 : 1 (8.3)*	1 : 1 (17.3)*
Picryl chloride	71.9	1 : 1 (34.5)	1 : 1 (3.5)	1 : 1 (10.5)*
2, 4, 6-Trinitroanisol	49.0	1 : 1 (−4.0)	∇	∇ or 1 : 1 (−20.0)
2, 4, 6-Trinitrophenetol	32.3	1 : 2 (−16.0)	1 : 2 (−17.2)	1 : 2 (−5.7)
Trinitrocresol	91.0	1 : 1 (58.8) or (3 : 2)	1 : 1 (15.3)	1 : 1 (32.8)*
Styphnic acid	—	1 : 1 U*	1 : 1 U*	2 : 1 (26.0) or (1 : 1)*
1, 2, 4, 6-Tetranitrobenzene	73.5	1 : 1 (26.0)	1 : 1 (6.5)	3 : 2 (41.1)
Tetryl	19.7	3 : 2 (−29.0)	m : n (−46.3) D	1 : 1 (−17.5)*

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., 122.

** Asahina, Yokoyama, *J. Chem Soc. Japan*, **56** (1925), 415.

(7) T. Asahina and C. Shinomiya, *J. Chem. Soc. Japan*, **59** (1938), 341; C. Shinomiya, *J. Chem. Soc. Japan*, **59** (1938), 833, 922; **60** (1939), 170.

(8) E. G. Cox, *Proc. Roy. Soc. (London)*, A, **135** (1932), 491.

(9) J. M. Robertson, *Proc. Roy. Soc. (London)*, A, **142** (1933), 674; **140** (1933), 79.

(10) R. C. Evans, "An Introduction to Crystal Chemistry", 335-349, Cambridge (1939).

Table 2. Binary Systems of Dinitro and Mononitro⁽¹¹⁾ Compounds.

Mol ratio A : B (τ) B	A	α-Naphthol	β-Naphthol	Naphthalene
2, 4-Dinitrobenzoic acid 2, 4-Dinitrochlorobenzene 2, 4-Dinitrophenol 2, 4-Dinitrobromobenzene 2, 4-Dinitrotoluene m-Dinitrobenzene 2, 4-Dinitroanisol 2, 4-Dinitroaniline Dinitromesitylene	1:1 U 1:1 (35.7) 1:1 (14.7) 1:1 (12.3)*** 1:1 (15.0) 1:1 (7.0) 1:1 (2.0) 1:1 (2:3) or U √	1:2 U or √ 1:1 (6.7) 1:1 (−8.3) 1:1 (−15.7)*** 1:1 (−19.5) 1:1 U* 1:1 (−22.0) 2:3 U √	1:1 U 1:1 (13.2) 1:1 (−4.0) 1:1 (−5.7)*** 1:1 (−14.5) 1:1 (−34.2) D* 1:1 (−33.5) 1:3 U √	
2, 6-Dinitrophenol 2, 6-Dinitrotoluene 2, 6-Dinitroaniline	1:1 (0.8) 1:1 U 1:1 U	1:1 (−16.7) √ 1:1 (12.0)	1:1 (−13.8) √* 1:1 U	
3, 5-Dinitrobenzoic acid 3, 5-Dinitroanisol	1:1 (41.5) 1:1 (−7.3)	1:1 (22.0) √	1:1 (39.5) 1:1 U	
2, 5-Dinitrophenol 2, 5-Dinitrotoluene p-Dinitrobenzene	1:1 (17.4) 1:1 (11.9) 1:1 U	1:1 (3.4) 1:1 (−8.5) 1:1 (−11.8) or (3:2)	3:2 (10.1) or (1:1 1:1 (−19.6) 1:1 (−7.5)*	
p-Nitrobenzoic acid m- ,, o- ,,	1:1 U 1:2 (3.3) √	1:2 U √ or 1:1 (−24.3) √	1:1 U 1:2 (10.2) √	
p-Nitrobenzaldehyde m- ,, o- ,,	3:2 (−21.6) 1:1 (−29.0) 1:1 U	1:1 (−37.0)* 1:1 U* √*	√ √ √	
p-Nitrochlorobenzene m- ,,	2:3 (−37.0) √	√ √	√ √	
p-Nitrophenol m- ,, o- ,,	√ √ √	√ √ √	√* √ √*	
p- or m-Bromobenzene	√	√	√	
p-Nitrotoluene m- ,,	√ —	√ —	√* √*	
Nitrobenzene	—	—	√*	
p-Nitroaniline m- ,, o- ,,	√ √ √	√ √ √	√ √* √	
p-Nitroanisol	√	√	√	

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., 122.

*** Data of the molecular compound obtained from the solution by Buehler, Hisey, Wood (*J. Am. Chem. Soc.*, 52 (1930), 1940.).

(11) Some of the liquidus in systems of simple eutectic type are in fairly good agreement with their ideal crystallisation curves.

(1) Compound ratio usually 1:1, except the following systems:

3 : 2 naphthalene — 1,2,4,6-tetranitrobenzene, α -naphthol — tetryl, naphthalene—2,5-dinitrophenol, α -naphthol — *p*-nitrobenzaldehyde;

2 : 3 naphthol—2,4-dinitroaniline, α -naphthol—*p*-nitrochlorobenzene;

1 : 2 naphthol — 2,4,6-trinitrophenetol, naphthalene — 2,4,6-trinitrophenetol, β -naphthol — 2,4-dinitrobenzoic acid, β -naphthol — *p* nitrobenzoic acid, α -naphthol—*m*-nitrobenzoic acid, naphthalene — *m*-nitrobenzoic acid;

1 : 3 naphthalene—2,4-dinitroaniline.

Except a few examples, ratios other than 1:1 are found in the case of rather feeble compound formations, in which case there sometimes happens to be another metastable equilibrium, the molecular ratio of which is given in Tables 1, 2 in parentheses.

(2) From Tables 1, 2, which are arranged in the order of decreasing tendency of compound formation, it will readily be seen by comparing the value of τ or ω that compounds of α -naphthol have higher "melting

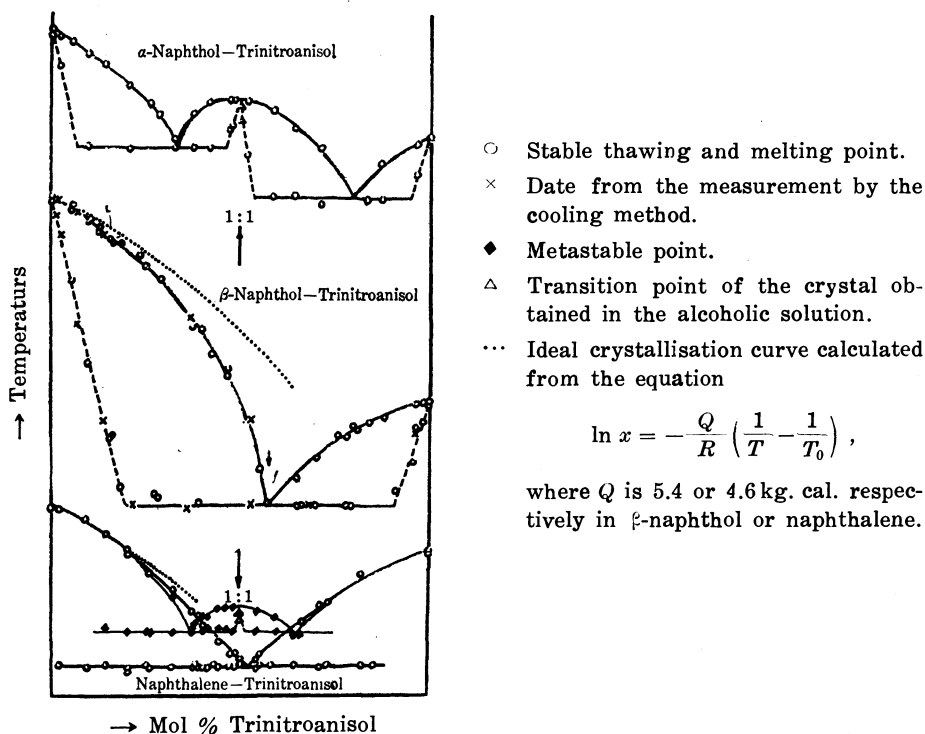


Fig. 2.

point elevation" and a wider compound existence range than those of β -isomer (the only exception being β -naphthol—2,6-dinitroaniline). Most of the naphthalene compounds have intermediate values of τ or ω .

It is interesting to compare, of the various feeble compound formation systems, α -naphthol compound with a β -isomer or naphthalene compound. Trinitroanisol which gives a compound of congruent melting point with α -naphthol, fails to give one with β -naphthol, while it gives with naphthalene a simple eutectic or a metastable compound. Analogous examples are to be seen in the compounds of *m*-nitrobenzoic acid.

In *m*-nitrobenzene, 2,4-dinitroaniline, 2,6-dinitrotoluene, 3,5-dinitroanisol, and *p*-, *m*- and *o*-nitrobenzaldehydes, the orders of compound formation are clearly systematized.⁽¹²⁾

(3) In comparing the columns of Tables 1 and 2, the order of compound formation is readily seen to be

trinitro compound > dinitro compound > mononitro compound,
and the effect of second substitution radical in the nitrated benzene nucleus,

sym-Trinitro compounds: $-\text{H} > \text{OH} > \text{NH}_2 > \text{CH}_3 > \text{Cl} > \text{OCH}_3,$
 $\text{OC}_2\text{H}_5,$

2,4-Dinitro compounds: $-\text{CO}_2\text{H} > \text{Cl} > \text{OH} > \text{Br} > \text{CH}_3 > \text{H} >$
 $\text{OCH}_3 > \text{NH}_2,$

Mononitro compounds: $-\text{CO}_2\text{H}, \text{CHO} > \text{Cl} > \text{Br} \dots$

The tendency of compound formation is the most marked in sym-trinitrobenzene, the substitution of any other radicals into it diminishes the tendency, presumably because of certain hindrances. In the case of less nitrated compounds, the effect of the substituent is profound, whether positive or negative. Of the molecular compounds of mononitrobenzenes, those of naphthalene somewhat differ in nature from those of naphthols.

(4) A comparison of isomers of equally nitrated components also gives a number of interesting results in connection with the affinity of molecular compounds. In di- and mono-nitrobenzenes, the orders are,

p-nitro compound, *m*-nitro compound > *o*-nitro compound;
2, 4-dinitro compound, 2, 5-dinitro compound, 3, 5-dinitro compound > 2, 6-dinitro compound.

More detailed results will be given in a later paper.

(5) These compounds⁽¹³⁾ showed distinctly halochromic phenomenon, and naphthols were more coloured than naphthalene, owing probably to the presence of the hydroxyl group. Between α - and β -naphthol, most of the α -compounds proved to be more halochromic than the β -isomers.

These molecular compound crystals were prepared from the solution, and most of them showed melting points identical with those obtained in the phase diagrams.

(12) Incongruent melting point was found not only in feeble combinations but also in systems, one component of which had a much higher melting point than the other.

(13) P. Pfeiffer, "Organische Molekulverbindungen", 2. Aufl., 338, Stuttgart (1927).

Experimental.

Determination of Solid-Liquid Transition Points. The phase diagram was obtained by improving the thawing and melting point method of H. Reinboldt ⁽¹⁴⁾, by which the least quantity of sample (10–100 mg.) could be investigated in a short time.

The apparatus consisted of the following parts.

- (a) A thermometer of very small diameter. A rod thermometer about 150 mm. long, 2–3 mm. diameter, with a mercury bulb of the same diameter 2–3 mm. long. Accuracy of temperature reading about 0.2°.
- (b) Sample tube. The glass tube shown in Fig. 3. The upper stem was made exactly to fit the thermometer inserted in it, in order to prevent the inner wall of the lower bulge from touching the sample throughout the observation.
- (c) Heating vessel (not illustrated). To regulate the heating, an air mantle was adopted and immersed in a liquid bath for which liquid paraffin or concentrated sulphuric acid was found to be convenient. The bath was provided with a thermometer and a stirrer.
- (d) Weighing. To save time, the sample could be weighed with a torsion or a micro spring balance (0.1–100 mg.). The present writer used a quartz spring balance that is a modification of Salvioni's microchemical balance.

The weighed sample was placed through a side hole in the sample tube, and the thermometer introduced. The substance was fused to a homogeneous mixture. After cooling, the sample tube containing the solidified substance was placed in the liquid bath, heated gradually and constantly, and the thawing point observed. The thawed sample was then further heated with a little stirring with the thermometer until it completely melted, when the melting point was observed. (Both thawing and melting point can be frequently observed, their values being usually the same.) Supercooling was avoided by rubbing or crystal seeding, which made it possible to obtain a detailed curve near the eutectic point ⁽¹⁵⁾. The observation was repeated by varying the composition, which was effected by slightly drawing up the thermometer (as in Fig. 3b) and adding one component to the mixture.

The capillary tube method ⁽¹⁶⁾ was also used in experimenting with readily sublimable or decomposable material. Some of the data obtained by the cooling curve method are included in the above mentioned tables.

Preparation of the Molecular Compound from the Solution. In the system, the molecular compound formation of which was observed on the diagram, the writer tried to obtain a crystal of the compound from the solution containing its components. From 0.1 to 0.2 g. of the components was weighed in a compound ratio, separately dissolved in alcohol, and the warmed solutions were mixed together, the mixture which, after a short heating, was slowly poured into 50–100 cc. of distilled water with vigorous stirring. The separated crystal was suctioned, washed with distilled water (if permitted), pressed between sheets of filter paper, and dried overnight in a desiccator. The yield of products seems to agree with the compound formation in the diagram.

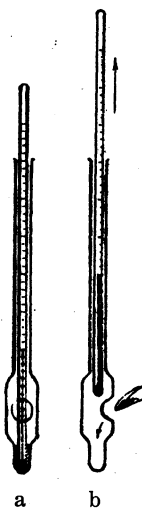


Fig. 3.

(14) H. Reinboldt, K. Henning and M. Kircheisen, *J. prakt. Chem.*, [2], **111** (1925), 246; C. Shinomiya, *J. Chem. Soc. Japan*, **58** (1937), 118.

(15) Supercooling is very frequent near the eutectic composition, in which case, supercooled viscous liquid was easily made to crystallise when some crystals of that component (not the other), which should give heterogeneous equilibrium with the liquid, were seeded. In this way, it is easy to determine whether the composition of the mixture lies on the A-component side or on the B-component side of the eutectic composition.

(16) A method devised and modified from the original by T. Asahina. (*Bull. Chem. Soc. Japan*, **9** (1934), 132.)

Special Part.

(1) α - or β -Naphthol—1,2,4,6-tetranitrobenzene.

These system are too unstable to enable a determination of diagrams.

With α -naphthol,

Eutectic point: 74.0°, 111.0°; 87 mol%, 13.5 mol% α -naphthol.

Compound (1:): brown red prisms, melting at 137.0°.

with β -naphthol,

Eutectic point: 95.0°, 110.0°; 82.6 mol%, 18 mol% β -naphthol.

Compound (1:1): brown red powder, melting at 130.5°.

(2) Naphthalene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 5.0 mg.

Mol% tetranitrobenzene	100.0	75.5	59.4	42.9	33.6	19.0	9.2
Melting point	126.0	128.0	135.0	138.0	138.0	129.0	92.0
Thawing point	125.0	—	111.0	129.0	—	73.0	73.0

Tetranitrobenzene: 7.6 mg.

Mol% tetranitrobenzene	88.4	67.7	49.2	34.7	24.1	18.1	12.5	6.4 ⁽¹⁷⁾	4.7
Melting point	119.0	132.0	138.0	139.0	—	—	116.5	75.0	74.0
Thawing point	114.0	114.0	—	108.0	75.0	74.0	74.0	74.0	76.5

Total naphthalene: 21.0 mg.

Mol% naphthalene	80.0	74.0	58.5	48.9	43.0	35.6	28.3
Melting point	—	—	139.5	138.0	139.0	139.0	—
Thawing point	74.0	74.0	134.0	114.0	114.0	120.0	74.0

Eutectic point: 74.0°, 114.0°; 93.7 mol%, 9 mol% naphthalene.

Compound (3:2): orange yellow prism melting at 139.5°.

This system was the most stable of the three, whereas with trinitro or dinitro compounds, α -naphthol usually formed the most stable compound. In Fig. 4, however, the curvature near the melting point is extremely flat, and considerable dissociation is expected.

The conclusion is that tetranitrobenzene is not a stable substance ⁽¹⁸⁾, its tendency of molecular compound formation with naphthalene and naphthols is not so marked as that with *sym*-trinitrobenzene.

(3) α -Naphthol—tetryl (Fig. 5).

Naphthol: 6.7 mg.

Mol% naphthol	95.7	88.1	75.6	69.8	59.0	44.0	34.3	27.0
Melting point	93.0	88.5	79.0	77.5	80.0	97.5	106.0	116.0
Thawing point	84.0	76.0	75.5	75.0	78.0	78.0	78.0	77.0

Tetryl: 7.1 mg.

Mol% tetryl	94.6	54.4	49.1	43.1	39.8	34.7	27.3	17.5	6.5
Melting point	126.0	90.0	83.0	80.0	80.0	79.5	76.0	85.5	92.3
Thawing point	117.0	77.0	77.0	77.0	—	77.0	75.0	75.0	76.0

Naphthol: 12.0 mg.

Mol% naphthol	75.4	66.9	61.3	57.5	52.7	50.4
Melting point	79.0	79.0	80.0	80.0	79.5	85.5
Thawing point	76.0	75.5	78.0	78.5	77.0	77.0

Eutectic point: 75.5°, 77.0°; 72.6 mol%, 52.9 mol% α -naphthol.

Compound (3:2): brown red prisms, melting at 80.0°.

(17) In the sample of 6.4 moles% tetranitrobenzene, its molecular compound crystal was recognized, while in that of 4.7 moles% tetranitrobenzene, naphthalene was seen in the last stage of melting. The arrow indicates the position of the eutectic point.

(18) 1, 2, 4, 6-Tetranitrobenzene was easily prepared by the method of W. Borsche (*Ber.* **56** (1923), 1939.). Instead of trinitrophenetol in alcoholic solution, trinitroanisol in methyl alcohol was used. The crude picryl hydroxylamine immediately nitrated, tetranitrobenzene was formed, which was decomposed considerably by repeated crystallisations in chloroform.

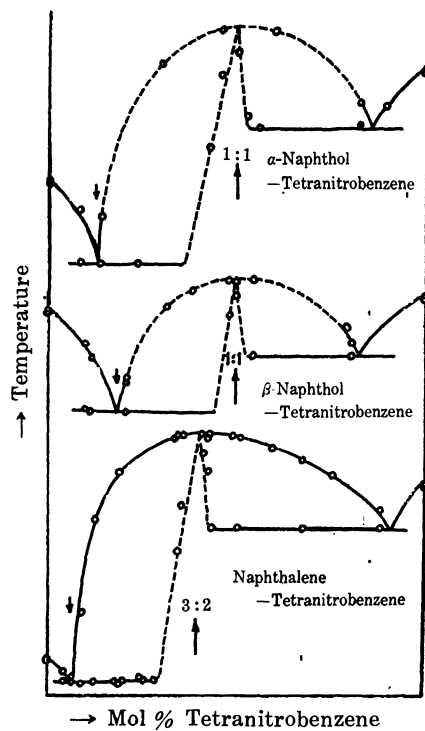


Fig. 4.

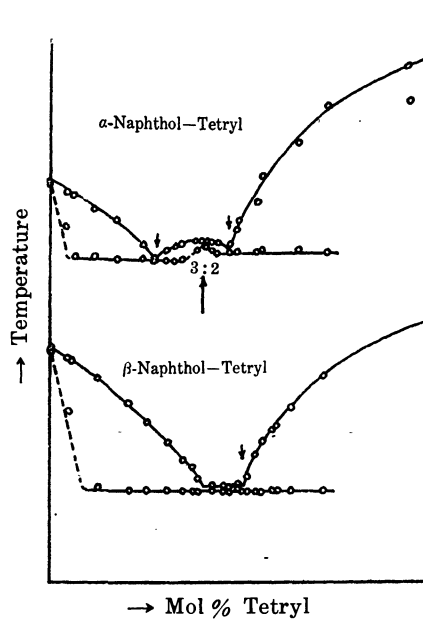


Fig. 5.

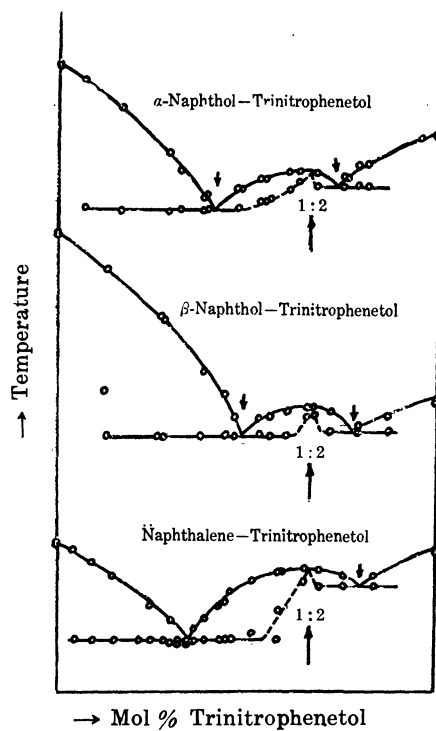


Fig. 6.

(4) β -Naphthol—tetryl (Fig. 5).

Total naphthol: 9.4 mg.

Mol% naphthol	94.5	79.9	87.8	74.8	65.2	54.1	50.6	46.2	40.6	27.9
Melting point	11.85	107.0	114.0	102.0	92.0	85.5	86.0	94.0	101.0	114.5
Thawing point	—	84.0	85.0	84.5	84.0	84.0	85.0	83.8	84.0	84.0

Tetryl: 17.2 mg.

Mol% tetryl	95.9	69.1	62.4	61.7	57.2	53.3	48.4	44.6	41.5	36.9
Melting point	119.0	97.0	90.5	87.0	86.0	85.0	88.0	97.0	100.0	106.0
Thawing point	105.0	84.0	84.0	84.0	84.0	84.0	84.0	83.8	83.8	84.0

This last mentioned system is of dissociation type. In the range of 59.6–49.6 mol% of β -naphthol, the melting curve was a straight line. The compound ratio was indistinct although brownish halochromy was very marked.

Notwithstanding the abundance of nitro groups, two tetranitro compounds have never shown any notable compound formation, probably owing to steric hindrances or ortho nitro effect. In these systems, it is noteworthy that the addition of naphthalene is more marked than that of the two naphthols.

(5) α -Naphthol—2,4,6-trinitrophenetol.

Trinitrophenetol: 5.0 mg.

Mol% trinitrophenetol	100.0	75.6	32.2	16.8	7.0
Melting point	78.0	66.0	68.0	84.8	92.0
Thawing point	77.0	—	57.5	57.8	58.0

Naphthol: 3.2 mg.

Mol% naphthol	60.5	51.3	43.8	35.2	31.8	18.0
Melting point	62.0	63.5	—	67.0	66.8	70.0
Thawing point	58.0	—	60.8	65.0	63.0	64.0

Total trinitrophenetol: 16.3 mg.

Mol% trinitrophenetol	96.0	63.8	55.0	60.9	53.7	47.3	38.5	29.3
Melting point	76.5	67.8	66.3	67.8	65.5	63.3	61.0	73.0
Thawing point	—	65.0	60.0	63.0	60.0	58.0	57.8	57.0

Naphthol: 1.5 mg.

Mol% naphthol	24.5	20.8
Melting point	67.0	70.0
Thawing point	64.3	64.0

Eutectic point: 57.5°, 64.0°; 58.3 mol%, 26.0 mol% α -naphthol.

Compound (1:2): orange prisms or powder, melting at 68.0°.

(6) β -Naphthol—2, 4, 6-trinitrophenetol.

Total trinitrophenetol: 9.3 mg.

Mol% trinitrophenetol	83.4	53.0	67.0	44.2	28.3
Melting point	71.5	73.0	75.0	79.5	99.5
Thawing point	—	68.5	73.0	69.0	68.0

Naphthol: 4.2 mg.

Mol% naphthol	87.2	72.4	61.6	53.1	44.7	39.8	34.5	27.8	20.8	12.8
Melting point	112.0	100.0	85.0	73.0	73.0	74.0	75.5	74.5	71.0	73.3
Thawing point	68.0	68.0	68.0	68.0	68.0	68.0	73.0	69.0	69.0	69.0

(80.0)

Eutectic point: 68.0°, 69.0°; 51.1 mol%, 21.7 mol% β -naphthol.

Compound (1:2): orange yellow prisms or powder, melting at 75.5°.

(7) Naphthalene—2,4,6-trinitrophenetol.

Trinitrophenetol: 6.3 mg.

Mol% trinitrophenetol	58.8	34.8	24.4	15.8	9.3	4.3
Melting point	72.0	54.0	63.0	—	75.0	78.0
Thawing point	62.0	53.0	54.0	54.0	54.0	54.0

(54.0)

Trinitrophenetol: 13.1 mg.

Mol% trinitrophenetol	83.4	75.7	69.3	65.2	59.3	51.8	46.0
Melting point	71.0	71.0	72.8	73.0	72.0	70.0	67.0
Thawing point	68.0	68.0	68.0	69.5	—	56.0	54.0

Trinitrophenetol: 3.1 mg. ⁽¹⁹⁾

Mol% trinitrophenetol	44.5	42.9	39.1	36.3	34.1	29.9	28.1	21.4	14.3
Melting point	64.0	63.0	60.0	57.0	—	59.0	—	64.0	71.0
Thawing point	54.0	54.0	54.0	54.0	54.0	53.0	54.0	54.0	54.0

Eutectic point: 54.0°, 68.0°; 64.9 mol%, 19.8 mol% naphthalene.

Compound (1:2): pale yellow powder or prisms, melting at 73.0°.

Three diagrams of trinitrophenetol are given in Fig. 6. The order of compound formation is naphthalene > α -naphthol > β -naphthol. It is related in character to tetranitro compounds, rather than to trinitroanisol. Substitution of ethyl by a methyl radical somewhat affects addition compound formation.

Summary.

The molecular compound of naphthalene and naphthols with mono-, di-, tri-, and tetra-nitro aromatic compounds are systematically compared, and the compound formation discussed with solid—liquid phase diagrams.

In conclusion, the writer wishes to express his sincere thanks to Prof. B. Kubota of the Tokyo Imperial University for his kind guidance and encouragement throughout this study and to Dr. T. Asahina for much valuable advice. Thanks are also due to the Hattori-Hokakai for a grant, with which the expenses connected with the study have been defrayed, and to Mr. R. Takagi for his gift of materials.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo
and
Kumamoto Higher Technical School.*

(19) This datum, together with the value of the cooling method in Fig. 2, is due to Mr. N. Sato, whom the writer wishes to thank for his assistance.

**On the Action of Phosphate upon Hexoses. IV.
Formation of Lactic Aldehyde side by side with Acetol.**

By RYOZO GOTO.

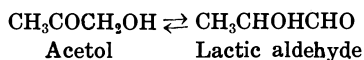
(Received February 9, 1940).

In the previous papers⁽¹⁾ of this series, it has been reported that when a mixture of glucose and a slightly acidic (*pH* 7-5) concentrated solution of potassium phosphate (about 40%) was distilled, acetol was

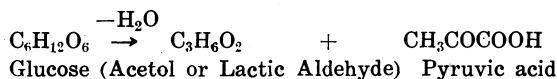
(1) R. Nodzu and his co-workers, this Bulletin, **10** (1935), 122; 467; *Mem. Coll. Sci. Kyoto Imp. Univ.*, **20** (1937), 197.

found in the distillate, accompanied by small quantities of methylglyoxal, diacetyl and some indistinct substances, and that pyruvic acid was present in the distillation residue. From these facts, we have postulated that under these conditions glucose molecule may split into acetol and pyruvic acid, as well as into others.

In the present work, the same distillation experiment was repeated with a larger amount of the materials and the distillate was studied more thoroughly. Besides acetol and the other products described above, the presence of lactic aldehyde and of pyruvic acid was confirmed. At first sight, the appearance of lactic aldehyde side by side with acetol was somewhat surprising, since it has long been known⁽²⁾ that the former transforms very easily into the latter. It was found, however, that by the same distillation process, not only lactic aldehyde did convert almost completely into acetol, but the reverse process also took place and a small portion of the acetol changed into lactic aldehyde. Hence, at least in the solution of phosphate, both substances seem to be in a relation of desmotropic equilibrium:



shifting far on the left hand side. It is accordingly indecisive which of the two is the precursor in the postulated scheme of cleavage of glucose molecule:



Experimental Part.

Glucose. The distillate⁽³⁾ (about 9 litres, about 5g. acetol) obtained from a mixture of 200g. glucose and 2 litres of 40% potassium phosphate solution (pH 5.2–5.6), was warmed on a boiling water bath for about half an hour with enough semicarbazide hydrochloride and sodium acetate to equal eight equivalents of the acetol content, was left to stand over night, and then filtered. The filtrate was evaporated⁽⁴⁾ to about 500 c.c. under a reduced pressure of carbon dioxide. After filtering off a yellowish white precipitate, the filtrate was concentrated further until an appreciable amount of precipitate reappeared and then filtered again. Repeating this process several times, four kinds of precipitates tabulated were obtained.

	m.p.	g.
I.	258°	0.7
II.	195°	4.8
III.	190°	2.35
IV.	239°	0.17

(2) Nef (*Ann.*, **335** (1904), 247.) has suggested that "Das Acetol ist mit Oxyaceton identisch; der isomere *n*-Milchsäurealdehyd, *n*-CH₃CHOHCHO, existiert nicht, sondern geht in Acetol über." A. Wohl, *Ber.*, **41** (1908), 3599.

(3) The distillation, and the estimation of the iodine-consuming substances such as acetol in the distillate were carried out in the same ways as described in the previous papers. (R. Nodzu, *loc. cit.*)

(4) During the course of evaporation, some iodine-consuming substance which has no reducing power for Fehling solution, was distilled. This distillate presents an interesting subject for research.

On further meticulous fractional crystallization of these precipitates from hot water, the followings were isolated: From I, diacetyl-bis-semicarbazone (m.p. 279–280°) and methylglyoxal-bis-semicarbazone (m.p. 262–264°); from II and III, mainly acetol semicarbazone (m.p. 197–198°), and pyruvic acid semicarbazone (m.p. 212–213°) and diacetyl-mono-semicarbazone (m.p. 227–228°) in a small quantity; from IV, lactic aldehyde semicarbazone (m.p. 246–247°) and acetol semicarbazone. Besides these semicarbazones, hydrazodicarbonamide (m.p. 257–258°) was isolated from II, III, and IV. These semicarbazones were all identified by the mixed melting point determinations. Another similar experiment at pH 6.2–6.6 was made with similar results, as will be seen in Table 1 in which the former results are also cited.

Table 1.

No.	Glucose g.	K-phosphate mixture 40%		Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.				
		pH.	c.c.			m.p. 278°	m.p. 261°	m.p. 245°	m.p. 211°	m.p. 197°
1	200	5.2–5.6	1000	9000	4.92	0.1	0.05	0.06	0.02	5.51
2	200	6.2–6.6	1000	9000	5.18	0.08	0.06	0.08	0.01	4.40

Acetol and Lactic aldehyde. Acetol (b.p. 53–54°/78mm.; semicarbazone m.p. 198–199°) was synthesized from monobromoacetone following A. Levene and A. Walti.⁽⁵⁾ Lactic aldehyde (m.p. 105–107°; semicarbazone m.p. 245–247°, Found N. 32.24 Calc. for $C_4H_5O_2N_3$: N. 32%; 2,4-dinitrophenylhydrazone m.p. 154–155°) was prepared by hydrolysis of monobromacetal, following R. Dwarzak and W. Prodinger.⁽⁶⁾ On treating with semicarbazide, the acetol gave only its semicarbazone and nothing of lactic aldehyde, and the lactic aldehyde also its semicarbazone only.

Thus it was confirmed that the acetol and the lactic aldehyde were free each from the other. The distillation of these substances with the phosphate solution and the analysis of distillates were carried out in the same ways as described in the case of glucose. The results of experiments are summarized in Tables 2 and 3.

Semicarbazones of methylglyoxal (m.p. 262–264°), lactic aldehyde (m.p. 246–247°) and acetol (m.p. 197–198°) in these tables, were respectively identified by the mixed melting point determination.

Table 2.

No.	Acetol g.	K-phosphate mixture 40%		Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.		
		pH.	c.c.			m.p. 262°	m.p. 246°	m.p. 197°
1	1.0	5.2–5.6	100	1200	0.64	0.02	0.02	1.15
2	1.0	6.2–6.6	100	1200	0.68	0.03	0.02	1.25

(5) A. Levene and A. Walti, *Organic Syntheses*, Vol. **10** (1930), 1.(6) R. Dwarzak and W. Prodinger, *Monatsh*, **48** (1927), 252; **50** (1928), 459.

Table 3.

No.	Lactic aldehyde g.	K-phosphate mixture 40%		Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.		
		pH.	c.c.			m.p. 262°	m.p. 246°	m.p. 197°
1	0.5	5.2—5.6	100	1500	0.43	Trace	0.1	0.35
2	0.5	5.2—5.6	100	1500	0.43	Trace	0.08	0.32
3	0.5	6.2—6.6	100	1500	0.4	Trace	0.1	0.4

In conclusion the writer wishes to express his sincere thanks to Prof. Dr. R. Nodzu for his valuable suggestions throughout this work.

*Chemical Laboratory, Faculty of Science,
Kyoto Imperial University.*

The Influence of Temperature on the Formation of Platinum-carbonyl Sol.

By Isamu SANO.

(Received February 10, 1940.)

On passing carbon monoxide through a dilute aqueous solution of chloroplatinic acid at ordinary temperature, a colloidal solution of red colour is obtained in a short time, the general description of the formation and behaviour of the sol being given in the foregoing paper.⁽¹⁾ From various facts^{(1), (2)} such as the oxidizing as well as decomposing action of air, oxygen and aqueous solution of bromine or hydrogen peroxide, the sol of red colour and the sol of black colour obtainable by dialyzing the red one or by letting it stand in the air, might be assumed to be composed of colloidal platinum-carbonyl and colloidal platinum respectively. The present paper deals with the influence of temperature together with concentration of the solution of chloroplatinic acid on the formation of the sol.

Experimental. Carbon monoxide was prepared by heating the mixture of formic acid and concentrated sulphuric acid and washed by bubbling it through alkaline hydroxide solutions. The aqueous solutions of

(1) I. Sano, this Bulletin, **9** (1934), 320.

(2) I. Sano, this Bulletin, **13** (1938), 118.

chloroplatinic acid were made by dissolving the acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) from Takeda in ordinary distilled water. The reaction vessel used was cleaned, prior to use, with chromic acid mixture and, if necessary, with aqua regia and steamed with water vapour.

A 50 c.c. of the chloroplatinic acid solution of a definite concentration was taken in each run of the experiments. The gas was, by way of a pre-heating device constructed of glass-tube, introduced into it at the desired temperatures and at a rate of 3 litres per hour constant throughout the runs of experiment, from a capillary glass-tube having a diameter short of 1 mm.

Results and its discussion. The colour of the chloroplatinic acid solution turns, with the formation of colloidal solution, from pale yellow into red, brown as well as black according to the temperature and the concentration of the solution. The transitional change in colour of the solution was observed with the naked eye under day-light with simultaneous recording of time during the passage of carbon monoxide through the solution. Some of the results obtained are given in the following tables (Table 1 to Table 6 inclusive), where c stands for the concentration of the starting aqueous solution of the acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) in per cent, θ the temperature of preparation in $^{\circ}\text{C}$., t the time elapsed from the commencement in minutes and h the hue of the solution observed at time t .

As can be seen from the tables, the chloroplatinic acid solutions assume, through the stages as under stated, a variety of colours according to the temperature of reaction as well as the concentration of solution in consequence of the passage of carbon monoxide. The transitional change in colour of the solution in any run may be summarily outlined as follows: In the incipient stage, the solution will faintly assume a shade of a black tint in a short course of time from the start—this tendency will be perceived appreciably in concentrated solutions and promptly at high temperatures and may be supposed to be due to the transient formation of a lower salt like platinumous chloride^{(1), (3)} soluble in hydrochloric acid.⁽⁴⁾ It will yield platinum carbonyl chloride in combination with carbon monoxide only to be so unstable in aqueous solution that it readily decomposes into platinum, carbon dioxide and hydrochloric acid—to be immediately followed by the colouration bearing brown as the predominant colour; this period being over, the solution will be of a tone of colour ranging from red to brown, and in the ultimate stage, will take, in accordance with the conditions concerned, a deep colour between purplish red and dark brown if observed in transmitted light, though tinged more or less deeply with black in reflected one. The colloidal solutions prepared from the acid solutions having larger concentrations such as 0.08 as well as 0.1% will be black in appearance and unstable, irrespective of the temperature of preparation, and settle in some measure presently after its formation. It was observed throughout the present experiment that

(3) F. C. Phillips, *Am. Chem. J.*, **16** (1894), 255.

(4) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 16, 251.

Table 1.

 $c: 0.02 \quad \theta: 20$

t	h
0	pale yellow
16	faintly tinged with dark
20	faintly tinged with darkish red
23	light red with a mere dash of purple
30	red with a dash of purple
40	"
60	"

Table 2.

 $c: 0.02 \quad \theta: 50$

t	h
0	pale yellow
9	faintly tinged with dark
11	light brown
17	brown with a dash of red
30	red having a tinge of brown
40	coloured more deeply
50	darkish red faintly tinged with brown
60	"

Table 3.

 $c: 0.02 \quad \theta: 80$

t	h
0	pale yellow
7	faintly tinged with dark
8	faintly tinged with darkish yellow slightly inclining to brown
10	light brown
25	tinged more deeply with dark
40	dark brown
60	"

Table 4.

 $c: 0.08 \quad \theta: 20$

t	h
0	light yellow
13	faintly tinged with dark
14	light yellow having a tinge of darkish red
16	brownish yellow with a mere dash of red
18	brown inclining to red
20	red with a tinge of brown
22	red with a dash of purple
60	"

Table 5.

 $c: 0.08 \quad \theta: 50$

t	h
0	light yellow
8	faintly tinged with dark
12	dark yellow
17	coloured more deeply
20	dark yellow with a dash of brown
40	dark brown slightly inclining to yellow
50	dark brown
60	"

Table 6.

 $c: 0.1 \quad \theta: 20$

t	h
0	light yellow
11	faintly tinged with dark
14	light brown slightly inclining to yellow
18	brown
19	brownish red faintly tinged with purple
21	red with a dash of purple
28	darkish red
40	darkish red with a tinge of brown
60	"

the more dilute the starting acid solutions, the more stable were the sols obtained.

A summary of the hues, h , of colloidal solutions obtainable under sets of conditions concerning the concentration, c , of the chloroplatinic acid solution and the temperature, θ , at which the passage of carbon monoxide was performed is given in Table 7. The relations among them are plotted on a graph with the values of the temperature, θ , in $^{\circ}\text{C}$. as ordinates and of the concentration, c , in % as abscissæ in Fig. 1.

Table 7.

$c: 0.01$		$c: 0.05$	
θ	h	θ	h
5	red with a dash of purple	5	red with a dash of purple
20	"	20	"
35	"	35	"
50	brownish red with a mere dash of purple	50	brown with a tinge of red
55	red slightly tinged with brown	55	brown
60	brown with a tinge of red	60	dark brown
65	brown	65	"
80	dark brown		
$c: 0.02$		$c: 0.08$	
θ	h	θ	h
5	red with a dash of purple	20	red with a dash of purple
20	"	25	brownish red faintly tinged with purple
35	"	35	brown slightly inclining to red
50	darkish red faintly tinged with brown	40	brown
55	darkish red with a tinge of brown	50	dark brown
60	brown		
65	dark brown		
80	"		
$c: 0.1$			
θ	h	θ	h
5	red with a dash of purple	5	red with a dash of purple
15	"	15	"
20	darkish red with a tinge of brown	20	darkish red with a tinge of brown
30	brown with a mere dash of red	30	brown with a mere dash of red
35	brown	35	brown
45	"	45	"
50	dark brown	50	dark brown

It is no wonder that the boundaries between the domains of hue should be somewhat wanting in clearness, the lines of demarcation, a , b and c , though drawn well-definedly in the figure, only indicating the approximate positions of them. It can be seen from the figure that a colloidal solution assuming red with a dash of purple will be produced at ordinary

temperatures from the chloroplatinic acid solution of lower concentration; the domain of its formation is reduced with the increasing concentration of the starting solution and extinguished at a limiting concentration,

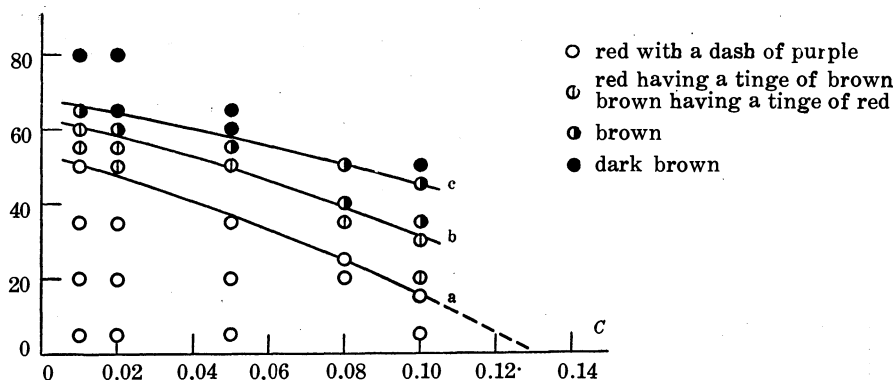


Fig. 1.

$c = 0.13$, as shown by the extension of the line a, and it points to the supposition, therefore, that there should be never produced stable sols of red inclining to purple beyond the limiting concentration at any temperature. F. C. Phillips⁽³⁾ observed that aqueous solutions of platinum chloride were slightly tinged with black by the action of carbon monoxide, cold or at $100^{\circ}\text{C}.$, to be subsequently followed by slow deposition of metallic platinum.

With the intention of acquiring further informations on the colouration effects above mentioned, the extinction coefficients of the sols were measured after they were left at room temperature out of contact with the air for the space of 2 hours from the close of preparation downward. The measurements were made with the Nutting's spectrophotometer at ordinary temperature, in that the extinction coefficient, ϵ , could be estimated with the aid of the formula

$$\epsilon = -2 \log (\cos \alpha) / c \cdot d,$$

where α denotes the angle of extinction for any visible ray to be determined through observation with the spectrophotometer, c the concentration and d the thickness of layer of the solution. The results obtained are diagrammatically depicted in Fig. 2, 3, 4, 5 and 6 in terms of the relationship between the extinction coefficient multiplied by the concentration, ϵc , per unit thickness in cm. of the sols concerned and the wavelength of the rays referred, λ , in $\text{m}\mu$ in company with the temperatures of preparation of the sols, θ , in $^{\circ}\text{C}.$ ϵc was taken in place of c on account of certain difficulties attending on the determination of concentration of the sols owing to their variability in the air. This will suffice to give informations on the extinction effects of the sols obtainable from the acid solution of one and the same concentration.

The dotted line in Fig. 6 represents the relation between ϵc and λ for a 0.1% solution of chloroplatinic acid; as compared with this, it is obvious for the colloidal solution to display a larger extinction effect.

The sols will turn black in due time, as already described,⁽¹⁾ by leaving it intact in the air owing to the disappearance of carbon monoxide or carbonyl group from colloidal particle due to volatilization towards as well as oxidation by the air. It might be considered for the extinction coefficient of the sol to exhibit a definite increase in magnitude as a consequence of the change in colour, this being manifestly indicated through the results given as the thick lines, full for the red sol as well as broken for the black one in Fig. 3.

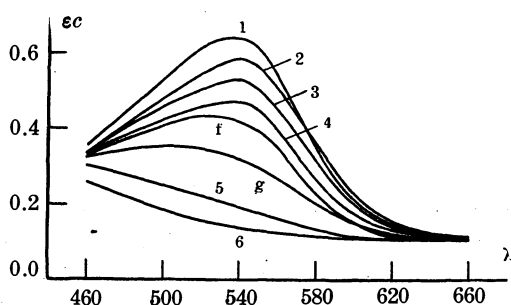


Fig. 2.

Curve	θ
1	5
a	15
2	20
b	25
c	30
3	35
d	40
e	45
4	50
f	55
g	60
5	65
6	80

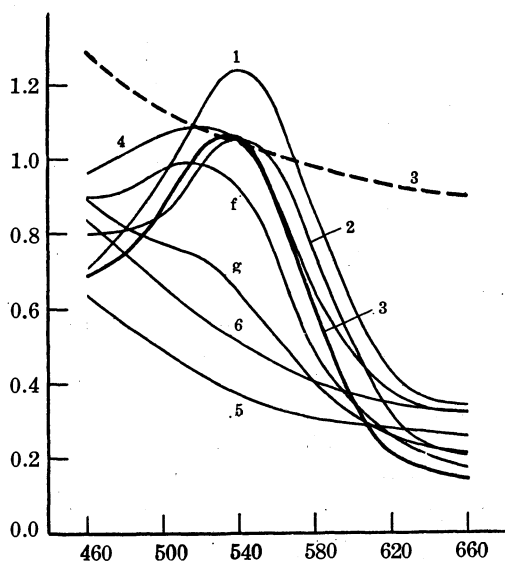


Fig. 3.

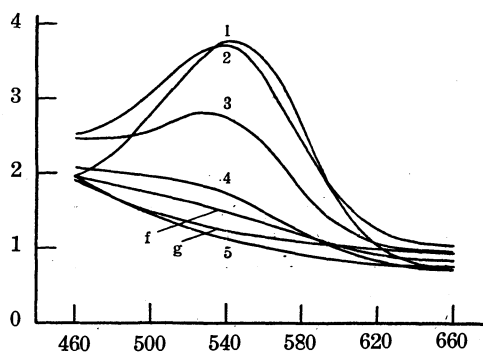


Fig. 4.

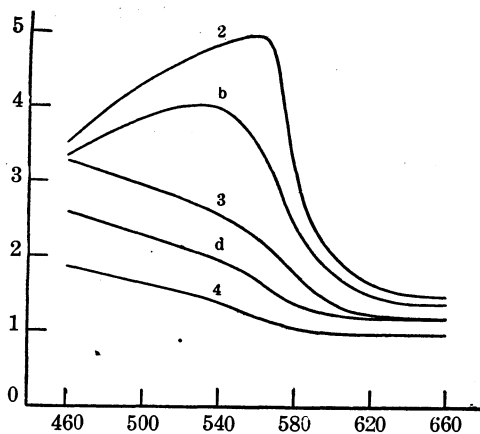


Fig. 5.

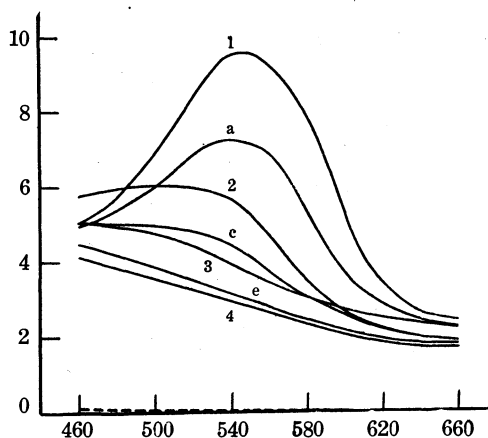


Fig. 6.

It can be distinctly seen from the figures that the extinction curves for the sols having a tinge of red reach a definite maximum at about 540 $m\mu$; while the curves for those with a tinge ranging from brown to black show monotonously decreasing gradient with increasing wave-length. It would seem, therefore, that the extinction effect could be reduced as the temperature of formation of the sol is raised, although beyond a certain limiting temperature depending on the concentration of solution this should attain a noticeable magnitude for the second time as the chloroplatinic acid solution passes immediately into a sol tinged with black by the action of carbon monoxide at higher temperatures as indicated in Fig. 1.

It must be added that the run of the extinction curves was taken into consideration in discriminating the shade and tone of a colour of the sol produced and establishing the influence of the temperature of preparation and the concentration of chloroplatinic acid solution on the formation of it as represented in Fig. 1.

Summary.

(1) The influence of the temperature of preparation on the formation of platinum-carbonyl sol from the chloroplatinic acid solution by the action of carbon monoxide were investigated at various temperatures between 5° and 80°C., together with the influence of the concentration of solution ranging from 0.01 to 0.1% with respect to $H_2PtCl_6 \cdot 6H_2O$.

(2) Stable sols having a tinge of red with a dash of purple may be produced from the solutions of concentrations between 0.01 and 0.08% in a wide range of temperature; sols of various colours such as brownish red, brown as well as dark brown may be formed in the same limits of concentration as the above at the elevated temperatures.

(3) Sols tinged with red slightly inclining to purple may be obtained, though unstable, from the 0.1% acid solutions only at lower temperatures.

(4) The colouration effects above-mentioned were spectroscopically analyzed with the Nutting's spectrophotometer, and it was found that

the extinction curves for the sols tinged with red reach a maximum at about $540\text{ m}\mu$, while those for the sols with a tinge varying from brown to black decrease monotonously with the increasing wave-length.

The author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance in the present experiment. It is also his pleasant duty to acknowledge the valuable advice offered by Dr. K. Yamasaki.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

The Effect of Reduced Nickel on the Addition of Hydrogen Bromide to Undecenoic Acid in Various Solvents.

By Matsuji TAKEBAYASHI.

(Received February 24, 1940).

In the previous work with Y. Urushibara⁽¹⁾ it was established that, while hydrogen bromide adds to pure undecenoic acid in toluene solution in the absence of oxygen to yield nearly pure 10-bromoundecanoic acid, the presence of reduced nickel reverses the direction of addition to some extent and, for instance, about one-third of the product formed in moderately dilute toluene solution is 11-bromoundecanoic acid (oxygen is far more potent in producing the same effect). In the previous experiments toluene was used exclusively as the solvent. The present paper records the results of the additions in the presence of reduced nickel in various solvents, which are summarized in the accompanying table.

Hydrogen bromide was passed into a solution of 1.0 g. undecenoic acid in 15 c.c. of the solvent in the presence of 2.3 g. of reduced nickel at 0°C. in the dark for one hour. The mixture was left to stand overnight and the product was examined. The reaction was always complete. The proportion of 10- and 11-bromoundecanoic acids in the reaction product was determined by observing the melting (clearing) point.

In benzene, toluene, ligroin, and carbon tetrachloride, reduced nickel suffered no change during the reaction, and the effect was as marked as previously observed in toluene (somewhat smaller in ligroin) (Exp. 1, 2, 3 and 7). On the other hand, in acetic acid and ether reduced nickel was attacked seriously by hydrogen bromide, the solution being coloured greenish, and the effect of the metal was found very weak (Exp. 4 and 5). In chloroform, the metal was attacked slightly but the solution was not

(1) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331, 404, 574.

Exp. No.	Solvent	Product	
		Melting point (°C.)	11-Bromo-acid (%)
1	Benzene	26.0	33
2	Toluene	25.8	33
3	Ligroin	27.3	28
4	Acetic acid	32.0	12
5	Ether	(liquid)	
6	Chloroform	29.8	20
7	Carbon tetrachloride	26.0	33

coloured, and the proportion of 11-bromo-acid in the product was intermediate (Exp. 6). These results appear to be in harmony with the previous experiences in the addition of hydrogen bromide to allyl bromide that the abnormal (reversely directed) addition was caused only by the metallic surface of the ferromagnetic metals, viz., nickel and iron, whereas their salts, viz., ferric chloride added,⁽²⁾ nickel bromide formed in case of the contamination of the metal by its oxide,⁽³⁾ and cobalt bromide produced owing to the little resistance of metallic cobalt to the attack by hydrogen bromide,⁽³⁾ promoted the normal addition. However, in view of the fact that the action of oxygen on the addition of hydrogen bromide to undecenoic acid was impeded in acetic acid and ether,⁽⁴⁾ the effect of reduced nickel might not be allowed to appear even if the metal were not attacked by hydrogen bromide in these solvents.

Experimental.

Materials. Undecenoic acid used was a commercial product (Kahlbaum, "extra pure") melting at 23.8° (corr.) and can be regarded fairly pure. It gave no colouration with ammonium thiocyanate and ferrous ammonium sulphate, being free from peroxide. Hydrogen bromide was generated by the action of bromine on hot tetralin, passed through cooled tetralin, over anhydrous calcium bromide and anthracene, and through a tube cooled with ice and salt, condensed in a vessel cooled with solid carbon dioxide and ether, and vaporized, the middle fraction only being used. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. and reduced again in the atmosphere of hydrogen at 350°C. in the reaction tube.

Benzene and toluene, free from thiophene, were redistilled over metallic sodium. Ligroin was washed with sulphuric acid, aqueous sodium carbonate, and water, dried over calcium chloride, and distilled over sodium (boiling point 80–95°C.). Acetic acid was refluxed with 2% of its weight of potassium permanganate, distilled, dried over phosphorus pentoxide, and purified by fractional distillation. Ether was washed repeatedly with concentrated sulphuric acid until the latter remained colourless, shaken with an alkaline aqueous solution of potassium permanganate, washed with water, dried over calcium chloride, and distilled. The ether purified in this way was free from peroxide. Chloroform was shaken several times with about half its volume of water and then dried over calcium chloride, and distilled over phosphorus pentoxide. Carbon tetrachloride was refluxed with an alkaline solution of potassium permanganate, washed with water, dried over calcium chloride, distilled, and redistilled with the addition of phosphorus pentoxide.

(2) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

(3) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 755; **12** (1937), 51.

(4) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

Apparatus and Experimental Procedures. The main part of the apparatus consists of a reaction tube (R) of 22 mm. diameter and 100 c.c. capacity, a side tube (S) of 22 mm. diameter and 90 c.c. capacity an inlet tube (I) for hydrogen bromide and hydrogen, and an outlet (O) for excessive hydrogen bromide and for evacuation. The whole is made of Pyrex glass.

Undecenoic acid (1.0 g.) was dissolved in a required amount (15 c.c.) of the solvent in S, the volume of the solution was marked on S, and further 5 c.c. of the solvent was added. Reduced nickel was placed in R. The whole system was evacuated at room temperature. Thus the excess of the solvent was distilled off through O. In this way air was driven out. When the volume of the solution reached the mark, the solution was frozen by cooling in liquid air while the nickel in R was heated to 350°C., evacuation being continued. The stopcock of O was closed, hydrogen introduced from I, and after a while the vessel evacuated again. This process was repeated several times, cooling of S and heating of R being continued. Then R was cooled to room temperature under evacuation. O was closed, and S taken out of liquid air. Then the solution in S was decanted on reduced nickel in R, and hydrogen bromide introduced.

Hydrogen bromide was passed at 0°C. in the dark for one hour. The mixture was left to stand at room temperature in the dark overnight. The solvent and the excess of hydrogen bromide were removed in vacuum at 50°C., and the remaining substance was collected with the solvent. The nickel was filtered off and washed with the solvent. The solution was again evaporated in vacuum at 60°C. The product was always obtained in quantitative yield, and did not decolourize bromine. The product was cooled to crystallization and pressed on cooled porous plates.

The proportion of 10- and 11-bromoundecanoic acids in the reaction product was determined by observing the melting (clearing) point. For this purpose the data of Ashton and Smith⁽¹⁾ for the binary mixtures of the two bromo-acids were employed.

The author expresses his hearty thanks to Prof. Y. Urushihara of the Imperial University of Tokyo for his kind guidance and to Prof. K. Ishikura, the director of the Osaka Higher School, for his encouragement. Thanks are also due to the Imperial Academy of Japan and to Hattori Hoko Kwai for grants.

*Chemical Laboratory,
Osaka Higher School.*

The Influences of Aldehydes and Hydroxyaldehydes on the Addition of Hydrogen Bromide to Undecenoic Acid in Presence and in Absence of Oxygen or Reduced Nickel.

By Matsuji TAKEBAYASHI.

(Received February 24, 1940).

While hydrogen bromide adds to undecenoic acid in benzene or toluene solution under the normal conditions to yield nearly pure 10-bromoundecanoic acid, oxygen⁽¹⁾ and reduced nickel^{(2) (3) (4)} reverse the direction of addition to give rise to the formation of more or less 11-bromoundecanoic acid. Impurities in the undecenoic acid originating in the preparation of the acid from ricinus oil increase the sensitiveness of the acid to oxygen,^{(1) (5)} while the effect of reduced nickel appears not to be influenced by the impurities.⁽⁵⁾ On the other hand, antioxidants such as catechol and hydroquinone inhibit the actions of both oxygen and reduced nickel.⁽³⁾ Ashton and Smith⁽¹⁾ showed that α -heptenylheptaldehyde formed by the action of alcoholic potash on heptaldehyde was a powerful agent to make undecenoic acid sensitive to oxygen and suggested that the heptaldehyde formed during the distillation of ricinus oil must be the origin of the powerful agent in the impure undecenoic acid.

The author has examined the influences of some aldehydes and hydroxyaldehydes, with a view to seeing if there could be a substance capable of exhibiting opposite influences on the effects of oxygen and of reduced nickel, but without finding any. Benzene instead of toluene was used as the solvent throughout the experiments described below, because it has been shown that they give similar results.^{(1) (4)}

The effects of some aldehydes alone on the addition were first examined. Hydrogen bromide was passed into a solution of pure undecenoic acid (1.0 g.) in benzene (15 c.c.) with the addition of the aldehyde (25 mols % to the acid) at 0°C. in the dark for one hour. The mixture was allowed to stand at room temperature in the dark overnight. The reaction was always complete. The composition of 10- and 11-bromo-undecanoic acids in the product was determined from the melting (clearing) point as previously. The results are given in Table 1. Compare them with the data quoted in Table 2 from the previous work.

Propylaldehyde, benzaldehyde and salicylaldehyde, which were practically free from peroxides, exhibited but a small influence, if any, on the addition of hydrogen bromide to undecenoic acid (Exp. 1, 3, and 4). On the other hand, the crotonaldehyde used contained peroxide, and accordingly the direction of addition was reversed to some extent (Exp. 2).

(1) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331.

(3) *Idem, ibid.*, **13** (1938), 404.

(4) M. Takebayashi, *ibid.*, **15** (1940), 113.

(5) Y. Urushibara and M. Takebayashi, *ibid.*, **13** (1938), 574.

Table 1.

Exp. No.	Aldehyde	Product	
		Melting point (°C.)	11-Bromo-acid (%)
1	Propylaldehyde, 0.1 g.	33.0	8
2	Crotonaldehyde containing peroxide, 0.1 g.	29.0	23
3	Benzaldehyde, 0.15 g.	33.2	8
4	Salicylaldehyde, 0.2 g.	33.3	7

Table 2. Undecenoic acid 3.68 g. in the first two exp., 2.5 g. in others. Toluene, 20 c.c.

In presence of	Product	
	Melting point (°C.)	11-Bromo-acid (%)
None (vacuum)	34.7	1
Air	48.7	97
Reduced nickel, 3.0 g.	25.5	34
Air+Catechol, 0.3 g. (22 mols %)	33.5	6
Reduced nickel, 3.0 g.+Catechol, 0.3 g.	33.0	8
Air+Hydroquinone, 0.3 g. (22 mols %)	34.2	3
Reduced nickel, 3.0 g.+Hydroquinone, 0.3 g.	32.6	10

The influences of aldehydes and hydroxyaldehydes on the effects of oxygen and reduced nickel were then examined. The results are summarized in Table 3. Hydrogen bromide was passed into a solution of

Table 3.

Exp. No.	In presence of	Product	
		Melting point (°C.)	11-Bromo-acid (%)
5	Air+Benzaldehyde, 0.15 g.	47.4	92
6	Reduced nickel, 2.3 g.+Benzaldehyde, 0.15 g.	26.3	32
7	Air+Salicylaldehyde, 0.2 g.	47.2	91
8	Reduced nickel, 2.3 g.+Salicylaldehyde, 0.2 g.	26.2	32
9	Air+Protocatechualdehyde, 0.2 g.	35.5	52
10	Reduced nickel, 2.3 g.+Protocatechualdehyde, 0.2 g.	29.2	22
11	Air+Vanillin, 0.2 g.	42.2	72
12	Reduced nickel, 2.3 g.+Vanillin, 0.2 g.	29.0	23

pure undecenoic acid (1.0 g.) in benzene (15 c.c.) at 0°C. in the dark in the presence of the aldehyde (25 mols % to the acid) and either air (Exp. 5, 7, 9, and 11) or reduced nickel (2.3 g.) (Exp. 6, 8, 10, and 12). Compare the results with Table 2.

Benzaldehyde and salicylaldehyde exhibited negligibly small influences on the actions of oxygen and of reduced nickel (Exp. 5, 6, 7, and 8). Protocatechualdehyde and vanillin exerted weak but noticeable inhibiting influences on the actions of both oxygen and reduced nickel (Exp. 9, 10, 11, and 12). Their inhibiting actions, however, were found far smaller than those of catechol and hydroquinone (compare Table 2).

Experimental.

Materials. Undecenoic acid, reduced nickel, hydrogen bromide, and benzene were the same as described in the previous paper.⁽⁴⁾ Propylaldehyde (Kahlbaum, "extra pure") was distilled carefully on the day of use. It gave a very faint colouration with ammonium thiocyanate and ferrous ammonium sulphate, being almost free from peroxide. Crotonaldehyde used was a commercial product containing peroxide in a quantity. Benzaldehyde, a pure product, was distilled in vacuum and used immediately. Salicylaldehyde, a commercial pure material, was distilled in vacuum. It was free from peroxide. Protocatechualdehyde and vanillin were commercial specimens (Kahlbaum, "extra pure") melting at 152° and 80.5°, respectively.

Apparatus and Experimental Procedures. The apparatus was the same that was used in the previous work.⁽⁴⁾ In experiments in the presence of aldehydes, undecenoic acid (1.0 g.) and the aldehyde (25 mols % to the acid) were dissolved in a required amount (15 c.c.) of benzene and further 5-6 c.c. of benzene was added. The excess of benzene was distilled off in vacuum at room temperature. In this way air was driven out. Hydrogen bromide was passed into the solution at 0°C. in the dark for an hour. The mixture was left to stand overnight at room temperature in the dark. The reaction mixtures were coloured. The solvent, the aldehyde, and the excess of hydrogen bromide, were removed in vacuum at 60°, and the remaining substance was collected with benzene. The solution was washed with water, dried over calcium bromide, decolourized with animal charcoal, and evaporated in vacuum at 60°.

In the additions in the presence of air and aldehydes, undecenoic acid and the aldehyde were dissolved in benzene. Protocatechualdehyde and vanillin were sparingly soluble in benzene and mostly remained undissolved. Hydrogen bromide was passed into the solution with cooling in ice water for one hour. The reaction mixture was treated as mentioned above. Salicylaldehyde was driven out by evacuation. Protocatechualdehyde and vanillin remaining as coloured solids in the solutions were filtered off at 0°C. after hydrogen bromide had been removed in vacuum.

In experiments with reduced nickel and aldehydes, undecenoic acid and the aldehyde were dissolved in benzene beforehand, and the experiments were carried out in the same way as described in the previous paper.⁽⁴⁾ The reaction mixture was treated as mentioned above.

The reaction was always complete and the product did not decolourize bromine. The composition of the product was determined from the melting point as previously.

The author expresses his hearty thanks to Prof. Y. Urushibara of the Imperial University of Tokyo for his kind guidance and to Prof. K. Ishikura, the director of the Osaka Higher School, for his encouragement. Thanks are also due to the Imperial Academy of Japan and to Hattori Hoko Kwai for grants.

*Chemical Laboratory,
Osaka Higher School.*

Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. VII. Der Austauschmechanismus der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calcium- oxyds.⁽¹⁾

Von Noriyoshi MORITA.

(Eingegangen am 5. Februar 1940.)

Inhaltsübersicht. Um über den Mechanismus der katalytischen Austauschreaktion der O-Atome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calciumoxyds eine nähere Kenntnis zu gewinnen, wird das Verhalten des Calciumoxyds in Sauerstoffatmosphäre, sowie die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff bzw. Wasserdampf und festem Calciumoxyd bei verschiedenen Temperaturen untersucht. Dabei wird festgestellt erstens, dass durch Erhitzung des Calciumoxyds in Sauerstoffgas von 2/3 at. Druck bis auf 600° keine nennenswerte Absorption bzw. Desorption des Sauerstoffs stattfindet. Ebenso wenig können wir die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und festem Calciumoxyd ausfindig machen, auch wenn die Versuchstemperatur bis auf 650° erhöht wird. Dagegen wird beim Einwirken des Wasserdampfes auf Calciumoxyd festgestellt, dass die Austauschreaktion der O-Atome zwischen beiden Substanzen, ebenso wie bei der katalytischen Austauschreaktion der O-Atome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calciumoxyds, erst bei 400° bemerkbar wird. Aber auch bei noch niedrigeren Temperaturen, wo der einwirkende Wasserdampf durch das Calciumoxyd restlos absorbiert aufgefangen wird, scheint der durch Erhitzung des so angefeuchteten Calciumoxyds bis auf 500° wieder befreite Wasserdampf seine O-Atome ganz gegen die des Calciumoxyds ausgetauscht zu haben. Aus einer einfachen Rechnung ergibt sich, dass bei dieser Art der Austauschreaktion etwa zwei Mol absorbierten Wassers gegen je ein Mol Calciumoxyd in Austauschreaktion geraten sind, ohne Unterschied ob man das Wasserdampf absorbierte Calciumoxid bei Zimmertemperatur oder bei erhöhten Temperaturen (100° bis 300°) über Nacht stehen lässt.

Aus allen diesen Versuchsergebnissen wird deshalb geschlossen, dass bei der katalytischen Austauschreaktion der O-Atome zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Calciumoxyds, ebenso wie bei früher untersuchtem Kupferoxyd, die aktivierte Adsorption des Wasserdampfes an der Oberfläche des Oxydkatalysators ein massgebender Prozess ist. Denselben Mechanismus können wir auch für die katalytische Austauschreaktion an der Oberfläche der Oxyde der anderen Erdalkalimetalle anwenden.

Einleitung. Bei dem früheren Versuche, wo die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche der Oxyde, die zur vierten Hauptreihe des periodischen Systems gehören, d.h. die Oxyde von Calcium, Titan, Vanadin, Chrom, Mangan, Eisen und Nickel, findet man, dass die Reaktion an der Oberfläche des Calciumoxyds etwa bei 390° bemerkbar wird (Austauschmass %A erreicht 10%) und oberhalb 600° ein vollständiges Austauschgleichgewicht schnell erreicht wird (vgl. IV. Mitteil.). Über

(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: ebenda, **13** (1938), 601; III. Mitteil.: ebenda, **13** (1938), 656; IV. Mitteil.: ebenda, **14** (1939), 9; V. Mitteil., Teil I: ebenda, **14** (1939), 520; Teil II: ebenda, **15** (1940), 1; VI. Mitteil., Teil I: ebenda, **15** (1940), 47; Teil II.: ebenda, **15** (1940), 71.

den Mechanismus dieser Reaktion haben wir damals die Vermutung geäußert, dass die aktivierte Adsorption des Wasserdampfes an der Oberfläche des Calciumoxyds ein massgebender Prozess sein dürfte. Derselbe Mechanismus kann aber auch für dieselbe katalytische Austauschreaktion an der Oberfläche der anderen Arten von Erdalkalioxyden angewendet werden, die bei den letzten Versuchen ergründet wurden (vgl. VI. Mitteil.). Dort wird nämlich festgestellt, dass die Temperatur, wo das Austauschmass %A erst 10% erreicht, 500° für Magnesiumoxyd, 380° für Strontiumoxyd und 350° für Bariumoxyd beträgt. Der Zweck der vorliegenden Versuche liegt deshalb darin, den direkten experimentellen Beweis für diesen vermuteten Mechanismus der katalytischen Austauschreaktion an der Oberfläche des Calciumoxyds oder im allgemeinen an der Oberfläche der Erdalkalioxyde zu suchen.

Falls nämlich die aktivierte Adsorption des Sauerstoffs an der Oberfläche des in Rede kommenden Oxyds dabei der massgebende Prozess wäre, dann würde die Adsorption bzw. Desorption des Sauerstoffs am betreffenden Oxyd eben bei der Temperatur deutlich bemerkbar werden, wo die katalytische Austauschreaktion zwischen Sauerstoff und Wasserdampf an demselben Oxyd erst bemerkbar wird, genau so wie dies beim früher untersuchten Manganoxyd der Fall war (vgl. V. Mitteil) und dasselbe gilt auch für die Austauschreaktion der O-Atome zwischen Sauerstoffgas und betreffendem Oxyd. Wenn dagegen der massgebende Prozess bei der katalytischen Austauschreaktion die aktivierte Adsorption des Wasserdampfes wäre, dann müsste die Austauschreaktion der O-Atome zwischen Wasserdampf und festem Oxyd eben bei der Temperatur mit wohl messbarer Geschwindigkeit stattfinden, wo die katalytische Austauschreaktion deutlich stattzufinden beginnt, wie man dies aus den früher durchgeführten Versuchen mit Kupferoxyd erwarten kann (vgl. III. Mitteil.). Aus diesem Grunde wird zunächst die Adsorption des Sauerstoffs an der Oberfläche des Calciumoxyds und dann die Austauschreaktion zwischen gasförmigem Sauerstoff bzw. Wasserdampf und festem Calciumoxyd resp. bei verschiedenen Temperaturen untersucht. Die dabei erhaltenen Versuchsergebnisse weisen aber eindeutig darauf hin, dass der massgebende Prozess bei der katalytischen Austauschreaktion der O-Atome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calciumoxyds, und höchstwahrscheinlich auch bei den anderen Arten von Erdalkalioxyden, wie erwartet, die aktivierte Adsorption des Wasserdampfes an der Oberfläche des in Rede kommenden Oxyds sein muss.

Experiment 1. Sorption des Sauerstoffs an Calciumoxyd. Die bei diesem Versuche benutzte Apparatur und Versuchsanordnung ist genau dieselbe, der man sich früher zum Sorptionsversuch mit Manganoxyd bediente (vgl. V. Mitteil. Teil 1).

Das Calciumoxyd, das chemisch rein aus dem Handel bezogen wird, wird zunächst sorgfältig zerkleinert und dann in einem Quarzrohr unter guter Evakuierung etwa drei Stunden lang bis auf 800° erhitzt. Aus dem so behandelten Oxyd werden nun 20.2 g im Sorptionsgefäß (Gefäß A in Abb. 1 in V. Mitteil.) eingewogen und die ganze Apparatur unter Erhitzung des Sorptions- und Vergleichsgefäßes (Gefäße A und B in Abb. 1 in V. Mitteil.) bis auf 800° etwa fünf Stunden lang

möglichst gut evakuiert. Nach der Abkühlung bis zu Zimmertemperatur wird die ganze Apparatur mit reinem Sauerstoffgas bis auf 2/3 at. Druck gebracht und dann die Temperatur des Sorptions- und Vergleichsgefäßes wieder langsam bis auf 600° erhöht. Nachdem die Apparatur auf diese Weise bei erhöhten Temperaturen etwa drei Stunden lang belassen worden ist, wird sie wieder bis auf Zimmertemperatur abgekühlt und das Sauerstoffgas in der Apparatur möglichst vollständig ausgepumpt. Diese Massnahme vor dem eigentlichen Sorptionsversuch wird deshalb vorgenommen, um dadurch irgendwelche oxydierbaren Verunreinigungen in der Apparatur möglichst vollständig zu beseitigen. Nach dieser Vorbehandlung wird die Apparatur wieder mit reinem Sauerstoffgas bis auf 2/3 at. Druck gefüllt und die Menge des von Calciumoxyd adsorbierten bzw. desorbierten Sauerstoffs nach der früher angegebenen Methode (Differentialmethode, vgl. V. Mitteil.) genau gemessen, indem man die Temperatur des Sorptions- und Vergleichsgefäßes langsam bis auf 600° steigen lässt.

Einige dabei gewonnene Ergebnisse sind in Tabelle 1 wiedergegeben, wo die letzte Spalte die Menge des Sauerstoffgases angibt, die von Anfang bis zu einem gewissen Zeitpunkt während des Versuches von ein Gramm Calciumoxyd adsorbiert (+) bzw. desorbiert (–) worden ist.

Tabelle 1. Sorption bzw. Desorption des Sauerstoffs an erhitztem Calciumoxyd bei verschiedenen Temperaturen.

Zeit in Stdn.	Temperatur °C	Sorptions- (+) bzw. Desorptions- (–) menge von O ₂ in ccm pro g CaO
0.00	17	—
3.00	207	–0.004
6.00	304	–0.002
22.0	303	+0.001
26.0	591	–0.003
30.0	597	–0.001
46.0	17	+0.001

Aus diesen Versuchen wird ohne weiteres ersehen, dass mindestens bis auf die höchste benutzte Temperatur (597°) keine nennenswerte Sorption bzw. Desorption des Sauerstoffs an der Oberfläche des Calciumoxyds stattfindet. Deshalb liegt schon aus diesem Sorptionsversuche die Annahme nahe, dass der massgebende Prozess bei der katalytischen Austauschreaktion zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calciumoxyds keine aktivierte Adsorption des Sauerstoffs sein kann. Diese Auffassung wird weiter durch die folgenden Versuche (Experiment 2) bestätigt, wo die Austauschreaktion zwischen gasförmigem Sauerstoff und festem Calciumoxyd untersucht wird.

Experiment 2. Austauschreaktion zwischen gasförmigem Sauerstoff und festem Calciumoxyd. Die Versuchsanordnung ist genau dieselbe wie beim früheren Versuch mit Kupferoxyd (vgl. III. Mitteil.).

Etwa 300 g Calciumoxyd, das auf dieselbe Weise wie bei oben angegebenem Experiment 1 vorbehandelt worden ist, wird in einer gut geschlossenen Flasche aufbewahrt und von diesem aufbewahrten Oxyd wird jedesmal 65 g zum Austausch-

versuch verwendet, indem man damit ein aus Pyrexglas geblasenes Reaktionsrohr⁽²⁾ beschickt und dadurch das schwere Sauerstoffgas, das aus der Elektrolyse des an schwerem Sauerstoff angereicherten Wassers entwickelt worden ist, bei einer bestimmten Temperatur durchströmen lässt. Dabei wird das frisch im Reaktionsrohr beschickte Calciumoxyd immer vor dem eigentlichen Austauschversuch unter Durchleitung des getrockneten Sauerstoffströmes aus des Elektrolyse des gewöhnlichen Wassers bis auf 600° über Nacht lang erhitzt, um dadurch die letzte Feuchtigkeit im Reaktionsrohr sowie im benutzten Oxyd restlos zu beseitigen.

Das zum Austauschversuch benutzte an schwerem Sauerstoff angereicherte schwere Wasser besitzt gewöhnlichem Wasser gegenüber den gesamten anfänglichen Dichteüberschuss von 41.4 γ , davon 43.4 γ auf die Anreicherung des schweren Sauerstoffs zurückgeführt werden kann.⁽³⁾ Das aus der Elektrolyse dieses schweren Wassers entwickelte schwere Sauerstoffgas wird zunächst mit reinem Stickstoffgas im Volumenverhältnis von $O_2:N_2=2:1$ vermischt und das so hergestellte Gasgemisch in das mit Calciumoxyd beschickte Reaktionsrohr eingeleitet. Die Strömungsgeschwindigkeit des Gasgemisches beträgt (bei Zimmertemperatur und unter gewöhnlichem Druck gemessen!) 30 ccm pro Minute. Das auf diese Weise aus dem Reaktionsrohr zusammen mit Stickstoffgas ausgeströmte schwere Sauerstoffgas wird dann mit reinem Bombenwasserstoff katalytisch bis zu Wasser verbrannt und das spezifische Gewicht des so rekombinierten Wassers, dessen Menge bei jedem einzelnen Versuch 10 ccm beträgt, zum Schluss nach sorgfältiger Reinigung mit gewöhnlichem Wasser verglichen. Die dritte Spalte der Tabelle 2 gibt den so gemessenen Dichteüberschuss des rekombinierten Wassers gewöhnlichem Wasser gegenüber wieder.

In dieser Tabelle 2 stellt der allererste Versuch Nr. 0 den Kontrollversuch, der ohne Beschickung des Reaktionsrohres mit Calciumoxyd durchgeführt wird, während die anderen vier die bei verschiedenen Temperaturen aber immer mit erneuertem Calciumoxyd durchgeführten

Tabelle 2. Austauschreaktion zwischen O_2 und festem CaO bei verschiedenen Temperaturen.

Versuchs-nr.	Temperatur °C	Dichteüberschuss des rekombinierten Wassers in γ	Dichteabnahme in γ	Austausch- mass % A
0	600	37.9	—	—
1	350	37.1	0.8	3
2	450	36.6	1.3	5
3	550	36.6	1.3	5
4	650	37.6	0.3	1

eigentlichen Austauschversuche dar. Wir können deshalb mit dem Unterschied des gefundenen Dichteüberschusses zwischen Kontrollversuch Nr. 0 und anderen eigentlichen Austauschversuchen, die in zweiter letzter Spalte der Tabelle angegeben sind, den Grad der in Rede kommenden Austauschreaktion zwischen Sauerstoff und Calciumoxyd messen. Falls nun die Austauschreaktion zwischen den angegebenen Mengen Sauerstoff und Calciumoxyd vollständig durchgeführt würde, dann müsste dieser Unterschied, wie eine einfache Rechnung zeigt, 24.6 γ

(2) Das Reaktionsrohr besitzt 40 cm Länge und 2 cm 1. W.

(3) Der Wasserstoff im benutzten schweren Wasser ist deshalb um 2.0 γ leichter als gewöhnlicher Wasserstoff.

betragen.⁽⁴⁾ Deshalb wird das in der letzten Spalte der Tabelle angegebene prozentuale Austauschmass %A durch Gl. (1) berechnet:

$$\%A = \frac{(\text{Gefundene Dichteabnahme})}{24.6} \times 100 \quad (1).$$

Das so berechnete Austauschmass %A überschreitet aber bei allen untersuchten Temperaturen, auch wo die früher untersuchte katalytische Austauschreaktion zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calciumoxyds lebhaft stattfindet (390°; vgl. IV. Mitteil.), kaum einige Prozente. Da aber solch eine kleine Abnahme der Dichte des verwendeten schweren Sauerstoffs schon als ein experimenteller Fehler betrachtet werden muss, darf wohl die Annahme zu Recht bestehen, dass kein Austausch der O-Atome zwischen gasförmigem Sauerstoff und festem Calciumoxyd mindestens innerhalb des benutzten Temperaturbereiches stattfindet.

Experiment 3. Austauschreaktion zwischen Wasserdampf und festem Calciumoxyd bei verschiedenen Temperaturen. Im Gegenteil zum oben angegebenen Versuche (Experiment 2) konnten wir beim vorliegenden Experiment 3 und auch beim weiter unten anzugebenden Experiment 4 untrüglich feststellen, dass Wasserdampf seine O-Atome sehr leicht gegen die des Calciumoxyds austauscht.

Das zu diesen Versuchen benutzte Calciumoxyd wird auf genau dieselbe Weise wie oben bereitet, und bei jedem Austauschversuch lässt man 65 g von diesen gereinigten Mengen Calciumoxyd gegen 10 g schweren Wasserdampf reagieren. Die dabei benutzte Versuchsanordnung ist im grossen und ganzen dieselbe wie beim oben angegebenen Experiment 2; das Reaktionsrohr wird mit den eben genannten Menge von Calciumoxyd beschickt und dadurch wird zunächst das Sauerstoffgas aus der Elektrolyse des gewöhnlichen Wassers unter Erhitzung des Rohres über Nacht geleitet. Nach dieser Vorbehandlung wird dann das Reaktionsrohr bei einer bestimmte Versuchstemperatur konstant erhitzt und durch dieses wird das Reaktionsgasgemisch von der Zusammensetzung $N_2:H_2O=2:1$ aus reinem Stickstoffgas und schwerem Wasserdampf mit der Geschwindigkeit von 60 ccm pro Minute (bei Zimmertemperatur und unter gewöhnlichem Druck gemessen!) durchströmen gelassen. Wenn auf diese Weise genau 10 ccm. schweren Wassers durch das Reaktionsrohr durchgeleitet worden ist, wird das ausgetauschte Wasser, das in einem dem Reaktionsrohr folgenden Gefriergefäss aufgefangen wird, auf übliche Weise sorgfältig gereinigt und dessen Dichte mit gewöhnlichem Wasser verglichen. Die dritte Spalte der Tabelle 3 gibt den so gemessenen Dichteüberschuss des schweren Wassers nach dem Versuch ($=\Delta s_e$) wieder.

Da das zu diesen Versuchen verwendete an schwerem Sauerstoff angereicherte schwere Wasser dasselbe ist, wie bei oben angegebenem Experiment 2 benutzt wurde, besitzt es, wie oberhalb der Tabelle 2 angegeben ist, den gesamten anfänglichen Dichteüberschuss von 41.4 γ ($=\Delta s_a$), wovon 43.4 γ ($=\Delta s_a(0)$) auf die Anreicherung des schweren Sauerstoffs zurückgeführt werden kann. Da aber bei jedem einzelnen Versuch in Tabelle 3 10 ccm dieses schweren Wassers gegen 65 g Calcium-

(4) Bei dieser Berechnung wird angenommen, dass der Verteilungsquotient des schweren Sauerstoffs zwischen CaO und O₂ gleich eins und der Sauerstoff im ersteren um 7 γ schwerer als gewöhnlicher Wassersauerstoff ist (Luftsauerstoff!).

Tabelle 3. Austauschreaktion zwischen gasförmigem H_2O und festem CaO bei verschiedenen Temperaturen.

$$\text{N}_2 : \text{H}_2\text{O} = 2 : 1, \quad \Delta s_a = 41.4 \gamma, \quad \Delta s_a(\text{O}) = 43.4 \gamma.$$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
1	400	27.2	14.2	58
2	450	37.7	3.7	15
3	500	34.7	6.7	27
4	550	39.3	2.1	9

oxyd ausgetauscht worden ist, müsste der gesamte Dichteüberschuss des schweren Wassers, genau so wie beim oben angegebenen Experiment 2, um 24.6 γ abnehmen, wenn die O-Atome dieses Wassers gegen die der benutzten Mengen Calciumoxyd bis zum Gleichgewicht ausgetauscht würden. Das in der letzten Spalte der Tabelle 3 angegebene prozentuale Austauschmass %A wird deshalb eben mit der dort angegebenen Gl. (1) berechnet.

Die Zahlenwerte des so berechneten %A weisen aber ohne Zweifel darauf hin, dass in diesem Fall eine ziemlich lebhaftete Austauschreaktion der O-Atome zwischen Wasserdampf und damit berührtem festem Calciumoxyd stattfindet. Doch merkwürdigerweise nimmt die Grösse des so gefundenen Austauschmasses %A, wie aus Tabelle 3 ohne weiteres zu ersehen ist, mit steigender Temperatur ziemlich stark ab. Diese Abnahme des gefundenen Austauschmasses mit steigender Temperatur ist aber kein Wunder, wenn man die Tatsache in Rechnung zieht, dass durch Calciumoxyd einmal absorbiertes schweres Wasser desto schwieriger daraus wieder befreit werden konnte je niedriger die Versuchstemperatur lag. Wird z.B. der schwere Wasserdampf zusammen mit Stickstoffgas in das mit Calciumoxyd beschickte und unterhalb 400° erhitzte Reaktionsrohr hineingeleitet, so findet man überhaupt nur Stickstoffgas aus dem anderen Ende des Rohres ausströmen; der Wasserdampf wird ganz durch das Calciumoxyd absorbiert aufgefangen. Selbst bei der in Tabelle 3 angegebenen niedrigsten Temperatur (400°), wo wir das grösste Austauschmass %A gefunden haben, konnte nur 70% der gesamten verwendeten Mengen des schweren Wassers (10 ccm!) nach der Beendigung des Versuches wieder im Gefriergefäss gefunden werden. Dagegen konnten wir bei den anderen Versuchen, die oberhalb 400° durchgeführt wurden und wobei sich immer ein kleines Austauschmass %A fand, fast die ganze Menge des verwendeten schweren Wassers ohne Verlust wieder erhalten. Alle diese Tatsachen weisen ohne Zweifel darauf hin, dass der Wasserdampf, der ins Reaktionsrohr eingeleitet wird, einmal durch das Calciumoxyd absorbiert und dann wieder befreit wird und die Tiefe, bis dazu der Wasserdampf in das Calciumoxyd hineindringt, mit steigender Temperatur allmählich abnimmt. Wenn man deshalb annimmt, dass die in Rede kommende Austauschreaktion eben in diesem absorbierten Zustand stattfindet, wird die oben gefundene Abnahme des Austauschmasses %A mit steigender Temperatur wohl begreifbar.

Experiment 4. Austauschreaktion zwischen festem Calciumoxyd und darin absorbiertem Wasserdampf. Um die oben erwähnte Annahme direkt zu bestätigen, dass die Austauschreaktion zwischen Wasserdampf und Calciumoxyd gerade im absorbierten Zustand stattfindet, führten wir einen besonderen Versuch aus. Dieser besteht nämlich darin, dass man eine bestimmte Menge schweren Wassers, dessen Gehalt an schwerem Sauerstoff wohl bekannt ist, durch eine ebenfalls bestimmte Menge Calciumoxyd absorbieren lässt und nachdem das so mit schwerem Wasser angefeuchtete Calciumoxyd bei einer bestimmten Temperatur, die aber wohl unterhalb 400° liegt (vgl. oben), eine bestimmte Zeitlänge stehen gelassen worden ist, den Wasserdampf durch Erhitzung des gefeuchteten Calciumoxyds wieder befreit und den Gehalt des so desorbierten Wassers an schwerem Sauerstoff mit dessen anfänglichem Wert vergleicht.

In der Praxis haben wir dabei folgendermassen verfahren. Etwa 20 g (aber wohl abgewogene Menge) reines Calciumoxyd wird in einem Reaktionsrohr aus Pyrexglas etwa zwei Stunden lang bis auf 500° unter guter Evakuierung erhitzt. Nach der Abkühlung wird dann zu diesem Calciumoxyd etwa 3 g (aber wohl abgewogene Menge) schweren Wassers in Dampfform absorbiert zugesetzt.⁽⁵⁾ Das dabei benutzte schwere Wasser ist dasselbe, das bei dem anderen oben angegebenen Versuche verwendet wird; es besitzt den gesamten anfänglichen Dichteüberschuss von 41.4γ , ($= \Delta s_a$), davon 43.4γ ($= \Delta s_a(O)$) von der Anreicherung des schweren Sauerstoffs herrührt. Nachdem auf diese Weise das mit schwerem Wasser angefeuchtete Calciumoxyd bei einer bestimmten Temperatur aber immer 24 Stunden lang stehen gelassen worden ist, wird das Wasser durch die Erhitzung des letzteren im Vakuum bis auf 500° wieder befreit und die Dichte des so desorbierten Wassers nach sorgfältiger Reinigung mit gewöhnlichem Wasser verglichen.

Bei diesem Entwässerungsprozess des mit schwerem Wasser angefeuchteten Calciumoxyds ergibt sich aber, dass kaum eine messbare Menge Wasserdampf verloren geht, so lange als die Erhitzungstemperatur unterhalb 370° liegt und erst oberhalb dieser Temperatur eine merkbare Desorption stattfindet. Deshalb haben wir bei der wirklichen Entwässerung des mit schwerem Wasser angefeuchteten Calciumoxyds das letztere, wie schon oben angegeben ist, immer bis auf 500° erhitzt.⁽⁶⁾ Die folgende Tabelle 4 gibt die dadurch gewonnenen Ergebnisse wieder, wo die zweite Spalte die Temperatur, bei welcher das schwere Wasser absorbierte Calciumoxyd 24 Stunden lang gehalten wird und die dritte Spalte (Δs_e) den Dichteüberschuss des aus diesem angefeuchteten Oxyd wieder befreiten Wassers anzeigt. Deshalb enthält die letzte Spalte ($\Delta s_a - \Delta s_e$) die Abnahme der Dichte des benutzten schweren Wassers, die von der Austauschreaktion der O-Atome zwischen Wasserdampf und Calciumoxyd herrührt.

Aus diesen Ergebnissen kommt man ohne weiteres zu dem Schluss, dass bei allen untersuchten Temperaturen eine lebhafte Austauschreak-

(5) Dieser Prozess wird auch in demselben Gefäss wie beim Entwässerungsprozess und ebenfalls in Vakuum durchgeführt.

(6) Da der geschwindigkeitsbestimmende Prozess bei der Austauschreaktion zwischen Wasserdampf und festem Calciumoxyd, wie darauf schon oben hingewiesen wurde, höchstwahrscheinlich die Diffusion des Wasserdampfes in festem Calciumoxyd ist, übt diese Erhitzung des mit Wasser angefeuchteten Calciumoxyds kurze Zeit bis auf 500° kaum einen Einfluss auf das Endresultat aus.

Tabelle 4. Austauschreaktion zwischen festem CaO und darin absorbiertem H₂O bei verschiedenen Temperaturen.

CaO = 20 g, H₂O = 3 g, $\Delta s_a = 41.4 \gamma$, $\Delta s_a(O) = 43.4 \gamma$.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ
1	Zimmertemp.	29.8	11.6
2	100	29.8	11.6
3	300	28.8	12.6

tion zwischen dem absorbierten Wasserdampf und Calciumoxyd stattfindet. Weiter wird festgestellt, wie dies aus dem konstanten Wert der Dichteabnahme $\Delta s_a - \Delta s_e$ bei allen untersuchten Temperaturen ersichtlich ist, dass die in Rede kommende Austauschreaktion immer bis zum Austauschgleichgewicht auftritt, ohne Unterschied ob man das hydratisierte Calciumoxyd bei Zimmertemperatur oder bei noch erhöhten Temperaturen stehen lässt. Aus einer einfachen Rechnung ergibt sich dabei,⁽⁷⁾ dass bei dieser Art Austauschreaktion ein Mol CaO seine O-Atome gegen mehr als ein Mol (etwa zwei Mol!) H₂O austauscht. Deshalb liegt die Annahme nahe, dass das Calciumoxyd mehr als ein Mol Wasser, d.h. mehr als der gewöhnlichen stöchiometrischen Zusammensetzung von Calciumhydroxyd Ca(OH)₂ entspricht, darin absorbiert und in diesem Zustand seine O-Atome gegen die des Wassers austauscht. Aber weil diese Austauschreaktion, wie darauf schon oben hingewiesen wurde, sehr glatt verläuft, darf man diesem Wasser in leicht austauschbarer Form absorbierte Calciumoxyd etwa die Formel von Polyhydrat CaO(H₂O)_x zuschreiben. In dieser Formel drückt x eine Zahl aus, die grösser als 1, höchstwahrscheinlich sehr nahe bei 2, liegt.

Diskussion. Wie darauf schon in der Einleitung hingewiesen wurde, muss der massgebende Prozess bei der katalytischen Austauschreaktion zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des Metalloxyds entweder die aktivierte Adsorption des Sauerstoffs oder die des Wasserdampfes am betreffenden Oxyd sein. Diese erste Möglichkeit, dass die aktivierte Adsorption des Sauerstoffs der massgebende Prozess ist, darf aber bei der in Rede kommenden Austauschreaktion an der Oberfläche des Calciumoxyds schon aus den oben angegebenen Ergebnissen von Experiment 1 und 2 sicher ausgeschlossen werden, dass weder die Adsorption (bzw. Desorption) noch die Austauschreaktion der O-Atome zwischen Sauerstoff und Calciumoxyd eben bei der Temperatur merklich stattfindet, wo die betreffende katalytische Austauschreaktion zwischen Sauerstoff und Wasserdampf an demselben Oxyd mit messbarer Geschwindigkeit auftritt (etwa oberhalb 400°!). Diese Annahme liegt um so näher als nach Blumenthal⁽⁸⁾ die Bildung des Peroxyds aus Calciumoxyd und gasförmigem Sauerstoff:

(7) Dabei wird der Verteilungsquotient des schweren Sauerstoffs zwischen CaO und H₂O gleich eins angenommen.

(8) A. Blumenthal, *J. chim. phys.*, **34** (1937), 627.



auch bei niedrigen Temperaturen äusserst schwer stattfindet; der Zersetzungsdruck von CaO_2 ist bereits bei 106° so gross wie ein at. Druck. Bei den anderen Arten Erdalkalioxyden können wir aber nicht so ohne weiteres denselben Schluss ziehen, weil z.B. die Reaktion:

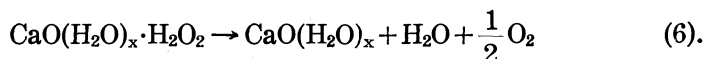
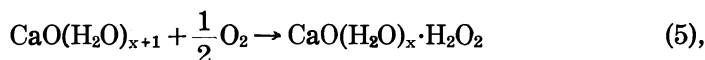
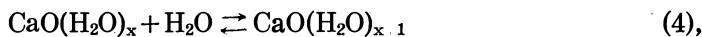


bei etwa 500° bis 800° nach beiden Seiten hin mit wohl messbarer Geschwindigkeit verläuft. Aber dass solch eine Peroxydbildung aus Metalloxyd und Sauerstoffgas bei der in Rede kommenden katalytischen Austauschreaktion zwischen Sauerstoff und Wasserdampf an Erdalkalioxyden keine Hauptrolle spielt, kann aus folgenden Gründen zwanglos verneint werden. Erstens wird z.B. bei den früher durchgeführten Versuchen gefunden, dass die katalytische Austauschreaktion an der Oberfläche des oben angegebenen BaO schon von 350° an sich deutlich bemerkbar macht (vgl. VI. Mitteil.). Diese Temperatur liegt aber viel niedriger als die oben angegebene Temperatur, wo die Peroxydbildung gemäss Gl. (3) mit wohl messbarer Geschwindigkeit stattzufinden beginnt. Zweitens liegt eben die Temperatur, wo die betreffende katalytische Austauschreaktion an jedem Erdalkalioxyd zuerst mit wohl messbarer Geschwindigkeit auftritt, einander sehr nahe; die Temperatur, wo das gefundene Austauschmass %A zuerst 10% erreicht, ergibt für MgO 500° , für CaO 390° , für SrO 380° und für BaO 350° (vgl. oben). Dagegen liegt die Temperatur, wo die Peroxydbildungsreaktion jedes betreffenden Erdalkalimetalls nach Schema (3) nach beiden Seiten lebhaft stattzufinden beginnt, ziemlich stark auseinander.⁽⁹⁾ Aus allen diesen Gründen darf wohl geschlossen werden, dass der massgebende Prozess bei der in Rede kommenden Austauschreaktion zwischen Sauerstoff und Wasserdampf an der Oberfläche der Erdalkalioxyde keine aktivierte Adsorption des Sauerstoffs an betreffenden Oxyden sein kann. Auf diese Weise bleibt nur noch eine Möglichkeit übrig, dass die aktivierte Adsorption des Wasserdampfes gerade diese massgebende Rolle spielt.

Diese letztere Annahme findet aber nun durch die Ergebnisse von Experiment 3 und 4 eine sichere Stütze. Aus Experiment 3 ergibt sich nämlich, dass die Austauschreaktion der O-Atome zwischen Wasserdampf und festem Calciumoxyd eben bei der Temperatur merklich stattzufinden beginnt, wo die katalytische Austauschreaktion zwischen Sauerstoff und Wasserdampf am betreffenden Oxyd erst mit wohl messbarer Geschwindigkeit auftritt (etwa 400° !). Weiter wird aus Experiment 4 festgestellt, dass bei der oben angegebenen Austauschreaktion zwischen Wasserdampf und Calciumoxyd höchstwahrscheinlich ein Polyhydrat von der Zusammensetzung $\text{CaO}(\text{H}_2\text{O})_x$ ($x > 1$) zwischen beiden Substanzen gebildet und gerade in diesem Zustand die O-Atome des Calciumoxyds gegen die des darin absorbierten Wasserdampfes ausgetauscht werden.

(9) A. Blumenthal, loc. cit.; M. Tzentnerschver und M. Blumenthal, *Bull. intern. acad. polonaise*, 1935 A, 540. Vgl. auch *Chem. Abstracts*, 30 (1936), 5862.

Bei diesem letzten Experiment 4 findet man ferner, dass die Desorption des Wasserdampfes aus dem mit schwerem Wasser angefeuchtetem Calciumoxyd erst oberhalb etwa 400° merklich stattfindet. Diese letztere Temperatur stimmt aber eben mit der überein, wo die in Rede kommende katalytische Austauschreaktion zwischen Sauerstoff und Wasserdampf an der Oberfläche des Calciumoxyds erst mit wohl messbarer Geschwindigkeit auftritt. Aus allen diesen Versuchsergebnissen liegt es deshalb sehr nahe, dass die katalytische Austauschreaktion der O-Atome zwischen Wasserdampf und gasförmigem Sauerstoff an der Oberfläche des Calciumoxyds, oder im allgemeinen an der Oberfläche der Erdalkalioxyde, nach folgendem Schema durchgeführt wird:



Die erste Reaktion (4) stellt die reversible Adsorption und Desorption des Wasserdampfes an der Oberfläche des mit Wasser schon teilweise hydratisierten Calciumoxyds dar und eben dieser Prozess (4) bildet die massgebende Stufe der ganzen Austauschreaktion. Dass nicht die aktivierte Adsorption des Wasserdampfes an wasserfreiem Oxyd CaO sondern die an dem mit Wasser schon teilweise hydratisierten „angefeuchteten“ Oxyd $\text{CaO}(\text{H}_2\text{O})_x$ dabei eine Rolle spielt, wird schon daraus ersichtlich, dass die Austrittstemperatur der katalytischen Austauschreaktion an einzelnen Erdalkalioxyden, wie darauf schon oben hingewiesen wurde, trotz der grossen Verschiedenheit des Zersetzungsdruckes der einfachen Hydroxyde aller Metalle nicht sehr voneinander abweicht. Die Temperatur, wo der Zersetzungsdruck des einfachen Hydroxyds jedes Erdalkalimetalls erst bis zu 9.2 mm Hg wächst, beträgt z.B. für $\text{Mg}(\text{OH})_2$ 175°, für $\text{Ca}(\text{OH})_2$ 369°, für $\text{Sr}(\text{OH})_2$ 452° und für $\text{Ca}(\text{OH})_2$ 630°. ⁽¹⁰⁾ Sie nimmt also gerade im Gegenteil zur Aufttrittstemperatur der katalytischen Austauschreaktion mit zunehmendem Atomgewicht stark zu. Eben aus diesem Grunde darf die aktivierte Adsorption des Wasserdampfes an wasserfreiem Oxyd als den massgebenden Prozess für die in Rede kommende katalytische Austauschreaktion ausgeschlossen werden. ⁽¹¹⁾

(10) J. Johnston, *Z. phys. Chem.*, **62** (1908), 330; W. F. GIAUQUE und R. C. ARCHIBALD, *J. Am. Chem. Soc.*, **59** (1937), 568.

(11) Die Annahme, dass die für die katalytische Austauschreaktion massgebende Rolle spielende aktivierte Adsorption des Wasserdampfes wirklich an der Oberfläche des teilweise hydratisierten Oxyds stattfindet, steht auch mit den bei den früher durchgeführten eigentlichen Austauschversuchen gefundenen Tatsachen im Einklang, dass Erdalkalioxyd desto schneller zusammengesintert wird je stärker seine katalytische Wirksamkeit ist; das Magnesiumoxyd, das die geringste Wirksamkeit besitzt, am schwersten dagegen das Bariumoxyd, das die grösste Wirksamkeit besitzt, am schnellsten zusammengesintert wird.

Die beiden anderen Reaktionen (5) und (6) in oben angegebenem Schema drücken den Austausch der O-Atome zwischen den so durch das teilweise hydratisierte Calciumoxyd aufgenommenen Wassermolekülen und den darauf weiter hineinfliegenden Sauerstoffmolekülen aus. Dabei wird weiter angenommen, dass Wasserstoffsuperoxyd als ein Zwischenprodukt in Reaktion (5) gebildet wird. Obwohl solch eine Zwischenbildung von Wasserstoffsuperoxyd, besonders in gut definierter Form, zur Deutung der in Rede kommenden Austauschreaktion zwischen aktiviert adsorbierten Wassermolekülen und darauf hineinfliegenden Sauerstoffmolekülen nicht immer angenommen zu werden braucht, so fehlen doch für die Entstehung irgendwelcher peroxydartigen Verbindungen aus angefeuchtetem Calciumoxyd und Sauerstoff keine experimentellen Beweise. So wird z.B. die Entstehung der peroxyartigen Verbindungen aus feuchtem Calciumoxyd und Luft von Tarugi⁽¹²⁾ analytisch nachgewiesen und weiter kürzlich von Hundeshagen⁽¹³⁾ festgestellt, dass in Gipsverputz und besonders in seinem wetterseitig gelegten Raum aktiver Sauerstoff (vermutlich Calciumperoxyd) entwickelt wird. Aus allen diesen Gründe ist deshalb die Annahme nicht von der Hand zu weisen, dass die Austauschreaktion zwischen aktiviert adsorbierten Wassermolekülen und darauf weiter hineinfliegenden Sauerstoffmolekülen durch die Zwischenbildung der Peroxyde vor sich geht.

Herrn Prof. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Nippon Gakuzyutu-Sinkōkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) sowie der Hattori-Hohkōkai (der Hattori-Stiftung), die durch Gewährung eines Stipendiums die Ausführung dieser Arbeit ermöglicht haben, bin ich auch zu grossem Dank verpflichtet.

Osaka Teikoku Daigaku
Rigaku-bu
Kagaku Kyositu
(Chemisches Institut
der Kaiserlichen Universität Osaka).

(12) N. Tarugi, *Gazz. chim. ital.*, **34** (1902), 254. Vgl. auch *Chem. Zentr.*, **1904**, 1531. Die Entstehung der Peroxyde aus feuchtem Calciumoxyd und Luft wurde von Vaubel (*Z. angew. Chem.*, **25** (1912), 2300; *J. prakt. Chem.*, **88** (1913), 61) zur Deutung des Zerfressens des in Kalkmörtel eingebetteten Bleirohres benutzt, obwohl diese letztere Annahme später von Ditz (*J. prakt. Chem.*, **87** (1913), 208; ebenda, **88** (1913), 443) als unzutreffend abgelehnt wurde.

(13) F. Hundeshagen, *Chem.-Ztg.*, **62** (1938), 328.

Absorptionsspektren von Metallkomplexsalzen des 2,2'-Dipyridyls. III.

Von Kazuo YAMASAKI.

(Eingegangen am 6. März 1940.)

Die vorliegende Arbeit ist die Fortsetzung der vorhergehenden Mitteilungen⁽¹⁾ über die Dipyridylkomplexsalze und ihre Lichtabsorptionen.

Wenn das Gemisch der wässrigen Lösung des Kobaltchlorids (1 Mol) und der alkoholischen Lösung des 2,2'-Dipyridyls (1 Mol) mit wenig HCl versetzt und im Exsikkator mit Wasserstoffatmosphäre eingedampft wird, so entstehen zuerst blaue Kristalle und dann eine Masse von kleinen grünen Kristallen. Diese Kristalle wurden mit Alkohol und Äther gewaschen und zur Analyse gebracht.

Blaue Verbindung. Die so erhaltene blaue Verbindung ist in Wasser unter roter Färbung löslich und nach einigen Sekunden schlägt die Farbe in Rotgelb um. Diese Verbindung ist schwer löslich in kaltem, aber ziemlich leicht in heissem Alkohol. Die Farbe ihrer alkoholischen Lösung in heissem Zustand ist blau, aber in kalten oder verdünnten Lösungen ist sie rot. Dieser Farbenwechsel ist gleich dem der Kobaltchloridlösung. Die Analyse dieser neuen blauen Verbindung ergibt: Gef. Co 16.35; N 7.78; Cl 39.80. Ber. für $\text{CoCl}_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2 \cdot 2\text{HCl}$ (2,2'-Dipyridyl = $\text{C}_{10}\text{H}_8\text{N}_2$) Co 16.43; N 7.80; Cl 39.36%. Die Analysenwerte stimmen somit auf die Formel $\text{CoCl}_2 \cdot \text{Dip} \cdot 2\text{HCl}$ ($\text{Dip} = 2,2'\text{-Dipyridyl}$). Diese Verbindung bildet himmelblaue feine Kristalle, die kein Kristallwasser enthält; die, erhitzt auf 120°, verliert 2HCl und entsteht eine blauviolette Verbindung welche die Zusammensetzung von CoDipCl_2 besitzt.

Die analogen Verbindungen $\text{CoCl}_2 \cdot \text{A} \cdot 2\text{HCl}$ (A bedeutet Pyridin oder Chinolin) wurden schon von Percival und Wardlaw⁽²⁾ durch die Einwirkung einer mit HCl gesättigten alkoholischen Lösung des Kobaltchlorids auf Pyridin oder Chinolin gewonnen und die Konstitutionsformel $[\text{CoCl}_4] (\text{HA})_2$ wurde von den genannten Autoren ihnen angegeben. Die blaue Verbindung von 2,2'-Dipyridyl kann auch nach demselben Verfahren hergestellt werden, d.h. man lässt in die mit HCl gesättigte eiskalte alkoholische Lösung von Kobaltchlorid (1 Mol) die alkoholische Lösung von 2,2'-Dipyridyl (1 Mol) einfließen. Dann scheiden sich blaue feine Kristalle ab, die scharf abgesaugt und mit Alkohol und Äther gut gewaschen werden. Nimmt man die beide Verbindungen von Pyridin und Dipyridyl miteinander ganz analog an, so kann man zur Dipyridylverbindung auch die gleichartige Konstitutionsformel $[\text{CoCl}_4] (\text{H}_2\text{Dip})$ angeben. Wie oben

(1) I. Mitt. dies Bulletin, **12** (1937), 390; II. Mitt. ebenda, **13** (1938), 538. In der II. Mitteilung ist ein Druckfehler: Seite 541, Zeile 12, lies $\lambda = 303 \text{ m}\mu$ statt $\lambda = 503 \text{ m}\mu$.

(2) E. G. V. Percival und W. Wardlaw, *J. Chem. Soc.* **1929**, 1505.

erwähnt, löst sie sich in Wasser mit rotgelber Farbe. Wenn diese rotgelbe Lösung auf dem Wasserbad eingedampft wird, scheidet sich eine grüne kristallinische Verbindung, welche sich identisch mit den oben beschriebenen grünen Kristallen erweist. Über diese grüne Verbindung wird unten genauer beschrieben.

Die blaue Dipyridylverbindung $[\text{CoCl}_4](\text{H}_2\text{Dip})$ ist beständig im Exsikkator, aber sie absorbiert Wasser aus der Luft und wandelt sich in die rote oder schwachrote Verbindung um, je nach dem Feuchtigkeitsgrad der Luft. Nämlich, wenn die Luft stark gefeuchtet ist, so entsteht die schwachrote Verbindung, während in etwas trockener Luft die rote Verbindung gebildet wird. Die beiden d.h. rote und schwachrote Verbindungen verlieren das Wasser über Phosphorpentoxyd oder bei 100° und gehen auf einer blauviolette Verbindung über. Diese blauviolette Verbindung ist identisch mit der, die von blauen Verbindung $[\text{CoCl}_4](\text{H}_2\text{Dip})$ unter HCl-Abspaltung entsteht. Die Identität dieser beiden Verbindungen wurde nach röntgenographischen Analyse (Pulverdiagramm) ermittelt⁽³⁾. Die Analyse der blauvioletten Verbindung ergibt: Gef. Co 20.40; N 10.09; Cl 24.70%. Berechnet für CoDipCl_2 : Co 20.60; N 9.79; Cl 24.79%. Die Analysenwerte stimmen also auf die Formel CoDipCl_2 . Bei Wasserverlust ergeben die rote und schwachrote Verbindungen die gleiche blauviolette Verbindung, wobei resp. die rote 0.75–1.0 H_2O und die schwachrote 3.85–3.9 H_2O verliert. Daraus kann man ihnen die folgenden Formeln zugeben: $\text{CoDipCl}_2 \cdot \text{H}_2\text{O}$ (rot) und $\text{CoDipCl}_2 \cdot 4\text{H}_2\text{O}$ (schwachrot). Diese rote und schwachrote Verbindungen lösen sich in Wasser mit gelber Farbe und beim Verdunsten auf dem Wasserbad scheiden sich die grüne Kristalle, die identisch mit der oben genannten grünen Verbindung ist. Die rote Färbung, die beim Auflösen der blauen Verbindung in Wasser erscheint, deutet an, dass die Umwandlung in die hydrierten roten Verbindung geschieht.

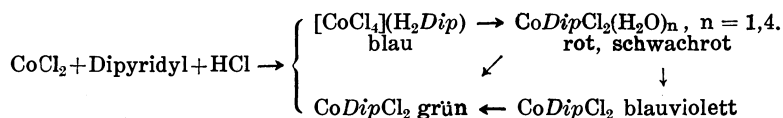
Auch im Falle von Pyridinverbindung $[\text{CoCl}_4](\text{HPy})_2$ findet diese HCl absplattende Reaktion im festen Zustand unter Bildung von der violette Verbindung $\alpha\text{-Co}(\text{Py})_2\text{Cl}_2$ statt.

Grüne Verbindung. Wie schon oben erwähnt, bei der Darstellung der blauen Verbindung werden grüne Kristalle aus ihrer Mutterlauge allmählig abgeschieden. Die letztere ist in Alkohol unlöslich; in Wasser löst es jedoch leicht mit gelber Farbe. Der Gewichtverlust an dieser Verbindung wird weder in vacuo über P_2O_5 noch bei Erhitzung auf 100° beobachtet. Diese grüne Verbindung wurde mit heissem Alkohol gut gewaschen, um die Beimengungen der blauen Verbindung und HCl möglichst völlig zu entfernen, und zur Analyse gebracht: Gef. Co 20.50; N 9.92; Cl 24.70%. Berechnet für CoDipCl_2 : Co 20.60; N 9.79; Cl 24.79%. Die Analysenwerte stimmen somit auf die Formel CoDipCl_2 . Die gleiche Analysenwert wurde gleichfalls für die grüne Verbindung erhalten welche beim Eindampfen der gelben Lösungen der oben genannten blauen oder roten Verbindung entsteht. Die wässrige Lösung dieser grünen Verbindung ist gelb und reagiert sauer. Diese Erscheinung deutet wahrscheinlich ein hydrolytische Strukturänderung an. Wird aber die gelbe Lösung

(3) Für deren Ausführung Dr. S. Shinoda bestens gedankt sei.

auf dem Wasserbad eingedampft, so kristallisiert die ursprüngliche grüne Verbindung wieder: das Hydrolyseprodukt der grünen Verbindung kann jedoch nicht isoliert werden.

Zusammenfassend lässt sich die Umwandlungsschema der oben beschriebenen Verbindungen folgenderweise wiedergeben:



Absorptionsspektren. (1) *In festem Zustand:* Da alle die blaue, rote, schwachrote, und grüne Verbindungen in wässriger Lösung immer die Farbumschläge durch vermutliche Strukturänderungen erleiden, so wurde ihre Lichtabsorption in festem Zustand nach der von Tsuchida und Kobayashi⁽⁴⁾ vorgeschlagenen Methode mit Hilfe des Mikroskops gemessen. Die Ergebnisse sind in Abb. 1 angegeben. Bei der blauen Verbindung ist das Licht um 480–570 m μ durchlässig und ihre Absorption ist ähnlich der der gleichen Verbindung in alkoholischen Lösung. Die rote Verbindung absorbiert um 500–540 m μ und die Lage der Absorptions-

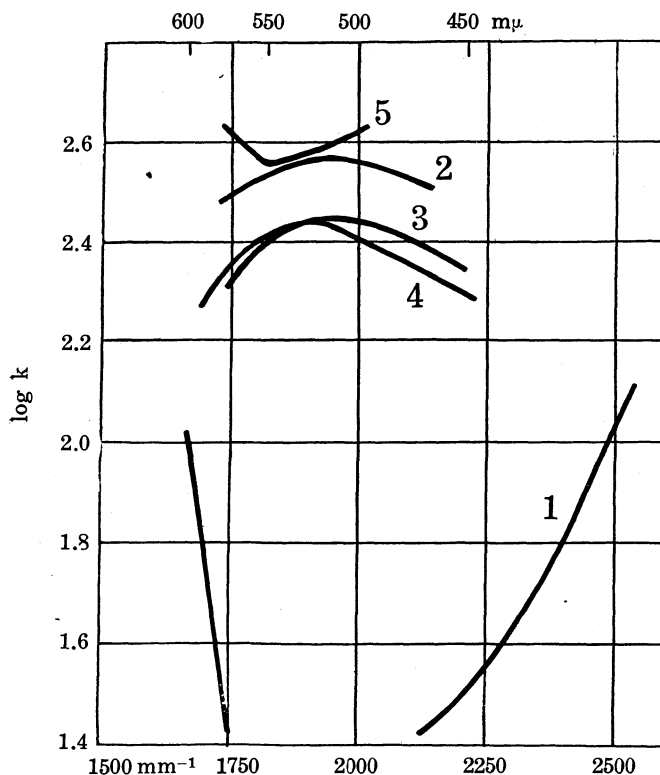


Abb. 1. Kurve 1: Blaue Verb., 2: Rote Verb., 3: Schwachrote Verb., 4: Kobaltchlorid, 5: Grüne Verb., k: Extinktionskoeffizient der Krystalle.

(4) R. Tsuchida und M. Kobayashi, dies Bulletin, **13** (1938), 619.

maximum stimmt mit den Banden ($520\text{ m}\mu$) des Kobaltchlorids überein, dagegen liegt die Absorption der schwachroten Verbindung um $480\text{--}540\text{ m}\mu$. Die grüne Verbindung lässt das Licht um $550\text{ m}\mu$ durch. Die Dicke der Kristalle, welche für diese Absorptionsmessungen verwendet wurden, ist resp. 0.17 (blau), 0.05 (rot), 0.06 (schwachrot), 0.05 (Kobaltchlorid) und 0.04 mm (grün).

(2) *In der Lösung*: Die Lichtabsorption im sichtbaren und ultravioletten Gebiet wurde mit Nuttingsche Spektrophotometer bzw. mit Quarzspektrographen (Hilger E2) gemessen. Die Ergebnisse bezüglich der alkoholischen Lösungen der blauen Verbindung $[\text{CoCl}_4](\text{H}_2\text{Dip})$ sind in Abb. 2 angegeben. Ihre Löslichkeit in kaltem Alkohol ist gering (die

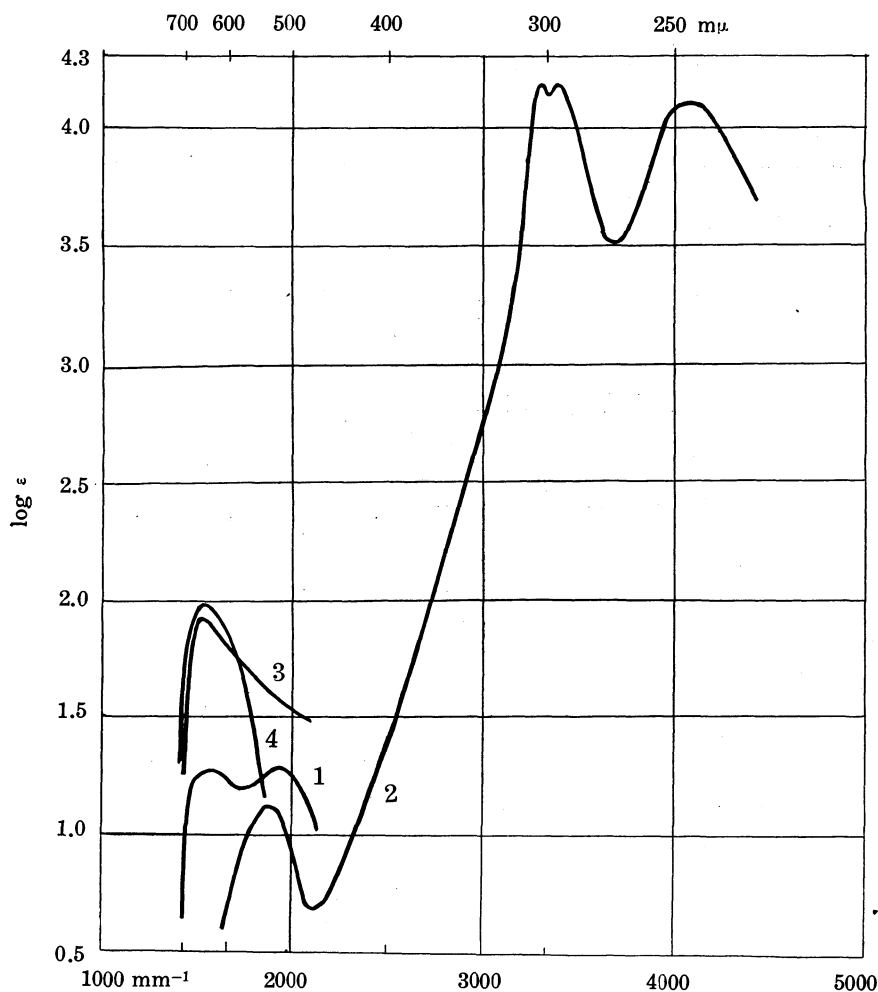


Abb. 2. Kurve 1: $1/320$ Mol, 2: $1/1000$ und $1/8000$ Mol (15°),
3: $1/1000$ Mol (50°), 4: Kobaltchlorid $1/80$ Mol.

gesättigte Lösung ist $1/320$ Mol). Die Farbe der gesättigten Lösung ist violett, aber durch Verdünnung ($1/1000$ Mol) wird sie rot. Im heißen Zustand (50°) wird die letzte Lösung blau, wobei die Vermehrung der

molarer Extinktionskoeffizient (ϵ) beobachtet wird. Dieser Farbenwechsel ist gleich dem der Kobaltchloridlösung. Die Lagen der Absorptionsbanden sind:

1/320 Mol(15°)	: 640 m μ (log ϵ = 1.3), 515 m μ (log ϵ = 1.3).
1/1000 Mol(15°)	: 530 m μ (log ϵ = 1.1).
„ (50°)	: 660 m μ (log ϵ = 1.9 ₄).
1/8000 Mol(15°)	: 305 + 295 m μ (log ϵ = 4.1 ₇), 246 m μ (log ϵ = 4.1 ₀).
Kobaltchlorid 1/89 Mol(15°)	: 650 m μ (log ϵ = 1.9 ₉).

Zum Vergleich wurde die Absorptionsband von Kobaltchlorid anbei gegeben. Wie die Kurve zeigt, ist die Absorption in 50° ähnlich der des Kobaltchlorids. Die ultraviolette Absorption wurde für die Lösungen von 1/1000 Mol und 1/8000 Mol beobachtet. Trotz der Annahme, dass in diesen verdünnten roten Lösungen sicherlich die Solvation stattfindet und die Formel $[\text{CoCl}_4](\text{H}_2\text{Dip})$ nicht mehr gültig zu sein scheint, wurde hier die Erfüllung des Beerschen Gesetzes beobachtet. Weiter stimmt die Lage der Absorptionsbanden im Ultraviolett dieser blauen Verbindung mit den Banden 305 + 295 m μ , 243 m μ des zweiwertigen Kobalto-Komplexe $[\text{Co}(\text{Dip})_3]\text{Cl}_2$ gut überein (Vgl. I Mitt.).

Wie oben erwähnt, lösen sich die blaue und grüne Verbindungen in Wasser mit rotgelber bzw. gelber Farbe. Die Absorptionskurven dieser Lösungen sind in Abb. 3 gezeigt. Da in wässrigen Lösungen dieser Verbindungen etwaige Strukturänderungen denkbar ist, wurde die Absorption nur nach der Hartley-Balysche Methoden qualitativ gemessen. Die Konzentrationen sind 1/50, 1/1000 und 1/10000 Mol.

Zum Vergleich sind die Absorptionskurven des $[\text{Co}(\text{Dip})_3]\text{Cl}_2$ und $[\text{Co}(\text{Dip})_3]\text{Cl}_3$ auch hier angegeben. Die Lagen der Banden sind:

Blaue Verb. $([\text{CoCl}_4](\text{H}_2\text{Dip}))$	: 492 m μ , 303 + 295 m μ , 243 m μ .
Grüne Verb. (CoDipCl_2)	: 450 m μ , 318 + 306 m μ .
$[\text{Co}(\text{Dip})_3]\text{Cl}_2$	: 305 + 295 m μ , 243 m μ .
$[\text{Co}(\text{Dip})_3]\text{Cl}_3$	: 450 m μ , 319 + 307 m μ .

Wie es aus der Abbildung ersichtlich ist, zeigt die rotgelbe wässrige Lösung der blauen Verbindung die gleichen Absorptionsbanden im Ultraviolett mit Kobalto-Salz $[\text{Co}(\text{Dip})_3]\text{Cl}_2$, während die Banden der grünen Verbindung im Ultraviolett sich mit der des Kobalti-Salz $[\text{Co}(\text{Dip})_3]\text{Cl}_3$ gut übereinstimmend beweisen.

Wenn die wässrige Lösung der blauen Verbindung, zwecks der Entfernung von der Salzsäure, auf dem Wasserbad eingedampft wird und so entstandene grüne Verbindung nochmals in Wasser gelöst wird, so zeigt die Lösung die gleichen Absorptionsbanden wie die Lösung des Kobalti-Salz. Diese etwas komplizierte Tatsache führt uns zur Vermutung, dass die grüne zweiwertiges Kobaltatom enthaltende Verbindung beim Auflösen in Wasser eine Oxydation erleidet und ihre Lösung so gut wie Kobalti-Salz absorbiert. Aber diese Vermutung wurde nicht durch das Experiment geprüft, in dem die grüne Verbindung in Baly-Rohr unter Wasserstoffatmosphäre in Wasser gelöst und deren Absorption beobachtet wird: nämlich wurde keine Verschiebung der Banden dabei bemerkt. Was die Aufklärung der widersprechenden Tatsache anbelangt, dass, obgleich die grüne Verbindung CoDipCl_2 ein Komplexsalz

des zweiwertigen Kobalts ist, ihre Absorption dagegen mit der des Kobalti-Salz $[\text{Co}(\text{Dip})_3]\text{Cl}_3$ einander ähnelt, so wird eine weitere Untersuchung darüber erforderlich sein.

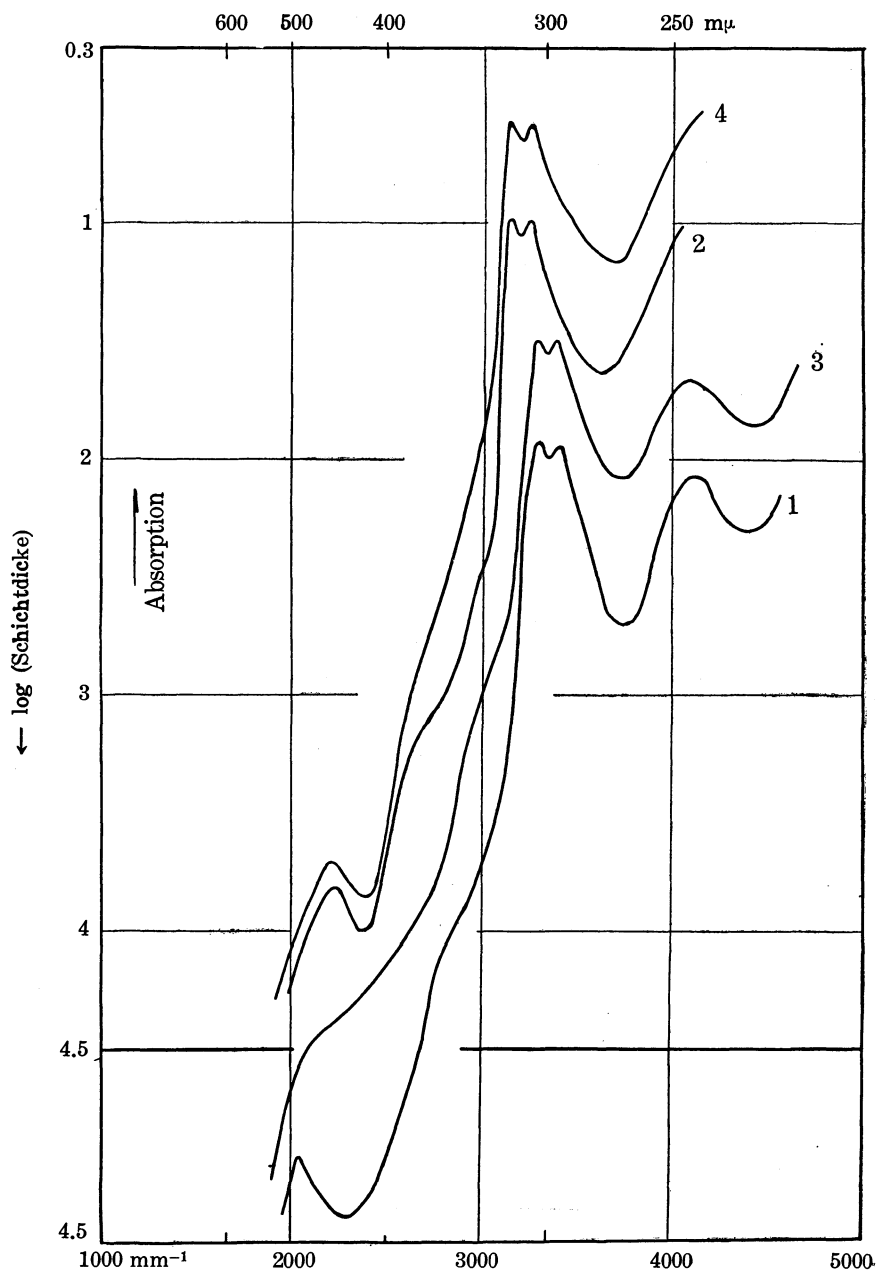


Abb. 3. Kurve 1: Blaue Verb., 2: Grüne Verb., 3: $[\text{Co}(\text{Dip})_3]\text{Cl}_2$,
4: $[\text{Co}(\text{Dip})_3]\text{Cl}_3$.

Auf der Ordinate wurde die Logarithmen der Schichtdicke (mm)
der Lösung entsprechend 1/10000 Mol aufgetragen.

Wie die Analysenwerte zeigen, besitzen die blauviolette und die grüne Verbindungen die gleiche Zusammensetzung CoDipCl_2 und sie müssen daher als die Isomeren betrachtet werden. Die blauviolette Verbindung ist unbeständig an der Luft und absorbiert Wasser, während es bei der grünen Verbindung nicht der Fall ist. Die beide werden also vorläufig als α -Form (die grüne), und β -Form (die blauviolette) voneinander unterschieden. Die Umwandlung der β -Form in das grüne α -Isomere wird leicht durch Eindampfen ihrer wässrigen Lösung erzielt, aber die gegenseitige Umwandlung ist keineswegs ermöglicht.

Die analogen Pyridinverbindungen dieser Reihe $\text{Co(Py)}_2\text{Cl}_2$ wurden schon von verschiedenen Autoren untersucht und auch zwei Isomeren α - und β -Form sind bekannt. Nach den röntgenographischen Untersuchungen von Cox und seine Mitarbeitern⁽⁵⁾ über die Struktur des $\text{Co(Py)}_2\text{Cl}_2$, besitzt die violette α -Form die ebene und zwar Trans-Konfiguration, während die der β -Form noch unerklärlich bleibt. Im Falle des 2,2'-Dipyridyls muss die Trans-Konfiguration unmöglich sein, weil ein 2,2'-Dipyridyl immer die Cis-Koordinationsstelle besetzt. Weder die röntgenographische Untersuchung über Strukturbestimmung noch die Ermittlung der Molekulargröße von jetzt gewonnenen 2,2'-Dipyridyl-Kobaltkomplexverbindungen gelangt es noch dem Autor. Die weitere Untersuchungen darüber werden fortgesetzt.

Zusammenfassung.

Einige neuen Komplexverbindungen des Kobaltchlorids mit 2,2'-Dipyridyl wurden dargestellt: $[\text{CoCl}_4](\text{H}_2\text{Dip})$, $\text{CoDipCl}_2 \cdot \text{H}_2\text{O}$, $\text{CoDipCl}_2 \cdot 4\text{H}_2\text{O}$, CoDipCl_2 (grüne α -Form und blauviolette β -Form).

Ihre Absorptionsspektren wurden in festem Zustand sowie auch in der Lösungen beobachtet.

Es sei mir gestattet, Herrn Prof. Yuji Shibata für seine freundliche Anleitung und Ratschläge bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

*Chemisches Institut,
Naturwissenschaftliche Fakultät,
Kaiserliche Universität zu Tokyo.*

(5) E. G. Cox, A. J. Shorter, W. Wardlaw und W. J. R. Way, *J. Chem. Soc.*, **1937**, 1556.

Studies on the Organic Molecular Compounds. Part II. The Influence of Nitro Radicals and Second Substitution Radicals on the Formation of the Aromatic—Nitroaromatic Molecular Compounds. II.

By Chiro SHINOMIYA.

(Received February 5, 1940.)

Molecular Compound Formations in the Equally Nitrated Isomers. In the previous paper⁽¹⁾, molecular compound formation was discussed in connexion with the number of nitro radicals, the number and variety of second substitution radicals in the nitro components, as also with the effects of the presence and the position of hydroxyl group in naphthalene α -, and β -naphthol. In this paper, a comparison is made of the nitro-components. Table 1 gives the essence of the binary systems of α -, β -naphthylamine, α -, β -naphthol, and naphthalene with various nitrobenzenes and their derivatives.

(1) Compound ratio principally 1:1⁽²⁾, except the following systems:

- 2 : 1 naphthalene—*vic*-trinitrobenzene, β -naphthylamine—*asym*-trinitrobenzene?, α -naphthylamine—2,4-dinitroanisol;
- 3 : 2 naphthylamine—2,3-dinitrophenol, naphthalene—2,5-dinitrophenol, β -naphthylamine—3,4-dinitrophenol;
- 2 : 3 β -naphthol—2,4-dinitroaniline;
- 1 : 3 naphthalene—2,4-dinitroaniline.
- 1 : 2 β -naphthol—2,4-dinitrobenzoic acid, β -naphthylamine—3,5-dinitrobenzoic acid;

(2) As mentioned in the previous paper, in the case of naphthylamine and naphthol, the compound formations of the α -isomers are superior to those of the β -isomers.

(3) The effect of second substitution radical in the nitrated benzene nucleus was the same as that described in Part I.

(4) The main part of this paper is taken up with comparisons of compound formations of various isomers of nitrated components. The sequences are⁽³⁾,

Trinitrobenzenes:—*sym*-compound > *asym*- or *vic*-compound,
 Dinitrobenzenes:—*p*- or *m*-compound > *o*-compound,
 Trinitrotoluenes:—2,4,6-compound > 2,3,4- or 2,4,5-compound,
 Dinitro-phenols or toluenes:—2,4-; 2,5- or 3,5-compound > 2,6-compound > 2,3- or 3,4-compound.

(1) This Bulletin, Vol. 15, No. 3.

(2) Stable nitro compounds usually combined in the ratio of 1:1. The order of stability of nitro compounds, calculated from their heat of combustion, are

p - > m - > o -dinitrobenzene; *sym*- > *asym*-trinitrobenzene; p - > m - > o -nitrotoluene; 2,4-, 3,5- > 2,6- > 2,5 > 2,3- > 3,4-dinitrotoluene; 2,4,6- > 2,4,5- > 2,3,4-trinitrotoluene.

(3) Some of the molecular compounds of trinitroxylenes that were examined were found to agree with this order.

Table 1. Mol ratio A : B, (τ), and Colour.***

A	B [Melting point]	Nitrobenzene	Dinitrobenzenes			
		 NO ₂ [5.7]	 NO ₂ [117.0]	 NO ₂ [90.0]	 NO ₂ [173.5]	
α -Naphthylamine	—	—	✓*	1:1 (−6.2)* Red	1:1 U*	1:1 U*
β - „	—	—	✓*	1:1 (−46.8)* Red	1:1 U*	1:1 U*
α -Naphthol	—	—	✓	1:1 (7.0) Orange yellow	1:1 U	1:1 U
β - „	—	—	✓	1:1 U*	1:1 (−11.8) or (3:2)	1:1 (−11.8) or (3:2)
Naphthalene	✓*	✓*	✓*	Orange yellow 1:1 (−34.2) D* Light yellow	Orange red 1:1 (−7.5)* Yellow	Orange red 1:1 (−7.5)* Yellow
A [Melting point]	B [Melting point]	Mononitrophenols				
		 OH NO ₂ [45.0]	 OH NO ₂ [96.5]	 OH NO ₂ [113.0]		
α -Naphthylamine	[50.0]	✓	1:1 (−17.5)* Yellow	1:1 (−13.1)* Yellow	1:1 (−13.1)* Yellow	1:1 (−13.1)* Yellow
β - „	[110.0]	✓	1:1 (−39.7)* Yellow	1:1 (−30.8)* Orange yellow	1:1 (−30.8)* Orange yellow	1:1 (−30.8)* Orange yellow
α -Naphthol	[96.0]	✓	✓	✓	✓	✓
β - „	[122.0]	✓	✓	✓	✓	✓
Naphthalene	[80.0]	✓*	✓	✓	✓	✓
A [Melting point]	B [Melting point]	Mononitrotoluenes				
		 CH ₃ NO ₂ —	 CH ₃ NO ₂ [15.5]	 CH ₃ NO ₂ [52.7]		
α -Naphthylamine	[50.0]	—	—	✓	✓	✓
β - „	[110.0]	—	—	✓	✓	✓
α -Naphthol	[96.0]	—	—	✓	✓	✓
β - „	[122.0]	—	—	✓	✓	✓
Naphthalene	[80.0]	—	✓*	✓*	✓*	✓*

Table 1.—(Continued)

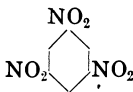
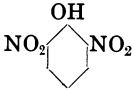
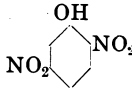
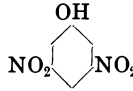
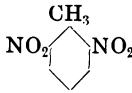
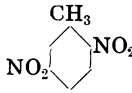
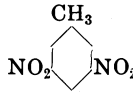
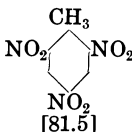
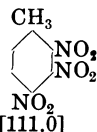
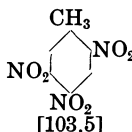
Trinitrobenzenes					
 [121]	 [57.0]			 [123.0]	
Viscous, decomposed Decomposed 1:1 (−6.5) Bright red 1:1 (−28.5) Brown 2:1 (14.5) Yellow	1:1 Ca. 7.5) Black 2:1 (−12) ?, decomposable Dark brown 1:1 (−9.5) Brown red 1:1 (−26.0) or (1:2) (−5.7) Orange red Brown red 1:1 (−16.0) Yellow			1:1 (127.5)** Dark red 1:1 (45.0)* Red 1:1 (84.0) Orange 1:1 (36.0) Orange yellow 1:1 (51.0)* Light yellow	
Dinitrophenols					
 [145.0]	 [63.3]	 [113.5]	 [106.0]	 [134.5]	 [123.0]
3:2 (17.0) Black 3:2 (−19.5) Black √ √ √	1:1 (40.3) Deep yellow 1:1 (18.3)** Deep yellow 1:1 (0.8) Bright red 1:1 (−16.7) Bright red 1:1 (−13.8) Bright yellow	1:1 (23.6)* Reddish brown 1:1 (−39.4)* Brown red 1:1 (14.7) Orange red 1:1 (−8.3) Orange red 1:1 (−4.0)* Yellow	1:1 (23.0) Black 1:1 (−11.5) Black 1:1 (17.4) Ruby red 1:1 (3.4) Ruby red 3:2 (10.1) or (1:1) Orange	1:1 (3.7) Yellowish brown 3:2 (−36.8) ? Yellowish brown √ √ √	1:1 (24.0) Brown yellow 1:1 (−19.5) Deep yellow 1:1 (−2.5) Yellowish orange 1:1 (−29.5) Orange yellow 1:1 U Light yellow
Dinitrotoluenes****					
 —	 [65.0]	 [71.0]	 [50.2]	 [59.0]	 [82.3]
√ √ √ √ √	√* √* 1:1 U Brown yellow √ √*	1:1 (1.5,* Bright red √ 1:1 (15.0) Orange yellow 1:1 (−19.5) Lemon yellow 1:1 (−14.5)* Light yellow	1:1 (0.0) Reddish purple √ 1:1 (11.9) Bright red 1:1 (−8.5) Orange red 1:1 (−19.6) Yellow	√* √* √ √ √*	1:1 (41.7)* 1:1 (−43.2) D* — — 1:1 (−18.7)*

Table 1.—

A [Melting point]	B [Melting point]	Trinitrotoluenes		
		 [81.5]	 [111.0]	 [103.5]
α -Naphthylamine	[50.0]	1:1 (76.5)** Reddish brown	—	—
β - " "	[110.0]	1:1 (16.2)* Red	—	Viscous, decomposed
α -Naphthol	[96.0]	1:1 (37.8) Orange	1:1 (—15.5) Brown red	1:1 (—17.8) Orange red
β - " "	[122.0]	1:1 (8.3)* Orange yellow	1:1 (—35.0) Brown red	1:1 (—2.8) Red
Naphthalene	[80.0]	1:1 (17.3)* Light yellow	1:1 (4.5) Yellow	1:1 (—2.8) Yellow

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., 122.

** The data of the crystal from the solution (Pfeiffer, "Organische Molekülverbindungen," 2 Aufl., 366, 356, Stuttgart (1927); Hertel and Mischnat, *Ann.*, 451 (1927), 197; Hepp, *Ann.*, 215 (1882), 378).

*** The colour of the melt (mixed in the compound ratio), not of the crystal obtained from the solution. Some of the colours of the latter are shown in bracket [].

In these aromatic—nitroaromatic binary systems, the ortho substitution radicals somewhat hinder molecular compound formation. Notwithstanding its excellent combination energy in solution or gas⁽⁵⁾, *o*-dinitrobenzene formed no crystalline molecular compound with aromatic ring⁽⁴⁾. Analogous results were noted in the *o*-dinitro-phenols and toluenes; the *o*-trinitro compounds (*vic*-, *asym*-trinitrobenzene, 2,3,4- or 2,4,5-trinitro-toluene, etc.) exerts only weak compound formation.

The influence of the ortho substituted second radical is not simple, but in 2,6-dinitro-phenol or toluene, the presence of a hydroxyl or methyl radical hindered compound formation⁽⁶⁾, while in the dinitrophenol—naphthylamine system, the tendency to form another type of molecular combination was increased, the *o*-dinitro, and even the mononitro compound, was a distinct molecular compound; "complex isomerism"⁽⁷⁾ was found especially in the cases of the 2,6- and 3,5-dinitrophenols.

(5) Although all the systems listed in Table 1 showed distinct halochromism when fused, in the case of a simple eutectic system, the phenomenon vanished on solidification.

Halochromism of these molecular compounds was greatly affected by the substituent (auxochrome) of their component. The sequence of the effects was

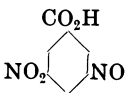
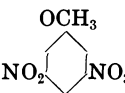
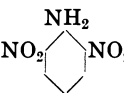
(4) G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur", 114, Stuttgart (1937).

(5) Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., 122.

(6) R. Kremann, and O. Rodinis, *Monatsh.*, 27 (1906), 130.

(7) E. Hertel, *Ann.*, 451 (1927), 197.

(Concluded)

Dinitrobenzoic acids		Dinitroanisols		Dinitroanilines	
 [178.5]	 [205.0]	 [87.0]	 [105.5]	 [179.5]	 [137.0]
— — 1:1 U Reddish orange 1:2 U or √ Red 1:1 U Orange	1:1, decomp. [Brown red] 1:2 U [Deep red] 1:1 (41.5) Brown 1:1 (22.0) Brown yellow 1:1 (39.5) Lemon yellow	2:1 (−4.3) Red √ 1:1 (2.0) Brown yellow 1:1 (−22.0) Yellow 1:1 (−33.5) Yellowish white	1:1 (−3.3) Ruby red √ 1:1 (−7.3) Orange yellow √ 1:1 U Yellowish white	1:1 U Dark red √ 1:1 (2.3) or U Orange yellow 2:3 U Brown yellow 1:3 U Chrom yellow	1:1 U Dark brown 1:1 (−34.0) Dark brown 1:1 U Brown red 1:1 (12.0) Brown red 1:1 U Light brown

**** The present writer devised an effective separation by adding α -naphthylamine or naphthol to the nitrated mixture of Sirks (*Rec. trav. chim.*, **27** (1908), 211.) in order to form a molecular compound only with the 2,5-dinitro isomer. The molecular compound, which easily crystallised, was filtered, and decomposed with acid or with ammonia according as whether naphthol or naphthylamine was used.

- (a) Variety of substituent: $\text{NH}_2 > \text{OH} > (\text{H}), \text{OCH}_3, \text{CH}_3$,
 (b) Position of substituent: α -position $>$ β -position (in naphthalene derivatives), o - or p -position $>$ m -position (in benzene derivatives).

In the nitro component with three substituents, this rule still seemed to hold, for example, *sym*-trinitrobenzene was less halochromic than the *vic*- or *asym*-isomer, presumably because of the meta position of the three nitro radicals in the former. Of the six isomers of dinitrophenol, the 2,3- or 2,5-compound having two nitro radicals in ortho or para position, and the nitro and hydroxyl radicals in ortho position, showed the most powerful halochromy, while the 3,5-compound, which has all the substituents in meta position, was the least halochromic. The 2,6- and 3,5-dinitrophenols with naphthylamines, which formed a less halochromic compounds than the *m*-dinitrobenzene, notwithstanding the presence of the hydroxyl radical, were found to be another type of molecular compound, as already shown (with 2,6-dinitrophenol and its derivatives) by Hertel⁽⁷⁾.

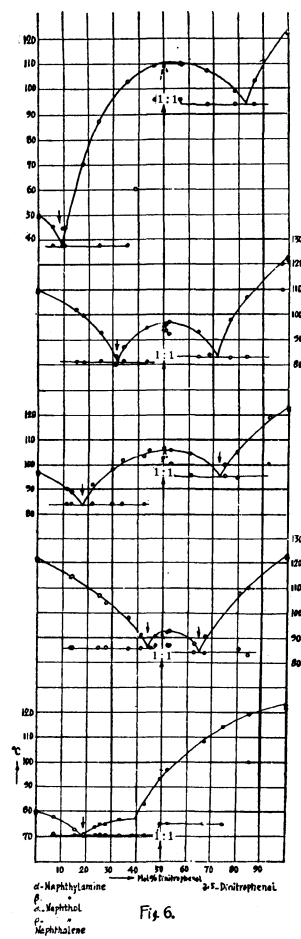
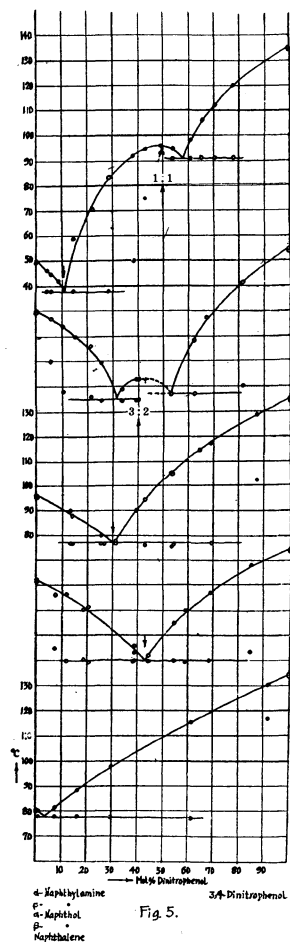
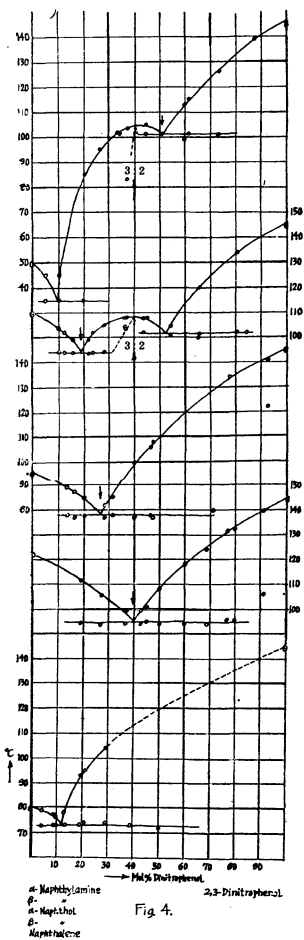
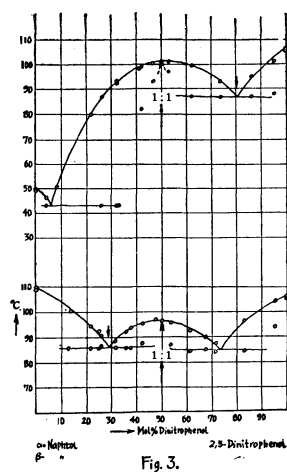
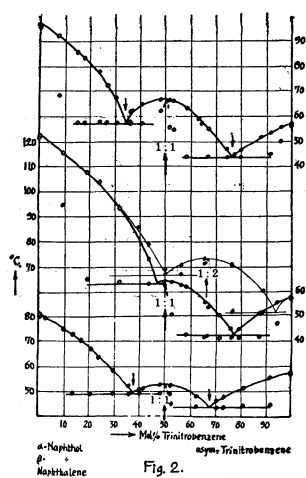
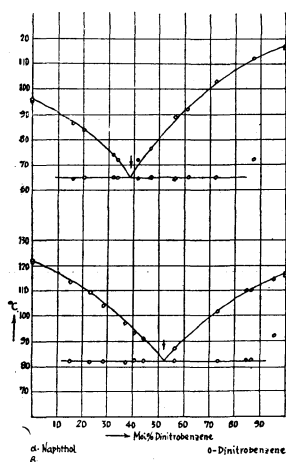
Experimental.

(1) α -Naphthol—*o*-dinitrobenzene (Fig. 1).

Dinitrobenzene: 8.0 mg.

Mol% dinitrobenzene	100.0	87.4	72.5	56.4	41.9	32.0	20.4
Melting point	117.0	112.0	103.0	89.0	72.0	74.0	84.0
Thawing point	116.0	72.0	65.0	64.0	64.5	65.2	65.0
Naphthol: 6.7 mg.							
Mol% naphthol	83.9	66.2	53.1	38.3			
Melting point	86.5	72.0	76.3	92.0			
Thawing point	64.5	65.0	65.0	65.0			

Eutectic point: 64.5°, 61.8 mol% α -naphthol.



(2) β -Naphthol—*o*-dinitrobenzene (Fig. 1).

Dinitrobenzene: 12.0 mg.

Mol% dinitrobenzene	84.4	59.2	40.5	23.0
Melting point	110.5	92.5	93.0	109.5
Thawing point	82.5	82.5	82.3	82.0

Dinitrobenzene: 9.8 mg.

Mol% dinitrobenzene	95.4	86.6	73.1	56.4	44.0	37.0	28.3	15.1
Melting point	114.5	110.0	101.5	87.0	91.0	97.0	104.0	113.5
Thawing point	92.0	82.5	81.8	82.0	82.0	81.8	82.0	82.0

Eutectic point: 82.0°, 48.0 mol% β -naphthol.

In the binary systems of *o*-dinitrobenzene, remarkable halochromic phenomenon was seen in the liquid state, which, however, vanished on solidification.

(3) α -Naphthol—*asym*-trinitrobenzene.

Trinitrobenzene: 9.5 mg.

Mol% trinitrobenzene	95.6	87.7	77.2	64.1	53.0	48.2	40.3	35.4	30.0	23.2	17.3
Melting point	55.8	52.0	45.0	57.0	66.0	66.5	64.8	62.0	67.0	77.3	83.0
Thawing point	50.0	—	—	—	54.5	62.0	57.0	57.8	57.0	57.5	57.0

Trinitrobenzene: 2.0 mg.

Mol% trinitrobenzene	100.0	77.2	62.8	51.0	36.0	26.2	14.8	7.4
Melting point	57.0	45.5	59.0	66.0	62.0	72.0	85.5	92.0
Thawing point	56.0	—	—	55.0	57.0	57.0	57.0	68.0

Trinitrobenzene: 4.7 mg.

Mol% trinitrobenzene	91.7	79.8	74.1	66.5	53.0
Melting point	53.5	46.5	47.2	55.0	63.0
Thawing point	45.0	43.5	43.7	43.8	43.8

Eutectic point: 57.0°, 43.7°; 66.5 mol%, 24.0 mol% α -naphthol.

Compound (1:1): brown red powder, melting at 67.0°.

(4) β -Naphthol—*asym*-trinitrobenzene.

Trinitrobenzene: 2.3 mg.

Mol% trinitrobenzene	72.0	58.4	52.7	39.3	24.1	9.5
Melting point	50.5	61.5	63.0	(85.0)	103.2	115.2
Thawing point	41.0	42.0	50.0	—	—	94.0

Trinitrobenzene: 9.7 mg.

Mol% trinitrobenzene	88.9	76.5	65.8	56.3	49.8 ⁽⁸⁾	43.2	32.0	19.1
Melting point	49.5	45.0	55.0	62.0	63.5	72.0	92.5	107.5
	(60.0)	(70.8)	(73.0)	(70.0)	(68.5)	(78.0)		
Thawing point	—	41.0	41.0	—	62.5	62.0	63.0	64.0
	(51.0)	(51.5)	(71.0)	(66.5)	(66.5)			

Trinitrobenzene: 5.1 mg.

Mol% trinitrobenzene	94.5	87.5	79.3	67.0
Melting point	55.0	51.0	45.0	53.0
Thawing point	46.5	41.5	41.0	42.0

In the stable system,

Eutectic point: 62.5°, 42.0°; 52.5 mol%, 22.8 mol% β -naphthol.

Compound (1:1) orange red powder, melting at 63.5°.

In the metastable system,

Eutectic point 66.5°, 51.0°; 49.2 mol%, 6.0 mol% β -naphthol.

Compound (1:2) brown red crystals, melting at 73.0°.

(5) Naphthalene—*asym*-trinitrobenzene.

Trinitrobenzene: 2.0 mg.

Mol% trinitrobenzene	70.3	52.3	41.4	23.6	16.7	9.1	2.4
Melting point	46.0	—	50.8	63.0	70.0	74.5	79.0
Thawing point	43.5	44.5	—	—	—	—	—

(8) At 63.5° the compound crystal disappeared, and upon stirring, the fused liquid soon solidified again to a more coloured mass, the thawing and melting points of which were 66.5° and 68.5° respectively.

Trinitrobenzene: 13.1 mg.

Mol% trinitrobenzene	91.8	80.6	73.0	62.1	52.2	48.1	39.7	35.4	29.2	20.6	13.1
Melting point	55.0	51.0	47.5	48.0	52.0	52.5	50.5	52.0	58.0	67.0	72.5
Thawing point	44.5	44.0	43.0	43.5	48.5	49.0	49.0	48.8	49.0	49.0	49.0

Eutectic point: 49.0°, 43.5°; 62.7 mol%, 32.8 mol% naphthalene.

Compound (1:1): yellow powder, melting at 52.5°.

Three systems of *asym*-trinitrobenzene are given in Fig. 2. The order of solubility of trinitrobenzene in naphthalene and naphthols did not quite agree with that of the value τ . In the diagram of β -naphthol—trinitrobenzene, a metastable compound (1:2) was once found by keeping the fused liquid for a long time above its melting point ⁽⁸⁾.

(6) α -Naphthylamine—2,5-dinitrophenol (Fig. 3).

Dinitrophenol: 8.1 mg.

Mol% dinitrophenol	95.4	86.3	74.0	62.3	53.0	47.0	41.5	32.6	22.3
Melting point	101.0	95.0	93.0	99.5	101.0	100.0	98.0	92.0	80.0
Thawing point	88.0	87.0	86.5	87.0	97.0	93.0	—	43.0	—

Naphthylamine: 9.8 mg.

Mol% naphthylamine	95.4	91.4	73.3	67.5	57.6	39.4
Melting point	46.3	51.0	87.0	93.5	99.0	101.0
Thawing point	43.0	—	43.0	43.0	70.0	100.0

Eutectic point: 43.0°, 87.0°; 93.5 mol%, 19.5 mol% α -naphthylamine.

Compound (1:1): long black needles, melting at 101.0°.

(7) β -Naphthylamine—2,5-dinitrophenol (Fig. 3).

Dinitrophenol: 4.3 mg.

Mol% dinitrophenol	67.6	47.5	35.8	24.8	12.3
Melting point	90.0	97.0	92.5	93.0	—
Thawing point	85.0	—	86.0	86.0	86.0

Dinitrophenol: 8.2 mg.

Mol% dinitrophenol	95.5	83.2	71.8	61.4	53.7	50.3	42.6	37.6	31.2	25.4	21.3	13.9
Melting point	104.0	96.5	87.8	92.5	95.5	96.2	95.5	94.0	89.0	91.0	95.0	101.0
Thawing point	94.0	84.0	84.0	84.5	87.0	94.0	88.0	86.0	86.5	87.0	86.0	86.0

Eutectic point: 86.0°, 85.0°; 70.8 mol%, 16.5 mol% β -naphthylamine.

Compound (1:1): black prisms or needles, melting at 96.5°.

2,5-Dinitrophenol forms a stable molecular compound with naphthalene and its derivatives.

(8) α -Naphthylamine—2,3-dinitrophenol.

Dinitrophenol: 5.2 mg.

Mol% dinitrophenol	100.0	87.0	59.9	34.8	20.6
Melting point	145.0	139.0	113.0	101.0	85.0
Thawing point	144.0	—	99.0	—	35.0

Dinitrophenol: 5.3 mg.

Mol% dinitrophenol	73.3	61.3	50.7	44.7	37.4	33.2	26.4	10.6	5.7
Melting point	126.0	115.0	101.0	105.0	103.0	101.5	95.0	45.0	44.5
Thawing point	101.0	101.0	101.0	101.0	83.0	—	—	35.0	35.0

Eutectic point: 35.0°, 101.0°; 90.0 mol%, 49.3 mol% α -naphthylamine.

Compound (3:2): black powder, melting at 105.0°.

(9) β -Naphthylamine—2,3-dinitrophenol.

Dinitrophenol: 7.5 mg.

Mol% dinitrophenol	83.9	65.3	45.1	36.4	23.7	15.8	10.3
Melting point	—	—	108.0	108.0	102.0	99.0	104.0
Thawing point	102.0	100.0	—	104.5	94.0	94.0	94.0

Dinitrophenol: 6.0 mg.

Mol% dinitrophenol	80.9	66.0	54.5	43.7	36.7	28.1	22.1	12.2
Melting point	134.0	120.2	104.5	107.8	108.0	105.0	99.3	102.0
Thawing point	102.0	101.5	101.0	102.0	103.5	94.0	93.5	94.0

Eutectic point: 94.0°, 101.5°; 80.5 mol%, 47.0 mol% β -naphthylamine.

Compound (3:2): black needles or powder, melting at 108.0°.

(10) α -Naphthol—2,3-dinitrophenol.

Dinitrophenol: 6.8 mg.

Mol% dinitrophenol	92.9	78.0	47.8	40.0	28.6	16.4
Melting point	140.5	134.0	108.0	100.0	82.0	87.0
Thawing point	122.0	92.0	77.0	77.0	77.0	77.0

Dinitrophenol: 5.4 mg.

Mol% dinitrophenol	71.4	46.4	31.8	20.1	13.8
Melting point	—	106.0	85.0	86.0	89.0
Thawing point	80.0	78.0	78.0	78.0	78.0

Eutectic point: 78.0°, 73.0 mol% α -naphthol.(11) β -Naphthol—2,5-dinitrophenol.

Dinitrophenol: 5.0 mg.

Mol% dinitrophenol	76.6	44.4	27.0	15.8
Melting point	132.0	101.0	105.0	112.0
Thawing point	96.0	95.0	96.0	96.0

Dinitrophenol: 12.4 mg.

Mol% dinitrophenol	90.6	79.5	68.3	59.9	49.8	42.2	35.4	26.7	18.7
Melting point	140.0	132.5	124.0	118.0	108.0	99.5	99.5	105.5	110.8
Thawing point	106.0	95.8	94.0	94.0	94.0	94.0	94.0	93.8	94.5

Eutectic point: 95.0°, 60.3 mol% β -naphthol.

(12) Naphthalene—2,3-dinitrophenol.

Dinitrophenol: 3.8 mg.

Mol% dinitrophenol	76.6	50.5	39.2	19.6	10.0	4.4
Melting point	—	—	—	93.0	76.0	79.0
Thawing point	100.0	72.0	73.0	73.0	73.0	73.0

Dinitrophenol: 4.6 mg.

Mol% dinitrophenol	29.3	21.1	13.3	9.0
Melting point	104.0	95.0	78.0	77.5
Thawing point	74.0	74.0	73.0	73.0

Eutectic point: 73.0°, 87.7 mol% naphthalene.

Owing to the considerable sublimation of naphthalene, melting points above 100° could not be observed.

Six diagrams of 2,3-dinitrophenol are shown in Fig. 5.

(13) α -Naphthylamine—3,4-dinitrophenol.

Dinitrophenol: 4.4 mg.

Mol% dinitrophenol	100.0	14.6	6.1
Melting point	134.5	59.0	45.0
Thawing point	133.5	38.0	38.0

Naphthylamine: 10.0 mg.

Mol% naphthyl- amine	95.5	90.9	78.6	71.2	62.9	56.8	50.7	45.7	38.9	34.5	29.2	22.0
Melting point	46.3	42.0	71.0	83.5	92.0	94.8	96.0	95.0	98.0	106.0	112.0	120.0
Thawing point	38.0	—	viscous	38.0	50.0	75.0	93.0	91.0	91.0	91.0	91.0	91.0

Eutectic point: 38.0°, 91.0°; 88.8 mol%, 41.8 mol% α -naphthylamine.

Compound (1:1): yellowish brown powder, melting at 96.0°.

(14) β -Naphthylamine—3,4-dinitrophenol.

Dinitrophenol: 4.0 mg.

Mol% dinitrophenol	81.4	67.2	49.9	40.2	21.4	10.4
Melting point	121.5	107.5	viscous	83.0	96.0	104.0
Thawing point	80.0	—	viscous	75.0	76.0	78.0

Naphthylamine: 9.8 mg.

Mol% naphthylamine	94.0	84.6	74.6	66.1	60.1	53.7	46.8	37.6
Melting point	107.0	99.5	89.0	79.0	83.0	viscous	77.0	98.5
Thawing point	90.0	—	74.7	74.5	74.3	viscous	—	77.0

Eutectic point: 75.0°, 77.0°; 68.6 mol%, 47.0 mol% β -naphthylamine.

Compound (3:2): yellowish brown prisms, melting at 83.0°.

In this system, the compound crystal was obtained, although with difficulty, by rubbing the viscous liquid at 50–60° with the thermometer inserted, but in the range of 47–59 mol% of β -naphthylamine, neither rubbing nor seeding had any effect.

(15) α -Naphthol—3,4-dinitrophenol.

Dinitrophenol: 3.4 mg.							
Mol% dinitrophenol	86.8	64.0	52.6	39.5	26.9	13.2	
Melting point	128.5	114.5	105.5	90.0	—	90.0	
Thawing point	102.0	—	75.5	—	77.0	77.0	
Naphthol: 6.8 mg.							
				↓			
Mol% naphthol	86.1	74.4	69.0	57.2	46.7	31.2	
Melting point	88.0	80.0	78.0	94.0	105.0	117.0	
Thawing point	77.0	77.0	77.0	76.0	76.0	77.0	

Eutectic point: 77.0°, 69.3 mol% α -naphthol.(16) β -Naphthol—3,4-dinitrophenol.

Dinitrophenol: 5.6 mg.							
Mol% dinitrophenol	84.4	58.6	38.6	20.4	11.7		
Melting point	128.5	110.0	96.0	111.5	116.5		
Thawing point	93.5	89.5	90.0	89.0	90.0		
Naphthol: 5.1 mg.							
Mol% naphthol	92.7	81.2	61.4	55.7	45.5	31.5	
Melting point	116.0	110.0	93.0	92.2	105.0	117.0	
Thawing point	95.0	90.5	89.8	89.8	90.0	90.0	

Eutectic point: 90.0°, 57.2 mol% β -naphthol.

(17) Naphthalene—3,4-dinitrophenol.

Naphthalene (mg.)	101.0	12.0	19.6	13.0	10.0	3.5	
Mol% naphthalene	99.3	92.5	83.4	70.0	38.5	8.4	
Melting point	80.0	81.0	88.0	97.5	115.5	130.0	
Thawing point	77.5	77.5	77.5	77.5	77.0	117.0	

Eutectic point: 77.5°, 96.3 mol% naphthalene.

In order to avoid considerable loss of naphthalene by sublimation, this system was observed by the capillary method.

Six diagrams of 3,4-dinitrophenol are shown in Fig. 4. They resemble somewhat the diagrams of 2,3-dinitrophenol. The solubility curve of dinitrophenol in α -naphthylamine and in α -naphthol almost agrees with that in the β -isomer.

(18) α -Naphthylamine—3,5-dinitrophenol.

Dinitrophenol: 8.0 mg.							
Mol% dinitrophenol	100.0	78.5	56.9	46.3	35.1	24.0	10.1
Melting point	123.0	99.0	110.0	109.0	103.0	87.0	55.0
Thawing point	121.5	94.0	96.0	96.0	38.0	38.0	38.0
Dinitrophenol: 4.0 mg.							
Mol% dinitrophenol	86.1	67.4	57.4	38.3	17.4	9.4	5.6
Melting point	103.0	107.5	109.5	—	70.0	45.0	46.0
Thawing point	94.0	94.0	103.0	60.0	—	38.0	38.0

Eutectic point: 38.0°, 94.0°; 91.1 mol%, 17.2 mol% α -naphthylamine.

Compound (1:1): brownish yellow needles, melting at 110.5°.

(19) β -Naphthylamine—3,5-dinitrophenol.

Dinitrophenol: 6.6 mg.							
Mol% dinitrophenol	77.3	64.8	52.7	43.7	34.6	25.5	15.7
Melting point	98.0	93.0	97.0	94.5	87.0	93.0	102.0
Thawing point	82.5	83.0	92.0	81.0	81.5	82.0	81.0
Dinitrophenol: 10.0 mg.							
Mol% dinitrophenol	98.0	83.9	69.2	51.8	31.4	18.5	
Melting point	120.0	107.0	—	97.0	83.3	100.0	
Thawing point	110.0	83.0	84.0	93.0	80.0	81.0	

Eutectic point: 81.0°, 83.0°; 68.0 mol%, 28.0 mol% β -naphthylamine.

Compound (1:1): orange yellow needles or powder, melting at 97.0°.

The above two molecular compounds of naphthylamines crystallised with some difficulty, another metastable compounds occasionally forming.

(20) α -Naphthol—3,5-dinitrophenol.

Dinitrophenol: 6.0 mg.

Mol% dinitrophenol	92.1	74.8	49.9	43.9	33.5	21.8	11.6
Melting point	119.0	100.0	106.0	105.0	101.0	91.0	89.0
Thawing point	100.0	95.0	102.0	100.0	83.0	83.0	83.0

Dinitrophenol: 5.0 mg.

Mol% dinitrophenol	79.8	61.0	52.8	42.0	29.8	13.5
Melting point	105.0	104.0	105.0	102.5	97.0	88.0
	(70.0)					
Thawing point	94.0	95.3	99.8	83.0	83.0	83.0

Eutectic point: 83.0°, 95.0°; 82.3 mol%, 27.2 mol% α -naphthol.

Compound (1:1): yellowish orange needles, melting at 107.0°.

(21) β -Naphthol—3,5-dinitrophenol.

Dinitrophenol: 7.1 mg.

Mol% dinitrophenol	81.0	53.6	45.7	35.6	24.6	14.0
Melting point	108.0	93.0	—	98.0	107.0	115.0
Thawing point	86.0	87.0	86.0	85.5	86.0	86.0
	(40)					

Dinitrophenol: 7.1 mg.

Mol% dinitrophenol	84.8	67.2	63.5	52.6	47.2	41.4	27.3	13.9
Melting point	110.0	91.0	88.0	92.5	90.5	91.5	104.0	114.5
Thawing point	83.0	84.0	84.0	87.0	87.0	86.0	86.0	86.0

Eutectic point: 86.0°, 84.0°; 55.3 mol%, 34.5 mol% β -naphthol.

Compound (1:1): orange yellow needles, melting at 93.0°.

(22) Naphthalene—3,5-dinitrophenol.

Dinitrophenol: 7.3 mg.

Mol% dinitrophenol	74.9	49.4	25.7	15.5	7.0
Melting point	114.0	93.0	75.0	—	78.0
Thawing point	75.0	75.0	71.0	70.5	71.0
	(51.0)				

Dinitrophenol: 8.3 mg.

Mol% dinitrophenol	85.2	67.3	52.6
Melting point	119.0	108.0	97.0
Thawing point	100.0	75.0	75.0

Dinitrophenol: 10.4 mg.

Mol% dinitrophenol	43.4	38.6	33.1	27.9	23.9	19.1	15.8
Melting point	83.0	—	77.0	75.0	74.0	71.0	73.0
Thawing point	70.5	70.5	70.5	70.5	70.5	70.5	70.5

Eutectic point: 70.5°, 81.2° mol% naphthalene.

Peritectic point: 77.0°, 60.5 mol% naphthalene.

Compound (1:1): light yellow needles with an incongruent melting point.

Six diagrams of 3,5-dinitrophenol are given in Fig. 6. The crystalline molecular compound was found in every case, although its crystallisation velocity was not great. Sometimes another metastable state was observed.

Summary.

The molecular compounds of various nitrobenenes with naphthylamines, naphthols, and naphthalene were systematically compared and the compound formations discussed by means of solid—liquid phase diagrams.

The writer wishes to express his sincere thanks to Prof. B. Kubota of the Tokyo Imperial University for his kind guidance and encouragement throughout this study and to Dr. T. Asahina for his valuable advices. Thanks are also due to the Hattori-Hokokai for the grant, with the aid of which the expenses of the study were defrayed.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.
Kumamoto Higher Technical School.*

Properties of Cobalt Oxide as an Active Material of Negative Electrode in Alkaline Storage Cell.

By Kyôji KINOSHITA.

(Received February 26, 1940.)

The author has reported previously, that the electrode plates of the alkaline storage cell could be made by using the metallic oxides such as silver oxide,⁽¹⁾ bismuth oxide,⁽²⁾ and mercury oxide,⁽³⁾ in the pasted form.

It was found recently, that cobalt oxide can be made into the negative electrode plate of the alkaline storage cell in the pasted form, just like other metallic oxides mentioned above. The present paper describes the results of the experiments dealt with cobalt oxide.

(1) **Experimental.** (a) *Preparation of the cobalt oxide.* Three kinds of the oxides of cobalt having the compositions, CoO , Co_2O_3 and Co_3O_4 are known. In preparing the electrode plate in the pasted form, it becomes a matter of question that, which oxide out of these three should be chosen as the material of the paste.

In the preparation of the electrode plate of the lead acid storage cell, oxides such as Pb_2O (lead suboxide), and PbO (litherge) are preferred as the material of the paste, and the oxide of higher degree of oxidation seemed to lack cohesive power to be used as the material for the paste. From the analogy of this fact CoO , which is low in degree of oxidation, was chosen as the cobalt oxide for the experimental purposes.

The CoO which was used for the experiments was prepared by heating pure CoCO_3 in an electric furnace under the reduced atmospheric pressure to red heat and decomposing CoCO_3 by the reaction of



Changes in weight in the course of above reaction show that, the above mentioned decomposing reaction proceeds stoichiometrically. In this manner an oxide of greenish brown in colour could be obtained.

(b) *Experiments on the electrode plates in the pasted form.* CoO thus prepared was made into paste mixing with 5N NH_4OH , or 5N NH_4Cl , and then the paste was applied to the grid made of silver plated lead antimony alloy. The size of the grid used was about 6.0 cm. $\times$ 1.5 cm. $\times$ 0.3 cm.. As the pasting liquid, solution of NH_4Cl seemed to be more suitable than NH_4OH , because the cohesion of the cobaltous oxide paste was found to be excellent in this case.

The plate which had been applied with the paste of cobaltous oxide by the above method was negatively electrolyzed in 20% KOH solution

(1) K. Kinoshita, this Bulletin, **12**, (1937), 164, 366.

(2) K. Kinoshita, *ibid.*, **15**, (1940), 59.

(3) K. Kinoshita, *ibid.*, **15**, (1940), 82.

and was converted into the negative electrode plate of the alkaline storage cell (process of "formation").

That is, the "formation" was undertaken by the current of 50 milliamperes in 20% KOH solution. But with the starting of the "formation" violent evolution of gas was observed at the electrode, thereby it was supposed that the progress of the electrolytical reducing reaction of the active material at the electrode do not proceed properly.

The "formation" process was continued for about 30 hours and then the electrode plate thus formed was combined with positive electrode plate of Nife alkaline accumulator, and dipped in 20% KOH solution. The open voltage of the cell was found to be 1.564 volts, but when the discharge was started by the discharge current of 200 milliamperes the terminal voltage fell to about 1.1 volts and in 30 minutes it reached zero volt, that is, its discharge capacity was 0.1 amperehours. Then after a full overcharge by the charge current of 200 milliamperes, the cell was discharged by the discharge current of 200 milliamperes. This time its discharge capacity was found to be 0.074 amperehours.

It was thought, from the above results, that the active material which consists of CoO alone seemed wanting in electrolytical reversible nature to be used as an active material in storage cell. The fact that the violent evolution of gas in the process of "formation" may be accounted for as one evidence of this. The poor electrical conductivity of the oxide may be the principal cause of this irreversible nature.

In order to improve the electrical conductivity, therefore, a little amount of graphite powder was added to CoO. The cobalt oxide, CoO, which was produced by the thermal decomposition of CoCO_3 was mixed with graphite powder amounting 20 to 30%, and was made into paste with 5 N NH_4Cl solution, and then finished into two electrode plates. The constitutions of these two plates are shown in Table 1.

Table 1.

Number of electrode plate	Constitution of paste (amount of graphite) %	Amount of paste applied to grids (in grams)	Amount of CoO applied to grids <i>w</i> (in grams)
1	20	3.71	2.97
2	30	3.87	2.72

The "formation" of these plates were undertaken in 20% KOH solution by the current of 100 milliamperes for about 70 hours. Immediately after the "formation" the plates were combined with the positive electrode plates of Nife accumulator and subjected to discharge by the current of 100 milliamperes for five times in 20% KOH solution. The results of experiments are shown in Table 2.

As seen in Table 2, the discharge capacity C of cell No. 1 at any cycles of discharge gradually decreases from the value of C in preceding cycle. The discharge capacity of cell No. 2 does not fall so markedly.

In the case of cell No. 1 appreciable amount of the active material fell off from the surface of the electrode plate, in the course of charges

Table 2.

Number of discharge n	Discharge current milli-amperes	Number of electrode plate			
		No. 1		No. 2	
		Discharge hour in hours	Discharge capacity C in ampere hours	Discharge hour in hours	Discharge capacity C in ampere hours
1	100	5.500	0.550	4.000	0.400
2	100	5.083	0.508	3.500	0.350
3	100	4.433	0.443	3.000	0.300
4	100	3.733	0.373	3.000	0.300
5	100	2.250	0.225	3.250	0.325

and discharges. In the cell No. 2 the active material fell off more or less, though not so much.

The discharge characteristic curves of the storage cell No. 1 are shown in Fig. 1.

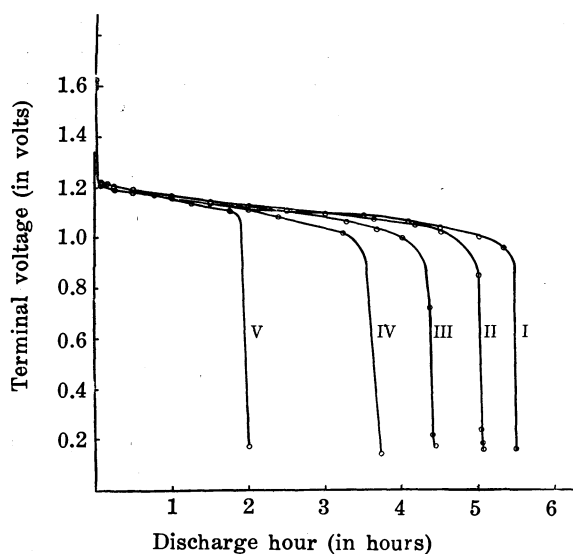


Fig. 1. Discharge characteristic curves of the cell No. 1. Numbers I, II,—V, correspond to the number of cycles.

Similar discharge characteristic curves can be obtained in the case of cell No. 2. The open voltage of the cell was about 1.5 volts or 1.6 volts. When discharged by the current of 100 milliamperes, the current density being about 5.5 milliamperes/cm², the terminal voltage lowered at first to about 1.2 volts, then kept on decreasing gradually, and then it dropped rather abruptly to zero volt at the last period of the discharge.

The type of this discharge characteristic curve is analogous in form to that of the lead acid storage cell, and it is noteworthy that the terminal voltage of cobaltous

oxide cell is found to be comparatively high as an alkaline storage cell.

Table 3 shows the discharge capacity per one gram of cobaltous oxide (C/w) which has been applied to grids.

(c) *Experiments on the plates in the pocketed form.* As described in the preceding paragraph the author has succeeded in making the electrode plates of alkaline storage cell with CoO, in the pasted form,

Table 3.

Number of discharge <i>n</i>	Discharge current milliamperes	Number of electrode plate	
		No. 1	No. 2
		Capacity per one gram of CoO	Capacity per one gram of CoO
		C/w in $\frac{\text{milliampere hour}}{\text{gram}}$	C/w in $\frac{\text{milliampere hour}}{\text{gram}}$
1	100	185	147
2	100	171	129
3	100	149	110
4	100	126	110
5	100	76	120

but the discharge capacities of the electrode plates thus prepared tended to decrease gradually. This tendency seemed to arise from the falling off of the active material. Therefore, the similar experiment was undertaken with an electrode which was prepared in the pocketed form.

The mechanical structure of the ordinary pocketed type electrode plate of alkaline accumulator is very complicated and is very difficult to reproduce in a laboratory, thereupon the author made use of the positive pocket of the Nife accumulator.

The positive pocket of the Nife alkaline accumulator was taken away from the electrode plate, and the active material packed in it was thoroughly removed, and then rinsed well. Then the mixture of CoO and graphite (percentage of graphite being 20) was sealed in an above cited empty tube, and made into electrode plate. Two electrode plates were thus prepared the constitution of which being as follow.

Number of plate	Amount of active material packed in (grams)	Amount of graphite %	Amount of CoO. (<i>w</i>) (grams)
A	8.96	20	7.17
B	8.82		7.06

The "formation" was undertaken by the current of 100 milliamperes for 59 hours in the case of No. A, and the same current for 35 hours in the case of No. B. The electrode plates A and B were combined with the positive electrode plates of Nife alkaline accumulator and dipped in 20% KOH solution, and then were subjected to discharges for nine cycles. Tables 4 shows the results of the experiments.

Cell A was discharged, in the second cycle, by the current of 100 milliamperes for 7 hours and then discharged again by the current of 200 milliamperes for 52 minutes, while cell B was discharged throughout by the current of 100 milliamperes. In the ninth cycle, both cells were discharged by the current of 160 milliamperes. In other cycles both cells were discharged by the current of 150 milliamperes and charged by the current of 100 milliamperes for about 18 hours.

Table 4.

Number of discharge n	Discharge current milli-amperes	Number of electrode plate			
		A		B	
		Time of Discharge hour (in hours)	Discharge capacity C in ampere hours	Discharge hour (in hours)	Discharge capacity C in ampere hours
1	150	5.450	0.818	3.700	0.555
2	100~200	7.866	0.873	5.700	0.570
3	150	5.900	0.885	3.500	0.525
4	150	6.183	0.936	3.333	0.500
5	150	5.833	0.875	3.166	0.475
6	150	5.916	0.887	2.800	0.420
7	150	5.883	0.882	2.666	0.400
8	150	6.100	0.915	2.883	0.433
9	160	5.400	0.854	2.633	0.421

As shown in Table 4 the value of C differs considerably notwithstanding the value of w is almost equal in both electrode A and B. This seems to have its cause in the fact that it is difficult to make the electrode plates in the pocketed form of the same conditions. Probably some insignificant difference in conditions in preparing the electrode plate, such as difference of compressed condition of active material or the different condition of "formation" may leave serious influence upon the discharge capacity of the electrode. Though there is a considerable difference in the value of C between the cell A and B, it does not vary so much according to the number of discharge in one cell.

With respect to the electrode A and B the discharge capacity per one gram of CoO (C/w) is calculated and tabulated in Table 5.

Table 5.

Number of discharge n	Discharge current milliamperes	Number of electrode plates	
		A	B
		Capacity per one gram of CoO C/w in $\frac{\text{milliampere hour}}{\text{gram}}$	Capacity per one gram of CoO C/w in $\frac{\text{milliampere hour}}{\text{gram}}$
1	150	114	79
2	100~200	122	81
3	150	124	74
4	150	131	71
5	150	122	67
6	150	124	59
7	150	123	52
8	150	128	61
9	160	119	60

The discharge characteristic curve is very similar to that which was shown in the case of the plates in the pasted form. The open voltage before the discharge was about 1.5 volts or 1.6 volts, then lowered to about 1.2 volts in the first period of discharge, and then it falls continuously in the vicinity of 1.1 volts and finally reaches the nearly zero voltage showing the end of discharge. After the sudden fall of the terminal voltage at the end of discharge, the lowering seemed to stop for a while at the point of about 0.3 volts and show a uniform voltage for a time, but this point was not touched in this experiment.

(2) **Conclusions.** The negative electrode plate of the alkaline storage cell can be prepared with CoO both in pasted and in pocketed forms.

Considerable discharge capacity can be obtained from these electrode plates, when combined with the positive electrode plate of Nife alkaline accumulator and dipped in 20% KOH solution.

The discharge characteristic curve shows about 1.5 volts in the open condition before the discharge, and during the discharge (the discharge current density being about 5.5 milliamperes/cm.²)⁽⁴⁾ it shows an average voltage of about 1.1 volts, and falls gradually, and then at last ends in the sudden fall of the terminal voltage.

In conclusion the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University, for his valuable advice on these experiments.

*Toyoda Research Laboratory,
Imperial Invention Society,
Shimomeguro Tokyo.*

(4) In the experiments on the plates in the pocketed form, material for calculating the exact current density are lacking. But it is considered to be nearly the same as that in the case of pasted form.

Lead Content of the Hot Springs of Japan.

By Kazuo KURODA.

(Received March 12, 1940.)

The lead content of the hot springs of Japan was determined and it was found that some of the hot springs showed fairly high content of lead.

Methods of Analysis. For the determination of lead in the mineral springs, the following methods were adopted.

(a) *Dithizone-Polarographic Method.* Ammonium citrate is added to a suitable quantity (500 to 1000 ml.) of the mineral water, adjust

to pH 8.5 with ammonium hydroxide (5:95), and shake with successive 10 ml.-portions of the purified carbon tetrachloride solution of diphenylthiocarbazone (dithizone). Wash the combined extracts with ammonium hydroxide (1:1000), run the carbon tetrachloride solution into a separating funnel, and shake with 6 N hydrochloric acid. Add 10 ml. of sodium chloride to the acid solution and evaporate to complete dryness. Dissolve the residue in 0.1 N potassium chloride solution and the total volume is made up to 10 ml. A part of the solution is brought to a small electrolysis vessel, freed from the air by a current of hydrogen, and then polarographically examined. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amounts of lead salt in a solution which is 0.1 N with respect to potassium chloride freed from atmospheric oxygen.

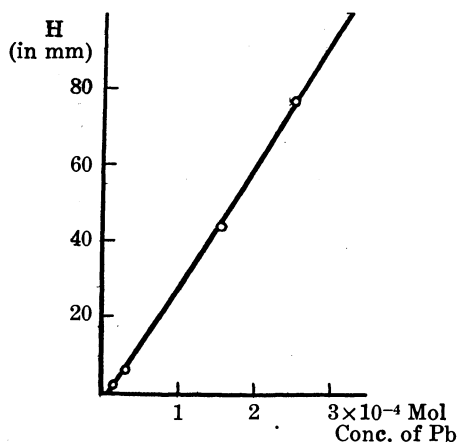


Fig. 1.

(b) *Dithizone Method.* Add 10 ml. of N ammonium citrate solution and 10 ml. of 10% potassium cyanide solution to a suitable quantity (250 ml. to 500 ml.) of the mineral water and render the solution distinctly alkaline with ammonium hydroxide (5:95). Add the purified carbon tetrachloride solution of diphenylthiocarbazone and shake in a separating funnel. Combine the carbon tetrachloride extracts and wash

them with 1% potassium cyanide solution to remove excess of the reagent. Add 6 N hydrochloric acid, shake, and compare the green colour with that obtained with standard lead solution.

The efficacy of the method was tested by adding known amounts of standard lead solution to 500 ml. of water and submitting the solutions to the complete process of extraction and colorimetric determination; the results obtained are shown in Table 1.

Table 1.

Lead added (γ)	Lead found (γ)	Error (γ)
12.0	12.2	+0.2
10.0	10.0	0.0
8.0	7.4	-0.6
6.0	5.9	-0.1

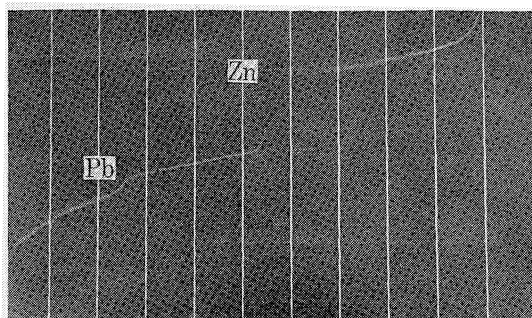


Fig. 2. The "waves" due to lead and zinc in the Monkawa hot spring. 0.1N with respect to KCl. In the hydrogen atmosphere, sensitivity $\frac{1}{2}$, 4V accumulator. Curve starts at E.M.F. = 0.

Results. The results of the determinations of the lead content, mainly of the hot springs of Japan, are collected in Table 2.

Table 2. Lead Content of the Hot Springs of Japan.

No.	Hot Spring	Pb γ /l	% (in total residue)	Method of Analysis
1	Hon-Onsen, Arima, Hyōgo Prefecture.	62.4	0.00037	(b)
2	Katakosi-Yu, Arima, Hyōgo Prefecture.	35.2	0.00015	(b)
3	Mito, Sizuoka Prefecture.	11.4	0.00088	(b)
4	Nanasigure, Iwate Prefecture.	8.0	0.00006	(b)
5	Monkawa, Kanagawa Prefecture.	3.6 7.0	0.00001 0.00002	(b) (a)
6	Yoemon-Yu, Yunohana-zawa, Hakone, Kanagawa Prefecture.	14.0	0.00070	(a)
7	Sea Water, Yosihama.	2.4	0.000007	(b)
8	Tap Water of Tokyo.	4.0	0.0042	(b)

The radium content of the above-mentioned springs was determined by T. Nakai.⁽¹⁾ In the Arima hot spring which showed the highest lead content, fairly much quantity of radium was also found.⁽²⁾ The average lead content of six samples was 22 γ per litre, or 0.00036% of the total residue. The presence of lead in sea water was detected by the dithizone method and the amount was estimated to be 2.4 γ per litre, but the determination by the polarographic method ended in failure.

Summary.

(1) The lead content of a number of hot springs in Japan was estimated by the dithizone method and the dithizone-polarographic method.

(2) The lead content of sea water was estimated.

The author wishes to express his hearty thanks to Prof. Kenjiro 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

(1) *J. Chem. Soc. Japan*, **59** (1938), 1179.

(2) $65-71 \times 10^{-12}$ g Ra/l.

Effect of the Rain on the Composition of the Hot Springs of Yunohanazawa, Hakone.

By Kazuo KURODA.

(Received March 12, 1940.)

In the previous paper,⁽¹⁾ the author reported the seasonal variations of radium, vanadium, chromium and molybdenum contents of the hot springs of Yunohanazawa, Hakone, Kanagawa Prefecture. The author found that it was beyond doubt that there were variations of composition as a result of abundant rain. In the present paper, the author describes the effect of the rain on the composition of the hot springs of Yunohanazawa.

The rainfall, water level, water temperature, *pH*, total residue, acidity, iron, manganese, sulphate and hydrogen sulphide were measured every day for six weeks. The methods of experiment will be briefly described.

(a) *Total residue*. A 100 ml. portion of the mineral water was evaporated to complete dryness, heated to 130°C. and weighed.

(b) *Acidity*. Acidity was determined by titration with standard solution of sodium carbonate using phenol red as the indicator.

(c) *Iron*. A 10 ml. portion of the mineral water was boiled with few drops of nitric acid and the potassium thiocyanate solution was added. The red colour was compared with that obtained with standard iron solution.

(d) *Manganese*. Nitric acid, phosphoric acid and potassium periodate were added to 20 ml. of the mineral water, and boiled for few minutes. The reddish violet colour was compared with that obtained with standard manganese solution.

(e) *Sulphate*. Sulphate was determined colorimetrically using barium chloride and potassium chromate.

(f) *Hydrogen sulphide*. A measured excess of iodine solution was added to the mineral water and titrated back to the end point with thiosulphate.

The results are collected in Table 1 and Table 2.

The results of the observation show that the hot springs of Yunohanazawa are affected strongly by the rainfall and that the salt content increases as a result of abundant rain. The changes of discharge, total residue, iron and sulphate content are noticed immediately after a rain-storm, whereas *pH* and acidity show the maximum values some time later. The changes of manganese and hydrogen sulphide is not so marked as that of iron. The Kōbō-yu spring is affected more strongly by the rainfall than the Gongen-yu spring. The maximum value of discharge and the minimum value of water temperature occurred immediately after heavy rains.

(1) This Bulletin, 15 (1940), 65.

Table 1. Effect of the rain on the composition of the Gongen-Yu spring.

Date	Rain-fall (mm.)	Water-level (cm.)	Temperature (°C.)	pH	Total Residue (g./l.)	Fe (g./l.)	Mn (g./l.)	SO ₄ (g./l.)	Acidity (N)	H ₂ S (g./l.)
July 31	0.2	17	48.5(29.0)	2.65		0.0014	0.0011	0.70	0.011	0.141
Aug. 1	14.2	17	48.8(26.1)	2.7		0.0023	0.0009	0.70	0.012	0.125
2	0.9	17	48.6(23.2)	2.75		0.0011	0.0010	0.71	0.012	0.144
3	8.9	17	49.0(22.0)	2.7		0.0012	0.0009	0.72	0.013	0.158
4	8.0	17	49.0(21.2)	2.75		0.0010	0.0010	0.69	0.013	0.148
5	11.0	17	48.9(20.2)	2.7		0.0010	0.0010	0.72	0.012	0.146
6	17.6	17	49.0(22.1)	2.7		0.0015	0.0010	0.72	0.013	0.132
7	2.45	17	49.0(26.0)	2.75		0.0036	0.0011	0.72	0.012	0.128
8	1.35	17	49.0(24.0)	2.75		0.0014	0.0010	0.71	0.012	0.135
9	0.8	17	49.0(24.0)	2.7		0.0011	0.0011	0.80	0.013	0.134
10	10.1	17	49.0(23.8)	2.75		0.0014	0.0011	0.80	0.011	0.132
11	6.0	17	49.0(24.0)	2.7		0.0016	0.0011	0.69	0.013	0.139
12	1.4	17	49.2(24.0)	2.75		0.0020	0.0010	0.74	0.012	0.146
13	4.0	17	49.0(24.0)	2.75		0.0021	0.0010	0.78	0.012	0.141
14	9.6	17	49.0(24.0)	2.75		0.0009	0.0010	0.76	0.012	0.139
15	2.0	17	49.3(24.0)	2.7		0.0009	0.0010	0.75	0.012	0.138
16	—	17	49.0(22.0)	2.7		0.0006	0.0011	0.75	0.012	0.117
17	—	17	49.0(22.5)	2.75	1.35	0.0012	0.0011	0.76	0.012	0.145
18	74.0	17	49.0(23.0)	2.75	1.32	0.0016	0.0010	0.74	0.013	0.134
19	76.4	17	49.1(19.5)	2.6	—	0.0016	0.0009	0.74	0.013	0.137
20	90.5	26	49.2(19.5)	2.6	1.32	0.0026	0.0009	0.82	0.013	0.141
21	1.5	26	49.6(23.8)	2.6	1.73	0.0009	0.0010	1.12	0.014	0.121
22	0.9	26	50.3(24.8)	2.6	—	0.0097	0.0009	1.14	0.016	0.141
23	—	26	50.5(20.5)	2.6	—	0.0087	0.0009	1.07	0.016	0.142
24	10.0	26	50.8(20.8)	2.55	1.23	0.0078	0.0009	1.07	0.016	0.129
25	4.5	26	50.7(22.0)	2.55	1.31	0.0072	0.0009	1.05	0.016	0.115
26	2.5	26	50.8(20.0)	2.55	—	0.0072	0.0009	1.03	0.017	0.108
27	5.5	27	51.0(21.1)	2.5	1.05	0.0068	0.0010	0.97	0.017	0.117
28	0.8	26	51.0(21.1)	2.5	1.00	0.0059	0.0011	0.89	0.017	0.114
29	6.3	26	51.0(19.2)	2.55		0.0054	0.0011	0.84	0.017	0.138
30	—	25	51.3(21.8)	2.6		0.0043	0.0010	0.84	0.017	0.119
31	—	25	51.4(22.0)	2.6		0.0041	0.0010	0.84	0.016	0.121
Sept. 1	—	25	51.6(21.0)	2.6		0.0034	0.0010	0.82	0.017	0.127
2	—	25	51.6(19.0)	2.6		0.0030	0.0010	0.79	0.016	0.107
3	—	24	51.8(19.2)	2.6		0.0018	0.0011	0.74	0.016	0.100
4	—	23	51.7(19.0)	2.6		0.0017	—	0.74	0.016	0.117
5	—	22	51.6(18.0)	2.6		0.0020	—	0.68	0.016	0.119
6	—	21	51.5(20.5)	2.7		0.0012	—	0.68	0.016	0.116
7	—	21	51.6(22.0)	2.7		0.0015	—	0.68	0.016	0.113
8	7.3	20	51.5(21.0)	2.6		0.0015	—	0.88	0.015	0.127
9	—	19	51.6(20.8)	2.6		0.0023	—	0.94	0.015	0.128

Table 2. Effect of the rain on the composition of the Kôbô-Yu spring.

Date	Rainfall	Discharge in l./min.	Temperature (°C.)	pH	H ₂ S (g./l.)
July 31	0.2		45.5(29.0)	2.8	0.079
Aug. 1	14.2	14.5	45.8(26.1)	2.7	0.079
2	0.9	14.3	45.8(23.2)	2.7	0.078
3	8.9	13.4	45.5(22.0)	2.6	0.080
4	8.0	13.4	45.5(21.2)	2.75	0.081
5	11.0	12.0	45.5(20.2)	2.75	0.078
6	17.6	11.4	45.5(22.1)	2.7	0.082
7	2.45	9.6	45.7(26.0)	2.65	0.072
8	1.35	12.0	45.8(24.0)	2.7	0.062
9	0.8	9.1	45.6(24.0)	2.7	0.068
10	10.1	10.5	45.5(23.8)	2.7	0.065
11	6.0	10.9	45.5(24.0)	2.8	0.065
12	1.4	10.9	45.4(24.0)	2.7	0.074
13	4.0	9.9	45.0(24.0)	2.7	0.068
14	9.6	9.5	45.4(24.0)	2.7	0.076
15	2.0	9.1	45.3(24.0)	2.7	0.063
16	—	8.4	45.1(22.0)	2.7	0.064
17	—	8.0	45.2(22.5)	2.7	0.063
18	74.0	7.6	45.2(22.5)	2.7	0.079
19	76.4	20.8	44.2(19.5)	2.7	0.083
20	90.5	33.4	43.5(19.5)	2.65	0.077
21	1.5	45.6	43.5(23.8)	2.7	0.079
22	0.9	47.5	44.8(24.8)	2.7	0.101
23	—	44.5	45.2(20.5)	2.65	0.104
24	10.0	42.1	45.5(20.8)	2.6	0.093
25	4.5	40.0	45.6(22.0)	2.6	0.092
26	2.5	39.8	46.0(20.0)	2.6	0.091
27	5.5	38.5	46.0(21.1)	2.6	0.086
28	0.8	37.7	46.0(21.1)	2.6	0.094
29	6.3	35.4	46.1(19.2)	2.6	0.093
30	—	31.4	46.3(21.8)	2.6	0.093
31	—	30.2	46.5(22.0)	2.6	0.090
Sept. 1	—	29.3	46.9(21.0)	2.7	0.090
2	—	29.0	47.0(19.0)	2.7	0.089
3	—	28.6	47.0(19.2)	2.7	0.096
4	—	27.8	47.0(19.0)	2.7	0.101
5	—	28.0	47.0(18.0)	2.7	0.110
6	—	27.0	47.0(20.5)	2.7	0.099
7	—	27.8	47.0(22.0)	2.7	0.099
8	7.3	26.4	47.0(21.0)	2.7	0.098
9	—	25.6	47.0(20.8)	2.7	0.106

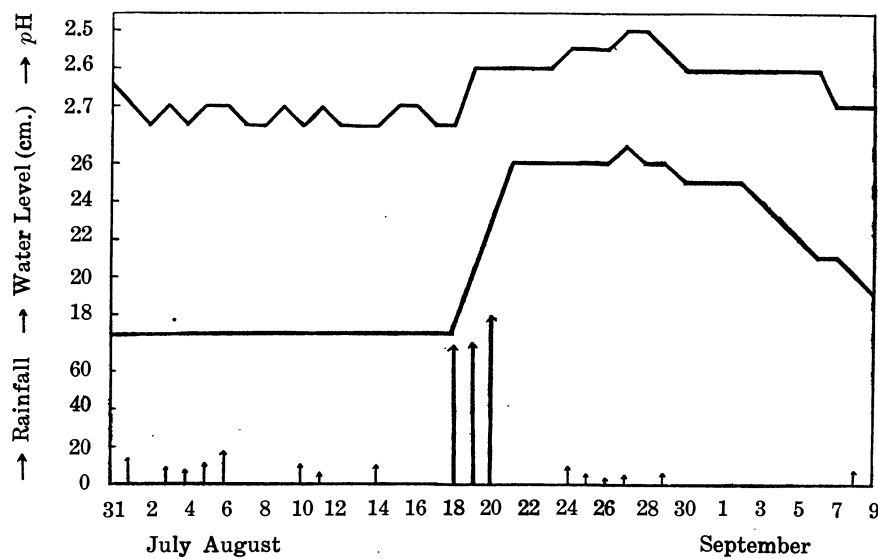


Fig. 1. Effect of the Rain on the Water Level and pH of the Gongen-Yu Spring.

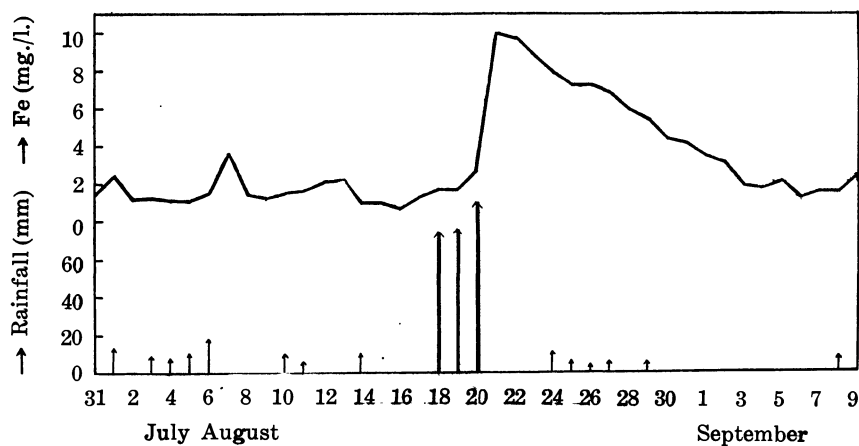


Fig. 2. Effect of the Rain on the Iron Content of the Gongen-Yu Spring.

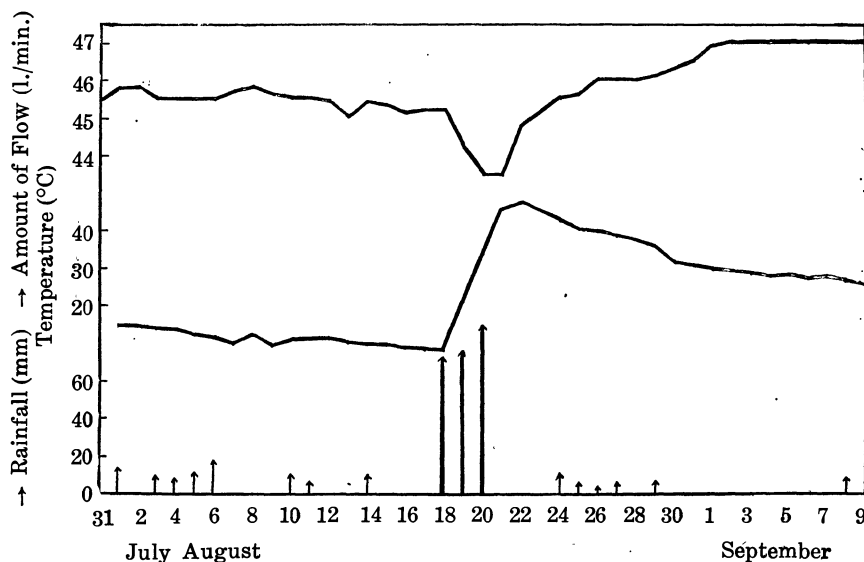


Fig. 3. Effect of the Rain on the Discharge and Temperature of the Kōbō-Yu Spring.

Summary.

The effect of the rain on the composition of the hot springs of Yunohanazawa was studied and it was found that the springs vary in composition according to the amount of rain falling.

The author expresses his hearty thanks to Prof. Kenjiro 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

Recherches sur la concentration des ions d'hydrogène contenus dans les solutions aqueuses des ammines-cobaltiques complexes et sur leurs spectres d'absorption. V. Solutions aqueuses des complexes renfermant le radical oxalique.⁽¹⁾

Par Taku UÉMURA et Naoichi HIRASAWA.

(Reçu le 2 avril 1940.)

Nous avons déjà publié dans un mémoire précédent⁽²⁾ le résultat de nos recherches concernant les onze sels contenant des molécules d'éthylènediamine dans le noyau complexe. Le présent mémoire a le même but que les études déjà exposées il y a quelques années⁽³⁾: faire connaître l'état des sels complexes en solution aqueuse en changeant la concentration des ions d'hydrogène (*pH*). La présente expérience a donc été faite également en utilisant un certain composé qui contient le radical oxalique (C_2O_4) dans le noyau complexe.

Corps étudiés et procédé expérimental. Nous avons synthétiquement préparé les sept complexes suivants qui renferment le radical oxalique dans leur noyau complexe.

- (1) $[Co(C_2O_4)_3]K_3.H_2O$
- (2) $[Co(C_2O_4)_2(H_2O)OH]K_2$
- (3) $[Co(C_2O_4)_2(NH_3)_2]K.H_2O$
- (4) $[Co(C_2O_4)(NH_3)_2(NO_2)_2]K.H_2O$
- (5) $[Co(C_2O_4)(NH_3)_3(H_2O)]Cl$
- (6) $[Co(C_2O_4)(NH_3)_4]Cl$
- (7) $[Co(C_2O_4)(NH_3)_5]Cl.HCl$

Nous avons mesuré les spectres d'absorption des solutions aqueuses pour les complexes ci-dessus nommés ayant les conditions expérimentales suivantes, à savoir: 5, 10 ou 20 mm. d'épaisseur des solutions avec 1/500, 1/2500 ou 1/10000 mol de concentration. L'électrode d'antimoine a été employée pour déterminer la concentration des ions d'hydrogène des solutions étudiées. Les photographies d'absorption ont été obtenues avec des plaques spéciales photographiques "Fuji" (marque japonaise) pour mesurer les coefficients d'extinction au moyen du spectrographe français en quartz comme auparavant.

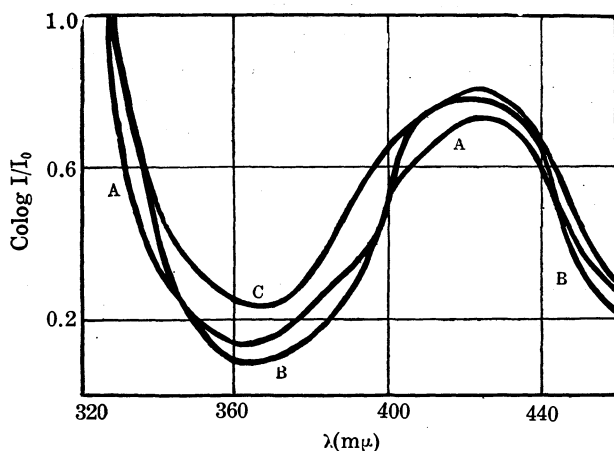
Relation entre la concentration des ions d'hydrogène (*pH*) et la courbe d'absorption des sels complexes. (1) $[Co(C_2O_4)_3]K_3.H_2O$, *Cobalti-trioxalate de potassium*. Ce corps préparé d'après la méthode

(1) Exposé fait à la réunion mensuelle de la Société chimique du Japon, le 13 mars 1937.

(2) T. Uémura et N. Hirasawa, ce bulletin, **13** (1938), 377.

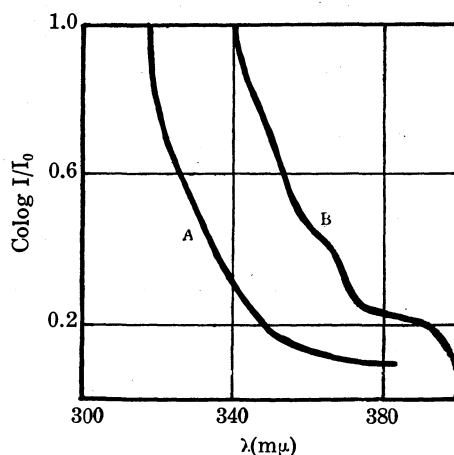
(3) T. Uémura et H. Suéda, ce bulletin, **10** (1935), 50, 85; H. Suéda, *ibid.*, **12** (1937), 71.

indiquée par Sørensen⁽⁴⁾ est un cristal bleu. Sa photographie d'absorption a été prise en employant la solution de 1/500 mol de concentration et de 20 mm. d'épaisseur. Ce composé racémique a déjà été étudié par la voie spectrochimique⁽⁵⁾. Nos résultats montrent, dans la figure 1, que l'absorption maximum se trouve au voisinage de la longueur d'onde de 420 m μ et minimum de 365 m μ (pH=3.1). Quand le pH passe à 2.2, par 1/500 titre HCl, et à 3.2, par 1/500 titre NaOH, la longueur d'onde qui indique l'absorption maximum ou minimum ne varie pas sensiblement. La solution aqueuse de ce complexe donne la précipitation colloïdale d'hydroxyde de cobalt par l'addition d'une faible solution alcaline. Quelques hydroxydes se sont déjà produits au pH 3.2.



[Co(C₂O₄)₃]K₃·H₂O (1/500 mol)
A: pH = 2.2 B: pH = 3.1 C: pH = 3.2

Fig. 1.



[Co(C₂O₄)₂(H₂O)OH]K₂ (1/500 mol)
A: pH = 2.7 B: pH = 5.6

Fig. 2.

(2) [Co(C₂O₄)₂(H₂O)OH]K₂, *Cobalti-aquo-hydroxo-dioxalate de potassium*. Ce complexe a été synthétisé par l'indication de Durrant⁽⁶⁾ et porte le nom de ce savant: le sel Durrant. Ce composé est un cristal vert et ne donne pas d'absorption sélective en région ultra-violette, même à la solution de 1/500 mol de concentration et de 5 mm. d'épaisseur. On peut facilement obtenir la précipitation d'hydroxyde de cobalt par l'addition d'une faible solution alcaline. Comme on le voit, dans la figure 2, la courbe présentée par sa solution aqueuse (pH=5.6) et celle donnée par l'addition de 1/500 titre HCl (pH=2.7) n'indiquent que le changement de position à la fin de l'absorption. La solution du petit pH comme 2.7 change de valeur au bout d'un certain temps, et il y a lieu de penser qu'il se produit une certaine réaction. Ce sel a été déjà étudié par Spacu et d'autres chimistes⁽⁷⁾ qui ont suggéré la décomposition par l'acide hydrochlorique en donnant le complexe [Co(C₂O₄)₂(H₂O)₂]K.

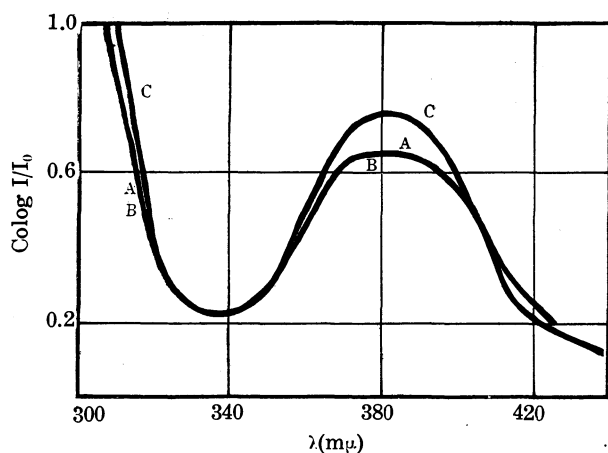
(4) S. P. L. Sørensen, *Z. anorg. Chem.*, **11** (1896), 1.

(5) J. Lifschitz et E. Rosenbohm, *Z. wiss. Phot.*, **19** (1920), 203; A. Mead, *Trans. Faraday Soc.*, **30** (1934), 1052.

(6) R. G. Durrant, *J. Chem. Soc.*, **87** (1905), 1785.

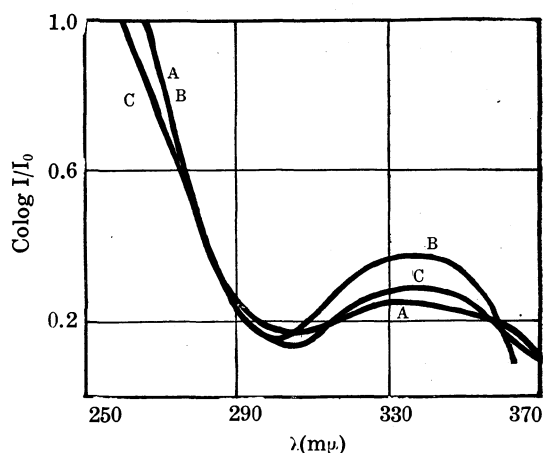
(7) G. Spacu, J. G. Murgulescu et M. Vancea, *Z. anorg. Chem.*, **220** (1934), 1.

(3) $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]\text{K}\cdot\text{H}_2\text{O}$, *Cobalti-diammonio-dioxalate de potassium*. En se référant à plusieurs mémoires publiés,⁽⁸⁾ nous avons réussi à préparer ce complexe cristallin violet. Nous l'avons photographié pour obtenir son spectre d'absorption avec sa solution de 1/500 mol de concentration et de 20 mm. d'épaisseur. La solution aqueuse de ce sel de 1/500 mol de concentration donne le pH 8.1 et cette valeur du pH passe à 2.3 par l'addition de 1/500 titre HCl et à 10.9 par celle de 1/500 titre NaOH. Puisque les solutions de ce corps complexe produisent difficilement la précipitation en l'additionnant même d'une solution alcaline de pH élevé, on peut conclure que la solution du sel actuel est assez stable en région du pH 2.3 à 10.9. Ces larges variations de valeur du pH n'ont pas influencé sensiblement la longueur d'onde d'absorption, le maximum se tenant presque toujours à 380 m μ et le minimum à 335 m μ . Les minima indiqués par les trois courbes d'absorption dans la figure 3 surtout coïncident bien l'un à l'autre. Riesenfeld et Klement⁽⁹⁾ ont déjà discuté sur la position trans occupée par les deux molécules d'ammoniaque qui se trouvent dans le noyau complexe de ce corps, et de plus le sel d'ammonium porté par le même noyau complexe a été déjà étudié par Kranig⁽¹⁰⁾.



$[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]\text{K}\cdot\text{H}_2\text{O}$ (1/500 mol)
A: pH = 2.3 B: pH = 8.1 C: pH = 10.9

Fig. 3.



$[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2(\text{NO}_2)_2]\text{K}$ (1/10000 mol)
A: pH = 2.5 B: pH = 7.4 C: pH = 11.0

Fig. 4.

(4) $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_2(\text{NO}_2)_2]\text{K}\cdot\text{H}_2\text{O}$, *Cobalti-diammonio-dinitro-oxalate de potassium*. Ce composé a été préparé suivant les méthodes indiquées par Jörgensen, Lamer et Mason⁽¹¹⁾. C'est un complexe rouge-brun et sa solution aqueuse montre le pH 7.4, mais ses pH passent respec-

(8) S. M. Jörgensen, *Z. anorg. Chem.*, **17** (1898), 477; A. Werner et R. Feenstra, *Ber.*, **39** (1906), 1540; E. H. Riesenfeld et R. Klement, *Z. anorg. Chem.*, **124** (1922), 11.

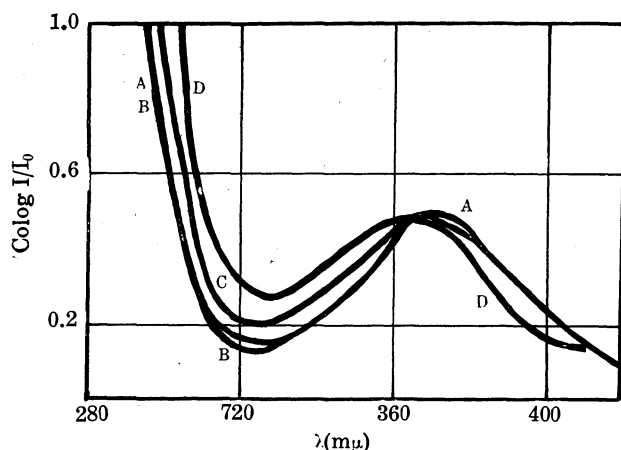
(9) E. H. Riesenfeld et R. Klement, *Z. anorg. Chem.*, **124** (1922), 2.

(10) J. Kranig, *Ann. chim.*, [10], **11** (1929), 53.

(11) S. M. Jörgensen, *J. prakt. Chem.*, [2], **23** (1881), 249; V. K. Lamer et C. F. Mason, *J. Am. Chem. Soc.*, **49** (1927), 413.

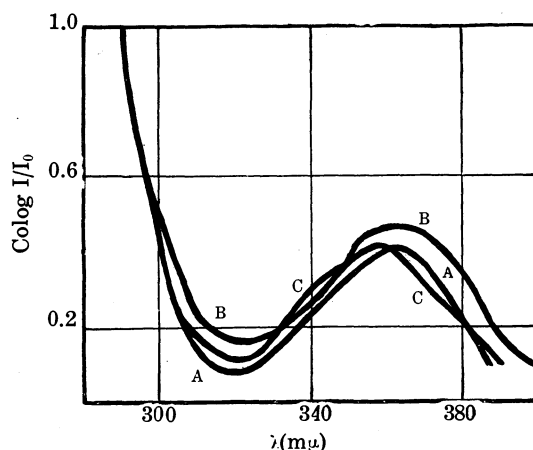
tivement à 2.5 en l'additionnant de 1/500 titre HCl et à 11.0 par 1/1000 titre NaOH. Comme son pouvoir absorbant est grand, nous avons utilisé ses solutions de 1/10000 mol de concentration et de 10 mm. d'épaisseur pour obtenir les photographies d'absorption. Les résultats observés montrent, dans la figure 4, que la variation du pH n'a pas eu une grande influence sur la position du maximum ou du minimum dans les courbes d'absorption. Le spectre d'absorption visible du complexe actuel a déjà été exposé par le Prof. Y. Shibata⁽¹²⁾, et la constitution stéréochimique a été aussi étudiée par Riesenfeld et Klement⁽⁹⁾ qui ont constaté de la position trans pour les molécules d'ammoniaque, et encore par Thomas⁽¹³⁾ qui a cru déterminer la position cis pour les molécules d'ammoniaque.

(5) $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_3(\text{H}_2\text{O})]\text{Cl}$, *Chlorure de cobalti-triammonio-aquo-oxalate*. Ce corps complexe obtenu suivant les indications proposées par Jørgensen et Werner⁽¹⁴⁾ est un cristal rouge-violet en poudre. Quand on dissout ce corps préparé dans l'eau, son pH donne la valeur de 7.3. On peut faire passer le pH à 2.2 par addition de 1/500 titre HCl, à 7.4 par addition de 1/1000 titre NaOH et à 8.2 par addition de 1/500 titre NaOH. Nous avons pris des photographies d'absorption avec la solution de 1/500 mol de concentration et de 20 mm. d'épaisseur. Ces recherches spectrochimiques nous ont montré que l'absorption maximum se trouve vers 370 m μ et le minimum, vers 325 m μ . On peut encore observer, dans la figure 5, que la variation du pH ne produit probablement pas de dif-



$[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_3(\text{H}_2\text{O})]\text{Cl}$ (1/500 mol)
A.: pH = 2.2 B: pH = 7.3 C: pH = 7.4 D: pH = 8.2

Fig. 5.



$[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_4]\text{Cl}$ (1/500 mol)
A: pH = 2.4 B: pH = 8.1 C: pH = 10.7

Fig. 6.

férences sur les courbes d'absorption. Nous pouvons montrer seulement, au pH 8.2, un changement de position d'absorption à une longueur d'onde plus courte. Comme Werner⁽¹⁴⁾ a déjà admis que par addition de NH_4OH , il se produit un sel hydroxo $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_3\text{OH}]$, nous

(12) Y. Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, **37** (1916), Art. 8, 14.

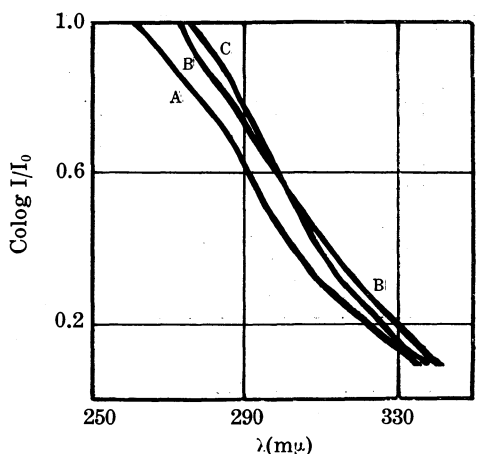
(13) W. Thomas, *J. Chem. Soc.*, **123** (1923), 617.

(14) S. M. Jørgensen, *Z. anorg. Chem.*, **11** (1896), 434, **14** (1897), 418; A. Werner, *Ann.*, **229** (1914), 405.

pouvons donc aussi supposer que ce composé actuel forme $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_3\text{OH}]$ par addition d'une solution alcaline qui fait varier le pH à 8.2 produisant quelque influence sur la courbe d'absorption. Werner a encore prétendu, dans son mémoire précité, donner la forme cis, mais nous ne pouvons cependant trouver aucune publication traitant de la forme trans.

(6) $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_4]\text{Cl}$, *Chlorure de cobalti-tétrammonio-oxalate*. Le complexe actuel, qui a été obtenu grâce aux indications données par Jörgensen⁽¹⁵⁾, est un cristal rouge et produit une solution aqueuse donnant le pH 8.1. Le pH de cette solution passe à 2.4 par 1/500 titre HCl et à 10.7 par 1/500 titre NaOH. Nous avons observé ses photographies d'absorption en utilisant la solution de 1/500 mol de concentration et 20 mm. d'épaisseur. La figure 6 nous montre que le maximum d'absorption se trouve à la longueur d'onde 360 $m\mu$ tandis que le minimum est à 320 $m\mu$. La variation du pH n'influence pas généralement la valeur d'absorption, mais la courbe donnée par la solution du pH 10.7 change peu dans une région de longueur d'onde plus basse. On peut trouver, sur ce complexe, de nombreuses études spectrochimiques qui ont déjà été exposées dans plusieurs publications.⁽¹⁶⁾

(7) $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_5]\text{Cl.HCl}$, *Chlorure de cobalti-pentammonio-oxalate (hydrochlorure)*. Ce corps synthétisé suivant la méthode de Jörgensen⁽¹⁷⁾ est une poudre jaune-orange et donne le pH 3.3 en solution aqueuse. Cette valeur du pH passe à 2.4 par addition de 1/500 titre HCl et à 10.6 par celle de 1/2500 titre NaOH. Nos photographies d'absorption ont été prises avec la solution de 1/2500 mol de concentration et 10 mm. d'épaisseur. Comme nous le montre la figure 7, l'absorption sélective dans la région ultraviolette n'apparaît pas, et la variation du pH ne produit qu'un faible changement de position à la fin de l'absorption. La solution fortement acide change un peu la position de la fin d'absorption dans une région de longueur d'onde plus courte. K. Matsuno⁽¹⁸⁾ a déjà étudié le spectre d'absorption du sel actuel dans la région visible.



$[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_5]\text{Cl.HCl}$ (1/2500 mol)
A : pH = 2.4 B : pH = 3.3 C : pH = 10.6

Fig. 7.

(15) S. M. Jörgensen, *J. prakt. Chem.*, **42** (1890), 211, *Z. anorg. Chem.*, **11** (1896), 420.

(16) Y. Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, **37** (1915), Art. 2, 13; G. Urbain et Y. Shibata, *Compt. rend.*, **170** (1920), 107; A. Uspensky et K. Tschibisoff, *Z. anorg. Chem.*, **164** (1927), 337; J. Kranig, *Ann. chim.*, [10], **11** (1929), 96.

(17) S. M. Jörgensen, *Z. anorg. Chem.*, **11** (1896), 426.

(18) K. Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, **45** (1925), Art. 8.

Résumé.

(1) Les deux composés $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})\text{OH}]\text{K}_2$ et $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_5]\text{Cl.HCl}$ n'ont pas manifesté d'absorption sélective dans la région ultra-violet.

(2) Les cinq autres complexes renfermant le radical oxalique qui donnent leur absorption sélective dans la région ultra-violet ne subissent pas de grande influence du fait de la variation de la concentration des ions d'hydrogène sur les courbes d'absorption.

(3) En prenant quatre sels complexes aux mêmes concentrations et aux mêmes épaisseurs (1/500 mol, 20 mm.) et comparant leurs spectres d'absorption, la longueur d'onde du centre d'absorption maximum devient plus élevée quand le radical oxalique augmente dans le noyau complexe.

(4) Les complexes ayant leur absorption maximum dans une région de longueur d'onde plus élevée sont peut-être aussi doués d'un pouvoir absorbant assez puissant.

(5) La valeur du pH de solution aqueuse du sel préparé a augmenté par l'addition d'une molécule d'ammoniaque dans le noyau complexe.

Les présentes recherches ont été menées à bien grâce à l'aide des autorités de la Faculté et à celle de la Société "Téjima Kôgyô-Shikindan" qui a bien voulu se charger d'une partie des frais de nos expérimentations. Nous tenons donc à leur exprimer ici notre vive reconnaissance.

*Laboratoire de Chimie minérale,
Faculté des Arts et Métiers de Tokyo
(Tokyo Kogyô-Daigaku).*

**Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs.
VIII. Der Einfluss der Kontaktdauer des reagierenden Gasge-
misches mit dem Katalysator auf dem Grad der Austausch-
reaktion.⁽¹⁾**

Von Noriyoshi MORITA.

(Eingegangen am 4. April 1940.)

Inhaltsübersicht. Betreffend der katalytischen Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Metalls bzw. Metalloxyds ist eine Formel abgeleitet worden (Gl. (19)), die die Beziehung zwischen der Kontaktdauer des reagierenden Gasgemisches mit dem Katalysator und dem Grad der

(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: *ebenda*, **13** (1938), 601; III. Mitteil.: *ebenda*, **13** (1938), 656; IV. Mitteil.: *ebenda*, **14** (1939), 9; V. Mitteil.: *ebenda*, **14** (1939), 520 und **15** (1940), 1; VI. Mitteil.: *ebenda*, **15** (1940), **47**, 71; VII. Mitteil.: *ebenda*, **15** (1940), 119.

dabei erzielten Austauschreaktion wiedergeben soll. Diese Formel, die uns auch die Bestimmung der Aktivierungsenergie der angegebenen Austauschreaktion ermöglicht, wird dann an Hand der mit metallischem Platin, Aluminiumoxyd und Platinschwamm durchgeführten Versuche geprüft und bestätigt. Weiter wird unter Benutzung dieser Formel festgestellt, dass die Temperatur $t(10\%)$, wo das prozentuale Austauschmass $\%A$ an der Oberfläche eines angegebenen Katalysators erst 10% erreicht und eben durch diese Temperatur die katalytische Wirksamkeit der verschiedenen Arten der Katalysatoren bisher verglichen worden sind, durch die Strömungsgeschwindigkeit des Reaktionsgasgemisches sowie die Menge des benutzten Katalysators nicht viel beeinflusst wird.

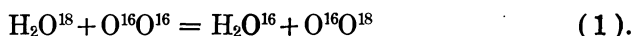
Einleitung. Bei den vorhergehenden Versuchen über die katalytische Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche der verschiedenen Arten der Metalle und Metalloxyde wird der Grad der Austauschreaktion dadurch gemessen, dass man die wirkliche gefundene Abnahme der Dichte des schweren Wassers nach der Austauschreaktion mit dem theoretischen Wert vergleicht, der sich beim vollständigen Austausch ergeben würde; wenn z.B. die erstere nur 10% des letzteren beträgt, wird der Grad der angegebenen Austauschreaktion mit dem Wort ausgedrückt, dass das „prozentuale Austauschmass“ der betreffenden Austauschreaktion $\%A=10\%$ beträgt.

Das so bestimmte prozentuale Austauschmass $\%A$ wächst aber an der Oberfläche eines bestimmten Katalysators mit zunehmender Temperatur zuerst allmählich aber von einer bestimmten Temperatur an ziemlich steil an. Wir können deshalb die katalytische Wirksamkeit eines angegebenen Katalysators mit solch einer Temperatur bestimmen, wo das gefundene Austauschmass erst einen bestimmten Betrag wie z.B. 10% erreicht. Dies haben wir bei dem vorhergehenden Versuche so durchgeführt, dass wir die katalytische Wirksamkeit der verschiedenen Arten der Katalysatoren mittels solch einer Temperatur $t(10\%)$ verglichen, bei der das gefundene Austauschmass erst 10% erreicht, weil sich aus experimentellen Erfahrungen ergeben hat, dass diese Temperatur $t(10\%)$ weder durch die Strömungsgeschwindigkeit des Reaktionsgasgemisches noch durch die Menge des benutzten Katalysators viel beeinflusst wird (vgl. IV. Mitteil.). Aber um diese Methode der Vergleichung der katalytischen Wirksamkeit durch die Temperatur $t(10\%)$ weiter auszuführen, ist es sehr wünschenswert nicht nur aus experimentellen Erfahrungen sondern auch auf theoretischem Wege zu bestätigen, dass die charakteristische Temperatur $t(10\%)$ hauptsächlich durch die Beschaffenheit des benutzten Katalysators bestimmt aber nicht viel durch die sonstigen Versuchsbedingungen beeinflusst wird.

Aus diesem Grunde wird in der vorliegenden Abhandlung zuerst eine Gleichung abgeleitet, die die Beziehung zwischen der Strömungsgeschwindigkeit bzw. der Kontaktdauer des reagierenden Gasgemisches mit dem Katalysator und dem dabei erzielten prozentualen Austauschmass $\%A$ wiedergeben soll. Die dadurch gewonnene Gleichung, nach der die Quantität $-\log\left(1 - \frac{\%A}{100}\right)$ mit der zunehmenden Strömungsgeschwindigkeit umgekehrt proportional abnehmen muss, wird dann an Hand der mit metallischem Platin und Aluminiumoxyd gewonnenen Versuchsergebnisse experimentell bestätigt. Zum Schluss wird unter Benutzung der so experimentell bestätigten Gleichung eine weitere Gleichung abgeleitet, die

die Beziehung zwischen der Strömungsgeschwindigkeit bzw. der Kontaktdauer und der charakteristischen Temperatur $t(10\%)$ wiedergeben soll. Diese Gleichung zeigt, dass die charakteristische Temperatur $t(10\%)$ wie erwartet weder durch die Strömungsgeschwindigkeit noch durch die Menge des Katalysators viel beeinflusst wird.

Mathematische Beziehung zwischen dem prozentualen Austauschmass %A und der Kontaktdauer bzw. der Strömungsgeschwindigkeit. Wegen der Kleinigkeit des Gehaltes des zum Austauschversuch benutzten schweren Wassers an schwerem Sauerstoff kann die in Rede kommende Austauschreaktion durch die Gl. wiedergegeben werden:



Dabei können wir die Gleichgewichtskonstante dieser Reaktion (1) gleich eins oder, in anderen Worten ausgedrückt, die Reaktionsfähigkeit der beiden Arten der O-Atome d.h. O^{16} und O^{18} miteinander gleich annehmen, weil das Atomgewicht beider Arten der O-Atome zueinander sehr nahe steht. Setzen wir nun die Anzahl der gesamten (d.h. leichten und schweren) Wassermoleküle in einer Volumeneinheit des reagierenden Gasgemisches gleich N und die der Sauerstoffmoleküle gleich $N'/2$,⁽²⁾ so bleibt die Anzahl dieser beiden während des Verlaufes eines Austauschversuches durchaus konstant, weil die analytische Zusammensetzung des Reaktionsgasgemisches durch die Austauschreaktion nicht verändert wird. Dagegen wird die (atomare) Konzentration des schweren Sauerstoffs im Wasserdampf u und die im Sauerstoffgas u' durch die Austauschreaktion (1) immer weiter verändert und zwar derart, dass die erstere u immer ab- und die letztere u' immer zunimmt, weil wir im praktischen Fall von vorn herein schweren Wasserdampf gegen gewöhnliches leichtes Sauerstoffgas austauschen lassen. Deshalb können wir die Geschwindigkeit der Austauschreaktion (1) entweder mit der Abnahme der O^{18} -Konzentration im Wasserdampf $(-du/dt)$, wie dies üblich der Fall ist, oder mit der Zunahme im Sauerstoffgas (du'/dt) quantitativ messen.

Wir können aber betreffend des Mechanismus der Austauschreaktion drei extreme Fälle unterscheiden, je nachdem ob die aktivierte Adsorption des Wasserdampfes, die des Sauerstoffgases bzw. die wirkliche Austauschreaktion in der Adsorptionsschicht den geschwindigkeitsbestimmenden Prozess bildet. Beim ersten Fall, wo die reversible Adsorption und Desorption des Wasserdampfes an der Oberfläche des Katalysators der langsamste Prozess ist, darf angenommen werden, dass der aus der Oberfläche des Katalysators desorbiert herauskommende Wasserdampf dieselbe isotopische Zusammensetzung wie das Sauerstoffgas besitzt, weil die Gleichgewichtskonstante der Reaktion (1) gleich eins angenommen wurde. Deshalb lässt sich in diesem Fall:

$$-Ndu = (u-u')dN_1 \quad (2)$$

setzen, wenn die Anzahl der aus einer mit einer Volumeneinheit Gasgemisch in Berührung stehenden Menge des Katalysators während einer

(2) Weil ein Sauerstoffmolekül zwei O-Atome während ein Wasserdampfmolekül nur ein solches enthält, kommen gegen eine Anzahl Wasserdampfmoleküle gerade eine Hälfte dieser Anzahl Sauerstoffmoleküle in Austausch.

kleinen Zeit dt desorbiert herauskommenden Wasserdampfmoleküle mit dN_1 bezeichnet wird. Aus dieser Gl. (2) erhält man als die Austauschgeschwindigkeit die Gl.:

$$-\frac{du}{dt} = (u-u') \frac{1}{N} \left(\frac{dN_1}{dt} \right) \quad (3).$$

Wirkt dagegen die reversible Adsorption und Desorption des Sauerstoffgases geschwindigkeitsbestimmend, so folgt auf ähnliche Weise wie oben die Gl.:

$$-\frac{du}{dt} = (u-u') \frac{1}{N} \left(\frac{dN_2}{dt} \right) \quad (4),$$

wenn die Desorptionsgeschwindigkeit der Sauerstoffmoleküle aus dem mit einer Volumeneinheit Reaktionsgasgemisch in Berührung stehenden Katalysator mit $\frac{1}{2} (dN_2/dt)$ ausgedrückt wird.⁽³⁾ Bei der letzten Möglichkeit, wo die Austauschreaktion in der Adsorptionsschicht selbst den langsamsten Prozess bildet, wird auf ähnliche Weise wie Gl. (2) die Gl. erhalten:

$$-Ndu = u(1-u')dN_3 - u'(1-u)dN_3 = (u-u')dN_3 \quad (5),$$

wenn die Anzahl der Wasserdampfmoleküle, die an der Oberfläche des mit einer Volumeneinheit Reaktionsgasgemisch in Berührung stehenden Katalysators während einer kleinen Zeit dt gegen Sauerstoffgas ausgetauscht werden, mit dN_3 ausgedrückt wird. Aus dieser Gl. (5) folgt deshalb als die Austauschgeschwindigkeit die Gl.:

$$-\frac{du}{dt} = (u-u') \frac{1}{N} \left(\frac{dN_3}{dt} \right) \quad (6).$$

Die so erhaltenen drei Gln. (3), (4) und (6), die bei den oben angegebenen drei extremen Fällen die Austauschgeschwindigkeit wiedergeben, können wir aber in einer einzigen Gl. (7) zusammenfassen:

$$-\frac{du}{dt} = (u-u') \frac{1}{N} \left(\frac{dN_o}{dt} \right) \quad (7),$$

wenn wir mit einem einzigen Ausdruck (dN_o/dt) den Ausdruck (dN_1/dt) in Gl. (3), (dN_2/dt) in Gl. (4) bzw. (dN_3/dt) in Gl. (6) representieren.

Nun wird aus der Versuchsbedingung, dass der gesamte O^{18} -Gehalt des Reaktionsgasgemisches immer konstant bleibt, die Gl. erhalten:

$$(u_o - u)N = (u' - u_o')N' \quad (8),$$

wenn man die O^{18} -Konzentration in Wasserdampf und Sauerstoffgas am Anfang des Experiments resp. mit u_o und u_o' bezeichnet. Aus diesen beiden Gln. (7) und (8) folgt deshalb unter Eliminierung von u' die Gl.:

(3) Vgl. Fussnote (2).

$$-\frac{du}{dt} = \left\{ \left(\frac{1}{N} + \frac{1}{N'} \right) u - \left(\frac{u_o'}{N} + \frac{u_o}{N'} \right) \right\} \left(\frac{dN_o}{dt} \right) \quad (9).$$

Da aber der Ausdruck (dN_o/dt) , die die Geschwindigkeit der Desorption des Wasserdampfes bzw. Sauerstoffgases oder der Austauschreaktion in der Adsorptionsschicht wiedergibt, mindestens so lange als die katalytische Wirksamkeit des angegebenen Katalysators unverändert bleibt als konstant angesehen werden kann, erhält man durch die Integration von Gl. (9) die Gl.:

$$u = \frac{u_o N + u_o' N'}{N + N'} + \frac{(u_o - u_o') N'}{N + N'} \exp \left\{ -\frac{N + N'}{NN'} \left(\frac{dN_o}{dt} \right) t \right\} \quad (10).$$

Das prozentuale Austauschmass %A wird aber nun als das prozentuale Verhältnis der wirklich gefundenen Abnahme des Dichteüberschusses des benutzten schweren Wassers bzw. der Abnahme des O¹⁸-Gehaltes des schweren Wasserdampfes $(u_o - u)$ gegen den theoretischen Wert, der sich beim vollständigen Austausch ergeben würde, definiert. Deshalb können wir unter der oben angegebenen Annahme, dass die Gleichgewichtskonstante der Reaktion (1) gleich eins ist, die Gl. ableiten:

$$\%A = \frac{u_o - u}{u_o - \frac{u_o N + u_o' N'}{N + N'}} \times 100 \quad (11).$$

Ersetzt man u in dieser Gl. (11) durch Gl. (10), so ergibt sich die Gl.:

$$\%A = \left[1 - \exp \left\{ -\frac{N + N'}{NN'} \left(\frac{dN_o}{dt} \right) t \right\} \right] \times 100 \quad (12),$$

oder in logarithmischer Form:

$$-\log \left(1 - \frac{\%A}{100} \right) = \frac{N + N'}{2.303 NN'} \left(\frac{dN_o}{dt} \right) t \quad (13).$$

Beim besonderen Fall, wo das gefundene prozentuale Austauschmass %A klein genug ist, können wir die obige Gl. (12) auch wie folgt vereinfachen:

$$\%A = \frac{N + N'}{NN'} \left(\frac{dN_o}{dt} \right) t \times 100 \quad (14).$$

Nach dieser Gl (14) nimmt nämlich das prozentuale Austauschmass %A mit der zunehmenden Kontaktdauer t linear zu. Dies wird tatsächlich, wie weiter unten gezeigt wird, durch das Experiment bestätigt. Aber bevor wir darauf eingehen, wollen wir die oben gewonnenen Gln. (13) und (14) in eine noch praktischere Formel umgestalten, indem man statt der experimentell schwer bestimmbar Kontaktdauer t die leicht messbare Strömungsgeschwindigkeit des Reaktionsgasgemisches anwendet.

Da unter der Kontaktdauer t solch eine Zeitlänge verstanden wird, die das Reaktionsgasgemisch im Katalysatorraum verbraucht, bevor das

erstere den letzteren verlässt, besteht zwischen der Kontaktdauer t und der an Ort und Stelle des Katalysatorraumes gemessenen Strömungsgeschwindigkeit des Reaktionsgasgemisches v' die Beziehung:

$$t = \frac{(V - V_0)}{v'},$$

falls man mit V das Gesamtvolumen des Katalysatorraumes und mit V_0 das eigentliche Volumen des Katalysators ausdrückt (vgl. Abb. 1).

Da aber beim wirklichen Austauschversuch die Strömungsgeschwindigkeit des Reaktionsgasgemisches nicht an Ort und Stelle des Katalysators sondern ausserhalb des Katalysatorrohrs und zwar bei Zimmertemperatur (etwa bei 25°) gemessen wird, besteht zwischen der so gemessenen Strömungsgeschwindigkeit v und der Kontaktdauer t offensichtlich die Beziehung:

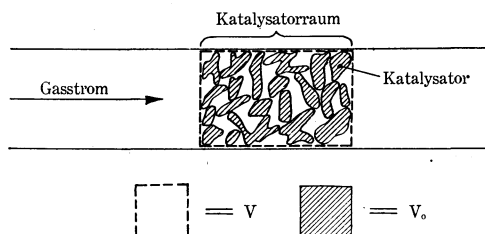


Abb. 1. Schematische Darstellung des Katalysatorraumes.

$$t = \frac{(V - V_0)}{v} \frac{298}{T} \times 60 \text{ Sec.} \quad (15),$$

wenn das Volumen V und V_0 beide in ccm, die Strömungsgeschwindigkeit v in ccm pro Min. und die Temperatur des Katalysatorraumes T in absoluter Einheit gemessen wird.

Setzt man weiter das Volumenverhältnis des Sauerstoffgases gegen den Wasserdampf im Reaktionsgasgemisch:

$$\text{O}_2 : \text{H}_2\text{O} = r : 1 \quad (16),$$

so folgt ohne weiteres:

$$N'/N = 2r,$$

weil wir mit $N'/2$ und N resp. die Anzahl der in einer Volumeneinheit Gasgemisch enthaltenen Sauerstoffmoleküle und Wasserdampfmoleküle ausdrückten (vgl. oben). Deshalb ergibt sich die Gl.:

$$\frac{N + N'}{NN'} = \frac{(2r + 1)}{2r} \frac{1}{N} \quad (17),$$

und weiter kann

$$N = \frac{N}{22400} \frac{273}{T} \frac{1}{r + 1} \quad (18),$$

gesetzt werden, wenn man mit N die Loschmidtsche Zahl bezeichnet.

Setzt man also die hier gewonnenen drei Gln. (15), (17) und (18) in die oben angegebene Gl. (13) ein, so erhält man zum Schluss die gewünschte Gl. (19):

$$-v \log \left(1 - \frac{\%A}{100} \right) = K \left(\frac{dN_o}{dt} \right) \text{ ccm/Min.} \quad (19).$$

Dabei ist

$$\begin{aligned} K &= \frac{60 \times 298 \times 22400}{2.303 \times 273} \frac{(2r+1)(r+1)}{2r} \frac{(V-V_o)}{N} \\ &= 637000 \frac{(2r+1)(r+1)}{2r} \frac{(V-V_o)}{N} \end{aligned} \quad (20).$$

Und auf ähnliche Weise erhält man aus Gl. (14) die Beziehung:

$$\%A = k \frac{1}{v} \quad (21),$$

wo

$$k = \frac{60 \times 298 \times 22400}{273} \frac{(2r+1)(r+1)}{2r} \frac{(V-V_o)}{N} \left(\frac{dN_o}{dt} \right) \quad (22),$$

ist.

Nach der ersten Gl. (19) können wir den Ausdruck $\left\{ -v \log \left(1 - \frac{\%A}{100} \right) \right\}$ als eine Quantität auffassen, die der wahren Austauschgeschwindigkeit (dN_o/dt) direkt proportional ist. Deshalb muss dieser Ausdruck als eine Konstante in Wegfall kommen, wenn der Austauschversuch bei konstanter Temperatur ausgeführt wird, weil in diesem Fall die Austauschgeschwindigkeit (dN_o/dt) offensichtlich unverändert bleibt. Die zweite Beziehung (21), die nur beim genügend kleinen Wert von $\%A$ gültig ist, zeigt weiter an, dass das prozentuale Austauschmass $\%A$ bei konstanter Temperatur mit der Strömungsgeschwindigkeit v umgekehrt proportional abnimmt. Diese beiden Folgerungen werden nun durch die weiter unter anzugebenden Versuche experimentell bestätigt.

Austauschversuche mit metallischem Platin bei verschiedenen Strömungsgeschwindigkeiten. Wir haben beim früheren Versuch, wo die Austauschreaktion zwischen Sauerstoffgas und Wasserdampf an der Oberfläche des metallischen Platins bei konstanter Temperatur (750°) aber bei verschiedener Strömungsgeschwindigkeit v untersucht wurde, tatsächlich gefunden, dass das prozentuale Austauschmass $\%A$, wie Gl. (21) verlangt, mit dem reziproken Wert der Strömungsgeschwindigkeit $1/v$ direkt proportional zunimmt (vgl. Abb. 2 in I. Mitteil.). Dadurch wird nämlich die Beziehung (21) experimentell bestätigt. Da aber diese Beziehung (21), wie schon oben hingewiesen wurde, nur beim genügend kleinen Wert von $\%A$ als streng gültig angesehen werden kann, haben wir unter Benutzung derselben Versuchsergebnisse (vgl. Tabelle 4 in I. Mitteil.) die genauere Beziehung (19) geprüft; nach dieser Gl. (19) muss nämlich der Ausdruck $\left\{ -v \log \left(1 - \frac{\%A}{100} \right) \right\}$ unabhängig von der Strömungsgeschwindigkeit konstant bleiben. Dass dies wirklich der Fall ist, kann aber aus der letzten Spalte der unten angegebenen Tabelle 1 ohne weiteres ersehen werden.

Tabelle 1. Austauschreaktion zwischen O_2 und H_2O auf metallischem Platin bei verschiedener Strömungsgeschwindigkeit (v) aber bei konstanter Temperatur (750°).

$$O_2 : H_2O = 2 : 1,$$

$$\Delta s_a = 34.7 \gamma$$

Versuchsnr.	v ccm / Min.	% A	$-\log\left(1 - \frac{\% A}{100}\right)$	$-v \log\left(1 - \frac{\% A}{100}\right)$
3	100	15	0.07	7.0
2	60	31	0.16	9.6
6	55	35	0.19	10.5
4	45	33	0.17	7.7
5	35	42	0.24	8.4
1	25	83	0.77	19.2 ?

Als den Mittelwert der in der letzten Spalte der Tabelle angegebenen Werte haben wir:⁽⁴⁾

$$-v \log\left(1 - \frac{\% A}{100}\right) = 8.6 \text{ ccm/Min.} = K \left(\frac{dN_o}{dt}\right) \quad (23).$$

Da aber nun bei der praktischen Ausführung der Versuche, wie oberhalb der Tabelle 1 angegeben ist, ein Reaktionsgasgemisch von der Zusammensetzung $O_2 : H_2O = 2 : 1$ verwendet wurde, kann $r=2$ gesetzt werden (vgl. Gl. (16)). Weiter wurde ein als Katalysator knäueförmig gerollter Platindraht in das Katalysatorrohr eingeschoben und dadurch wurde der Mittelteil des Rohres, das 2 cm l.W. besass, 1.5 cm lang besetzt. Deshalb können wir das Gesamtvolumen des Katalysatorraumes $V = \pi \times 2.0^2 \times 1.5/4 = 4.7$ ccm setzen (vgl. Abb. 1), während das eigentliche Volumen des Katalysators V_o sich auch aus der Gewichtsmenge des benutzten Katalysators (=3.3 g) als 0.15 ccm ergab. Setzt man deshalb den so gewonnenen Wert von r , V und V_o in Gl. (20) ein und dadurch wird die Konstante K in Gl. (23) mit ihrem Zahlenwert ersetzt, so folgt als die wahre Austauschgeschwindigkeit der Wert:

$$\left(\frac{dN_o}{dt}\right) = 4.8 \times 10^{17} \text{ Molekül Wasserdampf in ccm pro Sec.}$$

$$\text{bzw.} \quad = 2.4 \times 10^{17} \text{ Molekül Sauerstoff in ccm pro Sec.}^{(5)} \quad (24).$$

Weil aber beim früheren Versuch (I. Mitteil.) festgestellt wurde, dass bei der in Rede kommenden Austauschreaktion an der Oberfläche des metallischen Platins die aktivierte Adsorption des Sauerstoffs die geschwindigkeitsbestimmende Rolle spielt, kommen wir zu dem Schluss, dass die durch Gl. (24) angegebene Anzahl Sauerstoffmoleküle in einer Volumeneinheit Reaktionsgasgemisch jede Sekunde an der Oberfläche des Platindrahts adsorbiert (bzw. daraus desorbiert) werden. Der zum

(4) Ausgenommen den letzten Wert 19.2.

(5) Vgl. Fussnote (2).

Versuch benutzte Platindraht besitzt nun, wie sich aus seiner Gewichtsmenge (=3.3 g) und Dicke (=0.07 bis 0.08 mm) leicht errechnen lässt, eine gesamte Oberfläche von 82 cm². Deshalb steht mit einer Volumeneinheit Gasgemisch $82/(V-V_0)=82/(4.7-0.15)=18$ cm² Metalloberfläche in Berührung. Auf diese Grösse Metalloberfläche müssen aber jede Sekunde 1.8×10^{24} Molekül Sauerstoff aus einer Volumeneinheit Gasgemisch hineinfliegen, weil das Reaktionsgasgemisch die Zusammensetzung von O₂:H₂O=2:1 besitzt und unter atmosphärischem Druck und bei 750° steht. Aus dieser Anzahl der gesamten hineinfliegenden Moleküle des Sauerstoffs und der oben durch Gl. (24) angegebenen Anzahl der aktiviert adsorbierenden Sauerstoffmoleküle lässt sich die Stossausbeute der in Rede kommenden aktivierten Adsorption ohne weiteres errechnen:⁽⁶⁾

$$e^{-\frac{A}{RT}} = \frac{2.4 \times 10^{17}}{1.8 \times 10^{24}} = \frac{1}{7.5 \times 10^6} \quad (25).$$

Ein Sauerstoffmolekül wird nämlich bei jedem 7.5×10^6 -maligen Stossen auf die Platinoberfläche dadurch aktiviert aufgefangen. Aus dieser Gl. (25) ergibt sich also die Aktivierungsenergie der betreffenden aktivierten Adsorption:

$$A = 32 \text{ Kcal.} \quad (26).$$

Austauschversuch mit Aluminiumoxyd bei verschiedener Strömungsgeschwindigkeit. Dieser noch nicht ausführlich veröffentlichte Versuch ist insofern von Interesse, als in diesem Fall gerade im Gegenteil zu der oben angegebenen Austauschreaktion an der Oberfläche des metallischen Platins die aktivierte Adsorption des Wasserdampfes den geschwindigkeitsbestimmenden Prozess bildet (vgl. IV. und VI. Mitteil.). Der Versuch zeigte, dass die Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Aluminiumoxyds erst bei 520° bemerkbar wird und oberhalb 700° sehr schnell stattfindet. Da aber die ausführliche Beschreibung der Versuche später erfolgen soll, wollen wir hier nur den Teil der Versuche mitteilen, bei dem es sich um den Einfluss der Strömungsgeschwindigkeit auf den Grad der Austauschreaktion d.h. auf das prozentuale Austauschmass %A handelt.

Der Versuch wird mit dem chemische rein von Merck bezogenen Aluminiumoxyd unter ganz ähnlicher Anordnung wie beim oben angegebenen Versuch mit metallischem Platin ausgeführt. Etwa 10 g (12 ccm) Oxyd wird bei jedem einzelnen Versuch von neuem in das Katalysatorrohr eingeschoben und das so beschickte Oxyd wird vor dem Beginn des Austauschversuchs unter Durchleitung des elektrolytischen Sauerstoffs immer etwa drei Stunden lang erhitzt.

Die bei diesem Versuch gewonnenen Ergebnisse sind in Tabelle 2 zusammengestellt.

In dieser Tabelle 2 stellt die Versuchsnr. die zeitliche Reihenfolge der einzelnen Versuche und Δs_a und Δs_e den gewöhnlichem Wasser gegenüber gemessenen Dichtebereich des zum Versuch benutzten schweren Wassers vor und nach dem Versuch dar.

(6) Dabei wird der sterische Faktor als eins angenommen.

Deshalb drückt die Differenz $\Delta s_a - \Delta s_e$ die Abnahme der Dichte des schweren Wassers aus, die auf die Austauschreaktion zurückgeführt wird. Da aber aus einer einfachen Rechnung sich ergibt, dass diese Abnahme der Dichte des schweren Wassers beim vollständigen Austausch 30.3 γ betragen muss, wird das prozentuale Austauschmass %A gemäss der Gl. berechnet:

$$\%A = \frac{\Delta s_a - \Delta s_e}{30.3} \times 100 \quad (27).$$

Tabelle 2. Austauschreaktion zwischen O_2 und H_2O auf Aluminiumoxyd bei verschiedener Strömungsgeschwindigkeit aber bei konstanter Temperatur (570°).

$$O_2 : H_2O = 2 : 1,$$

$$\Delta s_a = 57.0 \gamma^{(7)}$$

Versuchsnr.	v ccm / Min.	$\Delta s_a - \Delta s_e$ in γ	% A	$-\log \left(1 - \frac{\% A}{100} \right)$	$-v \log \left(1 - \frac{\% A}{100} \right)$
5	120	5.2	17	0.08	9.6
3	80	6.9	23	0.11	8.8
1	60	8.7	29	0.15	9.0
2	40	10.8	36	0.19	7.6
4	20	16.7	59	0.39	7.8

Das so berechnete prozentuale Austauschmass %A nimmt aber, wie vierte Spalte der Tabelle zeigt, mit der abnehmenden Strömungsgeschwindigkeit v allmählich zu. Dagegen bleibt der in der letzten Spalte der Tabelle angegebene Ausdruck $\left\{ -v \log \left(1 - \frac{\% A}{100} \right) \right\}$ unabhängig von der Strömungsgeschwindigkeit ziemlich konstant und als Mittelwert erhält man:

$$-v \log \left(1 - \frac{\% A}{100} \right) = 8.6 \text{ ccm/Min.} = K \left(\frac{dN_o}{dt} \right) \quad (28).$$

Da aber nun das Gesamtvolumen des Katalysatorraumes $V=12$ ccm ist (vgl. Abb. 1 und S. 174) und das eigene Volumen des Katalysators (d.h. Aluminiumoxyds) sich aus seiner Gewichtsmenge (=10 g) und sp. Gewicht (=3.9) als $V_o=2.6$ ccm ergibt, lässt sich die wahre Austauschgeschwindigkeit (dN_o/dt) auf ähnliche Weise wie beim Fall mit metallischem Platin mit Hilfe der Gl. (19) errechnen. Diese ergibt nämlich:

$$\left(\frac{dN_o}{dt} \right) = 2.1 \times 10^{17} \text{ Moleküle in ccm pro Sec.} \quad (29).$$

Diese Anzahl muss aber gerade die Geschwindigkeit angeben, mit der die Wasserdampfmoleküle an der Oberfläche des in einer Volumeneinheit Katalysatorraum enthaltenen Aluminiumoxyds adsorbiert (bzw. daraus desorbiert) werden, weil in diesem Fall, wie schon oben erwähnt, die

(7) Von diesem gesamten Dichteüberschuss 57.0 γ rührt 36.3 γ von der Anreicherung des schweren Sauerstoffs her.

aktivierte Adsorption des Wasserdampfes für die Austauschreaktion massgebend wirkt.

Austauschversuch mit Platinschwamm bei verschiedener Temperatur. Um über die Temperaturabhängigkeit der Austauschgeschwindigkeit (dN_o/dt) zu einer Orientierung zu kommen, sehen wir Experiment 1 in I. Mitteil. als ein typisches Beispiel an, das mit Platinschwamm ausgeführt wurde. Dabei haben wir die bei verschiedenen Temperaturen gefundenen Werte des prozentualen Austauschmasses %A gegen die betreffenden Temperaturen eingezeichnet (vgl. Abb. 3 in I. Mitteil.). Werden deshalb aus dieser Kurvenangabe solche Temperaturen gesucht, wo das prozentuale Austauschmass %A bis zu einem gewissen Betrag wächst, so ergibt sich die folgende Tabelle 3, wo die Temperaturen T , bei denen das gefundene prozentuale Austauschmass %A resp. 10%, 20% u.s.w. erreicht wird, in absoluter Einheit angegeben sind.

Tabelle 3. Austauschreaktion zwischen O_2 und H_2O auf Platinschwamm bei verschiedener Temperatur aber bei konstanter Strömungsgeschwindigkeit (60 ccm/Min.).

% A	10	20	30	40	50	60	70	80	90
T abs.	643	678	693	708	723	733	748	768	803
$-\log\left(1-\frac{\%A}{100}\right)$	0.046	0.097	0.155	0.222	0.301	0.398	0.523	0.699	1.000

Da aber in diesem Fall die Strömungsgeschwindigkeit v immer konstant gehalten ist, muss der in der letzten Horizontalreihe der Tabelle 3 angegebene Ausdruck $\left\{-\log\left(1-\frac{\%A}{100}\right)\right\}$ der wahren Geschwindigkeit (dN_o/dt) der bei jeder betreffenden Temperatur stattfindenden Austauschreaktion direkt proportional sein (vgl. Gl. (19)). Wenn man aus diesem Grunde den Logarithmus dieses Ausdruckes gegen den reziproken Wert der absoluten Temperatur einzeichnet, erhält man eine gute gerade Linie, die durch die Gl. gut wiedergegeben wird (vgl. Abb. 2):

$$\log \left\{ -\log \left(1 - \frac{\%A}{100} \right) \right\} = 6.13 - \frac{4800}{T} \quad (30).$$

Nach Gl. (19) muss aber zwischen der wahren Austauschgeschwindigkeit (dN_o/dt) und dem Ausdruck $\log \left\{ -\log \left(1 - \frac{\%A}{100} \right) \right\}$ die Beziehung bestehen:

$$\log \left(\frac{dN_o}{dt} \right) = \log v - \log K + \log \left\{ -\log \left(1 - \frac{\%A}{100} \right) \right\} \quad (31).$$

Werden die Konstanten v und K in dieser Gl. gemäss der wirklich benutzten Versuchsbedingungen ($r = 2$, $v = 60$ ccm/Min., $V = 1.7$ ccm und $V_o = 0.2$ ccm) durch resp. Zahlenwerte ersetzt (vgl. Gl. (20) und weiter die oben gewonnene Beziehung (31) eingesetzt, so folgt die Gl.:

$$\log \left(\frac{dN_o}{dt} \right) = 25.13 - \frac{22,000}{4.576T} \quad (32).$$

Die Aktivierungsenergie der Austauschreaktion zwischen Wasserdampf und Sauerstoffgas an der Oberfläche des Platinschwamms beträgt also:

$$A = 22 \text{ Kcal.} \quad (33).$$

Vergleicht man nun diesen Wert mit dem oben mit metallischem Platin (und zwar bei einer Temperatur) gewonnenen Wert (=32 Kcal.), so wird ersichtlich, dass die Reaktion an der Oberfläche des Platinschwamms

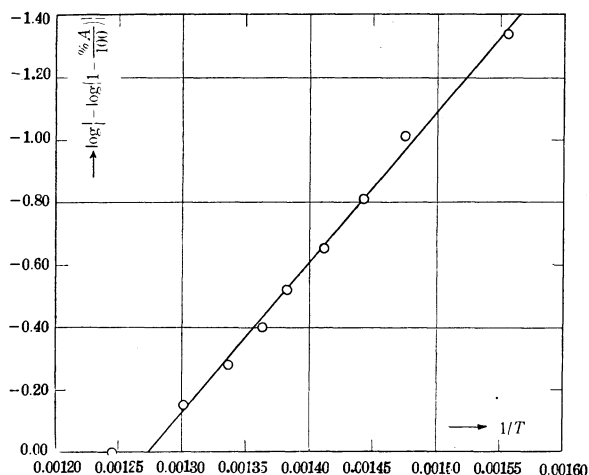


Abb. 2. Abhängigkeit der Austauschgeschwindigkeit von der Temperatur.

eine um etwa 10 Kcal. kleinere Aktivierungsenergie als beim metallischen Platin fordert. Dieses Ergebnis steht aber mit dem experimentellen Befund gut im Einklang, dass die Austauschreaktion an der Oberfläche des Platinschwamms schon bei 300° bemerkbar wird während die mit metallischem Platin erst oberhalb 500° mit wohl messbarer Geschwindigkeit stattfindet (vgl. Abb. 3 in I. Mitteil.), obwohl beim wirklichen Fall auch die Verschiedenheit der Oberflächengrösse beider Arten der Katalysatoren in Rechnung gezogen werden muss.

Mathematische Beziehung zwischen der Temperatur $t(10\%)$ und der Strömungsgeschwindigkeit v . Wir haben bei der Ableitung der Gl. (19), die die Beziehung zwischen der Strömungsgeschwindigkeit v und dem prozentualen Austauschmass $\%A$ wiedergeben soll, stillschweigend angenommen u. a., dass das Reaktionsgasgemisch immer so gut durchmischt ist, dass seine isotopische Zusammensetzung durch den ganzen Katalysatorraum gleichmässig zur Verteilung gelangt. Weiter wird angenommen, dass die Menge des Gases, das durch die angegebene Menge des Katalysators adsorbiert wird, im Vergleich mit dem in Gasphase frei bleibenden unmessbar so klein und deshalb die Veränderung der analytischen und isotopischen Zusammensetzung des letzteren durch die erstere kaum in Betracht kommt. Alle diese Annahmen entsprechen aber der

Wirklichkeit nur in erster Annäherung.⁽⁸⁾ Überdies ist der genaue Wert von %A nur sehr schwierig zu bestimmen und eine verhältnismässig kleine Schwankung im Werte von %A kann eventuell einen ziemlich merklichen Einfluss auf das Endresultat ausüben.⁽⁹⁾ Zieht man deshalb alle diese Momente in Rechnung, so darf wohl geschlossen werden, dass die Beziehung zwischen der Strömungsgeschwindigkeit v und dem prozentualen Austauschmass %A mittels Gl. (19) bzw. (31) befriedigend genau wiedergegeben wird. Andererseits haben wir bei dem zuletzt ausgeführten Versuch mit Platinschwamm gefunden, dass die Temperaturabhängigkeit der Austauschgeschwindigkeit (dN_o/dt) durch die Arrheniussche Gl. mit der Formel:

$$\log \left(\frac{dN_o}{dt} \right) = \log C - \frac{A}{4.576T} \quad (34)$$

gut ausgedrückt werden kann. Aus diesen beiden Gln. (31) und (34) können wir deshalb die mathematische Beziehung zwischen der Strömungsgeschwindigkeit v und der charakteristischen Temperatur $t(10\%)$ ohne weiteres ableiten.

Weil die charakteristische Temperatur $t(10\%)$, mit der wir die katalytische Wirksamkeit eines angegebenen Katalysators messen, solch eine Temperatur ausdrückt, wo das gefundene prozentuale Austauschmass %A erst 10% erreicht, kommt in diesem Fall das letzte Glied in der rechten Seite der Gl. (31) als eine Konstante in Wegfall.⁽¹⁰⁾ Wenn man deshalb diese Konstante mit $\log B$ bezeichnet, so ergibt sich die Gl.:

$$\log \left(\frac{dN_o}{dt} \right) = \log v - \log K + \log B \quad (35).$$

Setzt man nun die rechten Seiten der beiden Gln. (34). und (35) miteinander gleich, so folgt:

$$\log v = (\log K - \log B + \log C) - \frac{A}{4.576T_i} \quad (36).$$

In dieser Gl. (36) drückt T_i solch eine (in absoluter Einheit gemessene) Temperatur aus, wo das gefundene prozentuale Austauschmass %A bei einer angegebenen Strömungsgeschwindigkeit v erst 10% oder im allgemeinen $i\%$ erreicht. Wenn man deshalb mit T_i und T_i' resp. die (absolute) Temperatur bezeichnet, wo das prozentuale Austauschmass %A an einem

(8) Dazu wird offensichtlich vorausgesetzt, dass die Temperatur innerhalb des Katalysatorraumes überall gleichmässig ist.

(9) Wenn man z.B. die Dichteabnahme ($\Delta s_a - \Delta s_e$) des ausgetauschten schweren Wassers beim Experiment Nr. 6 in Tabelle 1 um etwa 0.5% grösser als der dort angegebene Wert (= 28.4%) setzt, nimmt das prozentuale Austauschmass %A bis zu 32% ab und folglich wird der Ausdruck $\left\{ -v \log \left(1 - \frac{\%A}{100} \right) \right\} = 9.2$. Dieser letzte Wert steht nun mit dem entsprechenden Werte der anderen Experimente sehr gut im Einklang.

(10) Wird nämlich %A = 10% gesetzt, so wird $\log \left\{ -\log \left(1 - \frac{\%A}{100} \right) \right\} = \log B = -1.339$.

angegebenen Katalysator bei zwei verschiedenen Strömungsgeschwindigkeiten v und v' ein und denselben Betrag $i\%$ erreicht, erhält man aus Gl. (36) ohne weiteres die Gl.:

$$\log \frac{v}{v'} = \frac{A}{4.576} \left(\frac{1}{T_i'} - \frac{1}{T_i} \right) \quad (37).$$

Aus dieser Gl. ersieht man, dass die Temperatur T_i , wo das gefundene prozentuale Austauschmass $\%A$ bis zu einem bestimmten Betrag $i\%$ wächst, durch die Strömungsgeschwindigkeit des Gasgemisches v nicht so viel beeinflusst wird. Dabei ist zu beachten, dass die Form dieser Gl. (37) von der absoluten Grösse von i unabhängig ist; dieselbe Beziehung (37) zwischen v und T_i besteht immer, ohne Unterschied ob man als i wie üblich 10% wählt oder irgendeinen anderen bestimmten Betrag wie z.B. 20%, 30% oder 40% benutzt. Wird deshalb die Gl. (37) z.B. auf dem oben angegebenen Versuch mit Platinschwamm angewendet, so ergibt sich die Gl.:

$$\log \frac{v}{v'} = 4800 \left(\frac{1}{T_i'} - \frac{1}{T_i} \right) \quad (38).$$

Die Temperatur $t(10\%)$, wo das gefundene Austauschmass zuerst 10% erreicht, wird bei diesem Versuch mit der Strömungsgeschwindigkeit von 60 ccm/Min. als 375° gefunden. Aber nach der oben angegebenen Gl. (38) wird diese Temperatur ($T_i - 273$) nur bis zu etwa 300° herabgesetzt, auch wenn die Strömungsgeschwindigkeit v sogar bis zu 6 ccm/Min. d.h. zehnmal verkleinert wird.

Eine ähnliche Beziehung wie zu Gl. (37) können wir auch zwischen den verwendeten Mengen des Katalysators und der charakteristischen Temperatur T_i ableiten, wenn man annimmt, dass bei konstant gehaltener Kontaktdauer die Menge des zu verwendeten Katalysators mit der zunehmenden Strömungsgeschwindigkeit umgekehrt proportional abnimmt. Werden nämlich mit T_i und T_i' solche Temperaturen bezeichnet, bis dazu ein angegebener Katalysator erhitzt werden muss, um mit zwei verschiedenen Mengen des Katalysators w und w' denselben Betrag ($i\%$) des prozentualen Austauschmasses zu gewinnen, so erhält man die Gl.:

$$\log \frac{w'}{w} = \frac{A}{4.576} \left(\frac{1}{T_i'} - \frac{1}{T_i} \right) \quad (39).$$

Die charakteristische Temperatur T_i bzw. $t(10\%)$ wird nämlich auch durch die benutzte Menge des Katalysators nicht so viel beeinflusst. Auf diese Weise kommen wir zu dem Schluss, dass die Temperatur T_i bzw. $t(10\%)$, bis sie die Erhitzung eines angegebenen Katalysators erforderlich macht, um das prozentuale Austauschmass $\%A$ an der Oberfläche des Katalysators bis zu einem bestimmten Betrag wie z.B. 10% anwachsen zu lassen, weder durch die Strömungsgeschwindigkeit des Reaktionsgasgemisches noch durch die Menge des benutzten Katalysators sehr viel beeinflusst wird. Wir dürfen deshalb mit dieser Temperatur T_i bzw. $t(10\%)$, wie dies bisher tatsächlich der Fall gewesen ist, die katalytische

Wirksamkeit verschiedener Arten der Katalysatoren vergleichen, mindestens so lange als die Strömungsgeschwindigkeit des Reaktionsgasgemisches sowie die Menge des Katalysators bei jedem Fall möglichst gleich gehalten ist.

Herrn Prof. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Nippon Gakuzyutu-Sinkōkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) sowie der Hattori-Hōkōkai (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung der vorliegenden Arbeit ermöglicht haben, bin ich zu grossem Dank verpflichtet.

*Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyositu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka).*

Über die Wirkung von Ultraschallwellen auf die Kolloid-erscheinungen. VII. Die Untersuchung der Wirkung auf die Lösung von Rohrzucker.

Von Naoyasu SATA und Yukio HARISAKI.

(Eingegangen am 11 April 1940).

(1) **Einleitung.** Parallel mit den Versuchen an typisch kolloide hochmolekulare Substanzen, wie Gelatine⁽¹⁾ bzw. Tannin,⁽²⁾ haben wir die Untersuchung auf echte Lösungen hochmolekularer Substanzen erweitert. Als ein Beispiel von solcher, wurde zuerst der Rohrzucker ausgewählt.

A. Szalay⁽³⁾ hat schon die Wirkung der USW. (Abkürzung von Ultraschallwellen) auf Zuckerlösung untersucht. Dadurch wurde gefunden, dass der Rohrzucker die Zersetzung erleidet, welche etwa 0.2% beträgt durch die 30 minutige Beschallung von USW. von 722 kHz.. Die Ergebnisse seitdem ausgeführter zahlreichen Untersuchungen betreffend der chemischen Wirksamkeit der USW. haben aber gezeigt, dass die Intensität gegenwärtiger USW. vielleicht noch nicht soweit genügen würde die Bindung beständiger Moleküle zu zerstören sondern höchstens an Substanzen kolloider Dimensionen die Wirkung ausüben könnte.⁽⁴⁾ Selbstverständlich ist es andere Frage, ihre Wirkung an unbeständige Verbindungen, metastabile Systeme usw.⁽⁵⁾

(1) N. Sata, *Kolloid-Z.*, **87** (1939), 185.

(2) N. Sata, *Kolloid-Z.*, **88** (1939), 182.

(3) A. Szalay, *Z. physik. Chem., A*, **164** (1933), 238

(4) G. Schmid, *Z. Elektrochem.*, **44** (1938), 723; G. Schmid u. O. Rommel, *Z. Elektrochem.*, **45** (1939), 659; *Z. physik. Chem., A*, **185** (1939), 97.

(5) L. Bergmann, *Der Ultraschall*, S. 179, Berlin (1937).

Ausserdem hat Szalay den Wert 0.2% durch chemische Zuckeranalyse erhalten, bei denen die Fehlergrenze kaum unter 0.2% abzuschätzen ist.⁽⁶⁾

Der nachstehende Versuch ist angestellt, um es von neuem zu kontrollieren, ob die USW. wirklich mit der Zuckerspaltung unmittelbar zu tun haben oder eine sonstige sekundäre Erscheinung darauf verantwortlich ist.

(2) **Versuch durch optische Methode.** Zuerst wollten wir die Rohrzuckerinversion, wie gewöhnlich, durch die Messung der optischen Drehung nachweisen. Da die grösste Möglichkeit der Fehlerquelle in Reinheit des Rohrzuckers zu liegen ist, wurde der Zucker vorher vorsichtig gereinigt. Nämlich der käufliche Rohrzucker in Kristallform haben wir aus frisch destilliertem Methylalkohol zweimal umkristallisiert, wobei für allen Behandlungen immer die Geräte aus geschmolzenem Quarz benutzt worden sind. Man nimmt nun ca. 25 ccm 10%-Lösung in einem Quarz-Reagenzrohr vom inneren Durchmesser 20 mm. und lässt kräftigen USW. von 450 kHz.⁽⁷⁾ beschallen. Um den Temperatureinfluss auszuschliessen wurde die USW.-Behandlung wie anderes Mal⁽¹⁾ durchgeführt, indem jeweils nach 1 Minute Beschallung 30 Sekunden abgekühlt wurde. Tabelle 1 stellt die Versuchsergebnissen das.

Tabelle 1.

Beschallungsdauer (Min.)		0	20	40	60
Abgelesener Winkel gleich nach Beschallung.		13.28	13.21	13.23	13.22
Abgelesener Winkel nach dem Stehenlassen von	1 Tag	13.28	—	—	13.13
	2 Tagen	13.26	—	—	13.00
	4 Tagen	13.29	—	—	12.98

Die Zahlen ergeben die absolute Drehungswinkeln, weil es in diesem Falle nur die Änderung der Drehung uns interessiert. Daraus ersieht man, dass die USW. auf die Drehung gar keine Wirkung ausüben, wenigstens gleich nach Beschallung. Aber es ist dabei bemerkenswert, dass die USW.-beschallte Lösung, nach dem Stehenlassen, die Tendenz zeigt die Drehung zu verändern, während die nicht beschallte Kontrolle immer unverändert bleibt. Über diesen Punkt hoffen wir in anderer Gelegenheit noch eingehend untersuchen können. Jedenfalls nur durch optischen Versuch kann man noch nicht entscheiden, dass die USW. auf Rohrzuckerlösung ohne Wirkung sind; denn wir haben mit Tanninlösung erfahren, dass es bei dieser Substanz durch Niederschlagbildung, Färbung usw. etwaige Änderung nicht verneinen ist, obwohl durch optische Messung keine Änderung des Drehungsvermögens zu erkennen war.

Wir haben dann versucht ob man die USW.-Wirkung nach chemisch-analytischer Methode nachweisen könnte.

(3) **Versuch nach Chemischer Analyse.** Da die analytische Methode zur genauen quantitativen Bestimmung der kleinen Menge

(6) I. M. Kolthoff, Die Massanalyse, Bd. II, S. 467, Berlin (1931).

(7) N. Sata, *Kolloid-Z.* **71** (1935), 53.

reduzierendes Zuckers, noch nicht vorhanden ist, haben wir vorläufig die Analyse nach Jodmetrie ohne,⁽⁸⁾ und unter Anwendung Fehlingscher Lösung⁽⁹⁾ durchgeführt. Einzelheiten der Ausführung der Analyse sind zwar folgende:

(a) *Jodmetrie*: Etwa 2.00 ccm Zuckerlösung (bezogen auf 10%-Glukose) verdünnt man mit destilliertem Wasser auf 100 ccm. Es wird dann genau 5.00 ccm 0.1 N Jodlösung, ca. 60 ccm 0.1 N NaOH zugesetzt und 5–10 Minuten stehen gelassen. Danach fügt man 5 ccm 2 N H₂SO₄ zu und das ausgeschiedene Jod wird mit 0.1 N Na₂S₂O₃ titriert.

(b) *Jodmetrie mit Fehlingscher Lösung*: 1–2 ccm Probe (bezogen auf 10%-Glukose) wird mit 20 ccm destilliertem Wasser verdünnt und mit 20 ccm Fehlingscher Lösung für 2 Minuten gekocht. Man kühlt sie schnell ab, fügt 3 g KJ hinzu und lässt das Jod mit 10 ccm 25%-H₂SO₄ ausscheiden, welches unmittelbar mit Thiosulfat-Lösung titriert wird. Wie bekannt, weil diese Methode keine exakte stöchiometrische Gründe besitzt,⁽¹⁰⁾ ist erhaltenes Resultat, nur vertraulich nach vorsichtiger Ausführung unter gleichen Versuchsbedingungen. Noch dazu in unserem Falle, haben wir zu tun mit sehr kleiner Menge invertiertes Zuckers in sehr grosser Menge nicht invertiertes Zuckers, welche auch die analytische Genauigkeit stört.⁽¹¹⁾

Schlussfolgerung dürfte deswegen nur gezogen werden, aus sorgfältigen vergleichenden Versuchen unter verschiedenen Bedingungen. So wird schon der Vorversuch in drei Arten ausgeführt. Nämlich, zuerst mit Jod allein, um den Einfluss des Stehdauers auf dem wiedermaligen Jod-Ausscheiden zu sehen. Zweitens mit 10%-Glukose, der Vorversuch in gewöhnlichem Sinne und drittens unter Zusatz von Rohrzucker. Die Prüfung der USW.-Wirkung wurde zuletzt parallel mit dem letzten Vorversuche durchgeführt. Die Ergebnisse sind in folgenden Tabellen ersichtlich.

(4) Versuchsergebnisse. I. *Jodmetrie ohne Fehlingscher Lösung.*

Tabelle 2. (Vorversuch mit 5.00 ccm Jod allein, ohne Zucker.)

Stehdauer (Min.)*	5	10	15	20	30	60
ccm Na ₂ S ₂ O ₃	4.97	4.93	4.98	4.96	4.97	4.97

* Stehdauer bedeutet der Zeitdauer des Stehenlassens nach Alkalizusatz.

Tabelle 3. (Vorversuch mit 10%-Glukose; Stehdauer 5 Min.)

ccm 0.1 N Jod.		15	20	25	30	40
ccm Na ₂ S ₂ O ₃ für 10%-Glukose von	1.00	3.73	8.63	13.57	--	--
	2.00	--	--	--	7.29	17.26
1.00 ccm Glukose entsprechende Jodmenge in ccm.		11.27	11.44	11.45	11.36	11.33

(8) R. Willstätter u. G. Schudel, *Ber.* **51** (1918), 780.

(9) *Loc. cit.* Die Massanalyse, S. 468.

(10) Ebendort, S. 467.

(11) Ebendort, S. 469.

Tabelle 4. (Vorversuch mit 10%-Rohrzucker.)

Für 5.00 ccm Jod, im Vorhandensein von 2.00 ccm Rohrzucker entsprechende ccm $\text{Na}_2\text{S}_2\text{O}_3$	Steh- dauer	Alter der Zuckerlösung (Tag.)								
		0*	1	2	3	4	5	6	7	8
	5	4.82	4.75	4.71	4.78	4.79	4.71	4.83	4.74	4.86
	10	4.59	4.76	4.66	4.72	4.79	4.61	4.76	4.65	4.75
	30	4.48	4.72	4.66	4.66	4.64	4.59	4.71	4.59	4.47
	60	4.49	4.69	4.43	4.63	—	—	—	—	—
	120	4.42	4.55	4.29	4.53	—	—	—	—	—

* Alter 0, bedeutet die Lösung gleich nach der Herstellung.

Tabelle 5. (USW.-Wirkung auf 10%-Rohrzucker.)

USW.—Besch.	30 Minuten.						60 Minuten.			
Vers. Nr.	1		2		3		4		5	
Stehdauer.	5	10	5	10	5	10	5	10	5	10
Für 2.00 ccm Rohrzucker (vor Beschallung) und 5.00 ccm Jod entsprechende ccm $\text{Na}_2\text{S}_2\text{O}_3$	4.83	4.73	4.81	4.69	4.80	4.70	4.88	4.81	4.87	4.70
	4.81	4.76	4.79	4.67	4.77	4.79	4.89	4.88	4.85	4.73
	4.84	4.76	4.78	4.68	4.80	4.79	4.89	4.89	4.86	4.69
	4.84	4.76								
	4.84	4.76								
	4.82	4.72								
	4.82	4.74								
Mittel	4.83	4.75	4.79	4.68	4.79	4.76	4.89	4.86	4.86	4.70
Wie oben, aber mit USW.—beschallter Zuckerlösung	4.72	4.65	4.69	4.61	4.73	4.70	4.88	4.77	4.81	4.61
	4.73	4.65	4.68	4.62	4.74	4.69	4.86	4.78	4.81	4.65
	4.74	4.66	4.70	4.61	4.74	4.68	4.86	4.79	4.77	4.58
	4.74	4.65								
	4.73	4.64								
	4.73	4.63								
	4.73	4.63								
Mittel	4.73	4.65	4.69	4.61	4.74	4.69	4.87	4.78	4.80	4.61
Differenz	0.10	0.10	0.10	0.07	0.05	0.07	0.02	0.08	0.06	0.09
%—Änderung	2.1	2.2	2.1	1.5	1.1	1.0	0.4	1.7	1.3	1.9

II. *Jodmetrie mit Fehlingscher Lösung.*

Tabelle 6. (Vorversuch.)

Menge zugegebenes Rohrzuckers.	ccm $\text{Na}_2\text{S}_2\text{O}_3$							
0	27.18	27.21	27.23	27.18	—	—	—	—
1.00 ccm (10%)	26.98	26.99	26.96	26.97	26.95	—	—	—
2.00 ccm (5%)	26.94	26.96	26.91	26.81	27.00	26.96	26.94	26.91

Tabelle 7. (USW.-Wirkung.)

Versuchsnr.	1	2	3
Beschallungsdauer	30	60	60
ccm $\text{Na}_2\text{S}_2\text{O}_3$ vor Beschallung	26.78	26.85	26.86
	26.72	26.87	26.85
	26.78	26.84	26.80
	—	26.88	26.79
Mittel	26.76	26.83	26.81
ccm $\text{Na}_2\text{S}_2\text{O}_3$ nach Beschallung	26.76	26.81	26.72
	26.75	26.77	26.59
	26.69	26.74	26.68
	26.68	26.82	26.66
Mittel	26.73	26.79	26.66
Differenz	0.03	0.04	0.15
%-Änderung	0.1	0.2	0.5

(5) **Erörterung.** Von den Versuchsergebnissen, könnte man ungefähr folgendes zusammenfassen.

(a) Die Vorversuche unter verschiedenen Bedingungen ergeben, in beiden Methoden, befriedigende Übereinstimmung. D.h., die Methoden sind zum Zweck der Analyse reduzierender Zuckerarten ganz gut brauchbar, wenn die Versuchsbedingungen richtig reguliert sind, obwohl sie keine stöchiometrische Gründe haben.

(b) Der Stehdauer nach Alkali-Zusatz bei der Methode ohne Fehlingscher Lösung und die Bedingung beim Sieden in der Methode mit Fehlingscher Lösung, scheinen die grösste Fehlerquelle zu verursachen.

(c) Von dem Vergleich der Ergebnissen der parallelen Versuche ohne und mit Zucker; vor und nach USW.-Beschallung ersieht man, dass der reine Rohrzucker in reinem destillierten Wasser schon eine sehr geringe reduzierende Kraft vor sich zeigt,⁽¹¹⁾ welche durch die Beschallung

eine Spur vermehrt wird. Diese Vermehrung des Reduktionsvermögens durch USW. liegt jedenfalls fast innerhalb der Fehlergrenze der analytischen Methoden, wie aus den Tabellen 5 bzw. 7 zu erkennen ist. Diese winzige Veränderung kann man doch nicht mit Sicherheit als USW.-Effekt entschliessen. Von der Natur der Wirkungsweise der USW., welche unmittelbar mit mechanischer Anregung verknüpft ist, sind im Ultraschallfeld die metastabile Zustände, wie Übersättigung, Unterkühlung usw. ganz ausgeschlossen.⁽⁵⁾ In anderen Worten, sollte der Effekt, entweder schnell der Sättigung erreichen oder mit Beschallungsdauer immer weiter zunehmend verlaufen. Die Ergebnisse vorhergehender Versuche^{(1), (2)} stimmen auch damit überein. Dagegen in diesem Falle, ist der Effekt, nicht nur in seinem absoluten Wert sehr klein, sondern zeigt kaum einen Unterschied nach 30-minütiger und 60-minütiger Beschallung.

Hier haben wir natürlich den anfangs erwähnten Fall von Tanninlösung erinnert, wobei die USW.-Zersetzung nicht zu verneinen ist, trotz des Konstantbleibens der optischen Drehung. Aber mit Rohrzuckerlösung konnten wir weder durch optische Messung noch durch chemische Analyse, die deutliche USW.-Wirkung nachweisen. Ausserdem bleibt die Lösung nach der Beschallung scheinbar ganz unverändert, vollkommen klar ohne irgendeine Trübung oder Färbung. Daraus möchten wir konstatieren, dass die hierzu angewandte USW. wenigstens mit dieser Intensität und Frequenz vielleicht noch nicht genügend sind um die Inversion des Rohrzuckers hervorzurufen.

Zusammenfassung.

(1) Die Wirkung von USW. auf Rohrzuckerlösung wurde nach optischer und chemischer Methode untersucht.

(2) Der Drehungswinkel zeigt keine Änderung nach der Beschallung bis 60 Minuten.

(3) Die jodmetrische Zuckeranalyse mit und ohne Fehlingscher Lösung wurde zuerst auf ihrer Genauigkeit unter verschiedenen Bedingungen geprüft, welche ein befriedigendes Resultat gegeben hat.

(4) Es wurde bestätigt, dass die wässrige Lösung von reinem Rohrzucker schon ein geringes Reduktionsvermögen besitzt, welches durch USW.-Beschallung eine Spur vermehrt wird.

(5) Da der gefundene USW.-Effekt nicht nur sehr klein ist, sondern mit zunehmendem Beschallungsdauer kaum zunimmt, wurde es konstatiert, dass die USW. wenigstens bei dieser Intensität und Frequenz keinen Einfluss auf die Rohrzucker-Inversion ausüben.

*Chemisches Institut der Kaiserlichen Universität
zu OSAKA und SIOMI-Forschungsinstitut
für Physik und Chemie.*

On the Absorption Spectra of Polynuclear Complex Salts.

By Yoshihiko OHYAGI.

(Received April 8, 1940).

The commercial 90% phosphoric acid dissolves many oxides or salts insoluble in water, and gives stable solutions. In the last year, H. Shiba and T. Inoue⁽¹⁾ found that the solution of cobaltic complex salt is also stable, and its absorption spectrum gives the same results with the aqueous solution: namely, the absorption maxima lie on the same wave-length of the spectrum.

In the present work the author attempted to examine the absorption spectra of the polynuclear complex salt of cobalt that is very unstable in the aqueous solution.

On this subject, there exist a few treatises previously, and among them the research of Y. Shibata⁽²⁾ on the acidic aqueous solution is the most attractive, but in the present work it is shown that the absorption spectra of the phosphoric acid solution do not always coincide with the result of Y. Shibata.

Apparatus. In the present work the author used a new micro type of Baly-tube as shown in Fig. 1. The sliding full rod and the window are made of quartz for the purpose of ultra-violet spectroscopy; and, drawing out the rod, the solution is let into the tube from the upper ditch that plays the part of reservoir. Now, with this tube, as the thickness (d) of solution varies from 4 cm to 0.4 mm, so a solution of 2.5-times of concentration should be prepared to get the corresponding result of ordinary Baly-tube; but when this solution is prepared, the next experiment with 1/10 concentration can be carried out with changing the thickness (d) of solution from 4 mm. to 0.04 mm. For this purpose the tube is clamped

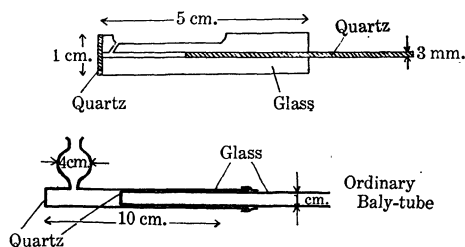


Fig. 1.

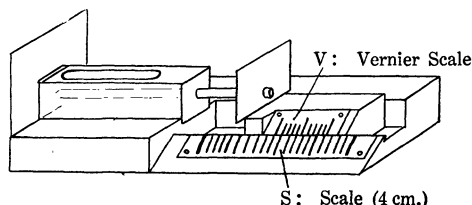


Fig. 2.

on a wooden stand with a vernier-scale as shown in Fig. 2, and is let to slide to any position desired. If this apparatus is used, the experiment is perfectly carried out with a little quantity of material as it requires about 0.5 to 1 c.c. of solution only.

(1) H. Shiba and T. Inoue, Unpublished result.

(2) Y. Shibata, *J. Faculty Sci., Imp. Univ. Tokyo*, Art II, **37** (1915), 6. *J. Chem. Soc. Japan*, **38** (1916), 99.

As the light source, a hydrogen Geissler-tube is used with 3000 volts and 150-milliamperes; it gives a fine continuous spectrum from 6500Å to about 2200Å.

Experimental and Discussion. The polynuclear cobalt complex salts are prepared in the method described by A. Werner.⁽³⁾ They are derived from the so-called "Melanochloride" and "Vortmann's Fusco-sulphate" with some exception. In this experiment the author studied on 23 salts as shown in Table 1.

Among them, however, $\left[\begin{array}{c} \text{CNS} \\ (\text{NH}_3)_4 \end{array} \text{Co}-\text{NH}_2\cdots\text{Co} \begin{array}{c} \text{Cl} \\ (\text{NH}_3)_4 \end{array} \right] (\text{CNS})_3$ is unstable in phosphoric acid. It decomposes at once with the evolution of gas, so the absorption spectrum cannot be observed. But this is not the characteristic property of this salt; other complex salts containing CNS-group are unstable or insoluble in the phosphoric acid also.

For the experiment, a solution of 0.025 mol. (for one atom of Co) is prepared to get the corresponding results of the ordinary condition of 0.01 mol., and the "Oriental" panchromatic plate is used; the duration of exposure is 30 seconds.

The commercial 90% phosphoric acid is a colourless viscous fluid. Its absorption curves has no selective absorption at all and the end absorption also lies in the range shorter than 2800Å. as shown in Fig. 3, so it may be used as a solvent without any refinement. This end absorption seems to be the effect of Fe^{+++} -ion, and with repeated recrystallization the absorption end are shifted slightly towards the shorter wave-length.

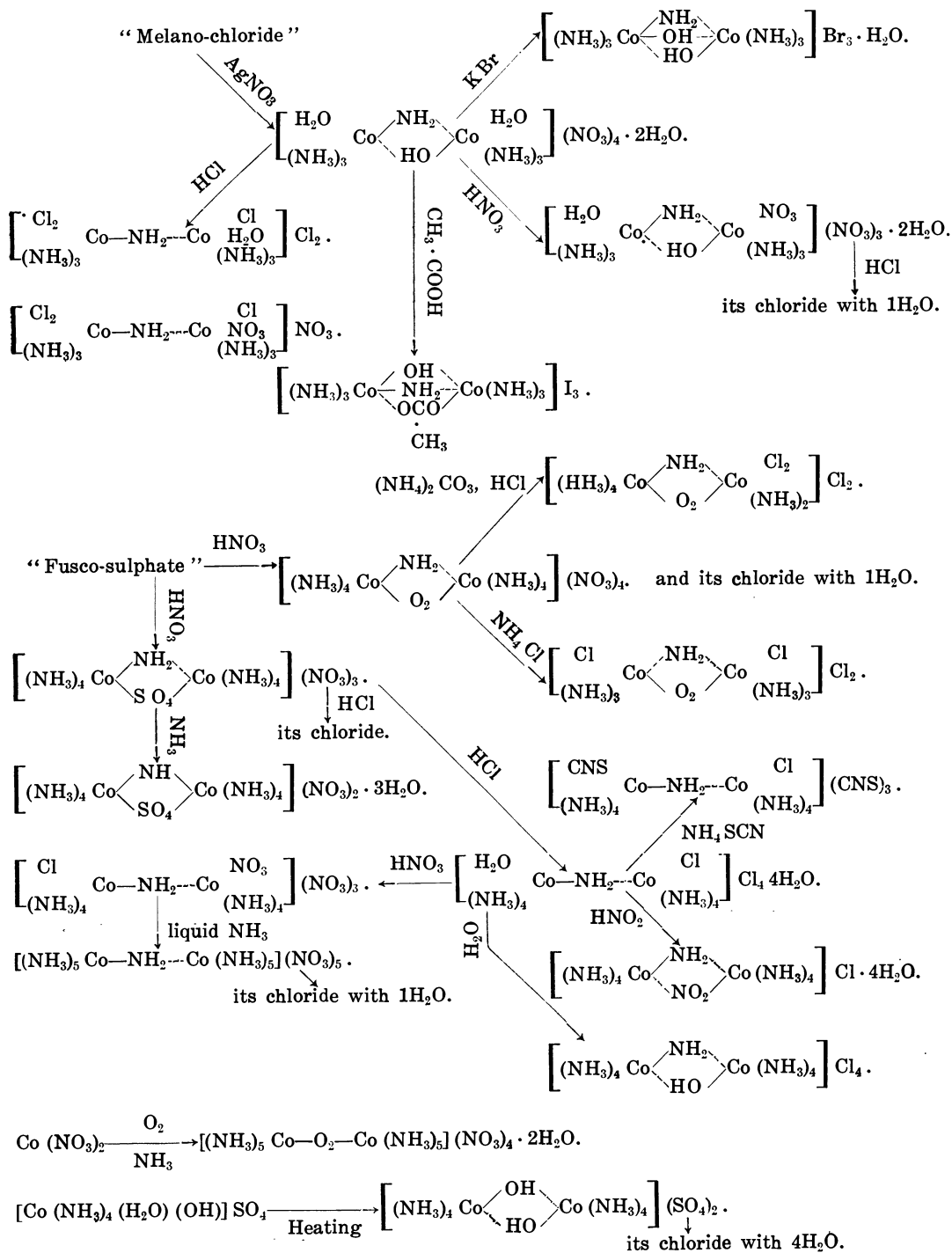
(1) $[(\text{NH}_3)_5\text{Co}-\text{NH}_2\cdots\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ and its chloride with $1\text{H}_2\text{O}$: The nitrate is a red needle with a bluish tint, and the chloride is a pink powder. The former gives a red phosphoric acid solution, and the absorption spectrum has three bands: viz., at 1900 mm^{-1} , 2780 mm^{-1} , and 3850 mm^{-1} as shown in Fig. 4. This third band was doubted to be the absorption of the nitrate ion at first; but, as the chloride has been proved to have the same absorption (Fig. 4) and NaNO_3 is found to have only a very small absorption at 3730 mm^{-1} with a 0.02 mol. solution (Fig. 10), this 3840 mm^{-1} absorption may be considered as the characteristic one for this quinquivalent cation.

(2) $\left[(\text{NH}_3)_4\text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{HO} \end{array} \text{Co}(\text{NH}_3)_4 \right] \text{Cl}_4$: This salt may be con-

sidered as the OH-derivative of the salt (1). Two molecules of ammonia of the latter are substituted with a OH-group. It is a brownish red crystal and gives a deep red phosphoric acid solution, the absorption curve of which is shown in Fig. 4 also. Its absorption maxima exist at 1825 mm^{-1} , 2710 mm^{-1} and 3410 mm^{-1} ; and from its shape the effect of one OH-group may be regarded as a bathochromic one especially for the third band and probably hypochromic for all these three bands, but this "hypochromic" effect is inconsistent a little with the result of the next salt.

(3) A. Werner and his co-workers, *Z. anorg. Chem.*, **16** (1898), 109; **21** (1899), 96; *Ber.*, **40** (1907), 2103, 4426, 4434, 4605, 4834; **41** (1908), 3879, 3912; *Ann.*, **375** (1910), 1.

Table 1.



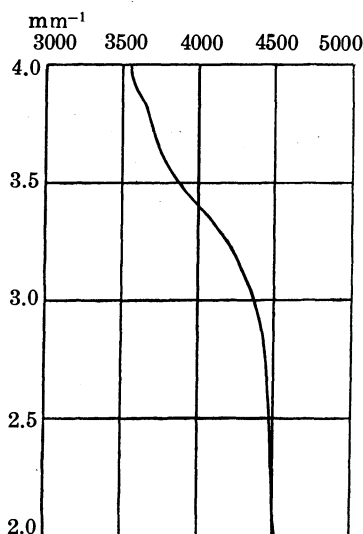


Fig. 3. Phosphoric acid. (90%)

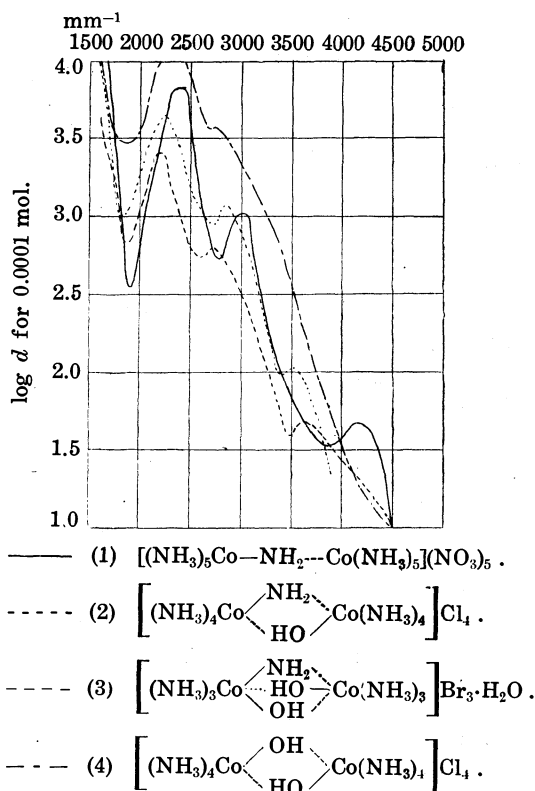
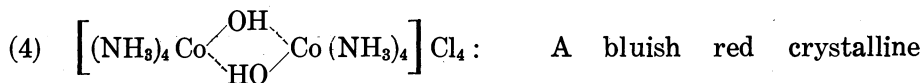


Fig. 4.

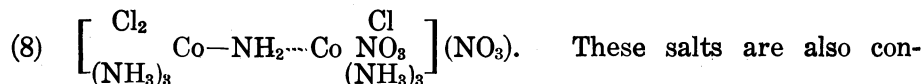
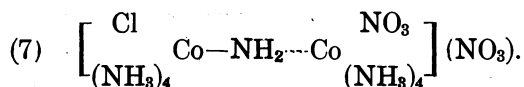
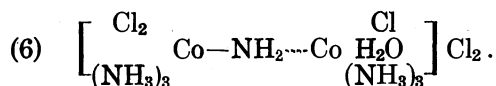
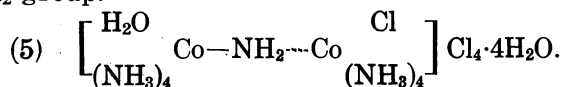
(3) $\left[(\text{NH}_3)_3\text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{HO} \quad \text{OH} \end{array} \text{Co}(\text{NH}_3)_3 \right] \text{Br}_3 \cdot \text{H}_2\text{O}$: This reddish brown

crystal dissolves in phosphoric acid with great difficulties and gives a dark red solution. And according to its small solubility, its 0.025 mol. solution cannot be prepared; so a 0.0125 mol. solution is used for the experiment and the results are rearranged for 0.025 mol. The absorption maxima exist on 1880 mm^{-1} , 2660 mm^{-1} and 3495 mm^{-1} ; these position are almost coincide with those of the salt (2) except the 2nd band, though they are much more hyperchromic than the latter. Now, this salt may be regarded as an OH-derivative of the salt (2), and from the above mentioned result, its absorption is expected to be a more hypochromic one than that of the salt (2) with the substitution of one more OH-group. Perhaps, however, this inconsistency has its base in the peculiar condition of the three bridging groups. On the other hand, this salt is regarded as a NH_2 -derivative of the next salt (4) also. Then, with the substitution of NH_2 -group the absorption of the latter brows to a very hyperchromic one, and moreover, a third band appears; namely, the NH_2 -group has a hyperchromic effect on the 1st and 2nd band, and causes a 3rd band to appear. So, the 3840 mm^{-1} -absorption of the salt (1) may also be regarded as the effect of the NH_2 -group probably.



powder. It gives a red phosphoric acid solution. The absorption curve has two bands: viz., at 1875 mm^{-1} , and 2670 mm^{-1} and they are much more hypochromic than the other salts as shown in Fig. 4.

And as it may be said that the OH-group in the complex ion causes an almost same result of hydrolysis to that ion, this diol-complex salt has a comparatively weak combination between two cobalt atoms and two OH-groups as compared with the other polynuclear complex salts. In the salt (3) this weak combination is strengthened probably with a NH_2 -group.



These salts are also considered as the derivatives of the salt (1), but the effect of the co-ordinated Cl-atom seems to be a profound one.

The salt (5) is a brownish violet crystal and the phosphoric acid solution is also brownish violet. The absorption maxima lie on 1820 mm^{-1} , 2750 mm^{-1} and 3400 mm^{-1} as shown in Fig. 5.

The salt (6) is a violet-black crystal and the phosphoric acid solution is deep violet. The absorption maxima lie on 1850 mm^{-1} , 2460 mm^{-1} and 3200 mm^{-1} .

The salt (7) is a brownish violet crystal lighter than the first, and the phosphoric acid solution is violet. The absorption maxima lie on 1830 mm^{-1} , 2650 mm^{-1} and 3400 mm^{-1} .

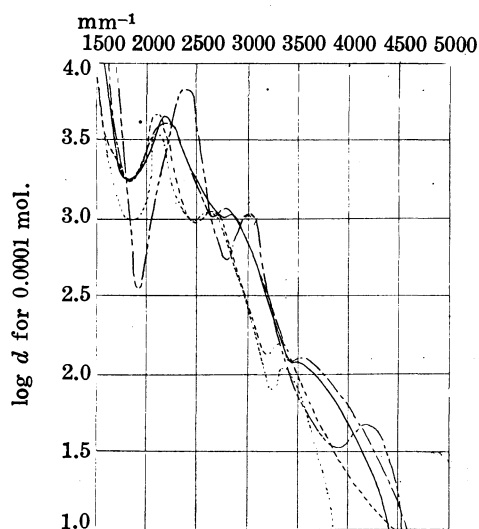
The salt (8) is a violet-black crystal and the phosphoric acid solution is dark violet. The absorption maxima lie on 1800 mm^{-1} , 2500 mm^{-1} and 3200 mm^{-1} .

The effect of Cl' is bathochromic for any band; especially for the 3rd band. But it seems that this bathochromic effect cannot be found on the 2nd band with single Cl' as compared the curve of (5) with that of (1).

On this case, the 2nd band is found more hypochromic but not bathochromic at all. In the next place, however, this band is shifted towards the longer wave-length region with a NO_3 -ion substituted in the place of H_2O (the case (7)), or with two more atoms of Cl co-ordinated one to every one cobalt atom (the case (6)). The bathochromic effect of Cl' is already known with the mononuclear complex-salt, but, from this result it may be doubted that in the case of the polynuclear complex salt this effect appears for the first time with another anion (in this case the NO_3 -ion) co-ordinated with the other cobalt atom.

However, this NO_3 -ion cannot change the third band of the salt (5): this band is shifted towards the longer wave-length for the first time with that two shared Cl-atoms (the case (6) and (8)).

(9) $\left[(\text{NH}_3)_4 \text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{array} \text{Co} (\text{NH}_3)_4 \right] \text{Cl}_4 \cdot \text{H}_2\text{O}$: This salt is a brownish orange crystal and gives an orange red phosphoric acid solution. Its absorption curve has three distinct bands as shown in Fig. 6: viz., at 2030 mm^{-1} , 2820 mm^{-1} and 3400 mm^{-1} .



- (5) $\left[\begin{array}{c} \text{H}_2\text{O} \\ \text{Co} \end{array} \begin{array}{c} \text{Cl} \\ \text{Co} \end{array} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{array} \right] \text{Cl}_4 \cdot 4\text{H}_2\text{O}$.
 - - - - (6) $\left[\begin{array}{c} \text{H}_2\text{O} \\ \text{Co} \end{array} \begin{array}{c} \text{Cl}_2 \\ \text{Co} \end{array} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{array} \right] \text{Cl}_2$.
 - - - - (7) $\left[\begin{array}{c} \text{Cl} \\ \text{Co} \end{array} \begin{array}{c} \text{NO}_3 \\ \text{Co} \end{array} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{array} \right] (\text{NO}_3)_3$.
 - - - - (8) $\left[\begin{array}{c} \text{Cl}_2 \\ \text{Co} \end{array} \begin{array}{c} \text{Cl} \\ \text{Co} \end{array} \begin{array}{c} \text{NO}_3 \\ \text{Co} \end{array} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{array} \right] (\text{NO}_3)_3$.
 - - - - (1) $[(\text{NH}_3)_5\text{Co}-\text{NH}_2-\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$.

Fig. 5.

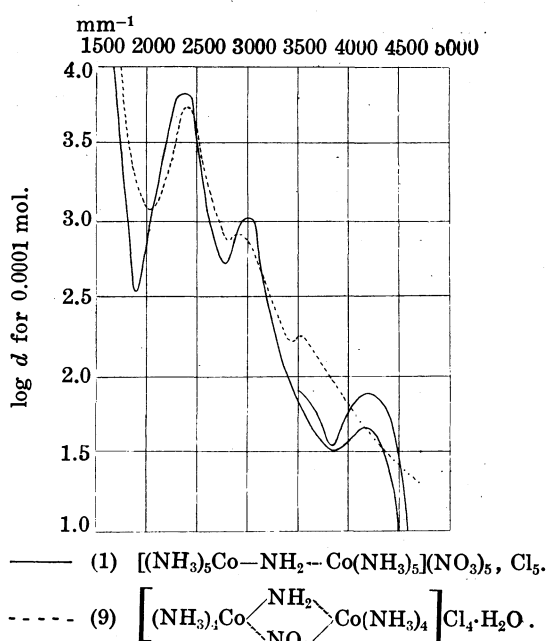


Fig. 6.

The effect of NO_2 -group is hypsochromic with the 1st band as it is in the mononuclear complex salt; but, on the contrary, with the 2nd band it is also hypsochromic. Perhaps this change is caused by the NH_2 -group co-ordinated in the cis-position to it. With the third band, the effect is found to be bathochromic.

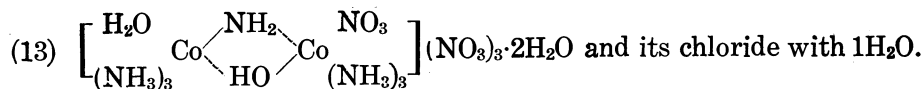
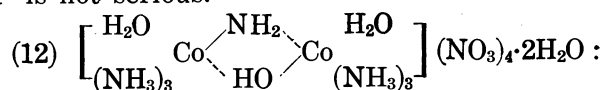
(10) $\left[(\text{NH}_3)_4 \text{Co} \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{SO}_4 \end{array} \text{Co} (\text{NH}_3)_4 \right] (\text{NO}_3)_3$ and its chloride.

(11) $\left[(\text{NH}_3)_4 \text{Co} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{SO}_4 \end{array} \text{Co} (\text{NH}_3)_4 \right] (\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: These three salts are all reddish violet fine crystals (the imino-salt is a little lighter coloured

than the other), and give violet phosphoric acid solutions. Their absorption curves are given in Fig. 7.

There are two distinct absorption bands at 1850 mm^{-1} and 2700 mm^{-1} , but the absorption of the imino-salt is a little more hypochromic than the other, and all of them have not the 3rd band: namely, the most conspicuous effect of the SO_4 -group is that it wipes out the 3rd band of the salt (1).

The effect on the 1st band is a little hypsochromic and on the 2nd band bathochromic. On the spectrum the difference between NH_2 - and NH - is not serious.



The former is a light reddish brown crystal and the latter two are reddish orange crystals. All these three give reddish orange phosphoric acid solution. Their absorption curves are shown in Fig. 8. The 1st salt at 1910 mm^{-1} , 2550 mm^{-1} and 3200 mm^{-1} ; the 2nd salt at 1910 mm^{-1} , 2560 mm^{-1} and 3390 mm^{-1} ; the 3rd chloride at 1910 mm^{-1} , 2530 mm^{-1} and 3350 mm^{-1} .

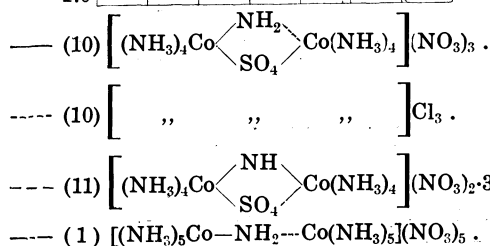
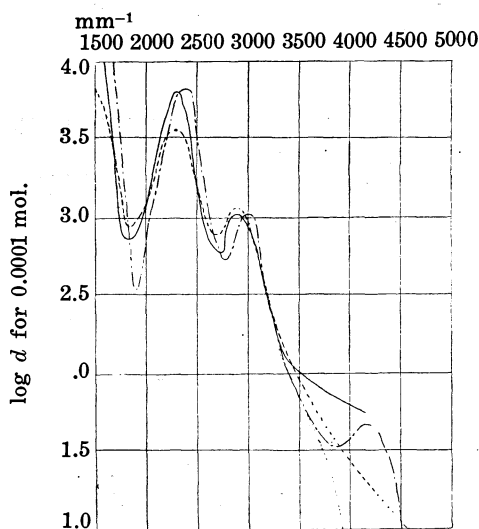


Fig. 7.

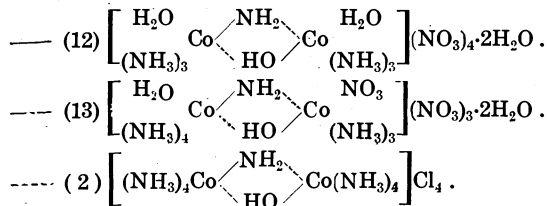
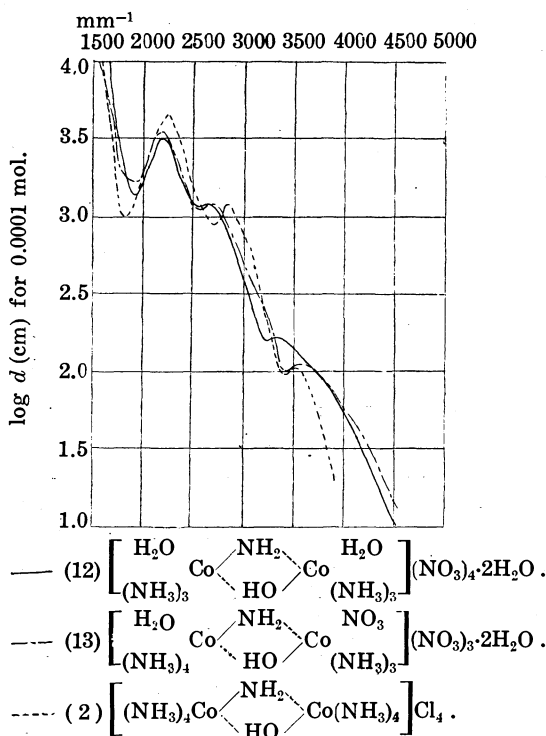
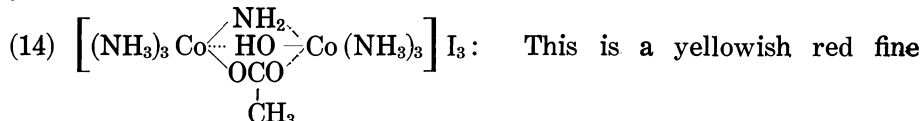


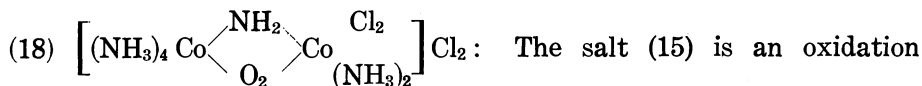
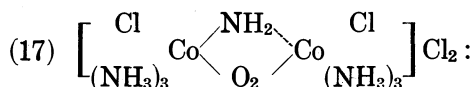
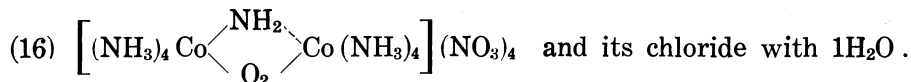
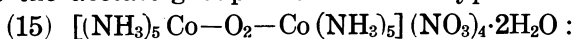
Fig. 8.

These three salts are regarded as derivatives of the salt (2), and from the result it is shown that in this case the effect of NO_3 -group appears only on the 3rd band: viz., it is hypo- and hypsochromic. The effect of H_2O -molecule is serious in this case as it is hypsochromic on the 1st band and bathochromic on the 2nd and 3rd band, moreover, it is hypsochromic for all of these three bands. So, the fact, that by the above mentioned salt (5) three bands are all found hypsochromic, is probably the effect of H_2O .



powder and gives an orange phosphoric acid solution. But as its solubility is very small, its 0.025 mol. solution cannot be prepared. So, a solution of 0.00625 mol. was used, and afterwards the result has been rearranged for the position of 0.025 mol. The absorption curve is shown in Fig. 9. It has three bands at 1890 mm^{-1} , 3310 mm^{-1} and 2650 mm^{-1} . This 3310 mm^{-1} -absorption is very distinct and seems to be the characteristic one for this "acetato" complex salt; and when this salt is considered to be the derivative of the salt (2), the acetato-group effects on the 3rd band of the latter as bathochromic.

The absorption at 2650 mm^{-1} is a very small one, and possibly seems to be an inflection point: but it is certainly the transformed 2nd band originally found in the salt (2). With all these results it may be said that the acetato-group effects much hyperchromic and bathochromic.



product of ammoniacal cobalt nitrate solution, and presents itself as a large dark greenish brown crystal.

It gives a greenish brown solution in the phosphoric acid, and its absorption curve has two great bands at 2000 mm^{-1} and 3360 mm^{-1} with a very fine one at 2900 mm^{-1} as shown in Fig. 10. The absorption at 3360 mm^{-1} is exceptionally hyperchromic, and, at first, it was doubted to be the absorption caused by the nitrate ion, but NaNO_3 has been proved to have a small one at 3730 mm^{-1} , this 3360 mm^{-1} -absorption may be regarded as the effect of the complex cation. Still more it seems to have another absorption in the infra-red region, but it cannot be observed for the sake of the small sensitivity of plate. That fine absorption at 2900 mm^{-1} is found in this salt only.

In the case of this salt, the absorption in the infra-red region is probably the first absorption band, and the apparently first 2000 mm^{-1} -absorption is really the second.

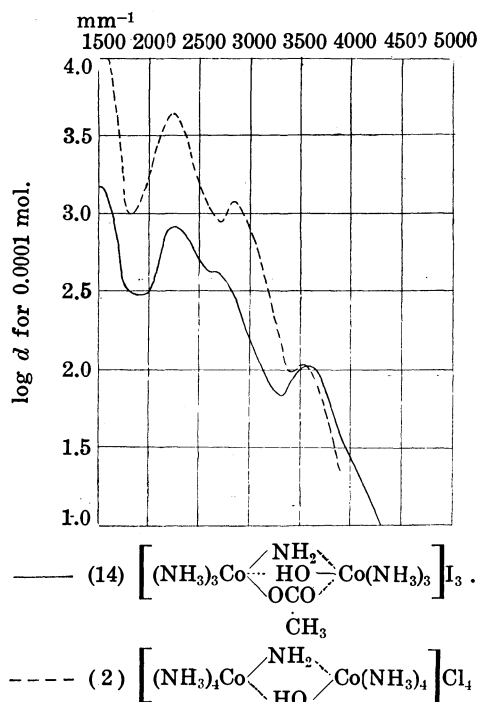


Fig. 9.

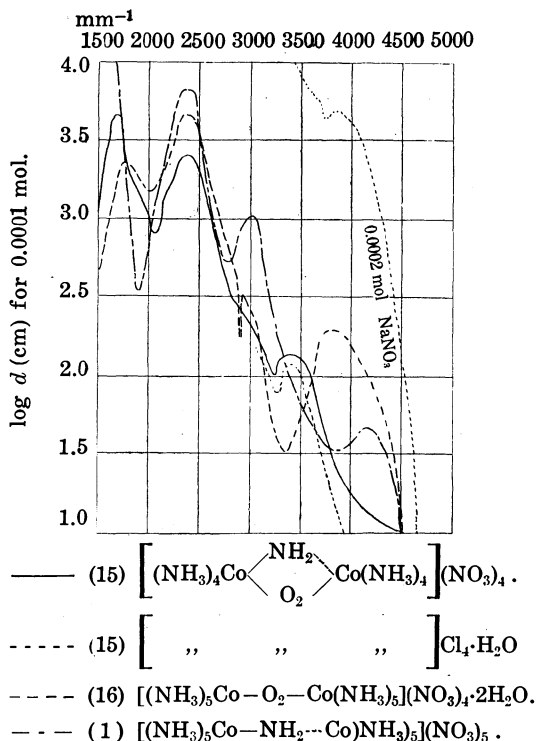


Fig. 10.

The salt (16) is regarded to be the intermediate compound of (1) and (16). It has a dark green colour and the phosphoric acid solution is greenish brown. Its absorption curve has also two distinct bands at 2080 mm^{-1} and 3270 mm^{-1} , and probably one more in the infra-red region as shown in Fig. 10., and there is almost no difference between nitrate and chloride. Its absorption at 3270 mm^{-1} is considerably more hypochromic than that of the salt (15).

Now, when to this salt (16) two Cl-atoms are entered, there appears two salts (17) and (18) according to the position of Cl-atoms: viz., if these two are co-ordinated together to one atom there yields the salt (18), and if co-ordinated apart to the different cobalt atoms, there yields the salt (17).

The former is a brownish violet crystalline powder and gives a dark greenish brown phosphoric acid solution. Its absorption maxima lie on 1920 mm^{-1} , 2640 mm^{-1} and 3140 mm^{-1} as shown in Fig. 11.

The latter is a green powder and gives a dark green solution with great difficulties. Its absorption maxima lie on 1950 mm^{-1} , 2885 mm^{-1} , 3150 mm^{-1} and 3560 mm^{-1} . But this 2885 mm^{-1} -absorption seems to be a little uncertain one. In either case, these two salts differ not only in their crystalline colour but also in their absorption. The 3150 mm^{-1} -absorption is common for these two salts and probably it is the third bands; it is a little more hypo- and bathochromic than that of (15). But for the other part of the absorption curve and for the existence of a quadrivalent cobalt atom, regularities have not yet been found.

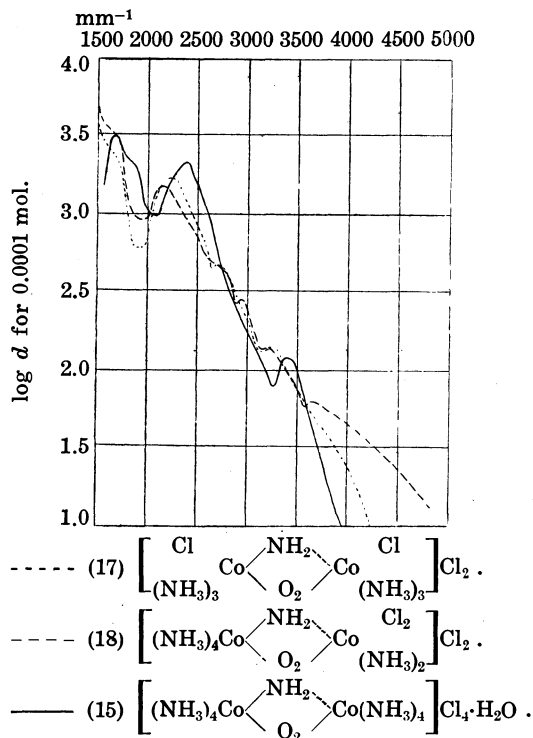


Fig. 11.

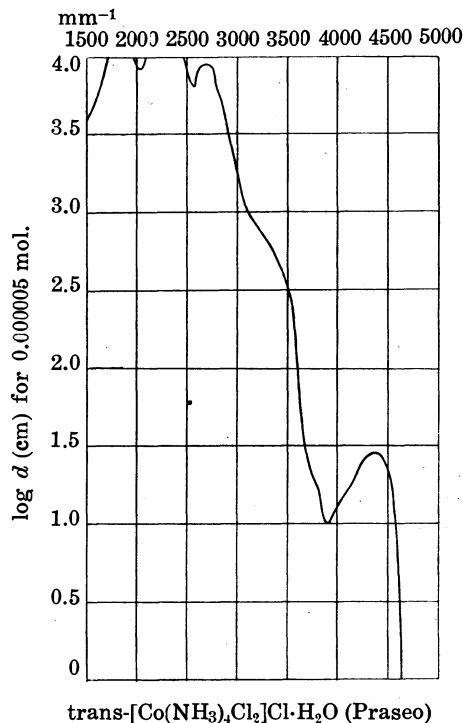


Fig. 12.

According to the opinion⁽⁴⁾ that the third band is caused with two anionic ligands co-ordinated in the trans-position, the author observed the absorption spectrum of the trans-[Co(NH₃)₄Cl₂]Cl·H₂O (Praseo-chloride) also in the phosphoric acid solution as shown in Fig. 12.; the results, however, are proved to be of no use. But this great band at 3900 mm⁻¹ is a very peculiar one.

Summary.

The absorption spectra of the polynuclear cobalt complex salts are observed in the phosphoric acid solution. They are stable in it, and give distinct absorption spectra.

In conclusion the author expresses his hearty thanks to Dr. H. Shiba and Dr. T. Inoue of The Institute of Physical and Chemical Research, and further to Prof. Y. Shibata of The Imperial University of Tokyo. This paper is dedicated to the soul of my late wife, Yoshiko, who had aided me very much and died on March 30th, 1940.

*The Institute of Physical and
Chemical Research, Tokyo.*

(4) R. Tsuchida, this Bulletin, **13** (1938), 388, 436. etc.

On the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum.

By Isamu SANO.

(Received March 28, 1940).

It is well known, as an established fact for a long time, that oxalic acid is appreciably decomposed in its aqueous solutions by a variety of agents such as light,⁽¹⁾ moulds⁽²⁾ as well as metals in finely divided state.⁽³⁾

In the last communication,⁽⁴⁾ the present writer made a description of the results obtained in the decomposition of the acid due to oxidation with the air, which is catalyzed by the colloidal platinum-carbonyl as well as by the colloidal platinum obtainable by leaving it alone in contact with the air. The sols of platinum-carbonyl tinged with red as well as of platinum tinged with black, were both used without subjected to dialysis, and therefore, they were contaminated with hydrochloric acid liberated from chloroplatinic acid through the reducing action of carbon monoxide, although the acid is likely to have little influence upon the stability of the sols thus produced.⁽⁵⁾

The red sols of platinum-carbonyl may be easily obtained, as already reported,⁽⁴⁾ by passing carbon monoxide through dilute aqueous solutions of chloroplatinic acid for some time at ordinary temperature. By dialyzing the red sol, it turns black in due time to convert into a sol of platinum.⁽⁵⁾

The present communication deals with the experiments on the decomposition of oxalic acid catalyzed by the black sol of platinum obtained by means of dialysis of the red one.

Experimental. A 0.05% aqueous solution of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was used in preparing the red sol in each run of the experiments. Carbon monoxide was produced by heating the mixture of formic acid instead of oxalic acid previously used and concentrated sulphuric acid, and then, purified by passing through alkaline hydroxide solutions. The passage of carbon monoxide through the acid solutions was done at nearly a constant rate of 3 litres per hour throughout the

(1) P. Carles, *Compt. rend.*, **71** (1870), 226; 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; T. Gigli, *Chem. Zentr.*, **64** (1893), I, 11; A. Richardson, *J. Chem. Soc.*, **65** (1894), 450; H. de Vries, *Z. angew. Chem.*, **1899**, 521; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521; S. Ishimaru, *J. Chem. Soc. Japan*, **43** (1922), 767; **53** (1932), 449; *Science Repts. Tohoku Imp. Univ.*, Ser. I, **24** (1935), 411.

(2) 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.

(3) O. Šulc, *Z. physik. Chem.*, **28** (1899), 719.

(4) I. Sano, this Bulletin, **14** (1939), 121.

(5) I. Sano, this Bulletin, **9** (1934), 320.

experiments. The red sol was dialyzed, immediately after its formation, with parchment paper for a few days with the frequent renewal of dialysate until freed from chlorine ions. Care was taken to keep the volume of the sol constant through the course of dialysis, this being conducted in a flanged glass-tube with graduation, open at both ends, over the bottom of which the membrane was tightly tied with a cord. Consequently, the black sol of platinum thus obtained might be reasonably inferred from calculation to contain 0.188 grams of platinum in one litre, the same as in the red sol of platinum-carbonyl so far as the content of platinum is concerned. It must be mentioned for reference that the sol was exposed, by way of precaution, to the action of ultrasonics for a few minutes prior to use in order to make sure of its dispersion, since the sol has a slight tendency, particularly if concentrated,⁽⁶⁾ to settle to some extent.

The reactions were carried out at 50.0°C. under diffused day-light. The procedures were the same as in the last communication.⁽⁴⁾ The reacting mixtures consisting of 10 c.c. of aqueous solution of oxalic acid of a definite concentration and 2 c.c. of the black sol were placed in test-tubes provided with a rubber stopper through which a capillary glass-tube was inserted as a line of communication of the air, and enough agitated at short intervals during the course of the run. The acid contents of the test-tubes were, by turns, titrated with a 0.1 N barium hydroxide solution at the desired intervals of time.

Results and Discussion. The results are given in Tables 1, 2, 3, 4 and 5, where t represents the time elapsed from the start in hours, c the titre of the reacting solution titrated with the barium hydroxide solution at time t in c.c. The meanings of c_k and t_k in the tables will be elucidated later.

With the intention of verifying the condition indispensable for the progress of the reaction accelerated through the existence of colloidal platinum that the reacting solution must be charged with dissolved oxygen, a number of runs were made at 50.0°C. in test-tubes hermetically sealed. The results are shown in Tables 6 and 7.

These results were plotted on a graph with the values of $c_0 - c$ as ordinates and of t as abscissæ in Fig. 1, 2, 3 and 4, where the figure attending on the curve states the number of the table referred to. If the reaction catalyzed by colloidal platinum should, in process of time, pass to proceed in conformity to the formula for a reaction of zero order

$$-dc/dt = k \quad \text{or} \quad c_0 - c = kt,$$

Table 1. Concentration of oxalic acid solution: 0.10 N

t	c	$c_k (t_k = 1)$
0	11.32 (c_0)	—
1	11.04	11.04
3	10.85	11.03
5	10.62	10.98
7	10.46	11.00
9	10.28	11.00
11	10.06	10.96
13	10.00	11.07
16	9.82	11.16
19	9.42	11.03
23	9.08	11.05
27	8.51	(10.84)
31	8.06	(10.75)

(6) I. Sano, this Bulletin, **15** (1940), 106.

Table 2. Concentration of oxalic acid solution: 0.10 N

t	c	$c_k (t_k = 4)$
0	11.28 (c_0)	—
2	10.88	—
4	10.51	10.51
6	10.28	10.47
8	10.15	10.53
10	9.96	10.53
12	9.74	10.51
15	9.49	10.54
20	8.97	10.50
24	8.58	10.49
27	8.17	(10.37)
31	7.57	(10.15)

Table 3. Concentration of oxalic acid solution: 0.05 N

t	c	$c_k (t_k = 1)$
0	5.72 (c_0)	—
1	5.46	5.46
3	5.26	5.44
5	5.08	5.43
7	4.91	5.44
9	4.74	5.46
12	4.56	5.53
15	4.20	5.44
20	3.76	5.44
24	3.40	5.43
27	3.24	5.54
30	2.87	5.43
32	2.52	(5.26)

Table 4. Concentration of oxalic acid solution: 0.025 N

t	c	$c_k (t_k = 1)$
0	3.03 (c_0)	—
1	2.82	2.82
3	2.64	2.80
5	2.45	2.78
7	2.34	2.83
9	2.02	2.67
12	1.92	2.82
15	1.57	2.72
19	1.42	2.89
22	1.16	2.88
25	0.79	2.73
28	0.69	2.90
32	0.30	2.84

Table 5. Concentration of oxalic acid solution: 0.025 N

t	c	$c_k (t_k = 2)$
0	3.02 (c_0)	—
1	2.81	—
3	2.50	2.59
4	2.38	2.56
6	2.27	2.63
10	1.91	2.62
12	1.68	2.57
16	1.34	2.58
20	1.06	2.66
24	0.51	2.47
28	0.27	2.58
32	0.19	(2.86)

Table 6. Concentration of oxalic acid solution: 0.10 N

t	c	$c_k (t_k = 1)$
0	11.30 (c_0)	—
1	10.96	10.96
2	10.86	10.93
3	10.78	10.92
6	10.60	10.96
9	10.34	10.92
12	10.19	10.98
15	9.90	10.61
21	9.88	—
24	9.85	—
27	9.82	—
30	9.76	—

Table 7. Concentration of oxalic acid solution: 0.025 N

t	c	$c_k (t_k = 1)$
0	3.10 (c_0)	—
1	2.67	2.67
3	2.60	2.75
6	2.24	2.62
9	2.06	2.67
12	1.86	—
15	1.78	—
18	1.62	—
21	1.58	—
24	1.50	—
27	1.45	—
30	1.28	—

where c_0 is the original concentration of the reacting solution and k the velocity constant, there should exist a portion of straight line in the curve representing the relation between $c_0 - c$ and t , and this is the actual case as shown in Fig. 1, 2 and 3. The reaction takes place immediately after the addition to the acid solution of the black sol dialyzed beforehand and proceeds smoothly, this forming a contrast to the progress of the reaction catalyzed by the red sol in which case there can be distinctly seen an induction period at the outset.⁽⁴⁾ Although the incipient part of Curves 1, 2, 3, 4 and 5 in the figures changes its course in a short time after the

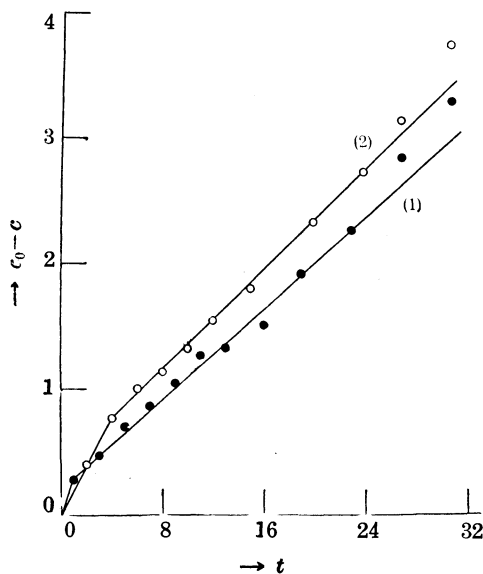


Fig. 1.

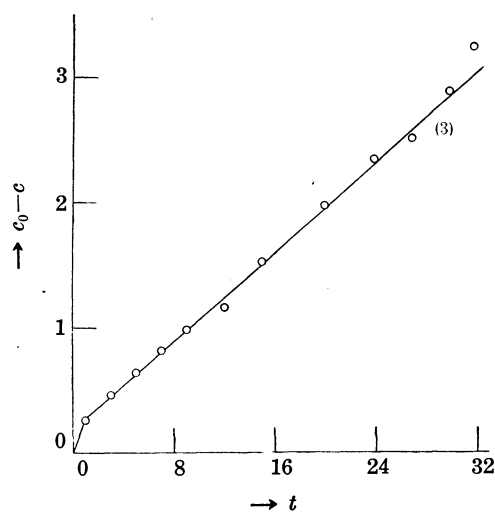


Fig. 2.

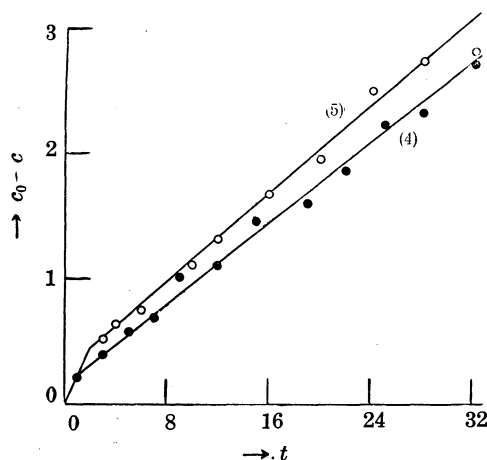


Fig. 3.

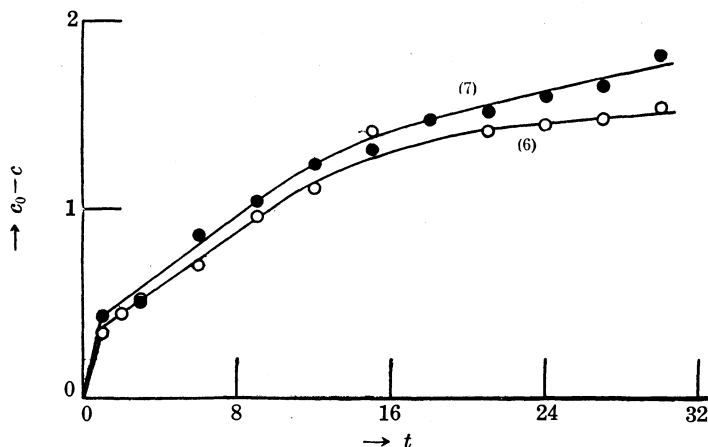


Fig. 4.

commencement of reaction, the subsequent part of it assumes a rectilinear figure within the range of measurement performed. The turning-point in the curve following on the heels of the transition period might make its appearance, as described in the last communication,⁽⁴⁾ in consequence of the coagulation of the sol by electrolyte and, in particular, by heat. The catalyzing ability of colloidal particle must be reduced to some extent through coagulation in the course of the transition period. It may be supposed for the coagulation to occur the more promptly and strongly, the more concentrated the oxalic acid solution and the higher the temperature of reaction is. It was observed as a matter of fact that in dilute solutions of the acid, the sol was apparently stable throughout one run of the experiments; while in concentrated solutions, it somewhat flocculated in due course of time to have a slight tendency to settle at the bottom. The magnitudes of the velocity constant corresponding for the linear portion of curve in the figures were found, however, to be approximately identical with one another as in the table shown below,

Number of table	Concentration of aqueous solution of oxalic acid (N)	$k = (c_0 - c) / t$
1	0.10	0.0895
2	0.10	0.0957
3	0.05	0.0883
4	0.025	0.0818
5	0.025	0.0889
6	0.10	0.0720
7	0.025	0.0767

this being in striking contrast to the results obtained with the sols not subjected to dialysis in advance, according to which it was very likely for the reactions to proceed in accordance with the formula for the type of first order, and moreover, it was undeniable for the velocity constant to be notably affected by the concentration of the acid solution. In the cases of the reactions with the sols dialyzed, it is found for them, as indicated above, to be rather

of the type of zero order. The applicabilities of the alternative types can be clearly seen particularly with dilute solutions of the acid.

This remarkable difference may be attributed to the singularity of conditions of the surface of colloidal particle due to dialysis by dint of

which the sol could be set free from contamination by electrolyte. It might be supposed for the colloidal particles to be invested with the enhanced adsorptive as well as catalytic ability through the process of dialysis, and in consequence, to be capable of adsorbing the reactant strongly and extensively; this implies that the available surface of particle may be practically saturated with reactant at the concentrations prevailing and the reaction velocity independent of concentration, the reaction being therefore of zero order. It can be definitely seen, however, that Curves 1, 2 and 3 are only approximately linear to go on increasing with the lapse of time, although Curves 4 and 5 are both of rectilinear figure throughout the course of reaction concerned.

The value of c_k tabulated previously was computed from k shown above in conformity to the formula for reaction of zero order

$$c_k - c = kt,$$

where c signifies the titre of oxalic acid solution as before at time t reckoned from a virtual starting-point of estimation denoted by t_k in the tables. It can be anticipated for c_k to take a constant value in each run of the experiments if the reaction concerned should be of zero order.

Taking these circumstances into account, some theoretical discussion of the subject will be made below. If θ_1 is the fraction of the available surface covered unimolecularly with molecules of oxalic acid and θ_2 with molecules of oxygen at any time, it will follow under the same assumptions as in the last communication⁽⁴⁾ that for equilibrium between the adsorbed layer consisting of both molecules of oxalic acid as well as oxygen and those in the surrounding medium

$$a_1 \mu_1 (1 - \theta_1 - \theta_2) = \nu_1 \theta_1 \quad \text{and} \quad a_2 \mu_2 (1 - \theta_1 - \theta_2) = \nu_2 \theta_2,$$

a_1 and a_2 being the fraction of the numbers of molecules of oxalic acid and oxygen, μ_1 and μ_2 , colliding with the surface of colloidal catalyst in unit time which remain, and $\nu_1 \theta_1$ and $\nu_2 \theta_2$ the numbers of molecules of oxalic acid and oxygen which leave the surface in unit time. The presence of molecules of water as solvent may be set at naught because of the hydrophobic nature of the colloidal particle involved.

Neglecting θ_2 in comparison with θ_1 under the assumption that the surface is covered only sparsely with molecules of oxygen, though to a much greater extent with molecules of oxalic acid, so that $\theta_2 \ll \theta_1 < 1$, it follows that

$$a_1 \mu_1 (1 - \theta_1) = \nu_1 \theta_1 \quad \text{and} \quad a_2 \mu_2 (1 - \theta_1) = \nu_2 \theta_2.$$

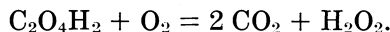
Solving these for θ_1 and θ_2 ,

$$\theta_1 = a_1 \mu_1 / (a_1 \mu_1 + \nu_1) \quad \text{and} \quad \theta_2 = \nu_1 a_2 \mu_2 / \nu_2 (a_1 \mu_1 + \nu_1).$$

Since it may be presumed for the rate of reaction, v , referred to the oxalic acid concentration, c , 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. This points to the rate-determining process suggested in the last communication⁽⁴⁾



Substituting θ_1 and θ_2 obtained from the above equations, it follows that

$$\begin{aligned} v &= k \left\{ a_1 \mu_1 / (a_1 \mu_1 + \nu_1) \right\} \cdot \left\{ \nu_1 a_2 \mu_2 / \nu_2 (a_1 \mu_1 + \nu_1) \right\} \\ &= k' a_1 \mu_1 \mu_2 / (a_1 \mu_1 + \nu_1)^2, \end{aligned}$$

where k' is set up of a combination of various constants such as k , ν_1 , ν_2 and a_2 .

Now, reference must be made to the aspect⁽⁷⁾ that there should exist a relationship shown by the formulation

$$Z = n \sqrt{RT/2\pi M}$$

between the number of molecules of any reactant, Z , striking unit area of the available surface of catalyst from its surrounding medium in unit time and the concentration, c , of the reactant in the medium, where n shows the number of molecules of reactant per c.c., R the gas constant, T the temperature and M the molecular weight of the reactant, this indicating Z to be proportional to c as assumed previously.^{(4),(8)}

Thus, the velocity equation mentioned above may be rewritten in the form

$$-dn/dt = k' a_1 s \kappa n \mu_2 / (a_1 s \kappa n + \nu_1)^2,$$

where κ stands for $\sqrt{RT/2\pi M}$, n the number of molecules of oxalic acid per c.c. at time t and s the total area of available surface of catalyst. Since μ_2 is presumed to be constant throughout the run of the experiments on account of the reacting system being continually supplied with oxygen from the outside, this reduces to

$$-dn/dt = k'' a_1 s \kappa n / (a_1 s \kappa n + \nu_1)^2,$$

k'' being a constant including μ_2 . On integration it follows that

$$(n_0 - n) \left\{ (a_1 s \kappa / 2) \cdot (n_0 + n) + 2\nu_1 + (\nu_1^2 / a_1 s \kappa) \cdot \ln (n_0 / n) / (n_0 - n) \right\} = k'' t,$$

where n_0 indicates the number of molecules of oxalic acid at the outset of reaction. Putting

$$K(n) = (a_1 s \kappa / 2) \cdot (n_0 + n) + 2\nu_1 + (\nu_1^2 / a_1 s \kappa) \cdot \ln (n_0 / n) / (n_0 - n)$$

$$K_1(n) = (a_1 s \kappa / 2) \cdot (n_0 + n) \quad \text{and} \quad K_2(n) = (\nu_1^2 / a_1 s \kappa) \cdot \ln (n_0 / n) / (n_0 - n)$$

the equation becomes

(7) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 22, Oxford (1933).

(8) I. Sano, this Bulletin, **13** (1938), 118.

$$n_0 - n = (k'' / K(n)) t.$$

This suggests the reaction to be of zero order, if $K(n)$ could be assumed to be constant, since $n_0 - n$ is proportional to $c_0 - c$, and this would be the actual case as is to be anticipated from the following consideration. The functions, $K_1(n)$ and $K_2(n)$, are monotonously increasing and decreasing with increasing n respectively, and accordingly, the function $K(n)$ would assume a roughly constant value over a certain range of varying n . This is schematically indicated in Fig. 5, Curves K_1 , K_2 and K speaking for the variation of the functions, $K_1(n)$, $K_2(n)$ and $K(n)$, with n respectively. Considered in this light, the reaction should proceed practically in line with the formula for the type of zero order.

It has been reported already that oxalic acid is decomposed in its aqueous solutions in the presence of oxygen. The effect is definitely shown by Curves 6 and 7 in Fig. 4. In these runs the reaction was performed in test-tubes hermetically sealed in order of keeping out the air from the outside. It can be explicitly seen the drift to occur in the course of time from want of oxygen.

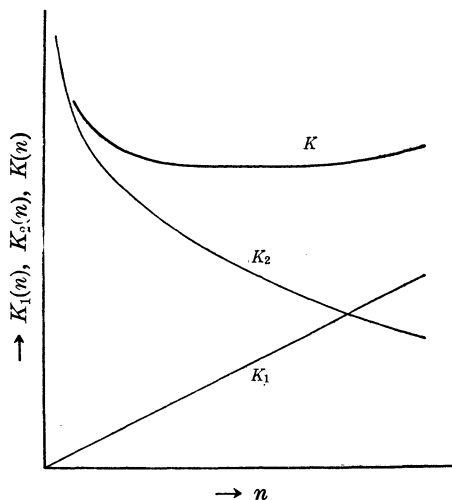
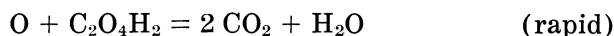
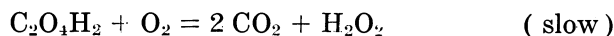
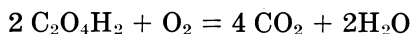


Fig. 5.

From what has been stated, the catalytic decomposition of oxalic acid in its aqueous solutions accelerated by colloidal platinum in the presence of oxygen may be accounted for in the same manner as described in the last communication⁽⁴⁾; that is,



Therefore, the velocity of the reaction



should be determined by the first step of decomposition.

Summary.

(1) The decomposition of aqueous solutions of oxalic acid (0.10, 0.05 and 0.025 N) due to oxidation accelerated by colloidal platinum obtained through the process of dialysis of colloidal platinum-carbonyl was investigated, in the presence of oxygen and diffused day-light, during a period extending over thirty hours at 50.0°C.

(2) It appears that the greater part of the course of reaction proceeds in accordance with the formula for the type of zero order after it passed incipiently through a short period of transition and the rate of reaction is scarcely influenced by the concentration of reacting solution.

(3) It was definitely shown that the reaction should be retarded if the supply of oxygen is cut off.

(4) The above results were explained in conformity with the mechanism of reaction previously proposed.

The author wishes to express his cordial thanks to Prof. J. Same-shima under whose kind guidance the present work has been carried out. 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.

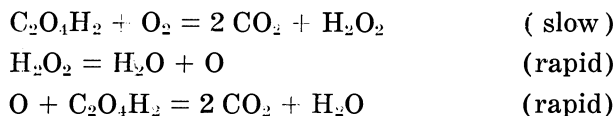
*Chemical Institute, Faculty of Science,
Tokyo Imperial University.*

The Effect of Gases upon the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum.

By Isamu SANO.

(Received March 23, 1940).

It was depicted in the foregoing papers^{(1),(2)} that the catalytic decomposition of oxalic acid in its aqueous solutions by colloidal platinum-carbonyl as well as colloidal platinum would be definitely suppressed in case of deficient supply of air, and consequently, the scheme of the reaction might be assumed to be given by



In the present experiments the influences of various gases, with which the reacting system was kept in contact throughout the course of reaction, upon the decomposition of the acid catalyzed by colloidal platinum were investigated with oxygen, nitrogen as well as air under reduced pressure as the charged gas.

The reactions were conducted under diffused day-light as it has been already confirmed to be of no influence upon the decomposition of the acid

(1) I. Sano, this Bulletin, **14** (1939), 121.

(2) I. Sano, this Bulletin, **15** (1940), 196.

solution. The experimental procedures were quite the same as described in the previous paper⁽²⁾ except the contrast of the gases touching the medium of reaction. The reacting mixtures composed of 10 c.c. of a 0.05 N aqueous solution of oxalic acid and 2 c.c. of the platinum sol obtained from a 0.05% aqueous solution of chloroplatinic acid in the same way as stated formerly⁽²⁾ were put in test-tubes, which, immediately afterwards, were thoroughly filled with the gas in question and tightly sealed with rubber stopper, and consecutively, they were brought without delay in a thermostat to be kept at 50.0°C. under diffused day-light for the desired space of time. Oxygen now used was produced from sodium

Table 1.
Filled with oxygen.

t	c
0	5.99 (c_0)
3	4.76
6	3.58
12	1.99
18	2.03
24	1.83
30	1.80
40	1.79

Table 2.
Filled with nitrogen.

t	c
0	5.99 (c_0)
3	5.78
6	5.77
12	5.78
18	5.82
24	5.79
30	5.78
40	5.78

Table 3.
Filled with air under
reduced pressure.

t	c
0	5.99 (c_0)
3	5.80
6	5.78
12	5.67
18	5.65
24	5.65
30	5.63
40	5.60

peroxide and water, and nitrogen from an aqueous solution of ammonium nitrite. The run of experiments with air under reduced pressure was performed in test-tubes furnished with rubber stopper through which a capillary tube was transfixed as a valve of exhaustion of air by means of water-pump. The degassing process was put, at intervals, in practice for some time at ordinary temperature.

The results are given in Tables 1, 2 and 3, where t indicates the time elapsed from the start in hours and c the titre of the reacting solution titrated with a 0.1 N barium hydroxide solution at time t in c.c. The variation of $c_0 - c$ with t is graphically represented in Fig. 1, where the numeral accompanying the curve shows the number of the table referred to.

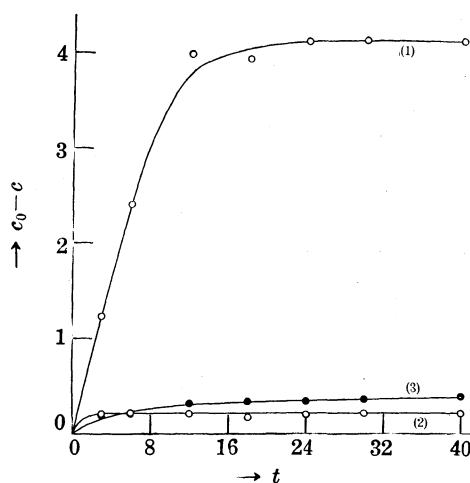
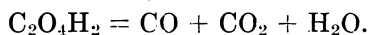


Fig. 1.

It can be seen from these that oxygen has a notable influence standing out in sharp contrast to those of nitrogen as well as air under reduced pressure. The retarding effect observed in the course of the reaction with oxygen may come from the increasing shortage of the gas with the progress of reaction. The appreciable decomposition of the acid at the inci-

cient stage as seen in the runs with nitrogen as well as air under reduced pressure would be attributable to the air dissolving originally in the acid solution. Since a small quantity of air would effect an entrance into the vessel of reaction during the degassing steps conducted frequently with water-pump in the run, the reaction with air under reduced pressure might progress, though slow, with the lapse of time, and this is the actual case as indicated by Curve 3 in the figure.

The evacuation was intended to clear the reacting system of carbon monoxide which would be produced and adsorbed by the surface of catalyst to keep the reaction from the progress if the decomposition of the acid should occur unimolecularly on the surface of catalyst in accordance with



It would seem, in view of the results obtained, that circumstances are rather adverse for the unimolecular decomposition.

To infer from the informations which have hitherto been acquired, it will follow that oxalic acid should be decomposed, in the presence of oxygen as well as colloidal platinum, in line with the mechanism above-mentioned.

Summary.

(1) The influences of gases such as oxygen, nitrogen as well as air under reduced pressure upon the decomposition of aqueous solution of oxalic acid (0.05 N) were, in the existence of colloidal platinum obtained from colloidal platinum-carbonyl through dialysis and under diffused daylight, examined at 50.0°C.

(2) Oxygen alone has a marked effect in accelerating the decomposition, but the two others none.

(3) This gives support to the mechanism of reaction previously discussed.

The author wishes to express his sincere thanks to Prof. J. Same-shima for his kind guidance 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.

*Chemical Institute, Faculty of Science,
Tokyo Imperial University.*

On the Dialysis of Platinum-carbonyl Sol.

By Isamu SANO.

(Received April 19, 1940.)

It was described, in the preceding paper⁽¹⁾, that the platinum-carbonyl sol obtainable at ordinary temperature from a dilute aqueous solution of chloroplatinic acid by the action of carbon monoxide would, if left alone in the air for some time or submitted to dialysis, turn black from red colour to yield a platinum sol. This could be interpreted to be caused by the disappearance of carbon monoxide from colloidal particles owing to its volatilization towards as well as oxidation by the air during these processes. In fact, the red sol is so stable, if kept in touch with carbon monoxide, that it would be tinged, as it is, with red slightly inclining to purple for a long period. For instance, a platinum-carbonyl sol prepared from a 0.05% solution of the acid and hermetically sealed with the gas in a test-tube was scarcely charged with any appreciable change in colour for more than two years, though colloidal particles in the sol would come to display sedimentation in due course of time. The aspect of the red sol at several months after its preparation is illustrated in Fig. 1. Although the sol settled almost wholly about two years later, it could disperse with facility, if exposed to the action of supersonics, to be the same in appearance as ever.

It may be presumed from these facts that, if dialyzed in the atmosphere of carbon monoxide, platinum-carbonyl sol will be set free, assuming red as it is, from hydrochloric acid liberated, in process of preparation, from chloroplatinic acid in consequence of its reduction by carbon monoxide. This was verified to be the actual case by the present experiment.

Experimental. The apparatus used is schematically shown in Fig. 2. Shortly after its formation, the red sol is transferred quickly and smoothly into the dialyzer, and immediately, subjected to dialysis, passing continually carbon monoxide through the sol as well as the dialyzate in turn. The dialysis was conducted with frequent changes of the dialyzate until freed from chlorine ions for a long space of time extending over fifteen days at room temperature, making use of a sheet of viscose in tubular form as the dialyzing membrane (M). Whenever the dialyzate was taken out through the cock (C) to be tested of chlorine ion, it was immediately supplied through the tube (T) from the reservoir (R) provided with a compression-valve (V). The conclusive test of chlorine ion was made directly with the sol in such a manner that a small portion of it was pipetted out from the dialyzer, converted by heating to a black sol of platinum, separated from suspending particles by dint of centrifuge, and now, submitted to the trial on chlorine ion.

(1) I. SANO, this Bulletin, 9 (1934), 320.

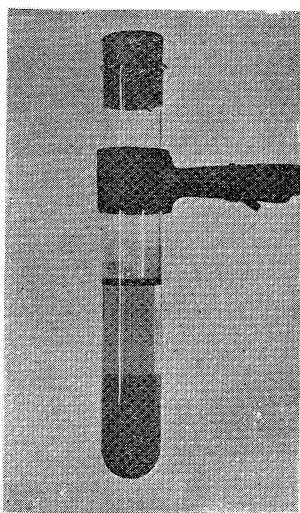


Fig. 1.

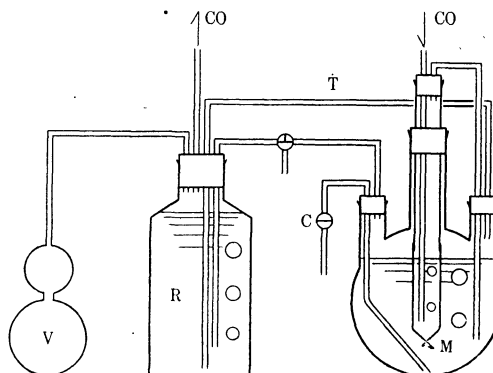


Fig. 2.

The experiments were made with the sols prepared at ordinary temperature in the same way as previously from 0.02 as well as 0.05% solutions of chloroplatinic acid. The sols obtained through the process of dialysis are the very same as they were before, not only in appearance but also in behaviour. For example, they assume a red colour which is slightly tinged with purple, decompose readily with the addition of bromine water or turn black, if left in the air or heated to some extent, to produce platinum sols. According to electrophoretic investigation, they are negatively-charged sols as ever.

It may be concluded from the results that the particles in the red sol, dialyzed or not, are composed only of platinum and carbon monoxide. The possibility of compounds containing chlorine as an essential constituent such as discussed in the preceding paper⁽¹⁾ would be not worth consideration. The formation of colloidal platinum surrounded by molecules of platinum-carbonyl has already⁽¹⁾ been substantially denied from various facts.

Summary.

The platinum-carbonyl sols of red colour prepared from 0.02 as well as 0.05% aqueous solutions of chloroplatinic acid were dialyzed in the atmosphere of carbon monoxide, as they would turn black to convert into platinum sols when treated in the air, until freed from chlorine ions.

The sols obtained through the process were just the same in appearance as well as in behaviour as they were formerly. This implies that the particles in the red sols, dialyzed or not, are fundamentally constituted from platinum and carbon monoxide or platinum-carbonyl.

The author wishes to express his sincere thanks to Prof. J. Sameshima for his kind guidance.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

The Action of Weak Alkalies upon Glucose. II.

By Ryuzaburo NODZU and Ryoze GOTO.

(Received April 26, 1940.)

The formation of acetol from glucose by the action of various alkaline reagents has been often reported. Concerning the mechanism of the formation, there have been two different views. Nef⁽¹⁾ postulated that the acetol is a reduction product of methylglyoxal which is formed from glucose through glyceric aldehyde. Pinkus⁽²⁾, on the contrary, assumed it to be a primary decomposition product of the sugar. The former view has been supported by several investigators among whom Neuberg⁽³⁾ put forward an opinion that methylglyoxal transforms disproportionately into acetol and pyruvic acid.

In the previous paper⁽⁴⁾, it was confirmed chemically and spectrographically that when a mixture of glucose and 1/25 mol solution of sodium carbonate (alone or with sodium sulphite) was distilled, acetol appeared along with diacetyl in the distillate. In the present work, aqueous solutions of glucose, glyceric aldehyde, methylglyoxal, and acetol were respectively distilled with sodium carbonate and the distillates analyzed (as semicarbazones), by methods similar to those described in the previous paper. In Table 1 the experimental results are tabulated.

Table 1.

No.	Sample		Na ₂ CO ₃ 1 25 mol sol. c c.	Na ₂ SO ₃ g.	Dis- tillate c.c.	Iodine con- suming sub- stance as acetol g.	Semicarbazones g.	
	Name	g.					Diacetyl m.p. 278-80°	Acetol m.p. 196-7°
1	Glucose	5	250	15	1200	0.146	0.021	0.084
2	„	5	250	0	1400	0.159	0.020	0.092
3	Methyl- glyoxal	3	250	15	1500	0.072	0.043	0
4	„	3	250	0	1500	0.055	0.031	0
5	Glyceric- aldehyde	2	250	15	1500	0.075	0.014	0
6	„	3	250	15	1000	0.117	0.023	Trace
7	„	2	250	0	1500	0.068	0.011	0
8	„	3	250	0	1000	0.093	0.020	0.010
9	Acetol	1	250	15	1500	0.382	0.001	0.411
10	„	1	250	0	1500	0.343	0.002	0.400

(1) J. U. Nef, *Ann.*, **335** (1904), 247; **357** (1907), 214.

(2) G. Pinkus, *Ber.*, **31** (1898), 31.

(3) C. Neuberg, *Biochem. Z.*, **49** (1913), 502.

(4) R. Nodzu and R. Goto, this Bulletin, **11** (1936), 381.

As will be seen from the table, methylglyoxal gave not even a trace, glyceric aldehyde only a trace of acetol, and glucose an abundance of acetol. It was also found that the yield of acetol from glucose (Table 1. No. 1, 2.) was not increased by the addition of methylglyoxal in similar distillation experiments (Table 2.). Moreover, the origin of acetol from glyceric aldehyde (Table 1. No. 6, 8.) should rather be attributed to a hexose⁽⁵⁾ which may be derived from the latter during the experiment in an alkaline medium.

Table 2.

No.	Sample		Na ₂ CO ₃ $\frac{1}{25}$ mol sol. c.c.	Na ₂ SO ₃ g.	Dis- tillate c.c.	Iodine con- suming sub- stance as acetol g.	Semicarbazones g.	
	Name	g.					Diacetyl m.p. 278-80°	Acetol m.p. 196-7°
1	Glucose Methyl- glyoxal	5 1	250	15	1500	0.213	0.055	0.060
2	Glucose Methyl- glyoxal	5 1	250	0	1500	0.193	0.045	0.045

The acetol, therefore, is formed from glucose neither through glyceric aldehyde nor through methylglyoxal, showing that at least here, the postulations of Nef and others are untenable.

It is noteworthy that methylglyoxal distilled over from the weak alkaline solution as diacetyl, but not as itself, contradicting the assumption often made. It is very likely that under such conditions nearly all the methylglyoxal transforms easily into lactic acid and diacetyl (or acetoin).

Experimental Part. Materials. Methylglyoxal (b.p. 35°-38°/10 mm) was obtained by oxidation of acetone by means selenium dioxide⁽⁶⁾; and glyceric aldehyde (m.p. 130°) was prepared by way of acrolein acetal from glycerin following the Witzemann's method.⁽⁷⁾ Acetol (b.p. 53°-54°/18 mm.) was synthesized from monobromoacetone by the method of Levene and Walti⁽⁸⁾.

Distillation and Analysis. The distillation⁽⁹⁾, the estimation of iodine consuming substances in the distillate, and the analysis of distillate were done in the same ways as described in the previous papers. The experimental results are tabulated in Tables 1 and 2. The distillation residue from methylglyoxal was evaporated to syrup under reduced pressure and the syrup was made strongly acidic by sulphuric acid. Then it was extracted with ether for about 30 hours, following⁽¹⁰⁾ Evans' method.

(5) E. Schmitz, *Ber.*, **46** (1913), 2327; H. O. L. Fischer, *Helv. Chim. Acta*, **19** (1936), 519.

(6) H. L. Riley, J. F. Morley and N. A. C. Friend, *J. Chem. Soc.*, **1932**, 1875.

(7) E. J. Witzemann, *J. Am. Chem. Soc.*, **36** (1914), 1908.

(8) "Organic Syntheses." Vol. X, p. 1, (1930).

(9) During the distillation of methylglyoxal (alone or with glucose), 1/25 mol solution of Na₂CO₃ was supplied from time to time in order to keep a weak alkalinity of the distilling flask content.

(10) W. L. Evans and co-workers, *J. Am. Chem. Soc.*, **48** (1926), 2665.

From the ether extract, lactic acid was isolated in the form of its zinc salt (found: H_2O , 18.2; Zn 21.6; Calc. for $\text{ZnC}_6\text{H}_{10}\text{O}_6 + 3\text{H}_2\text{O}:\text{H}_2\text{O}$, 18.18; Zn 21.89%). Also, the acid was quantitatively titrated following Tanaka and Endo⁽¹¹⁾. The analytical results are cited in Table 3.

Table 3.

No.	Methylglyoxal g.	Na_2CO_3 $\frac{1}{25}$ mol sol. c.c.	Na_2SO_3 g.	Distillate c.c.	Lactic acid in residue	
					g.	%
1	3	250	15	1500	0.654	21.8
2	3	250	0	1500	1.013	34.4

In conclusion, the expense of this work was defrayed by a grant (Sizenkagaku Kenkyu-hi.) from the Department of Education, to which the authors are deeply indebted.

*Chemical Institute, Faculty of Science,
Kyoto Imperial University.*

(11) S. Tanaka and M. Endo, *Biochem. Z.*, **210** (1929), 120.

Acetylformoin. I. Its Preparation.

By Ryuzaburo NODZU and Sango KUNITIKA.

(Received April 30, 1940.)

Benzoylformoin⁽¹⁾ has long been known, but acetylformoin (a provisional formula $\text{CH}_3\text{COCHOHCOCOCH}_3$) has not previously been reported. It may be anticipated to be an interesting substance not only from the point of view of its structure, but also of sugar chemistry, being a possible dehydration product of the hexoses. In the present work, the preparation was effected by applying the principle of benzoin condensation to methylglyoxal.

From the condensation product of methylglyoxal in the presence of potassium cyanide, a yellow crystalline substance was isolated by means

(1) H. G. Söderbaum, *Ber.* **24** (1891), 1386, 3033.

P. H. Abenius and H. G. Söderbaum, *Ber.*, **25** (1892), 3470.

W. Abenius, *Ber.*, **27** (1894), 706.

P. Karrer and A. v. Segesser, *Helv. Chim. Acta*, **18** (1935), 273.

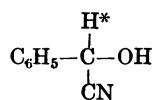
P. Karrer and C. Musande, *Helv. Chim. Acta*, **18** (1935), 1140.

P. Karrer and F. Litwant, *Helv. Chim. Acta*, **19** (1936), 829.

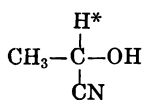
A. H. Blatt, *J. Am. Chem. Soc.*, **57** (1935), 1103; **58** (1936), 1894.

of vacuum distillation. On recrystallization from cold benzene, it formed pale yellow needles and melted at 81–82°. This substance has a molecular formula $C_6H_8O_4$ and may be either acyloin or aldol of methylglyoxal. Under similar experimental conditions, however, it was not formed by the action of hydroxyl ion alone—a proper catalyst for aldolization, indicating that the simultaneous presence of cyanide ion is essential for its formation. It was also observed that its behaviour towards various oxidizing agents—Fehling's solution, ferric chloride and potassium permanganate, was quite similar to that of benzoylformoin. From these evidence, it may be concluded that it has a structure analogous to benzoylformoin and may properly be called acetylformoin.

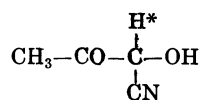
By the action of aqueous alkali cyanide, aliphatic aldehydes, in general, give aldols, but no acyloin. The success in synthesizing acetylformoin seems at first sight to be somewhat surprising. In the previous articles,⁽²⁾ however, we showed that it may be an essential condition for benzoin condensation that the hydrogen atom H^* of a well accepted



(I)



(II)



(III)

intermediate—benzaldehyde cyanhydrine (I) is sufficiently acidic. The failure in the acyloin condensation of aliphatic aldehyde may, therefore, be attributed to a lack of acidity of the typical hydrogen in the intermediate, e.g., (II) being CH_3 a group far inferior to the C_6H_5 group in acidifying effect. On the other hand, the hydrogen atom of methylglyoxal cyanhydrine (III) would be sufficiently acidic, taking into consideration a powerful electromeric effect—an acidifying effect—of the CH_3-CO group. Methylglyoxal should therefore condense to acetylformoin, as it did in the actual case.

It should be noted that the aqueous solution of acetylformoin was fermented by Fleischmann's yeast, leaving the solution laevo-rotatory.

Experimental Part. *Methylglyoxal.* This was prepared from acetone by oxydation with selenium dioxide⁽³⁾. 850 c.c. of pure acetone was refluxed with 250 g. selenium dioxide for about 3 hours during which the liquid gradually became clear. After cooling the reaction liquid, the selenium powder deposited was filtered off and the filtrate distilled on a boiling water bath. The distillation residue was again distilled under reduced pressure and the fraction b.p. 39–41°/15 mm. was taken as methylglyoxal (yield 40 g.).

Acetylformoin. A methylglyoxal solution (40 g. in 200 c.c. water) and a potassium cyanide (3.1 g. mol ratio to methylglyoxal 0.083) solution were both cooled in ice water and then mixed. The mixture was made

(2) R. Nodzu and co-workers, *J. Chem. Soc. Japan*, **58** (1937), 313; **59** (1938), 1237.

(3) H. L. Riley, *J. Chem. Soc.*, **1932**, 1875.

J. Hahn and O. Schales, *Ber.*, **67** (1934), 1821.

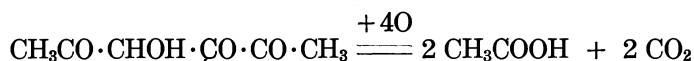
T. Bersin, *Ber.*, **69** (1936), 560.

just alkaline ($pH = 7.3$) by addition of solid sodium bicarbonate, and kept for 30 minutes in ice water. After acidifying with syrupy phosphoric acid, it was evaporated under reduced pressure until inorganic salt began to crystallize out and then absolute alcohol (ca. 150 c.c.) was added. The deposited inorganic crystals were filtered off and the filtrate was evaporated to a syrup under reduced pressure. To the syrup, ether (ca. 350 c.c.) was added and the solution was filtered. The filtrate was dehydrated with anhydrous sodium sulphate and the ether driven away. The yellow syrupy residue was now subjected to a vacuum (5 mm.) distillation. At first an oily substance (ca. 4 g., b.p. $35-50^{\circ}$) distilled and as the thermometer rose from 60° to 70° , yellow crystals appeared in the condenser and on cold parts of the distilling flask. The crystals were gathered, and found to amount to about 4.5 g. They were recrystallized from cold benzene in fine pale yellow needles (m.p. 82°). Found: C, 50.1; H, 5.6; M, (in acetic acid) 142. Cal. for $CH_3COCHOHCOCOCH_3$: C, 50.0; H, 5.6%; M, 144.)

So far as studied under various conditions—of temperature, times and pH ,—the reaction conditions described above were the best.

It was very auto-oxidizable, quickly darkened and liquefied in the course of 2 hours, when exposed to the air. It reduced Fehling's solution in the cold, and on addition of ferric chloride solution gave a greenish blue coloration which instantaneously faded when the solution was shaken.

Oxidation of acetylformoin. A solution of acetylformoin (0.12 g.) in 5% sulphuric acid (25 c.c.) was warmed on a boiling water bath, adding drop by drop 3% solution of potassium permanganate until no more decoloration of the oxidant took place. 8 c.c. of the permanganate solution was used. The reaction product was distilled, keeping its volume constant by the addition of water and the distillate was received in N/10 sodium hydroxide solution (25 c.c.). The distillation was continued until the distillate no longer reddened methylorange. On titration, it was found that it contained acid amounting to 0.0945 g. as acetic acid which corresponds to about 95% of the value calculated by the following equation



The amount of permanganate solution used was almost equal to what the theory requires (7.3 c.c.). From another experiment with 0.554 g. acetylformoin similar results were obtained, i.e., 34 c.c. (theoretically 33 c.c.) of the potassium permanganate solution was consumed and 0.425 g. acetic acid (92% of the theoretical) was formed. The distillates gave acetotoluidide (m.p. 147°).

Benzoylformoin (1 g.) was similarly oxidized (35 c.c. of 3% potassium permanganate solution) and benzoic acid (0.81 g.) was obtained with a yield of 96% of the theoretical value.

Action of potassium carbonate upon methylglyoxal. A solution of methylglyoxal (30–50 g. in 200 c.c. water) was made alkaline (pH 7.4–9.0) by potassium carbonate and kept for various intervals (0.5–15 hours) at $0-2^{\circ}$. After acidifying the reaction product with phosphoric acid, it was evaporated and extracted with ether. The ether extract was

evaporated and the residue was then distilled under reduced pressure without any sign of the appearance of acetylformoin. With ferric chloride the distillate (36–60°/3–5 mm.) did not show the characteristic greenish blue coloration of acetylformoin but rather a persistent red.

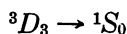
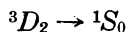
*Chemical Institute, Faculty of Science,
Kyoto Imperial University.*

Studies on Luminescent Materials. Part 2. On the Fluorescence Spectra of Zinc Sulphide-Copper Crystalphosphors at -185° , 20° , and 150°C^* .

By Yasuo UEHARA.

(Received May 6, 1940.)

1. Introduction. In the previous paper⁽¹⁾, the author reported the theory of fluorescence, photoconductivity and the other properties of ZnS/Cu phosphors, based on the quantum mechanical theory of solid state. By the theory of the author, we can expect two fluorescence bands corresponding to the electronic transitions



of the Cu^+ ion in the activation centre of the ZnS/Cu phosphors.

In order to prove this expectation, the author carried out measurements of the fluorescence spectra of ZnS/Cu phosphors at -185° , 20° , and 150°C .

2. Experiments. (A) *Preparation of phosphors.* As raw materials, Kahlbaum's sample (guaranteed reagents for analytical purpose) were always used. These materials were purified by repeated recrystallizations or distillations. Zinc sulphide precipitate was prepared by a method similar to that of K. Mamm⁽²⁾ and it was washed about fifty-times with distilled water. Then it was dried at 70°C . in an electric air bath with automatic regulator.

The resulting product is perfectly white fine powder. KCl was used as a flux and cupric sulphate water solution was added as an activator.

* Read before the Annual Meeting of the Chem. Soc. Japan, April 5, 1939 and reported on the *J. Chem. Soc. Japan*, **60** (1939), 675.

(1) Y. Uehara: *Bull. Chem. Soc. Japan*, **14** (1939), 539; *J. Chem. Soc. Japan*, **60** (1939), 133.

(2) K. Kamm: *Ann. Physik*, **30** (1937), 333.

Finely ground mixtures whose compositions are shown in Table 1, were placed in a white alumina crucible which was placed in a larger crucible. They were heated in the sulphur vapour at $1100^{\circ} \pm 10^{\circ}\text{C}$. in an electric furnace with automatic regulator for 15 minutes and they were cooled rapidly.

(B) *Observation of fluorescence spectra.* In the measurements of fluorescence spectra, ZnS phosphor coated on a quartz tube, i.e. an inner tube in the Fig. 1, was irradiated by Hg 3650 Å (triplet) line and the emitted fluorescence light was introduced in about right angle in a spectrograph.

For the measurement at -185°C ., the quartz tube covered with the phosphor was placed in a larger quartz tube and sealed with Apiazon W-wax at *D* in Fig. 1. After the space between the inner and the outer tube was evacuated, liquid air was poured into the inner tube.

For the experiments at 150°C ., a furnace shown in Fig. 2 was used. In Fig. 2, *E* is ZnS phosphor placed in a quartz tube *C*, *F* and *D* are

Table 1. Composition of pure ZnS and ZnS/Cu phosphors.

No. of Sample	Activator	Flux
	Cu (gram atom)	KCl (mol)
ZnS-1	0	0
ZnS-2	0	1/10
ZnS-3	1×10^{-3}	1/10
ZnS-4	1×10^{-4}	1/10
ZnS-5	1×10^{-5}	1/10
ZnS-6	1×10^{-6}	1/10
ZnS-7	1×10^{-5}	0

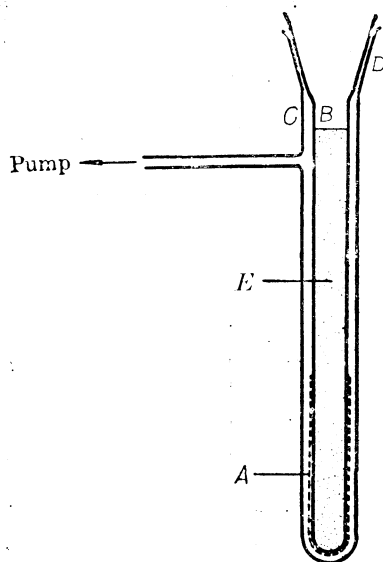


Fig. 1. Quartz tube for the measurements of the fluorescence spectra of ZnS phosphors. A: ZnS phosphor, B: inner quartz tube, C: outer quartz tube, D: Apiezon W-wax seal. E: liquid air.

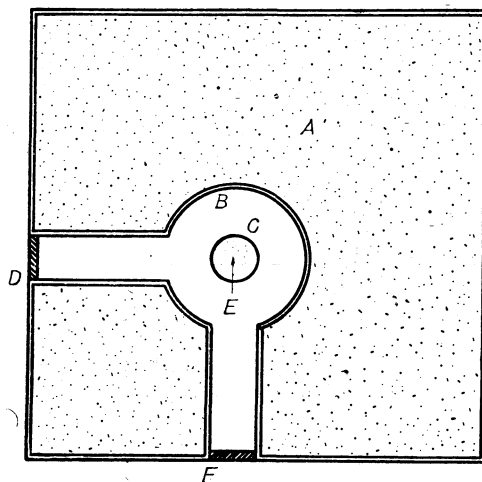


Fig. 2. Electric furnace for the measurements of Fluorescence spectra of ZnS phosphors at 150°C . A: electric furnace, B: aluminium metal wall, C: quartz tube, E: ZnS phosphor, D, F: quartz plate window.

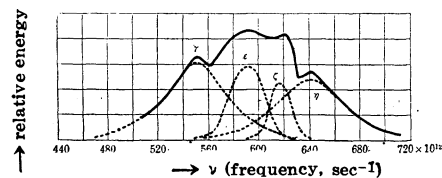


Fig. 3. Fluorescence spectra of ZnS—I
(Cu=0, KCl=0) at -185°C .

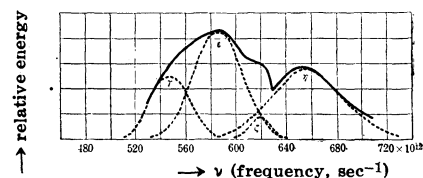


Fig. 4. Fluorescence spectra of ZnS—II
(Cu=0, KCl=1/10) at -185°C .

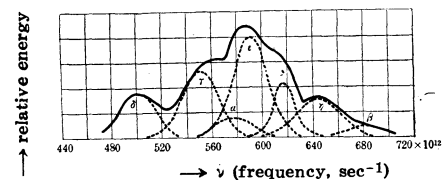


Fig. 5. Fluorescence spectra of ZnS—VII
(Cu= 1×10^{-5} , KCl=0) at -185°C .

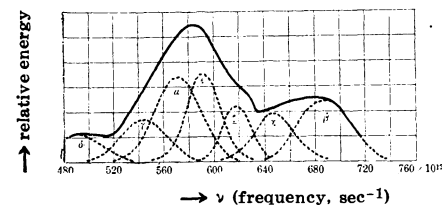


Fig. 6. Fluorescence spectra of ZnS—VI
(Cu= 1×10^{-6} , KCl=1/10) at -185°C .

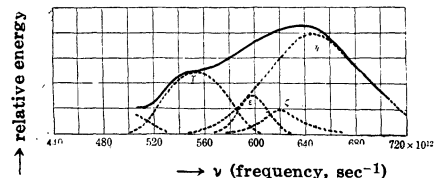


Fig. 10. Fluorescence spectra of ZnS—I
(Cu=0, KCl=0) at 20°C .

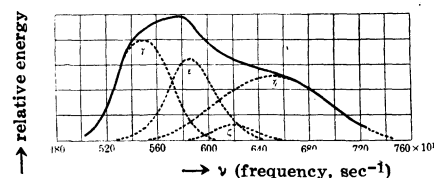


Fig. 11. Fluorescence spectra of ZnS—II
(Cu=0, KCl=1/10) at 20°C .

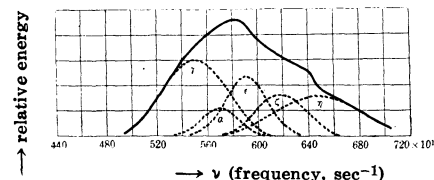


Fig. 12. Fluorescence spectra of ZnS—VII
(Cu= 1×10^{-5} , KCl=0) at 20°C .

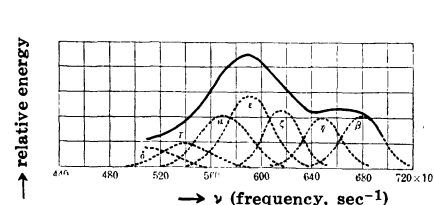


Fig. 13. Fluorescence spectra of ZnS—VI
(Cu= 1×10^{-6} , KCl=1/10) at 20°C .

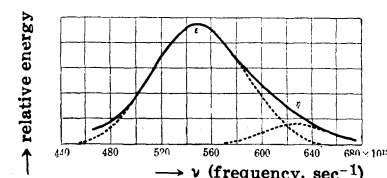


Fig. 17. Fluorescence spectra of ZnS—I
(Cu=0, KCl=0) at 150°C .

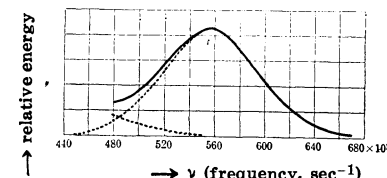


Fig. 18. Fluorescence spectra of ZnS—II
(Cu=0, KCl=1/10) at 150°C .

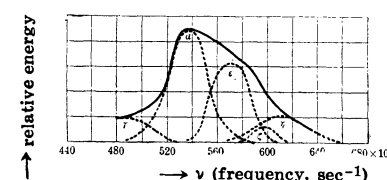


Fig. 19. Fluorescence spectra of ZnS—VII
(Cu= 1×10^{-5} , KCl=0) at 150°C .

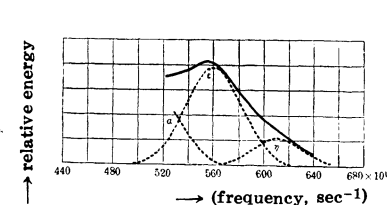


Fig. 20. Fluorescence spectra of ZnS—VI
(Cu= 1×10^{-6} , KCl=1/10) at 150°C .

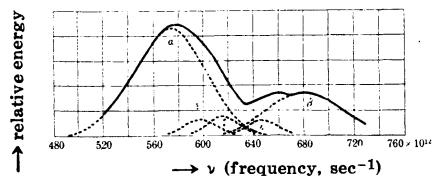


Fig. 7. Fluorescence spectra of ZnS-V
($\text{Cu}=1 \times 10^{-5}$, $\text{KCl}=1/10$) at -185°C .

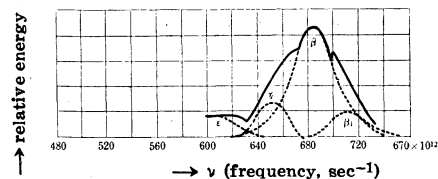


Fig. 8. Fluorescence spectra of ZnS-IV
($\text{Cu}=1 \times 10^{-4}$, $\text{KCl}=1/10$) at -185°C .

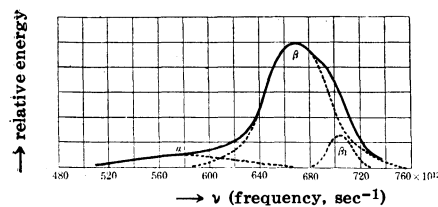


Fig. 9. Fluorescence spectra of ZnS-III
($\text{Cu}=1 \times 10^{-3}$, $\text{KCl}=1/10$) at -185°C .

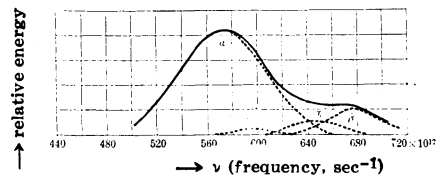


Fig. 14. Fluorescence spectra of ZnS-V
($\text{Cu}=1 \times 10^{-5}$, $\text{KCl}=1/10$) at 20°C .

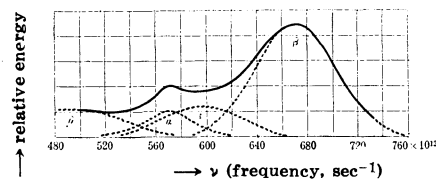


Fig. 15. Fluorescence spectra of ZnS-IV
($\text{Cu}=1 \times 10^{-4}$, $\text{KCl}=1/10$) at 20°C .

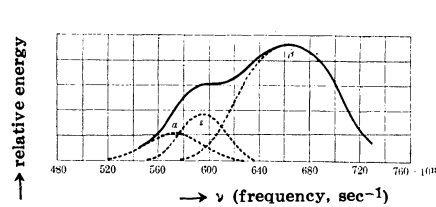


Fig. 16. Fluorescence spectra of ZnS-III
($\text{Cu}=1 \times 10^{-3}$, $\text{KCl}=1/10$) at 20°C .

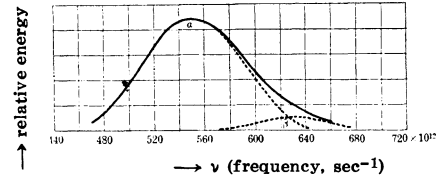


Fig. 21. Fluorescence spectra of ZnS-V
($\text{Cu}=1 \times 10^{-5}$, $\text{KCl}=1/10$) at 150°C .

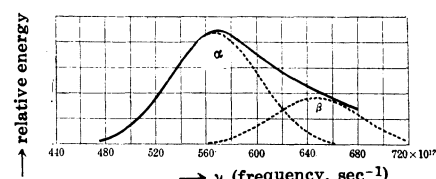


Fig. 22. Fluorescence spectra of ZnS-IV
($\text{Cu}=1 \times 10^{-4}$, $\text{KCl}=1/10$) at 150°C .

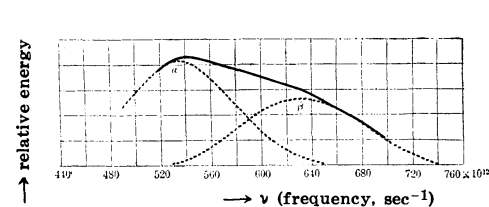


Fig. 23. Fluorescence spectra of ZnS-III
($\text{Cu}=1 \times 10^{-3}$, $\text{KCl}=1/10$) at 150°C .

quartz plate windows. The furnace in which the ZnS phosphor is contained, is kept at 150°C. by means of automatic regulator.

As the excitation light source, a high pressure mercury discharge tube in connection with a wood filter yielding practically only line of 3650 Å (triplet), was used.

Photographic spectrophotometry of the fluorescence spectra was made by means of Zeiss three glass prism spectrograph (focal length of camera lens: 27 cm.) in connection with a Zeiss fifth stepped filter and tungsten lamp as a standard light source.

The observed energy distribution curves of the fluorescence spectra were given in Fig. 3 ~ Fig. 23. In these figures thick lines show the observed energy distribution curves of the fluorescence spectra and broken lines show the energy distribution curves of the partial fluorescence bands resolved by the similiar method to that of P. Borrisow⁽³⁾, O. Schellenberg⁽⁴⁾ and H. Nitka⁽⁵⁾.

3. Theoretical Interpretation of the Experimental Results.

(A) *Fluorescence of pure ZnS phosphors.* Fluorescence of pure ZnS phosphors containing no activator was observed first by A. Schleede⁽⁶⁾ and later by N. Riehl⁽⁷⁾ and by S. Rothschild⁽⁸⁾. Rothschild⁽⁸⁾ reported that pure ZnS phosphors which contain NaCl as a flux but no activator, show only one fluorescence band with a maximum at 466 mμ. In the pure ZnS phosphors containing no flux and no activator, however, the author observed four (partial fluorescence bands with maxima at 4670 Å, 4870 Å, 5085 Å and 5455 Å at -185°C., as shown in Fig. 3. The author proposes to give a following nomenclature for these four fluorescence bands,

$$\eta = 4670 \text{ Å} \quad \zeta = 4870 \text{ Å} \quad \epsilon = 5085 \text{ Å} \quad \text{and} \quad \gamma = 5455 \text{ Å}.$$

In these bands, $\eta=4670 \text{ Å}$ band will probably correspond to the band 466 mμ observed by Rothschild.

Tomaschek⁽⁹⁾ observed four bands in the ZnS phosphor activated by by Cu, $\alpha = 520 \text{ mμ}$, $\beta = 437 \text{ mμ}$, $\gamma = 570 \text{ mμ}$, and $\delta = 600 \text{ mμ}$. Rothschild⁽⁸⁾ assumed that $\gamma = 570 \text{ mμ}$ band observed by Tomaschek will not be due to Cu activator but to Mn activator which might be involved as impurities in this phosphor. The author, however, observed $\gamma = 5455 \text{ Å}$ band in the pure ZnS phosphor containing no impurities. $\gamma = 5455 \text{ Å}$ band will probably correspond to $\gamma = 570 \text{ mμ}$ band observed by Tomaschek. Then we can conclude that γ band is not due to Cu activator or Mn activator but to Zn atom activator diffused in this phosphor, as shown in our previous paper.⁽¹⁾

(3) P. Borrisow: *Ann. Physik.* **42** (1913), 1321.

(4) O. Schellenberg: *Ann. Physik.* **13** (1932), 249.

(5) H. Nitka: *Ann. Physik.* **16** (1933), 720.

(6) A. Schleede and H. Rupp: *Die Leuchtmassen und ihre Verwendung*, Borntraeger (1937), 153.

(7) N. Riehl: *Ann. Physik.* **29** (1937), 637.

(8) S. Rothschild: *Z. Physik.* **108** (1937), 24.

(9) R. Tomaschek: *Ann. Physik.* **65** (1931), 212.

It is pointed out by Seitz⁽¹⁰⁾ that the presence of excess of Zn atom is responsible for the fluorescence of pure ZnS phosphors. But Seitz's mechanism of fluorescence of pure ZnS phosphors is different from that of the author, as shown already in the previous paper.⁽¹⁾

The author has pointed out in the previous paper⁽¹⁾ that the resonance radiation (in its wide meaning) in the activation centre is responsible for the fluorescence of pure ZnS phosphors as well as ZnS phosphors activated by Cu. Fig. 24 shows schematically the energy levels of pure ZnS phosphors and of ZnS phosphors activated by Cu. (cf. Uehara.⁽¹⁾)

The energy levels of normal Zn atom lies in the forbidden region between conduction band and $S-3p^6$ band. The energy levels of excited Zn atom lies immediately below the conduction band or on the position overlapping partially each other. Fig. 25 show the potential curve of Zn atom in the activation centre schematically. A represents an equilibrium position of the normal Zn atom in the activation centre. After an electron in this position has absorbed light quanta, it makes a transition to one of the excited states of Zn atom. Then it moves into a new equilibrium position of the excited states. The transition of the electron from the excited states to the ground state gives rise to the four fluorescence bands in the pure ZnS phosphors. But it is very difficult to predict which of these transitions corresponds to each band of these four fluorescence bands. Therefore, we assume that the four fluorescence bands observed by the author may be correlated with following electronic transitions, (cf. Fig. 25),

$$^1P_1 \rightarrow ^1S_0 (a \rightarrow i) = 4670 \text{ \AA} = \eta$$

$$^3P_2 \rightarrow ^1S_0 (b \rightarrow h) = 4870 \text{ \AA} = \zeta$$

$$^3P_1 \rightarrow ^1S_0 (c \rightarrow g) = 5085 \text{ \AA} = \epsilon$$

$$^3P_0 \rightarrow ^1S_0 (d \rightarrow f) = 5455 \text{ \AA} = \gamma.$$

the photoconductivity and of the intensity of the fluorescence of pure ZnS phosphors as well as ZnS phosphors activated by Cu, as we shall see in the following paper.

(B) Fluorescence of ZnS/Cu phosphors.

As we see in Table 2 ~ Table 4, there exists three fluorescence bands α , β and β_1 due to activator in the ZnS phosphors activated by Cu, Fig. 26

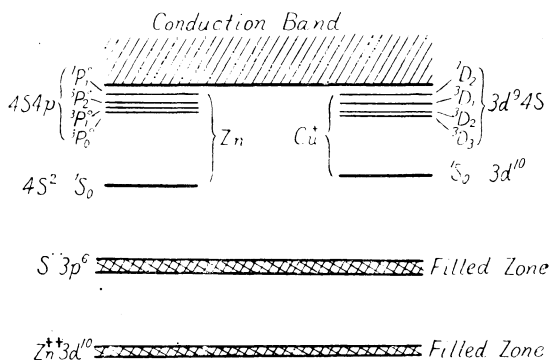


Fig. 24. Energy level diagram of the pure ZnS and ZnS/Cu phosphor.

The reason for this assumption will be given to some extent in the following discussion about the fluorescence of ZnS/Cu phosphors.

By using this mechanism of the fluorescence of pure ZnS phosphors, the author could calculate theoretically the temperature dependence of

(10) F. Seitz: *J. Chem. Phys.* **6** (1938), 150.

Table 2. Fluorescence band of pure ZnS and ZnS/Cu phosphors at -185°C . (Wave length unit $\text{\AA}$)

Activator	Flux	Fluorescence bands							
Cu (gr atom)	KCl (mol)	β_1	β	η	ζ	ϵ	α	γ	δ
0	0	—	—	4670	4870	5085	—	5445	—
0	1/10	—	—	4585	4840	5120	—	5475	—
1×10^{-5}	0	—	4410	4660	4870	5085	5300	5455	6120
1×10^{-6}	1/10	—	4380	4645	4870	5085	5270	5535	6120
1×10^{-5}	1/10	—	4410	4645	4885	5050	5225	—	—
1×10^{-4}	1/10	4225	4375	4615	—	—	—	—	—
1×10^{-3}	1/10	4265	4480	—	—	—	—	—	—
	Mean	4245	4410	4635	4865	5085	5260	5480	6120

Table 3. Fluorescence bands of pure ZnS and ZnS/Cu phosphors at 20°C . (Wave length unit $\text{\AA}$)

Activator	Flux	Fluorescence bands						
Cu (gr atom)	KCl (mol)	β	η	ζ	ϵ	α	γ	δ
0	0	—	4645	4855	5035	—	5455	—
0	1/10	—	4600	4840	5120	—	5475	—
1×10^{-5}	0	—	4645	4855	5085	5270	5455	—
1×10^{-6}	1/10	4410	4645	4870	5085	5265	5555	—
1×10^{-5}	1/10	4445	4645	—	5050	5245	—	—
1×10^{-4}	1/10	4480	—	—	5040	5265	—	6120
1×10^{-3}	1/10	4520	—	—	5050	5265	—	—
	Mean	4465	4635	4855	5065	5260	5485	6120

Table 4. Fluorescence bands of pure ZnS and ZnS/Cu phosphors at $+150^{\circ}\text{C}$. (Wave length unit $\text{\AA}$)

Activator	Flux	Fluorescence bands				
Cu (gr atom)	KCl (mol)	β	η	ζ	ϵ	α
0	0	—	4840	—	5475	—
0	1/10	—	—	—	5415	—
1×10^{-5}	0	—	4920	5035	5265	5595
1×10^{-6}	1/10	—	4920	—	5355	—
1×10^{-5}	1/10	4760	—	—	—	5455
1×10^{-4}	1/10	4645	—	—	—	5300
1×10^{-3}	1/10	4760	—	—	—	5595
	Mean	4755	4895	5035	5375	5485

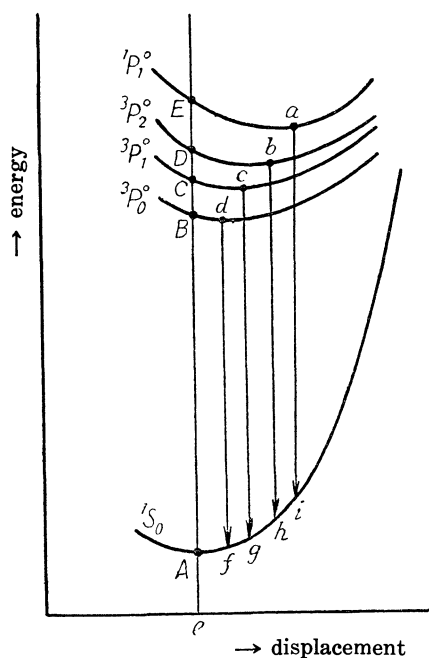


Fig. 25. Potential curve of Zn atom in the activation centre of the pure ZnS phosphor.

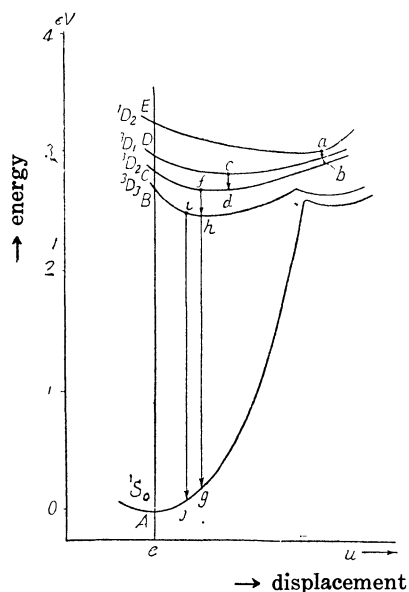


Fig. 26. Potential curve of Cu^+ ion in the activation centre of the ZnS/Cu phosphor.

shows the potential curve of Cu^+ ion in the activation centre, which has been already given by the author.⁽¹⁾ When an electron in the equilibrium position of one of the excited states of Cu^+ ion in the activation centre makes a transition to the ground state of Cu^+ ion, fluorescence will be observed. For example, the electronic transitions $f \rightarrow g$ or $i \rightarrow j$ give rise to fluorescence. On the other hand, the transition $f \rightarrow h$ will occur with radiation of elastic vibration wave and this transition will be more probable compared with the transition $f \rightarrow g$, when the coupling between the electron and lattice vibrations is strong.

Therefore, the transition $f \rightarrow g$ will become more probable compared with the transition $i \rightarrow j$, when the amplitude of the elastic vibrations in the activation centre becomes small. In other words, the lower the temperature is, the stronger the fluorescence band corresponding to the transition $f \rightarrow g$ becomes. As we see in Fig. 4 ~ Fig. 23, when the temperature decreases the blue β (and β_1) band becomes stronger compared with the green α band. Therefore, we can say that α and β band may be correlated with the following transitions.

$$^3D_2 \rightarrow ^1S_0 (f \rightarrow g) = \beta$$

$$^3D_3 \rightarrow ^1S_0 (i \rightarrow j) = \alpha$$

By the same reason, the transition $^3D_1 \rightarrow ^1S_0$ may be responsible for the band β_1 , which has the shortest wave length. $\delta = 6120 \text{ \AA}$ band

observed by the author in some of the ZnS/Cu phosphors will probably correspond to the $\delta = 600 \text{ m}\mu$ band observed by Tomaschek. But nothing can be predicted about the origin of the δ band at present, for the measurements of the fluorescence spectra of the other phosphors have not yet been carried out thoroughly in this region of the spectrum.

(C) *Effect of the amount of activator on the fluorescence spectra.* The ionic radius of Cu^+ ion is smaller than that of S^{2-} ion. Hence the larger the amount of the Cu activator is, the smaller becomes the overlapping of their eigenfunctions in the activation centre. Therefore, when a large amount of Cu^+ activator is introduced in the phosphor, the coupling between the excited states of Cu^+ ion and lattice vibrations will become weaker. Then β -band should occur more intensively, when the amount of Cu activator becomes larger. In fact, it is the case in our observations, as seen in Fig. 4 ~ Fig. 23.

(D) *Effect of the flux on the fluorescence spectra.* It could not be observed any appreciable variations of the wave length of the maxima of the partial fluorescence band between the ZnS phosphors containing no flux and that of ZnS phosphors containing KCl as a flux. But relative intensity of each fluorescence band varies very much by adding KCl as a flux. As the results, the energy distribution curves of the fluorescence spectra vary remarkably by the influence of the flux.

From these results, we can consider that K^+ (or Cl^-) ion may diffuse into the crystal lattice and it changes the transition probability of the electron from the excited states to the ground state in the activation centre.

(E) *Temperature effect on the fluorescence spectra.* It has been already pointed out by the author that the fluorescence band of ZnS phosphors should show a wide breadth by the molecular vibrations coupled with the elastic vibrations of the lattice.⁽¹⁾ Therefore, the breadth of the bands should become larger when the temperature is raised, which was actually the case in the observations by the author. Further it could be confirmed experimentally that the wave length of the maxima of the partial fluorescence bands make a shift from blue to red with increasing temperature above the room temperature.

Summary.

(1) Energy distribution curves of the fluorescence spectra of pure ZnS and ZnS/Cu phosphors were measured at -185° , 20° , and 150°C .

(2) Four fluorescence bands were observed in the pure ZnS phosphors containing no activator and no flux. It was pointed out that these four fluorescence bands may be correlated with the transitions

$$^1P_1 \rightarrow ^1S_0 = 4670 \text{ \AA} = \eta$$

$$^3P_2 \rightarrow ^1S_0 = 4870 \text{ \AA} = \zeta$$

$$^3P_1 \rightarrow ^1S_0 = 5085 \text{ \AA} = \epsilon$$

$$^3P_0 \rightarrow ^1S_0 = 5455 \text{ \AA} = \gamma$$

of the electron of the Zn atom in the activation centre.

(3) In the ZnS phosphors activated by Cu, three bands α , β and β_1 were observed. These three fluorescence bands may be correlated with the transitions

$$^3D_3 \rightarrow ^1S_0 = 5260 \text{ \AA} = \alpha$$

$$^3D_2 \rightarrow ^1S_0 = 4410 \text{ \AA} = \beta$$

$$^3D_1 \rightarrow ^1S_0 = 4245 \text{ \AA} = \beta_1$$

of the electron of the Cu^+ ion in the activation centre.

(4) The effect of the temperature and of the amount of the activator, and flux on the fluorescence spectra were discussed.

The author wishes to express his sincere thanks to Mr. B. Imamura, Vice-Director of this institute, for his generous help and to Prof. S. Mizushima of Tokyo Imperial University for his kind advice and encouragement.

*Laboratory, Tokyo Shibaura Electric Co.
Mazda Division, Kawasaki.*

Catalytic Activity of Phthalocyanines in the Autoxidation of Linseed Oil and Methyl Linoleate.

By Bunichi TAMAMUSHI and Shizuo TOHMATSU.

(Received May 13, 1940.)

Phthalocyanine and its related compounds have been in these ten years extensively studied by Linstead and his co-workers.⁽¹⁾ Among many remarkable results obtained concerning these compounds, their catalytic properties are of special interest. Polanyi and his co-workers⁽²⁾ have found that metal-free phthalocyanine as well as copper phthalocyanine are capable to activate molecular hydrogen and to catalyse the conversion of para-hydrogen into normal hydrogen. Cook⁽³⁾ has recently demonstrated that iron phthalocyanine and its related compounds have similar catalytic properties as haemin and other iron-containing compounds of porphyrin group, which are important from a biochemical point of view. They possess namely catalase and oxidase properties and are capable of catalysing the decomposition of hydrogen peroxide, the

(1) R. P. Linstead, Phthalocyanine und verwandte Verbindungen, ein zusammenfassend. Vortrag., *Ber.* **72** (1939), A, 93.

(2) M. Polanyi, M. Calvin and E. G. Cockbain, *Trans. Faraday Soc.* **32** (1936), 1436, 1443.

(3) A. H. Cook, *J. Chem. Soc.* **1938**, 1761, 1763, 1774, 1845.

oxidations of hydrogen iodide, benzaldehyde and a number of olefinic compounds and the chemiluminescent reaction of luminol.

According to our own observations, a weak luminescence came out, when 0.05%-luminol solution in 5%-aqueous NaOH was treated with 3%-hydrogen peroxide in the presence of a small amount of chloriron phthalocyanine, while with copper- or magnesium phthalocyanine the reaction occurred so feebly that the emitted light was only just discernible. The catalase activities of these compounds were examined in aqueous solution of hydrogen peroxide in which a small amount of catalyst was suspended, the course of decomposition being normally followed by titration with potassium permanganate. The first order velocity constant thus determined at 20°C. are approximately 0.01 min.⁻¹ for chloriron phthalocyanine, 0.001 min.⁻¹ for magnesium- and copper phthalocyanine, whereas the velocity constant of haemin is about 0.05 min.⁻¹. The catalase activity of chloriron phthalocyanine is therefore about 1/5 of that of haemin, which is in accordance with the fact that chloriron phthalocyanine is highly surpassed by haemin in the catalytic influence upon the luminescent oxidation of luminol.

Now, some of the compounds of phthalocyanine are used as colours. They are valuable because of their beauty of appearance, strong colouring power, unusual stability against light, heat, alkali, and acid and insolubility in ordinary solvents. Granted that they have more or less the oxidase activity, it is a matter of interest to examine whether they themselves act as driers, when they are used as colours in paints. Mr. Akiyama, who kindly afforded us metallic phthalocyanines⁽⁴⁾ and other materials used in the present experiment, made some preliminary observations on this subject. Among the metallic phthalocyanines, chloriron phthalocyanine was found to be effective as a drier, though its efficiency was not so great as that of Co-Pb-naphthenate ("Soligen") of I. G., a well known drier.

We first determined the rate of drying of linseed oil at 50°C. in air, once with Co-Pb-naphthenate and then with metallic phthalocyanines, the oil being well mixed with a small quantity (0.05 g. per 1 c.c. oil) of catalyst. The linseed oil with Co-Pb-naphthenate dried in about 3 hours, while with chloriron phthalocyanine in about 7 hours and with copper or magnesium phthalocyanine in about 25 hours.

We then made some experiments concerning the catalytic action of metallic phthalocyanines as compared with that of Co-Pb-naphthenate of I. G. towards the autoxidation of methyl linoleate and linseed oil. Methyl linoleate has been prepared from cotton seed oil as follows:⁽⁵⁾ 1 kg. cotton-seed oil is saponified and fatty acids thereby obtained are dissolved in 1500 c.c. ligroin, into which bromine is added under cooling until a red colour comes to stay. The bromination product is recrystallized from ligroin. The bromide together with methyl alcohol and zinc granules is then heated till the mixture boils, and into it is added methyl alcoholic

(4) The method of preparation of metallic phthalocyanines adopted by Mr. Akiyama is principally the same as that of Linstead and his co-workers. Compare *J. Chem. Soc.*, **1934**, 1017-1031.

(5) Beilstein, *Organische Chemie*, Bd. II, 496.

hydrochloric acid: the mixture is again boiled for an hour. On cooling, the methyl ester of linoleic acid separates itself, which is extracted with petroleum ether and washed with water several times and dried by means of sodium sulphate: petroleum ether is then expelled by evaporation. The pure product is obtained by distillation in vacuo.

Linseed oil as well as methyl linoleate were dissolved in carbon tetrachloride with catalyst (0.015 g. catalyst in 50 c.c. solution) in a reaction vessel with upright cooling condenser, into this mixture air was gently passed through for 20–24 hours, during which time the reaction vessel was maintained at a constant temperature of 20°C. From time to time, a small portion of the solution was pipetted out, of which the iodine number was determined according to the method of Wijs and thus we compared the rate of autoxidation.

The results are given in the following tables, one for methyl linoleate and another for linseed oil, where chloriron phthalocyanine and Co-Pb-naphthenate are compared as to their catalytic activity.

Table 1. Autoxidation of Methyl Linoleate.

With chloriron phthalocyanine as catalyat		With Co-Pb-naphthenate as catalyat	
Time (hours)	Iodine number	Time (hours)	Iodine number
0	174	0	174
3	130	3	104
10	92	10	85
20	75	20	70

Table 2. Autoxidaton of Linseed Oil.

With chloriron phthalocyanine as catalyst		With Co-Pb-naphthenate as catalyst	
Time (hours)	Iodine number	Time (hours)	Iodine number
0	175	0	175
3	140	2.5	136
10	91	10	90
24	62	24	61

The accuracy of the determination of iodine number was not the same in all cases and allowance should be made for errors due to the variation of concentration of the reacting mixture in the course of the reaction time. The general features of the matter are nevertheless evident. Chloriron phthalocyanine has, as is shown above, really a marked catalytic activity towards the autoxidation of methyl linoleate as well as of linseed oil; its activity is almost as powerful as that of Co-Pb-naphthenate, although the latter always excels the former.

Out of other metallic phthalocyanines copper phthalocyanine was chosen and examined, whose activity was, however, found to be much weaker than that of chloriron phthalocyanine, the iodine number of methyl linoleate decreasing from 174 to 110 in 20 hours while that of linseed oil from 175 to 120 in the same time.

Summary.

The catalytic action of metallic phthalocyanines towards the autoxidation of linseed oil and methyl linoleate is demonstrated. Chloriron phthalocyanine is remarkably effective as catalyst, whereas copper- and magnesium phthalocyanine are slightly effective.

We deeply acknowledge our indebtedness to Mr. H. Akiyama of Nippon Oil and Fat Co. for his kind supply of materials as well as his valuable advices. We also thank the Nippon Gakuzyutu Sinkokai for a grant.

*Nedzu Chemical Laboratory
Musashi Higher School, Tokyo.*

**Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs.
IX. Die Herstellungsmethode und die katalytische Wirksamkeit des Katalysators: die mischkatalytische Wirkung der Verunreinigungen.⁽¹⁾**

Von Noriyoshi MORITA.

(Eingegangen am 15. Mai 1940.)

Inhaltsübersicht. Der mögliche Einfluss der Verunreinigungen, die bei der Herstellung des Katalysators eintreten können, auf die katalytische Wirksamkeit des letzteren für die Austauschreaktion zwischen Wasserdampf und Sauerstoffgas wird durch ein besonderes Experiment untersucht, das unter Benutzung der auf verschiedene Weise hergestellten Arten der Kupferoxyde durchgeführt wurde. Dabei wird festgestellt:

(a) Die vier Arten der Kupferoxyde, die resp. auf verschiedene Weise hergestellt wurden und voneinander ziemlich stark verschiedene äusserliche Beschaffenheit besitzen, weisen fast gleich hohe katalytische Wirksamkeit auf.

(b) Dagegen zeigen die beiden Arten der Kupferoxyde, von denen das eine das aus Kupfersulfat und Natronlauge auf nassem Wege hergestellte pulverförmige und das andere zuerst mit verdünnter Natronlauge getränkte und dann getrocknete drahtförmige Kupferoxyd war, beide gleich abnorm hohe katalytische Wirksamkeit.

(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: *ebenda*, **13** (1938), 601; III. Mitteil.: *ebenda*, **13** (1938), 656; IV. Mitteil.: *ebenda*, **14** (1939), 9; V. Mitteil.: *ebenda*, **14** (1939), 520 und **15** (1940), 1; VI. Mitteil.: *ebenda*, **15** (1940), 47, 71; VII. Mitteil.: *ebenda*, **15** (1940), 119; VIII. Mitteil.: *ebenda*, **15** (1940), 166.

(c) Der ebenfalls mit Natronlauge getränkte und dann getrocknete Bimsstein ist auch für die in Rede kommende Austauschreaktion katalytisch wirksam, obwohl der Bimsstein an sich allein keine katalytische Wirksamkeit besitzt. Die Wirksamkeit des so mit Natronlauge behandelten Bimssteins ist aber viel kleiner als die des oben in (b) beschriebenen Natriumhydroxyd-tragenden Kupferoxyds.

Aus diesem Versuchsergebnisse kommt man zu dem Schluss:

(a) Die katalytische Wirksamkeit des Kupferoxyds wird weder durch die Herstellungsmethode noch durch die äusserliche Beschaffenheit viel beeinflusst, so lange als es chemisch rein bleibt.

(b) Die anormal hohe Wirksamkeit des auf nassem Wege unter Benutzung von Natronlauge hergestellten Kupferoxyds lässt sich vielleicht durch die Wirkung des in minimaler Menge zurückgebliebenen Natriumhydroxyds bzw. -oxyds erklären.

(c) Da die katalytische Wirksamkeit des mit Natronlauge behandelten Kupferoxyds nicht nur die des reinen Kupferoxyds sondern auch die des Natriumhydroxyd-tragenden Bimssteins übertrifft, hat man beim ersten Fall mit der mischkatalytischen Wirkung von Kupferoxyd und Natriumhydroxyd zu rechnen.

Einleitung. Wir haben bisher die katalytische Wirkung verschiedener Arten der Oxyde und Metalle auf die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf untersucht.

In der Praxis führten wir die Versuche im allgemeinen so aus, dass man unter Benutzung des bei verschiedenen Temperaturen direkt gemessenen prozentualen Austauschmasses $\%A$ solch eine Temperatur $t(10\%)$ interpoliert, wo das prozentuale Austauschmass $\%A$ an der Oberfläche des angegebenen Katalysators erst 10% erreicht, und die so bestimmte charakteristische Temperatur $t(10\%)$ der verschiedenen chemischen Arten der Katalysatoren untereinander vergleicht.

Während dieser Reihe der Versuche fanden wir oft, dass die Arten der Katalysatoren, die miteinander chemisch identisch sind aber auf voneinander verschiedene Weise hergestellt wurden, in einigen Fällen fast die gleiche dagegen in anderen Fällen wieder ziemlich beträchtlich abweichende katalytische Wirksamkeit manifestieren. So z.B. geben zwei Arten der Chromoxyde, Cr_2O_3 -I und Cr_2O_3 -II, die nach voneinander verschiedener Methode dargestellt wurden,⁽²⁾ fast die gleiche hohe charakteristische Temperatur $t(10\%)$ an: $t(10\%)$ von Cr_2O_3 -I beträgt 380° , während die von Cr_2O_3 -II bei 420° liegt. Dagegen zeigen die ebenfalls auf zwei verschiedene Wege bereiteten Arten der Zinnoxide, SnO_2 -I und SnO_2 -II,⁽³⁾ zueinander ganz abweichende katalytische Wirksamkeit: $t(10\%)$ von SnO_2 -I beträgt 400° , während die von SnO_2 -II bei 670° liegt. Als eine plausible Ursache für diesen grossen Unterschied der katalytischen Wirksamkeit zwischen den beiden Arten der Zinnoxide haben wir damals die Promotor- bzw. mischkatalytische Wirkung der Verunreinigungen angenommen, die bei der Herstellung der ersten Art Zinnoxid SnO_2 -I unbewusst und in minimaler Menge eingetreten sind.

(2) Cr_2O_3 -I wird durch die thermische Entwässerung des aus wässriger Lösung von $\text{Cr}(\text{NO}_3)_3$ durch Versetzung mit verdünnter Ammoniaklösung abgeschiedenen Niederschlags von $\text{Cr}(\text{OH})_3$ erhalten. Dagegen wird Cr_2O_3 -II durch die thermische Zersetzung von $(\text{NH}_4)_2\text{CrO}_4$ hergestellt (Näheres darüber vgl. dies Bulletin, **14** (1939), 10 und **15** (1940), 53).

(3) SnO_2 -I wird aus dem käuflichen Zinnoxid bloss durch die starke Erhitzung bereitet, während SnO_2 -II durch die thermische Zersetzung des Carbonats, das aus SnCl_4 unter Benutzung von Natronlauge und Kohlensäure hergestellt wurde, gewonnen wird (Näheres darüber vgl. dies Bulletin, **15** (1940), 51).

Dabei kommt als solch eine Verunreinigung, die die katalytische Wirksamkeit des angegebenen Zinnoxys $\text{SnO}_2\text{-I}$ anormal erhöhte, vor allem das Alkalihydroxyd in Frage, das bei der Herstellung des Oxyds verwendet aber daraus nicht vollständig befreit worden war. Diese Annahme liegt um so näher, als das betreffende Oxyd $\text{SnO}_2\text{-I}$ nichts anders als das käufliche Oxyd war, das direkt vor dem Versuch durch blosse Erhitzung möglichst vollständig getrocknet wurde, während das andere weniger wirksame Oxyd $\text{SnO}_2\text{-II}$ das unter besonderer Sorgfalt im eigenen Laboratorium synthetisch hergestellte Präparat war. Um diese Annahme sofort zu bestätigen haben wir deshalb in der vorliegenden Arbeit verschiedene Arten der Kupferoxyde auf verschiedene Wege hergestellt und ihre katalytische Wirksamkeit für die Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf miteinander sowie mit dem mit einer kleinen Menge Ätznatron absichtlich versetzten Kupferoxyd verglichen. Da wir aber bei diesem Versuch, wie erwartet, die stark erhöhte Wirksamkeit der mit Natriumhydroxyd möglicherweise bzw. absichtlich verunreinigten Kupferoxyde gefunden haben, wird weiter der mit Natronlauge getränkte Bimsstein betreffend seiner katalytischen Wirksamkeit für die in Rede kommende Austauschreaktion untersucht.

Darstellung der Katalysatoren. Die in der vorliegenden Arbeit verwendeten Arten der Katalysatoren werden auf folgende Weise hergestellt:

Kupferoxyd-I, CuO-I .—Als dieses wird das „Kupferoxyd drahtförmig“ von Merck direkt zum Versuch verwendet.

Kupferoxyd-II, CuO-II .—Pulverförmiges reines Kupferoxyd aus dem Handel wird direkt zum Versuch benutzt.

Kupferoxyd-III, CuO-III .—Reines Kupfernitrat aus dem Handel wird in einem Porzellantiegel sorgfältig erhitzt bis keine Entwicklung von Stickstoffdioxid mehr nachgewiesen wird. Das so erhaltene Kupferoxyd wird weiter in einem Quarzrohr unter Evakuierung bei etwa 500° einige Stunden lang erhitzt.

Kupferoxyd-IV, CuO-IV .—Reines basisches Kupfercarbonat aus dem Handel wird in einem Becherglas so lange erhitzt bis sich keine Kohlensäure mehr entwickelt. Dann wird das Oxyd in einem Quarzrohr ebenfalls wie beim CuO-III in Vakuum and bei 500° einige Stunden lang erhitzt.

Kupferoxyd-V, CuO-V .—Dieses Oxyd wird aus Kupfersulfat und Natronlauge dadurch bereitet, dass man den Niederschlag von Kupferoxyhydrat, der bei der Versetzung der wässrigen Lösung von reinem Kupfersulfat mit Natronlauge abgeschieden wird, durch Erhitzung entwässert. Den Niederschlag wäscht man nämlich zuerst gründlich mit destilliertem Wasser so lange, bis keine Sulfationen im Filtrat mehr nachgewiesen werden können. Dann wird der so gewaschene Niederschlag, nachdem er im Trockenschrank zuerst bei 80° aber zum Schluss bei 120° sorgfältig getrocknet worden ist, in einem Quarzrohr und zwar unter Evakuierung bei etwa 500° einige Stunden lang erhitzt, bis das Oxydhydrat sich vollkommen in Oxyd verwandelt.

Mischkatalysator aus Kupferoxyd und Ätznatron, CuO-NaOH .—Etwa 20 g „Kupferoxyd drahtförmig“ von Merck, d.h. dasselbe Präparat wie

CuO-I, wird, nachdem es bei etwa 400° gut getrocknet worden ist, in 200 ccm 0.1 normaler Natronlauge eingeführt und darin etwa eine Stunde lange unter Vermeidung des Abdampfens des Wassers gekocht. Dann wird das Oxyd von der Lösung abfiltriert und ohne weiteres bei 400°C getrocknet. Das so behandelte Kupferoxyd dürfte höchstens 0.2% NaOH enthalten.

Ätznatron tragender Bimsstein, Bimsstein-NaOH.— „Bimsstein gekörnt“ von Kahlbaum wird zunächst mit konzentrierter Salzsäure dreimal behandelt und dann mit destilliertem Wasser gründlich gewaschen, bis keine Chlorionen mehr im Filtrat sich nachweisen lassen. Der so gereinigte Bimsstein wird nun, nachdem er sorgfältig getrocknet worden ist, mit der 0.1 N Natronlauge auf genau dieselbe Weise wie oben bei der Herstellung des Kupferoxyd-Ätznatron-Mischkatalysators behandelt.

Versuchsergebnisse. Die Ergebnisse der Austauschversuche, die unter Verwendung der so hergestellten Arten Katalysatoren durchgeführt wurden, sind in Tabellen 1 bis 7 zusammengestellt, wo die Versuchsnr. in der ersten Spalte die zeitliche Reihenfolge der einzelnen Austauschversuche angibt und die sonstigen Buchstaben und Abkürzungen folgende Bedeutung haben:

Δs_a und Δs_e : der gewöhnlichem Wasser gegenüber gemessene Dichteüberschuss des zum Versuch verwendeten an schwerem Sauerstoff angereicherten schweren Wassers vor (Δs_a) und nach (Δs_e) dem Versuch.

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

%A: das „prozentuale Austauschmass“, d.h. das prozentuale Verhältnis der wirklich gefundenen Dichteabnahme ($\Delta s_a - \Delta s_e$) des schweren Wassers nach der Austauschreaktion gegen den theoretischen Wert, der sich beim vollständigen Austausch ergeben würde.

M: Gewichtsmenge des zum Versuch verwendeten Katalysators.

Das zu jedem Versuch benutzte Reaktionsgasgemisch besitzt, wie üblich, die Zusammensetzung von $O_2:H_2O = 2:1$ und das im Katalysatorrohr beschickte Kupferoxyd wird bei jedem einzelnen Versuch direkt vor dem Beginn des Versuches immer bis auf etwa 800° unter Durchleitung des elektrolytischen Sauerstoffgases einige Stunden lang erhitzt.

Tabelle 1. CuO-I. $\Delta s_a = 54.2 \gamma$, $\Delta s_a(O) = 34.5 \gamma$, $M = 15 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	500	53.6	0.6	2
4	600	50.3	3.9	14
1	700	36.5	17.7	61
3	800	25.6	28.6	99

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 2. CuO-II. $\Delta s_a = 54.2 \gamma$, $\Delta s_a(O) = 34.5 \gamma$, $M = 9 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	500	53.2	1.0	3
4	600	48.9	5.3	18
1	700	26.5	27.7	96
3	800	25.9	28.3	98

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 3. CuO-III. $\Delta s_a = 54.2 \gamma$, $\Delta s_a(O) = 34.5 \gamma$, $M = 15 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
5	400	54.2	0.0	0
2	500	54.3	0.1	0
4	600	51.3	2.9	10
1	700	27.8	26.4	91
3	800	25.0	29.2	101

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 4. CuO-IV. $\Delta s_a = 54.2 \gamma$, $\Delta s_a(O) = 35.4 \gamma$, $M = 6.5 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
5	400	53.6	0.6	2
2	500	53.4	0.8	3
4	600	43.0	11.2	39
1	700	25.0	29.2	101
3	800	24.8	29.4	102

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 5. CuO-V. $\Delta s_a = 54.2 \gamma$, $\Delta s_a(O) = 34.5 \gamma$, $M = 10 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
7	400	52.8	1.4	5
2	500	38.9	15.3	53
5	500	40.7	13.5	47
4	600	28.6	25.6	89
6	600	27.3	26.9	93
1	700	25.0	29.2	101
3	800	24.3	29.9	103

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 6. CuO-NaOH. $\Delta s_a = 54.2 \gamma$, $\Delta s_a(O) = 34.5 \gamma$, $M = 15 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
5	300	53.0	1.2	4
2	400	50.9	3.3	11
4	500	52.1	2.1	7 ⁽⁴⁾
1	600	27.9	26.3	91
3	700	23.9	30.3	105

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 7. Bimsstein-NaOH. $\Delta s_a = 57.0 \gamma$, $\Delta s_a(O) = 36.3 \gamma$, $M = 6 \text{ g.}$

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass %A
2	500	55.4	1.6	5
1	600	51.8	5.2	17
3	700	51.3	5.7	19

$$\%A = \frac{\Delta s_a - \Delta s_e}{30.3} \times 100$$

Diskussion der Ergebnisse. Aus den oben angegebenen Versuchsergebnissen 1 bis 7 werden die von 1 bis 5; die unter Verwendung der fünf Arten der präparativ reinen Kupferoxyde ausgeführt wurden, in untenstehender Abb. 1 graphisch wiedergegeben. Dabei werden auch die Versuchsergebnisse, die bei einem früheren Versuch unter Benutzung zweier Arten von Kupferoxyden gewonnen⁽⁵⁾ und in III. Mitteil. berichtet wurden, zum Vergleich durch punktierte Linien eingezeichnet. Aus dieser graphischen Darstellung lässt sich aber ohne weiteres ersehen, dass die %A-Temperatur-Kurven aller untersuchten Arten der Oxyde, ausgenommen die des letzten Oxyds CuO-V, sehr nahe zueinander liegen: die charakteristische Temperatur $t(10\%)$ der in der vorliegenden Arbeit untersuchten Arten der Oxyde, CuO-I bis CuO-IV, liegen etwa zwischen 550° und 600° und die der früher untersuchten beiden Arten der Oxyde liegen auch nicht viel weiter von diesem Temperaturgebiet. Der eventuell erkennbare kleine Unterschied der katalytischen Wirksamkeit zwischen

(4) Dieses abnorm kleine %A von Versuchsnr. 4 kann vielleicht dadurch erklärt werden, dass ein Teil des an der Oberfläche des Kupferoxyds anhaftenden Natriumhydroxyds aus irgend einem Grund verloren geht.

(5) Das eine Kupferoxyd, das damals CuO-I genannt wurde, ist nichts anderes als das „Kupferoxyd drahtförmig“ von Merck, das aber vor der Benutzung im Sauerstoffstrom bis auf 700° bis 800° über Nacht erhitzt wurde. Das andere Oxyd, das damals CuO-II genannt wurde, wird dagegen aus demselben käuflichen Präparat wie CuO-I dadurch bereitet, dass man dies, nachdem es zunächst mittels Wasserstoffgases vollständig bis zu Kupfer reduziert worden ist, wieder durch Erhitzung im Sauerstoffstrom bis zum Oxyd verwandelt (Näheres darüber vgl. dies Bulletin, 13 (1938), 658).

den betreffenden Arten der Oxyde⁽⁶⁾ kann auf die verschiedene Oberflächenbeschaffenheit bzw. Oberflächengrösse zurückgeführt werden,⁽⁷⁾ weil das in dem vorliegenden Versuch benutzte CuO-I drahtförmig, CuO-III feinkörnig, CuO-II und CuO-IV beide pulverförmig waren und die zu jedem Versuch benutzte Menge des Oxyds bei dem vorliegenden Versuch 7 bis 15 g während sie beim früheren Versuch (punktierte Linien I' und II' in Abb. 1!) etwa 65 g betrug.

Gegen diese Übereinstimmung der katalytischen Wirksamkeit der ersten vier Arten der Oxyde, CuO-I bis CuO-IV, die in dem vorliegenden Versuch untersucht wurden, zeigt das zuletzt untersuchte Oxyd, CuO-V, das ebenfalls präparatisch als reines Kupferoxyd angesehen werden kann, viel höhere Wirksamkeit als die anderen Arten der Oxyde: die charakteristische Temperatur $t(10\%)$ dieses letzteren Oxyds CuO-V liegt sogar um 100° bis 150° niedriger als die anderen (vgl. Abb. 1). Diese grosse

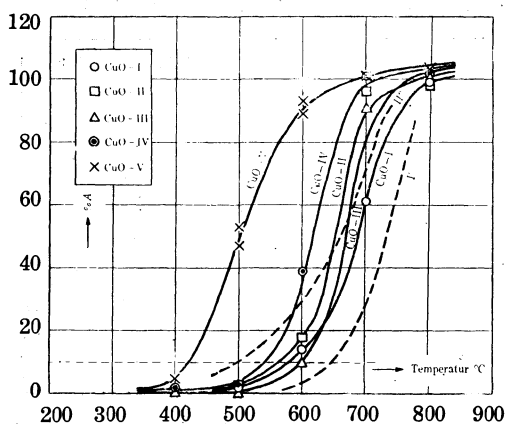


Abb. 1. Die Abhängigkeit des Austauschmasses von der Temperatur (CuO-I bis CuO-V).

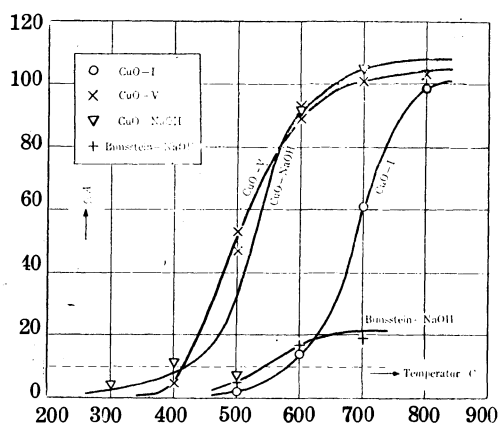


Abb. 2. Die Abhängigkeit des Austauschmasses von der Temperatur (CuO-I, CuO-V, CuO-NaOH und Bimsstein-NaOH).

Diskrepanz der katalytischen Wirksamkeit zwischen den präparatisch als gleich reines Kupferoxyd anzusehenden Katalysatoren, die uns an den ähnlichen Unterschied zwischen den früher untersuchten beiden Arten der Zinnoxide erinnern lässt, legt uns die Annahme nahe, dass es sich dabei um die mischkatalytische Wirkung handelt, die von der bei der Herstellung des in Rede kommenden Oxyds CuO-V benutzten Natronlauge herrührt. Aus diesem Grunde wird in der nebenstehenden Abb. 2 die %A-Temperatur-Kurve dieses letzteren Oxyds CuO-V mit der von CuO-

(6) Aus den %A-Temperatur-Kurven in Abb. 1 ergibt sich, dass die charakteristische Temperatur $t(10\%)$ von CuO-III = 600° , die von CuO-I = 580° , die von CuO-II = 560° und die von CuO-IV = 550° ist; die katalytische Wirksamkeit der einzelnen Arten der Oxyde nimmt nämlich in dieser Reihe allmählich zu.

(7) Je grösser die Oberfläche des angegebenen Katalysators wird, desto schneller muss die katalytische Austauschreaktion verlaufen. Dazu kommt aber noch die Möglichkeit, dass die störende Austauschreaktion zwischen schwerem Wasserdampf in der Gasphase und dem an der Oberfläche des Katalysators in minimaler Menge zurückhaftenden Sauerstoff bzw. Wasserdampf mit zunehmender Oberflächengrösse des Katalysators mehr in den Vordergrund tritt.

NaOH verglichen, das bei seiner Herstellung absichtlich mit einer kleiner Menge von NaOH versetzt worden ist. Die Abb. zeigt uns aber deutlich, dass die katalytische Austauschreaktion an der Oberfläche dieser beiden Arten der Katalysatoren fast gleich leicht stattfindet: die charakteristische Temperatur $t(10\%)$ beider Arten der Oxyde liegt sehr nahe nebeneinander. Aus diesem Ergebnisse wird deshalb zwanglos geschlossen, dass die enorm hohe Wirksamkeit von CuO-V wie erwartet vom Natriumhydroxyd herrührt, das bei der Herstellung des genannten Oxyds verwendet aber daraus nicht vollständig befreit worden war. Dabei können wir aber nicht ohne weiteres entscheiden, ob es sich um die direkte Wirkung des Natriumhydroxyds allein handelt oder ob irgendwelche von seinen Abarten, wie z.B. Natriumsalze d.h. Natriumionen eine Rolle spielen. Jedoch können wir in jedem Fall aus dem Versuchsergebnis, das unter Benutzung des mit Natriumhydroxyd getränkten Bimssteins gewonnen wurde, wohl schliessen, dass das Natriumhydroxyd auch in sehr verdünntem Zustand ziemlich starke katalytische Wirkung ausübt; die Kurve Bimsstein-NaOH in Abb. 2 zeigt, dass der Bimsstein, der an sich selbst fast keine katalytische Wirkung für die in Rede kommende Austauschreaktion besitzt (vgl. II. Mitteil.), fast ebenso gut wirksam wie das reine Kupferoxyd wird, wenn man den ersteren mit verdünnter Natronlauge behandelt.⁽⁸⁾ Das oben angegebene CuO-NaOH wird ebenfalls mit Natronlauge von derselben Konzentration wie diese behandelt. Aber trotzdem ergibt die katalytische Wirksamkeit dieses Oxyds CuO-NaOH ebenso wie CuO-V, dass sie nicht nur die des reinen Kupferoxyds (d.h. von CuO-I bis CuO-IV) sondern auch die des NaOH-tragenden Bimssteins übertrifft. Dieser Befund legt uns deshalb die Annahme nahe, dass man durch die oben angegebene abnorm hohe Wirksamkeit des durch Natriumhydroxyd absichtlich (CuO-NaOH) bzw. unbewusst (CuO-V) verunreinigten Kupferoxyds mit einer mischkatalytischen Wirkung des Kupferoxyds und Natriumhydroxyds zu rechnen hat.

Den merklichen Unterschied der katalytischen Wirksamkeit, der oft zwischen den Arten der Katalysatoren gefunden wurde, die chemisch miteinander identisch sind aber auf verschiedene Weise hergestellt wurden, wie z.B. SnO₂-I und SnO₂-II, haben wir uns auch höchstwahrscheinlich aus demselben Grund wie oben, d.h. durch die mischkatalytischen Wirkung der unbewusst eingetretenen minimalen Mengen Verunreinigungen zu erklären. Aber andererseits können wir aus den Versuchsergebnissen mit den ersten vier Arten der Kupferoxyde CuO-I bis CuO-IV zwanglos zu dem Schluss kommen, dass der chemisch identische Katalysator ohne Unterschied seiner Herstellungsmethode und äusserlichen Beschaffenheit immer fast gleich hohe katalytische Wirksamkeit zeigt, so lange als er nicht nur als chemisch sondern auch katalytisch rein angesehen werden kann. Die früher gefundene Gleichheit der katalytischen Wirksamkeit der beiden Arten der Chromoxyde Cr₂O₃-I und Cr₂O₃-II, die auf verschiedene Weisen hergestellt wurden, gehört auch zu diesem letzteren Fall.

(8) Der verhältnismässig niedrige Wert von $\%A$, das mit Bimsstein-NaOH bei 700° gefunden wurde (vgl. Tabelle 7 Versuchsnr. 3), kann eventuell aus demselben Grund wie beim Versuch Nr. 4 mit CuO-NaOH bei 500° (in Tabelle 6), d.h. durch das Verlorengehen eines Teils von NaOH erklärt werden (vgl. Fussnote (4)).

Herrn Prof. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Nippon Gakuzyutu-Sinkōkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschung) sowie der Hattori-Hōkōkai (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung dieser Arbeit ermöglicht haben, bin ich auch zu grossem Dank verpflichtet.

Osaka-Teikoku-Daigaku Rigaku-bu
Kagaku-Kyositu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka).

The Occurrence of Gallium in the Hot Springs of Japan.

By Kazuo KURODA.

(Received May 27, 1940.)

Gallium is widely distributed in nature in minute quantities, and it is detected spectroscopically in many rocks and minerals. It is, however, rarely reported in the mineral waters. J. Bardet⁽¹⁾ found this element in some French mineral waters, and S. Piña de Rubies and C. Sirvent d'Argent⁽²⁾ in Spanish mineral waters. According to V. M. Goldschmidt,⁽³⁾ the atomic ratio of gallium to aluminium in the aluminium minerals varies from 1:10 to 1:100000. The present author found the occurrence of gallium in a number of hot springs, mainly of acid alum-vitriol springs of Japan. Their gallium content was spectroscopically estimated.

Arc Spectrographic Estimation of Gallium. Pure gallium metal was dissolved in hydrochloric acid and the solutions containing 1, 0.1, 0.01, 0.001 and 0.0001 mg. of gallium per c.c. were prepared. Sodium chloride (10 mg.) 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 and 0.0001 mg. of gallium 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.

(1) J. Bardet, *Compt. rend.* **157** (1913), 224.

(2) S. Piña de Rubies, C. Sirvent d'Argent, *Anal. s. soc. españ. fís. quim.* **29** (1931), 235; *Chem. Abstracts*, **25** (1931), 3104.

(3) V. M. Goldschmidt, Cl. Peters, *Nachr. Ges. Göttingen, Math.-physik. Klasse* **1931**, 165-85 (1931).

Table 1. Spectral Lines at Different Concentrations.

λ (Å)	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.	0.0001 mg.
2255.03	F				
2259.23	F				
2294.20	W	F			
2297.87	W	F			
2338.60	S	W			
2371.33	S	W			
2418.70	S	W	F		
2450.08	S	S	W		
2500.71	S	S	W	F	
2659.87	S	S	W	F	
2719.66	S	S	W	F	
2874.24	S	S	S	S	F
2943.7	S	S	S	S	W
2944.18	S	S	W	F	
4033.01	S	S	S	F	
4172.06	S	S	W	F	

Gallium Content of the Hot Springs of Japan. Aluminium oxide (10 mg.) obtained from the suitable quantities (5 to 50 c.c.) of the mineral water was subjected to arc excitation. The following gallium lines were found (Table 2). Table 2 shows that seven samples (out of eleven samples) contained about 0.1 γ of gallium in 10 mg. of aluminium oxide. The gallium content of the hot springs was calculated from their aluminium content. The results are shown in Table 2 and Table 3.

Except the hot springs of Yunohanazawa, gallium was always found in the above-mentioned acid alum-vitriol springs of Japan. The atomic

Table 2. Spectral Lines of Gallium.

Hot Spring	Prefecture	2874.24 Å	2943.7 Å
(1) Kinbu.	Yamanashi	—	W
(2) Seki-no-Yu, Kusatu.	Gumma	W	S
(3) Sirahata-no-Yu, Kusatu.	Gumma	F (?)	W
(4) Zizo-no-Yu, Kusatu.	Gumma	—	W
(5) Wasi-no-Yu, Kusatu.	Gumma	—	W
(6) Takayu.	Yamagata	—	F
(7) Kinkei.	Totigi	—	—
(8) Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—
(9) Kōbō-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—
(10) Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—
(11) Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	—	—

Table 3. Gallium Content of the Hot springs of Japan.

Hot Spring	Gallium Contents (g./l.)
(1) Kinbu.	$1 \sim 5 \times 10^{-5}$
(2) Seki-no-Yu, Kusatu.	$5 \sim 10 \times 10^{-6}$
(3) Sirahata-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$
(4) Zizo-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$
(5) Wasi-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$
(6) Takayu.	$1 \sim 5 \times 10^{-6}$
(7) Kinkei.	$5 \sim 10 \times 10^{-7}$
(8) Gongen-Yu, Yunohanazawa.	less than 10^{-7}
(9) Kōbō-Yu, Yunohanazawa.	less than 10^{-7}
(10) Yoemon-Yu, Yunohanazawa.	less than 10^{-7}
(11) Daruma-Zigoku, Yunohanazawa.	less than 10^{-7}

ratio of gallium to aluminium in the hot springs is considered to be 1:100000. Expressed in percentages to total residue, the gallium content of these hot springs is between 0.001 and 0.00001.

Summary.

(1) An arc spectrographic detection and estimation of gallium was studied.

(2) The gallium content of a number of hot springs of Japan was estimated.

The author expresses his hearty thanks to Prof. Kenjiro 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

The Occurrence of Beryllium in the Hot Springs of Japan.

By Kazuo KURODA.

(Received May 27, 1940.)

In the previous paper,⁽¹⁾ the author reported the beryllium content of the hot springs of Matunoyama in Niigata Prefecture. Beryllium has recently been detected spectroscopically in a number of hot springs,

Table 1. Spectral lines of Beryllium.

Hot Spring	Prefecture	2348.6Å	2494.7Å	2650.8Å	3131.1Å
(1) Kinbu.	Yamanasi	W	—	F	F
(2) Seki-no-Yu, Kusatu.	Gumma	W	—	—	—
(3) Sirahata-no-Yu, Kusatu.	Gumma	W	—	—	F
(4) Zizo-no-Yu, Kusatu.	Gumma	—	—	—	—
(5) Wasi-no-Yu, Kusatu.	Gumma	F	—	—	—
(6) Takayu.	Yamagata	—	—	—	—
(7) Kinkei.	Totigi	F	—	—	—
(8) Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—	—	—
(9) Kōbō-Yu, Yunohanazawa, Hakone.	Kanagawa	W	F (?)	F	F
(10) Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	F	—	—	—
(11) Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	W	F	F	F

Table 2. Beryllium Content of the Hot Springs of Japan.

Hot Spring	Beryllium Content (g./l.)
(1) Kinbu.	$5 \sim 10 \times 10^{-5}$
(2) Seki-no-Yu, Kusatu.	1×10^{-6}
(3) Sirahata-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$
(4) Zizo-no-Yu, Kusatu.	less than 10^{-7}
(5) Wasi-no-Yu, Kusatu.	$5 \sim 10 \times 10^{-7}$
(6) Takayu.	less than 10^{-7}
(7) Kinkei.	$5 \sim 10 \times 10^{-7}$
(8) Gongen-Yu, Yunohanazawa.	less than 10^{-7}
(9) Kōbō-Yu, Yunohanazawa.	$1 \sim 5 \times 10^{-6}$
(10) Yoemon-Yu, Yunohanazawa.	$5 \sim 10 \times 10^{-7}$
(11) Daruma-Zigoku, Yunohanazawa	$1 \sim 5 \times 10^{-6}$

(1) This Bulletin, **14** (1939), 305.

mainly of acid alum-vitriol springs of Japan. The amount of beryllium in these hot springs was spectroscopically estimated.

Aluminium oxide (10 mg.) obtained from the suitable quantities (5 to 50 c.c.) of the mineral water was subjected to arc excitation, and the following beryllium lines were found (Table 1.). The amount of beryllium was estimated from the table of the spectral lines of beryllium at different concentrations, which was described in the previous paper.⁽¹⁾ The results of the experiment are shown in Table 2.

The results of the experiment show that the atomic ratio of beryllium to aluminium in most of acid springs above-mentioned is considered to be 1:100000. Expressed in percentages to total residue, the beryllium content of these hot springs is between 0.001 and 0.00001.

Summary.

The beryllium content of a number of hot springs of Japan was estimated.

The author expresses his hearty thanks to Prof. Kenjiro 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

Über die Bestimmung der Verteilung der Kristallite in Fasern auf direktem und indirektem Wege.

Von Yukichi GO.

(Eingegangen am 5. Mai 1940.)

Inhalt.

1. Einleitung	239
2. Direktbestimmung der Kristallitverteilung	240
a) Direktbestimmungsversuche unter Benutzung der diatropen Reflexe von einer Schiefaufnahme	240
b) Röntgengoniometer für die Polykristalluntersuchung	242
(i) Kratky'sches Goniometer	242
(ii) Experimentelle Schwierigkeiten des Apparates	243
c) Direktbestimmung der Kristallitverteilung aus den diatropen Reflexen mit einer Schwenkkamera	244
d) Anwendungsmöglichkeiten der diatropen Reflexe für die Direkt- Bestimmung	246
3. Indirektbestimmung der Kristallitverteilung	247
a) Vereinfachung der Intensitätsformel $I \propto \left \frac{d\omega_1}{d\delta} \right + \left \frac{d\omega_2}{d\delta} \right $	248
b) Verallgemeinerung der Kratky'schen Intensitätsformel	250
c) Vereinfachte Ableitung nach dem Matano'schen Prinzip unter Be- nutzung des Reflexionskreises und Netzebenenkreises	252
d) Zusammenstellung und Vergleich der drei verschiedenen Ableitungs- prinzipien und zwei Intensitätsformeln	254
e) Experimentelle Prüfung unter Anwendung von Doppeldreh-Kristall- Aufnahmen des Pentaerythrit-Einkristalls	254
4. Zusammenfassung	258

1. Einleitung. Um den Ordnungsgrad der Kristallite in Fasern quantitativ zu messen und zu vergleichen, habe ich vor einiger Zeit für Zwecke der Praxis eine nach röntgenographischer Methode erhaltene Grösse II für den Parallelitätsgrad der Kristallite vorgeschlagen.⁽¹⁾ Wie damals schon gesagt wurde, ist es sehr wichtig, eine geeignete Interferenz für die Intensitäts-Photometrierung auszuwählen. Obwohl die Interferenz der diatropen Ebene hierfür theoretisch am richtigsten ist, wurde eine stärkste Aequator-Interferenz für die praktische Messung angewendet, weil erstens die diatrope Interferenz die Intensitätsverteilung gerade am Pol der Lagenkugel nicht richtig zeigt, zweitens ihre schwache Intensität ungünstig ist und drittens der Einfluss der Nachbarinterferenzen unvermeidlich wird.

Der Parallelitätsgrad der Kristallite wurde nach folgender Gleichung aus der Halbwertsbreite H° der Energie-Verteilungskurve längs des Debye-Scherrer-Kreises einer stärksten Aequator-Interferenz berechnet:

$$\text{Parallelitätsgrad} \quad II = \left(\frac{90^\circ - H^\circ/2}{90^\circ} \right) \times 100 \quad (1)$$

(1) Y. Go und T. Kubo, *J. Soc. chem. Ind. Japan*, **39** (1936), 458.

Einerseits wurde nun, unter Anwendung der oben angegebenen Grösse H , eine Diskussion der mechanischen Eigenschaften der Fasern sowie des Einflusses der Herstellungsweise der künstlichen Seide und Zellwolle und auch des Einflusses von chemischen und mechanischen Einwirkungen auf den Orientierungsgrad der Kristallite vorgenommen, und zwar hauptsächlich vom Standpunkt der Praxis aus.

Die theoretisch exakte Behandlung der Beziehung zwischen der Verteilung der Kristallite und den mechanischen Eigenschaften der Fasern ist keine leichte Aufgabe und die Grösse H ist natürlich nicht für diesen Zweck, sondern nur für den praktischen

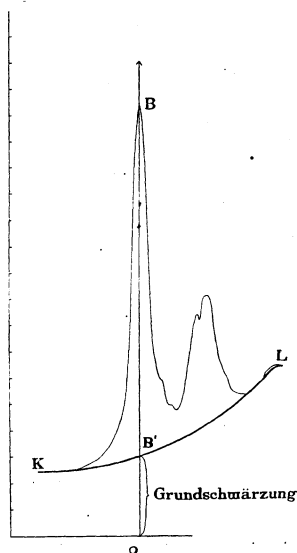


Fig. 1.

Vergleich entwickelt worden. Für die praktische Messung ist es vor allem notwendig, dass sie zunächst einmal möglichst einfach ist und dass die erhaltenen Resultate soweit wie möglich von subjektiven Fehlern frei sind. Durch die Photometrierung nach radialer Richtung kann man doch die Grundschwärzung gerade für den angewendeten Debye-Scherrer-Kreis feststellen, wie es in Fig. 1 zu sehen ist, und es ist doch möglich, wie es von W. A. Sisson und G. L. Clark⁽²⁾ schon im Jahre 1933 versucht worden ist, auf verschiedene Weise den Orientierungsgrad der Kristallite unter Berücksichtigung der Grundschwärzung quantitativ zu vergleichen. Aber leider ergibt sich hier die Möglichkeit von subjektiven Fehlern, weil man die Kurve der Grundschwärzung $LB'K$ durchziehen muss, und wenn man diesen Fehler ausschalten will, ist es notwendig, nicht nur nach einer radialen Richtung, sondern nach verschiedenen radialen Richtungen zu photometrieren und aus den ganzen Messungen die wahrscheinlichste Grundschwärzung festzustellen. Aber ein solches Vorgehen ist wegen seiner Langwierigkeit für die praktische Messung schon nicht mehr geeignet. Über die Natur der Verteilungskurve der Kristallite in nativen und künstlichen Fasern wird bei anderer Gelegenheit noch näher diskutiert werden.

Andererseits wurden theoretische Erörterungen über die Intensitätsverteilung der Faserdiagramme vorgenommen, und zwar hauptsächlich für den Fall der indirekten Bestimmung der Verteilung der Kristallite.

Im Folgenden werden nun neue Versuche zur direkten Bestimmung der Kristallitverteilung durch Verbesserung der Aufnahmetechnik besprochen und nachher werden die von verschiedenen Autoren abgeleiteten mathematischen Behandlungen für die Indirekt-Bestimmung der Kristallitverteilung weiter entwickelt und ihre Ableitungsprinzipien verglichen.

2. Direktbestimmung der Kristallitverteilung. (a) *Direktbestimmungsversuche unter Benutzung der diatropen Reflexe von einer Schiefaufnahme.* Obwohl die Anwendung der diatropen Reflexe für die praktische Messung aus den oben schon erwähnten drei Gründen nicht geeignet ist, kann man für den Zweck der theoretisch exakten Untersuchung doch weiter versuchen, die diatropen Reflexe auszunutzen. Wie in Fig. 2 zu sehen ist, liegen die Repräsentationspunkte der diatropen Reflexe auf der Lagenkugel (die Durchstossunkte der Normalen der diatropen Ebenen an der Kugeloberfläche) bei einer realen einfachen

(2) W. Sisson und G. L. Clark, *Ind. Eng. Chem. Anal. Edition*, **5** (1933), 296.

Faserstruktur in der Nähe des Poles F. Die Dichteverteilungskurve D dieser Punkte zeigt definitionsgemäss die Verteilung der Normalenrichtungen von den in Frage kommenden diatropen Ebenen und gleichzeitig auch die wirkliche Verteilung der Kristallite in der Faser.

Die Kurve der Intensitätsverteilung der diatropen Reflexe auf den Faserdiagrammen ist aber nicht identisch mit der Kurve D, sondern sie zeigt nur die Dichteverteilung der Repräsentationspunkte längs des Reflexionskreises R auf der Lagenkugel an, also nur die Form des

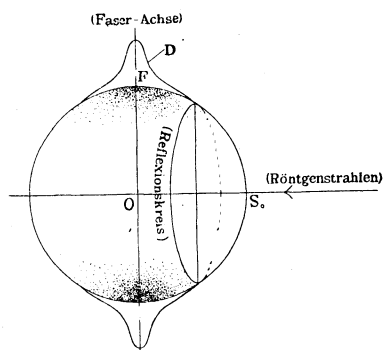


Fig. 2.

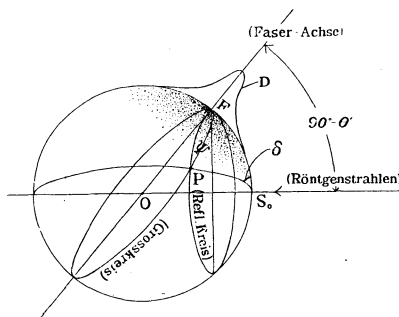


Fig. 3.

Fusses der Verteilungskurve D. Dieses kann man sich bei räumlicher Betrachtung der Verhältnisse auf der Lagenkugel leicht klar machen. Wenn aber eine Schiefstellung der Faser zur Röntgenstrahlenrichtung im Winkel von $90^\circ - \theta^\circ$ vorgenommen wird, wie es in Fig. 3 gezeigt ist, so geht der Reflexionskreis R gerade durch den Pol F der Lagenkugel. Hierbei wird θ aus der Bragg'schen Formel

$$n\lambda = 2d \sin \theta$$

berechnet (wobei d der Netzebenenabstand der in Frage kommenden Reflexe und λ die Wellenlänge der Röntgenstrahlen ist). Zum Zwecke der Uebertragung vom Reflexionskreis, längs dessen die Dichteverteilung gemessen wird, auf den Grosskreis der Lagenkugel müssen nun nur noch die Winkel nach der trigonometrischen Gleichung (2) umgerechnet werden.

$$\cos \psi = \cos \delta \cdot \cos \theta \quad (2)$$

Hierbei ist δ der Richtungswinkel einer Reflexionsstelle auf dem Debye-Scherrer-Kreis,

ψ der Polabstand der entsprechenden Stelle P auf der Lagenkugel.

Für die Aufnahmen zur Bestimmung der Intensitätsverteilung längs des Debye-Scherrer-Kreises wurde die zylindrische, welche für die Messung der H -Werte konstruiert worden war,⁽³⁾ benutzt. Nur wurde das Ende der Blende schief geschnitten, um die Achse des direkt darauf

(3) Y. Go und T. Kubo, *J. Cell. Inst. Tokyo*, **12** (1936), 79.

geklebten Faserbündels gerade im Winkel $90^\circ - \theta^\circ$ zur Röntgenstrahlenrichtung zu neigen (Fig. 4).

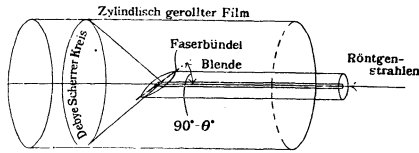


Fig. 4.

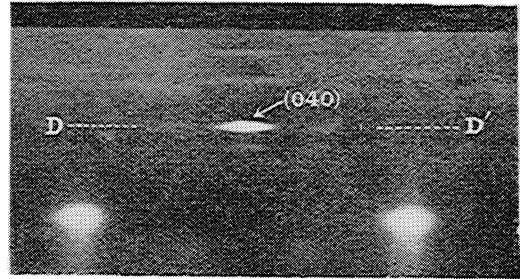


Fig. 5.

Fig. 5 zeigt eine solche Aufnahme von der Ramiefaser. Der markierte Reflex ist einer der diatropen Ebene (040) und der Neigungswinkel der Faserachse zur Röntgenstrahlenrichtung war $17^\circ 24'$. Fig. 6a zeigt die Intensitätsverteilungskurve dieses Reflexes längs der dem Debye-Scherrer-Kreis entsprechenden geraden Linie DD' und die daraus nach

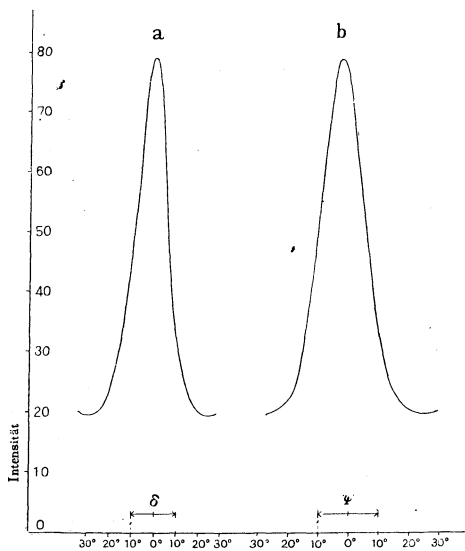


Fig. 6.

Formel (2) umgerechnete wirkliche Verteilungskurve der Kristallite in der Faser ist als Fig. 6b gezeigt. Wie man an der Aufnahme Fig. 5 und auch an der Kurve Fig. 6a deutlich sieht, ist leider der Einfluss der Nachbarinterferenzen doch nicht ganz vermeidlich. Die Verteilungskurve Fig. 6b ist deswegen nicht für den ganzen Bereich der Kurve ausnutzbar und muss daher für den Fussteil der Kurve durch andere Messungen ergänzt werden.

(b) *Röntgengoniometer für die Polykristalluntersuchung.* (i) *Kratky'sches Goniometer:* Für die Polykristalluntersuchung hat O. Kratky bereits früher ein Röntgengoniometer konstruiert.

Der in Fig. 7 abgebildete Apparat ist nach dem Kratky-schen Prinzip gebaut: das Präparat dreht sich um eine die Röntgenstrahlen schneidende Achse, deren Neigung gegen die Strahlenrichtung verändert werden kann. Es wird ein Debye-Scherrer-Kreis ausgeblendet und auf einem zylindrischen Film aufgefangen, dessen Achse mit der Richtung der Röntgenstrahlen zusammenfällt und der sich in dieser Richtung in zwangsläufiger Kupplung mit der Präparatendrehung hin und her bewegt. Die Ausblendung geschieht mittels der „Auswahlblende“. Diese

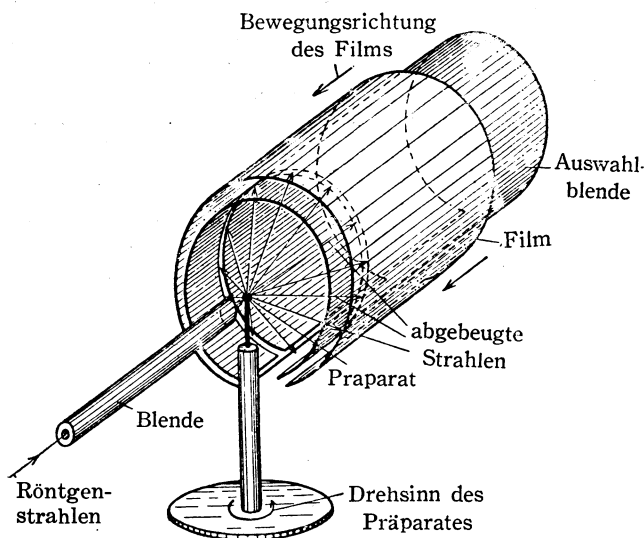


Fig. 7.

ist ein dem Film koaxialer Hohlzylinder, der einen schmalen, kreisförmigen Spalt besitzt, der parallel zur Basis verläuft und durch Verschieben des Zylinders längs seiner Achse in eine solche Lage gebracht werden kann, dass nur den zu einem bestimmten Debye-Scherrer-Kreis gehörigen Strahlen der Durchtritt gestattet ist. Indem sich das Präparat und mit ihm die Lagenkugel dreht, der Reflexionskreis aber fest bleibt, bestreicht dieser bei einer vollen Umdrehung eine Kugelzone, und alle in dieser gelegenen Repräsentationspunkte der betreffenden Ebene gelangen daher in Reflexionsstellung.

Ein grosser Vorteil dieser Aufnahmetechnik ist es, dass der Debye-Scherrer-Kreis nach dem Aufrollen des Filmes eine gerade Linie bildet, sodass seine Photometrierung, ebenso wie die in radialer Richtung, längs einer geraden Linie erfolgen kann, was eine grosse Vereinfachung bedeutet.

(ii) Experimentelle Schwierigkeiten des Apparates: Trotz der prinzipiellen Richtigkeit dieser Aufnahmemethode und des erwähnten Vorteils bei der Photometrierung, ist leider über eine praktische Anwendung des Goniometers für die Polykristalluntersuchung nichts bekannt geworden. Meiner Meinung nach ist dies aber wohl nur auf die konstruktiven und experimentellen Schwierigkeiten dieses Apparates zurückzuführen.

Die erste Schwierigkeit ist die Justierung der zwei koaxialen Achsen, nämlich der Achse der Blende und des gerollten Filmes, besonders mit Rücksicht auf die Bewegung des Filmes. Eine kleine Abweichung drängt den Debye-Scherrer-Kreis bei der schmalen Ausblendung sehr leicht heraus, und bei einer kleinen Abweichung des Filmes von der genauen zylindrischen Form bildet der Debye-Scherrer-Kreis nach Aufrollen des Filmes nicht mehr eine gerade Linie, und die Photometrierung wird somit schon nicht mehr gut durchführbar.

kassette K und ihrem Tisch K' dreht. Hier ist also keine mechanische Verkuppung zwischen der Bewegung des Filmes und des Präparates notwendig. Wegen des Zusammenstossens der Filmkassette K mit der Blende B bei einer ganzen Umdrehung wurden die Präparate nur im notwendigen Winkelbereich hin und her geschwenkt.

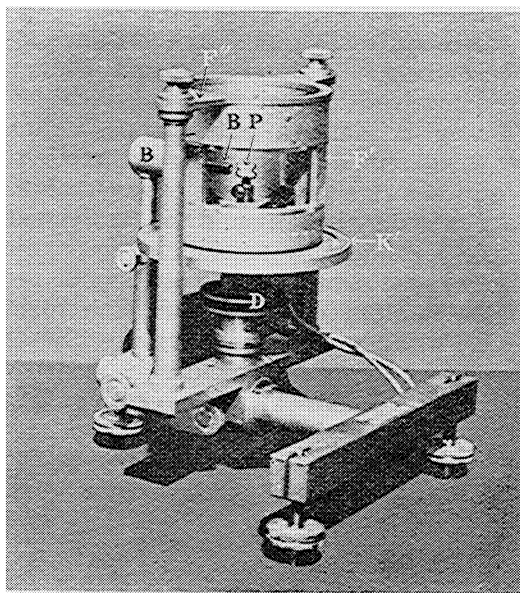


Fig. 9 a.

Fig. 9, a und b, sind photographische Aufnahmen dieser Kamera von der Seite und von oben.

Die Verhältnisse auf der Lagenkugel sind in Fig. 10 dargestellt. Man sieht gleich die Möglichkeit, dass man durch diese Aufnahmemethode die Kristallitverteilung gerade am Pol der Lagenkugel feststellen und gleichzeitig längs eines Grosskreises verfolgen kann.

Fig. 11 zeigt die aus der Photometerkurve umgerechnete Kristallitverteilungs-

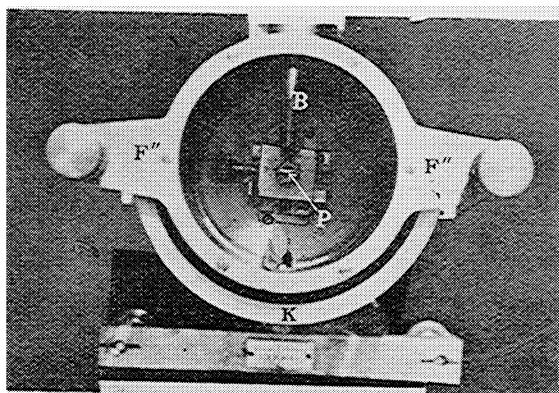


Fig. 9 b.

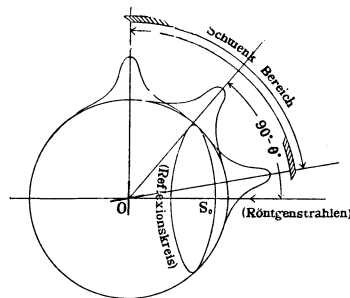


Fig. 10.

kurve der Ramiefaser. Die Photometrierung wurde unter Verwendung des diatropen Reflexes (040) durchgeführt. Das mit der oben erklärten Schwenkkamera aufgenommene Röntgenbild ist in Fig. 12 als a dargestellt. Der Schwenkwinkel war 60° und die Pfeile zeigen die Photometrierungsrichtung. Fig. 12b ist eine absichtlich in sechs Einzelaufnahmen zerlegte Aufnahme desselben Reflexes. Die nebeneinander liegenden Aufnahmen stellen sechs zeitlich nacheinander, bei stehender Kamera, aber unter verschiedenen Winkeln aufgenommene

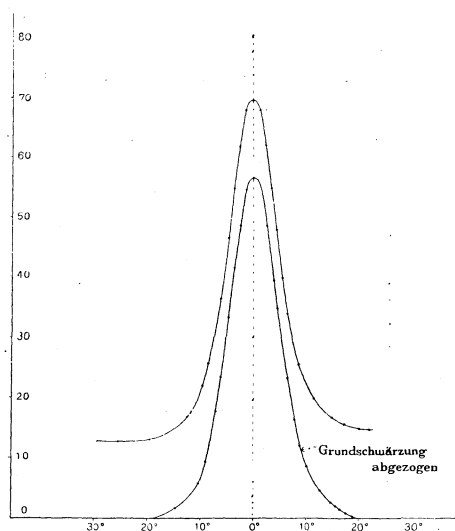


Fig. 11.

Röntgenbilder dar. Wie man sieht, zeigt jede einzelne Aufnahme einen Bogen, welcher der durch die Fensterblende herausgeschnittene Teilausschnitte des Debye-Scherrer-Kreises ist. Der durch Zusammenschmelzen dieser bogenförmigen Einzelreflexe bei kontinuierlich bewegter Kamera entstehende Reflex 12a kann daher keine symmetrische Intensitätsverteilung in wagerechter Richtung haben und es ist daher leider nicht vermeidlich, dass die daraus erhaltene Photometerkurve immer ein wenig—wenn auch nicht viel—unsymmetrisch wird. Dieser Nachteil würde sich durch Verwendung des Kratky'schen Goniometers vermeiden lassen, weil dabei der

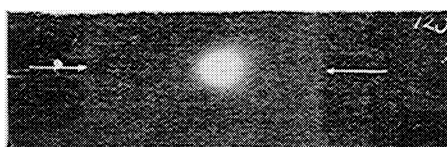


Fig. 12 a.

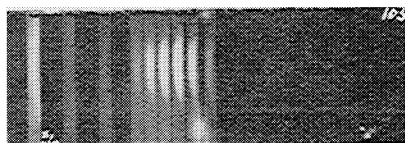


Fig. 12 b.

Debye-Scherrer-Kreis nicht bogenförmig, sondern geradlinig aufgenommen wird.

(d) *Anwendungsmöglichkeiten der diatropen Reflexe für die Direkt-Bestimmung.* Wie im vorhergehenden Teil erörtert wurde, kann man versuchen, durch Anwendung geeigneter Methoden direkter, ohne mathematische Ausrechnung, die Kristallitverteilung festzustellen.

Dabei stösst man jedoch auf einige Schwierigkeiten allgemeiner Art, durch welche die Anwendungsmöglichkeiten der diatropen Reflexe für die Direkt-Bestimmung beschränkt werden. Die Hauptschwierigkeit ist der Einfluss der Nachbarinterferenzen, welche in der Nähe der angewandten diatropen Reflexe liegen. Die Lage der Nachbarinterferenzen hängt aber von der Art der Kristallitengitter ab; in günstigen Fällen, wenn die diatropen Reflexe keine störenden Nachbarinterferenzen in der Nähe haben, kann man sie natürlich ohne weiteres für die Direkt-Bestimmung verwenden.

Die zweite Schwierigkeit hängt mit der Kristallitverteilung zusammen. Je ungeordneter die Kristallite in der Faser verstreut sind, umso grösser sind die Möglichkeiten der Störungen durch Nachbarinterferenzen.

Es folgt daraus, dass:

1) Bei den Fasern, welche einen grossen $//$ -Wert besitzen, also bei den hoch orientierten Fasern, ist es sehr gut möglich, die Verteilungskurve lediglich durch Schiefaufnahme störungsfrei festzustellen. Natur-

lich kann man in diesem Falle auch die Schwenkkamera verwenden und dann die beiden erhaltenen Verteilungskurven vergleichen.

2) Als nächste Stufe kann man einen Fall ansehen, bei welchem der Orientierungsgrad ziemlich hoch ist, am Fuss der Verteilungskurve aber sich ein geringer Einfluss einer anderen Interferenz findet (wie bei Fig. 5 und 6).

In diesem Fall besteht noch die Möglichkeit, die ganze Verteilungskurve durch Schwenkaufnahme noch störungsfrei zu verfolgen (wie bei Fig. 12a).

3) Bei schlecht orientierten Fasern kommen ganz Nachbarinterferenz-freie diatrophe Reflexe nur noch selten vor. Die Schwenkkamera ist auch nicht mehr für den ganzen Verteilungsbereich brauchbar wegen ihrer mechanischen Konstruktion. Und es ist hier auch leicht möglich, dass noch Störungen von anderen Interferenzen hinzukommen. Auf der in Fig. 12b dargestellten Aufnahme sieht man z.B. an der linken Seite den Reflex (320), welcher bei einer schlechten Orientierung der Kristallite den Reflex (040) genügend hätte beeinflussen können. Diese Störung ist aber mit der Kratky'schen Vorrichtung prinzipiell auch nicht vermeidbar.

Für die Direkt-Bestimmung der Kristallitverteilung sind die diatropen Reflexe also gut anwendbar, allerdings nur in günstigen Fällen, wenn die Reflexe von Störungen durch Nachbarinterferenzen frei sind.

Andererseits kann man auch versuchen, die Verteilungskurven indirekt unter Verwendung der Aequatorreflexe mathematisch auszurechnen und die so erhaltenen Kurven mit den aus den diatropen Reflexen direkt festgestellten Verteilungskurven zu vergleichen. Die Richtigkeit der mathematischen Behandlung des Problems kann erst durch einen solchen Vergleich genau geprüft werden.

3. Indirektbestimmung der Kristallitverteilung.

Ausser den diatropen Reflexen gibt es keine Reflexe, aus welchen die Kristallitverteilung direkt ohne mathematische Ausrechnung festgestellt werden kann. Es ist daher zunächst die genaue Kenntnis der betreffenden mathematischen Beziehung erforderlich, und erst dann kann die wirkliche Kristallitverteilung in der Faser indirekt aus der Intensitätsverteilung im Faserdiagramm ausgerechnet werden.

In der letzten Veröffentlichung wurden die von O. Kratky⁽⁵⁾ zum ersten Mal abgeleiteten und später von I. Sakurada und K. Futino,⁽⁶⁾ dann von C. Matano⁽⁷⁾ und schliesslich von Y. Go mit I. Kakinoki und S. Nagata^{(8) (9)} weiter entwickelten mathematischen Beziehungen miteinander verglichen und auch kurz über einige experimentelle Prüfungen berichtet. Im Folgenden sollen die inzwischen weiter entwickelten mathematischen Behandlungen und weitere, experimentell erhaltene Ergebnisse näher diskutiert werden.

(5) O. Kratky, *Kolloid-Z.* **64** (1933), 213.

(6) I. Sakurada und K. Futino, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **24** (1934), 193.

(7) C. Matano, *J. Soc. Chem. Ind. Japan*, **39** (1936), 478.

(8) Y. Go, Kakinoki, und S. Nagata, *Rept. Japan. Assoc. Adv. Sci.*, **12** (1937), 128.

(9) Y. Go, S. Nagata und J. Kakinoki, *this Bulletin*, **13** (1938), 198.

(a) Vereinfachung der Intensitätsformel, $I \propto \left| \frac{d\omega_1}{d\delta} \right| + \left| \frac{d\omega_2}{d\delta} \right|$

Unter Zugrundelegung der Annahme, dass die Intensität an einem Punkte auf dem Debye-Scherrer-Kreis proportional ist der Anzahl der Kristallite, welche auf den entsprechenden kleinen Bereich des Reflexionskreises ihre Wirkung ausüben ($I \propto \frac{d\omega}{d\delta}$), wurde die folgende Beziehung abgeleitet:⁽⁸⁾

$$I \propto \left| \frac{1}{v_1} \right| + \left| \frac{1}{v_2} \right|$$

$$v_1 = \left(\frac{d\delta}{d\omega} \right)_{\omega=\omega_1}$$

$$= \frac{A}{A^2 - B_1^2} \left\{ \cos \varphi B_1 + \kappa_1 \frac{(\cos \rho B_1 - \sin \theta A \sqrt{\sin^2 \varphi A^2 - B_1^2})}{\sqrt{A^2 \cos^2 \theta - B_1^2 - A^2 \cos^2 \rho + 2 \cos \rho \sin \theta A B_1}} \right\}$$

$$v_2 = \left(\frac{d\delta}{d\omega} \right)_{\omega=\omega_2} = (B_1 \text{ und } \kappa_1 \text{ sind durch } B_2 \text{ und } \kappa_2 \text{ zu ersetzen}) \quad (3)$$

wobei:

$$A = 1 - \cos^2 \delta \cos^2 \theta$$

$$B_1 = \sin \theta \cos \rho - \cos \varphi \cos \delta \sin \theta \cos \theta + \cos \theta \sin \delta \sqrt{C}$$

$$B_2 = \sin \theta \cos \rho - \cos \varphi \cos \delta \sin \theta \cos \theta - \cos \theta \sin \delta \sqrt{C}$$

$$C = \sin^2 \varphi - \cos^2 \rho - \cos^2 \theta \cos^2 \delta + 2 \cos \rho \cos \varphi \cos \theta \cos \delta$$

$$\kappa_1 \text{ und } \kappa_2 \text{ sind } +1 \text{ oder } 1-$$

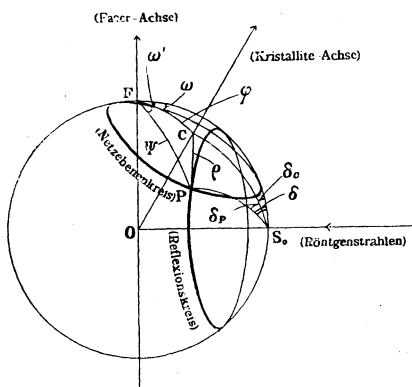


Fig. 13.

Bei dieser früheren Ableitung war der Richtungswinkel auf dem Reflexionskreis in zwei Teile (δ_c und δ_p) unterteilt worden (vergl. Fig. 13).

Im Folgenden soll jedoch eine andersartige Ableitung der Intensitätsformel gebracht werden, welche sogar zu einer noch einfacheren Formel führt, jedoch unter Zugrundelegung der gleichen Annahme bezüglich der Intensität und der Kristallitverteilung ($I \propto \frac{d\omega}{d\delta}$):

$$\text{Aus } \Delta \text{ FPC folgt } \cos(\omega' - \omega) = \frac{\cos \rho - \cos \varphi \cos \psi}{\sin \varphi \sin \psi} \quad (4)$$

wobei: $\omega' = \omega_1$, oder $\omega' = \omega_2$, und ψ der Polabstand des Punktes P ist.

Der Netzebenenkreis geht bei einer vollen Umdrehung der Kristallachse C zweimal durch den Punkt P.

Wenn C links vom Punkte P liegt, vom Pol F aus gesehen, nämlich wenn $\omega' > \omega$ ist, setzen wir $\omega' = \omega_1$, und wenn C rechts vom Punkte P liegt, nämlich wenn $\omega' < \omega$ ist, setzen wir $\omega' = \omega_2$.

$$\text{Aus } \angle FPS_0 \text{ folgt } \cos \delta = \frac{\cos \psi}{\cos \theta} \quad (5)$$

$$\cos \omega' = \frac{\sin \theta}{\sin \psi} \quad (6)$$

Wenn man (5) und (6) in (4) einsetzt, und eliminiert und das Differential $\frac{d\omega}{d\delta} (\theta, \rho, \varphi = \text{Konst.})$ ausrechnet, so ergibt sich

$$\frac{d\omega}{d\delta} = \frac{\cos \theta (\cos \varphi \sin \delta - \sin \varphi \cos \delta \sin \omega)}{\sin \varphi (\cos \theta \sin \delta \cos \omega - \sin \theta \sin \omega)} \quad (7)$$

Wenn man ω' aus (4) und (6) eliminiert und in (7) einsetzt, so erhält man die Formel für den allgemeinsten Fall, nämlich:

Spiralfaser $\varphi \neq 90^\circ$
allgemeine Reflexe $\rho \neq 90^\circ$

$$I \propto \left| \frac{d\omega_1}{d\delta} \right| + \left| \frac{d\omega_2}{d\delta} \right|$$

$$\frac{d\omega_1, d\omega_2}{d\delta} = \frac{\cos \theta (\sin \delta (\cos \varphi - \cos \theta \cos \delta \cos \rho) \pm \sin \theta \cos \delta \sqrt{C}}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{C}} \quad (8)$$

Für die speziellen Fälle ergibt sich:

Spiralfaser $\varphi \neq 90^\circ$, Aequator Reflexe $\rho = 90^\circ$

$$\frac{d\omega_1, d\omega_2}{d\delta} = \frac{\cos \theta (\sin \delta \cos \varphi \pm \sin \theta \cos \delta \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta})}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}} \quad (9)$$

Ringfaser $\varphi = 90^\circ$, allgemeine Reflexe $\rho \neq 90^\circ$

$$\frac{d\omega_1, d\omega_2}{d\delta} = \frac{\cos \theta (\sin \delta \cos \delta \cos \theta \cos \rho \mp \sin \theta \cos \delta \sqrt{\sin^2 \rho - \cos^2 \theta \cos^2 \delta})}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \rho \cos^2 \theta \cos^2 \delta}} \quad (10)$$

Ringfaser $\varphi = 90^\circ$, Aequator Reflexe $\rho = 90^\circ$

$$\frac{d\omega_1, d\omega_2}{d\delta} = \frac{\sin \theta \cos \theta \cos \delta}{1 - \cos^2 \theta \cos^2 \delta} \quad (11)$$

Beim letzteren Fall ergibt sich:

$$I \propto \frac{\sin \theta \cos \theta \cos \delta}{1 - \cos^2 \theta \cos^2 \delta} = \frac{\cot \theta \cos \delta}{1 + \cot^2 \theta \sin^2 \delta}$$

Dies stimmt mit dem Sakurada—Futino'schen Ergebnis überein, aber das beruht natürlich auf der Gleichheit der beiden Ableitungsprinzipien ($I \propto \frac{d\omega}{d\delta}$).

Die Formeln werden noch einfacher, wenn folgende Beziehung erfüllt ist:

$$[\sin \delta (\cos \varphi - \cos \theta \cos \delta \cos \rho) \pm \sin \theta \cos \delta \sqrt{C}] \leq 0$$

Dann ergibt sich für:

Spiralfaser, allgemeine Reflexe

$$I \propto \frac{\cos \theta \sin \delta (\cos \varphi - \cos \theta \cos \delta \cos \rho)}{(1 - \cos^2 \theta \cos^2 \delta) \sqrt{C}} \quad (12)$$

Spiralfaser, Aequator Reflexe

$$I \propto \frac{\cos \theta \cos \varphi \sin \delta}{(1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}} \quad (13)$$

Ringfaser, allgemeine Reflexe

$$I \propto \frac{\cos^2 \theta \cos \rho \cdot \sin \delta \cos \delta}{(1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}} \quad (14)$$

Ringfaser, Aequator Reflexe

$$I \propto \frac{\sin \theta \cdot \cos \theta \cdot \cos \delta}{1 - \cos^2 \theta \cos^2 \delta} \quad (15)$$

(b) *Verallgemeinerung der Kratky'schen Intensitätsformel.* O. Kratky hat die Intensitätsformel nur für die Aequator Reflexe abgeleitet,⁽⁵⁾ aber hier soll versucht werden, sein Ableitungsprinzip für die allgemeineren Fälle weiter zu entwickeln. Das Kratky'sche Ableitungsprinzip beruht auf dem schrittweisen Vorgehen in drei Stufen. Zunächst lässt man den Netzebenenkreis $N_{(\delta, \rho)}$ der in Frage kommenden Netzebene, bei einem konstanten Spiralwinkel φ , um 360° auf der Lagenkugel rotieren (Fig. 14). Dabei bestreicht der Netzebenenkreis die Kugelzone (Z),

welche den Verteilungsbereich der Normalen auf der Lagenkugel zeigt. Zweitens berechnet man die Dichteverteilung der Normalen auf dieser Zone längs dem Grosskreis $\left(\frac{dl}{d\psi}\right)$.

Schliesslich wird drittens die auf der Zone längs dem Grosskreis berechnete Normalenverteilung einfach durch Winkelumrechnung ($\cos \psi = \cos \delta \cos \theta$) auf den Reflexionskreis (Kleinkreis) übertragen. Dieses Ableitungsprinzip wurde damals von O.

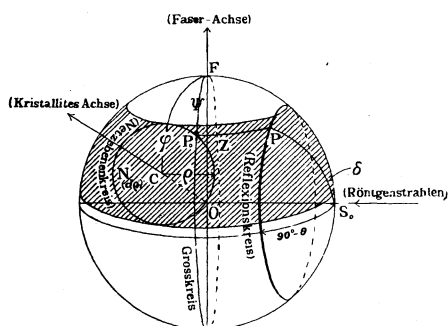


Fig. 14.

Durch Eliminierung von x aus diesen Gleichungen ergibt sich:

$$\sin \beta = \frac{\cos \psi - \cos \rho \cos \varphi}{\sin \rho} \quad (21)$$

und durch Differenzierung:

$$\frac{d\beta}{d\psi} = -\frac{\sin \psi}{\sin \rho \sin \beta} \quad (22)$$

Durch Vereinigung von (21) (22) mit (20) erhält man:

$$\frac{dl}{d\psi} = -\frac{\sin \rho \sin \psi}{\sqrt{\sin^2 \rho \sin^2 \varphi - \cos^2 \psi - \cos^2 \rho \cos^2 \varphi + 2 \cos \rho \cos \varphi \cos \psi \cos \varphi}}$$

und nach der Beziehung $\cos \psi = \cos \delta \cos \theta$:

$$\frac{dl}{d\psi} = -\frac{\sin \rho \sin \psi}{\sqrt{\sin^2 \varphi - \cos^2 \rho - \cos^2 \theta \cos^2 \delta + 2 \cos \rho \cos \varphi \cos \theta \cos \delta}} = -\frac{\sin \rho \sin \psi}{\sqrt{C}}$$

wobei $C = \sin^2 \varphi - \cos^2 \rho - \cos^2 \theta \cos^2 \delta + 2 \cos \rho \cos \varphi \cos \theta \cos \delta$ ist.

Also ergibt sich nunmehr nach (16):

$$I \propto J_{\varphi} \cdot \sin \varphi \cdot \frac{1}{\sin \psi} \cdot \frac{\sin \rho \sin \psi}{\sqrt{C}} = J_{\varphi} \cdot \sin \varphi \frac{\sin \rho}{\sqrt{C}} \quad (23)$$

Bei idealer Spiralfaserstruktur sind J_{φ} und $\sin \varphi$ konstant, und die Beziehung stimmt mit der von Matano überein. Die Ableitungsprinzipien von Kratky und Matano sind verschieden, aber wir sehen hier, dass die abgeleiteten Resultate auch für die allgemeinen Reflexe übereinstimmen, wie es für die Aequator Reflexe schon in der letzten Publikation gezeigt worden war.

(c) Vereinfachte Ableitung nach dem Matano'schen Prinzip unter Benützung des Reflexionskreises und Netzebenenkreises. Ohne den Reflexionskreis und Netzebenenkreis anzuwenden, hat C. Matano⁽⁷⁾ die Intensitätsverteilungsfunktion nach eigener Rechnungsweise abgeleitet, aber wenn man die Ableitungsprinzipien von verschiedenen Autoren untereinander vergleichen will, so muss mindestens zunächst die mathematische Arbeitsweise vereinheitlicht werden. Also soll im Folgenden die Intensitätsformel nach dem Matano'schen Ableitungsprinzip, aber unter Anwendung des Reflexions- und Netzebenenkreises—wie bei den anderen Autoren seit Polanyi üblich—abgeleitet werden. Wir finden die Ableitung dabei sogar noch einfacher als die von C. Matano selbst durchgeführte.

Nach der Matano'schen Ableitung (vergl. Fig. 16) nimmt man θ , ρ und δ als Konstante und ω und φ als Variable an. Wenn man den Linienelement des geometrischen Ortes von Punkt C (Kristallitachse) auf dem Grosskreis der Langenkugel als bezeichnet, so ist:

$$ds = \sqrt{d\varphi^2 + \sin^2 \varphi d\omega^2} \quad (24)$$

$$I \propto N_{(\omega, \varphi)} \cdot \sin \varphi \cdot \frac{\sin \rho}{\sqrt{C}} \quad (30)$$

Wie man sieht, zeigen die Beziehungen (30) und (23) exakte Uebereinstimmung.

(d) *Zusammenstellung und Vergleich der drei verschiedenen Ableitungsprinzipien und zwei Intensitätsformeln.* In der Tabelle I sind die drei verschiedenen Ableitungsprinzipien und die aus ihnen abgeleiteten Intensitätsformeln zusammengestellt und verglichen. Während das Prinzip I zu der komplizierten Intensitätsformel A führt, ergeben die beiden anderen Prinzipien II und III übereinstimmend die viel einfachere Formel B. Hier tritt sehr klar der grundsätzliche Unterschied zwischen dem Ableitungsprinzip I einerseits und II und III andererseits in der Verschiedenheit ihrer Differential-Ausdrücke hervor, welcher darauf beruht, dass im ersten Falle längs des Reflexionskreises (Kleinkreises), im zweiten Falle aber längs des Grosskreises differenziert wird.

In Tabelle II werden dann die Formeln A und B noch einem genaueren Vergleich unterzogen, und zwar werden hier die Maximum- und Minimum-Werte sowie ihre Richtungswinkel für die verschiedenen Fälle untereinander verglichen.

- (1) Maximum- und Minimum-Punkte (d.h. die Richtungswinkel δ bei denen die Funktionen Maximum- bzw. Minimum-Werte zeigen).

Hierbei zeigt sich, dass die Lage der Maximum-Punkte in allen Fällen übereinstimmt. Bei den Minimum-Punkten zeigt sich ebenfalls Uebereinstimmung bis auf den Fall der Spiralfaserstruktur, allgemeine Reflexe (in der Tabelle doppelt eingerahmt).

- (2) Maximum- und Minimum-Werte (Intensitätswerte).

Hier zeigt sich, dass die Maximum-Wert für den Fall

$|\rho - \varphi| \geq 0$ immer unendlich werden. Für den Fall

$|\rho - \varphi| < 0$ sind die Maximum-Werte dagegen alle verschieden.

Die Minimum-Werte sind ebenfalls sämtlich verschieden (alle diese verschiedenen Werte sind in der Tabelle einfach eingerahmt).

(e) *Experimentelle Prüfung unter Anwendung von Doppeldreh-Kristall-Aufnahmen des Pentaerythrit-Einkristalls.* Es ergeben sich also zwei Möglichkeiten, die Richtigkeit der Intensitätsformeln experimentell nachzuprüfen, und zwar:

- (1) Feststellung des Minimum-Punktes bei dem Fall Spiralfaserstruktur, allgemeine Reflexe.
- (2) Messung und Vergleich der Minimum-Intensitäts-Werte.

Weil es seinerzeit schwierig war, einen geeigneten Einkristall für die erste Methode zu finden, wurde damals⁽⁹⁾ zunächst die Ramie-Faser angewendet und es wurde dann über die so erhaltenen Ergebnisse berichtet, wobei die experimentell erhaltene Intensitätskurve mit der mathematisch errechneten Kurve verglichen wurde. Die erhaltene Kurve stimmte damals ganz gut mit der nach Formel A errechneten überein, aber dieses Ergebnis kann doch nur einen sehr beschränkten

Tabelle 1.

Ableitungs- prinzip	$I = \int N_{\varphi} \cdot \sin \varphi \cdot \left \frac{d\omega}{d\delta} \right \cdot d\varphi \dots\dots\dots (I)$	$I = \int N_{(\varphi, \omega)} \cdot ds = \int N_{(\varphi, \omega)} \times \sqrt{1 + \left(\sin \varphi \frac{d\omega}{d\varphi} \right)^2} \cdot d\varphi \dots\dots\dots (II)$	$\dots\dots\dots (III)$
Differential	$\left \frac{d\omega}{d\delta} \right :$ Kristallitenzahl ($d\omega$) an einem Punkt P längs Reflexionskreis (Kleinkreis) ($d\delta$) (Fig. 13)	$\left \frac{d\omega}{d\psi} \right :$ Normalenzahl ($d\psi$) an einem Punkt P längs Grosskreis ($d\psi$) (Fig. 15)	$\left \frac{d\omega}{d\varphi} \right :$ Kristallitenzahl ($d\omega$) an einem Punkt C längs Grosskreis ($d\varphi$) (Fig. 16)
Allgemeine Formel für Reale Faser- struktur	$I = \int N_{\varphi} \cdot \sin \varphi \left\{ \left \frac{d\omega_1}{d\delta} \right + \left \frac{d\omega_2}{d\delta} \right \right\} \cdot d\varphi$ $\frac{d\omega_1, \omega_2}{d\delta} = \frac{\cos \theta \{ \sin \delta (\cos \varphi - \cos \theta \cos \delta \cos \varphi) \pm \sin \theta \sin \delta \sqrt{C} \}}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{C}} \dots\dots\dots (A)$	$I = \int N_{\varphi} \cdot \sin \varphi \cdot \frac{\sin \rho}{\sqrt{C}} \cdot d\varphi$ $C = \sin^2 \varphi - \cos^2 \rho - \cos^2 \theta \cos^2 \delta + 2 \cos \theta \cos \rho \cos \varphi \cos \delta$	$\dots\dots\dots (B)$
Spiralfaser $\varphi \neq 90^\circ$ allgemeine Reflexe $\rho \neq 90^\circ$	$I \propto \left \frac{d\omega_1}{d\delta} \right + \left \frac{d\omega_2}{d\delta} \right $ $\frac{d\omega_1, \omega_2}{d\delta} = \frac{\cos \theta \{ \sin \delta (\cos \varphi - \cos \theta \cos \delta \cos \varphi) \pm \sin \theta \sin \delta \sqrt{C} \}}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{C}}$ $\frac{d\omega_1, \omega_2}{d\delta} = \frac{\cos \theta \{ \sin \delta \cos \varphi \pm \sin \theta \cos \delta \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta} \}}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}}$	$I \propto \frac{\sin \rho}{\sqrt{\sin^2 \varphi - \cos^2 \rho - \cos^2 \theta \cos^2 \delta + 2 \cos \theta \cos \rho \cos \varphi \cos \delta}} = \frac{\sin \rho}{\sqrt{C}}$ (N_{φ} und $\sin \varphi$ sind Konstant)	
Äquator $\rho = 90^\circ$	$\frac{d\omega_1, \omega_2}{d\delta} = \frac{\cos \theta \{ \sin \delta \cos \varphi \pm \sin \theta \cos \delta \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta} \}}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}}$	$I \propto \frac{1}{\sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}}$	
Ringfaser $\varphi = 90^\circ$ allgemeine Reflexe $\rho \neq 90^\circ$	$\frac{d\omega_1, \omega_2}{d\delta} = \frac{\cos \theta \{ \sin \delta \cos \varphi \pm \sin \theta \cos \delta \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta} \}}{\pm (1 - \cos^2 \theta \cos^2 \delta) \sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}}$	$I \propto \frac{\sin \rho}{\sqrt{\sin^2 \varphi - \cos^2 \theta \cos^2 \delta}}$	
Äquator $\rho = 90^\circ$	$\frac{d\omega_1, \omega_2}{d\delta} = \frac{\sin \theta \cos \theta \cos \delta}{1 - \cos^2 \theta \cos^2 \delta}$	$I \propto \frac{1}{\sqrt{1 - \cos^2 \theta \cos^2 \delta}}$	

Tabelle 2.

			$ \rho - \varphi \geq 0$				$ \rho - \varphi < 0$			
			Maximum		Minimum		Maximum		Minimum	
			Richtungs- winkel, δ	Inten- sität	Richtungs- winkel,	Intensität	Richtungs- winkel, δ	Intensity	Richtungs- winkel, δ	Intensität
$\varphi \neq 90^\circ$ Spiral Faser	$\rho \neq 90^\circ$ all- gemeine Reflexe	B	$\cos^{-1} \left\{ \frac{\cos(\rho - \varphi)}{\cos \theta} \right\}$	∞	$\cos^{-1} \left\{ \frac{\cos \rho \cos \varphi}{\cos \theta} \right\}$	$\frac{1}{\sin \varphi}$	0°	$\frac{\sin \rho}{\sqrt{C}}$	$\cos^{-1} \left\{ \frac{\cos \rho \cos \varphi}{\cos \theta} \right\}$	$\frac{1}{\sin \varphi}$
		A	„	„	?	?	„	$2 \cot \theta$	?	?
	$\rho = 90^\circ$ Äquator	B	$\cos^{-1} \left(\frac{\cos \varphi}{\cos \theta} \right)$	∞	90°	$\frac{1}{\sin \varphi}$	0°	$\frac{1}{\sqrt{\sin^2 \varphi - \cos^2 \theta}}$	90°	$\frac{1}{\sin \varphi}$
		A	„	„	„	$\frac{2 \cos \varphi \cos \theta}{\sin \varphi}$	„	$2 \cot \theta$	„	$\frac{2 \cos \varphi \cos \theta}{\sin \varphi}$
$\varphi = 90^\circ$ Ring Faser	$\rho \neq 90^\circ$ all- gemeine Reflexe	B	$\cos^{-1} \left(\frac{\sin \rho}{\cos \theta} \right)$	∞	90°	1	0°	$\frac{\sin \rho}{\sqrt{\sin^2 \rho - \cos^2 \theta}}$	90°	1
		A	„	„	„	0	„	$2 \cot \theta$	„	0
	$\varphi = 90^\circ$ Äquator	B					0°	$\frac{1}{\sin \theta}$	90°	1
		A					„	$2 \cot \theta$	„	0

Wert beanspruchen, weil erstens die Ramiefaser keine ideale Faserstruktur besitzen kann und zweitens die Form der Kurve in der Nähe des Minimum-Punktes ziemlich flach und daher für einen einwandfreien Vergleich nicht günstig ist. Es mussten daher weitere Prüfungen mit einem geeigneten Einkristall gemacht werden. Nachdem ein solcher im Pentaerythrit gefunden worden war, wurden damit Doppeldreh-Kristall-Aufnahmen (101), $\varphi=53^\circ$ gemacht.

Die hierbei experimentell erhaltene Kurve (Fig. 17) bestätigt die nach der Formel B errechnete Kurve. Die nach Formel A und B errechneten Kurven sind in Fig. 18 dargestellt.

Es ist natürlich klar, dass die mit einem solchen Einkristall erhaltenen Resultate sicherer sind als die unter Verwendung von Ramiefaser erhalte-

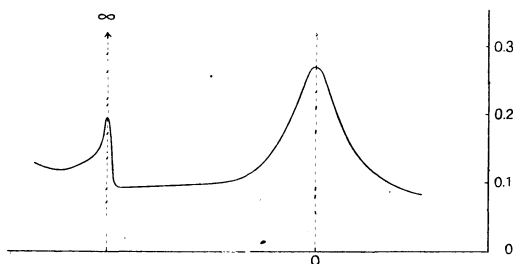


Fig. 17.

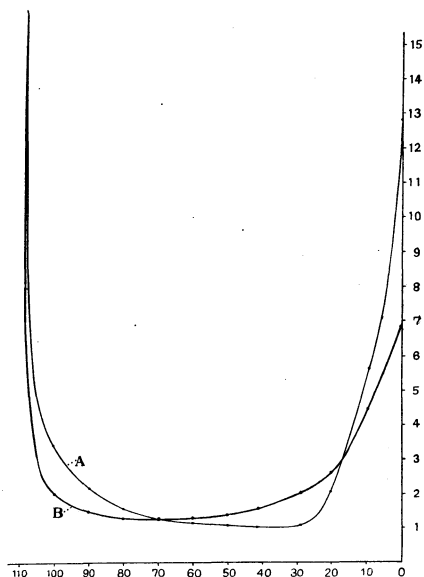


Fig. 18.

nen, aber da man auch hier die sich aus der Flachheit der Kurve in der Nähe des Minimum-Punktes ergebende Unsicherheit berücksichtigen muss, so erscheint es angebracht, noch weitere Experimental-Ergebnisse abzuwarten, bevor eine endgültige Entscheidung für eine der beiden Formeln gefällt werden kann.

Man könnte für die weitere Prüfung die sich nach den beiden Formeln ergebenden Unterschiede für die Minimum-Werte der Intensitäten benutzen, und zwar am bequemsten im Falle der Ringfaserstruktur, wobei nach A der Wert $=0$, nach B $=1$ wird.

Leider kann man aber wegen der sich aus der Konstruktionsart der Doppeldreh-Kristall-Kamera sich ergebenden Aufnahmeschwierigkeit den Fall der Ringfaserstruktur nicht vollständig unter Benutzung des Einkristalls aufnehmen. Dagegen kann die Aufnahme mit einem aus Ramiefaser hergestellten Papier durchgeführt werden. Allerdings stösst man hierbei wieder auf die schon früher hervorgetretene Unsicherheit, die sich aus der Realfaserstruktur der Ramiefaser an Stelle der Idealfaserstruktur ergibt.

Man kann allerdings versuchen, die Ergebnisse unter Berücksichtigung einer bestimmten Verstreuung zu korrigieren. Vergleicht man die experimentell erhaltene Kurve mit der unter Annahme einer Verstreuung

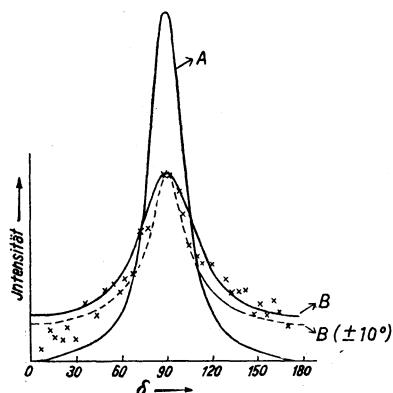


Fig. 19.

von $\pm 10^\circ$ errechneten*⁽¹⁰⁾, so zeigt sich, dass sie auch in diesem Falle eine gute Uebereinstimmung mit der nach Formel B erhaltenen Kurve zeigt. (Fig. 19).

Zusammenfassung.

Die Benutzung der diatropen Reflexe zur Bestimmung der Kristallitverteilung in der Faser bietet den Vorteil, dass man direkt ohne mathematische Ausrechnung die Kristallitverteilung bestimmen kann. Es wurde erstens die Schiefaufnahme zur Bestimmung der Kristallitverteilung aus

den diatropen Reflexen herangezogen, und zweitens wurde eine neue Schwenkkamera mit sich bewegendem Film konstruiert. Unter Benutzung dieser Kamera wurden weitere Versuche zur Direktbestimmung der Kristallitverteilung durchgeführt, und schliesslich wurden dann noch die Anwendungsmöglichkeiten der diatropen Reflexe näher diskutiert.

Die Benutzung der allgemeinen Reflexe bei dem Indirekt-Bestimmungs-Verfahren erfordert eine mathematische Ausrechnung, welche bisher von verschiedenen Autoren nach verschiedenen Ableitungsprinzipien versucht worden ist. Diese Ableitungsprinzipien wurden zusammengestellt und verglichen, und die Richtigkeit der sich aus ihnen ergebenden Werte durch Vergleich mit experimentell erhaltenen Resultaten weiter zu prüfen versucht. Hierbei ergab es sich, dass die bisher vorliegenden Ergebnisse mit der aus der Formel B errechneten Kurve besser übereinstimmen als mit der aus der Formel A errechneten, sodass der Formel B welche nach den Ableitungsprinzipien von O. Kratky und C. Matano abgeleitet wurde, die grössere Wahrscheinlichkeit zuzuschreiben ist.

*Institut für Faserforschung,
Kaiserliche Universität zu Osaka.*

* Die Rechnung für diesen Fall hat O. Kratky neulich ausgeführt und mir freundlicherweise zugeschickt, wofür ich ihm auch an dieser Stelle meinen herzlichen Dank aussprechen möchte.

(10) O. Kratky, *Österreich. Chem.-Z.* 8 (1939), 1.

Studies on the Organic Molecular Compounds. Part III. On the Molecular Compound-Formation of Aromatic Hydrocarbons with Nitro-Compounds and with Antimony Trihalides.

By Chiro SHINOMIYA.

(Received May 20, 1940.)

It has been shown by a number of investigators that many condensed or non-condensed aromatic ring compounds, such as naphthalene, phenanthrene, anthracene, durene, hexamethylbenzene, diphenyl, dibenzyl, tolane, etc., form addition compounds with nitro compounds and similar substances. The writer has discussed this matter in connexion with compound-formation and halochromism in previous papers.⁽¹⁾

I. Binary Systems of Condensed Ring Substances. All the aromatic hydrocarbons mentioned here either have been proved or are considered to have the construction, as a whole, of a plane ring molecule, and may be seen to form similar binary phase diagrams with a nitro component. It may therefore be concluded that, in these binary systems, compound-formation is due to the affinity between the unsaturated carbon linkings and the nitro radicals. In the solid crystalline state, however, another condition may be necessary, namely, the formation of a crystal lattice of the addition compound, a condition that is disregarded in the liquid or gaseous state. Consequently, organic molecular compound-formation in the crystalline state is greatly affected by the structure of the component, particularly, the shape of the molecule. All the systems studied showed distinct halochromism when fused, pointing to the presence of molecular compounds in the liquid state, of which, however, only half the number gave crystalline compounds. The result is given in Table 1.

(1) The compound ratio was 1:1, except in the following cases:⁽²⁾

- 3 : 1 phenanthrene—*p*-dinitrobenzene;
- 2 : 1 naphthalene—styphnic acid, benzene—trinitrobenzene, benzene—picryl chloride;
- 3 : 2 naphthalene—tetranitrobenzene, acenaphthene—picramide;
- 2 : 3 pyrene—styphnic acid, fluorene—trinitrobenzene;
- 1 : 2 fluorene—tetranitrobenzene;
- 2 : 3 & 1 : 1 phenanthrene—tetranitrobenzene;
- 1 : 1 & 1 : 2 pyrene—*m*-dinitrobenzene.

(2) The order of compound-formation of nitro compounds with these hydrocarbons was almost the same as that was shown in the previous paper.⁽¹⁾

(1) This Bulletin, 15 (1940), 92, 137.

(2) As to the metastable compound, a more detailed report will be published at a not distant date.

Table' 1.

A:B (Melting point) Black areas: Value of Shaded areas: Value of B (Melting point)	 {80.0}	 {150.0}	 {109.5}	 {96.0}	 {100.5}	 {5.5}*	 {116.0}	 {217}	 {251}
Trinitrobenzene {123.0}	1:1 {152.5}*	1:1* {59.5}	1:1 {205.0}	1:1 {168}	1:1 {198}	2:1 {77}* or 1:1*	2:3 {105.0}	1:1 {165}	1:1 {186}
Picric acid {122.0}	1:1 {191.5}	1:1 {218}	1:1 {183}	1:1 {160.5}	1:1 {145}	1:1 U*	1:1 {84.5}	1:1 U*	1:1* U
Tetranitrobenzene {126.0}	3:2 {139.5}	1:1 {162.5}	1:1 {134.0}	1:1 {110.5}	2:3 {139.0} 1:1 U (1:2)	—	1:2 {130.0}	1:1 {77.0}	1:1 U ? Decomposed
Picramide {188.5}	1:1 {165}	1:1 {236.0}	1:1 {191.5}	3:2 {97.0} or 1:1*	1:1* {166.0}	1:1*	1:1 U*	1:1* {163.5}	1:1 U
Trinitroresol {108.5}	1:1 {126.0}	1:1 {165.0}	1:1 {144.0}	1:1 {117.5}	1:1 {113.0}	—	1:1 {107.2}	Decomposed*	1:1 U
Styphnic acid {182.0}	2:1 {146.0} or 1:1*	2:3 {150.0} or 1:1	1:1 {78.5} or 2:3	1:1 {154}	1:1 {120}	—	1:1 U*	or 1:1*	V
Trinitrotoluene {81.5}	1:1 {98}	1:1 {164.5}	1:1 {133.0}	1:1 {109.0}	1:1 {94}	—	1:1 {85}	V*	V
Picryl chloride {83.0}	1:1 {92}	1:1 {184.0}	1:1 {120.0}	1:1 {113.2}	1:1 {98}	2:1 {39}* or 1:1*	1:1 {64.0}	1:1 {141.0}	V
2,4-Dinitrophenol {113.5}	1:1 {92.5}	1:1 {146.5}	1:1 {92.0}	1:1 {86.0}	V*	—	V*	V*	V
2,4-Dinitrotoluene {71.0}	1:1 {61}	1:1 {92.5}	1:1 {75.5}	1:1 {61}* or V*	V*	V*	V*	V*	V
Trinitroanisol {68.0}	V or {1154.0}	1:1 {104.5}	1:1 {75.0}	V	V	—	V	V	V
p-Dinitrobenzene {173.5}	1:1 {119.0}	1:1 U	V	V*	3:1 {81}	V*	V*	V*	V
m-Dinitrobenzene {90.0}	1:1 {50.5} D*	1:1 {82.0} 1:2 {91.5}	1:1 {77.0}	1:1 {72.5}	V*	V*	V*	V*	V
o-Dinitrobenzene {117.0}	V*	V	V	V*	V*	V*	V*	V*	V
2,6-Dinitrotoluene {65.0}	V*	V	V	V*	V*	V*	V*	V*	V
3,4-Dinitrotoluene {59.0}	V*	V	V	V*	V*	V*	V*	V*	V
p-Nitrophenol {113.0}	V*	V	V	V*	V	—	V	V*	V
m-Nitrophenol {96.5}	V	V	V	V*	V	—	V	V or 1:1*	V
o-Nitrophenol {45.0}	V*	V	V	V*	V	—	V	V*	V

× The data from literature.

A : B (Melting point) shows the value of the crystal from solution.

- (3) The hydrocarbon sequence was usually naphthalene, pyrene, fluoranthene > acenaphthene > phenanthrene, benzene > fluorene > anthracene, chrysene.

Certain irregularity was found in the molecular compounds of tetranitrobenzene and styphnic acid.

- (4) Halochromic phenomenon was seen in the following order, pyrene, acenaphthene, anthracene > phenanthrene, fluorene > chrysene > fluoranthene > naphthalene > benzene.

(5) It is interesting to note that the molecular compound of dissociation type and incongruent type in this Table, lay between the simple eutectic system and the lowest "melting point elevation" system of the congruent type.

II. Binary Systems of Non-Condensed Ring Substances. The tendency to form molecular compounds of methyderivatives of benzene seemed to become very marked according as the increase of the number of substituents, while their compounds ratios were not simple, showing sometimes a phase diagram of "partially miscible type." In the case of certain compounds having two aromatic rings separated, as each of the separated ring can unite with one molecule of the nitro component, one molecule combine with two molecules of the nitro components.⁽³⁾ Since in these cases, the shape of the component molecules greatly affects the compound-formation, it is not possible to discuss the matter merely on the basis of the plane formula commonly used in the organic chemistry.

Table 2.

	Mesitylene	Prehnitene	Durene	Pentamethylbenzene	Hexamethylbenzene
Trinitrobenzene	—	—	2:1 [101.0°] PM 1:1 (U)*	3:2 [121.0°] PM (1:1)	1:1 (175°)*
Picric acid	m:n*	1:1 (U)*	∇ [E: 64.5°]	3:2 [124.0°] PM or 1:1 (131°)*	1:1 (170°)*

	Diphenyl	p, p'-Ditoluyl	Dibenzyl	Stilbene	Tolane
Trinitrobenzene	1:1 [U]*	1:1 [D: 91.0°]	1:2 (102°)*	1:2* [121.5°]	1:2 (96°)*
Picric acid	∇*	∇ [E: 93.0°]	∇*	1:1 [U: 93.0°]	1:2 (111°)*

	Diphenylmethane	Triphenylmethane	Diphenylamine	Azobenzene	p-Aminoazobenzene
Trinitrobenzene	—	PM	1:2 (100.0°)	1:2 (132°)*	1:2 [158°]
Picric acid	∇*	PM*	1:2 [U: 70.0°] or 1:1 [U]*	∇*	Decomposed

* Data from literature.

D: Dissociation type.

U: Incongruent type.

PM: Partially miscible type, the molecular compound of which separates two non-miscible liquids at melting point.

∇: Simple eutectic type whose eutectic point is E.

() Melting points in parentheses represent those of crystals obtained from solution.

III. Molecular Compounds of Antimony Trihalides. The relationships just described were found to hold true of the organic-inorganic molecular compounds of Menshutkin,⁽⁴⁾ some of which, with the writer's

(3) J. J. Sudborough, *J. Chem., Soc.*, **109** (1916), 1339.

(4) B. Menshutkin, *Chem. Zentr.* **1910**, II, 378; **1911**, II, 751; **1912**, I, 408; II, 1436; **1913**, I, 804.

Table 3.

A : B (τ) A \ B	B	SbCl ₃	SbBr ₃	A : B (τ) A \ B	B	SbCl ₃	SbBr ₃
C ₆ H ₃ (CH ₃) ₃ 1, 3, 5	{1:2 (45.0) 1:1 U	{1:2 (25.0) 1:1 U		C ₆ H ₅ OH	1:2 (-25.3)	1:2 U	
C ₆ H ₆ *	1:2 (28.5)	1: (28.0)		C ₆ H ₅ OCH ₃	{1:2 (4.4) 1:1 U	1:1 (0.5)	
C ₆ H ₃ (CH ₃) ₃ 1, 2, 4	{1:2 (26.5) 1:1 U or [1:1 (-15.6)]	{1:2 U 1:1 U [1:2 (-17.5)]		C ₆ H ₅ OC ₂ H ₅	1:1 (19.9)	1:1 (16.0)	
C ₆ H ₅ CH ₃	{1:2 (25.5) 1:1 U	{1:2 U 1:1 U		C ₆ H ₅ COH	1:1 (14.0)	1:1 (1.5)	
C ₆ H ₄ (CH ₃) ₂ 1, 4	1:2 (16.9) or 1:1 U	1:2 (0.4)		C ₆ H ₅ COCH ₃	1:1 (1.0) or ∇	1:1 (-19.5)	
C ₆ H ₅ C ₂ H ₅	{1:2 (19.3) 1:1 (49)	1:1 U		C ₆ H ₄ ·CH ₃ ·NO ₂ 1, 2	1:1 (2.5)	1:1 U	
C ₆ H ₄ (CH ₃) ₂ 1, 3	{1:2 (8.3) 1:1 U or [1:1 (0)]	1:1 U		C ₆ H ₅ CN	[1:1 (-8.5)]	[1:1 (-2.5)]	
C ₆ H ₄ (CH ₃) ₂ 1, 2	{1:2 (-5.2) 1:1 (-3.2)	1:1 (-8.5)		C ₆ H ₄ ·CH ₃ ·Cl 1, 2	1:1 (-15.4)	∇	
CH ₃ ·C ₆ H ₄ ·CH(CH ₃) ₃ 1, 4	{1:2 U 1:1 U	1:1 U or [1:1 (0.5)]		C ₆ H ₄ ·CH ₃ ·NO ₂ 1, 2	Viscous, glassy	∇	
C ₆ H ₅ (CH ₂) ₂ CH ₃	1:2 U or 1:1 (-13.3)	1:1 U		C ₆ H ₅ NO ₂	[1:1 (-45.5)D] or ∇	∇	
				C ₆ H ₄ ·CH ₃ ·NO ₂ 1, 4	[1:1 (-55.0)]	∇	
				C ₆ H ₄ (NO ₂) ₂ 1, 3	∇ or [1:1 U]	∇	
				C ₆ H ₅ F, C ₆ H ₅ Cl, } C ₆ H ₅ Br	1:1 U	∇	
				C ₆ H ₅ I	[1:1 U] or ∇	∇	
				C ₆ H ₄ ·CH ₃ ·Cl 1, 3	[1:1 U]	∇	
				C ₆ H ₄ ·CH ₃ ·Cl 1, 4, C ₆ H ₄ Cl ₂ 1, 4, C ₆ H ₄ Br ₂ 1, 4, C ₆ H ₅ CO ₂ H, C ₆ H ₅ COCl, C ₆ H ₅ SO ₃ H	∇	∇	

A : B (τ) A \ B	B	SbCl ₃	SbBr ₃
C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅	{1:4 (8.7) 1:2 U	1:4 (1.9)	
C ₆ H ₅ NNC ₆ H ₅	1:4 (8.7)	1:4 U	
(C ₆ H ₅) ₂ CH ₂	1:2 (42.3)	1:2 (18.3)	
C ₆ H ₅ CHCHC ₆ H ₅	1:2 (7.3)	1:2 Viscous	
C ₆ H ₅ C ₆ H ₅	1:2 (-1.2)	1:2 U	
(C ₆ H ₅) ₃ CH	1:1 U	∇	

* In the writer's experiment pentamethylbenzene and durene gave superior compound-formation, their τ are almost 85 and 31 in type 1:2. Methylation of the benzene nucleus seems to increase compound-formation, while that of the side chain reverses the result.

additional data, are given in Table 3. Like a nitro compound, antimony trichloride or tribromide gives a combination of a type similar to an aromatic ring. By an arrangement of the antimony trihalide molecular compounds in the order of "melting point elevation", compound-formation was clearly shown to be closely related to the configuration of the aromatic compound. These systems were proved from the diagram to have usually two sets of compounds. Of these two compounds the less stable one (ratio 1:2) was obtained only when the aromatic component exhibited a superior compound-formation. It was moreover found that antimony chloride was more strongly additive than the bromide, and that compound-formation of the benzene derivatives decreased when atoms of halogen or of negative groups having properties similar to the halogens were introduced into the benzene nucleus. Certain regularity was also found in Table 3, between compound-formation and the substitution of benzene nucleus.

Experimental.

I. *Binary Systems of Pyrene and of Fluoranthene.* Pyrene and fluoranthene exhibited compound-formations that closely resemble each other, the former slightly more marked than the latter. See Figs. 1, 2 for diagrams.

(1) Pyrene—2,4,6-trinitrobenzene.

Pyrene: 9.0 mg.								
Mol% pyrene	100.0	84.0	55.3	48.6	37.3	26.0	17.2	
Melting point	150.0	193.5	244.0	245.5	241.5	227.0	204.0	
Thawing point	149.0	141.2	210.0	244.5	165.0	106.0	105.0	

Pyrene: 20.0 mg.								
Mol% pyrene	95.5	87.5	77.8	67.9				
Melting point	148.0	166.0	209.3	235.5				
Thawing point	142.0	141.6	142.0	146.0				

Trinitrobenzene: 20.0 mg.								
Mol% trinitrobenzene	95.0	82.6						
Melting point	147.0	205.0						
Thawing point	116.0	116.0						

Eutectic point: 141.5°, 116.0° (metastable: 105.5°); 90.0 mol%, 2.0 mol% pyrene.

Compound (1:1): reddish orange prisms, melting at 245.5°. Sublimable by heating.

(2) Fluoranthene—2,4,6-trinitrobenzene.

Trinitrobenzene: 9.8 mg.								
Mol% trinitrobenzene	73.8	58.1	46.9	30.1	16.1			
Melting point	188.5	203.0	204.0	—	124.5			
Thawing point	103.0	117.0	149.0	98.0	97.0			

Fluoranthene 4.3 mg.								
Mol% fluoranthene	100.0	95.1	71.7	62.4	51.1	28.6	17.2	10.7
Melting point	109.5	106.0	183.0	200.0	204.5	188.3	164.5	139.8
Thawing point	108.5	98.0	99.0	99.0	202.0	103.0	103.0	103.0

Eutectic point: 98.5°, 103.0°; 86.8 mol%, 4.0 mol% fluoranthene.

Compound (1:1): bright yellow prisms or needles, melting at 205.0°. Difficultly sublimable. Light voluminous crystals were obtained from the alcoholic solution.

Pyrene and fluoranthene gave the most stable compounds with trinitrobenzene. When fused they scarcely dissociated; by further heating, the molecular compounds sublimed without decomposing.

(3) Pyrene—picramide.

Pyrene: 9.4 mg.

Mol% pyrene	94.7	88.2	65.4	52.0	50.3	38.6	26.9	16.6
Melting point	145.0	174.0	228.5	235.5	236.0	231.0	213.5	195.5
Thawing point	138.0	141.0	139.5	231.0	225.0	181.0	180.5	180.5

Pyrene: 17.0 mg.

Mol% pyrene	91.5	81.4	73.8	62.3
Melting point	169.0	199.0	213.0	232.3
Thawing point	139.0	139.5	139.0	—

Eutectic point: 139.5°, 180.5°; 92.0 mol%, 12.2 mol% picramide.

Compound (1:1): brown prisms or plates, melting at 236.0°. Stable, difficultly sublimable.

(4) Fluoranthene—picramide.

Picramide: 8.2 mg.

Mol% picramide	77.7	51.5	38.4	26.2	15.8
Melting point	171.5	191.0	187.5	168.0	141.0
Thawing point	166.0	186.0	138.0	—	102.0

Total fluoranthene: 12.6 mg.

Mol% fluoranthene	90.1	94.7	64.8	51.8	35.2
Melting point	117.5	105.0	186.0	191.0	180.5
Thawing point	101.0	102.0	107.0	184.0	166.0

Eutectic point: 102.0°, 166.0°; 92.8 mol%, 26.7 mol% fluoranthene.

Compound (1:1): fine brownish yellow needles or powder, melting at 191.5°. Stable, difficultly sublimable.

(5) Pyrene—trinitroresol.

Trinitroresol: 5.6 mg.

Mol% trinitroresol	69.9	57.8	44.9	29.0
Melting point	153.5	161.0	161.0	152.0
Thawing point	83.0	144.0	151.0	135.0

Pyrene: 7.3 mg.

Mol% pyrene	89.1	76.5	47.1	24.6	15.3
Melting point	140.0	148.0	163.0	147.0	132.5
Thawing point	135.0	134.5	158.0	100.0	102.0
				(80.0)	(82.0)

Eutectic point: 135.0°, 101.0°; 84.8 mol%, 7.5 mol% pyrene.

Compound (1:1): reddish brown powder, melting at 163.0°.

(6) Fluoranthene—trinitroresol.

Trinitroresol 11.8 mg.

Mol% trinitroresol	89.0	67.7	48.3	36.4
Melting point	110.0	139.0	144.0	139.0
Thawing point	101.0	101.0	140.0	—

Fluoranthene: 19.6 mg.

Mol% fluoranthene	96.2	88.3	86.2	78.6	56.8	43.1	38.9
Melting point	107.8	105.0	112.0	126.5	143.0	143.0	—
Thawing point	100.8	101.0	101.0	101.0	105.0	126.0	1018

Eutectic point: 110.0°, 110.0°; 89.0 mol%, 8.2 mol% fluoranthene.

Compound (1:1) yellow needles, melting at 144.0°.

Trinitroresol gave the widest existence range (*w*).

(7) Pyrene—2,4,6-trinitrotoluene.

Pyrene: 9.1 mg.

Mol% pyrene	97.1	84.4	76.1	68.5	56.9	51.8	45.0	33.0	21.0
Melting point	148.0	132.0	142.5	154.0	163.5	164.5	163.0	153.5	135.5
Thawing point	127.0	126.0	126.0	126.0	128.0	158.0	98.0	75.0	75.0

Trinitrotoluene: 30.0 mg.

Mol% trinitrotoluene	94.4	89.0	83.5	74.1
Melting point	81.0	102.0	127.0	144.0
Thawing point	74.0	75.0	76.0	—

Eutectic point: 126.0°, 75.0°; 81.2 mol%, 4.8 mol% trinitrotoluene.

Compound (1:1): orange plates or prisms, melting at 164.5°.

(8) Fluoranthene—2,4,6-trinitrotoluene.

Trinitrotoluene 5.7 mg.

Mol% trinitrotoluene	63.9	44.3	28.5
Melting point	126.0	131.5	113.0
Thawing point	70.0	92.0	89.0

Fluoranthene: 11.5 mg.

Mol% fluoranthene	86.2	78.8	73.7	56.4	43.3	29.2	20.8
Melting point	100.2	90.0	107.0	132.0	132.0	114.0	95.0
Thawing point	88.5	89.0	88.6	89.0	75.5	72.0	72.8

Eutectic point: 89.0°, 72.5°; 78.8 mol%, 15.0 mol% fluoranthene.

Compound (1:1): fine yellow needles or powder, melting at 133.0°.

(9) Pyrene—picryl chloride.

Picryl chloride: 9.1 mg.

Mol picryl chloride	70.0	57.0	42.6	30.1
Melting point	145.0	152.0	150.0	136.0
Thawing point	73.0	134.0	135.0	125.0

Pyrene: 4.9 mg.

Mol% pyrene	91.0	71.2	49.1	22.4	8.7
Melting point	143.8	134.5	153.5	128.5	79.0
Thawing point	126.0	125.5	152.5	73.0	74.0

Eutectic point: 125.0°, 73.5°; 77.0 mol%, 8.0 mol% pyrene.

Compound (1:1): brownish red prisms or powder, melting at 154.0°.

(10) Fluoranthene—picryl chloride.

Picryl chloride: 9.1 mg.

Mol% picryl chloride	82.7	63.6	46.0	33.0
Melting point	73.5	111.0	119.0	106.0
Thawing point	67.0	—	110.0	80.0

Fluoranthene: 8.1 mg.

Mol% fluoranthene	84.6	62.5	53.6	42.6	26.1
Melting point	98.0	112.0	119.0	117.0	97.0
Thawing point	80.0	80.0	106.0	73.0	67.0

Eutectic point: 80.0°, 67.0°; 73.8 mol%, 15.6 mol% fluoranthene.

Compound (1:1): orange yellow prisms or plates, melting at 120.0°.

(11) Pyrene—2,4-dinitrophenol.

Total dinitrophenol: 11.1 mg.

Mol% dinitrophenol	80.5	92.4	61.0	50.6	44.8	33.5
Melting point	113.0	109.0	143.0	146.5	145.0	134.5
Thawing point	101.0	101.0	101.5	143.0	125.0	120.0

Pyrene: 8.0 mg.

Mol% pyrene	92.3	82.0	54.4	47.0
Melting point	143.0	132.5	146.0	146.0
Thawing point	120.0	120.0	120.0	—

Eutectic point: 120.0°, 101.0°; 73.6 mol%, 15.6 mol% pyrene.

Compound (1:1): reddish orange prisms or plates, melting at 146.3°.

(12) Fluoranthene—2,4-dinitrophenol.

Fluoranthene: 16.6 mg.

Mol% fluoranthene	94.7	72.5	60.5	49.5	37.8
Melting point	105.0	83.0	88.0	91.0	87.0
Thawing point	85.5	75.0	74.5	86.0	84.0

Dinitrophenol: 8.4 mg.

Mol% dinitrophenol	87.4	79.0	69.5	60.0	49.1	30.3	27.6	15.5
Melting point	106.0	101.8	94.0	87.5	92.0	78.2	83.0	99.0
Thawing point	85.0	84.5	84.0	84.5	90.5	75.0	75.0	75.5

Eutectic point: 75.0°, 85.0°; 68.8 mol%, 38.8 mol% fluoranthene.

Compound (1:1): yellow prisms, melting at 92.0°.

(13) Pyrene—2,4-dinitrotoluene.

Pyrene: 5.2 mg.

Mol% pyrene	90.2	75.8	61.8	49.4	31.1	21.2
Melting point	142.5	124.5	106.5	92.5	82.0	64.0
Thawing point	90.0	89.0	89.0	89.0	57.5	57.5

Dinitrotoluene: 7.2 mg.

Mol% dinitrotoluene	73.0	55.1	48.1	41.7	35.9	24.2	17.7
Melting point	121.0	90.8	92.0	90.3	85.5	69.0	60.5
Thawing point	89.0	89.0	86.0	63.0	57.5	57.5	57.5

Eutectic point: 89.0°, 57.5°; 54.4 mol%, 19.7 mol% pyrene.

Compound (1:1): yellow prisms, melting at 92.5°.

(14) Fluoranthene—2,4-dinitrotoluene.

Fluoranthene: 14.8 mg.

Mol% fluoranthene	91.0	80.2	59.8	54.8	44.8	36.4	25.3
Melting point	102.5	90.0	74.0	75.5	73.5	69.5	61.0
Thawing point	68.0	68.0	67.8	68.0	60.0	57.0	57.0

Dinitrotoluene: 15.5 mg.

Mol% dinitrotoluene	94.1	85.3	77.0	69.5	54.3	22.1
Melting point	68.0	63.0	59.0	65.5	74.5	74.5
Thawing point	57.0	57.0	57.0	57.0	61.0	68.0

Eutectic point: 68.0°, 57.0°; 64.0 mol%, 22.4 mol% fluoranthene.

Compound (1:1): light yellow powder, melting at 75.5°.

(15) Pyrene—2,4,6-trinitroanisol.

Trinitroanisol: 7.0 mg.

Mol% trinitroanisol	79.6	66.0	53.2	34.6	22.2
Melting point	92.0	100.0	104.0	112.0	128.0
Thawing point	61.0	65.0	98.0	98.0	98.0

Pyrene: 5.8 mg.

Mol% pyrene	87.5	62.4	52.9	43.1	21.8	13.3
Melting point	140.5	104.5	104.5	103.0	92.5	83.0
Thawing point	99.0	98.5	98.0	87.0	—	60.5

Eutectic point: 98.5, 60.5; 60.5 mol%, 3.0 mol% pyrene.

Compound (1:1): yellowish orange prisms or plates, melting at 104.5°.

(16) Fluoranthene—2,4,6-trinitroanisol.

Total fluoranthene: 11.0 mg.

Mol% fluoranthene	87.3	72.0	46.3	66.2	54.6	35.3	24.5
Melting point	101.5	86.5	74.0	75.0	74.0	71.5	64.5
Thawing point	70.0	67.0	67.5	68.0	69.0	54.5	54.5

Trinitroanisol: 26.3 mg.

Mol% trinitroanisol	92.8	86.5	79.2	62.7	51.2
Melting point	65.0	61.5	59.0	72.8	75.0
Thawing point	55.0	55.0	55.5	55.0	70.0

Eutectic point: 68.5°, 55.0°; 63.0 mol%, 18.5 mol% fluoranthene.

Compound (1:1): light yellow leafy or powdery crystals, melting at 75.0°.

Trinitroanisol was crystallised with difficulty from the fused liquid without seeding.

(17) Pyrene—*p*-dinitrobenzene.

Total pyrene: 18.4 mg.

Mol% pyrene	93.4	74.0	66.0	59.8	54.0	46.4	56.5	58.7	60.5	64.0	65.1	66.8
Melting point	144.0	122.3	111.0	113.0	115.0	127.5	114.0	113.0	112.0	109.5	111.3	115.0
Thawing point	115.0	107.5	107.5	107.5	107.5	—	107.8	108.0	107.5	107.5	107.5	107.5

Dinitrobenzene: 4.0 mg					
Mol% dinitrobenzene	81.8	71.5	66.6	57.5	
Melting point	159.0	149.5	142.0	—	
Thawing point	115.5	114.5	114.0	114.0	
Dinitrobenzene: 3.0 mg.					
Mol% dinitrobenzene	62.2	55.4	48.4	41.9	28.4
Melting point	141.0	130.0	116.0	113.5	129.0
Thawing point	114.0	113.0	109.0	108.0	108.5
Eutectic point: 107.5°, 63.7 mol% pyrene.					
Pertectic point: 114.5°, 52.0 mol% pyrene.					
Compound (1:1): bright red needles with an incongruent melting point.					

(18) Fluoranthene—*p*-dinitrobenzene.

Fluoranthene: 9.6 mg.				
Mol% fluoranthene	94.4	83.4	59.4	43.2
Melting point	106.0	97.0	115.0	138.0
Thawing point	92.3	80.0	80.0	80.0
Total fluoranthene: 12.5 mg.				
Mol% fluoranthene	66.7	76.9	32.6	29.4
Melting point	97.0	90.0	—	153.0
Thawing point	80.0	81.5	80.5	80.5

Eutectic point: 80.0°, 70.1 mol% fluoranthene.

The solubility of *p*-dinitrobenzene in fluoranthene was rather small.(19) Pyrene—*m*-dinitrobenzene.

Total dinitrobenzene: 13.9 mg.										
Mol% dinitrobenzene	85.4	91.3	83.1	76.2	66.5	62.1	58.6	56.3	55.4	49.9
Melting point	81.0	85.0	84.0	87.0	89.3	89.0	90.5	91.5	91.8	92.5
Thawing point	79.0	79.0	79.0	79.0	88.0	88.0	88.0	88.0	90.0	91.0
(82.0)										
						47.6	44.9	43.0	39.1	27.7
						92.0	91.0	94.0	103.0	122.5
						89.0	89.0	88.0	89.0	89.0

Pyrene: 7.7 mg.

Mol% pyrene	65.9	57.1	50.4	29.8	21.0
Melting point	111.0	94.0	92.8	89.0	86.5
Thawing point	88.0	88.0	88.5	81.0	79.0

Eutectic point: 89.0°, 88.0°, 79.0°; 56.5 mol%, 36.6 mol%, 13.0 mol% pyrene.

Compound (1:1): orange yellow needles, melting at 92.7°.

Compound (1:2): bright yellow powder, melting at 89.3°.

(20) Fluoranthene—*m*-dinitrobenzene.

Fluoranthene: 8.4 mg.										
Mol% fluoranthene	57.0	47.8	39.9	34.5	26.0					
Melting point	76.0	76.5	76.0	74.0	69.0					
Thawing point	68.5	—	68.0	68.0	67.0					
Total dinitrobenzene: 22.6 mg.										
Mol% dinitrobenzene	87.9	78.4	63.3	75.2	73.0	69.0	56.8	50.2	38.5	30.7
Melting point	83.0	77.0	74.8	73.0	71.5	69.0	76.5	77.0	76.0	79.5
Thawing point	68.0	67.8	67.5	67.5	66.8	67.5	68.0	74.0	71.0	71.0

Eutectic point: 71.0°, 68.0°; 56.0 mol%, 29.0 mol% fluoranthene.

Compound (1:1): light yellow powder, melting at 77.0°.

II. Binary System of 1,2,4,6-Tetranitrobenzene. 1,2,4,6-Tetranitrobenzene showed somewhat irregular compound-formation with the hydrocarbons.

Systems of compound ratio 1:1:—

pyrene, fluoranthene, acenaphthene, anthracene (and chrycene).

Systems of compound ratio other than 1:1:—

naphthalene, phenanthrene, and fluorene.

The molecular compounds of the latter type seem to dissociate considerably on melting, giving a flat liquidus near the dystectic point in the diagram, Fig. 3.

(21) Pyrene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 9.7 mg.

Mol% tetranitrobenzene	90.4	66.1	50.3	40.6	25.1	16.2
Melting point	125.0	162.0	168.0	162.0	141.0	130.0
Thawing point	122.0	122.0	160.0	130.0	—	—

Pyrene: 7.9 mg.

Mol% pyrene	95.8	79.5	62.0	49.0	40.6	22.3
Melting point	147.0	127.0	158.0	168.0	166.5	—
Thawing point	126.0	125.5	125.5	161.0	—	122.0

Eutectic point: 125.0°, 122.0°; 81.0 mol%, 8.5 mol% pyrene.

Compound (1:1): dark red powder, melting at 168.5°. Stable.

(22) Fluoranthene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 11.0 mg.

Mol% tetranitrobenzene	83.6	68.0	52.2	36.0	20.2	12.7
Melting point	116.0	120.0	132.0	124.0	88.0	98.0
Thawing point	110.0	110.0	119.0	84.0	84.0	84.0

Tetranitrobenzene: 6.4 mg.

Mol% tetranitrobenzene	93.9	67.2	56.1	50.1	40.2	28.4	21.7	14.2
Melting point	123.0	120.0	132.0	134.0	130.0	110.0	97.0	94.0
Thawing point	111.0	110.0	110.0	129.0	84.0	84.0	84.0	83.7

Eutectic point: 84.0°, 110.0°; 80.1 mol%, 25.3 mol% fluoranthene.

Compound (1:1): brown powder, melting at 134.0°.

(23) Acenaphthene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 10.0 mg.

Mol% tetranitrobenzene	80.2	70.6	57.2	42.9	29.0	11.8	0.0
Melting point	115.0	109.0	108.5	108.0	99.0	75.0	96.0
Thawing point	102.0	103.0	101.8	78.0	75.0	87.0	95.0

Tetranitrobenzene: 3.4 mg.

Mol% tetranitrobenzene	47.0	23.5	9.9
Melting point	110.0	89.5	88.5
Thawing point	92.0	76.0	77.0

Eutectic point: 76.0°, 102.0°; 81.0 mol%, 35.8 mol% acenaphthene.

Compound (1:1): reddish brown prisms, melting at 110.5°.

(24) Anthracene—1,2,4,6-Tetranitrobenzene.

Tetranitrobenzene: 8.5 mg.

Mol% tetranitrobenzene	93.5	84.2	69.3	48.7	43.0	35.4	27.1
Melting point	125.0	145.0	163.0	171.0	168.5	176.0	189.0
Thawing point	121.0	—	119.0	162.0	162.0	162.0	162.0

Tetranitrobenzene: 5.5 mg.

Mol% tetranitrobenzene	60.4	44.7	30.1
Melting point	169.0	—	186.0
Thawing point	120.5	163.0	163.0

Eutectic point: 163.0°, 120.5°; 60.5 mol%, 5.8 mol% anthracene.

Compound (1:1): deep red prisms or needles, melting at 171.0°.

(25) Phenanthrene—1,2,4,6-tetranitrobenzene.

Tetranitrobenzene: 7.4 mg.

Mol% tetranitrobenzene	94.0	81.0	62.3	53.7	40.2	23.8	13.6	0.0
Melting point	—	121.0	125.0	123.0	118.0	99.0	87.0	100.5
Thawing point	115.0	115.0	121.0	115.0	83.0	78.0	79.0	100.0

Tetranitrobenzene: 5.1 mg.

Mol% tetranitrobenzene	92.1	81.5	72.0	54.9	41.3	32.0	20.7	11.4
Melting point	121.0	121.0	123.3	123.5	118.0	111.5	91.0	90.0
Thawing point	115.0	—	115.0	115.0	90.0	78.0	79.0	78.0

(117.0)

Tetranitrobenzene: 5.3 mg.

Mol% tetranitrobenzene	69.6	57.5	48.5	43.8
Melting point	123.5	124.5	122.5	120.5
	(125.5)			(118.5)
Thawing point	115.0	120.0	116.0	106.0
	(118.0)	(115.0)		

Eutectic point: 79.0°, 115.0°; 82.2 mol%, 12.0 mol%, phenanthrene.

Pertectic point: 115.0°, 61.5 mol% phenanthrene.

Compound (2:3): orange red needles, melting at 125.0°.

Compound (1:1): reddish orange needles with an incongruent melting point.

Under certain conditions of heating, the thawing and melting points were not uniform, another metastable combination (1:2) can thus be expected.

(26) Fluorene—1,2,4,6-tetranitrobenzene.

Total fluorene: 9.1 mg.

Mol% fluorene	100.0	76.9	55.0	39.4	35.1	27.5	45.7
Melting point	116.0	97.0	124.5	129.0	130.0	129.0	128.3
Thawing point	115.0	90.0	91.0	111.0	125.5	117.5	91.0

Tetranitrobenzene 8.7 mg.

Mol% tetranitrobenzene	90.3	82.4	67.4	60.2	27.2	17.0	8.6
Melting point	120.5	125.0	130.0	129.5	108.0	100.2	190.0
Thawing point	118.0	117.5	126.0	116.0	91.0	91.0	92.0

Eutectic point: 91.0°, 117.5°; 78.0 mol%, 12.0 mol% fluorene.

Compound (1:2): orange red prisms or needles, melting at 130.0°.

Summary.

As in the case of the nitro components discussed in Parts I and II, on the formation of crystalline molecular compounds, regularity was found also in the aromatic hydrocarbon components of condensed or non-condensed ring structure. The predominant tendency to compound-formation seems to be affected by the structure of both components, although it differs considerably from that in solutions. All the observed systems were almost halochromic when fused, about half the number of which gave crystalline compounds, some of which are shown in the phase diagrams. The effect of substituents of benzene ring in the binary systems containing antimony trihalides was also studied.

The writer wishes to express his sincere thanks to Prof. B. Kubota and to Prof. Y. Shibata of the Tokyo Imperial University for their kind guidance and encouragement throughout this study and to Dr. T. Asahina for much valuable advice. Thanks are also due to the Hattori-Hôkôkai for the grant, with the aid of which the expenses of the study were defrayed.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo
and
Kumamoto Higher Technical School.*

Über die unregelmässige Reihe der kolloiden Lösungen durch Elektrolyten. II. Untersuchung an Mastix-Sol.

Von Naoyasu SATA und Sigeru ITÔ

(Eingegangen am 1. Juni 1940.)

(1) **Einleitung.** Um den Mechanismus des Stabilisierens (Pep-tisierens) und Koagulierens der kolloiden Lösungen klar zu machen haben wir angefangen die sogenannte „unregelmässige Reihe“ bei der Koagulation eingehend systematisch zu untersuchen.

Einfachheitshalber wurde zuerst die unregelmässige Reihe von HgS-Sol durch AgNO_3 studiert.⁽¹⁾ Bekanntlich gibt es noch eine Reihe der kolloiden Lösungen, wie z.B. die Sole von Mastix, Pt, Au, u.s.w., welche auch unregelmässige Reihe durch Zusatz hochwertiger Elektrolyten wie Eisen- bzw. Aluminiumchlorid⁽²⁾ vor sich zeigen. Da diese Elektrolyten selbst schon die Tendenz haben, unter bestimmten Bedingungen, durch Hydrolyse, sich in kolloider Lösungen betreffender Oxyde zu verwandeln,⁽³⁾ lässt es sich vermuten, dass die unregelmässige Reihe in diesen Fällen nicht nur einfach als gegenseitige Wirkung zwischen kolloiden Teilchen und aktiven Ionen zu behandeln sei, sondern man müsste durch Hydrolyse entstandene Kolloidteilchen auch in Rücksicht nehmen. Gerade deswegen, wurden diese Gegenstände bis jetzt bei Seite gelassen. Mit der Fortschreitung der Untersuchung an HgS-Sole, ist aber uns allmählich erwünscht die unregelmässige Reihe dieser Art parallel zu untersuchen. Nachstehend wird der Versuch von der unregelmässigen Reihe des Mastix-Sols durch FeCl_3 berichtet.

(2) **Versuchsmaterial und Versuchsanordnung.** Der käufliche Mastix ist gelbbraunes halbdurchsichtiges Harz, welche in Körnern von 3–5 mm Durchmesser geliefert wird. Auf einer gewogenen Menge des Harzes fügt man absoluten Äthylalkohol zu. Es löst sich nicht vollkommen im Alkohol, sondern man erhält eine klare gelbe Lösung mit weisse klebrige kautschukartige Masse, welche ungelöst am Boden bleibt. Nach dem Filtrieren wird 200 ccm dieser alkoholischen Lösung im 1 Liter destillierten Wasser unter ständigem Umrühren dispergiert. So wird das Mastix-Sol dargestellt, welches, wie wohl bekannt, milchweiss undurchsichtig in Aussicht und orange-rot in Durchsicht ist. Das Eisenchlorid ist ein E. Mercksches Präparat " $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, kristallisiert, zur Analyse." Zum Koagulationsversuch haben wir 0.1, 0.01 und 0.001 Mol./Lit.-Lösungen benutzt, welche unmittelbar durch Wägung separat hergestellt sind. Das Wasser ist ein zweimal destilliertes Leitfähig-

(1) N. Sata u. Y. Niwase, *Kolloid-Z.*, **84** (1938), 314.

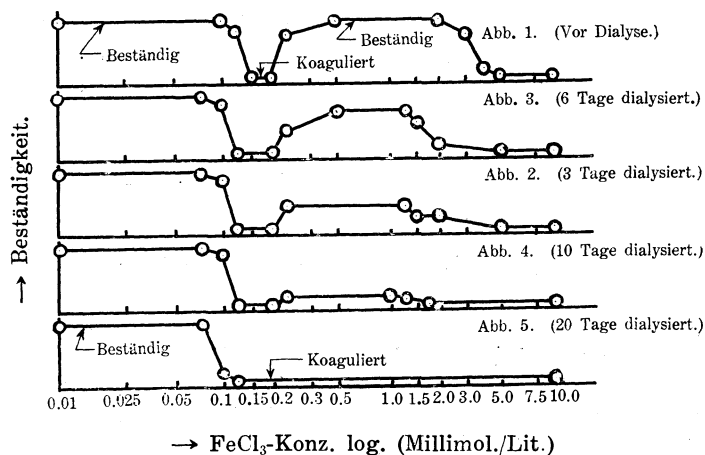
(2) H. Bechold, *Z. physik. Chem.*, **48** (1904), 418; H. Buxton u. P. Schaffer, *ibid.*, **57**, (1907) 59; H. Buxton u. O. Teagüe, *ibid.*, **57** (1907), 72; H. Mayanagi, *Kolloid-Z.*, **39** (1926), 319.

(3) H. Freundlich, *Kapillarchemie*, Bd. II (Leipzig, 1932) S. 270.

keitswasser⁽⁴⁾ und um die gelöste Gase auszutreiben wurde es vor dem Gebrauch nochmals ausgekocht. Trotzdem wird nur die 0.01 mol-Lösung durch Hydrolyse nach 2 Tagen schon trübe, während die 0.1 und 0.001 mol-Lösung immer unverändert bräunlich vollkommen klar blieben:

(3) **Beziehung zwischen unregelmässiger Reihe und Sol-Reinheit.** Die Koagulationsversuche wurden mit 5.0 ccm Sol und 5.0 ccm Salzlösungen verschiedener Konzentrationen ausgeführt.

Die nach oben erwähneter Weise hergestellte Mastix-Suspension ergibt schon ohne Reinigung die Koagulationskurve unregelmässiger Reihe. Da sie durch beigemengte Elektrolyten oder andere fremde Substanzen stark abhängig ist,⁽¹⁾ haben wir die Änderung der Koagulationskurve durch fortlaufende Reinigung durch Dialyse nachfolgt. Die Dialyse wurde gegen destilliertem Wasser mit Membran von Schweinblase ausgeführt. Während ersten einigen Tage ist das Cl-Ion in Aussenflüssigkeit deutlich nachweisbar. Die Versuchsergebnisse sind in Abb. 1–5 zusammengestellt. Die Abszisse ergibt die FeCl_3 -Konzentration in logarithmischem Mass und auf Ordinate wird die Sol-Beständigkeit übertragen.



Die Koagulationswerte (in Millimol/Lit.) des Sols mit Chloride verschiedener Kationen vor und nach der Dialyse sind in Tabelle 1 ersichtlich.

Tabelle 1.

	Sol- Konz. (gr./Lit.)	NaCl	CaCl_2	AlCl_3
Vor Dialyse	6.8	20	4	0.4
Nach Dialyse Von 22 Tage	6.2	125	10	0.4

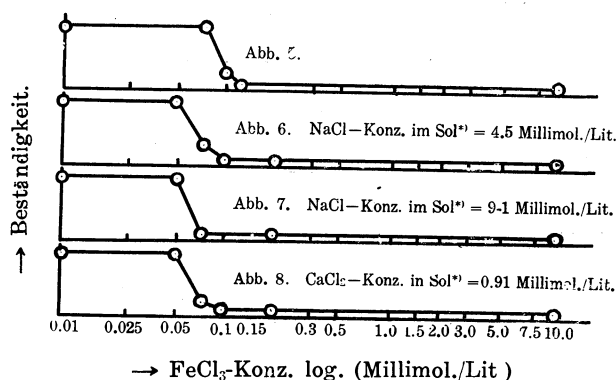
(4) N. Sata, *Kolloid-Z.*, **71** (1935), 49; R. Bourdillon, *J. Chem. Soc. London*, **1913**, 791.

Also die unregelmässige Reihe verschwindet sich durch die Dialyse von etwa 20 Tage und die Koagulationskurve geht zu einer gewöhnlichen Kurve mit einzigem Koagulationspunkt über. (Siehe Abb. 1 und 5).

Daraus könnte man schliessen, dass die unregelmässige Reihe in diesem Falle durch etwaige dialysierbare Substanz verursacht wird.

(4) **Über die Wirkung von Elektrolyten.** Wir haben eben gefunden, dass die unregelmässige Reihe von Mastix-Sol einfach durch Dialyse vernichtet wird. Als dialysierbare Substanzen kommen vorerst die anorganische Elektrolyten in Frage. Die Zunahme der Koagulationswerte nach der Dialyse (Tabelle 1) unterstützt auch die Tatsache, dass im Sol eine merkbare Menge der Elektrolyten vorhanden ist. Weil wir schon während der Dialyse, die Cl-Ionen nachgewiesen haben, wurde der Einfluss derselben auf die unregelmässige Reihe demnächst untersucht.

Zu diesem Zwecke, haben wir zu einem dialysierten Sol einige Fraktionen des Koagulationswertes entsprechende Menge der Chloride (d.h. die Sol-Beständigkeit nicht störende Menge) zugefügt und danach die unregelmässige Reihe mit FeCl_3 geprüft. Die erhaltene Koagulationskurven sind fast unverändert wie vor dem Salzzusatz d.h. das Vorhandensein der Chloride hilft nicht das Auftreten der unregelmässigen Reihe. Abb. 6, 7, und 8 ergeben die Resultate. Abb. 5 ist zum Vergleich nochmals angegeben.

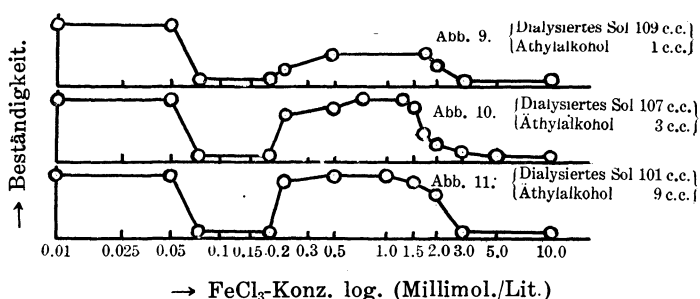


*) Die salzhaltige Sole sind folgendermassen hergestellt: Zuerst konzentriert man im H_2SO_4 -Exsikkator das dialysierte Sol bis auf Hälfte Volumens. 55 cc n dieses konzentrierten Sols wurde dann mit derselben Menge des Wassers bestimmter Salzkonzentration verdünnt.

(5) **Über den Einfluss des Lösungsmittels.** Oben ausgeführter Versuch zeigt uns, dass im Sol vorhandene Elektrolyten mit der unregelmässigen Reihe unmittelbar nicht zu tun haben. Die eingehende Überlegung lässt uns darauf erinnern, dass das hier zum Versuch angewandte Sol durch Wechseln des Lösungsmittels⁽⁵⁾ hergestellt ist und zwar das Dispersionsmittel nicht reines Wasser, sondern etwa 10% Äthylalkohol beigemischt ist. Dann müsste man überlegen, dass der Alkohol obwohl

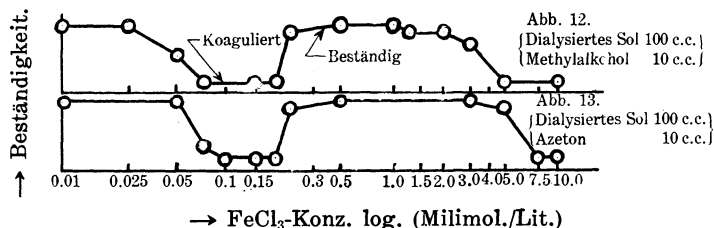
(5) P.P. von Weimarn, Die Allgemeinheit des Kolloidzustandes, S. 202 (Dresden und Leipzig, 1923); *Kolloid-Z.*, 8 (1911), 216.

er kein Elektrolyt ist, die Dialyse-Membran ohne Schwierigkeit durchgehen kann. So haben wir nun versucht die unregelmässige Reihe mit dialysiertem Sol, unter Zufügen verschiedener Menge von Äthylalkohol, zu prüfen. Wie aus den Abb. 9, 10 und 11 zu sehen ist, tritt die durch Dialyse verschwindete unregelmässige Reihe durch Zusatz des Alkohols wieder auf.



Jetzt ist es uns soweit klar, dass die der unregelmässigen Reihe verantwortliche dialysierbare Substanz in diesem Falle nicht ein Elektrolyt, sondern der Äthylalkohol ist.

(6) **Versuche mit anderen Lösungsmitteln.** Wie oben bestätigt, zur unregelmässigen Reihe des Mastix-Sols, der als Lösungsmittel benutzte Äthylalkohol spielt eine wichtige Rolle. Aber vom kolloidchemischen Standpunkt aus, hat der Alkohol dabei nur die Bedeutung als ein Lösungsmittel, welches das Mastix löst und mit Wasser leicht mischbar ist, und so die Kolloidsynthese durch Wechseln des Lösungsmittels erzieht. Dann ist es ohne weiteres interessant zu prüfen, ob andere Lösungsmittel, welche zur Herstellung des Mastix-Sols brauchbar sind, auch dasselbe Resultat ergeben würden. Nach dieser Ansicht, haben wir mit Alkoholverwandten Lösungsmitteln, namentlich Methylalkohol und Azeton den ähnlichen Versuch angestellt. Unter Anwendung dieser Lösungsmitteln erhält man gleicherweise die beständige Mastix-Sole, wie mit Äthylalkohol. Sie ergeben auch die unregelmässige Reihe, welche durch Dialyse verschwindet und durch Zufügen betreffendes Lösungsmittels wiederhergestellt wird. Die Ergebnisse sind in Abb. 12 und 13 veranschaulicht.



(7) **Schlussbemerkung.** Im Gegenteil zu HgS-Sol, bei welchem die unregelmässige Reihe unerwartet kompliziert vor sich läuft,⁽¹⁾ haben

wir mit Mastix-Sol gefunden, dass durch einfache Dialyse und wieder-maliges Zugeben des Lösungsmittels, die unregelmässige Reihe ziemlich einfach umkehrbar vernichtet und wiederhergestellt werden können. Daraus folgt, dass die unregelmässige Reihe hier nicht nur durch Adsorption hochwertiger Elektrolyten verursacht wird, sondern dass die Eigenschaften der Teilchenoberfläche, wo die Adsorption stattfindet, noch wichtigere Faktoren sind. Von seiner Herstellungsweise müsste das Mastix-Sol als eine Art „Emulsoides Kolloid“ angenommen werden und zwar die Teilchen nicht allein aus reiner Mastix bestehen, sondern eine kleine Menge des als Lösungsmittel benutzten Alkohol noch darin festgehalten wird. Dann ist dabei eine sehr komplizierte Verteilung von Alkohol zwischen Teilcheninnere, dessen Oberfläche, und Dispersionsmittel zu erwarten, und welche zur Untersuchung der unregelmässigen Reihe vor allem berücksichtigt werden müsste. Die Adsorption der zugefügten Elektrolyten usw. kommt erst danach in Frage.

Die Untersuchung wird in dieser Richtung, parallel mit dem Versuch an HgS-Sol fortgesetzt.

Zusammenfassung.

(1) Die unregelmässige Reihe von Mastix-Sol durch FeCl_3 wurde untersucht.

(2) Das Sol ergibt nicht mehr die unregelmässige Reihe, wenn man es durch Dialyse auf etwa 20 Tage reinigt.

(3) Sie wird nicht wiederhergestellt durch Zusatz der Elektrolyten, welche in Aussenflüssigkeit der Dialyse gefunden worden sind.

(4) Sie wird aber einfach wiederhergestellt durch Zufügen des als Lösungsmittel benutzten Äthylalkohol.

(5) Die Alkohol-verwandte Lösungsmittel, wie z.B. Methylalkohol und Azeton ergeben auch gleiches Resultat.

(6) Daraus wurde konstatiert, dass zur unregelmässigen Reihe nicht nur die aktive Elektrolyten, sondern die Oberflächeneigenschaften der Teilchen selbst auch eine wichtige Rolle spielen.

*Chemisches Institut der Kaiserlichen Universität zu
OSAKA und SIOMI-Institut für physikalische
und chemische Forschung.*

On the Theory of Diffusion, Viscosity, and Electrolytic Conduction.

By Seiji KANEKO.

(Received June 4, 1940.)

In this report, problems on diffusion, viscosity, electrolytic conduction are treated as examples of the theory of reaction velocity. The results obtained are of a rather qualitative nature and require further development.

1. Diffusion.⁽¹⁾⁽²⁾ The phenomena of diffusion and viscosity are very intimately connected with electrolytic conduction. In recent theory, particles in a liquid are always vibrating about an equilibrium position and occasionally jump from one place to another. This occurs when particles have sufficient energy to cross the potential barrier surrounding the vibrating particles. Let us first investigate the relation between the diffusion constant K , the number of jumps per unit time k_1 and the length of one jump λ .

According to Einstein's theory of diffusion⁽³⁾ the probability dP that the particle in the solution will move from the original place and lie between x and $x+dx$ after a time t is as follows:

$$dP = \left(\frac{1}{4\pi Kt} \right)^{\frac{1}{2}} e^{-\frac{x^2}{4Kt}} dx \quad (1).$$

When the above relation is extended to the case of three dimensions, the probability that the particle will lie between r and $r+dr$ is

$$dP = \left(\frac{1}{4\pi Kt} \right)^{\frac{3}{2}} e^{-\frac{r^2}{4Kt}} 4\pi r^2 dr \quad (2).$$

According to Rayleigh⁽⁴⁾, when N lines of length λ are connected at random, the probability that the last point will lie at a distance of r to $r+dr$ from the initial point is as follows:

$$dP = 3\sqrt{\frac{6}{\pi}} \frac{N^{-\frac{3}{2}}}{\lambda^3} e^{-r^2/\frac{2}{3}N\lambda^2} r^2 dr \quad (3).$$

Consequently, if we denote the length of one jump by λ and the number of jumps per unit time by k_1 , the probability that the particle will lie, after a time t , between r and $r+dr$ is

(1) S. Kaneko, *J. Chem. Soc. Japan*, **59** (1938), 673.

(2) S. Kaneko, *J. Chem. Soc. Japan*, **59** (1938), 1093.

(3) A. Einstein, *Ann. Physik.*, **17** (1905), 549.

(4) Lord Rayleigh, *Phil. Mag.*, **37** (1919), 321.

$$dP = 3\sqrt{\frac{6}{\pi}} \frac{(k_1 t)^{-\frac{3}{2}}}{\lambda^3} e^{-r^2/2 k_1 t} r^2 dr \quad (4).$$

Comparing (2) and (4) we have the following:

$$K = \frac{k_1 \lambda^2}{6} \quad (5).$$

The above relation has been obtained by Eyring,⁽⁵⁾ but since his verification is not rigorous, the factor 1/6 is missing.

The value k_1 may then be calculated. Eyring calculated this value as the reaction velocity constant. Here k_1 is calculated by Horiuti's theory⁽⁶⁾ of reaction velocity, and the result is somewhat different from Eyring's. Horiuti's general formula of reaction velocity is expressed by

$$k_1 = kT \frac{\int^S \cdots \int e^{-\frac{E^*}{kT}} dq_2 dq_3 \cdots dq_n dp_2 dp_3 \cdots dp_n}{\int^V \cdots \int e^{-\frac{E}{kT}} dq_1 dq_2 \cdots dq_n dp_1 dp_2 \cdots dp_n} \quad (6).$$

where k denotes Boltzmann's constant, T the absolute temperature, V the volume occupied by the initial system, S the surface of the transition state; $q_1, q_2, q_3, \dots$ are the coordinates of particles relating to position, and $p_1, p_2, p_3, \dots$ the coordinates relating to momentum. E the sum of the potential and kinetic energies of the particles, E^* the difference between the total energy E and the kinetic energy in the direction vertical to S . S in this case is a spherical surface of radius $\lambda/2$ surrounding the particle, and V is the so-called free volume per molecule v_f . Under this condition the integral of (6) becomes

$$k_1 = \sqrt{\frac{kT}{2\pi m}} \frac{\pi \lambda^2}{v_f} e^{-\frac{U^*}{kT}} \quad (7)$$

where m is the mass of the particle and U^* the activation energy. If the particle is vibrating according to Hooke's law we have the relation

$$v_f = \iiint_{-\infty}^{\infty} \exp \left\{ -\frac{f(x^2 + y^2 + z^2)}{2kT} \right\} dx dy dz = \left(\frac{2\pi kT}{f} \right)^{\frac{3}{2}} \quad (8)$$

where f is the force constant. Between f and the number of vibrations ν there is the following relation:

$$(2\pi\nu)^2 = \frac{f}{m} \quad (9).$$

Introducing (9) into (8) we have

(5) H. Eyring, *J. Chem. Phys.*, **4** (1936), 283.

(6) J. Horiuti, this Bulletin, **13** (1938), 210.

$$v_f = \left(\frac{kT}{2\pi\nu^2 m} \right)^{\frac{3}{2}} \quad (10)$$

2. **Viscosity.** By definition the viscosity of a liquid is given by

$$\eta = \frac{f\lambda_1}{\Delta v} \quad (11)$$

where η is the viscosity, f the force acting between the neighbouring molecular layers sliding over each other per unit area, Δv the difference of velocity between these layers, and λ_1 the distance between them. If we denote the mean distance of molecules in the sliding direction by λ_2 and the mean distance of molecules in the direction vertical to λ_1 , λ_2 , by λ_3 , then the force acting on a molecule from the neighbouring molecular layer is $f\lambda_2\lambda_3$. The value of Δv is therefore given by

$$\Delta v = f\lambda_2\lambda_3\omega \quad (12)$$

where ω is the reciprocal of the friction coefficient of the molecule in the liquid. According to Einstein's theory⁽³⁾ of diffusion there is the relation

$$K = \omega kT \quad (13)$$

between K and ω .

From (11), (12), (13) and (5), we have

$$\eta = \frac{6\lambda_1 kT}{\lambda^2 \lambda_2 \lambda_3 k_1} \quad (14)$$

The above relation has been obtained by Eyring⁽⁵⁾ from a somewhat different standpoint, but the numerical coefficient 6 is lacking. By substituting (7) into (14), the value of η can be calculated. Considering that the factor $\exp(-U^*/kT)$ varies greatly with temperature as compared to the other factors, η can be approximately expressed by the following equation.

$$\log \eta = A + \frac{B}{T} \quad (15)$$

where A and B are constants.

3. **Electrolytic Conduction.**⁽¹⁾⁽²⁾⁽⁷⁾⁽⁸⁾ Ordinarily, the ions in a liquid are vibrating incessantly and jump occasionally from one place to another as already described. Since the jumps of ions occur uniformly in all directions, there is no current in the solution. But when an electric field is applied, the number of jumps increases in the direction of the field and decreases in the opposite direction, thus giving rise to an electric current. If we denote the strength of the field by E , the charge

(7) S. Kaneko, *Bull. Electrotechn. Laboratory*, **2** (1938), 664.

(8) S. Kaneko, *Bull. Electrotechn. Laboratory*, **3** (1939), 99.

of an electron by ε , and the valency of the ions by z , then the activation energy is decreased in the direction θ by the amount

$$\frac{1}{2} \varepsilon z E \lambda \cos \theta$$

and the number of jumps increases in the following proportion:

$$\exp\left(\frac{1}{2} \varepsilon z E \lambda \cos \theta / kT\right).$$

Thus in a unit volume the number of jumps between θ and $\theta + d\theta$ is

$$d\nu = \frac{1}{2} n k_1 \exp\left(\frac{\varepsilon z E \lambda \cos \theta}{2kT}\right) \sin \theta d\theta \quad (16)$$

where n is the number of ions per unit volume in the solution. The electricity transported by these ions is

$$\varepsilon z \lambda \cos \theta d\nu.$$

Summing up the above quantity we obtain the formula for specific conductivity

$$\kappa = \int_0^\pi \frac{1}{2} n \varepsilon z \lambda k_1 \exp\left(\frac{\varepsilon z E \lambda \cos \theta}{2kT}\right) \sin \theta \cos \theta d\theta \quad (17)$$

Carrying out the integration, we have

$$\kappa = \frac{n \varepsilon^2 z^2 \lambda^2 k_1}{6kT} \Xi(x) \quad (18)$$

$$\begin{aligned} \Xi(x) &= \frac{z}{x^2} \cosh x - \frac{3}{x^3} \sinh x \\ &= 1 + \frac{3 \cdot 4}{5!} x^2 + \frac{3 \cdot 6}{7!} x^4 + \frac{3 \cdot 8}{9!} x^6 + \dots \end{aligned} \quad (19)$$

$$x = \frac{\varepsilon z \lambda E}{2kT} \quad (20)$$

The value of k_1 is already given by (7).

When E is very small (18) may be simplified as follows.

$$\kappa = \frac{n \varepsilon^2 z^2 \lambda^2 k_1}{6kT} \quad (21)$$

This is Ohm's law in electrolytic conduction. As in the case of viscosity $\log \kappa$ and $1/T$ have the linear relationship

$$\log \kappa = A - \frac{B}{T} \quad (22)$$

where A and B are empirical constants.

The above relation has been obtained by Rasch-Hinrichsen⁽⁹⁾ from experiments on fused salts, glass, and other insulators.

When E is very large κ can be expressed by the following formula.

$$\log \kappa = a + bE \quad (23)$$

where a and b are constants. This is the empirical formula discovered by Poole^{(10) (11)} from the measurement of the conductivities of mica, glass, and other solid dielectrics.

Equation (21) can be easily derived in another way. By definition the specific conductivity is given by

$$\kappa = n e^2 z^2 \omega \quad (24)$$

Introducing (5) and (13) into (24) we obtain (21) at once.

*Electrotechnical Laboratory,
Department of Communication.*

(9) E. Rasch and F. W. Hinrichsen, *Z. Elektrochem.*, **14** (1908), 41.
(10) H. H. Poole, *Phil. Mag.*, **32** (1916), 112.
(11) H. H. Poole, *Phil. Mag.*, **42** (1921), 488.

Studies on the Organic Molecular Compounds. Part IV. The Relation between Compound-Formation and the Substituent in the Monosubstitution Products of Several Aromatic Hydrocarbons.

By Chiro SHINOMIYA.

(Received May 20, 1940.)

According to the writer's studies, in the two series of binary systems of aromatic—nitroaromatic compound and of aromatic compound—antimony trihalide, the formation of crystalline molecular compounds is closely related not only to the nature of the aromatic ring, but also to the position, the number, and the variety of its substituents.⁽¹⁾ The influence of the substituent in the aromatic monosubstitution products on the formation of molecular compounds will now be discussed.

I. Greater Tendency of Compound-Formation of the α -Naphthalene Monosubstitution Products. It is supported by a number of facts that naphthalene α -monosubstitution products are generally more reactive than the β -isomers. Of the binary systems in previous reports, α -naphthol was generally proved to be more strongly additive than β -naphthol⁽²⁾ on compound-formation. Besides, as will be seen in Table 1, the foregoing relation holds also with naphthalene monosubstitution derivatives of simple substituent.⁽³⁾

Trinitrobenzene, picric acid, and tetranitrobenzene, arranged in the order of the tendency, were all used as a nitro component of greater tendency of compound-formation. Some irregularities were found in the systems of tetranitrobenzene (the system of α -methyl naphthalene having a lower τ than that of the β -isomer). At the same time in the systems of this nitrobenzene, the compound ratios other than 1:1, have been observed. A like ratio was found also in the systems of naphthoic acid.

In Table 1 a comparison of the compound-formation of two series of naphthalene monosubstitution products with each other and with that of naphthalene, brought out the interesting result that the α -compound had either a higher or lower "melting point elevation," while that of all the β -isomers were usually lower than that of naphthalene, from which it is concluded that substitution of any radical in the β -position of the naphthalene nucleus hindered compound-formation of this type.⁽³⁾ Similar results were noted in the anthracene and phenanthrene molecular compounds, with trinitrobenzene and picric acid, respectively, as the nitro component.⁽⁴⁾ The sequences are

(1) This Bulletin, **15** (1940), 92, 137, 259.

(2) Parts, I, II of these studies, *ibid.*, **15** (1940), 92, 137.

(3) This type of combination seems to be formed by the affinity of the aromatic ring—nitro radical or aromatic ring—antimony trihalide; the effects of substituents in the latter case were described in Part III.

(4) These compounds are distinctly halochromic (Beilstein, "Handbuch der organischen Chemie," 4 Aufl., B. VI, 704; Erstes ergänz. B. VI, 339.).

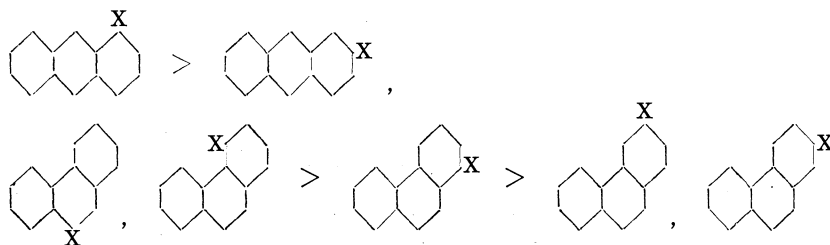
Table 1.

A [Melting point]	Mol ratio A:B [Melting point]	B [Melting point]	Trinitrobenzene	Picric acid	Tetranitrobenzene
			[123.0]	[122.0]	[126.0]
α -Naphthylamine		[50.0]	1:1 (214,* 127.5	{1:1 (161,* 75}	Decomposed
β - " "		[110.0]	1:1 [161]* 45.0	{1:1 (190)* 74}	Decomposed
α -Methylnaphthalene		[-22]*	1:1* [148.5] 98.0	1:1 (142)* 92	1:1 [U: Ca. 86]
β - " "		[35.0]	1:1 (123)* 44	1:1 (117,* 38.5	1:1 [127.0] 46.5
α -Naphthol		[96.0]	1:1 [193.5] 84.0	1:1 [190.5]* 81.5	1:1 [137.0] 26.0
β - " "		[122.0]	1:1 [158.5] 36.0	1:1 [156.3]* 34.3	1:1 [130.5] 6.5
α -Ethylnaphthalene		[<-14]*	—	1:1 (98)* > 44	—
β - " "		[-19]*	—	1:1 (71)* 19.5	—
α -Methoxynaphthalene		[-10]*	1:1 (138)* 82	—	—
β - " "		[73.0]	1:1* [94.0] - 4.0	1:1* [115.0] 17.5	2:1 [100] 9.3
α -Chloronaphthalene		[-17]*	1:1 [132.5] 79.5	1:1 [125.7]* 73.2	1:1 [U: 62.0] (1:1 [73.0] 18.5)
β - " "		[58.5]	1:1 [94.0] 3.2	1:1 [81.5]* - 8.8	3:2 [U: 93.0]
α -Bromonaphthalene		[5]*	1:1* [134.0] 70.0	1:1* [129.6] 66.1	—
β - " "		[59]*	—	1:1 [83.5]* - 7.0	—
α -Ethoxynaphthalene		[54]*	1:1 (125.5)* 61.3	—	—
β - " "		[37]*	1:1 (95)* 15.0	—	—
Naphthalene		[80.0]	1:1 [152.5]* 51.0	1:1 [151.5]* 50.5	3:2 [139.5] 41.1
α -Naphthoic acid		[160.0]	2:1* [191.5] 43.8	2:1 [193.5] 46.2	4:1 [165.0] 11.8
β - " "		[182.5]	3:2 [U: 142.0]	3:2 [U: 143.0]	✓ or (4:1 [U: 156])
β -Naphthylacetate		[68.0]	1:1 [71.0] - 24.5	1:1 [PM: 80.0]	1:1 [79.5] - 17.5
β -Methylnaphthoate		[75.0]	1:1* [105.5] 5.5	1:1 [72.5] - 26.0	✓ [E: 49.5]
α -Phenoxynaphthalene		[56]*	1:1 (112.5)* 23.0	—	—
β - " "		[93]*	1:1 (105.5)* - 2.5	—	—
α -Naphthonitril		[37.0]	1:1* [88.0] 8.0	1:1 [97.5] 18.5	2:1 [72.0] 5.3
β - " "		[66.0]	1:1* [95.0] 0.5	1:1 [79.0] - 15.0	2:1 [84.0] - 2.0
α -Naphthophenone		[75.5]*	1:1 (89)* - 10.3	—	—
β - " "		[82]*	—	1:1 (113,* 11	—
α -Nitronaphthalene		[57.0]	2:1 [PM: 70.0]	1:1* [U: 70.0]	✓ [E: 42.0]
β - " "		[78.0]	1:1* [71.0] - 19.0	✓ [E: 52.0]	✓ [E: 57.0]

* Data from literature.

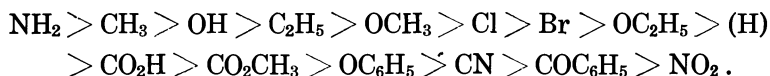
() Melting points in parentheses represent those of molecular compounds obtained from solution.

{ } Data in brackets are those of other types of molecular compounds.

where X is OH, OC₂H₅, or OCH₃.⁽⁴⁾

Since the real shape of these molecules are regarded as not to differ much from the above formula, i.e. each benzene ring being considered a regular hexagon, the "projection" of substituent X from the aromatic nucleus, which is more prominent in β -position, may interfere with the compound-formation of this type; and in the case of five phenanthrene derivatives, it will be easily understood that the substituent X should be in a freer state (consequently a more hindering state) in the 2- or 3-position than in the 4- or 9-position.

II. The Relation between Compound-Formation and the Substituent in the Monosubstituted Naphthalene Derivatives. From the results enumerated in the second column of Table 1, the effect of substituents on compound-formation in the systems of naphthalene α -derivatives with trinitrobenzene may be given in the following order;



This order, which is virtually the same as that in the case of the β -isomer, also holds in the systems of picric acid or tetranitrobenzene. The foregoing order is also related to that of the function groups in the substitution rule of benzene and in other cases.⁽⁵⁾ Since the tendency of compound-formation runs parallel with that of the positivity of the substituents, α - and β -nitronaphthalene have the least affinity with three polynitro derivatives of benzene.⁽⁶⁾ Such a weakening effect upon affinity seems to be in parallel with the magnitude of the substituents. This is marked in the substituents of analogous constitution, for example, $\text{CH}_3 > \text{C}_2\text{H}_5$; $\text{OH} > \text{OCH}_3 > \text{OC}_2\text{H}_5 > \text{OC}_6\text{H}_5$; $\text{CO}_2\text{H} > \text{CO}_2\text{CH}_3$; $\text{Cl} > \text{Br}$; etc.^{(7) (8)} These relations are observed in the case of the inorganic—organic molecular compound, of which by Menshutkin the data of some naphthalene derivatives were given in Table 2, together with those observed by the writer.⁽⁹⁾

In the systems dealt in this paper, halochromism appeared regularly. But in the case of crystalline molecular compounds of the naphthylamines with picric acid, it was less halochromic (greenish yellow or yellow) than with trinitrobenzene (dark red or red), from which the existence of another type of compound may be expected.⁽¹⁰⁾

(5) This roughly agrees with the diminishing order of dipole moment of these substituents in the aromatic nucleus; and this order is reproduced in the serial measurements of oxidation-reduction potentials of phenanthraquinone derivatives whose 1- or 3-position is occupied by those substituents. (L.F. Fieser, *J. Am. Chem. Soc.* **51** (1929), 3101.).

(6) In the binary and ternary systems of polynitroaromatic compounds only, a few systems belong to a very feeble compound type, and the others to a simple eutectic type.

(7) The number could be increased, for example, $\text{CHO} > \text{COCH}_3 > \text{COC}_6\text{H}_5$; $\text{Br} > \text{I}$.

(8) It will be rather difficult to attribute a plane shape to a whole molecule of naphthalene derivatives of such a large group as $-\text{CO}_2\text{H}$, $-\text{CO}_2\text{CH}_3$, $-\text{OCOCH}_3$, $-\text{COC}_6\text{H}_5$.

(9) Details will be reported in a future paper.

(10) Naphthylamine—trinitroresol and naphthylamine—styphnic acid were produced and they were confirmed to be of the same type of molecular compound,

Table 2.

A \ B Mol ratio A:B [Melting point] τ		
	SbCl ₃	SbBr ₃
Naphthalene	1:2 [86] 10.7	1:2 [66] -23.3
α -Naphthol ⁽⁹⁾	1:2 [77.5] -3.2	—
β - „ „ ⁽⁹⁾	✓	—
α -Nitronaphthalene	1:1 [39] -26.0	(1:1 [38.2] -37.3) or ✓
β - „ „ ⁽⁹⁾	1:1 [44.0] -31.5	—
α -Chloronaphthalene	1:2 [46] 3.0	✓
β - „ „	1:1 [29.5] -35.0	✓
α -Bromonaphthalene	1:1 [34.5] -3.5	✓

Experimental.

(1) α -Nitronaphthalene—trinitrobenzene.

Trinitrobenzene: 6.6 mg.

Mol% trinitrobenzene	88.5	76.0	55.6	52.7	48.0	39.8	22.8	15.3	12.1
Melting point	113.0	102.0	—	70.0	71.0	70.0	68.0	65.0	62.5
				(56.0)					
Thawing point	70.0	69.0	69.0	69.0	69.0	68.0	52.0	52.0	52.0
				(46.0)					

Total nitronaphthalene: 22.7 mg.

Mol% nitronaphthalene	100.0	97.3	90.0	73.9	70.4	65.6	60.4	52.7	50.1
Melting point	57.0	55.0	59.0	70.0	70.0	70.2	70.0	71.0	71.0
Thawing point	56.0	52.5	51.5	59.0	66.5	69.0	68.3	69.0	(52.0), 70.0
						47.6	44.8	41.4	58.2
						71.0	78.0	82.0	70.2
						70.0	70.0	70.0	68.8

Eutectic point: 52.0°, 69.0°, 70.0°; 94.5 mol%, 56.0 mol%, 47.3 mol% α -nitronaphthalene.

Compound (1:1): yellowish powder, melting at 71.0°.

Compound (2:1): yellowish powder, melting at 70.0° into two mutually non-miscible liquids.

Range of partial miscibility on liquidus: 75.0 mol%~57.0 mol% α -nitronaphthalene.(2) α -Nitronaphthalene—picric acid.

Nitronaphthalene: 7.8 mg.

Mol% nitronaphthalene	93.7	73.5	54.5	49.3	40.7	34.5	21.1
Melting point	53.0	61.0	72.0	(72.0)	(84.5)	(93.0)	108.0
		(47.0)					
Thawing point	49.0	48.0	66.0	69.0	69.0	69.0	69.0
		(40.0)					

Total picric acid: 26.5 mg.

Mol% picric acid	64.4	60.2	54.5	50.5	46.8	41.9	36.9	32.7	60.7
Melting point	(92.0)	88.0	83.0	78.0	72.5	71.5	70.0	67.0	90.8
Thawing point	69.8	70.0	70.0	70.0	69.0	—	50.0	48.0	70.0

Eutectic point: 48.0°, (70.0°); 85.0 mol%, (46.5 mol%) α -nitronaphthalene.Pertectic point: 72.0°, 53.5 mol% α -nitronaphthalene.

Compound (1:1): pale yellow powder with an incongruent melting point (its unstable congruent melting point: 72.0°).

(3) α -Nitronaphthalene—tetranitrobenzene.

Tetranitrobenzene: 7.0 mg.

Mol% tetranitrobenzene	73.4	43.1	23.3	11.1
Melting point	112.5	81.0	48.0	50.0
Thawing point	45.0	—	43.0	—

Nitronaphthalene: 5.1 mg.

Mol% nitronaphthalene	96.4	88.3	70.4	38.4
Melting point	54.0	49.0	60.5	101.0
Thawing point	43.0	42.0	41.8	42.8

Eutectic point: 42.0°; 80.0 mol% α -nitronaphthalene.(4) β -Nitronaphthalene—trinitrobenzene.

Total nitronaphthalene: 7.2 mg.

Mol% nitronaphthalene	100.0	83.4	74.8	47.1
Melting point	78.0	69.0, 65.5	59.0, 68.0	—, 75.5
Thawing point	77.0	45.0, —	46.0, 62.0	46.0 $\rightarrow$ 74.0
	54.8	41.2	26.6	
	—, 75.0	—, 80.0	101.0	
	—, 66.0	—, 73.0	46.0 $\rightarrow$ 73.0	

Trinitrobenzene: 10.8 mg.

Mol% trinitrobenzene	93.5	77.2	62.4	54.6	51.7	47.8	41.1
Melting point	117.0	103.5	87.0	77.0, —	73.0	66.5, —	—, 74.5
Thawing point	90.0	45.0	46.0, —	46.0, —	—	46.0, —	—, 62.0
	37.5	33.5	29.7	23.0	17.2		
	—, 74.0	51.0, 73.0	—, 71.0	61.0, 65.5	68.0, —		
	46.0 $\rightarrow$ 62.0	46.0 $\rightarrow$ 62.0	46.0 $\rightarrow$ 62.0	—, 62.0	46.0 $\rightarrow$ 62.0		

In the simple eutectic type,

Eutectic point: 46.0°, 63.0 mol% β -nitronaphthalene.

In the congruent type,

Eutectic point: 62.0°, 73.5°; 80.5 mol%, 44.4 mol% β -nitronaphthalene.

Compound (1:1): slightly halochromic powdery crystals, melting at 75.5°.

(5) β -Nitronaphthalene—picric acid.

Nitronaphthalene: 4.8 mg.

Mol% nitronaphthalene	92.7	77.0	65.8	55.0	45.3	29.5	12.0
Melting point	73.5	—	—	—	79.0	100.0	114.0
Thawing point	53.5	52.0	52.0	52.0	51.5	51.5	52.0

Picric acid: 5.0 mg.

Mol% picric acid	80.8	57.4	44.0	34.4	28.9	22.1	13.8
Melting point	109.0	85.0	66.0	54.0	58.0	62.5	70.0
Thawing point	52.0	52.0	51.5	52.0	52.0	52.0	52.0

Eutectic point: 52.0°, 64.0 mol% β -nitronaphthalene.(6) β -Nitronaphthalene—tetranitrobenzene.

Nitronaphthalene: 3.9 mg.

Mol% nitronaphthalene	90.7	81.8	66.7	49.0	22.7
Melting point	71.0	63.5	70.0	92.5	114.0
Thawing point	57.0	58.0	58.0	—	—

Tetranitrobenzene: 3.4 mg.

Mol% tetranitrobenzene	60.3	32.3	25.7	18.8	9.4
Melting point	101.3	68.5	57.0	63.0	71.0
Thawing point	57.0	57.0	57.0	56.0	57.0

Eutectic point: 57.0°, 74.3 mol% β -nitronaphthalene.

(11) Distinct transition was observed; it is indicated by a horizontal arrow.

In the foregoing six systems (Fig. 1), the hindering effect of substituent in the benzene and naphthalene nucleus was very marked. The presence of nitro radicals in the aromatic rings of both components in the binary system, does not increase the tendency of compound-formation; α - and β -nitronaphthalene showed very little affinity with trinitrobenzene, less with picric acid, and the least with tetranitrobenzene. With the same nitro component, β -nitronaphthalene had less affinity than the α -isomer, presumably the β -isomer has a more reactive nitro radical than the α -isomer.

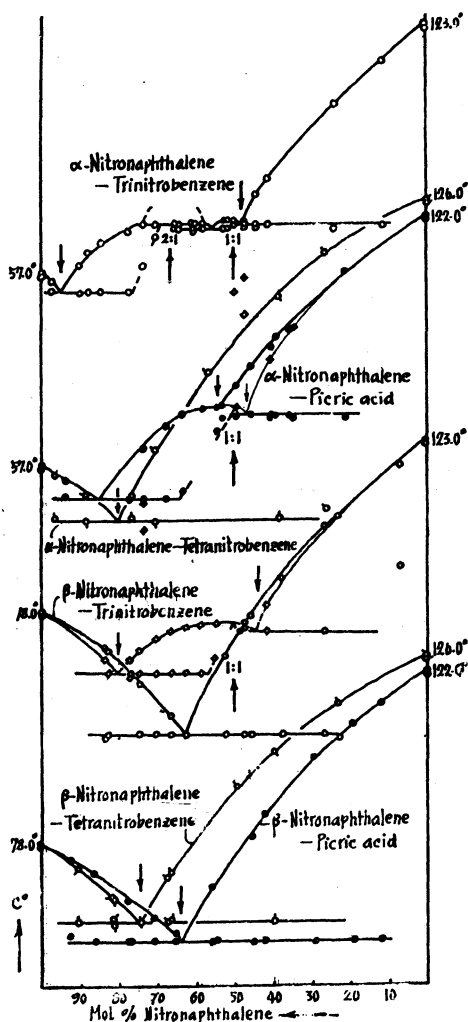


Fig. 1.

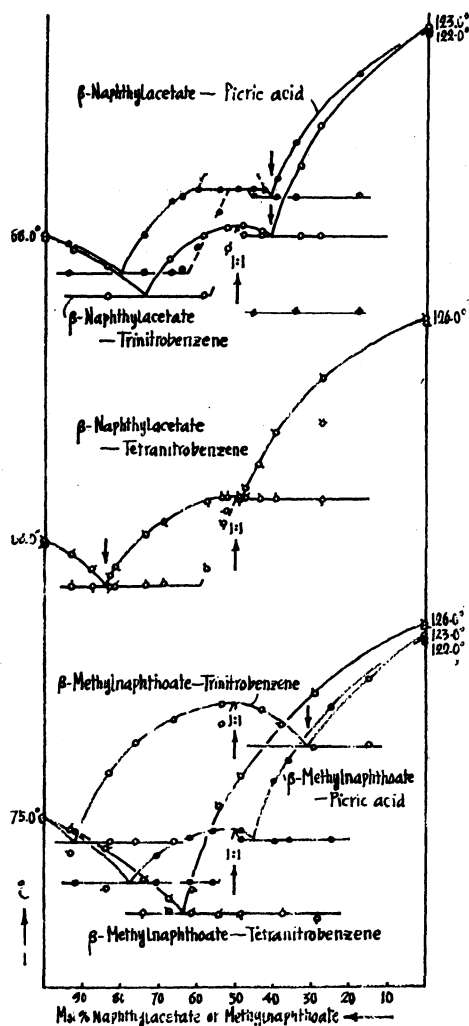


Fig. 2.

(7) β -Naphthylacetate—trinitrobenzene.

Naphthylacetate: 8.4 mg.

Mol% naphthylacetate	100.0	92.2	83.5	67.2	58.8	52.4	48.2	43.8	33.2	28.1
Melting point	68.0	64.0	60.0	62.0	68.0	70.0	70.8	69.0	86.8	97.0
Thawing point	67.5	58.5	52.0	viscous	52.0	64.5	68.0	68.0	68.0	68.0

Eutectic point: 52.0°, 68.0°; 73.7 mol%, 41.8 mol% β -naphthylacetate.

Compound (1:1): light yellow leafy or powdery crystals, melting at 71.0°.

(8) β -Naphthylacetate—picric acid.

Naphthylacetate: 8.8 mg.

Mol% naphthyl-										
acetate	93.8	74.0	66.3	54.3	45.3	42.5	34.5	27.6	17.9	
Melting point	66.0	68.0	77.0	80.0	80.3	80.0	92.8	102.5	111.0	
Thawing point	58.0	58.0	58.0	—	(47.0) → 78.5	—	(48.0) → 78.0	78.0	(48.0) → 79.0	

Picric acid: 6.5 mg.

Mol% picric acid	60.8	54.6	50.2	45.2	40.0	36.0
Melting point	83.0	80.0	80.0	80.0	80.0	78.0
Thawing point	78.0	78.5	80.0	74.0	65.0	59.0

Eutectic point: 58.0°, 78.0°; 80.0 mol%, 41.0 mol% β -naphthylacetate.

Compound (1:1): yellow powder, melting at 80.0° into two mutually non-miscible liquids.

Range of partially miscibility on liquidus: 61.5~42.0 mol% β -naphthylacetate.(9) β -Naphthylacetate—tetranitrobenzene.

Naphthylacetate: 5.6 mg.

Mol% naphthylacetate	92.9	82.9	73.4	68.3	57.7	53.3	47.4	39.3	27.1	
Melting point	64.5	59.0	69.8	73.0	78.0	79.5	82.0	96.5	(99.0), 111.0	
Thawing point	56.0	56.0	56.5	57.0	60.5	72.5	79.0	79.0	78.5	

Total tetranitrobenzene: 6.2 mg.

Mol% tetranitrobenzene	51.0	47.5	56.1	18.1	12.6
Melting point	79.5	79.5	88.0	61.0	60.5
Thawing point	79.0	76.0	79.0	56.0	56.0

Eutectic point: 56.0°, 79.0°; 84.0 mol%, 48.5 mol% β -naphthylacetate.

Compound (1:1): yellow powder, melting at 79.5°.

(10) β -Methylnaphthoate—trinitrobenzene.

Trinitrobenzene: 5.9 mg.

Mol% trinitrobenzene	85.2	71.0	57.6	47.0	34.5	24.6	17.6	0.0
Melting point	111.0	—	104.0	105.0	101.0	95.0	87.0	75.0
Thawing point	94.5	94.0	101.0	100.0	69.0	69.0	69.0	74.0

Eutectic point: 69.0°, 94.3°; 91.5 mol%, 31.0 mol% β -methylnaphthoate.

Compound (1:1): fine light yellow needles, melting at 105.5°.

(11) β -Methylnaphthoate—picric acid.

Total methylnaphthoate: 16.5 mg.

Mol% methylnaphthoate	91.2	70.2	48.1	39.6	61.8	55.7	35.8	24.6
Melting point	72.0	65.0	72.0	85.0	70.0	72.0	90.0	104.0
Thawing point	58.0	58.0	69.5	69.0	58.0	58.0	69.5	69.5

Eutectic point: 58.0°, 69.5°; 77.5 mol%, 45.5 mol% β -methylnaphthoate.

Compound (1:1): yellow prisms, melting at 72.5°.

(12) β -Methylnaphthoate—tetranitrobenzene.

Methylnaphthoate: 5.6 mg.

Mol% methylnaphthoate	92.9	83.8	67.2	61.3	48.3	37.8
Melting point	71.8	66.5	53.0	56.0	86.0	99.8
Thawing point	65.5	56.0	50.0	49.5	49.5	49.5

Tetranitrobenzene: 6.2 mg.

Mol% tetranitrobenzene	71.2	45.7	26.0
Melting point	107.5	78.0	58.0
Thawing point	48.0	49.0	49.5

Eutectic point: 49.5°, 63.7 mol% β -methylnaphthoate.

In the behaviour of compound-formation of β -naphthylacetate and its isomer, namely, β -methylnaphthoate, the former resembles naphthol and the latter naphthoic acid, as will be seen from Table 1 and Fig. 2.

Summary.

The effect of the substituents in the aromatic (naphthalene) ring on compound-formation was studied in connexion with "aromatic—nitro-aromatic combination," the results of which were in good agreement with those previously reported.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo and
Kumamoto Higher Technical School.*

Studies on the Oiliness of the Liquids. IX. Measurements of the Static Friction Coefficients of Cyclic Compounds for Glass Surfaces.

By Toshizo ISEMURA.

(Received June 12, 1940.)

The measurements of the static friction coefficients of many organic liquids for glass or silver surfaces had been reported in the preceding communications.⁽¹⁾ The liquids which had been tested, were mostly normal chain compounds such as aliphatic hydrocarbons, alcohols, acids, ketones and esters. It was recognised that long chain compounds, especially long chain acids, are suitable as lubricant for the boundary lubrication. In practice, such compounds are often added to the lubricating oil in order to increase the oiliness of it. Concerning the oiliness of the cyclic compounds, few results are hitherto reported. In this connection, the present experiments were undertaken to study the oiliness of some cyclic compounds. The friction coefficients have been measured for fifteen compounds of both isocyclic and heterocyclic series, and as the results it has been noticed that in cyclic compounds is there not a good lubricant. However, two of them, namely *m*-cresol and hexahydrophenol, are moderately active as lubricant.

The experiments were conducted by the balance method for the measurement of the static friction coefficient. The friction surfaces consisted of an optical glass plate and a glass of spherical surface whose radius of curvature is 6.5 cm. The method of measuring the friction and the conditions were the same as described in the preceding papers. The samples of liquids were purified as described in the following lines. Decahydronaphthalene was first shaken with the mixture of concentrated

(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; T. Isemura, *ibid.*, **14** (1939), 270, 297.

surphuric acid and fuming sulphuric acid and with sodium carbonate solution and then with distilled water. After drying on metallic sodium, it was fractionated by distillation. Nitrobenzene was recrystallised and distilled several times in vacuum after drying with calcium chloride. Benzyl alcohol was purified by careful fractional distillation in reduced pressure with exclusion of air by passing nitrogen gas. Cyclohexanone was purified by the formation of the addition compound with sulphite which then decomposed with sodium carbonate and distilled in vacuum. All the other samples were purified by repeated distillation under atmospheric pressure or in vacuum after drying with appropriate drying agents (CaCl_2 or P_2O_5 for halogenated benzenes and methyl salicylate, KOH for aniline, its derivatives and quinoline, and anhydrous Na_2SO_4 for cyclohexanol) prior to each experiment.

The results obtained are summarized in the following table. In the table, W denotes the weight of slider in gram, F the tangential force acting on slider in gram and μ the static friction coefficient.

As it has been mentioned, all the substances investigated showed poor lubricating activity, namely the friction coefficients of them were larger than 0.66. Above all, decahydronaphthalene showed a very large friction coefficient as high as 0.87. This value is the highest friction coefficient of all liquids for glass surface excepting that of water. The aliphatic saturated hydrocarbons are poor lubricants, however, still they show somewhat lower friction coefficients than this.⁽²⁾ For good lubrication, adsorption of the lubricants by the friction surfaces is a necessary condition although adsorption alone is not a sufficient one. The poor lubricating activities of both chain and cyclic hydrocarbons are ascribable to the lack of a polar group by which the lubricant molecule can be adsorbed on the sliding surfaces. *m*-Cresol and cyclohexanol have moderate activity as lubricant. They were the most active lubricants among the cyclic compounds. Hardy by using bismuth surfaces showed in his experiment that *m*-cresol and cyclohexanol have relatively low friction coefficients among the ring compounds.⁽³⁾ In this point the results with bismuth surface and those with glass surface are consistent with each other. Although benzyl alcohol is inferior to these compounds with respect to their lubricating activities, it shows also relatively low friction coefficient among the cyclic compounds. At any rate, it will be noticed that the compounds which have a OH-group in the molecule, show comparatively low friction coefficient. By analogy with the results on the aliphatic compounds, the acids of cyclic series may also be good lubricants.⁽²⁾ However, all the acids of cyclic series, such as benzoic acid and toluic acid are unfavorably solid, and they have not been tested. Chloro-, bromo- and iodobenzene show almost the same friction coefficient irrespective to the considerable differences among their molecular weights. Nitrobenzene has almost no lubricating activity. It has a very large dipole moment. If the adsorption of the lubricant by the friction surfaces was achieved by the dipole force, nitrobenzene may perhaps be strongly adsorbed by the friction surfaces, for the dipole moment of it is exceedingly large. Therefore, a little more lubricating activity may be expected for this substance. This is contrary

(2) This Bulletin, **11** (1936), 659; **13** (1938), 127.

(3) *Phil. Mag.*, **40** (1920), 201.

Table 1.

	<i>W</i>	<i>F</i>	μ		<i>W</i>	<i>F</i>	μ
Decahydro-naphthalene	23.40	19.78	0.85	Methyl salicylate	15.70	11.15	0.71
	23.50	21.25	0.91		23.60	18.47	0.78
	23.75	21.93	0.92		23.70	18.22	0.77
	24.10	20.90	0.87		26.05	23.02	0.77
	26.90	22.60	0.84		27.90	21.02	0.75
	27.75	23.20	0.84		28.00	21.55	0.77
			0.87				0.76
<i>m</i> -Cresol	23.00	15.25	0.66	Aniline	23.20	17.80	0.77
	24.20	15.20	0.63		26.05	18.27	0.70
	26.40	16.97	0.64		26.30	19.85	0.76
	31.90	23.10	0.65		26.80	20.00	0.75
	31.00	20.00	0.65		27.20	19.03	0.70
	33.40	24.40	0.73		27.90	19.30	0.69
			0.66				0.73
Cyclohexanol	20.90	13.51	0.65	<i>o</i> -Toluidine	21.80	15.78	0.73
	24.65	15.79	0.64		26.25	18.80	0.72
	25.50	17.28	0.68		26.70	20.62	0.80
	26.85	16.87	0.63		23.80	21.10	0.74
	23.90	20.74	0.72		30.30	22.40	0.74
			0.66				0.75
Benzyl alcohol	22.20	15.90	0.72	Dimethyl aniline	21.55	15.83	0.74
	26.35	18.25	0.69		24.50	18.30	0.75
	26.35	20.60	0.78		25.15	18.86	0.75
	26.25	19.50	0.74		25.20	18.93	0.75
	27.80	23.60	0.74		28.50	21.30	0.75
	30.30	22.00	0.73		29.50	24.20	0.82
			0.73				0.76
Chlorobenzene	22.55	18.50	0.82	<i>o</i> -Chlor-aniline	22.65	20.65	0.91
	23.25	19.30	0.83		24.40	21.78	0.89
	25.00	19.75	0.79		25.55	22.41	0.88
	25.50	20.90	0.82		25.65	22.01	0.83
	25.90	21.16	0.82		23.65	24.75	0.87
	27.60	22.23	0.81				0.86
	29.50	23.00	0.78				
			0.81				
Bromobenzene	21.35	16.00	0.75	Quinoline	19.80	15.40	0.78
	21.55	16.61	0.77		20.60	16.03	0.78
	22.40	18.40	0.82		21.55	18.48	0.86
	23.05	17.55	0.76		23.00	18.50	0.80
	24.30	19.00	0.78		26.30	20.80	0.79
	26.25	20.40	0.73		23.70	24.90	0.87
			0.78				0.82
Iodobenzene	23.90	18.75	0.78	Cyclohexanone	21.25	17.40	0.82
	24.00	17.95	0.82		22.00	16.58	0.76
	21.90	17.95	0.82		24.00	18.60	0.78
	20.70	17.00	0.82		25.65	20.28	0.79
			0.81		27.95	22.60	0.81
							0.79
Nitrobenzene	25.40	21.30	0.84				
	26.00	22.00	0.85				
	27.80	22.60	0.81				
	28.75	24.00	0.84				
			0.84				

to the experimental fact. Accordingly nitrobenzene may not be adsorbed by glass surface and the adsorption is not attained only by the dipole force.⁽⁴⁾

Aniline and its derivatives show somewhat smaller friction coefficients than the compounds just mentioned. However, *o*-chloroaniline has an exceptionally high friction coefficient among them. Quinoline shows also a high friction coefficient. It was already reported that aliphatic ketones are poor lubricants.⁽⁵⁾ The cyclic ketones can not be exceptional, cyclohexanone shows also a high friction coefficient. Hardy states⁽³⁾ that the most interesting substances which he had investigated are the hydroxy-acids with OH and COOH groups. This conjunction almost destroys the lubricating action in the case of the ring compounds such as salicylic acid. Owing to the existence of two polar groups, the present author had expected a high friction coefficient also in the case of methyl salicylate. Nevertheless, the friction coefficient is not so high as the author had expected. Although salicylic ester has two polar groups in the molecule, the ester group has probably no or little ability of anchoring on the friction surfaces. And the molecule behaves as if it were a phenol derivative.

It is considered that the adsorption by the friction surface by only one active group is a necessary condition for good lubrication, though not a sufficient one. Regular arrangement of the lubricant molecules or adequate orientation of the molecules is an important factor for good lubrication. Further discussion on the lubricating activity of liquids and friction will be given in a later paper.

In conclusion, the author expresses his hearty thanks to Prof. J. Sameshima for his kind guidance and encouragement throughout the present work. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokai (Japan Society for the Promotion of Scientific Research), to which author's thanks are due. The author's acknowledgement is also due to Hattori Hokokai for a grant.

Summary.

(1) The measurements of the static friction coefficients of cyclic compounds for glass surfaces were reported.

(2) It is noticed that no cyclic compound is a good lubricant, however, among them *m*-cresol and cyclohexanol are moderately active as lubricant.

*Chemical Institute, Faculty of Science,
Tokyo Imperial University, Tokyo.*

(4) This fact has been recently verified by Mr. Akamatsu in our laboratory by the direct measurement of adsorption of nitrobenzene by glass powder from its toluene solution with a very sensitive method.

(5) This Bulletin, **14** (1939), 270:

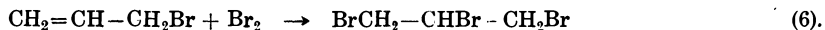
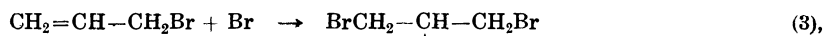
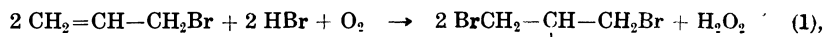
The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds and the Influence of Catechol.

By Osamu SIMAMURA.

(Received July 8, 1940.)

The addition of hydrogen bromide to allyl bromide and to undecenoic acid follows the Markownikoff rule in the absence of peroxides and oxygen to yield the normal products, 1,2-dibromopropane and 10-bromoundecanoic acid respectively, while in the presence of peroxides or oxygen the direction of addition is reversed, the abnormal products, 1,3-dibromopropane and 11-bromoundecanoic acid respectively, being formed; and the presence of an antioxidant, e.g. catechol, hydroquinone, diphenylamine, etc., in the reacting mixture gives rise to the formation of the normal products even in the presence of peroxides or oxygen.⁽¹⁾ The peculiar effect of oxygen in co-operation with hydrogen bromide has been found also in the isomerization of isostilbene⁽²⁾ and methyl allo-cinnamate⁽³⁾ to their respective geometrical isomerides, catechol being likewise effective in inhibiting the reaction.⁽²⁾

A contribution to the explanation of the oxygen effect was made by Y. Urushibara and O. Simamura⁽⁴⁾ when they passed hydrogen bromide and oxygen into allyl bromide in the dark at 0°C. and observed the complicated reactions to take place. As the result of the reactions free bromine, water, 1,2,3-tribromopropane, and an organic peroxide, were formed along with 1,3-dibromopropane, the main product. Thus it was indicated that bromine is liberated from hydrogen bromide and oxygen in the presence of the ethenoid compound and the reactions involved were represented as follows:



The starting reaction is the oxidation of hydrogen bromide by oxygen with allyl bromide as a necessary acceptor of bromine atoms to yield hydrogen peroxide and a dibromoisopropyl radical. The radical thus

(1) Compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461; *Ann. Rep.*, **1939**, 219.

(2) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507; **13** (1938), 566.

(3) O. Simamura, *ibid.*, **14** (1939), 294.

(4) Y. Urushibara and O. Simamura, *ibid.*, **14** (1939), 323.

formed reacts with hydrogen bromide to produce 1,3-dibromopropane and a bromine atom, and the latter combines with allyl bromide to give another dibromoisopropyl radical, thus the abnormal addition of hydrogen bromide to allyl bromide proceeding by a chain process. The organic peroxide may be such that is to be formed by the action of oxygen on the dibromoisopropyl radical. The hydrogen peroxide and hydrogen bromide produce free bromine and water, and the bromine combines with allyl bromide to yield 1,2,3-tribromopropane.

If oxygen is present only in a limited amount, reaction (1), consequently also reactions (4), (5), and (6), occur only to a small extent and thus the formation of the peroxide, water, bromine, and tribromopropane, may be imperceptible, while the abnormal addition giving 1,3-dibromopropane can proceed by the propagation of the chain reaction, (2) and (3). The inhibiting action of the antioxidants on the abnormal addition was formerly considered to consist in capturing the bromine atom and thus interrupting the propagation of the chain reaction. In the *cis-trans* isomerization caused by hydrogen bromide and oxygen a bromo-radical is likewise formed intermediately from the unsaturated molecule and a bromine atom delivered by hydrogen bromide and oxygen, and the change proceeds by a chain reaction carried by the bromine atom. The inhibition of this isomerization by an antioxidant was also attributed to the break of the chain reaction due to the capture of the bromine atom.

The present paper records the results of experiments on the action of the mixture of hydrogen bromide and oxygen on various ethenoid compounds, some being incapable of adding bromine at all and others adding bromine only to a limited extent. The influence of catechol on the reactions has been examined with the result that the hypothesis on the inhibiting action of the antioxidant on the oxygen effect has been corrected.

Materials. Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a bottle containing cold tetralin and a tube filled with anthracene, and dried with phosphorus pentoxide. Oxygen was taken from a bomb and dried with phosphorus pentoxide.

Tetraphenylethylene was prepared from benzophenone according essentially to the direction of J. Lévy and R. Lagrave.⁽⁵⁾ 1,1,1,2-Tetraphenylethanol-(2) (7 g.) was heated with acetyl chloride (30 c.c.) in a sealed tube at about 160° for four hours and tetraphenylethylene produced was recrystallized from benzene, m.p. 225–226°; yield 4.5 g.

Dimethylmaleic anhydride was prepared according to E. Ott.⁽⁶⁾ Dimethyl dimethylfumarate and dimethyl dimethylmaleate were synthesized by refluxing dimethylfumaric acid and dimethylmaleic anhydride respectively with methanol containing 10% of concentrated sulphuric acid. The dimethylfumarate melted at 42–44° after recrystallization from petroleum ether and the dimethylmaleate boiled at 98° under a pressure of 6 mm., n_D^{20} 1.4570. Dimethylfumaric acid was obtained by boiling dimethylmaleic anhydride with concentrated aqueous sodium hydroxide according to Fittig,⁽⁷⁾ m.p. 250–251°.

(5) J. Lévy and R. Lagrave, *Bull. soc. chim.*, [4], **43** (1928), 440.

(6) E. Ott, *Ber.*, **61** (1928), 2131.

(7) R. Fittig, *Ann.*, **304** (1899), 158.

Tetraethyl α,γ -dicarboxy- α -bromoglutaconate and tetraethyl α,γ -dicarboxy- α -methylglutaconate were prepared by the action of bromine⁽⁸⁾ and methyl iodide⁽⁹⁾ respectively on tetraethyl α,γ -dicarboxy- α -sodioglutaconate obtained from diethyl malonate, chloroform and sodium ethoxide.

1,1-Diphenylethylene was prepared by the method described in the "Organic Syntheses." Allyl bromide was purified by washing with dilute aqueous sodium carbonate and then with water, drying with anhydrous calcium chloride, and distilling in dim light. The product thus purified was free from peroxide (no colouration with ferrous ammonium sulphate and ammonium thiocyanate). Catechol was a product of Merck and phenanthrene of Schering-Kahlbaum.

The Action of the Mixture of Hydrogen Bromide and Oxygen on the Ethenoid Compounds. Tetraphenylethylene does not add bromine,⁽¹⁰⁾ and it has also been shown that the action of hydrogen bromide on tetraphenylethylene glycol results in the formation of tetraphenylethylene and free bromine instead of tetraphenylethylene dibromide.⁽¹¹⁾ Into a solution of tetraphenylethylene (0.2 g.) in benzene (50 c.c.) the mixture of hydrogen bromide and oxygen was passed for one hour in the dark at room temperature. No liberation of bromine was noticed. On removal of benzene in vacuum at room temperature the starting material was recovered. The elevation of the temperature to 40–50° did not cause any reaction.

With dimethylmaleic anhydride (0.6 g. in 30 c.c. of benzene) which adds no bromine,⁽¹²⁾ no reaction took place under similar conditions.

In phenanthrene the bond between carbon atoms 9 and 10 has a pronounced double bond character as is shown, for example, by the formation of a dibromide.⁽¹³⁾ When phenanthrene (0.8 g. in 30 c.c. of benzene or 0.1 g. in 30 c.c. of carbon tetrachloride) was treated with hydrogen bromide and oxygen for one hour, no liberation of bromine occurred and from the solutions thus treated the original material was recovered.

When the gas mixture was passed into a carbon tetrachloride solution of tetraethyl α,γ -dicarboxy- α -bromoglutaconate (0.35 g.–0.6 g. in 30 c.c.), which adds bromine to a small extent,⁽¹⁴⁾ an immediate and copious formation of bromine was observed. The amount of bromine liberated, however, did not seem to increase indefinitely even when the passage of the gas mixture was continued.

With tetraethyl α,γ -dicarboxy- α -methylglutaconate (0.64 g. in 30 c.c. carbon tetrachloride), which adds bromine to some extent,⁽¹⁵⁾ only a small

(8) M. Guthzeit and E. Hartmann, *J. prakt. Chem.*, **81** (1910), 329.

(9) F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99** (1911), 2196.

(10) H. Biltz, *Ann.*, **296** (1897), 219; H. Finkelstein, *Ber.*, **43** (1910), 1533.

(11) W. Madelung and M. Oberwegner, *Ber.*, **60** (1927), 2469.

(12) A. Michael, *J. prakt. Chem.*, **46** (1892), 382.

(13) L. F. Fieser and C. C. Price, *J. Am. Chem. Soc.*, **58** (1936), 1834.

(14) Private communication from Y. Urushibara: When bromine and the bromo-ester are mixed, the change in the colour intensity and the evolution of heat are hardly noticed, but on removing the free bromine by washing the mixture in ethereal solution with aqueous sodium sulphite and evaporating the ethereal solution, bromine is split off, showing that an addition product has been formed and exists in equilibrium with the unsaturated bromo-ester and free bromine. Thus the behaviour of the bromo-ester towards bromine is qualitatively the same as that of tetraethyl α,γ -dicarboxy- α -methylglutaconate⁽¹⁵⁾ but the bromine addition takes place to a smaller extent.

(15) Y. Urushibara, this Bulletin, **3** (1928), 200.

amount of bromine was liberated, and after removal of carbon tetrachloride there remained an unstable oily product having a content of bromine corresponding to the addition of one molecule of hydrogen bromide.

1,1-Diphenylethylene (0.1 g.) in carbon tetrachloride (30 c.c.) liberated bromine on treatment with hydrogen bromide and oxygen.

Dimethyl dimethylfumarate was found to add neither bromine nor hydrogen bromide in carbon tetrachloride in the dark, but on treatment of the ester with hydrogen bromide and oxygen bromine was liberated: A carbon tetrachloride solution containing 0.0010 mole of bromine and 0.0009 mole of the ester in 100 c.c. and a control solution containing only bromine were prepared in the dark and the intensities of the colour of the two solutions were compared with a Pulfrich photometer; after 116 days' standing in the dark any difference were still imperceptible. Into a carbon tetrachloride solution of the dimethylfumarate (0.4 g. in 30 c.c.) hydrogen bromide was passed for one hour; and the ester was recovered unchanged on evaporation of the solvent. On passing hydrogen bromide and oxygen under similar conditions the formation of bromine was rapid and proceeded similarly as with tetraethyl α,γ -dicarboxy- α -bromogluconate. On removal of carbon tetrachloride in vacuum, a viscous oil remained, which liberated bromine gradually. (For quantitative experiment see below.) Dimethyl dimethylmaleate behaved towards the mixture of hydrogen bromide and oxygen in a similar manner.

A further instance of bromine liberation in the presence of an ethenoid compound which adds no bromine is afforded by a compound, $C_{30}H_{42}O_{16}$, m.p. 86° , obtained by the action of iodine on tetraethyl α,γ -dicarboxy- α -sodio-glutaconate.^{(8) (16)} M. Guthzeit and E. Hartmann⁽⁸⁾ ascribed to this substance a bicyclobutane structure, which was deduced on the basis of a series of peculiar changes it showed. It is remarkable that it exhibited no indication of unsaturation. More recently C. K. Ingold and coworkers⁽¹⁷⁾ examined the substance and also the corresponding methyl ester and they confirmed the saturated character of the compound except that they obtained oxalic acid and tetraethyl ethanetetra-carboxylate by ozonolysis. They explained the remarkable behaviours by assuming a mesomerism between the following structures:



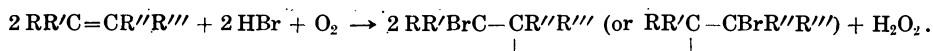
Now, the introduction of hydrogen bromide and oxygen into a carbon tetrachloride solution of the compound in question (0.58 g. in 30 c.c.) caused an immediate liberation of bromine, thus revealing the unsaturation of the compound.

The experimental results described above, although they give no simple rule for the relation between the bromine addition of an ethenoid compound and the liberation of bromine on treating it with hydrogen

(16) Private communication from Y. Urushibara: The same dimeric derivative is formed along with tetraethyl α,γ -dicarboxy- α -sodio-glutaconate, free iodine, and sodium bromide on heating tetraethyl α,γ -dicarboxy- α -bromogluconate with sodium iodide in alcoholic solution.

(17) C. K. Ingold, M. M. Parekh, and C. W. Shoppee, *J. Chem. Soc.*, **1936**, 142.

bromide and oxygen, can be well understood from the reaction mechanism as developed for the case of allyl bromide. The bromine liberation must be preceded by the starting reaction, which depends on the nature of the ethenoid compound. If the ethenoid compound is unable to take up a bromine atom to form a bromo-radical, then no reaction takes place at all. If the ethenoid compound is able to act as an acceptor of the bromine atom, then a bromo-radical and hydrogen peroxide are formed as in the case of allyl bromide:



The hydrogen peroxide produces free bromine by acting on hydrogen bromide. The free bromine appears at once if the ethenoid compound does not add the bromine or the bromine addition product is easily dissociable. If the ethenoid compound gives a stable bromine addition product, then free bromine remains as such only after, or just when, all the unsaturated compound has disappeared, but, as hydrogen peroxide can not be produced without the unsaturated compound, the bromine liberation can never be carried on beyond a certain limit. The bromo-radical may form a peroxide with oxygen on one hand, and, on the other, may either start the chain reaction of an abnormal addition of hydrogen bromide, or take up another bromine atom to form a dibromide, or split off the bromine atom to regenerate the double bond, according to its nature. In any case the liberation of bromine on treatment with hydrogen bromide and oxygen may be regarded as a possible, if not always occurring, symptom of the ethenoid double bond.

The Influence of Catechol on the Reactions. When the mixture of hydrogen bromide and oxygen was passed for one hour into a solution of dimethyl dimethylfumarate (0.33 g., 0.002 mole) in carbon tetrachloride (30 c.c.) with the addition of a small amount (15 mg., 7 moles per cent to the ester) of catechol and the solvent was removed in vacuum at room temperature, there remained a mass of crystals. This was extracted with water and then with ether. On evaporating the two extracts catechol and dimethyl dimethylfumarate were recovered. Thus catechol inhibited completely the liberation of bromine from hydrogen bromide and oxygen in the presence of dimethyl dimethylfumarate. On the other hand, on passing the gas mixture into a carbon tetrachloride solution of 0.0024 mole of the ester in absence of catechol about 0.0014 gram atom of bromine was set free besides 0.0026 gram atom combined in the oily product. The enormous capacity of catechol to inhibit the reaction was further demonstrated by an experiment with allyl bromide:

The remarkable reactions of allyl bromide with the mixture of hydrogen bromide and oxygen have been described briefly above or in details in the previous paper.⁽⁴⁾ The addition of a small amount of catechol caused a complete inhibition of the reactions: The gas mixture was passed into 20.2 g. (0.17 mole) of allyl bromide containing 20 mg. (0.00018 mole, about 0.001 mole to 1 mole of allyl bromide) for six hours in the dark at 0°, and the reaction mixture was washed several times with water, dried with calcium chloride, and distilled. The whole passed over at the boiling point of allyl bromide (70°). Thus, it has been shown that, although

an unlimited amount of oxygen is available, a very small amount of catechol is capable of inhibiting totally all the reactions observed in the absence of catechol. It seems that the normal addition, being slow compared with the abnormal, was unnoticeable in six hours at 0°.

In the previous experiments without catechol, one mole of allyl bromide gave the organic peroxide in an amount corresponding to 0.1 to 0.2 gram atom of iodine. The mechanism represented above requires the formation of at least 0.1 to 0.2 gram atom of bromine, to which the amount of tribromopropane obtained in practice nearly corresponded. Nevertheless, it is very evident that 0.001 mole of catechol can never match 0.1 to 0.2 gram atom of bromine in any chemical process whatever.

Further it was ascertained that catechol can not inhibit the reaction of hydrogen bromide and hydrogen peroxide (in aqueous solution).

All the facts point that the very starting reaction (1) is inhibited in the presence of catechol, thus suggesting some analogy with the inhibiting action of antioxidants on the autoxidation of aldehydes.

As for the mechanism of the inhibition by the antioxidants, what has been said of the experiments with an unlimited excess of oxygen applies at once to those with a limited amount of oxygen. Thus it is clear that the antioxidants inhibit the oxygen effect, not by capturing bromine atoms carrying the chain reaction of the abnormal addition or the isomerization, but by stopping the starting reaction giving a bromo-radical and hydrogen peroxide from an ethenoid compound, hydrogen bromide and oxygen.

The inhibiting actions of antioxidants on the effect of reduced nickel and on the light effect must be quite different matters. Reduced nickel produces an effect similar to that of oxygen not only in the addition reaction⁽¹⁸⁾ but also in the isomerization,⁽²⁾ and catechol prevents the effect. In this case the cause of the inhibition may be found in the adsorption of catechol on reduced nickel or in the capture of bromine atoms by catechol.⁽¹⁹⁾ Isostilbene is isomerized to stilbene by hydrogen bromide in sunlight in absence of oxygen, and catechol inhibits this isomerization in sunlight.⁽²⁰⁾ In this case it must be assumed that the bromine atoms, produced from hydrogen bromide by the action of light and responsible for the isomerization, are consumed by the catechol, and no alternative explanation seems possible. An experiment on the relation between the amounts of hydrogen bromide and of catechol will throw light on this problem.

The author expresses his hearty thanks to Prof. Y. Urushibara for his kind guidance and frequent discussions made on the results obtained. Thanks are also due to the Japan Society for the Promotion of Scientific Research and to the Ozi Seisi Co. for grants.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

(18) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51; **13** (1938), 331, 400, 404, 574; M. Takebayashi, *ibid.*, **15** (1940), 113, 116.

(19) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), 717.

(20) Y. Urushibara and O. Simamura, this Bulletin, **13** (1938), 566.

**Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs.
X. Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Aluminiumoxyds.
Der Einfluss der Zusammensetzung des Reaktionsgasgemisches auf dem Grad der Austauschreaktion.¹⁾**

Von Noriyoshi MORITA.

(Eingegangen am 5. Juli, 1940.)

Inhaltsübersicht. Die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Aluminiumoxyds wird nicht nur bei verschiedenen Temperaturen sondern auch unter Verwendung des Reaktionsgasgemisches verschiedener Zusammensetzung untersucht. Aus der ersten Reihe der Versuche, die mit dem Reaktionsgasgemisch der konstanten Zusammensetzung von $O_2:H_2O=2:1$ bei verschiedenen Temperaturen ausgeführt werden, wird gefunden, dass diese Reaktion erst bei etwa 520° bemerkbar und oberhalb 700° sehr schnell bis zum Gleichgewicht verläuft. Dagegen wird bei den Versuchen, die unter Verwendung des Reaktionsgasgemisches verschiedener Zusammensetzung durchgeführt werden, festgestellt, dass die Austauschgeschwindigkeit durch die Zusammensetzung des Reaktionsgasgemisches fast unbeeinflusst bleibt. Aus diesen letzteren Versuchsergebnissen liegt deshalb die Annahme nahe, dass bei der in Rede kommenden Austauschreaktion die Desorption des Wasserdampfes aus der Oberfläche des Aluminiumoxyds die massgebende Rolle spielt. Weiter wird aus der Temperaturabhängigkeit der Reaktionsgeschwindigkeit die Aktivierungsenergie zu 18 bis 22 Kcal. bestimmt.

Einleitung. Hinsichtlich der Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf an der Oberfläche des Aluminiumoxyds haben wir in dieser Reihe der Versuche schon an einigen Stellen Aufschluss gegeben. So wird über den Einfluss der Strömungsgeschwindigkeit auf dem Grad der Reaktion in VIII. Mitteil. ausführlich mitgeteilt und in IV. Mitteil. wird aus der Tatsache, dass die charakteristische Temperatur $t(10\%)$ des Aluminiumoxyds, d.h. die Temperatur, wo das prozentuale Austauschmass $\%A$ der in Rede kommenden katalytischen Austauschreaktion an der Oberfläche des betreffenden Oxyds zuerst 10% erreicht, gerade zwischen der des Calciumoxyds und Titanoxyds liegt, die Vermutung geäußert, dass bei der Reaktion auf Aluminiumoxyd höchstwahrscheinlich die Aktivierung des Wasserdampfes den geschwindigkeitsbestimmenden Prozess bildet.⁽²⁾ Bei den vorliegenden Versuchen handelt es sich nun erstens um den Einfluss der Temperatur und zweitens um den der Zusammensetzung des Reaktionsgasgemisches auf die betreffende Austauschreaktion. Die Ergebnisse der Versuche geben aber eine weitere Stütze für die oben angegebene Annahme, dass bei dieser Reaktion die aktivierte Desorption des Wasserdampfes geschwindigkeitsbestimmend wirkt.

(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: *ebenda*, **13** (1938), 601; III. Mitteil.: *ebenda*, **13** (1938), 656; IV. Mitteil.: *ebenda*, **14** (1939), 9; V. Mitteil.: *ebenda*, **14** (1939), 520 und **15** (1940), 1; VI. Mitteil.: *ebenda*, **15** (1940), 47 und 71; VII. Mitteil.: *ebenda*, **15** (1940), 119; VIII. Mitteil.: *ebenda*, **15** (1940), 166; IX. Mitteil.: *ebenda*, **15** (1940), 226.

(2) Vgl. dazu VI. und VII. Mitteil.

Austauschreaktion mit dem Reaktionsgasgemisch konstanter Zusammensetzung bei verschiedenen Temperaturen. Da die in dem vorliegenden Versuche benutzte Versuchsanordnung im grossen und ganzen dieselbe ist wie früher oft verwendet wurde, werden alle Einzelheiten auf die I. Mitteil. verwiesen. Als Aluminiumoxyd wird „Aluminiumoxyd, reinst, wasserfrei“ von Merck verwendet. Etwa 10 g dieses Oxyds (dessen scheinbares Volumen etwa 12 ccm beträgt) wird in den Mittelteil des Katalysatorrohres eingeschoben und darüber das Reaktionsgasgemisch bei verschiedenen Temperaturen aber immer mit konstanter Geschwindigkeit geleitet.

Das Reaktionsgasgemisch besteht bei dieser ersten Reihe der Versuche wie üblich aus zwei Volumenteilen elektrolytischen Sauerstoffs und einem Volumenanteil an schwerem Sauerstoff angereichertem Wasserdampf, und die Strömungsgeschwindigkeit (bei Zimmertemperatur und unter atmosphärischem Druck gemessen) beträgt 60 ccm pro Min. Das dazu benutzte schwere Wasser besitzt gewöhnlichem Wasser gegenüber den anfänglichen Dichteüberschuss (Δs_a) von 57.0 γ und von diesem gesamten Dichteüberschuss wird 36.3 γ auf die Anreicherung des schweren Sauerstoffs zurückgeführt (d.h. $\Delta s_a(O) = 36.3 \gamma$). Deshalb wird das in der zweiten letzten Spalte der Tabelle 1 angegebene prozentuale Austauschmass %A mittels der Gl. berechnet:

$$\%A = \frac{\Delta s_a - \Delta s_e}{30.3} \times 100 \quad (1).$$

In dieser Gl. drückt Δs_e den nach jedem Austauschversuch gemessenen Dichteüberschuss des schweren Wassers und der Zahlenwert 30.3 γ im Nenner die theoretisch berechnete Abnahme des Dichteüberschusses des schweren Wassers aus, die beim vollständigen Austausch sich ergeben würde.

Tabelle 1. Austauschreaktion zwischen O_2 und H_2O auf Aluminiumoxyd bei verschiedenen Temperaturen.

$O_2 : H_2O = 2 : 1$, Strömungsgeschw. = 60 ccm pro Min.,
 $\Delta s_a = 57.0 \gamma$ und $\Delta s_a(O) = 36.3 \gamma$.

Versuchs- nr.	Temperatur in °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austausch- mass %A	$-\log \left(1 - \frac{\%A}{100}\right)$
1	390	55.5	1.5	5	0.022
4	430	57.0	0.0	0	0.000
2	450	55.7	1.3	4	0.018
3	490	53.7	3.3	11	0.051
5	530	54.7	2.3	8	0.036
7	540	53.3	3.7	12	0.066
6	570	48.3	8.7	29	0.149
8	600	48.5	8.5	28	0.143
10	640	42.5	14.5	48	0.284
9	660	35.7	21.3	70	0.523
11	710	31.2	25.8	85	0.824

Das Aluminiumoxyd im Katalysatorrohr wird nach der Beendigung eines jeden Austauschversuches durch ein frisches Präparat ersetzt und dies wird direkt vor dem Beginn des nächsten Versuches unter Durchleitung des getrockneten elektrolytischen Sauerstoffs etwa drei Stunden lang bei jeder betreffenden Versuchstemperatur erhitzt. Die dabei gewonnenen Versuchsergebnisse sind in Tabelle 1 zusammengestellt.

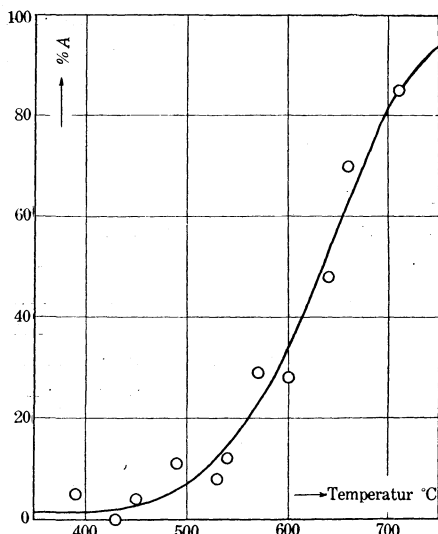


Abb. 1. Abhängigkeit des Austauschmasses %A auf Aluminiumoxyd der Temperatur.

Trägt man die so gefundenen Werte von %A bei verschiedenen Temperaturen gegen die letztere ein, so erhält man die Kurve, die in Abb. 1 wiedergegeben ist. Aus dieser Abb. 1 wird die charakteristische Temperatur $t(10\%)$ des Aluminiumoxyds, d.h. die Temperatur, wo das gefundenen prozentuale Austauschmass %A zuerst 10% erreicht, als 520° bestimmt.⁽³⁾ Aus dem in Spalte der Tabelle 1 angegebenen Werte von $\{-\log(1-\%A/100)\}$ können wir weiter die Aktivierungsenergie der betreffenden Reaktion ermitteln. Aber bevor wir darauf eingehen, wollen wir die Ergebnisse der zweiten Reihe der Versuche mitteilen, die unter Verwendung des Reaktionsgasgemisches verschiedener Zusammensetzung durchgeführt wurden.

Austauschreaktion mit Reaktionsgasgemische verschiedener Zusammensetzung bei verschiedenen Temperaturen. Bei dieser zweiten Reihe der Versuche wird nicht nur die Versuchstemperatur sondern auch die Zusammensetzung d.h. das Mischungsverhältnis des Sauerstoffs und Wasserdampfes im Reaktionsgasgemisch in möglichst weitem Masse verändert. In der Praxis haben wir so verfahren, dass man bei einer bestimmten Versuchstemperatur (d.h. bestimmten Temperatur des Katalysators) nicht eine Art des Reaktionsgasgemisches von der gewöhnlichen Zusammensetzung $O_2:H_2O = 2:1$ sondern vier Arten der Gasgemische verschiedener Zusammensetzung, d.h. $O_2:H_2O = 9:1, 4:1, 2:1$ und $1:1$, nacheinander, aber separat durch das Katalysatorrohr leitet. Die sonstigen Versuchsbedingungen sind genau dieselben wie oben bei der ersten Reihe der Versuche: die Strömungsgeschwindigkeit des Gasgemisches beträgt (bei Zimmertemperatur und unter gewöhnlichem Druck gemessen) 60 ccm pro Min. und das Aluminiumoxyd im Katalysatorrohr wird jedesmal (d.h. bei jedem Versuch von bestimmter Temperatur und mit einem Reaktionsgasgemisch von bestimmter Zusammensetzung) durch das frische Präparat ersetzt. Das in der vorliegenden Reihe der Versuche benutzte Reaktionsgasgemisch von bestimmter Zusammensetzung wird auf folgende Weise bereitet.

(3) Der früher in IV. Mitteil. vorläufig mitgeteilte Wert von $t(10\%) = 470^\circ$ soll durch diesen neueren Wert ersetzt werden.

Wenn z.B. das Reaktionsgasgemisch von der Zusammensetzung $O_2:H_2O=r:1$ bereitet werden soll, wird das Sättigungsgefäß (S. in Abb. 1 in I. Mittel) bis auf solch eine Temperatur konstant erwärmt, wo der Sättigungsdruck des schweren Wassers⁽⁴⁾ gerade $1/(r+1)$ atm. Druck beträgt. Lässt man nun durch das so erwärmte Sättigungsgefäß den aus der Elektrolyse des destillierten Wassers entwickelten Sauerstoffstrom mit der Geschwindigkeit von $60 \times (r/(r+1))$ ccm pro Min. durchblasen, so entsteht der Strom des Gasgemisches aus Sauerstoff und Wasserdampf, das offensichtlich die gewünschte Zusammensetzung ($O_2:H_2O=r:1$) und die Strömungsgeschwindigkeit (60 ccm pro Min.) besitzt. Die zur Bereitung der oben angegebenen vier Arten der Reaktionsgasgemische benutzten Versuchsbedingungen, d.h. die Temperatur, bis darauf das Sättigungsgefäß erwärmt wird und die Stärke des Gleichstroms, der zur Entwicklung des Sauerstoffstroms durch den Elektrolyseur geschickt wird,⁽⁵⁾ sind in Tabelle 2 wiedergegeben. Auf die Bedeutung der in den letzten drei Spalten der Tabelle angegebenen Faktoren kommen wir später zurück.

Tabelle 2. Versuchsbedingungen, die zur Herstellung der Arten der Reaktionsgasgemische verschiedener Zusammensetzung benutzt werden.

Zusammensetzung des Reaktions- gasgemisches $O_2 : H_2O$ ($r : 1$)	Temperatur des Sättigungs- gefäßes °C	Stromstärke durch den Elektrolyseur in Amp.	$\frac{(2r+1)(r+1)}{r}$	$\frac{(2r+1)}{r}$	$(2r+1)$
9 : 1	47	14.1	21.1	2.11	19.0
4 : 1	61	12.5	11.3	2.25	9.0
2 : 1	72	10.5	7.5	2.50	5.0
1 : 1	82	7.9	6.0	3.00	3.0

Die Ergebnisse der unter Verwendung der so bereiteten vier Arten der Reaktionsgasgemische bei drei verschiedenen Temperaturen durchgeführten Versuche sind in Tabelle 3 bis 5 zusammengestellt. Dabei wird das in der letzten Spalte der Tabellen angegebene prozentuale Austauschmass %A für das Reaktionsgasgemisch von der Zusammensetzung

$$O_2 : H_2O = 9 : 1 \quad \text{mittels der Gl.} \quad \%A = \frac{\Delta s_a - \Delta s_e}{35.9} \times 100,$$

$$,, \quad = 4 : 1 \quad ,, \quad \%A = \frac{\Delta s_a - \Delta s_e}{33.7} \times 100,$$

$$,, \quad = 2 : 1 \quad ,, \quad \%A = \frac{\Delta s_a - \Delta s_e}{30.3} \times 100,$$

$$\text{und} \quad ,, \quad = 1 : 1 \quad ,, \quad \%A = \frac{\Delta s_a - \Delta s_e}{25.3} \times 100 \quad (2)$$

(4) Da das wirklich verwendete schwere Wasser sehr verdünnt ist, kann sein Dampfdruck praktisch identisch mit dem des gewöhnlichen Wassers angesehen werden.

(5) Da zur elektrolitischen Entwicklung des Sauerstoffstromes mit der konstanten Strömungsgeschwindigkeit von 60 ccm pro Min. (bei 25° und unter atmosphärischem Druck gemessen!) der Gleichstrom von 15.7 Amp. erforderlich ist, haben wir die Stromstärke durch den Elektrolyseur konstant bei $15.7 \times (r/(r+1))$ Amp. gehalten, um das Reaktionsgasgemisch der Zusammensetzung von $O_2:H_2O=r:1$ zu bekommen.

berechnet, die mit Hilfe der analytischen Zusammensetzung des betreffenden Gasgemisches und der isotopischen Zusammensetzung des dabei benutzten schweren Wassers ohne weiteres abgeleitet werden.

Tabelle 3. Austauschversuch mit Reaktionsgasgemische ($O_2 + H_2O$) verschiedener Zusammensetzung bei 540° .

Strömungsgeschw. = 60 ccm pro Min., $\Delta s_a = 57.0 \gamma$, $\Delta s_a(O) = 36.3 \gamma$.

Zusammensetzung des Gasgemisches	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	%A	$-\log \left(1 - \frac{\%A}{100} \right)$
9 : 1	46.2	10.8	30	0.155
4 : 1	50.9	6.1	18	0.086
2 : 1	53.3	3.7	12	0.056
1 : 1	54.2	2.8	11	0.051

Tabelle 4. Austauschversuch mit Reaktionsgasgemische ($O_2 + H_2O$) verschiedener Zusammensetzung bei 600° .

Strömungsgeschw. = 60 ccm pro Min., $\Delta s_a = 57.0 \gamma$, $\Delta s_a(O) = 36.3 \gamma$.

Zusammensetzung des Gasgemisches	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	%A	$-\log \left(1 - \frac{\%A}{100} \right)$
9 : 1	38.3	18.7	52	0.319
4 : 1	44.6	12.4	37	0.201
2 : 1	48.5	8.5	28	0.143
1 : 1	52.0	5.0	20	0.097

Tabelle 5. Austauschversuch mit Reaktionsgasgemische ($O_2 + H_2O$) verschiedener Zusammensetzung bei 640° .

Strömungsgeschw. = 60 ccm pro Min., $\Delta s_a = 57.0 \gamma$, $\Delta s_a(O) = 36.3 \gamma$.

Zusammensetzung des Gasgemisches	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	%A	$-\log \left(1 - \frac{\%A}{100} \right)$
9 : 1	28.0	29.0	81	0.721
4 : 1	36.4	20.6	61	0.409
2 : 1	42.5	14.5	48	0.284
1 : 1	47.1	9.9	39	0.215

Theoretische Behandlung der Beziehung zwischen prozentualem Austauschmass %A und der Zusammensetzung des Reaktionsgasgemisches. Da wir oben in Tabelle 3 bis 5 den Einfluss der Zusammensetzung des Reaktionsgasgemisches ($O_2 + H_2O$) auf dem prozentualen Austauschmass %A experimentell festgestellt haben, wollen wir diese Ergebnisse vom theoretischen Standpunkt behandeln. Zu diesem Zweck kommt die früher abgeleitete Gl. in Betracht:

$$-v \log \left(1 - \frac{\%A}{100} \right) = K \left(\frac{dN_o}{dt} \right) \quad (3),$$

die die Beziehung zwischen dem prozentualen Austauschmass $\%A$ und der Geschwindigkeit der Austauschreaktion (dN_o/dt) d.h. der Zahl der Sauerstoff- bzw. Wasserdampfmoleküle angibt, die in einer Volumeneinheit des Reaktionsgasgemisches jede Sekunde ausgetauscht werden. In dieser Gl. (3) wird die Grösse der Konstante K durch die Gl. bestimmt:

$$K = 637000 \frac{(2r+1)(r+1)}{2r} \frac{(V-V_o)}{N} \quad (4),$$

vorausgesetzt, dass die Zusammensetzung des in Rede kommenden Reaktionsgasgemisches durch die Gl. angegeben:

$$O_2 : H_2O = r : 1 \quad (5),$$

weiter die Strömungsgeschwindigkeit v in ccm pro Min., die Austauschgeschwindigkeit (dN_o/dt) in Molekül pro Sek., das Volumen V des Katalysatorraumes und das V_o des Katalysators beide in ccm gemessen und mit N die Loschmidtsche Zahl ausgedrückt wird. Wir können aber Gl. (3) mit Hilfe der Gl. (4) ohne weiteres wie folgt umformen:

$$-\log \left(1 - \frac{\%A}{100} \right) = K' \frac{(2r+1)(r+1)}{r} \left(\frac{dN_o}{dt} \right) \quad (6).$$

Dabei wird die neue Konstante K' offensichtlich durch die Gl. bestimmt:

$$K' = 637000 \frac{(V-V_o)}{2Nv} \quad (7).$$

Die Beziehung zwischen dem prozentualen Austauschmass $\%A$ und der Zusammensetzung r des Reaktionsgasgemisches wird im allgemeinen durch diese Gl. (6) angegeben. Da aber die Austauschgeschwindigkeit (dN_o/dt) selbst auch eventuell durch die Zusammensetzung des Reaktionsgasgemisches beeinflusst werden kann, kann der auf der linken Seite der Gl. (6) stehende Ausdruck $\{-\log(1-\%A/100)\}$ durch die Veränderung der Zusammensetzung des Reaktionsgasgemisches auf verschiedene Weise und Art beeinflusst werden. Falls z.B. die Austauschgeschwindigkeit (dN_o/dt) ohne Rücksicht auf die Zusammensetzung r des Reaktionsgasgemisches immer konstant bleibt, kann Gl. (6) wie folgt vereinfacht werden:

$$-\log \left(1 - \frac{\%A}{100} \right) \propto \frac{(2r+1)(r+1)}{r} \quad (8),$$

$$\text{bzw.} \quad \frac{-\log \left(1 - \frac{\%A}{100} \right)}{\frac{(2r+1)(r+1)}{r}} = F_1(\%A, r) = \text{Konst.} \quad (9).$$

Dies tritt u. a. in dem Fall auf, wenn der eine der Reaktionsteilnehmer, d.h. Sauerstoff- bzw. Wasserdampfmoleküle, durch das Aluminiumoxyd sehr stark adsorbiert wird und die Desorptionsgeschwindigkeit der so ausgetauschten Sauerstoff- bzw. Wasserdampfmoleküle aus der Oberfläche des Katalysators oder die Geschwindigkeit der Austauschreaktion in der Adsorptionsschicht selbst den Verlauf der ganzen Reaktion beherrscht. Wenn das aber nicht der Fall ist, d.h. die Austauschgeschwindigkeit (dN_o/dt) mehr oder weniger durch die Zusammensetzung des Reaktionsgasgemisches beeinflusst wird, bleibt der Ausdruck F_1 in Gl. (9) offensichtlich nicht mehr konstant und statt dessen muss die andere Form der Beziehung zwischen $\%A$ und r bestehen. Weil aber die Form dieser Beziehung je nach der Art und Weise der Abhängigkeit der Austauschgeschwindigkeit von der Zusammensetzung des Gasgemisches im allgemeinen sehr kompliziert sein muss, wollen wir hier nur zwei einfache Fälle auswählen. Die eine einfache Beziehung dabei besteht, wenn die Austauschgeschwindigkeit (dN_o/dt) mit dem Teildruck des Wasserdampfes im Reaktionsgasgemisch direkt proportional wächst. In diesem Fall folgt aus Gl. (6) ohne weiteres die Gl.:

$$\frac{-\log\left(1 - \frac{\%A}{100}\right)}{\frac{(2r+1)}{r}} = F_2(\%A, r) = \text{Konst.} \quad (10),$$

weil der Teildruck des Wasserdampfes im Reaktionsgasgemisch offensichtlich der Grösse $1/(r+1)$ direkt proportional ist. Wächst dagegen die Austauschgeschwindigkeit (dN_o/dt) mit dem Teildruck des Sauerstoffs ($r/(r+1)$) direkt proportional, so muss die Beziehung bestehen:

$$\frac{-\log\left(1 - \frac{\%A}{100}\right)}{(2r+1)} = F_3(\%A, r) = \text{Konst.} \quad (11).$$

Obwohl auch viele andere Formen der Beziehungen gemäss der Abhängigkeitsweise der Austauschgeschwindigkeit von der Zusammensetzung des Reaktionsgasgemisches denkbar sind,⁽⁶⁾ wollen wir vorläufig die oben abgeleiteten drei Beziehungen (9) bis (11) mit den wirklich erhaltenen Versuchsergebnissen vergleichen. So werden die drei Arten der Ausdrücke F_1 , F_2 und F_3 in Gln. (9), (10) und (11) unter Benutzung der in Tabellen 2 bis 5 angegebenen Daten berechnet und in Tabelle 6 wiedergegeben.

Die Rechnungsergebnisse in Tabelle 6 zeigen ziemlich deutlich, dass der erste Ausdruck F_1 (vgl. Gl. (9)) fast unabhängig von der Zusammensetzung des Reaktionsgasgemisches konstant bleibt. Daraus darf wohl geschlossen werden, dass die in Rede kommende Austauschreaktion mindestens innerhalb der benutzten Versuchsbedingungen unabhängig von

(6) Um eine eventuell vorhandene Abhängigkeit der Reaktionsgeschwindigkeit der Zusammensetzung des Reaktionsgasgemisches herauszufinden, hat man vielleicht die letztere noch in viel weitere Grenze als die vorliegende variieren zu lassen.

Tabelle 6. Experimentelle Prüfung der Beziehungen zwischen dem prozentualen Austauschmass %A und der Zusammensetzung des Reaktionsgasgemisches r .

Zusammensetzung des Gasgemisches $O_2 : H_2O$ ($r : 1$)	540°			600°			640°		
	$F_1 \cdot 10^3$	$F_2 \cdot 10^2$	$F_3 \cdot 10^3$	$F_1 \cdot 10^3$	$F_2 \cdot 10^2$	$F_3 \cdot 10^3$	$F_1 \cdot 10^3$	$F_2 \cdot 10^2$	$F_3 \cdot 10^3$
9 : 1	7.3	7.3	8.2	15.1	15.1	16.8	34.2	34.2	28.0
4 : 1	7.6	3.8	9.1	17.8	8.9	21.2	36.3	18.2	45.5
2 : 1	7.5	2.2	11.2	19.1	5.7	28.6	37.9	11.4	56.8
1 : 1	8.5	1.7	17.0	16.1	3.2	32.2	35.8	7.2	71.7
Mittel	7.7	—	—	17.0	—	—	36.1	—	—

der Zusammensetzung des Reaktionsgasgemisches mit konstanter Geschwindigkeit verläuft. Dieses Ergebnis kann aber, wie darauf schon oben hingewiesen wurde, mindestens auf dreierlei Weise gedeutet werden: entweder die Desorption der ausgetauschten Wassermoleküle bzw. Sauerstoffmoleküle aus der Oberfläche des Katalysators oder die Austauschreaktion in der Adsorptionsschicht selbst wirkt massgebend. Zwischen diesen drei Möglichkeiten können wir bloss aus dem vorliegenden Versuchsergebnisse nicht so ohne weiteres zu einer Unterscheidung kommen. Aber aus der wohl bekannten Tatsache, dass der Wasserdampf durch das Aluminiumoxyd viel stärker als das Sauerstoffgas adsorbiert wird (aktivierte Adsorption!),⁽⁷⁾ liegt die Annahme sehr nahe, dass bei der in Rede kommenden katalytischen Austauschreaktion die Desorption der aktiviert adsorbierten Wasserdampfmoleküle der geschwindigkeitsbestimmende Prozess ist, d.h. die aktive Oberfläche des Aluminiumoxyds durch die Wasserdampfmoleküle fast bis zur Sättigung bedeckt wird und die Geschwindigkeit, mit der die so aktiviert adsorbierten und folglich gegen die aus der Gasphase hineinfliegenden Sauerstoffmoleküle bis zum Gleichgewicht ausgetauschten Wasserdampfmoleküle wieder desorbiert werden, den Verlauf der ganzen Reaktion beherrscht. Unter dieser Voraussetzung sind wir in der Lage diese Desorptionsgeschwindigkeit der aktiviert adsorbierten Wasserdampfmoleküle mit Hilfe der Gl. (6) zu berechnen, weil die Austauschgeschwindigkeit (dN_o/dt) in dieser Gl. der eben angegebenen Annahme nach nichts anders als die in Rede kommende Desorptionsgeschwindigkeit der Wasserdampfmoleküle aus der Oberfläche des Aluminiumoxyds ausdrückt.

Setzt man also in Gl. (7) den in Tabelle 6 angegebenen Wert von F_1 bei resp. Temperatur ein (vgl. Gl. (9)) und wird weiter gemäss der wirklich benutzten Versuchsbedingungen $v = 60$ ccm pro Min., $V = 12$ ccm und $V_o = 10/3.9 = 2.6$ ccm gesetzt, so ergibt sich der gewünschte Wert von (dN_o/dt), der in Tabelle 7 wiedergegeben ist.

(7) H.S. Taylor und A.J. Gould, *J. Am. Chem. Soc.*, **56** (1934), 1685; L.A. Munro und F.M.G. Johnson, *J. Phys. Chem.*, **30** (1926), 172.

Tabelle 7. Die Austauschgeschwindigkeit bzw. die Aktivierungs-
geschwindigkeit des Wasserdampfes an der Oberfläche
des Aluminiumoxyds.

Temperatur °C	540°	600°	640°
$(dN_o/dt) \cdot 10^{-17}$ Moleküle pro Sek.	0.94	2.07	4.38

Bei einem früheren Versuch (vgl. VIII. Mitteil.), wo die Geschwindigkeit derselben Austauschreaktion in Abhängigkeit von der Strömungsgeschwindigkeit des Reaktionsgasgemisches untersucht wurde, kamen wir zu dem Ergebnis, dass die Austauschgeschwindigkeit (dN_o/dt) bei 570° 2.1×10^{17} Moleküle pro Sek. beträgt. Die oben in Tabelle 7 angegebenen Werte von (dN_o/dt) stehen mit diesem letzteren befriedigend im Einklang.

Ermittlung der Aktivierungsenergie. Wir haben oben in Tabelle 1 das prozentuale Austauschmass %A in Abhängigkeit von der Temperatur gefunden. Da aber bei diesem Versuch die Strömungsgeschwindigkeit v und die Zusammensetzung r des Reaktionsgasgemisches konstant gehalten wird, muss der Ausdruck $\{-\log (1-\%A/100)\}$ gemäss Gl. (6) der wahren Austauschgeschwindigkeit (dN_o/dt) direkt proportional sein. Aus diesem Grunde wird in Abb. 1 der in der letzten Spalte der Tabelle 1 angegebene Wert von $\log \{-\log (1-\%A/100)\}$ gegen den reziproken Wert der absoluten Temperatur $1/T$ eingezeichnet. Die so erhaltene gerade Linie kann aber durch die Gl. befriedigend wiedergegeben werden:

$$\log \left\{ -\log \left(1 - \frac{\%A}{100} \right) \right\} = 3.8 - \frac{18,000}{4.576T} \quad (12).$$

Weil aber nun die Konstante K' in Gl. (6) durch Gl. (7) bestimmt wird, kann der Ausdruck $\log \{-\log (1-\%A/100)\}$ in obiger Gl. (12) mit Hilfe dieser beiden Gln. (6) und (7) durch die Austauschgeschwindigkeit (dN_o/dt) ersetzt werden, indem man in der letzteren Gl. (7) gemäss der wirklich benutzten Versuchsbedingungen $v=60$ ccm pro Min., $V=12$ ccm, $V_o=2.6$ ccm und $r=2$ setzt:

$$\log \left(\frac{dN_o}{dt} \right) = 22.0 - \frac{18,000}{4.576T} \quad (13).$$

Nach dieser Gl. beträgt die Aktivierungsenergie der vorliegenden katalytischen Austauschreaktion 18 Kcal. Diese letztere Energie kann aber auch mit Hilfe der in Tabelle 7 angegebenen Werte von (dN_o/dt) bei verschiedenen Temperaturen ohne weiteres ermittelt werden. Zu diesem Zweck wird wie üblich in der nebenstehenden Abb. 3 der Logarithmus von (dN_o/dt) gegen den reziproken Wert der absoluten Temperatur $1/T$ eingetragen. Dabei werden neben der in Tabelle 7 angegebenen Werte von (dN_o/dt) bei drei verschiedenen Temperaturen auch der früher bei 570° gefundene eingezeichnet (vgl. oben). Die so eingetragenen vier Punkte in Abb. 3 lassen sich aber durch die Gl. wiedergeben:

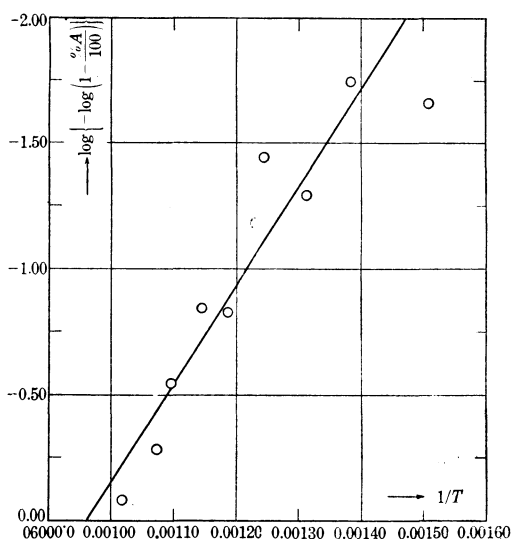
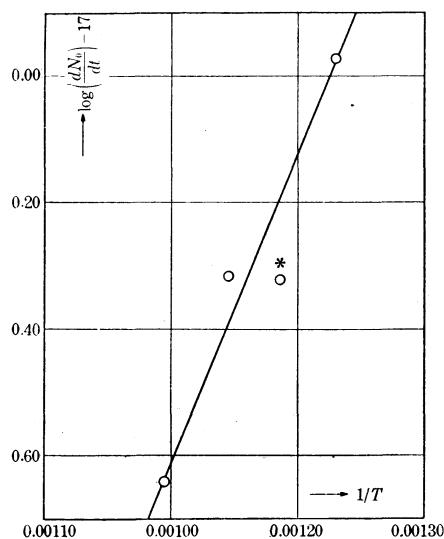


Abb. 2. Abhängigkeit des Austauschmass
%A der Temperatur T .



* Früheres Experiment
(Vgl. VIII. Mitteil.).

Abb. 3. Abhängigkeit der Aus-
tauschgeschwindigkeit (dN_0/dt)
der Temperatur T .

$$\log \left(\frac{dN_0}{dt} \right) = 23.1 - \frac{22,000}{4.576T} \quad (14).$$

Der Stossfaktor sowie die Aktivierungsenergie in dieser Gl. (14) stimmen mit den in obiger Gl. (13) befriedigend überein. Die Aktivierungsenergie A der vorliegenden Reaktion beträgt also etwa 18 bis 22 Kcal.:

$$A = 18 \sim 22 \text{ Kcal.} \quad (15).$$

Diese Energie muss aber nach dem oben angenommenen Mechanismus der vorliegenden Reaktion gerade dazu verbraucht werden, um die an der Oberfläche des Aluminiumoxyds adsorbierten Wassermoleküle bis zur Desorption zu aktivieren. Nach dem Versuch von Taylor und Gould⁽⁷⁾ beträgt die Adsorptionswärme der aktivierten Adsorption des Wasserdampfes an der Oberfläche des Aluminiumoxyds 14.6 bis 18.3 Kcal. Aus diesen beiden Energiewerten folgt ohne weiteres, dass die Aktivierungsenergie für die aktiviert Adsorption des Wasserdampfes an der Oberfläche des Aluminiumoxyds (als Unterschied zwischen der Aktivierungsenergie für die Desorption und der Adsorptionswärme) 3 bis 5 Kcal. beträgt. Diese Energie wurde bis jetzt, wenigstens so weit wir wissen, nicht direkt gemessen. Aber aus den anderen ähnlichen veröffentlichten Daten zu urteilen,⁽⁸⁾ erscheint uns der eben gefundene Wert (3 bis 5 Kcal.) von sehr plausibler Grösse als Aktivierungsenergie für die aktivierte

(8) Vgl. z.B. H.S. Taylor und A.T. Williamson, *J. Am. Chem. Soc.*, **53** (1931), 813, 2168.

Adsorption zu sein. Dieses Ergebnis darf deshalb als eine weitere Stütze für die oben angegebene Annahme angesehen werden, dass bei der katalytischen Austauschreaktion zwischen Wasserdampf und Sauerstoff an der Oberfläche des Aluminiumoxyds die Desorption der aktiviert adsorbierten Wasserdampfmoleküle eine massgebende Rolle spielt.

Herrn Prof. T. Titani möchte ich für sein warmes Interesse an dieser Arbeit ergebenst danken. Der Nippon Gakuzyutu-Sinkōkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hōkōkai (der Hattori-Stiftung), die durch Gewährung des Stipendiums die Ausführung dieser Arbeit ermöglicht haben, bin ich auch zu grossem Dank verpflichtet.

Osaka Teikoku Daigaku Rigaku-bu
Kagaku Kyositu
(Chemisches Institut der wissenschaftlichen
Fakultät der Kaiserlichen Universität Osaka)

Studies on the Organic Molecular Compounds. Part V. On the Formation of Some Crystalline Organic Molecular Compounds.

By Chiro SHINOMIYA.

(Received May 20, 1940.)

The formation of "Molecular lattice" construction in the crystalline state is not confined to ordinary organic compounds but organic molecular compounds with fairly simple molecular ratio of parent components, probably also form certain regularly ordered crystal lattices. Zachariasen⁽¹⁾ and Robertson⁽²⁾, from X ray analysis of oxalic acid dihydrate, found a unit lattice of $(\text{CO}_2\text{H})_2$ and $2\text{H}_2\text{O}$ being regularly arranged and oriented, and Hertel (earlier but in less detail) studied the crystal lattice of aromatic-nitroaromatic molecular compounds⁽³⁾.

Of the unit lattice of molecular compounds, numerous variations in the lattice type are possible, owing to the differences of the number of included molecules, their arrangement and their orientation. Although these differences may be due to the molecular structure of their components, it is nevertheless not an easy matter to treat them comprehensively and conclusively. The theories offered and experiments made with a view to solve this problem are yet too scanty, although from experimental induction and by comparing a number of organic molecular compounds very similarly constituted, it was found that the compound-formation, namely, the formation of crystalline molecular compounds, is most closely related to the configuration, particularly, to the molecular shape (as a whole) of the components. Although compound-formation in the crystalline state differs from that of the simple molecular compounds formed in the dilute solution, the former has also a regularity in structure.

The following two types of combination exist, for example, in the binary systems of naphthalene monosubstitution products with nitro compounds:



It is seen that nitro radicals combine with the unsaturated carbon linkings in (I), and that hydroxyl radical combines with the substituent of naphthalene nucleus in (II), these two types being called here for convenience "the compound of the first and the second type" respectively. Some of the differences in the two types, especially, halochromic phenomenon (prominent in the first type but not in the second), has often been used as a criterion to distinguish the two types.

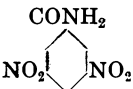
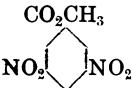
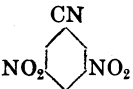
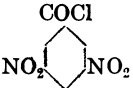
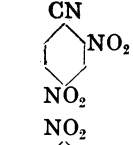
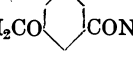
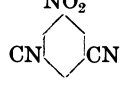
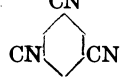
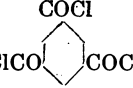
(1) W. H. Zachariasen, *Z. Kryst.*, **89** (1934), 529.

(2) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, **1936**, 1817.

(3) E. Hertel and H. Kleu, *Z. physik. Chem.*, B, **11** (1931), 59; E. Hertel and K. Schneider, *Z. physik. Chem.*, B, **13** (1931), 387.

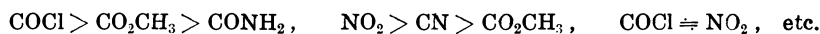
The writer compared, chiefly in compounds Type I, the compound-formation of naphthalene monosubstitution products⁽⁴⁾ between them, and pointed out the greater tendency of compound-formation of the α -isomer and so the stronger hindering effect of the β -isomer, the results being shown in Tables 1⁽⁵⁾ and 2⁽⁶⁾.

Table 1. Molecular Compounds obtained from Solution by Bennet.

Mol ratio A : B (Melting point) τ Colour B [Melting point]	A			
		α -Naphthylamine	β -Naphthylamine	Naphthalene
 [183]		1 : 1 (149) 32.5 Scarlet	—	—
 [112]		1 : 1 (120) 39 Deep red	1 : 1 (90) —21 Orange	1 : 1 (80) —16 Lemon yellow
 [127]		1 : 1 (169) 80.5 Dark red	1 : 1 (113.5) —5.0 Deep red	1 : 1 (123) 19.5 Pale yellow
 [74]		—	—	1 : 1 (127) 50 Pale yellow
 [100]		m : n Strong halochromic	1 : 1 [135]* 29.1 Strong halochromic	m : n Halochromic
 [>300]		m : n Strong halochromic	m : n Strong halochromic	—
 [205]		1 : 1 (149) 21.5 Deep red	1 : 1 (107.5) —50.0 Dark red	m : n Halochromic
 [263]		1 : 1 (167) 10.5 Dark yellow	m : n Halochromic	✓ Not halochromic
 [37]		—	—	1 : 1 (101) 42.5 Almost colourless

* This system, and all those in Table 2—5, were verified by phase diagrams.

Bennet noted the following orders of diminishing tendency of substituents to promote compound-formation :



(4) Part IV, This Bulletin, **15**, (1940), 281.

(5) G. M. Bennet and R. L. Wain, *J. Chem. Soc.*, **1936**, 1109.

(6) Data from the literature with writer's additional data.

Table 2. Binary Systems of Type I.

Mol ratio A : B [Melting point] τ	A	α -Naphthol	β -Naphthol
B			
Acetophenone		1 : 1 [13] -44.9	1 : 1 U
Benzophenone		1 : 1 [38]	✓
Chalkone		✓	✓
Dibenzalacetone		2 : 1 [68] -33.3	✓
Dianisalacetone		3 : 2 [69] -40.2	3 : 2 [74] -50.8
<i>p</i> -Quinone		1 : 1 [100] -6.0 or 2 : 1 [120] 7.3 or 1 : 2	1 : 1 [85] -34.0 or 2 : 1 or 1 : 2
Fenchone		1 : 1 [60.5]	1 : 1 U
Antipyrine		1 : 2 [73]	1 : 1 [79.5]
Dimethylpyrone		{ 1 : 1 [69.8] 3 : 2 [79.1]	{ 2 : 1 [44.6] 3 : 2 [39.5]
Cineole*		1 : 1 [75]	1 : 1 [48]

* Some more cyclic ethers were synthesized, and the superior compound-formation of α -naphthol investigated (Bennet, Wain, *J. Chem. Soc.*, 1936, 1114.).

The molecular compounds shown in Table 1, synthesized and observed by Bennet, had a halochromium similar to those of nitro molecular compounds, the order of compound-formation given by him being in good agreement with that of the value τ in Table 1. The quinones, which are very halochromic in these combinations, were investigated in a series of experiments by Pfeiffer, and proved by him to belong to this type⁽⁷⁾. It is noteworthy that, as in the *p*-quinone, which is regarded as one of the cyclic ketones, the ketones also form more easily a compound with α - than with β -naphthol.

The substitution radical in combination Type I that showed no direct effects upon the formation of molecular compounds, ought to function as the point of contact in combination Type II, and consequently there must be here a greater tendency of compound-formation in β -position. This was actually confirmed by the data of Tables 3⁽⁶⁾ and 4⁽⁶⁾.

When the compounds of a binary system have substituents either the same or similar to each other, then the tendency of compound-formation diminishes to a marked degree. For example, in Table 5, the binary system was of simple eutectic type, or of a eutectic type with two solid solutions⁽⁸⁾, or it was of a very feeble compound type.

(7) P. Pfeiffer, "Organische Molekülverbindungen," 2 Aufl., 282, Stuttgart (1927).

(8) The so-called "Roseboom's MKV Type" which seemed to be less compound-formable than the compound type, together with those of other solid solutions.

Table 3. Binary Systems of Type II.

Mol ratio A : B [Melting point] τ B	α -Naphthol	β -Naphthol
Trimethylcarbinol	1 : 2 [1] -48.0	1 : 2 [24] -33.7
Diphenylcarbinol	✓	2 : 3 [62] -27.6
Triphenylcarbinol	✓	✓
<i>m</i> -Aminophenol	✓	1 : 1 [99] -23.5
Aniline	{ 1 : 1 [32] -12.9 1 : 2 [28] 0.1	1 : 1 [82] 24.1
<i>p</i> -Toluidine	1 : 1 [53.6] -16.3	1 : 1 [81.2] -1.7
<i>o</i> -Phenylenediamine	1 : 1 [60] -39.9	1 : 1 [86] -26.9
<i>m</i> - " "	1 : 1 [35] -44.4	2 : 1 [114] 11.7
<i>p</i> - " "	2 : 1 [110] -0.6	2 : 1 [150.5] 22.6
α -Naphthylamine	1 : 4 [43] -16.2	2 : 3 [66] -12.8
β - " "	✓	2 : 1 [123] 5.0
Acridine	{ 1 : 1 [116] 14.0 1 : 2 U	{ 3 : 2 [135] 18.6 1 : 2 U
Carbazol, Azobenzene, } Diphenylamine, } Benzamide, Urea }	✓	✓
Acetamide	✓	1 : 1 [63]
Succinimide	✓	1 : 1 [87.5]

Table 4. Binary Systems of Type II.

Mol ratio A : B [Melting point] τ B	α -Naphthylamine	β -Naphthylamine
Trimethylcarbinol	{ 2 : 1 [30.5] -11.3 1 : 2 [24] -9.7 1 : 6 [16] -13.0	{ 2 : 1 [95] 13.2 1 : 2 U
Triphenylcarbinol	6 : 1 [41] -25.1	2 : 1 [D : 92] -35.5
Diphenylcarbinol	✓	✓
Pyrogallol	2 : 1 U	2 : 1 [121.5] 3.5
Catechol	1 : 2 [43.4] -43.3 or 1 : 1	1 : 1 [77.6] -29.9
Resorcinol	1 : 1 U ?	1 : 1 [81.3] -28.7
Hydroquinol	1 : 1 U	1 : 2 [142] -8.3
Phenol	1 : 1 [28.6] -16.9	1 : 1 [83.5] 8.0
<i>m</i> -Aminophenol	✓	1 : 1 [D : 91] -25.5
Salicylic acid	1 : 1 U	1 : 1 U
Benzoid acid, } Cinnamic acid }	✓	✓
Succinic acid	✓	1 : 1 [133.5] -14.0
Acetic acid	✓	✓

The guaiacol and the three cresols are formed of exceptionally inferior compound-formation with β -naphthylamine, which has a relatively high melting point compared with the above mentioned four substances.

Naphthols and naphthylamines are believed to have an ester or salt type of combination with alcohols, amines, and acids.

Table 5. Binary Systems of *sym*-Trinitrobenzene and its Derivatives.

*** A:B B	A							
	✓*	✓* or 1:1*	✓*	✓*	✓*	✓* or 2:3 D*	—	✓*
	✓**	✓**	✓ [59.5] 8%	(MKV) [50] 16%	MKV [55] 9%?	✓**	MKV [34.0] 45%	
	MKV [61.5] 35%	MKV*	MKV [72.5] 10%	MKV [55.0] 34%	MKV [65.0] 11%	2:1 [77] or 1:1*		
	1:1 [D:60]?**	✓* [58.5]	MKV [75.0] 9%	✓*	✓* or (MKV) [71.5] 11%			
	✓* or (MKV [104.0] 81%	MKV*	MKV	✓ [68.8]*				
	MKV [67.0] 49%	✓*	MKV [94.0] 20%					
	MKV [110.0] 67%	MKV*						
	✓**							

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., 122.

** The writer's value, with corrections (Shinomiya, Asahina, *J. Chem. Soc. Japan*, 57 (1936), 732; 58 (1937), 118.).

*** Type A—B, [Melting point or eutectic point], weight % of A in the eutectic point, are here noted.

Trinitrotoluene was found to form some molecular compounds in these combinations.

Bennet, who noticed that there was no crystalline molecular compound of picric acid with *p*-quinone⁽⁹⁾, similarly proved *sym*-trinitrobenzene—antimony trichloride to be a simple eutectic system.

The writer showed also that the hindering effect was due to the magnitude of the substituent radicals as the result of chelation or of steric causes⁽⁴⁾. By substituting a long aliphatic chain in the naphthalene ring, the aromatic character diminished and the characteristic aliphatic properties progressively increased⁽¹⁰⁾.

Needless to say, in the case of formation of crystalline molecular compounds in the binary systems, the influence of association, not the combination of the two component molecules A—B, but of the same component molecules A—A or B—B, is also to be considered. Although this is generally not pronounced, qualitatively speaking, substitution of a radical with strong association in the α -position of naphthalene ring results especially in considerable rise in the melting point of the α -substitution product. In case that such atomic groups, for example, as $-\text{CONH}_2$, or $-\text{CONH}-$ (regarded as the most strongly associated), are introduced in the α -position, we cannot expect the greater tendency of combination even in Type I. Experimental researches together with remarks on these problems will be treated in a separate paper.

Summary.

Compound-formation in the crystalline state was found to be most closely related to the configuration, especially, to the molecular shape of the two components. Molecular compounds of different types were distinguished by the mode of compound-formation, such as the type of phase diagrams, "melting point elevation", and halochromism.

The writer wishes to express his sincere thanks to Prof. B. Kubota and to Prof. Y. Shibata of the Tokyo Imperial University for their kind guidance and encouragement throughout this study and to Dr. T. Asahina for much valuable advice. Thanks are also due to the Hattori-Hôkôkai for the grant, with the aid of which the expenses of the study were defrayed.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo
and
Kumamoto Higher Technical School.*

(9) G. M. Bennet and G. H. Willis, *J. Chem. Soc.*, **1929**, 261.

(10) Not yet published.

Polymerisation of Tung Oil. II. Gelation of Tung Oil by Catalytic Action of Iodine.

By Monzi TATIMORI.

(Received August 13, 1940.)

The author hitherto studied about the polymerisation and gelation of tung oil at high temperature such as 260–280°C. and obtained several interesting results.⁽¹⁾ When neutral substances were added to tung oil, the reciprocals of gelation times of the mixture had a linear relation to the amount of addition and from which the values of ∞ , the amount of addition necessary to make the gelation time of tung oil infinitely long, were obtained. This value is considered to be proportional to the gelation accelerating action of the added reagent.⁽²⁾ It has been proved also that these conclusions could be applied to the other drying oils which have similar constitution to that of tung oil.⁽³⁾ But in the presence of the catalytically acting substances such as S, Se, the gelation was strongly retarded and the relation between the gelation time and the amount of addition was different from that of neutral substances and the logarithm of gelation time was proportional to the amount of addition⁽⁴⁾.

It is known that several acidic substances such as I_2 , HNO_3 , HCl , $FeCl_3$, S_2Cl_2 , $AlCl_3$, $ZnCl_2$, $SbCl_3$, have gelation accelerating action upon tung oil at room temperature⁽⁵⁾. These facts were used usually as the identification and estimation of tung oil, but reports were not published in details.

Experimentals. Iodine as catalyser and chloroform as solvent were used at first and the measurements were carried out at 25°C. Tung oil (density at 25°C. 0.9356) was weighed in a 200 c.c. three necked bottle into which chloroform solution of iodine was poured under stirring and the gelation time was measured. When the polymerisation of tung oil proceeded considerably, a small gelatinous mass floated on the surface of the sample and after a while the whole mass stuck to the stirring rod, this instant was noted as the gelation time. Between the times of gelation beginning and gelation finishing the difference of 3–10% was observed. As the gelation of tung oil at low temperature is a kind of catalytic reaction, the degree of mixing of tung oil and iodine has a considerable effect on the absolute value of gelation time. The dimension of the apparatus used in this experiment is shown in Fig. 1.

(1) M. Tatimori, this Bull., **13** (1938), 142; *J. Soc. Chem. Ind. Japan*, Suppl. Bd., **41** (1938), 39, 100; **42** (1939), 162; **43** (1940), 102, 136.

(2) The summarizing report of the gelation of tung oil will be published later.

(3), (4) Not yet published.

(5) J. Marcusson, *Angew. Chem.*, **33** (1920), 235; Melhiny, *Ind. Eng. Chem.*, **4** (1912), 96; Nagel and Grüss, *Wissenschaft. Veröff. Siemens Konzern*, **4** (1925), 284; M. Th. François, *Bull. Sci. Pharmacol.*, **41** (1934), 269.

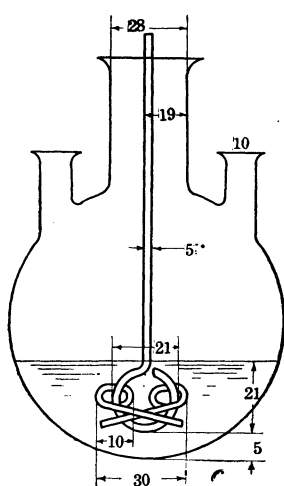


Fig. 1.

The gelation time is affected by the velocity of stirring and decreases according to the increase of the velocity of revolution. In the following experiments the revolution of 360 per minute was used.

From the results of the several experiments, the next relation has been found,

$$\log t = ax + b/zx \quad (1).$$

Where t is the gelation time in second, x the volume of tung oil, $(30-x)$ the volume of solvent, z the weight of iodine in gram, a and b the constants.

It is known that $\log t$ has a minimum value at $x = b/za$, by differentiating the equation (1) and when x is kept constant the relation between $\log t$ and $1/z$ is linear. These are proved experimentally.

Experiments were conducted with the systems of tung oil—chloroform—iodine, tung oil—glacial acetic acid—iodine, and tung oil—soya bean oil—chloroform—iodine.

The above formula could be applied to all these systems. One of the examples were shown in Table 1.

Table 1.

Volume of oil (Tung oil 95% Soya bean oil 5%) x c.c.	Volume of Solvent. $(30-x)$ c.c.	Amount of Iodine z g.	Gelation time t (sec.)	$\log t$	$\frac{1}{x}$	$\frac{1}{z}$
10	20	0.1775	838	2.923	0.1030	5.634
12	18	„	521	2.717	0.0833	„
15	15	„	442	2.645	0.0677	„
20	10	„	650	2.813	0.0500	„
23	7	„	932	2.969	0.0435	„
10	20	0.3550	46	1.663	0.1000	2.817
10	20	0.3195	70	1.845	„	3.130
10	20	0.2340	108	2.033	„	3.521
10	20	0.2485	172	2.236	„	4.024
10	20	0.2130	308	2.489	„	4.693

Next the effects of solvent were examined. The gelation times of the systems of 10 c.c. of tung oil and 20 c.c. of solvents were measured at 25°C. The results were shown in Table 2.

From Table 2 it was noticed that iodine in the solvents containing halogens has great accelerating action upon the gelation of tung oil and in the solvents containing oxygen has no or very weak gelation accelerating action. It is a very remarkable fact that the colour of iodine solution

Table 2.

Solvent	Amount of iodine	Gelation time (sec.)
Pentane	Saturated solution	11450
Hexane	"	3340
Cyclohexane	0.355 g. (a)	2745
Tetraline	a	7890
Benzene	"	286
Toluene	"	680
Xylenes	Saturated sol.	>18000
Petroleum ether	"	>16800
Benzin	"	1340
Mineral spirit	"	430
Kerosine	"	5030
Solvent naphtha	"	965
Chloroform	a	61
Carbon tetrachloride	"	125
Bromoform	"	1595
Ethylene dichloride	"	11.5
Trichloroethylene	"	50
Ethylene dibromide	"	92
Chlorobenzene	"	15
Para-aldehyde	"	4150
Glycerine dichlorohydrine	"	22
Glacial acetic acid	"	15.2
Acetic acid anhydride	"	10.2
Lactic acid	Saturated sol.	1545
Triacetin	a	135
Ethyl acetate	"	6560
Nitrobenzene	"	2.5
Carbon disulphide	"	280
Ether	"	> 9600
Acetone	"	> 7800
Methyl ethyl ketone	"	>15000
Butyl alcohols	"	> 6600
Benzyl alcohol	"	> 7000
Butyl acetates	"	> 9600
<i>m</i> -cresol	"	>30000
Aniline	"	>19800
<i>o</i> -toluidine	"	>18000

in the oxygen containing solvent is yellowish brown, on the other hand the colour of the iodine solutions which have strong gelation accelerating action are of violet tint. But the solvents from glycerine dichlorohydrine to nitrobenzene in Table 2 are exceptions and in spite of yellowish brown tint, have a strong gelation accelerating action.

In Table 3 the colour of iodine solutions were shown.

The solvents not shown in the Table have the violet tint as that of chloroform. The colour of the solution was determined by the Rovibond's Tintometer using 1/16 inch cell.

Table 3.

Solvent	Amount of iodine	Yellow	Red	Blue
Chloroform	0.355 g. (a)	—	54.0	0.8
Xylenes	Saturated sol.	20.0	28.0	—
Ethyl acetate	a	10.0	45.0	—
Butyl acetates	,,	20.0	23.0	—
Benzyl alcohol	,,	22.0	32.0	—
Acetone	,,	30.0	8.5	—
Methyl ethyl ketone	,,	30.0	4.4	—
Butyl alcohol	,,	7.0	33.0	—
<i>m</i> -cresol	,,	4.6	52.6	—
Aniline	,,	0.5	0.1	—
Glycerine dichlorohydrine	,,	20.0	33.0	—
Lactic acid	Saturated sol.	30.0	9.0	—
Acetic acid anhydride	a	14.0	30.0	—
Glacial acetic acid	,,	40.0	25.0	—
Triacetin	,,	35.0	21.0	—
Para-aldehyde	,,	12.0	35.0	—
Nitrobenzene	,,	5.2	40.0	—

It is a new fact that the violet solutions of iodine have strong gelation accelerating action. The gelation times of the mixture of two solvents were shown in Tables 4 and 5.

Table 4.

Solvent	Gelation time (sec.)	Dielectric constant at 25°C	Abbreviation (see Fig. 3)
(1) Benzene-nitrobenzene (% of nitrobenzene)			
0	286	2.28	—
5	105	3.10	105
10	47.5	4.25	110
15	22.5	5.45	115
25	10.5	8.08	125
50	7.5	14.9	150
75	6.0	24.0	175
100	2.5	35.0	—
(2) Benzene-chloroform (% of chloroform)			
25	158	2.74	225
50	115	3.25	250
75	87.5	3.91	275
(3) Benzene-chlorobenzene (% of chlorobenzene)			
25	128	3.18	325
50	65.5	3.96	350
75	33.5	4.79	375

Table 5.

Solvent	Gelation time (sec.)	Colour		
		Yellow	Red	Blue
Chloroform-acetone (% of acetone)				
5	128	—	66.0	—
10	268	5.0	66.0	—
15	623	7.0	55.0	—
25	2700	25.0	34.0	—
50	No gelation	40.0	13.0	—
75	„	51.0	9.5	—
Chloroform-ether (% of ether)				
5	78	—	62.0	0.5
15	228	—	57.0	0.5
25	1028	—	56.0	0.5
50	3170	10.0	38.0	—
75	>9600	15.0	30.0	—
Chloroform-butyl acetates (% of butyl acetates)				
5	178	1.0	87.5	—
10	433	3.0	87.0	—
15	1093	5.0	66.0	—
25	3280	5.0	73.0	—
50	>9000	12.0	51.0	—
75	No gelation	20.0	40.0	—
Chloroform-benzyl alcohol (% of benzyl alcohol)				
5	713	—	66.0	0.4
10	2218	—	63.0	0.3
15	5550	3.0	56.0	—
25	22200	—	54.0	0.4
50	No gelation	2.0	46.0	—
75	„	12.0	40.0	—
Chloroform- <i>m</i> -cresol (% of <i>m</i> -cresol)				
25	113	—	63.0	—
50	6780	5.0	56.0	—
75	No gelation	7.0	54.0	—
Chloroform-aniline (% of aniline)				
25	No gelation	2.0	2.0	—
50	„	3.0	0.5	—
75	„	2.5	0.4	—
100	„	2.0	0.3	—

According to the increase of the amount of solvent containing oxygen both the yellowish tint and gelation time of tung oil increase. And the gelation time increases according to the increase of yellowish tint of iodine solution.

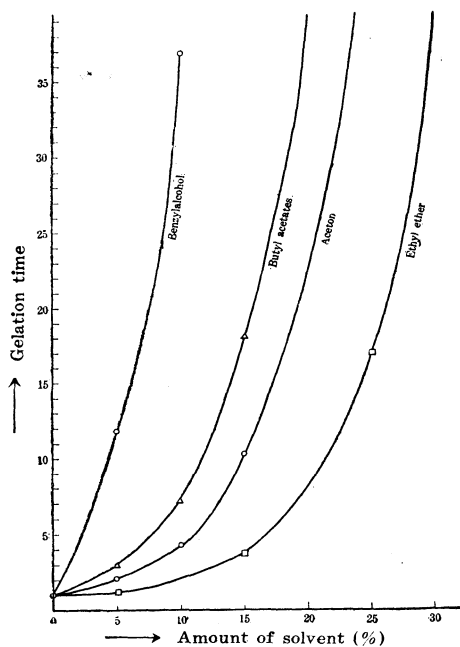


Fig. 2.

proved by the catalytic action of iodine solutions upon the gelation of tung oil.

Generally speaking the gelation accelerating action of iodine is strong in solvents having high dielectric constant.

The relations between dielectric constants and gelation times were shown in Fig. 3, both in logarithmic scale.

Greater part of solvents situate on a smooth curve.

Summary.

(1) The gelation times of tung oil catalysed by iodine in various organic solvents were measured.

(2) The relation between gelation time t , concentration of tung oil x and amount of iodine z is expressed by the formula

$$\log t = ax + b/zx.$$

(6) Lachmann, *J. Am. Chem. Soc.*, **25** (1903), 50; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", vol. II, p. 110.

(7) H. Gautier and G. Charpy, *Compt. rend.*, **111** (1890), 645.

L. Carcano, *Bull. Chim. Farm.*, **47** (1908), 5.

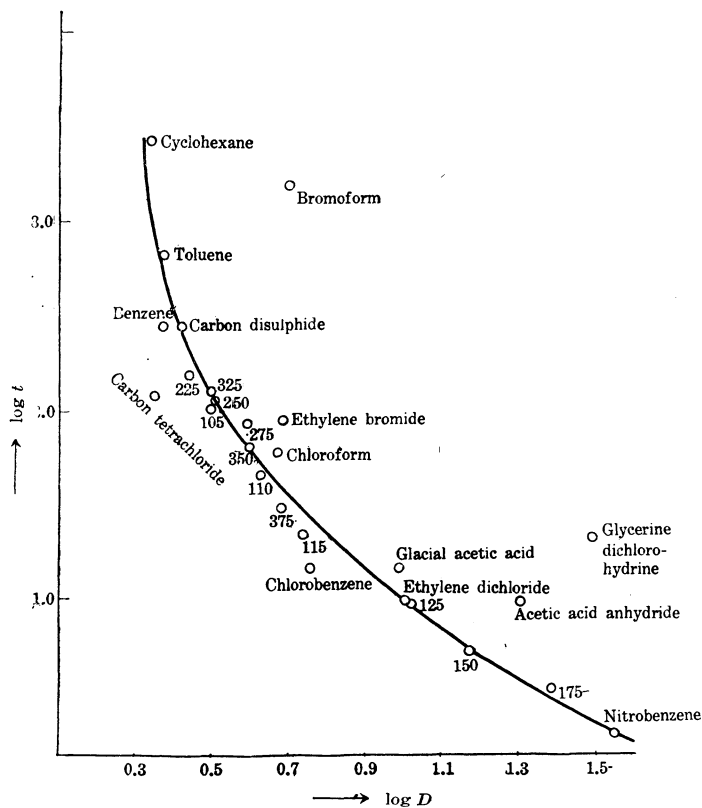


Fig. 3.

(3) In the solution having violet tint, iodine has a strong gelation accelerating action, but in the yellowish brown solution the accelerating action of iodine is very weak.

(4) Organic acids and nitrobenzene are exceptions of the above fact (3) and in spite of yellowish brown tint, have strong gelation accelerating action.

(5) In the iodine solutions of mixed solvents the gelation time increases with the increase of yellowish tint.

(6) Difference in catalytic action of iodine solutions is considered to be due to the difference of molecular state of iodine in the solution. Generally solvated solution of iodine has poor catalytic action.

(7) Generally iodine in the solvent having high dielectric constant shows strong gelation accelerating action.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

*Laboratory of Hitachi Works,
Hitachi Ltd., Hitachi.*

The Relation between Kolbe's Reaction and Hydrogen Ion Concentration. VIII.

By Ryoichi MATSUDA and Shigetaro IKUTA.

(Received August 16, 1940.)

Anodic oxidation of acetate and propionate was studied in the foregoing parts⁽¹⁾ of this paper, and, later on, electrolytic formation of persulphate was investigated by one of the present writers (R.M.) and his collaborators⁽²⁾. The present paper describes a study of preceding two electrolyses combined together, i.e., anodic reactions which take place by electrolysing a mixture of acetate and sulphate. Anolytes which contained sulphuric acid, ammonium sulphate, acetic acid, and ammonium acetate in various proportions were electrolysed with sulphuric acid as the catholyte and the anodic gases and peroxidic substances produced in the anolytes were investigated. The results of the gas analyses lead to an assumption that there is contained in it a new gaseous substance which was not known hitherto with a chemical formula $(\text{CO}_2)_2$, and which seems to have an important bearing on the peroxide theory.

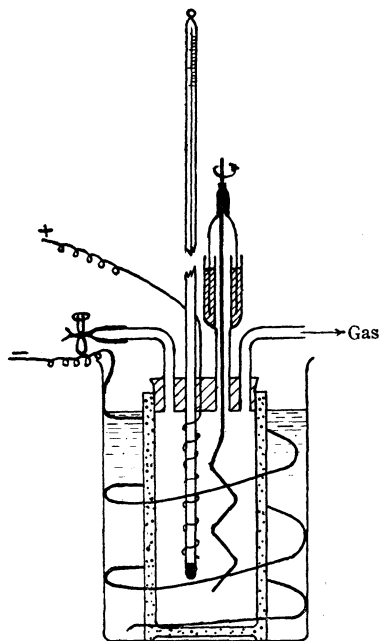


Fig. 1.

Experimental. The interior of a porcelain cylinder makes the anode chamber, which is equipped with a rubber stopper to which a platinum-wire anode, a thermometer, a stirrer and two bent tubes are inserted. The platinum anode is 0.5 mm. thick and 20.7 cm. long with a total effective surface of 3.25 cm², which makes a spiral surrounding the thermometer (Fig. 1).

The cathode also consists of a platinum-wire which is as thick as the anode and 45 cm. long. The electrolytic cell, which is a glass beaker, is surrounded with ice water to keep the temperature of the anolyte at 10°C. Current is so regulated as to supply a nearly definite amount of electricity which is measured by means of a copper coulometer. Anodic current density, D_A , is varied

(1) R. Matsuda and his collaborators, *J. Chem. Soc., Japan*, **51** (1930), 126; *ibid.*, **51** (1930), 632; *ibid.*, **52** (1931), 249: 756; this Bulletin, **7** (1932), 18, 297; *Compl. Abstr. J. Chem. Lit.*, Ser. 2, **6** (1932), 85 B.

(2) R. Matsuda and his collaborators, this Bulletin, **11** (1936), 1, 650; *ibid.*, **12** (1937), 331, 425; *ibid.*, **14** (1939), 72.

from 0.05 to 0.80 amp./cm². The porcelain cylinder is filled with an anolyte which measures 65 c.c., the two bent tubes being filled, as well, with the same solution at the beginning of the electrolysis. The catholyte consists of 90 c.c. 6 N sulphuric acid, unless otherwise mentioned.

The electrolysed anolyte is first tested qualitatively for hydrogen peroxide by titanium sulphate and then Caro's acid, persulphuric acid and

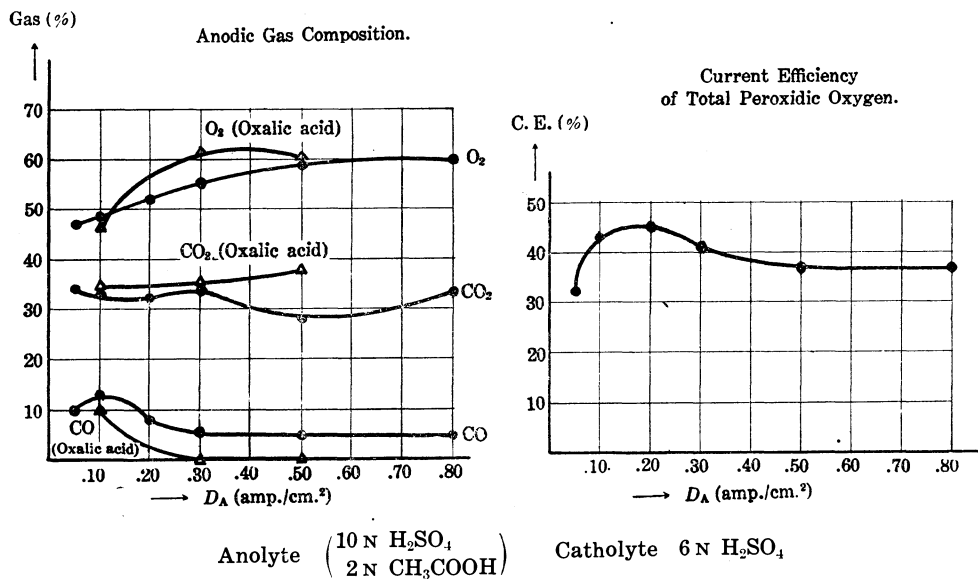


Fig. 2.

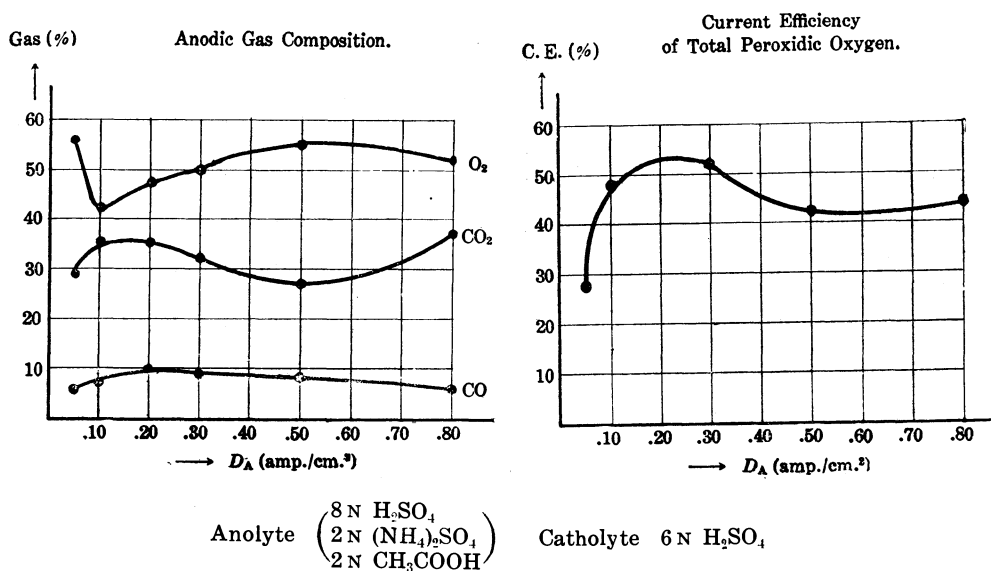


Fig. 3.

hydrogen peroxide are titrated after K. Glen's method⁽³⁾, but the *pH* of the anolyte is not determined. The anodic gas collected over a solution which is saturated with sodium chloride as well as with coal gas, is analysed according to Hempel's method. The oxygen used for explosion analysis is proved to be pure, containing neither nitrogen nor carbon dioxide.

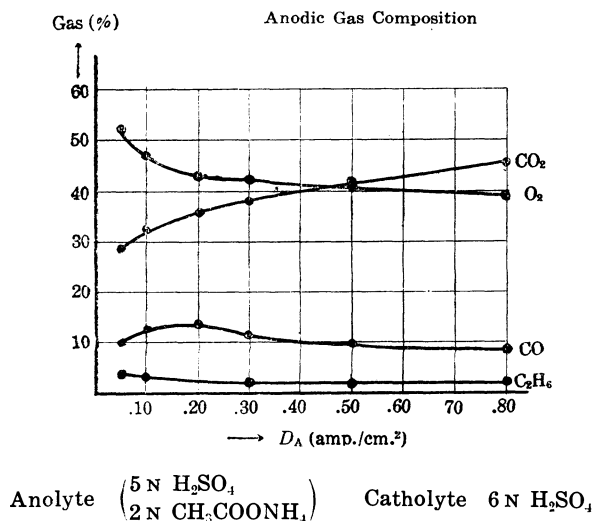


Fig. 4.

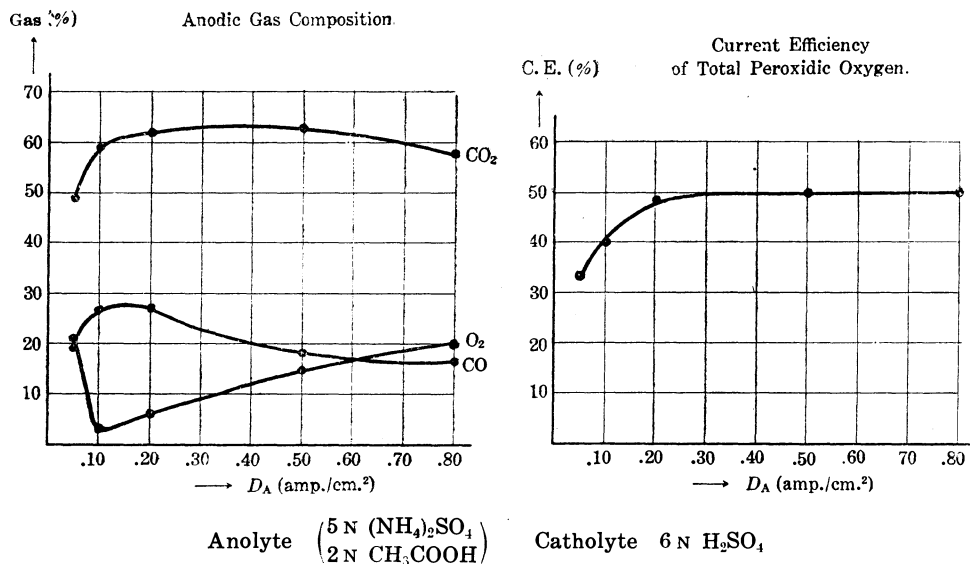


Fig. 5.

(3) *Z. anorg. u. allg. Chem.*, **195** (1931), 61.

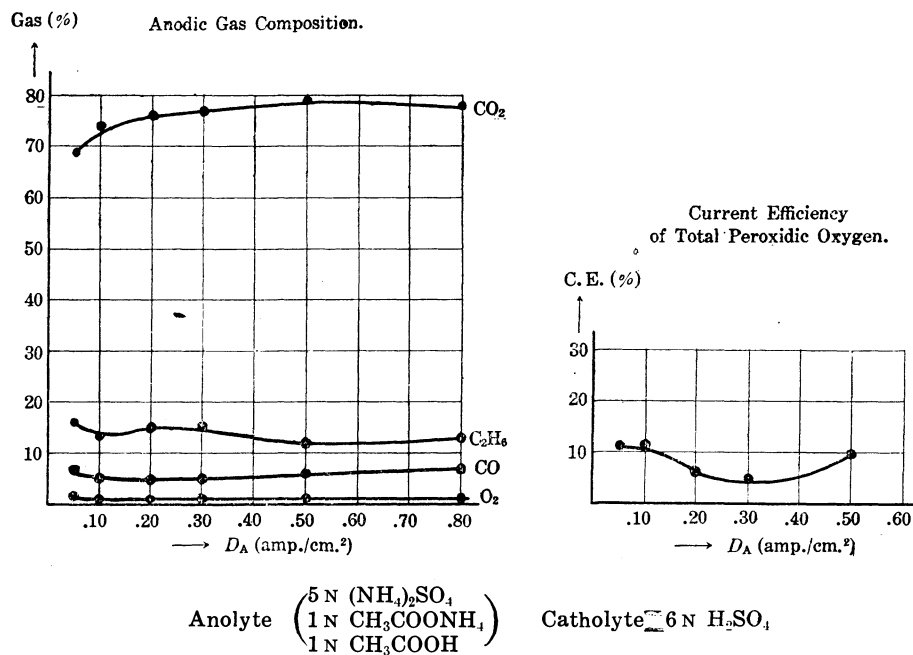


Fig. 6.

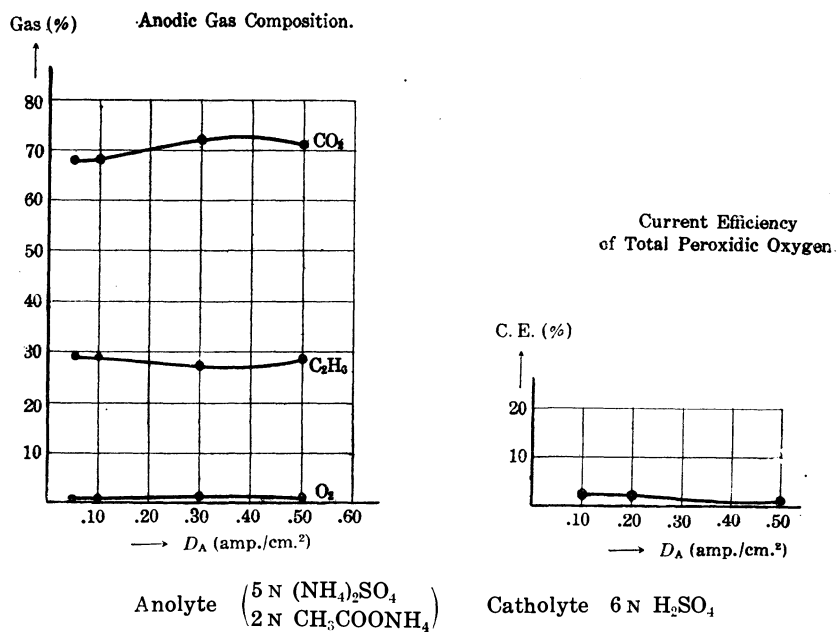


Fig. 7.

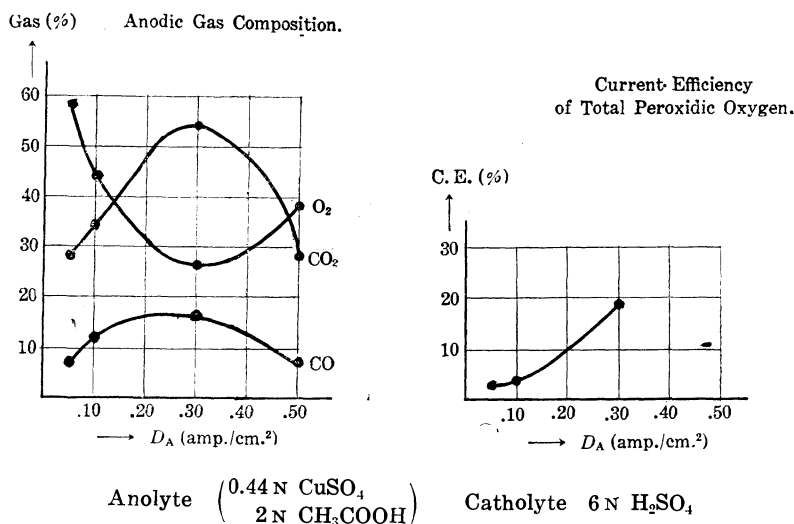


Fig. 8.

Following generalisations can be drawn from the data in Table 1. Carbon dioxide is produced from all the anolytes, No. 1 to No. 7, that is to say, complete oxidation takes place in each anolyte. And the lower the acidity of the anolyte, the more carbon dioxide is produced. Heavy hydrocarbon is not produced from any of the anolytes mentioned above. But when a solution which contains only acetate is electrolysed, Kolbe's reaction takes place and the anodic gases are shown to contain a little heavy hydrocarbon beside ethane. Oxygen is always evolved from the anolytes, but its proportion is small in some cases, e.g., 1 to 2%, and less than 1% in the anolytes No. 5 and No. 6 respectively. And the higher the acidity of the anolyte, the more oxygen is evolved. Carbon monoxide which is a product of incomplete oxidation is evolved in all cases but the anolyte No. 6. When the three anolytes, No. 4, 5, and 6 which contain no free sulphuric acid are compared, the proportion of carbon monoxide increases with the acidity of the anolyte.

Ethane is not produced from free acetic acid, but it is formed, if the anolyte contains ammonium acetate, even in the presence of free sulphuric acid. $(\text{CO}_2)_2$, which is a hypothetical substance, is produced to a small extent from the anolyte No. 3 which is acid with sulphuric acid, and to a less extent from the anolyte No. 5 which is acid with acetic acid, but none from the neutral anolyte No. 6 which nevertheless produces ethane. Nor it is formed from any anolyte which does not produce ethane.

The total volume of anodic gases increases, in general, as the acidity of the anolyte lowers. The total volume of oxygen at S. T. P. evolved from an anolyte which contains free sulphuric acid per 0.67 amp.-hour is remarkably large, and though it is comparatively small from an anolyte which contains no free sulphuric acid, it increases with the acidity of the anolyte.

Table 1.

Anolyte	Anodic Gases								Total Gas Vol. per 0.67 amp.-h.	Total O ₂ Vol. per 0.67 amp.-h.
	Approximation on an average in %									
	CO ₂	C _n H _{2n}	O ₂	CO	C ₂ H ₆	(CO ₂) ₂	unkn.	Total		
No. 1 $\left(\begin{array}{l} 10 \text{ N } \text{H}_2\text{SO}_4 \\ 2 \text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	32	0	55	6	0	0	7	100	25~50 c.c.	14~28 c.c.
No. 2 $\left(\begin{array}{l} 8 \text{ N } \text{H}_2\text{SO}_4 \\ 2 \text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 2 \text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	33	0	52	7	0	0	8	100	20~45 "	10~23 "
No. 3 $\left(\begin{array}{l} 5 \text{ N } \text{H}_2\text{SO}_4 \\ 2 \text{ N } \text{CH}_3\text{COONH}_4 \end{array} \right)$	40	0	42	10	3	<1	5	100	10~27 "	4~11 "
No. 4 $\left(\begin{array}{l} 5 \text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 2 \text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	60	0	15	20	0	0	5	100	24~45 "	4~7 "
No. 5 $\left(\begin{array}{l} 5 \text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 1 \text{ N } \text{CH}_3\text{COONH}_4 \\ 1 \text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	76	0	1	6	14	<1	3	100	220~240 "	2~3 "
No. 6 $\left(\begin{array}{l} 5 \text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 2 \text{ N } \text{CH}_3\text{COONH}_4 \end{array} \right)$	70	0	<1	0	28	0	2	100	280~440 "	<1 "
No. 7 $\left(\begin{array}{l} 0.44 \text{ N } \text{CuSO}_4 \\ 2 \text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	40	0	40	12	0	0	8	100	85~147 "	34~65 "

Table 2. Current Efficiency in % of Peroxidic Oxygen.

Anolyte C_A (amp./cm. ²)		0.05	0.10	0.20	0.30	0.50	0.80
No. 1 $\left(\begin{array}{l} 10\text{ N } \text{H}_2\text{SO}_4 \\ 2\text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	H_2SO_5	0.3	0.3	0.2	0.1	0.3	0.1
	H_2O_2	0.1	0.1	0.1	0.1	0.1	0.1
	$\text{H}_2\text{S}_2\text{O}_8$	31.1	42.1	44.5	41.1	37.2	36.5
	Total	31.5	42.5	44.8	41.3	37.6	36.7
No. 2 $\left(\begin{array}{l} 8\text{ N } \text{H}_2\text{SO}_4 \\ 2\text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 2\text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	H_2SO_5	0.1	0.1	0.2	0.1	0.1	0.1
	H_2O_2	0	0.1	0.1	0.1	0.1	0
	$\text{H}_2\text{S}_2\text{O}_8$	28.3	47.6	55.6	51.9	41.8	43.6
	Total	28.4	47.8	55.9	52.1	42.0	43.7
No. 4 $\left(\begin{array}{l} 5\text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 2\text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	H_2SO_5	0.1	0.1	0.1	—	0.1	0.1
	H_2O_2	0.1	0.1	trace	—	trace	0.1
	$\text{H}_2\text{S}_2\text{O}_8$	33.2	40.1	49.0	—	51.2	49.2
	Total	33.4	40.3	49.1	—	51.3	49.4
No. 5 $\left(\begin{array}{l} 5\text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 1\text{ N } \text{CH}_3\text{COONH}_4 \\ 1\text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	H_2SO_5	0.5	0.5	0.5	0.5	0.5	—
	H_2O_2	trace	trace	0	trace	trace	0
	$\text{H}_2\text{S}_2\text{O}_8$	10.4	10.4	5.4	4.5	9.1	—
	Total	10.9	10.9	5.9	5.0	9.6	—
No. 6 $\left(\begin{array}{l} 5\text{ N } (\text{NH}_4)_2\text{SO}_4 \\ 2\text{ N } \text{CH}_3\text{COONH}_4 \end{array} \right)$	H_2SO_5	—	0.3	0.5	—	0.2	—
	H_2O_2	—	0	0	—	0	—
	$\text{H}_2\text{S}_2\text{O}_8$	—	1.3	1.6	—	1.3	—
	Total	—	1.6	2.1	—	1.5	—
No. 7 $\left(\begin{array}{l} 0.44\text{ N } \text{CuSO}_4 \\ 2\text{ N } \text{CH}_3\text{COOH} \end{array} \right)$	H_2SO_5	0	0.3	—	0.1	—	—
	H_2O_2	0.5	0.4	—	trace	—	—
	$\text{H}_2\text{S}_2\text{O}_8$	2.7	3.5	—	18.5	—	—
	Total	3.2	4.2	—	18.6	—	—

The current efficiencies with respect to each of the peroxidic substances are given in Table 2. As methyl orange changed yellow, the titration of the anolyte No. 3 was not possible. The maximum current efficiency of the total peroxidic oxygen is 55% (the anolyte No. 2) and the minimum is 2% (the anolyte No. 6). It is observed that the total peroxidic oxygen increases with the acidity of the anolytes, when various anolytes are compared, and also that it decreases when oxygen evolution prevails and vice versa, when it is compared over the whole range of D_A . The bulk of the peroxidic oxygen is due to persulphuric acid, and Caro's acid comes next to it, hydrogen peroxide being found very little in each case. Hydrogen peroxide is produced in traces from the anolyte

No. 5 which is weakly acid, but none from the neutral anolyte No. 6, and generally speaking, the more acid the anolyte, the more it is found.

On $(\text{CO}_2)_2$ ⁽⁴⁾. When a gas sample, which was assumed to contain $(\text{CO}_2)_2$, was treated with the potash pipette to estimate carbon dioxide at the beginning of gas analysis, white fume was observed to take place. When an explosion sample out of the combustible residue after removal of carbon dioxide, heavy hydrocarbon, oxygen, and carbon monoxide was mixed with an excess of oxygen and subjected to electric discharge, it was observed that white and dense fume continued to appear for some time between the electrodes, falling down on the surface of mercury in the pipette. And then explosion followed, but never before. Some sample did not explode in spite of continued discharge by which white fume was yet produced. When the gases after explosion were treated with the potash pipette, another white fume was observed to take place. The electrodes of the pipette were covered with brownish black coating.

Table 3. Results of some Explosion Analyses.

Anolyte No. 3 $\left(\begin{array}{l} 5 \text{ N } \text{H}_2\text{SO}_4 \\ 2 \text{ N } \text{CH}_3\text{COONH}_4 \end{array} \right)$
 $D_A = 0.80 \text{ amp./cm}^2$

Sample	No. 1 (c.c.)	No. 21 (c.c.)	No. 24 (c.c.)	No. 27 (c.c.)
The volume of the sample	2.3	1.7	1.8	1.8
Contraction on explosion	1.4	1.0	1.1	1.2
CO ₂ produced on explosion	1.4	1.2	1.1	1.3
The volume of residue	1.6 (1.6)	1.1 (1.1)	1.2 (1.25)	1.2 (1.15)
O ₂ consumption	2.1 (2.1)	1.6 (1.6)	1.6 (1.65)	1.9 (1.86)
C ₂ H ₆	0.6	0.46	0.47	0.53
(CO ₂) ₂	0.1	0.14	0.08	0.12

The ratios in volume of the contraction to the carbon dioxide on combustion of methane and ethane are as follows:

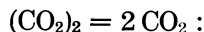
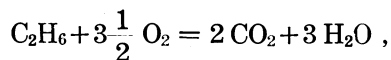
$$\frac{\text{contraction}}{\text{CO}_2} = 2.0 \quad \text{for} \quad \text{CH}_4,$$

and

$$\frac{\text{contraction}}{\text{CO}_2} = 1.25 \quad \text{for} \quad \text{C}_2\text{H}_6.$$

The corresponding ratios obtained from figures in Table 3, however, are equal to or less than unity. It is eventually assumed that a gas with a chemical formula $(\text{CO}_2)_2$, is hypothetically present with ethane if the latter is the only hydrocarbon in the sample and also that explosion results in the two reactions as shown by the following equations:

(4) R. Matsuda, *J. Chem. Soc., Japan*, **61** (1940), 638.



one is the complete oxidation of ethane which brings about contraction, and the other is the decomposition of $(\text{CO}_2)_2$ into carbon dioxide which brings about expansion, both reactions producing carbon dioxide.

Let x = volume of ethane,
and y = volume of $(\text{CO}_2)_2$:
 a = contraction on explosion,
and b = volume of carbon dioxide produced.

Then,

$$2\frac{1}{2}x - y = a,$$

$$\text{and } 2x + 2y = b.$$

Therefore,

$$x = \frac{1}{7}(2a + b),$$

$$\text{and } y = \frac{1}{2}(b - 2x).$$

The calculated volumes of both of the residue and the oxygen consumption which are shown in brackets in the table agree well with the corresponding observed values.

Discussion. Although carbon monoxide is found in considerable proportion in all cases in this experiment, it was not the case in Kolbe's reaction or one related to it which are generally known in the literature, as seen from the following illustrations. Ammonium and potassium acetates were electrolysed by R. Matsuda and his collaborators⁽⁵⁾ and in both cases 1% at most carbon monoxide was produced.

H. Hofer and M. Moest⁽⁶⁾ obtained an anodic gas which consisted of carbon dioxide and ethane by electrolysing sodium acetate in the presence of sodium perchlorate, but nothing was mentioned about either oxygen or carbon monoxide. According to the same authors electrolyses of sodium acetate in the presence of sodium sulphate, and also of potassium acetate in the presence of potassium bicarbonate resulted in very little carbon monoxide production.

R. E. Gibson⁽⁷⁾ obtained an anodic gas which consisted of 87% carbon dioxide, 3% carbon monoxide, 9% oxygen and 1% methane by electrolysing a mixture of 20 c.c. concentrated sulphuric acid, 100 c.c. acetic anhydride and 5 c.c. water. O. J. Walker and G. L. E. Wild⁽⁸⁾ stated

(5) R. Matsuda and his collaborators, (1), (2).

(6) H. Hofer and M. Moest, *Ann.*, **323** (1902), 284.

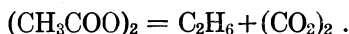
(7) R. E. Gibson, *J. Chem. Soc.*, **127** (1925), 483.

(8) O. J. Walker and G. L. E. Wild, *ibid.*, **1935**, 207.

that decomposition of acetyl peroxide produced a gaseous mixture which contained 1% carbon monoxide. The present writers electrolysed oxalic acid: the anolyte was the saturated solution (0.29N) of oxalic acid in 10 N sulphuric acid, and the catholyte 6 N sulphuric acid (vide Fig. 2). At $D_A=0.10$ amp./cm²., the anodic gas was nearly of the same composition as that of the anolyte No. 1, but at $D_A=0.30$ and 0.50 amp./cm². it was not. Though it will be interesting to compare the nature of acetic acid in sulphuric acid solution towards the anodic action with those of other substances in order to study the mechanism by which carbon monoxide is formed, further experiments are reserved for another occasion.

Walker and Wild obtained a gaseous mixture by decomposing acetyl peroxide which consisted of 27–40% methane, 55–64% carbon dioxide, ca. 9% oxygen, and ca. 4% ethane. S. Glasstone and A. Hickling⁽⁹⁾ studied the reaction between barium peroxide and acetic anhydride with and without water which, in both cases, produced a gaseous mixture which consisted of 65.9% carbon dioxide, 6.1% oxygen, 12.0% methane and 6.1% ethane. These are the reasons why they can not agree with the peroxide theory as the mechanism of Kolbe's reaction. The above two cases of decomposition of acetyl peroxide, however, are under very different conditions from that which will take place at a platinum-anode.

It was proposed already in Parts V, VI, and VII that the peroxide theory which assumes acetyl peroxide as the intermediate to produce ethane is preferable to other mechanisms, and it has been assumed in the present work that a gas which has a chemical formula $(CO_2)_2$, is formed by the anodic reaction. Now if ethane be produced by the decomposition of acetyl peroxide it will not be impossible that this new substance is formed as a by-product, as in the following equation:



Though the existence of $(CO_2)_2$ has to be confirmed by further tests from different angles, it seems to the present writers that it is a new evidence for the peroxide theory, if it exists at all.

The writers wish to express their heartfelt thanks to Prof. Motooki Matsui, D. Sc., for his unfailing encouragement. Thanks are also due to the Department of Education for a grant (Kwagaku Kenkyu Hi) for the sake of the present work.

*The Department of Applied Chemistry,
Tokushima Technical College.*

(9) S. Glasstone and A. Hickling, *J. Soc. Chem. Ind.*, **53** (1934), 512.

Radium Content of Mineral Springs in Japan.

By Toshio NAKAI.

(Received April 15, 1940.)

Contents.

	PAGE
I. Introduction	334
II. Methods of Analysis	335
The principle of the method	335
Apparatus	335
Natural leak	336
Determination of radium in mineral water	337
Determination of radium in sediments from mineral springs.....	339
III. Results of Determinations	339
Results of determinations	339
Geographical distribution of radium content	339
Comparison of the radium content of mineral waters in Japan with those in other countries	340
IV. Mineral Springs of Masutomi, Yamanashi Prefecture	363
Geographical distribution of radium and radon contents	366
Relation between the radium content and the radon content of spring waters	367
Variation in radon and radium contents	368
Relation between the radium and radon contents and the orifice temperature of spring waters	370
Relation between the radium and radon contents and the pH value of spring waters	371
Relation between the radium content and the amount of total solid matter in spring waters	372
The mineral springs of Yuzawa	372
Radium discharge	373
V. Hot Springs of Misasa, Tottori Prefecture	373
Geographical distribution of radium content	376
Relation between the radium content and the orifice temperature of spring waters	376
Relation between the radium content and the pH value of spring waters	377
Radium discharge	377
VI. Thermal Springs of Itō, Sizuoka Prefecture	377
VII. Thermal and Mineral Springs of Arima, Hyōgo Prefecture	379
VIII. Hot Springs of Beppu, Ōita Prefecture	381
IX. Relation between the Radium and the Radon Contents of Spring Waters.	384
X. Relation between the Radium Content and the Orifice Temperature of Mineral Springs	392
XI. Relation between the Radium Content and the Chemical Qualities of Spring Waters	394
Chemical classification of mineral springs and their radium contents.	394
Relation between the radium content and the quantities of dissolved solid constituents of spring waters	407
Relation between the radium content and the pH value of spring waters	408
XII. Radium Content of Brines from Oil Fields	412
Brines from oil fields	412
Hot springs from oil fields	417

Mineral waters of brine type	419
XIII. Radium Content of Sinter Deposits from Mineral Springs	419
XIV. Extraction of Radium from Mineral Waters	420
Methods	421
Results	422
Discussions	423

I. Introduction. Since K. Manabe and H. Isitani first undertook, in 1909, to determine the presence of radioactivity in the mineral springs of Japan, a number of reports have been made by R. Ishizu⁽¹⁾, Y. Kinugasa and other investigators, but no determination of the radium content in the mineral springs of Japan has yet been made. To do so is considered important for the following reasons:

First, it will help in solving certain problems in geochemistry. The quantitative analysis of radium in natural waters is indispensable for investigating the distribution of this element in the hydrosphere. Besides, studies of the rare elements, such as that of radium in spring waters, often play an important role in ascertaining their origin and history. It is also very important to know the conditions under which radium migrates when the spring waters act on the rocks through which they pass or when sinter deposits are precipitated from them.

Second, it is helpful in our search for the natural sources of this rare element. It has been reported⁽²⁾ that the quantity of radium brought up by a group of springs in a single district of North Caucasus, Russia, often amounts to more than one gram per year. Today the supply of radium depends entirely upon radium ores, such as pitchblende, carnotite, etc. Much to our disappointment, these radium ores are very scarce in Japan. If, therefore, a natural water of extraordinarily high radium content is found and a technique for separating the radium from such natural waters without having to use a large quantity of reagents could be developed, it may turn out to a valuable source of radium.

Third, there is the problem of hot-spring therapeutics. Studies in radioactivity have shown that the activity from mineral spring is one of the most effective of therapeutic agents. It is of course known that some of the physiological reactions of spring waters are believed to be due to the presence of very small quantities of the heavy metals, such as copper, arsenic, etc. According to T. Misawa, the mineral springs of Kinkei, Totigi Prefecture, have proved very efficacious in anaemia, because they contain a very small quantity of copper in addition to iron. Thus the minor constituents of mineral springs, although their quantities are very small, cannot be ignored. In this respect, the radium of mineral springs may have also some therapeutic effects.

Samples of water for the radium determination were collected from various parts of the country. Those of the waters from the mineral springs of Kasio and Tadati in Nagano Prefecture; Ena, Naegi and Kasagi in Gifu Prefecture; Masutomi in Yamanashi Prefecture; Ikeda in Simane Prefecture; and of those from the hot springs of Misasa, Sekigane, Hamamura and Katimi in Tottori Prefecture; and Sigaku, Koyabara and

(1) R. Ishizu, "The Mineral Springs of Japan," (1915).

(2) I. D. Kurbatov, *J. Phys. Chem.*, **38** (1934), 521.

Yugakai in Simane Prefecture were obtained by the writer. The waters from the mineral springs of Arima in Hyōgo Prefecture, were sampled by Y. Nemoto of the Tokyo Imperial Industrial Research Institute and K. Yamasaki of the Chemical Institute of the Tokyo Imperial University, and that from the hot springs of Tuta in Aomori Prefecture; Matunoyama in Niigata Prefecture; Sionoha and Yosino in Nara Prefecture; and those of Katuura, Yukawa, Yuzaki and Higasi-sirahama in Wakayama Prefecture, were collected by K. Kuroda of the Chemical Institute of the Tokyo Imperial University. The brines from the oil fields in Akita and Niigata Prefectures and that from the natural gas field in Tiba Prefecture were collected by K. Hosino of the Tokyo Imperial Industrial Research Institute. Through the courtesy of the Hot Spring Society of Japan, all the other samples of water were collected by the Hot Spring Owners' Association at each hot spring, for all of which courtesies the writer tenders his warmest thanks.

The samples of water for radium determination were usually drawn direct from the source at each spring. If the orifice of a spring happened to be at the bottom of a bath-tub, samples were drawn after bailing out the water, if that was possible. At the mineral springs of Wadegawara No. 2 in Masutomi, Yamanashi Prefecture, the writer measured the radon content of the water taken from the surface and that direct from the source of the spring. The result in the former case was 1133 Mache's units, whereas that of the latter was 1343 Mache's units. As there may be also some difference in the radium content of water drawn from the source of a spring and that of the surface water, although not so marked as in the case of the radon content, special precautions are necessary in sampling.

For sampling the water, a large bottle of about 2 liters capacity is completely filled with the water, except for the few c.c. of air at the neck to allow for temperature changes. The samples were sent to the Tokyo Imperial Industrial Research Institute, where their radium contents were determined.

II. Methods of Analysis. *The principle of the method.* For determining the radium in mineral waters, the so-called "emanation method" was adopted. The principle of this method is to compute the radium concentration in the sample of water by comparing the radioactivity of the radon that is expelled from the water sample (the radon in it being in equilibrium with the radium) with that produced by the radon from a known amount of radium.

The sample of water, after the sediments in it have been completely dissolved, is collected in a flask, sealed, and left to stand for twenty-eight days and more. When equilibrium is practically established between the radium in the specimen and its radon, all the radon present in it are swept into a previously evacuated ionization chamber by means of the vacuum-boiling method. Its radioactivity is then measured when it becomes maximum, which state is attained three hours after the admittance of radon.

Apparatus. The essential parts of the apparatus are an emanation electroscope and a radon-receiver. A reliable emanation electroscope,

made by the Institute of Physical and Chemical Research, Tokyo, was used. The arrangement is shown in Fig. 1.

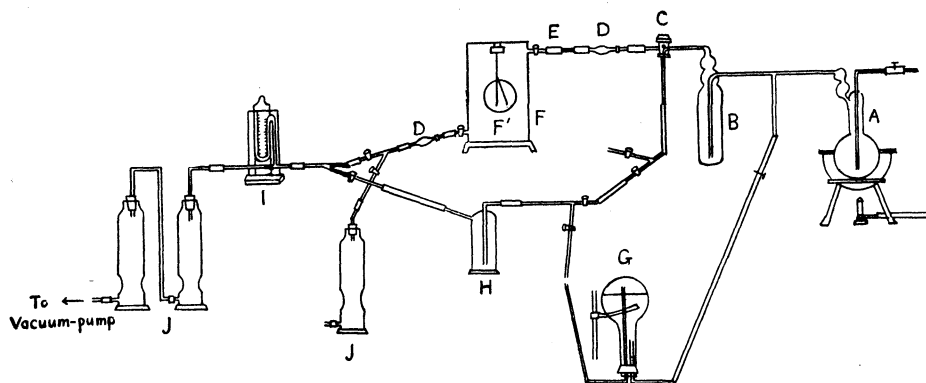


Fig. 1. Arrangement for Emanation Method.

A, which is a preserving flask of about 600 c.c. capacity (curie bottle) containing the solution to be examined, has two side-tubes drawn to a thin end. One of them is connected to the radon-receiver B (see figure), which has a capacity of about 400~500 c.c. and serves as a temporary receiver for the air containing the emanations and the vapour. Thoron disintegrates almost completely during its suspension in B, while radon survives, owing to its longer life, until its activity is measured. On being transferred to the ionization chamber F, the gases, including radon, are passed through a tail stopcock C, a calcium chloride drying tube D, and a capillary tube E. F is a cylindrical brass vessel of about 1500 c.c. capacity, which contains a gold-leaf F'. The reading is done by means of a low power microscope provided with a microscale in its image plane, across which the gold-leaf is observed to move.

G is a flask containing the distilled water that is poured into the radon-receiver B in order to drive the radon in it into the electroscope chamber.

H is a wash bottle, I a manometer, and J a gas-drying apparatus.

Natural leak. Before each determination, the natural leak of the electroscope, which varies from time to time, must be measured, for which purpose the ionization chamber is evacuated and fresh air introduced through the dryers. As soon as there is atmospheric pressure in the ionization chamber, readings are made and continued at intervals of 15 to 20 minutes for 1 to 3 hours until the leak becomes practically constant.

Since variation in the natural leak interferes with the accuracy of determination, whatever the cause, it is desirable to maintain the laboratory at a state as constant as possible. Should the air that is introduced into the ionization chamber contain even the slightest trace of moisture, the natural leak is liable to be affected to a very marked degree. Special precautions are, therefore, necessary for properly controlling the drying apparatus.

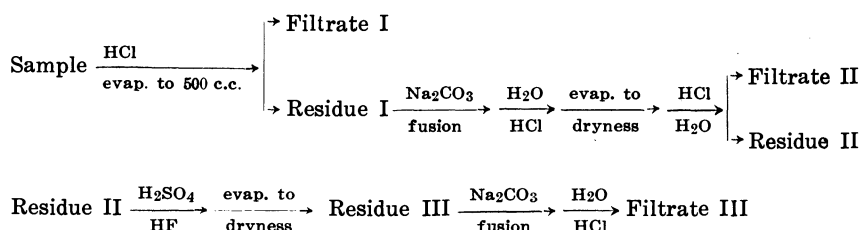
Determination of radium in mineral water. The first method. For determining the radium, about 2 liters of water are used for each sample. After adding a few c.c. of hydrochloric acid, it is evaporated to 500 c.c. on a water bath. Any insoluble residue is collected on the filter paper and the filtrate sealed into the curie bottle, leaving a space of about 100 c.c. for subsequent boiling. The sample sealed, is then allowed to stand for twenty-eight days or more, during which time equilibrium is practically reestablished between the radium in the specimen and its radon.

The solution in the curie bottle is vigorously boiled and the free radon that accumulates in the bottle is swept into a previously evacuated radon receiver and then introduced through the drying tube and the capillary tube into a previously evacuated ionization chamber. When all the air containing radon is expelled from the receiver, air for washing out is introduced through the drying tube into the ionization chamber to sweep away the radon remaining in C, D and E into the ionization chamber until there is an atmospheric pressure in the chamber. The reading is taken when the rate of fall of the leaf becomes maximum, which state is attained three hours after the admittance of radon. The rate of fall of the gold-leaf across the scale is expressed in terms of one scale division per minute. From this must be subtracted the natural leak, determined immediately before the determination, the figure thus obtained corresponding to the radioactivity from the solution in the curie bottle. By comparing the radioactivity produced by the radon with a known amount of radium, the radium content of the solution is readily computed. The standard solution used in the present investigation was prepared in the laboratory of S. Iimori, at the Institute of Physical and Chemical Research, Tokyo.

After completion of the determination, the ionization chamber is exhausted and dried air again introduced. By repeating this process several times, the ionization chamber is completely washed. The next determination is made after the radioactive deposits that have formed in it have completely decayed away.

The insoluble residue on the filter paper mentioned above is converted into solution by the following method. It is ignited and fused with anhydrous sodium carbonate. The fused mass is treated first with distilled water and then with hydrochloric acid. The solution is evaporated to dryness to render the silica insoluble, the salts thus obtained being moistened with concentrated hydrochloric acid and dissolved in water. The insoluble residue, mostly silica, is ignited and treated with a mixture of sulphuric and hydrofluoric acids. If a residue still remains, the operation just described must be repeated until no residue can be detected. The solution thus obtained is placed into a curie bottle and sealed and its radium content determined by the method already described. The sum of this result and that obtained from Filtrate I is the radium content of the original specimen. The amount of radium absorbed by Residue I is usually negligible.

The maximum observational uncertainty in the radium determination by this method is $0.01\sim0.02\times10^{-12}\text{g. Ra}$ per liter of water when 2 liters of sample of water are used.



The second method. With some water samples, the following method was adopted. About 2 liters of the water preserved in the bottle is filtered. 500 c.c. of the filtrate is taken and put into a curie bottle and sealed. The total residue, together with that remaining in the bottle, is dissolved in hydrochloric acid. The insoluble residue in hydrochloric acid is dissolved by the method described in the preceding section. The solutions thus obtained are separately put into curie bottles and sealed. The radium contents of the solution in each curie bottle are determined. The sum of these results, each result being calculated to that of 1 liter, is the radium content of the original specimen.

As will be seen from Table 1, the amount of radium adsorbed in the process of precipitation, deposited from the water after sampling, differs greatly with the spring water, in some of which this value is very large, so that they cannot be ignored.

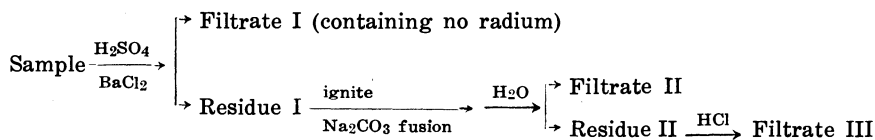
Table 1.

Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	
			in water	in sediment
Monkawa-Onsen	Monkawa	Kanagawa	0.41	0.00
Yuzawa No. 1	Masutomi	Yamanashi	71.74	0.07
Toyotomi-Onsen	Toyotomi	Hokkaidō	9.62	0.48
Totikubo No. 1	Masutomi	Yamanashi	16.60	16.02
Kaimonzi-Kōen-Onsen	Beppu	Ōita	0.13	0.12
Tuganerō No. 1	Masutomi	Yamanashi	14.57	49.96
Makiyama-Kōsen	Makiyama	Mie	0.17	1.63
Matudaira-no-yu	Masutomi	Yamanashi	0.00	1.52

The third method. To the water sample a few c.c. of sulphuric acid are added, followed by a solution of barium chloride (about 0.5 g.). Radium is precipitated from the water as radium sulphate, along with barium sulphate. The quantity of radium contained in the water of mineral springs is so small that the solubility product is not attained despite the high sulphate ion concentration, but by adding barium chloride, radium is precipitated along with barium sulphate in the form of mixed crystals.

The precipitated sulphate, after it is filtered off, is ignited and fused

with anhydrous sodium carbonate. The fused mass is leached with distilled water in order to dissolve the sodium sulphate. The insoluble residues of barium carbonate and radium carbonate are dissolved in hydrochloric acid. The two solutions thus obtained, the alkaline solution of sodium sulphate (Filtrate II) and the acidic solution of barium and radium chlorides (Filtrate III) are separately put into curie bottles and sealed and their radium contents determined.



As will be seen from Table 2, the results obtained by this method agree fairly well with those obtained by the first method. Since this method, however, is more troublesome than the other two, in the present experiments only the first and second methods were used, almost all the samples being determined by the first method.

Table 2. Comparison of the two methods of determination.

Method	Sample	Radium content g./l. $\times 10^{12}$
First	Yakendo-Kōsen, Arima,	61.57
Third	„	61.50
First	Hon-Onsen, Arima	64.97
Third	„	64.88
First	Netu-no-yu, Matunoyama	6.43
Third	„	6.44

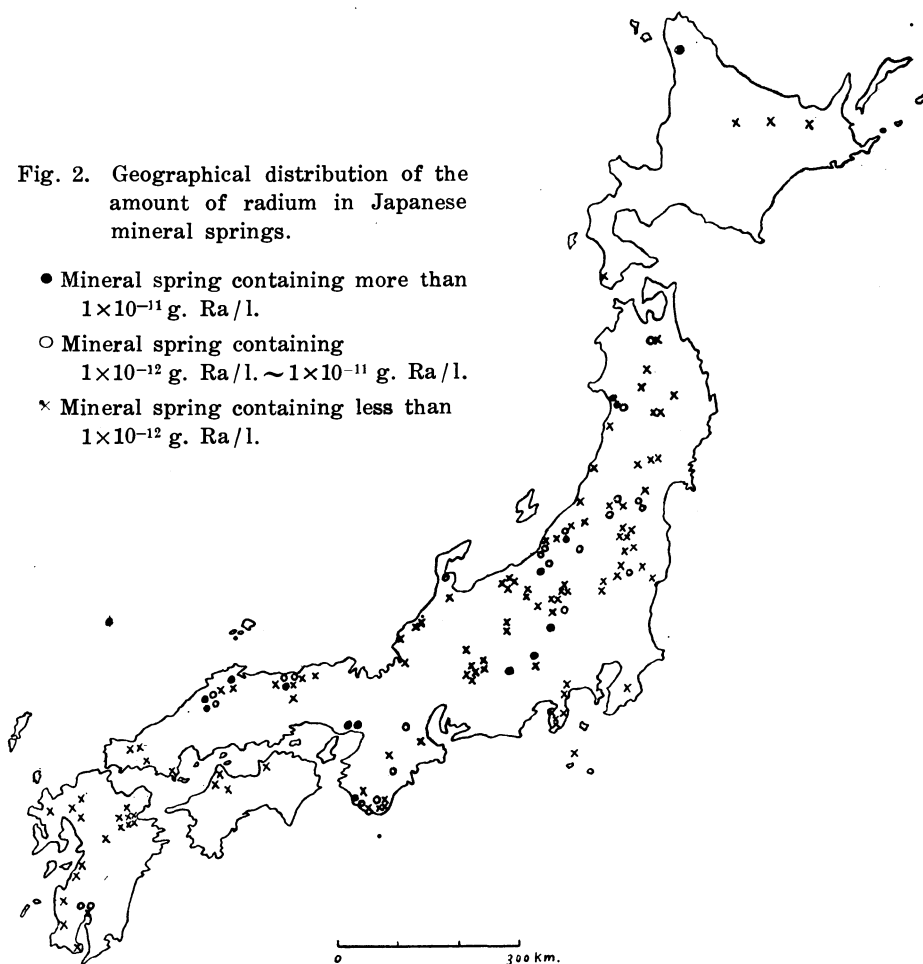
Determination of radium in sediments from mineral springs. About 10 g. of the sample is dissolved in hydrochloric acid. The insoluble residue is ignited and then fused with anhydrous sodium carbonate. The fused mass is then dissolved by the method described in a previous section. The solutions thus obtained are separately placed in curie bottles and sealed and their radium contents determined.

III. Results of Determinations. *Results of Determinations.* 477 water samples drawn from various mineral springs in Japan and 15 brine samples from the oil fields in Akita and Niigata Prefectures and from the natural gas field in Tiba Prefecture, were determined for radium content, with results shown in Table 3. The orifice temperatures of these spring waters as measured at time of sampling are also given for reference in the table.

Geographical distribution of radium content. The geographical distribution of the radium content of Japanese springs is shown on the accompanying map, Fig. 2, the radium content of each group of springs

Fig. 2. Geographical distribution of the amount of radium in Japanese mineral springs.

- Mineral spring containing more than 1×10^{-11} g. Ra/l.
- Mineral spring containing 1×10^{-12} g. Ra/l. $\sim 1 \times 10^{-11}$ g. Ra/l.
- × Mineral spring containing less than 1×10^{-12} g. Ra/l.



being represented by their highest values, from which it will be seen that the mineral springs of high radium concentration are usually localized—an interesting fact.

Comparison of the radium content of mineral waters in Japan with those in other countries. The radium contents of mineral waters in Japan will be compared with those in other countries.

The largest amount of radium in the water of mineral wells and springs previously known was discovered by B. A. Nikitin⁽³⁾ in the salt water from Grosny petroleum district, North Caucasus, Russia. It amounts to 1.83×10^{-8} g. of radium per liter of water. In the Far East, S. Gōda recently found the extraordinary high concentration of radium in salt water from Tzeliutsing, Szechwan, China. It amounts to 7.26×10^{-10} g. of radium per liter of water. In Table 4 are given for comparison the highest concentrations of radium in the world's mineral springs, and in Table 5 for those in Japan.

(3) W. Chlopin and B. Nikitin, *Compt. rend. acad. Sci., U.R.S.S.*, A **1930**, 393.

Table 3. Radium content of mineral waters in Japan.

1. Radium content of the mineral springs of Japan.

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
1	Katura-no-yu	Sōunkyō	Sōunkyō	Kamikawa	Kamikawa	Hokkaidō	0.12		Aug. 1937
2	Reikō-no-yu (Onna-yu)	"	"	"	"	"	0.08		"
3	" (Otoko-yu)A	"	"	"	"	"	0.08		"
4	" (")B	"	"	"	"	"	0.10		"
5	Hana-no-yu	"	"	"	"	"	0.12		"
6	Kawayu-Onsen	Kawayu	Kawayu	Tesikaga	Kawakami	"	0.00		
7	Ponyu-Onsen	Ponyu	Ponyu	Aiuti	Tokoro	"	0.00		Aug. 1937
8	Toyotomi-Onsen	Toyotomi	Kami-sarobetu, Saru	Horonobe	Tesio	"	10.10		"
9	Kozima-Kōsen No. 1	Kozima	Kozima	Nebuta	Matumae	"	0.00		July 1937
10	" No. 2	"	"	"	"	"	0.00		"
11	Netu-no-yu	Sukayu	Sukayu-sawa, Arakawa	Arakawa	Higasi- tugau	Aomori	0.32		Aug. 1937
12	Hie-no-yu	"	"	"	"	"	0.15		"
13	Sika-no-yu	"	"	"	"	"	0.17		"
14	Sibu-rokubu-no-yu	"	"	"	"	"	0.00		"
15	Sin-yu	Sinyu	Arakawa	"	"	"	0.05		"
16	Tetu-Kōsen No. 1	"	"	"	"	"	1.16		"
17	" No. 2	"	"	"	"	"	0.63		"
18	Megusuri-no-yu	"	"	"	"	"	0.07		"
19	Tuta-Onsen	Tuta		Towada	Kamikita	"	0.24	46.0	Aug. 1939
20	Nanasigure-Kōsen	Nanasigure	Nanasigure	Terada	Iwate	Iwate	0.60		
21	Hanamaki-Onsen	Hanamaki	Itini-tiwari	Yumoto	Hienuki	"	0.00	72.0	Aug. 1937
22	Usi-no-yu (Ō-yu)	Yumoto	Yumoto	Yuta	Waga	"	0.08		
23	Taki-no-yu	"	"	"	"	"	0.05		

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan.—(Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
24	Ōkama-no-yu	Tamagawa	Sibukuro-zawa,	Tazawa	Senhoku	Akita	0.60		Nov. 1937
25	Yuze-Onsen	Yuze	Tamagawa	Miyakawa	Katuno	"	0.00		
26	Onogawa-Onsen	Onogawa	Yubata	Misawa	Minami- okitama	Yamagata	8.37	76.0	Aug. 1939
27	Kyokuato-gensen	Akayu	Onogawa	Akayu Town	Higasi- okitama	"	0.09	62.0	"
28	Matusima-kwan-no-yu	"	"	"	"	"	0.09	54.0	"
29	Turuzune-Onsen	Kaminoyama	"	Kaminoyama Town	Minami- murayama	"	1.07		July 1939
30	Sin-moto-yu	"	"	"	"	"	0.27		"
31	Tukioka-hotel No. 1	"	"	"	"	"	1.58		"
32	" No. 2	"	"	"	"	"	1.07		"
33	Kawara-no-yu	Takayu	Takayu	Hotta	"	"	0.23	42.0	Aug. 1939
34	Gensen	Akakura	Akakura, Tomizawa	Higasi-Oguni	Mogami	"	0.12	65.0	Aug. 1937
35	Gensen No. 1	Sin-akakura	"	"	"	"	0.10	65.0	"
36	" No. 2	"	"	"	"	"	0.15	67.0	"
37	" No. 3	"	"	"	"	"	0.17	67.0	"
38	Kyōdō-yokuzyō-no-yu	Atumi	Atumi	Atumi	Nisi-tagawa	"	0.58		Jan. 1938
39	Kawanaka-no-yu	"	"	"	"	"	0.87		"
40	Kamasaki-no-yu	Kamasaki	Kamasaki, Kuramoto	Hukuoka	Katta	Miyagi	1.00		Aug. 1937
41	Mogamiya-no-yu	"	"	"	"	"	1.37		"
42	Kimuraya-no-kyū-yu	"	"	"	"	"	3.03		"
43	Kimuraya-no-sin-yu	"	"	"	"	"	2.58		"
44	Ō-yu	Aone	Aone	Kawasaki	Sibata	"	0.55		"
45	Nagō-no-yu	"	"	"	"	"	1.39		"
46	Sin-yu	"	Nomadaira	"	"	"	0.80		"

47	Kawara-no-yu	Sakunami	Sakunami	Hirose	Miyagi	Miyagi	0.21	54.0	Aug. 1939
48	Takaku-ryokwan-no-yu	Kawatabi	Kawatabi, Ōguti	Kawatabi	Tamatukuri	"	0.26		
49	Takatō-ryokwan-no-yu	"	"	"	"	"	0.08		
50	Huzisima-ryokwan-no-yu	"	"	"	"	"	0.07		
51	Itagaki-ryokwan-no-yu	"	"	"	"	"	0.00		
52	Private bath (A. Yosida)	"	"	"	"	"	0.00		
53	Tansan-sen	Naruko		Naruko Town	"	"	0.06		Aug. 1937
54	Tanaka-ryokwan No. 1	"		"	"	"	0.23	79.0	Aug. 1939
55	Moto-yu	Kasi	Teradaira, Mafune	Nisigō	Nisi-sirakawa	Hukusima	0.53		
56	Tengu-no-yu	"	"	"	"	"	0.41		
57	Yuzin-no-yu	"	"	"	"	"	0.75		
58	Mamegara-hudō-no-yu	Sirakawa	Sekikawakubo	Sirakawa Town	"	"	1.27		Oct. 1937
59	Moto-yu No. 1	Bobata	Hida, Bobata	Bobata	Isikawa	"	0.11		Aug. 1937
60	" No. 2	"	"	"	"	"	0.09		"
61	Naka-no-yu	Takano	Takano	Minowa	Iwaki	"	0.00		Nov. 1937
62	Moto-yu	Iwasiro-atami	Takatama	Takakawa	Adati	"	0.00		
63	Itiriki-hotel-no-yu	"	"	"	"	"	0.00		
64	Kamiya-ryokwan-no-yu	"	"	"	"	"	0.08		
65	Sin-yu	"	"	"	"	"	0.00		
66	Private bath (K. Hasimoto)	"	"	"	"	"	0.05		
67	" (T. Matumoto)	"	"	"	"	"	0.00		
68	" (M. Ōgosi)	"	"	"	"	"	0.08		
69	Yosino-ya-no-yu	"	"	"	"	"	0.02		
70	Takatama-Onsen	Takatama	Akogasima	Marumori	Asaka	"	0.02	42.5	
71	Sin-nozi-Onsen	Sin-nozi	Wasikurayama	Tutiyu	Sinobu	"	0.00		Aug. 1937
72	Spring No. 1	Wasikura	"	"	"	"	0.00	50.0	"
73	" No. 2	"	"	"	"	"	0.00	94.0	"
74	" No. 3	"	"	"	"	"	0.07	48.0	"
75	Numaziri-Onsen	Numaziri	Numaziriyama	Azuma	Yama	"	0.84		

1940]

Radium Content of Mineral Springs in Japan.

343

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
76	Naka-no-yu	Yokomuki	Wakamiya	Azuma	Yama	Hukusima	0.00	24.0	Aug. 1937
77	Iwasakiya-no-yu	Ōsio	Ōsio	Ōtaki	Ōnuma	"	3.72		
78	Kyōdō-no-yu	"	"	"	"	"	4.26		
79	Moto-yu	Kawazi	Kawazi	Huziwara Town	Sioya	Totigi	0.10		
80	Hudō-no-yu	"	"	"	"	"	0.61		
81	Iwa-no-yu	"	"	"	"	"	0.07		
82	Yakusi-no-yu	"	Asamayama, Kawazi	"	"	"	0.00		"
83	Komoti-no-yu	"	"	"	"	"	0.10		"
84	Kinkei-Kōsen	Kinkei	"	Huziwara	"	"	0.00		Aug. 1937
85	Kakkō-Onsen	Nasu	Nasudake, Yumoto	Nasu	Nasu	"	0.00		
86	Sika-no-yu	"	Huruyasiki, "	"	"	"	0.55		
87	No. 1 Nomi-yu	Ikao	Ikao	Ikao Town	Gumma	Gumma	0.00		
88	No. 2	"	"	"	"	"	0.00		
89	No. 3	"	"	"	"	"	0.06		
90	No. 4 Ohaguro-no-yu	"	"	"	"	"	0.09		"
91	No. 5 Hukiage-no-yu	"	"	"	"	"	0.00		"
92	No. 6 Ōseki-no-yu	"	"	"	"	"	0.00		"
93	Wasi-no-yu	Kusatu	Takisita, Kusatu	Kusatu Town	Agatsuma	"	0.05		"
94	Tiyo-no-yu	"	"	"	"	"	0.10		"
95	Nikawa-no-yu	"	"	"	"	"	0.03		"
96	Zizō-no-yu	"	Zizō, Kusatu	"	"	"	0.01		"
97	Netu-no-yu	"	Nisi-mati, "	"	"	"	0.15		"
98	Sirahata-no-yu	"	"	"	"	"	0.16		"

Table 3. — (Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
128	Moti-no-yu	Yugawara		Yugawara Town	Asigara-simo	Kanagawa	0.28		
129	Monkawa-Onsen	Monkawa	Monkawa	"	"	"	0.41		Sept. 1937
130	Senami-Onsen	Senami	Hamasinden	Senami Town	Iwahune	Niigata	0.11		"
131	Spring No. 1	Murasugi	Murasugi	Sasaoka	Kita-kambara	"	0.51		"
132	" No. 2	"	"	"	"	"	0.04		"
133	" No. 3	"	"	"	"	"	0.04		"
134	Netu-no-yu	Matunoyama	Yumoto	Matunoyama	Higasi-kubiki	"	6.43	68.0	Aug. 1939
135	Hii-no-yu	"	"	"	"	"	6.49	83.0	"
136	Kagami-no-yu	"	"	"	"	"	14.30	72.5	"
137	Usagiguti-Onsen	"	"	"	"	"	6.17	36.8	"
138	Tamago-no-yu	"	"	"	"	"	0.29	17.0	"
139	Komeya-no-yu	"	"	"	"	"	2.62		"
140	Yumoto-Onsen	"	"	"	"	"	7.16		Apr. 1938
141	Myōkō-Onsen	Myōkō	Sekikawa	Nakayama	Naka-kubiki	"	0.24	60.0	Aug. 1939
142	Akakura-Onsen	Akakura	Akakura	"	"	"	0.02		"
143	Moto-yu	Seki	Seki	Sekiyama	"	"	0.09		"
144	Iwō-no-yu	Tubame	Tubame	"	"	"	0.00		Aug. 1937
145	Moto-yu	"	"	"	"	"	0.00		"
146	Nagae-Kōsen	Nagae	Kōno, Tyōkeizi	Takaoka City		Toyama	0.42		"
147	Gotairan-no-yu	Wakura	Wakura	Wakura Town	Kasima	Isikawa	6.04		"
148	Moto-yu	"	"	"	"	"	5.89		"
149	Sin-yu	"	"	"	"	"	4.83		"
150	Hōsi-no-yu	Awazu	Awazu	Awazu	Nomi	"	0.21		"

151	Sō-yu	Awazu	Awazu	Awazu	Nomi	Isikawa	0.15		
152	Hurō-no-yu	"	"	"	"	"	0.14		
153	Yamasiro-Onsen	Yamasiro	Yamasiro	Yamasiro Town	Enuma	"	0.13		Aug. 1937
154	Zinbara-ryokwan-no-yu	Awara	Hunatu	Awara	Sakai	Hukui	0.56		
155	Simbo-Onsen	Simbo	Simbo	Simbo Town	Turuga	"	0.20	30.0	Oct. 1937
156	Hatu-yu	Sibu	Hirao	Hirao	Simo-takai	Nagano	0.08		Aug. 1937
157	O-yu No. 1	"	"	"	"	"	0.11		"
158	" No. 2	"	"	"	"	"	0.03		"
159	Yamada-Onsen	Yamada		Yamada	Kami-takai	"	0.25		Oct. 1937
160	Yamasio-Kōsen	Kasio	Kasio	Ōzika	Simo-ina	"	18.5	12.1	May 1936
161	Kosibu-no-yu	"	"	"	"	"	0.0		"
162	Hukagasawa-Kōsen	"	"	"	"	"	0.0		"
163	Nasihara-Kōsen	"	"	"	"	"	0.0		"
164	Me-no-yu	Asama	Asama	Hongō	Higasi-tikuma	"	0.06		June 1939
165	Higasiyama-Onsen	Higasiyama	Izibora, Asama	"	"	"	0.08		
166	Iriyamabe-Kōsen	Iriyamabe		Iriyamabe	"	"	0.43		
167	Itozawa-no-izumi	Itozawa	Itozawa	Yamaguti	Nisi-tikuma	"	0.0	13.0	May 1936
168	Siogasawa-Kōsen	Tadati		Tadati	"	"	0.0	12.0	"
169	Ōsiba	Masutomi		Masutomi	Kita-koma	Yamanasi	2.68	22.5	Oct. 1936
170	Ginsentō-huru-yu	"		"	"	"	9.39	31.0	"
171	Ginsentō-kami-no-yu	"		"	"	"	7.35	28.5	"
172	Ginsentō-naka-no-yu	"		"	"	"	0.43	22.0	"
173	Ginsentō-simo-no-yu	"		"	"	"	3.42	17.0	"
174	Wadegawara No. 1	"		"	"	"	6.76	18.0	"
175	" No. 2	"		"	"	"	11.62	19.5	"
176	Hattyōdaira No. 1	"		"	"	"	0.11	17.0	"
177	" No. 2	"		"	"	"	26.93	14.9	Apr. 1937
178	Yokote-no-yu	"		"	"	"	0.71	15.0	"
179	Higasiobi-no-izumi	"		"	"	"	35.65	25.0	Oct. 1936

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring	Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
180	Nibuzawa	Masutomi	Masutomi	Kita-koma	Yamanashi	6.22	24.0	Oct. 1936
181	Sio-no-sawa-tugane-yu	„	„	„	„	1.33	20.0	„
182	Gantō-hunsen	„	„	„	„	2.46	20.0	„
183	Kuridaira No. 1	„	„	„	„	0.77	22.0	„
184	„ No. 1. B	„	„	„	„	0.73	17.0	„
185	Kuridaira-tennenburo	„	„	„	„	26.05	23.3	„
186	Yunokubo No. 1	„	„	„	„	7.56	21.0	„
187	Kuridaira No. 3	„	„	„	„	6.56	19.4	„
188	Tuganerō No. 1	„	„	„	„	64.53	28.0	„
189	„ No. 2	„	„	„	„	29.39	30.8	„
190	Tuganerō-naka-no-yu	„	„	„	„	31.61	23.0	Apr. 1937
191	Tuganerō-kasikiri-no-yu	„	„	„	„	23.95	25.6	„
192	Tuganerō-simo-no-yu	„	„	„	„	25.05	22.2	„
193	Umamiti-zawa	„	„	„	„	4.93	15.8	Oct. 1936
194	Totikubo No. 1	„	„	„	„	32.62	27.0	„
195	Kinsentō	„	„	„	„	29.30	31.0	„
196	Hiuke-sui	„	„	„	„	39.16	11.2	Apr. 1937
197	Iwaana-zawa	„	„	„	„	0.76	13.8	„
198	Yuzawa No. 1	„	„	„	„	71.81	13.7	„
199	„ No. 2	„	„	„	„	1.93	17.7	„
200	„ No. 3	„	„	„	„	1.76	18.5	„
201	„ No. 4	„	„	„	„	0.00	13.7	„
202	„ No. 5	„	„	„	„	0.00	11.5	„

203	Dōbuti-no-yu	Masutomi		Masutomi	Kita-koma	Yamanasi	0.63	9.0	Apr. 1937
204	Siokawa-asiai-no-yu	"		"	"	"	1.20	17.5	Oct. 1936
205	Siokawa-nisida-no-yu	"		"	"	"	0.0	17.8	Apr. 1937
206	Siobuti-no-yu	"		"	"	"	11.06	14.5	Oct. 1936
207	Nakazima-no-izumi	"		"	"	"	2.94	14.3	Apr. 1937
208	Wada-matuba-Kōsen	"		"	"	"	82.66	13.0	Oct. 1936
209	Siozawa-kuromori-Kōsen	"		"	"	"	11.57	12.0	"
210	Siozawa-kuromori-yosino-kwan	"		"	"	"	0.00	8.5	Apr. 1937
211	Simo-no-daira-no-yu	"		"	"	"	13.00	7.8	"
212	Kamase-hudō-no-yu	"		"	"	"	0.00	2.2	"
213	Matudaira-no-yu	"		"	"	"	1.52	7.0	"
214	Kōhu-Onsen	Kōhu	Nisiki-mati	Kōhu City		"	0.08	39.0	Nov. 1939
215	Yukawa-no-yu	Itō	Yukawa	Itō Town	Takata	Sizuoka	0.16	44.0	Sept. 1937
216	Private bath (T. Ōkawa)	"	"	"	"	"	0.04	41.9	"
217	Matubara-no-yu	"	Matubara	"	"	"	0.16	42.0	"
218	Tennen-yu	"	"	"	"	"	0.19	43.7	"
219	Tōkyō-kwan-no-yu	"	"	"	"	"	0.04	52.0	"
220	Masuya-ryokwan-no-yu	"	"	"	"	"	0.51	48.0	"
221	Daitō-kwan-no-yu	"	"	"	"	"	0.17	45.7	"
222	Private bath (K. Iizima)	"	"	"	"	"	0.27	40.5	"
223	Hōsen-kwan-no-yu	"	"	"	"	"	0.39	42.0	"
224	Private bath (S. Naruto)	"	Kusumi	"	"	"	0.14	38.0	"
225	Tennen-yu	"	"	"	"	"	0.11	44.3	"
226	Enpanrō-no-yu	"	"	"	"	"	0.09	47.7	"
227	Arai-kwan-no-yu	"	"	"	"	"	0.26	40.5	"
228	Yōki-kwan-no-yu	"	Oka	"	"	"	0.18	51.0	"
229	Tōkai-kwan-no-yu	"	"	"	"	"	0.17	51.2	"
230	Private bath (K. Satō)	"	"	"	"	"	0.27	52.3	"
231	" (M. Aoki)	"	"	"	"	"	0.20	52.8	"

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
232	Private bath (T. Suzuki)	Itō	Oka	Itō Town	Takata	Sizuoka	0.28	44.8	Sept. 1937
233	„ (Wakatuki)	„	„	„	„	„	0.25	45.0	„
234	„ (Toyosima)	„	Kamata	„	„	„	0.08	51.0	„
235	Ō-yu	Yosina	Yosina	Kami-kano	„	„	0.10		„
236	Moto-yu	„	„	„	„	„	0.06		„
237	Higasi-no-yu	„	„	„	„	„	0.00		„
238	Kikusui-Onsen	„	„	„	„	„	0.00		„
239	Hōsen-Onsen	„	„	„	„	„	0.02		„
240	Kane-no-yu	„	„	„	„	„	0.06		„
241	Kan-no-yu	„	„	„	„	„	0.00		„
242	Kiku-no-yu	„	„	„	„	„	0.23		„
243	Seko-no-yu	Yugasima	Yugasima	„	„	„	0.10		Jan. 1939
244	Kidati-no-yu	„	„	„	„	„	0.30		„
245	Sagasawa-Onsen	Sagasawa	Sakasita, Kadonohara	„	„	„	0.21		Aug. 1937
246	Mito-Onsen	Mito	Mito	Utiura	„	„	0.50	42.0	
247	Radium-Kōsen	Ena	Yunosima, Takayama	Hukuoka	Ena	Gihu	0.0	13.1	May 1936
248	Itigaku-Kōsen	Itigaku	Momoyama	Nakatu Town	„	„	0.0	12.1	„
249	Yogarasu-Kōsen	Yogarasu	Ōiwa	„	„	„	0.0	14.0	„
250	Kitatani-no-izumi	Naegi	Kitatani	Naegi Town	„	„	0.0	12.3	„
251	Sika-no-yu	Kasagi	Kerokubo	Kasagi	„	„	0.0	15.1	„
252	Syō-no-yu	„	„	„	„	„	0.0	13.6	„
253	Iwō-sen	Gero	Simoyasiki	Gero Town	Masuda	„	0.00		Aug. 1937
254	Yunosima-Onsen	„	Yunosima	„	„	„	0.00		„

255	Hon-Onsen	Sakakibara	Hamada, Sakakibara	Sakakibara	Issi	Mie	0.17		
256	Makiyama-Kōsen	Makiyama	Makiyama	Tamataki	Ayama	"	1.80		
257	Yosino-Onsen	Yosino	Yosinoyama	Yosino	Yosino	Nara	0.43		Nov. 1939
258	Sionoha-Onsen	Sionoha			"	"	5.52		"
259	Kowase-no-yu	Katuura		Katuura Town	Higasi-muro	Wakayama	0.06	28.0	"
260	Kosi-no-yu No. 1	"		"	"	"	0.19	41.5	"
261	Obatakeyama- no-yu No. 1	"		"	"	"	0.13	35.0	"
262	Yukawarō-no-yu	Yukawa	Yukawa	Nati	"	"	0.10	40.2	"
263	Kawayu-Onsen	Kawayu	Kawayu, Minasegawa	Ukegawa	"	"	2.53		
264	Reimei-no-yu	Yuzaki		Sedo-no- kanayama	Nisi-muro	"	8.44	57.3	Nov. 1939
265	Higasi-sirahama-Onsen	Higasi- sirahama		"	"	"	15.91		"
266	Sin-tubaki-no-yu	Tubaki	Tubaki	Higasi- tomita	"	"	0.26	33.5	
267	Kami-no-yu	Ryūzin	Ryūzin	Ryūzin	Hidaka	"	0.57	48.0	
268	Simo-no-yu	"	"	"	"	"	0.15		
269	Tomiya-ryokwan-no-yu	Yumura		Onsen	Mikata	Hyōgo	0.79		
270	Hon-Onsen	Arima		Arima Town	Arima	"	64.97	43.0	Aug. 1939
271	Hana-no-bō-no-yu	"		"	"	"	47.08	34.5	"
272	Tansan-sen	"		"	"	"	0.76	16.0	"
273	Radium-Kōsen	"		"	"	"	12.68	27.5	"
274	Katakosi-Kōsen	"	Karato	Arino	"	"	111.05	21.0	"
275	Yakendo-Kōsen	"	Yakendo	"	"	"	61.57	22.0	"
276	Kyū-Onsen	Takarazuka	Yumoto, Takarazuka	Ryōgen	Mukō	"	26.46		Aug. 1937
277	Iwai-Onsen	Iwai	Iwai	Iwai Town	Iwami	Tottori	0.56	51.0	Oct. 1937
278	Itō-no-yu	"	"	"	"	"	0.75	34.0	"
279	Simo-no-yu	Yosioka	Higasi-sita- mati, Yosioka	Yosioka	Kedaka	"	0.61		
280	Suzukiya-no-yu	Hamamura	Hamamura	Seizyō	"	"	1.63	49.0	Aug. 1939
281	Tabakoya-no-yu	"	"	"	"	"	2.40	63.0	"
282	Hamanoya-no-yu	"	"	"	"	"	2.95	61.0	"
283	Kyōdō-yu	"	"	"	"	"	0.60	48.0	"

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
284	Seirei-no-yu	Hamamura	Hukutaziri, Katimi	Seizyō	Kedaka	Tottori	0.23	41.0	Aug. 1939
285	Sagi-no-yu	Katimi	Katimi	"	"	"	1.93	58.0	"
286	Nakataya-no-yu	"	"	"	"	"	0.73	42.0	"
237	Kabu-yu	Misasa	Misasa	Misasa	Tōhaku	"	1.14	45.0	"
288	Otyaya-no-yu	"	"	"	"	"	0.28	61.0	"
239	Private bath (M. Yamamoto)	"	"	"	"	"	0.25	52.5	"
290	Naka-no-yu	"	"	"	"	"	0.35	66.0	"
291	Hanaya-no-yu	"	"	"	"	"	0.85	68.0	"
292	Nakaya-no-yu	"	"	"	"	"	0.90	64.0	"
293	Bun-aburaya-no-yu	"	"	"	"	"	2.24	70.5	"
294	Hasizuya-no-yu	"	"	"	"	"	1.00	66.0	"
295	Yakusidō-no-yu	"	"	"	"	"	3.82	74.5	"
296	Saiki-honkwan-no-yu	"	"	"	"	"	2.37	71.0	"
297	Akazakiya-no-yu	"	"	"	"	"	5.25	69.0	"
298	Ryōyōzyo-gensen	"	"	"	"	"	2.89	72.0	"
299	Iwa-yu (Otoko-yu)	"	"	"	"	"	2.95	57.0	"
300	" (Onna-yu)	"	"	"	"	"	3.61	68.0	"
301	" (Makura-yu)	"	"	"	"	"	2.90	60.0	"
302	Eirakuan-no-yu	"	"	"	"	"	0.37	66.5	"
303	Aburaya-uti-yu	"	"	"	"	"	0.89	55.0	"
304	Aburaya-soto-yu (Mitu-yu)	"	"	"	"	"	0.21	51.5	"
305	Iwasaki-no-yu No. 2	"	"	"	"	"	2.81	68.0	"
306	Kiya-kazoku-yu	"	"	"	"	"	3.72	70.0	"

		Misasa	Misasa	Misasa	Tōhaku	Tottori			Aug. 1939
307	Haikyūzō-no-yu	Misasa						62.0	
308	Seitō-kwan-no-yu	"	"	"	"	"		60.0	"
309	Iwasaki-no-yu No. 1	"	"	"	"	"		54.5	"
310	Bansuirō-no-yu	"	"	"	"	"		48.0	"
311	Onsen-hotel-no-yu	"	"	"	"	"		68.5	"
312	Tennen-gankutu-no-yu	"	"	"	"	"		79.5	"
313	" No. 1	"	"	"	"	"		69.0	"
314	" No. 2	"	"	"	"	"		79.0	"
315	Ōhasi-ryōkwan-soto-yu	"	"	"	"	"		56.5	"
316	Yamadaku-no-yu	Yamada	"	"	"	"		64.0	"
317	Kōyōen-no-yu	"	"	"	"	"		46.0	"
318	Sinsen-ryō-no-yu	"	"	"	"	"		53.0	"
319	Misasa-kwan-no-yu	"	"	"	"	"		51.5	"
320	Okayamada-ryōyō-zyo-no-yu	"	"	"	"	"		46.0	"
321	Gunzihogoin-ryōyōzyo-no-yu	"	"	"	"	"		41.0	"
322	Kabu-yu	Sekigane	"	"	"	"		46.3	"
323	Kami-no-yu	"	"	"	"	"		46.0	"
324	Kame-no-yu	"	"	"	"	"		45.5	"
325	Turu-no-yu	"	"	"	"	"		45.3	"
326	Tokiwa-no-yu	"	"	"	"	"		39.5	"
327	Tama-no-yu	"	"	"	"	"		42.0	"
328	Yōzyō-kwan-no-yu	Tōgō	"	"	"	"		47.5	"
329	Tyūsei-kwan-no-yu No. 1	Hikizi	"	"	"	"			
330	" No. 2	Tyūkōzi	"	"	"	"			
331	Harada-ryōkwan-no-yu	"	"	"	"	"			
332	Doi-ryōkwan-no-yu	"	"	"	"	"			
333	Watanabe-ryōkwan-no-yu	"	"	"	"	"			
334	Kawamoto-ryōkwan-no-yu	"	"	"	"	"			
335	Private bath (H. Huzita)	"	"	"	"	"			
336	No. 1	"	"	"	"	"			
337		"	"	"	"	"			
338		"	"	"	"	"			
339		"	"	"	"	"			
340		"	"	"	"	"			
341		"	"	"	"	"			
342		"	"	"	"	"			
343		"	"	"	"	"			
344		"	"	"	"	"			
345		"	"	"	"	"			
346		"	"	"	"	"			
347		"	"	"	"	"			
348		"	"	"	"	"			
349		"	"	"	"	"			
350		"	"	"	"	"			
351		"	"	"	"	"			
352		"	"	"	"	"			
353		"	"	"	"	"			
354		"	"	"	"	"			
355		"	"	"	"	"			
356		"	"	"	"	"			
357		"	"	"	"	"			
358		"	"	"	"	"			
359		"	"	"	"	"			
360		"	"	"	"	"			
361		"	"	"	"	"			
362		"	"	"	"	"			
363		"	"	"	"	"			
364		"	"	"	"	"			
365		"	"	"	"	"			
366		"	"	"	"	"			
367		"	"	"	"	"			
368		"	"	"	"	"			
369		"	"	"	"	"			
370		"	"	"	"	"			
371		"	"	"	"	"			
372		"	"	"	"	"			
373		"	"	"	"	"			
374		"	"	"	"	"			
375		"	"	"	"	"			
376		"	"	"	"	"			
377		"	"	"	"	"			
378		"	"	"	"	"			
379		"	"	"	"	"			
380		"	"	"	"	"			
381		"	"	"	"	"			
382		"	"	"	"	"			
383		"	"	"	"	"			
384		"	"	"	"	"			
385		"	"	"	"	"			
386		"	"	"	"	"			
387		"	"	"	"	"			
388		"	"	"	"	"			
389		"	"	"	"	"			
390		"	"	"	"	"			
391		"	"	"	"	"			
392		"	"	"	"	"			
393		"	"	"	"	"			
394		"	"	"	"	"			
395		"	"	"	"	"			
396		"	"	"	"	"			
397		"	"	"	"	"			
398		"	"	"	"	"			
399		"	"	"	"	"			
400		"	"	"	"	"			
401		"	"	"	"	"			
402		"	"	"	"	"			
403		"	"	"	"	"			
404		"	"	"	"	"			
405		"	"	"	"	"			
406		"	"	"	"	"			
407		"	"	"	"	"			
408		"	"	"	"	"			
409		"	"	"	"	"			
410		"	"	"	"	"			
411		"	"	"	"	"			
412		"	"	"	"	"			
413		"	"	"	"	"			
414		"	"	"	"	"			
415		"	"	"	"	"			
416		"	"	"	"	"			
417		"	"	"	"	"			
418		"	"	"	"	"			
419		"	"	"	"	"			
420		"	"	"	"	"			
421		"	"	"	"	"			
422		"	"	"	"	"			
423		"	"	"	"	"			
424		"	"	"	"	"			
425		"	"	"	"	"			
426		"	"	"	"	"			
427		"	"	"	"	"			
428		"	"	"	"	"			
429		"	"	"	"	"			
430		"	"	"	"	"			
431		"	"	"	"	"			
432		"	"	"	"	"			
433		"	"	"	"	"			
434		"	"	"	"	"			
435		"	"	"	"	"			
436		"	"	"	"	"			
437		"	"	"	"	"			
438		"	"	"	"	"			
439		"	"	"	"	"			
440		"	"	"	"	"			
441		"	"	"	"	"			
442		"	"	"	"	"			
443		"	"	"	"	"			
444		"	"	"	"	"			
445		"	"	"	"	"			
446		"	"	"	"	"			
447		"	"	"	"	"			
448		"	"	"	"	"			
449		"	"	"	"	"			
450		"	"	"	"	"			
451		"	"	"	"	"			
452		"	"	"	"	"			
453		"	"	"	"	"			
454		"	"	"	"	"			
455		"	"	"	"	"			
456		"	"	"	"	"			
457		"	"	"	"	"			
458		"	"	"	"	"			
459		"	"	"	"	"			
460		"	"	"	"	"			
461		"	"	"	"	"			
462		"	"	"	"	"			
463		"	"	"	"	"			
464		"	"	"	"	"			
465		"	"	"	"	"			
466		"	"	"	"	"			
467		"	"	"	"	"			
468		"	"	"	"	"			
469		"	"	"	"	"			
470		"	"	"	"	"			
471		"	"	"	"	"			
472		"	"	"	"	"			
473		"	"	"	"	"			
474		"	"	"	"	"			
475		"	"	"	"	"			
476		"	"	"	"	"			
477		"	"	"	"	"			
478		"	"	"	"	"			
479		"	"	"	"	"			
480		"	"	"	"	"			
481		"	"	"	"	"			
482		"	"	"	"	"			
483		"	"	"	"	"			
484		"	"	"	"	"			
485		"	"	"	"	"			
486		"	"	"	"	"			
487		"	"	"	"	"			
488		"	"	"	"	"			
489		"	"	"	"	"			
490		"	"	"	"	"			
491		"	"	"	"	"			
492		"	"	"	"	"			
493		"	"	"	"	"			
494		"	"	"	"	"			
495		"	"	"	"	"			
496		"	"	"	"	"			
497		"	"	"	"	"			
498		"	"	"	"	"			
499		"	"	"	"	"			
500		"	"	"	"	"			

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
335	Private bath (H. Huzita) No. 2	Tōgō	Tyūkōzi	Tōgō	Tōhaku	Tottori	2.63		
336	Turuya-no-yu.	"	"	"	"	"	0.12		
337	Private bath (Y. Itō)	Matusaki		Matusaki	"	"	0.57		
338	Tyōrakuen-no-yu	Tamatukuri	Tamatukuri	Tamayu	Yatuka	Simane	3.17	72.0	Oct. 1937
339	Matu-no-yu	"	"	"	"	"	97.14		
340	Ameya-ryokwan-no-yu	Usio		Usio	Ōhara	"	0.06		
341	Usio-no-ido	Susa		Higasi-susa	Ihisi	"	0.30		
342	Moto-yu	Sigaku	Sigaku	Sahime	Anno	"	1.02	45.0	Aug. 1939
343	Abura-yu	"	"	"	"	"	0.80	39.5	"
344	Koyabara-Onsen	Koyabara	Koyabara	"	"	"	6.15	38.3	"
345	Radium-Kōsen No. 1	Ikeda	Ikeda	"	"	"	36.43	21.7	"
346	" No. 2	"	"	"	"	"	19.46	17.7	"
347	Yugakai-Onsen No. 1	Yugakai	Yugakai	Kasubuti	Ōti	"	35.06	32.3	"
348	" No. 2	"	"	"	"	"	30.57	27.3	"
349	" No. 3	"	"	"	"	"	13.45	25.9	"
350	Sagi-no-yu	Yunogō	Yunogō	Yunogō	Katuda	Okayama	0.62		Aug. 1937
351	Sin-sagi-no-yu	"	"	"	"	"	0.50		
352	Yamano-Onsen	Yamano		Yamano	Hukayasu	"	0.00		
353	Nisimuraya-no-yu	Yuda	Yuda	Yamaguti City		Yamaguti	0.00	62.0	Aug. 1937
354	Mizuno-ryokwan-no-yu	"	"	"	"	"	0.22		"
355	Hisanoya-no-yu	"	"	"	"	"	0.00		"
356	On-yu	Yumoto	Hukagawa, Yumoto	Hukagawa Town	Ōtu	"	0.68		"
357	Rei-yu	"	"	"	"	"	0.13		"

358	Mati-no-yu	Tawarayama	Yumati	Tawarayama	Otu	Yamaguti	0.00		Sept. 1937
359	Kawa-no-yu	"	"	"	"	"	0.00		"
360	Syō-no-yu	"	"	"	"	"	0.00		"
361	Kami-no-yu	Yanai		Yanai Town	Kuga	"	0.29		
362	Simō-no-yu	"		"	"	"	0.63		
363	Yuyama-Kōsen	Yuyama		"	"	"	0.34		
364	Gogōtani-Kōsen	Gogōtani		Gogō	Mitoyo	Kagawa	0.10		
365	Kami-no-yu	Dōgo		Dōgo Town	Onsen	Ehime	0.08		Aug. 1937
366	Yōzyō-yu	"		"	"	"	0.03		"
367	Donkobori-no-yu	"		"	"	"	0.03		"
368	Siunsen	Kaisyō	Kaisyō	Kawakami	"	"	0.21	20.0	Nov. 1937
369	Nibukawa-Kōsen	Nibukawa	Nibukawa	Nibukawa	Oti	"	0.14		Aug. 1937
370	Spring No. 1	Musasi		Hutukaiti Town	Tukusi	Hukuoka	0.15		Sept. 1937
371	" No. 2	"		"	"	"	0.17		"
372	Hunagoya-Kōsen No. 1	Hunagoya	Hunagoya	Mizuta	Yame	"	0.02		Aug. 1937
373	" No. 2	"	"	"	"	"	0.00	22.0	"
374	Hyōgami-Onsen			Obuti	"	"	0.00		Apr. 1939
375	Reityō-sen	Beppu	Beppu	Beppu City		Ōita	0.22	60.0	Aug. 1937
376	Kotobuki-Onsen	"	"	"		"	0.18	46.5	Sept. 1937
377	Yanagi-Onsen	"	"	"		"	0.64	49.5	"
378	Kusunoki-Onsen	"	"	"		"	0.39	44.5	Aug. 1937
379	Hurō-sen	"	"	"		"	0.32	59.0	"
380	Ta-no-yu A	"	"	"		"	0.18	57.0	"
381	" B	"	"	"		"	0.15	43.0	"
382	Kaigan-suna-yu	"	"	"		"	0.04	58.5	Sept. 1937
383	Takegawara-Onsen	"	"	"		"	0.74	64.5	Aug. 1937
384	Umezono-Onsen	"	"	"		"	0.75	61.5	Sept. 1937
385	Kitamati-Onsen	"	"	"		"	0.30	55.0	"
386	Kaimonzi-Kōen-Onsen	"	"	"		"	0.25	62.0	"

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Continued)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
387	Matogahama-Onsen	Beppu	Beppu	Beppu City		Ōita	0.76	49.5	Sept. 1937
388	Yumimatu-Onsen	"	"	"		"	0.25	62.0	"
389	Yumigahama-Onsen	"	"	"		"	0.59	49.0	"
390	Unsenzi-Onsen	"	"	"		"	0.21	51.0	Aug. 1937
391	Hinode-Onsen	"	"	"		"	0.17	50.5	Sept. 1937
392	Syōzyu-sen	"	"	"		"	0.48	47.0	"
393	Nagesi-Onsen	"	"	"		"	0.72	52.5	"
394	Kamiya-Onsen	"	"	"		"	0.11	51.0	"
395	Hamawaki-Onsen	"	Hamawaki	"		"	0.14	46.5	Aug. 1937
396	Sira-yu	Kwankaizi	Kwankaizi	"		"	0.22	43.0	Sept. 1937
397	Kwankaizi-Onsen	"	"	"		"	0.00	55.5	"
398	Horita-Onsen	Horita	Horita	"		"	0.09	81.0	"
399	Bōtyō-sen	Kita-isigaki	Kita-isigaki	"		"	0.00	63.0	"
400	Si-no-yu	Kamegawa	Kamegawa	"		"	0.00	54.0	"
401	Kiyō-sen	"	"	"		"	0.11	56.8	"
402	Hamada-Onsen	"	"	"		"	0.24	80.5	"
403	Gomusō-Onsen	"	"	"		"	0.04	45.0	"
404	Suzi-yu	"	"	"		"	0.00	58.0	"
405	Sibaseki-Onsen	"	Sibaseki, Kamegawa	"		"	0.00	67.0	"
406	Netu-no-yu	Kannawa	Kannawa	"		"	0.00	48.0	"
407	Sibu-yu	"	"	"		"	0.00	91.0	"
408	Umi-zigoku	"	"	"		"	0.54	90.5	1939
409	Zizō-Onsen	Myōban	Myōban	"		"	0.00	60.0	Sept. 1937

410	Kakuzyu-sen	Myōban	Myōban	Beppu City		Oita	0.27	70.0	Sept. 1937
411	Yakusi-Onsen	"	"	"		"	0.27	87.0	"
412	Tanakaiti-Onsen	Yuhuin	Tanakaiti	Minami-yuhuin	Hayami	"	0.00		
413	Yunotubo-Onsen	"		Kita-yuhuin	"	"	0.09		
414	Otomaru-Onsen	"		"	"	"	0.06		
415	Tukahara-Onsen	Tukahara	Tukahara	"	"	"	0.00		
416	Ō-yu (Kin-no-yu)	Yunohira	Tanigawa	Yunohira	Oita	"	0.24	92.0	Aug. 1937
417	Hana-no-yu-Onsen	"	"	"	"	"	0.19	78.0	"
418	Sirataki-Onsen	"	"	"	"	"	0.56	65.0	"
419	Kotobuki-Onsen	"	"	"	"	"	0.20	69.0	"
420	Suna-yu	"	"	"	"	"	0.13	63.0	"
421	Simizu-Onsen	"	"	"	"	"	0.12	72.5	"
422	Yunoto-Onsen	"	"	"	"	"	0.01	38.0	"
423	Hidaya-Onsen	"	"	"	"	"	0.10		"
424	Turuya-no-yu	"	"	"	"	"	0.07		"
425	Turuya-intaku-no-yu	"	"	"	"	"	0.05		"
426	Sinya-Onsen	"	"	"	"	"	0.00		"
427	Ōiwa-Onsen	"	"	"	"	"	0.04		"
428	Azumaya-no-yu	"	"	"	"	"	0.09		"
429	Migimaru-ryokwan-no-yu	"	"	"	"	"	0.11		"
430	Kitabeya-Onsen	"	"	"	"	"	0.00		"
431	Private bath (S. Asō)	"	"	"	"	"	0.00		"
432	" (K. Maki)	"	"	"	"	"	0.00		"
433	" (I. Asō)	"	"	"	"	"	0.08		"
434	Nagaiki-no-yu	Nagayu	Nagayu	Nagayu	Naori	"	0.58	42.0	Oct. 1937
435	Kōyōkwan-no-yu	"	"	"	"	"	0.47		"
436	Tōkyōya-no-yu	Takeo	Takeo	Takeo Town	Kinosima	Saga	0.89	52.0	
437	Huruyu-Onsen	Huruyu	Motomura, Huruyu	Minami-yama	Kosiro	"	0.05		
438	Tosita-Onsen No. 1	Tosita	Tosita, Kawayu	Tyōyō	Aso	Kumamoto	0.04		

Table 3.—(Continued)

1. Radium content of the mineral springs of Japan. (Concluded)

No.	Spring		Section	Village	County	Prefecture	Radium content g./l. $\times 10^{12}$	Temp. of spring °C	Date of sampling
439	Tosita-Onsen No. 2	Tosita	Tosita, Kawayu	Tyōyō	Aso	Kumamoto	0.10		
440	Gozen-no-yu	Hinaku	Hinaku	Hinaku Town	Asikita	"	0.08		Aug. 1937
441	Moto-yu-Onsen	Yunoura	Yunoura	Yunoura	"	"	0.04	45.0	Oct. 1937
442	Matu-no-yu-Onsen	"	"	"	"	"	0.07	42.0	"
443	Hukamizu-Onsen	"	"	"	"	"	0.02	43.0	"
444	Iwa-no-yu-Onsen	"	"	"	"	"	0.06	45.0	"
445	Kotobuki-Onsen	"	"	"	"	"	0.02		"
446	Sinohara-Onsen	"	"	"	"	"	0.06		"
447	Private bath (H. Yamamoto)	"	"	"	"	"	0.00		"
448	Mura-no-yu-Onsen	Ibusuki		Ibusuki Town	Ibusuki	Kagosima	0.89		Aug. 1937
449	Yaziga-yu-Onsen	"		"	"	"	0.55		"
450	Misuzi-no-yu	"		"	"	"	0.51		"
451	Sikorogahama-Onsen	"		"	"	"	0.89		"
452	Kaisuien-Onsen	"		"	"	"	1.05		"
453	Kairakuen-Onsen	"		"	"	"	1.18		"
454	Kabusiki-Onsen	Kabusiki	Yunoura	Isaku Town	Hioki	"	0.00		"
455	Private bath (K. Huzita)	Miyanozyō	Yuda	Miyanozyō Town	Satuma	"	0.06		Sept. 1937
456	" (K. Hayasida)	"	"	"	"	"	0.06		"
457	" (T. Kamizono)	"	"	"	"	"	0.00		"
458	" (A. Kamizono)	"	"	"	"	"	0.04		"
459	" (M. Morita)	"	"	"	"	"	0.00		"
460	Zairai-no-yu	"	"	"	"	"	0.06		"
461	Tansan-sen	Kirisima, Iwōdani	Simo- nakatugawa	Makizono	Aira	"	0.00		"

462	Sio-no-yu	Kirisima, Iwōdani	Simo- nakatugawa	Makizono	Aira	Kagosima	0.01		Sept. 1937
463	Myōban-sen	"	"	"	"	"	0.01		"
464	Iwōsen No. 1	"	"	"	"	"	0.00		"
465	" No. 2	"	"	"	"	"	0.00		"
466	Hayasida-Onsen	Kirisima, Eino-o	Eino, Simo- nakatugawa	"	"	"	0.39	71.0	"
467	Enrui-sen	"	"	"	"	"	3.52		"
468	Tetubun-sen	"	"	"	"	"	0.15		"
469	Maruya-ryokwan-no-yu	"	"	"	"	"	0.31		"
470	Ramune-Onsen No. 1	Ramune	Tozaki	"	"	"	0.20		Aug. 1937
471	" No. 2	"	"	"	"	"	0.18		"
472	Taisyō-kwan-no-yu	Hinatayama	Hinatayama	Hayato Town	"	"	0.00		
473	Hukuya-no-yu	"	"	"	"	"	0.00		
474	Ansintei-no-yu	"	"	"	"	"	0.00		
475	Sinkyū-no-yu	"	"	"	"	"	0.00		
476	Yuno-o-Onsen	Yuno-o		Hisikari	Isa	"	1.53		Sept. 1937
477	Kamii-kwan-no-yu	On-yō		Onyō-men	Gazan	Tyūsei-nan- dō, Korea	0.00	46.0	Oct. 1937

2. Radium content of brines from Japanese oil fields and
natural gas field.

No.	Oil-field (Natural gas field)*	County	Prefecture	Petroleum well			Radium content g./l. $\times 10^{12}$	pH**	Date of sampling
				No.	Depth m.	Flow of water 10 ³ l./day			
1	Omonogawa	Kawabe	Akita	1	310	4.0	11.05	7.0	July 1937
2	"	"	"	25	226	1.4	7.14	7.9	"
3	Araya	"	"	1	278	2.3	10.02	7.8	"
4	Aburaden	"	"	1	297	21.0	7.02	7.2	"

Table 3.—(Concluded)

2. Radium content of brines from Japanese oil fields and
natural gas field. (Concluded)

No.	Oil-field (Natural gas field)*	County	Prefecture	Petroleum well			Radium content g./l. $\times 10^{12}$	pH**	Date of sampling
				No.	Depth m.	Flow of water 10^3 l./day			
5	Oguni	Yuri	Akita	R 32	770	0.6	0.0	8.3	Nov. 1935
6	Oguti	Naka-kanbara	Niigata	R 97	381	5.6	0.0	8.5	"
7	Ōmo	Minami-kanbara	"	R 4	894	1.8	12.8	7.9	"
8	Ōguti	"	"	C 1	559		1.10	11.1	Oct. 1937
9	Yoita	Santō	"		426		0.04		Aug. 1939
10	Takamati	Kariha	"	R 36	1399	7.9	2.2	7.6	Oct. 1935
11	Iriwada	"	"	R 5	971	1.1	1.5	7.2	"
12	Nagamine	"	"	C 93	502	0.03	0.0	5.5	Nov. 1935
13	Okano	"	"	R 1	78		2.47		Mar. 1939
14	"	"	"	"	108		2.84		"
15	Ōtaki*	Isumi	Tiba				0.0		

** The pH value of the water was measured by K. Hosino with the sample he brought to the laboratory.

As will be seen from these tables, compared with the mineral springs in other countries, those in Japan are very poor in radium, which may be owing to the poverty in radium of Japanese rocks. Table 6 shows the radium contents of granite and basalt in Japan and those in other countries, from which the mean radium contents of rocks in Japan seem to be somewhat smaller than the mean for those in other countries as obtained by a number of investigators.

Table 4. Springs with the highest concentration of radium in the world.

Spring	Radium content g./l.	Author and date
Pit-holes No. 1/28, 3/28, 1/31. Petroleum district of Grosny. North Caucasus, Russia.	1.8×10^{-8}	B. A. Nikitin ⁽³⁾ (1930)
Pit-hole "Kasennaya No. 1." Petroleum district of Uchta. Northeastern European Russia.	7.4×10^{-9}	V. I. Baranov, ⁽¹⁾ I. D. Kurbatov, A. A. Cherepeunikov (1928)
Radium pit-hole of Heidelberg in Germany.	1.8×10^{-9}	A. Becker ⁽⁵⁾ (1918)
Tzeliutsing, Szechwan, China.	7.3×10^{-10}	S. Gōda ⁽⁶⁾ (1939)
Pit-hole Stolb Bereclej. Petroleum district of Dagestan. Caucasus, Russia.	3.0×10^{-10}	A. A. Cherepeunikov ⁽⁴⁾ (1928)
Spring Slavyanovsky. Watering place of Gelesnovodsk. North Caucasus, Russia	2.2×10^{-10}	I. D. Kurbatov, ⁽⁷⁾ V. Baranov (1928)
Bath, England.	1.4×10^{-10}	W. Ramsay ⁽⁸⁾ (1912)
Saratoga, New York, America.	1.1×10^{-10}	H. Schlundt ⁽⁹⁾ (1909)
Karlsbad, Germany	1.0×10^{-10}	W. Kolhorster ⁽¹⁰⁾ (1912)

Table 5. Springs with the highest concentrations of radium in Japan.

Spring	Location	Prefecture	Radium content g./l. $\times 10^{11}$
Katakosi-Kōsen	Arima	Hyōgo	11.11
Matu-no-yu	Tamatukuri	Simane	9.71
Wadamatuba-Kōsen	Masutomi	Yamanasi	8.44
Yuzawa No. 1	"	"	7.18

(4) A. Cherepeunikov, Trans. Geol. Survey (Leningrad), No. 4 (1928).

(5) A. Becker, *Z. anorg. allgem. Chem.*, **209** (1923), 131.

(6) S. Gōda, *Bull. Shanghai Nat. Sci. Research Lab.*, **8** (1939), 252.

(7) I. D. Kurbatov, *Compt. rend. acad. sci.*, U.R.S.S., **1930**, 452.

(8) W. Ramsay, *Chem. News*, **134** (1913), 105.

(9) H. Schlundt, *J. Phys. Chem.*, **18** (1914), 662.

(10) W. Kolhorster, *Verhandl. deut. physik. Ges.*, **14** (1912), 356.

Table 5.—(Concluded)

Spring	Location	Prefecture	Radium content g./l. $\times 10^{11}$
Hon-Onsen	Arima	Hyōgo	7.13
Hana-no-bō-no-yu	„	„	6.85
Tuganērō No. 1	Masutomi	Yamanasi	6.45
Yakendo-Kōsen	Arima	Hyōgo	6.16
Hiuke-sui	Masutomi	Yamanasi	3.92
Radium-Kōsen No. 1	Ikeda	Simane	3.64
Higasiobi-no-izumi	Masutomi	Yamanasi	3.57
Yugakai-Onsen No. 1	Yugakai	Simane	3.51
Totikubo No. 1	Masutomi	Yamanasi	3.26
Tuganērō-naka-no-yu	„	„	3.16
Yugakai-Onsen No. 2	Yugakai	Simane	3.06
Tuganērō No. 2	Masutomi	Yamanasi	2.94
Kinsentō	„	„	2.93
Hattōdaira No. 2	„	„	2.69
Kyū-Onsen	Takarazuka	Hyōgo	2.65
Kuridaira-tennen-buro	Masutomi	Yamanasi	2.61
Tuganērō-simo-no-yu	„	„	2.51
Tuganērō-kasikiri-no-yu	„	„	2.40
Radium-Kōsen No. 2	Ikeda	Simane	1.95
Yamasio-Kōsen	Kasio	Nagano	1.85
Okayamada-ryōyōzyo-no-yu	Misasa	Tottori	1.77
Kōyōen-no-yu	„	„	1.61
Ōhasi-ryokwan-soto-yu	„	„	1.60
Higasi-sirahama-Onsen	Higasi-sirahama	Wakayama	1.59
Alkali-sen	Isobe	Gumma	1.55
Misasa-kwan-no-yu	Misasa	Tottori	1.50
Kagami-no-yu	Matunoyama	Niigata	1.43
Onsen-hotel-no-yu	Misasa	Tottori	1.35
Yugakai-Onsen No. 3	Yugakai	Simane	1.35
Simono-daira-no-yu	Masutomi	Yamanasi	1.30
Petroleum well No. R4	Ōmo oil field	Niigata	1.28
Tansan-sen	Isobe	Gumma	1.16
Wadegawara No. 2	Masutomi	Yamanasi	1.16
Siozawa-kuromori-Kōsen	„	„	1.16
Siobuti-no-yu	„	„	1.11
Petroleum well No. 1	Omonogawa oil field	Akita	1.11
Toyotomi-Onsen	Toyotomi	Hokkaidō	1.01
Tennen-gankutu-no-yu No. 1	Misasa	Tottori	1.01
Petroleum well No. 1	Araya oil field	Akita	1.00

Table 6. Comparison of mean radium contents of granite and basalt in Japan and those in other countries.

Author	Granite		Basalt	
	Number of specimens	Radium content g./g. $\times 10^{12}$	Number of specimens	Radium content g./g. $\times 10^{12}$
Japan				
Z. Hatuda, ⁽¹¹⁾ T. Asayama ⁽¹²⁾ H. Hamaguti, ⁽¹³⁾ T. Nakai ⁽¹³⁾	41	1.41	6	0.12
Europe and America				
J. Joly ⁽¹⁴⁾	86	3.01	18	1.40
R. J. Strutt ⁽¹⁵⁾	10	2.79	8	0.44
E. H. Büchner ⁽¹⁶⁾	5	3.70	1	0.50
C. S. Piggot ⁽¹⁷⁾	24	1.75	13	0.96
R. D. Evans ⁽¹⁸⁾			2	0.33

IV. The Mineral Springs of Masutomi, Yamanashi Prefecture. The Masutomi Mineral Springs surpass all other Japanese cold springs in their radon content.⁽¹⁹⁾ Compared with those of strongest radioactivity in Europe, they are inferior only to Oberschlema, Brambach, Lurisia and Joachimsthal, but superior to Gastein, Landeck, Baden-Baden, etc., so that they no doubt hold the fifth position in the world.

With the object of studying these radioactive mineral springs, the writer stayed at this spa from October 15 to 19, 1936, and again from April 24 to 30, 1937. The temperature, the radon content⁽²⁰⁾ and the flow of the waters were measured at 45 springs in this region, direct at the source, and water samples for radium determination were also drawn direct from the source.

All these determinations are given in Table 7. The pH values of these waters were determined by K. Kuroda in July 1939. The amount of total evaporated residue was determined by S. Okauti for the samples taken in October 1936.

-
- (11) Z. Hatuda, *Mem. Coll. Sci.*, Kyōto Imp. Univ., B, **10** (1934), 63; **12** (1936), 1.
 (12) T. Asayama, *Jap. J. Astronomy and Geophysics*, **14** (1936), 19.
 (13) T. Nakai, *J. Chem. Soc. Japan*, **61** (1940), 149.
 (14) J. Joly, *Phil. Mag.*, (6) **24** (1912), 694.
 (15) R. J. Strutt, *Proc. Roy. Soc.*, **76 A** (1905), 88.
 (16) E. H. Büchner, *Jahr. f. Radioakt.*, **10** (1913), 516.
 (17) C. S. Piggot, *Am. J. Sci.*, **35**, A (1938), 227; **25** (1933), 229.
 (18) R. D. Evans, *Am. J. Sci.*, **29** (1935), 445.
 (19) In October 1939, S. Matuura and I. Iwasaki of the Kyūsyū Imperial University found a very strong radioactive mineral spring at Ikeda, Simane Prefecture, the radon content of which is almost equal to that of Masutomi (v. Table 18).
 (20) For measuring the radon content of water, the IM Fontactoscope, made by the Institute of Physical and Chemical Research, Tokyo, was used.

Table 7. Mineral springs of Masutomi and neighbourhood.

No.	Spring	Temp. of spring °C	Temp. of air °C	Radium content g./l. $\times 10^{12}$	Radon per liter of water in Mache's units	pH	Total residue g./l.	Flow of water hl./day	Radium discharge 10^{-3} g. (mg.)/year
1	Ōsiba	22.5	18.0	2.68	362	6.4	9.40	49	0.005
2	Ginsentō-huru-yu	31.0	18.3	9.39	153	6.5	10.30	22	0.008
3	Ginsentō-kami-no-yu	28.5	16.5	7.35	104	6.5	9.64	13	0.004
4	Ginsentō-naka-no-yu	22.0	16.5	0.43	11.6	6.7	9.72	19	0.000
5	Ginsentō-simo-no-yu	17.0	14.0	3.42	42.2		9.78	16	0.002
6	Wadegawara No. 1	18.0	15.6	6.76	588	6.5	3.25		
7	Wadegawara No. 2	19.5	16.5	11.62	1343	6.2	7.12	2	0.001
8	Hattō-daira No. 1	17.0	17.0	0.11	17.5		3.76	49	0.000
9	Hattō-daira No. 2	14.9	15.7	26.93*				4	0.004
10	Yokote-no-yu	15.0	15.7	0.71*				20	0.001
11	Higasiobi-no-izumi	25.0	17.0	35.65	8.9	6.3	9.69	22	0.029
12	Nibuzawa	24.0	20.5	6.22	330		7.25	77	0.018
13	Sio-no-sawa-tugane-yu	20.0	17.0	1.33	193		4.89	45	0.002
14	Gantō-hunsen	20.0	17.0	2.46	10.9		2.92		
15	Kuridaira No. 1	22.0	11.5	0.77	576	6.0	3.62		
16	Kuridaira No. 1. B	17.0	12.5	0.73	304		2.32		
17	Kuridaira-tennen-buro	23.3	17.0	26.05	7.4	6.4	8.56	32	0.030
18	Yunokubo No. 1	21.0	18.0	7.56	202		3.08		
19	Kuridaira No. 3	19.4	11.9	6.56	355*		7.65		
20	Tuganerō No. 1	28.0	16.5	64.53	4.9	6.4	8.53	175	0.412
21	Tuganerō No. 2	30.8	15.6	29.39	4.0	6.4	8.99	31	0.033
22	Tuganerō-naka-no-yu	23.0	16.3	31.61*				9	0.010
23	Tuganerō-kasikiri-no-yu	25.6	14.4	23.95*	6.5*			36	0.032
24	Tuganerō-simo-no-yu	22.2	14.0	25.05*				1	0.001
25	Umamiti-zawa	15.8	14.5	4.93	6.4		3.63		
26	Totikubo No. 1	27.0	13.3	32.62	25.6	6.3	9.42	81	0.006

Table 7.—(Concluded)

No.	Spring	Temp. of spring °C	Temp. of air °C	Radium content g./l. $\times 10^{12}$	Radon per liter of water in Mache's units	pH	Total residue g./l.	Flow of water hl./day	Radium discharge 10^{-3} g. (mg.) /year
27	Kinsentō	31.0	16.0	29.30	3.3	6.3	7.49	410	0.460
28	Hiuke-sui	11.2	15.7	39.16*			4.05	2	0.003
29	Iwaana-zawa	13.8	12.3	0.76*	0.0*		0.17		
30	Yuzawa No. 1	13.7	12.8	71.81*	16.1*			59	0.155
31	„ No. 2	17.7	12.8	1.93*					
32	„ No. 3	18.5	12.8	1.76*					
33	„ No. 4	13.7	12.8	0.00*					
34	„ No. 5	11.5	13.8	0.00*					
35	Dōbuti-no-yu	9.0	15.7	0.63*			2.45		
36	Siokawa-asiyai-no-yu	17.5	16.5	1.20	1.5*		3.81	64	0.003
37	Siokawa-nisida-no-yu	17.8	20.6	0.0*	0.4*				
38	Siobuti-no-yu	14.5	16.5	11.06	3.9*		5.10	32	0.013
39	Nakazima-no-izumi	14.3	18.3	2.94*	1.7*				
40	Wada-matuba-Kōsen	13.0	16.0	82.66	6.1*	6.4	13.34	2	0.006
41	Siozawa-kuromori-Kōsen	12.0	16.0	11.57	1.8*		4.46	8	0.003
42	Siozawa-kuromori-yosi- no-kwan	8.5	11.0	0.00*	1.2*				
43	Simo-no-daira-no-yu	7.8	15.0	13.00*	2.3*			26	0.012
44	Kamase-hudō-no-yu	2.2	17.8	0.00*	1.0*				
45	Matudaira-no-yu	7.0	15.5	1.52*					
Total:									1.343

The orifice temperature was measured on the same sample as that which was determined for the radium content.

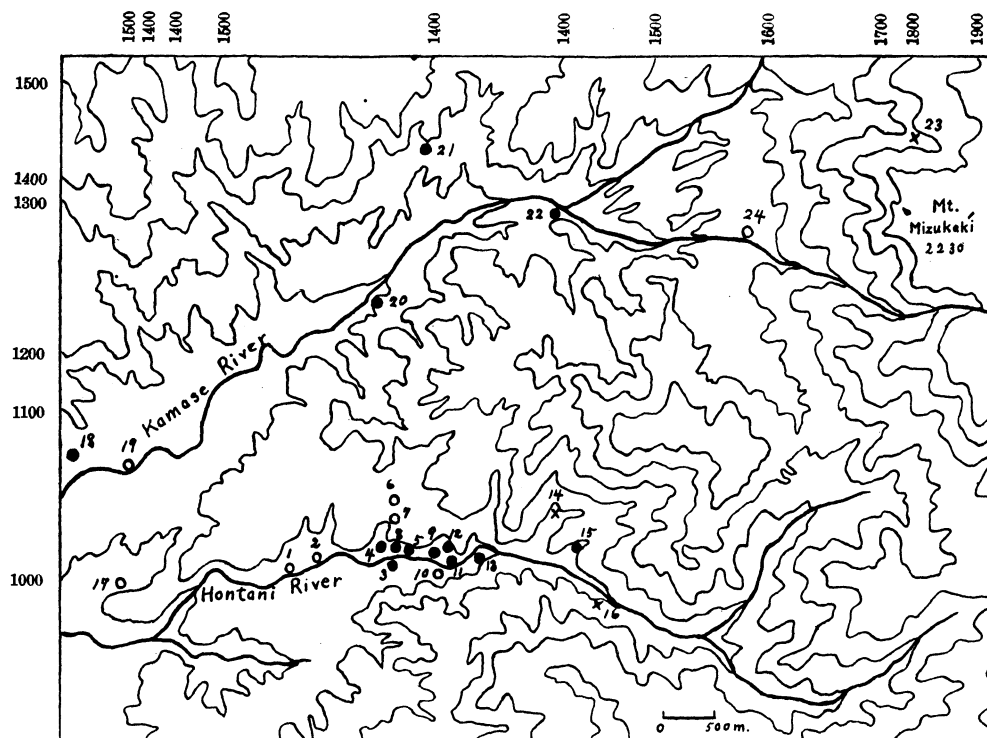
The radium content of the water was determined with the sample taken in October, 1936. Sampling of the waters started was made in April, 1937.

The radon content of the water was measured in October, 1936 and that of the sample started in April, 1937.

The flow of water was measured in April, 1937.

The pH value was determined by Kuroda in July, 1939.

The total residue was determined by Okauti from sample drawn October, 1936.

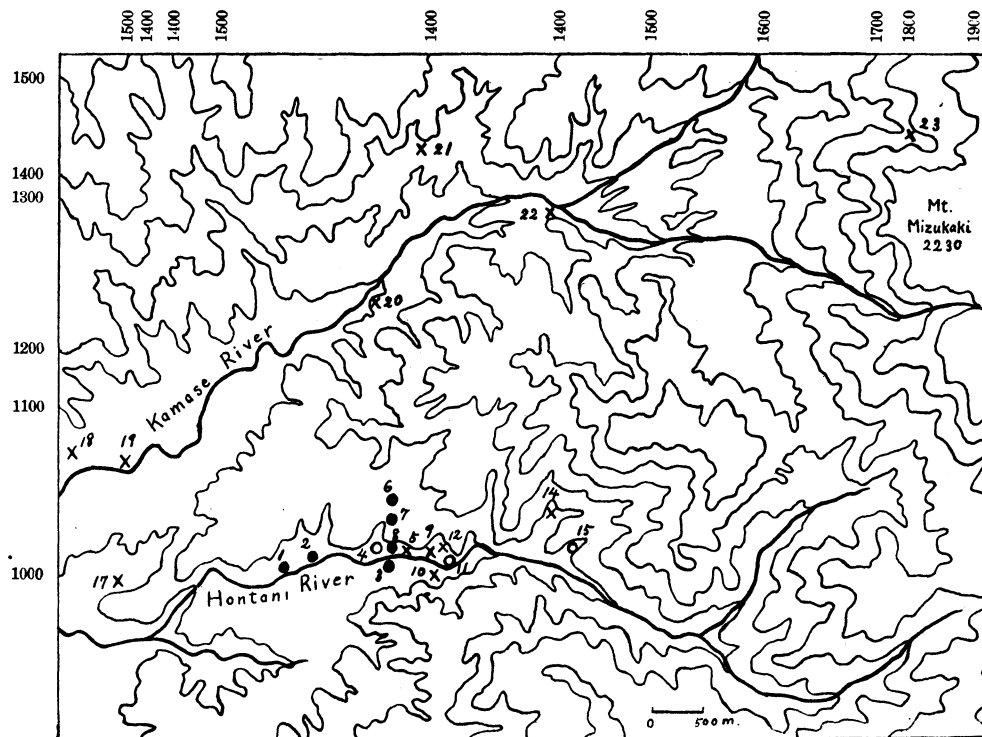


- Mineral spring containing more than 1×10^{-11} g. Ra/l.
- Mineral spring containing 1×10^{-12} g. Ra/l. $\sim 1 \times 10^{-11}$ g. Ra/l.
- × Mineral spring containing less than 1×10^{-12} g. Ra/l.

1. Ōsiba	13. Hiukesui
2. Ginsentō	14. Iwaanazawa
3. Wadegawara	15. Yuzawa
4. Hattōdaira	16. Dōbuti-no-yu
5. Higasiobi-no-izumi	17. Siokawa-no-yu
6. Nibuzawa	18. Siobuti-no-yu
7. Sio-no-sawa-tugane-yu	19. Nakazima-no-izumi
8. Kuridaira	20. Wada-matuba-Kōsen
9. Tuganerō	21. Siozawa-kuromori-no-yu
10. Umamiti-zawa	22. Simono-daira-no-yu
11. Totikubo	23. Kamase-hudō-no-yu
12. Kinsentō	24. Matudaira-no-yu

Fig. 3. Geographical distribution of the amount of radium in the Masutomi mineral springs.

Geographical distribution of radium and radon contents. The geographical distribution of radium and radon contents is shown on the accompanying maps, Figs. 3 and 4, from which it will be seen that almost all the springs, especially those with high radium and radon contents, are distributed along the two rivers, Hontani and Kamase. It shows that these spring waters flow out along these weak points of the earth's crust. It is also interesting to note as will be seen from these figures that, whereas those springs that are situated along the Hontani River are rich in both radium and radon, those along the Kamase River show compara-



The numerals against the black circle, open circle or cross are the mineral spring numbers in the Fig. 3.

- Mineral spring containing more than 100 Mache's units of radon.
- Mineral spring containing 10~100 Mache's units of radon.
- × Mineral spring containing less than 10 Mache's units of radon.

Fig. 4. Geographical distribution of the amount of radon in the Masutomi mineral springs.

tively low radio-activity notwithstanding their extraordinary high radium concentration.

Relation between the radium content and the radon content of spring waters. As will be seen from Table 7, the amount of radium in all the mineral waters was found to be much less than that required for radioactive equilibrium with the radon that is present in them. Even in the mineral waters at Wadamatuba, which shows the highest radium content, the amount of radium found was 0.83×10^{-10} g. per liter of water and the radon content 22.2×10^{-10} curie per liter, showing that the radon in the water is about 27 times greater than what the radium present in the water can produce.

According to Mache and Schweidler, the radioactivity of spring water is mainly due to the geological structure of the strata through which they last passed. The probable sources of the radium contained in spring waters are also largely the rocks where the waters originate and through which they pass, from which consideration the above results, showing that the amount of radium in spring waters is remarkably small compared

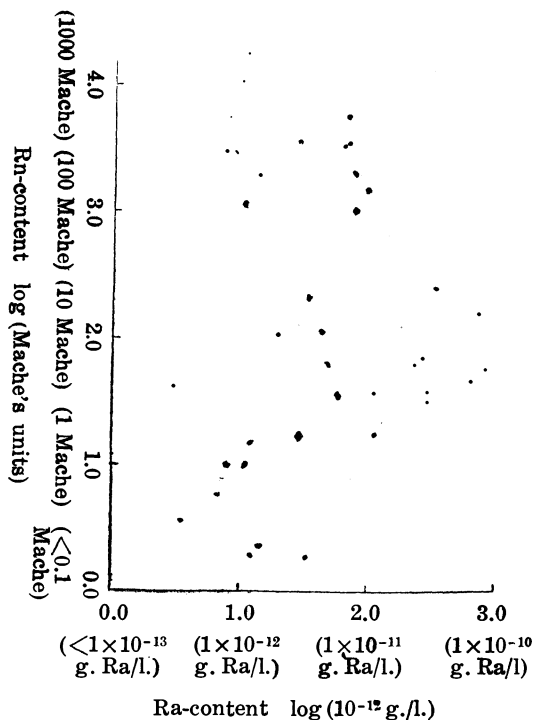


Fig. 5. Relation between the Ra-content and the Rn-content of the Masutomi mineral springs.

The radon content of some of the springs was measured at intervals of several years, namely, first in August, 1914, by R. Ishizu, then in October, 1936, and in April, 1937, by the writer, and most recently, in July, 1939, by Oana and Kuroda, the results of which are shown in Table 8. Most of them varied but little during these intervals of time, although a few showed remarkable variations, especially the mineral waters of Wade-gawara No. 2.

The radon concentration in spring waters may be affected by various factors, such as the temperature and volume output of water, weather conditions, especially the amount of rainfall, and also by the alterations in the underground water and changes in the rocks through which the waters pass. K. Noguti,⁽²¹⁾ after measuring the seasonal changes in radioactivity, temperature and flow of spring waters at Zigokudani near Volcano Asama, continuously during the period from June 1936 to June 1937, reported that their radioactivity increases with increase in flow of the water and decreases with rise in temperature of the water. S. Gōda⁽²²⁾ also, upon measuring the radioactivity, temperature, pH value, turbidity, and flow of water of a well in Shanghai, China, and the amount of rainfall there continuously from February 1933 to December 1936, reported that its radon concentration reaches maximum in summer and

with that of radon, may be simply explained by the difference in their solubilities in water. It indicates that spring waters usually contain an excess of free radon which they adsorb from rocks independently of radium, besides that which have their origin in radium dissolved in waters.

In Fig. 5, the radium content of spring waters is plotted against their radon content. No correlation can be established between them. Mineral waters with high radium content do not always show a corresponding high radon concentration, while those with high radon content do not always contain a large amount of radium. It also indicates that the radon from mineral waters is not due to the dissolved radium alone, as stated above.

Variation in radon and radium contents. Radon content.

(21) K. Noguti, *J. Chem. Soc. Japan*, **60** (1939), 7.

(22) S. Gōda, *Bull. Shanghai Nat. Sci. Research Lab.*, **8** (1939), 269.

Table 8. Variations in the radioactivity of springs in Masutomi.

No.*	Spring	Radon per liter of water in Mache's units							
		August 1914 (R. Ishizu)		October 1936		April 1937		July 1939 (S. Oana and K. Kuroda)	
		Temp. of Spring °C	Mache	Temp. of Spring °C	Mache	Temp. of Spring °C	Mache	Temp. of Spring °C	Mache
1	Osiba	19.0	277	22.5	362				
2	Ginsentō-huru-yu	29.5	103	31.0	153				
6	Wadegawara No. 1	14.0	657	18.0	588				
7	„ No. 2	21.5	828	19.5	1343	16.0	708	20.5	1085
11	Higasiobi-no-izumi			25.0	8.9			24.5	9.0
12	Nibuzawa	23.5	394	24.0	330				
13	Sio-no-sawa- tugane-yu	17.5	236	20.0	193				
15	Kuridaira No. 1	16.0	590	22.0	576				
16	„ No. 1. B.	20.0	318	17.0	304				
18	Yunokubo No. 1	17.0	248	21.0	202				
19	Kuridaira No. 3					19.4	355	21.4	233
20	Tuganerō No. 1			28.0	4.9			30.1	4.3
21	„ No. 2			30.8	4.0			29.6	3.5
25	Umamiti-zawa	12.0	2.9	15.8	6.4				
26	Totikubo No. 1			27.0	25.6			28.0	16.1
27	Kinsentō	31.5	2.2	31.0	3.3			31.0	2.1

* Numbers correspond to those used in Table 7.

minimum in winter and furthermore, that the variation in radioactivity runs parallel to that of the pH value, turbidity, and flow of water, from all which he concluded that the variation in radon concentration is due to the activity of underground water movement as the result of the amount of rainfall.

The variation in the radioactivity of spring water at Masutomi also can be explained only after much data of such factors as have just been mentioned have been obtained, so that, for the present, we shall leave this problem merely as a suggestion and wait the accumulation of further data.

Radium content. The radium content of some of the mineral springs in Masutomi was determined in October, 1936, by the writer and again in July, 1939, by Kuroda, the results being given in Table 9. - Some of them show remarkable variation. In this case their radium contents also are considered to be affected by numerous factors, as in the case of radon.

There seems to be no relation between the variation in radium content of these mineral waters and that of their temperature and the amount of solid matter held, although it is worthy of note that, as will be seen from Tables 8 and 9, the variation in radium content of these waters runs parallel to that of their radon content. In every case, the radium content

was higher in October, 1936, than in July, 1939. Parallel with this result, the radon concentration of the former is also higher than that of the latter.

Table 9. Variations in radium content of the Masutomi springs.

No.	Spring	October 1936			July 1939 (K. Kuroda)		
		Temp. of spring °C	Ra content g./l. $\times 10^{12}$	Total residue g./l.	Temp. of spring °C	Ra content g./l. $\times 10^{12}$	Total residue g./l.
1	Ōsiba	22.5	2.68	9.40	22.6	1.93	
2	Ginsentō-huru-yu	31.0	9.39	10.30	30.0	6.50	11.18
3	Ginsentō-kami-no-yu	28.5	7.35	9.64	28.5	5.86	
4	Ginsentō-naka-no-yu	22.0	0.43	9.72	27.0	0.58	10.61
5	Ginsentō-simo-no-yu	17.0	3.42	9.78		2.05	11.33
6	Wadegawara No. 1	18.0	6.76	3.25	22.0	8.20	5.63
7	„ No. 2	19.5	11.62	7.12	20.5	8.20	7.32
11	Higasiobi-no-izumi	25.0	35.65	9.69	24.5	18.89	10.17
12	Nibuzawa	24.0	6.22	7.25	24.0	7.73	16.20
13	Sio-no-sawa-tugane-yu	20.0	1.33	4.89	20.9	0.58	4.84
14	Gantō-hunsen	20.0	2.46	2.92	26.0	1.74	4.11
15	Kuridaira No. 1	22.0	0.77	3.62	21.2	1.46	3.72
16	„ No. 1. B.	17.0	0.73	2.32		0.58	10.00
17	Kuridaira-tennen-buro	23.3	26.05	8.56	23.6	14.06	8.95
19	Kuridaira No. 3	19.4	6.56	7.65	21.4	5.56	6.67
20	Tuganerō No. 1	28.0	64.53	8.53	30.1	24.61	9.39
21	„ No. 2	30.8	29.39	8.99	29.6	30.31	9.66
26	Totikubo No. 1	27.0	32.62	9.42	28.0	26.95	3.07
27	Kinsentō	31.0	29.30	7.49	31.0	21.97	8.33
28	Hiuke-sui	11.2*	39.16*		14.7	28.71	4.05
29	Iwaana-zawa	13.8*	0.76*		13.0	0.41	0.17
35	Dōbuti-no-yu	9.0*	0.63*		16.0	1.93	2.45
40	Wada-matuba-Kōsen	13.0	82.66	13.34	11.5	84.36	15.06

* Sampling in April 1937.

** Numbers correspond to those used in Table 7.

Relation between the radium and radon contents and the orifice temperature of spring waters. From the results thus far obtained we shall consider the relation between the radon and radium contents of the springs in Masutomi and their temperature. Looked at as a whole, the quantities of both the radium and radon in the waters seem to bear no general relation to the temperature of the waters.

We shall next attempt to compare springs that are situated close together within a distance of about 100 meters. The radium and radon contents and the temperature of these spring waters are given in Table 10.

A tendency will be seen from this table (excluding the case of Group IV and Group V) for the radium content of the waters to increase with

Table 10. Relation between the radium and radon contents and the temperature of springs.

Spring	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Radon per liter of water in Mache's units
Group I			
Ginsentō-huru-yu	31.0	9.39	153
Ginsentō-kami-no-yu	28.5	7.35	104
Ginsentō-naka-no-yu	22.0	0.43	11.6
Ginsentō-simo-no-yu	17.0	3.42	42.2
Group II			
Wadegawara No. 2	19.5	11.62	1343
„ No. 1	18.0	6.76	588
Group III			
Kuridaira-tennen-buro	23.3	26.05	7.4
Kuridaira No. 1	22.0	0.77	576
„ No. 1. B.	17.0	0.73	304
Group IV			
Tuganerō No. 2	30.8	29.39	4.0
„ No. 1	28.0	64.53	4.9
Tuganerō-kasikiri-no-yu	25.6	23.95	6.5
Tuganerō naka-no-yu	23.0	31.61	
Tuganerō-simo-no-yu	22.2	25.05	
Group V			
Yuzawa No. 3	18.5	1.76	
„ No. 2	17.7	1.93	
„ No. 1	13.7	71.81	16.1
„ No. 4	13.7	0.00	
„ No. 5	11.5	0.00	
Group VI			
Siozawa-kuromori-Kōsen	12.0	11.57	1.8
Siozawa-kuromori-yosinokwan	8.5	0.00	1.2

rise in their temperature. In the spring waters of Group IV, their radio-activity increases with fall in temperature, which may naturally be expected from the variation in the solubility of radium and radon with temperature.

Relation between the radium and radon contents and the pH value of spring waters. As will be seen from Table 7, all the spring waters in this region are weakly acidic, showing a pH value of 6.0~6.7. The maximum is 6.7 in the water of Ginsentō-naka-no-yu and the minimum 6.0 in that of Kuridaira No. 1. The difference in pH values for each spring water is consequently too small for comparison with the radium and radon contents.

Relation between the radium content and the amount of total solid matter in spring waters. The radium content and the amount of total evaporated residue (determined by Okauti) of the spring waters in Masutomi are given in Table 7. Plotting the amount of total residue as abscissae and the radium content as ordinates, we get Fig. 6. There seems to be a tendency here for the samples of high radium content to have fairly large proportions of solid matter.

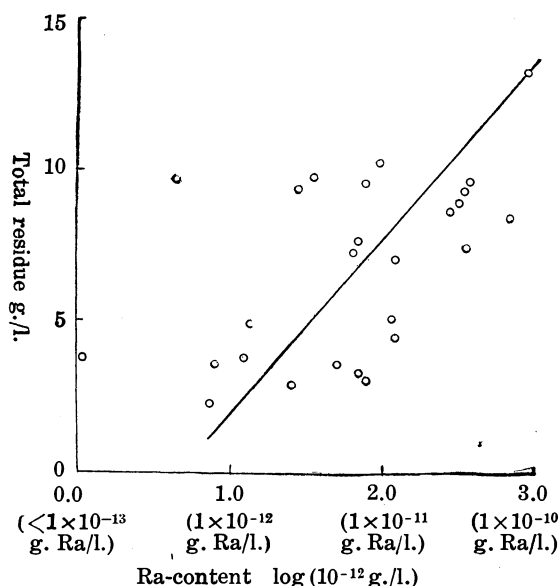


Fig. 6. Relation between the Ra-content and the amount of total residue in the Masutomi mineral springs.

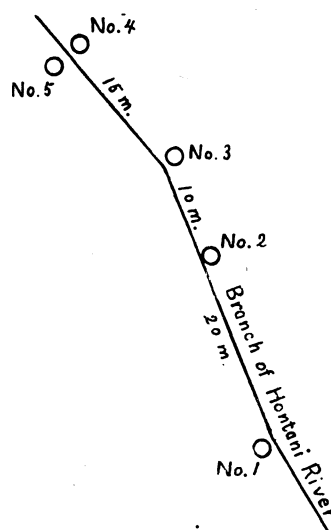


Fig. 7. Mineral springs of Yuzawa (Masutomi).

The mineral springs of Yuzawa. The five mineral springs of Yuzawa are located along a branch of the Hontani River, close together, being separated by distances of only 10 or 20 meters (V. Fig. 7), but as will be seen from Table 10, the radium content varies remarkably in this group of closely related springs. Notwithstanding that the radium content of the water at Spring No. 1 exceeds 7×10^{-11} g. radium per liter of water, no radium is detected in that of Springs Nos. 4-5, showing that they may pass through different strata, although they gush out to the surface of the earth within only a few meters of each other.

On the other hand, B. A. Nikitin⁽²³⁾, after studying the waters of the Ribí-Eibat oil field, reported that although water obtained from the same strata are closely related chemically, they contain different quantities of radium, in view of which it is not certain whether the waters in Yuzawa do not also come from different strata. This question can be answered only after a sufficient number of investigations have been made on the mineral waters and of the geological formations through which they pass.

Similar examples are found in the other groups of springs in this region (V. Table 10). Although the three springs of Kuridaira lie at

(23) B. A. Nikitin, *Tras. inst. ètat radium* (U.S.S.R.), **2** (1933), 160.

distances of less than 10 meters from one another, the radium content of the waters at Tennen-buro is about 40 times those of the other two, whereas the radon content of the latter is much higher than that of the former.

While the distance between the sources of two springs in Wadegawara is only one or two meters, the radium and radon contents of Spring No. 2 are nearly twice that of Spring No. 1.

Radium discharge. The radium discharge is calculated for each spring from its radium content and daily flow of water, the results of which are shown in Table 7. The radium brought up by a group of springs in this district amounts to about one milligram per year.

V. Hot Springs of Misasa, Tottori Prefecture. The Misasa Hot Springs, the most radioactive in Japan, ranks second only to Ischia in Italy. They are almost equal to the most radioactive hot spring in Gastein, which surpasses all the other hot springs of the world in radon content.

It is situated on the western and eastern banks of the Misasa River (V. Fig. 8). The region itself is flat with only a slight inclination, and of limited area. In this small space gush out in series a large number of hot springs of high radon content and high temperature, their sources being located mostly near the stream. (A large number of hot springs gush out in the stream too.) No less than 50 springs are found in this district, not very distant from one another.

The writer, who spent about a week here in August, 1939, observed the temperature, pH value, and the flow of water of the 34 springs direct at the source and took samples of water for radium determination direct from the source, the results of all which are given in Table 11. For some of them the radioactivity was measured by Ishizu and Hattori and the total evaporated residues were determined by Kuroda and the Imperial Hygienic Laboratory of Tokyo, the results of which are also given in this table for reference.

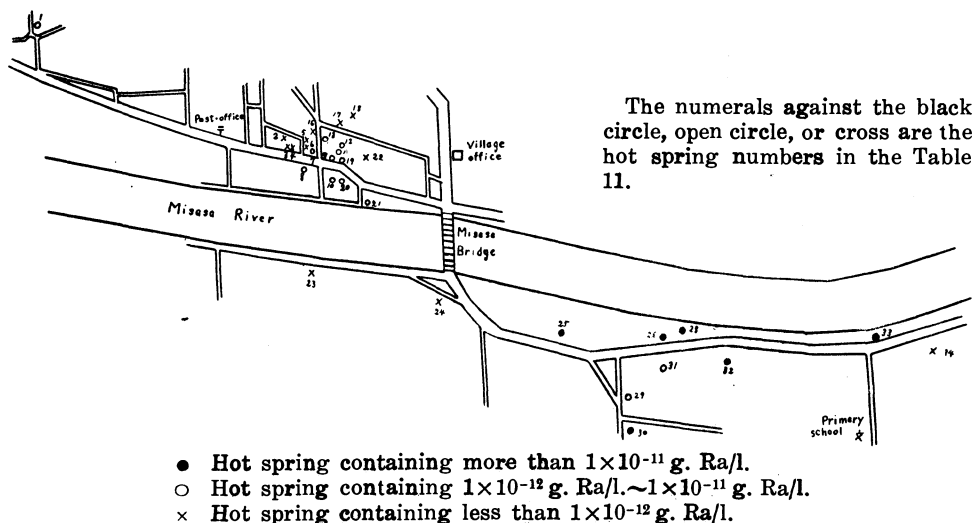


Fig. 8. Geographical distribution of the amount of radium in the Misasa hot springs.

Table 11. Hot springs of Misasa.

No.	Spring	Temp. of spring °C	Temp. of air °C	Radium content g./l. $\times 10^{12}$	Radon per liter of water in Mache's units (R. Ishizu Y. Hattori)	pH	Flow of water hl./day	Radium discharge 10^{-3} g. (mg.)/year	Total residue g./l. (K. Kuroda)
Misasa Group									
1	Kabu-yu (Public bath)	45.0	24.4	1.14	10.2*	6.9	1967	0.082	
2	Otyaya-no-yu	61.0	26.1	0.28	27.9*	6.9			
3	Private bath (M. Yamamoto)	52.5	26.9	0.25		6.7	98	0.001	
4	Naka-no-yu (Public bath)	66.0	28.3	0.35	11.0*	7.0	625	0.008	1.24**
5	Hanaya-no-yu	68.0	25.9	0.85	74.4	6.8	567	0.018	
6	Nakaya-no-yu	64.0	27.2	0.90	24.5*	6.8	407	0.013	
7	Bun-aburaya-no-yu	70.5	28.9	2.24	24.5*	7.0	44	0.004	
8	Hasizuya-no-yu	66.0	26.4	1.00	15.5*	6.9			
9	Yakusidō-no-yu	74.5	28.6	3.82	14.5	7.2	75	0.010	0.86**
10	Saiki-honkwan-no-yu	71.0	26.1	2.37		7.5	1832	0.158	
11	Akazakiya-no-yu	69.0	26.8	5.25	53.4	7.0	861	0.165	
12	Ryōyōzyo-gensen	72.0	28.7	2.89	130.5	6.8	1094	0.115	1.31**
13	Iwa-yu (Otoko-yu)	57.0	25.0	2.95	36.0*	6.8	825	0.035	
14	„ (Onna-yu)	68.0	28.7	3.61	34.5	6.9	536	0.071	1.23**
15	„ (Makura-yu)	60.0	25.0	2.90		6.9	62	0.007	
16	Eirakuan-no-yu	66.5	25.3	0.37	48.8	7.1	475	0.006	
17	Aburaya-uti-yu	55.0	29.0	0.89	19.2*	6.9	176	0.006	

18	Aburaya-soto-yu (Mitu-yu)	51.5	29.0	0.21		6.8	152	0.001	
19	Iwasaki-no-yu No. 2	68.0	27.2	2.81	19.3	7.2	496	0.051	1.16**
20	Kiya-kazoku-yu	70.0	26.7	3.72	28.4*	7.0	172	0.023	
21	Haikyūzyo-no-yu	62.0	28.8	2.32		6.8	684	0.058	0.92
22	Seitō-kwan-no-yu	60.0	26.3	0.14	85.6	7.0	610	0.003	
23	Iwasaki-no-yu No. 1	54.5	26.5	0.37	15.1	7.1	88	0.001	0.64
24	Bansuirō-no-yu	48.0	26.3	0.26		7.2	87	0.001	1.57
Yamada Group									
25	Onsen-hotel-no-yu	68.5	26.8	13.48		6.5			0.72
26	Tennen-gankutu-no-yu No. 1	79.5	26.8	10.06	42.9	6.4	142	0.052	
27	„ No. 2	69.0	26.8	7.11		6.3			
28	Ōhasi-ryokwan-soto-yu	79.0	30.7	15.95		6.6			
29	Yamadaku-no-yu (Public bath)	56.5	25.4	3.65	168.6	6.6	392	0.052	
30	Kōyōen-no-yu	64.0	28.5	16.06		6.2	47	0.028	
31	Sinsen-ryō-no-yu	46.0	32.0	2.12		6.3			
32	Misasa-kwan-no-yu	53.0	26.8	15.01		6.4			
33	Okayamaidai-ryōyōzyo-no-yu	51.5	27.4	17.67		6.8			1.53
34	Gunzihogoin-ryōyōzyo-no-yu	46.0	27.4	0.64		7.4	276	0.006	1.21
Total:								0.975	

Data on radon content of the water obtained by Y. Hattori⁽²⁴⁾ in October, 1935; that starred by R. Ishizu⁽²⁵⁾ in February and March, 1914.

** Determined by the Imperial Hygienic Laboratory of Tokyo.

(24) Y. Hattori, *Bull. Imp. Hygienic Lab.*, **52** (1939), 142.

(25) R. Ishizu, "*The Mineral springs of Japan*," (1916), 135.

Geographical distribution of radium content. The geographical distribution of radium content is shown on the accompanying map, Fig. 8. The springs in this district may be divided into two groups, the Misasa and Yamada. The 24 springs, Nos. 1-24, belong to the former and the 10 springs Nos. 25-34 to the latter.

As will be seen from Fig. 8, all the waters of the Yamada group have fairly high radium content compared with that of the Misasa group, with the exception of spring No. 34, the chemical quality of which also differs from the others of this group, as will be shown later.

Relation between the radium content and the orifice temperature of spring waters. We shall consider the 24 springs of the Misasa group, the radium contents of which are plotted in Fig. 9 against their

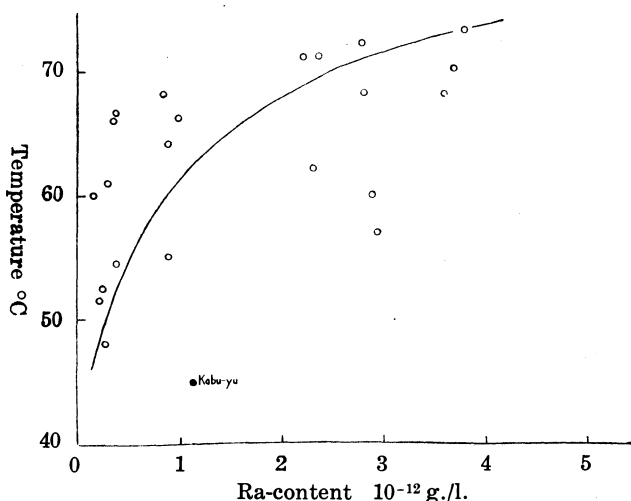
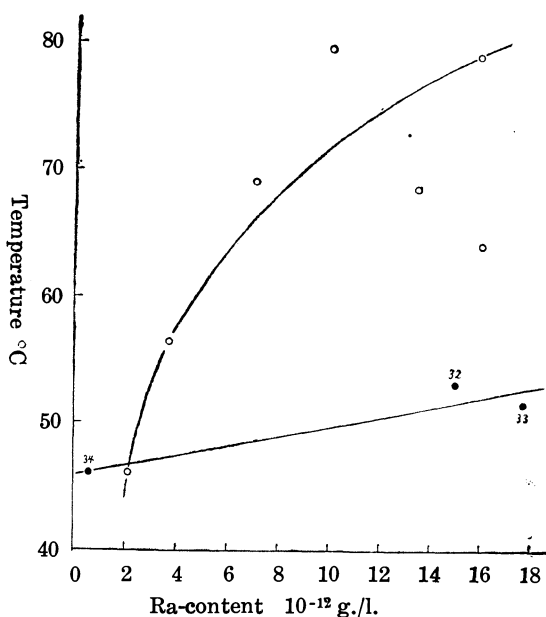


Fig. 9. Relation between the Ra-content and the orifice temperature of the springs of the Misasa group.

orifice temperatures, excluding the spring of Kabu-yu, seeing that it is situated far away from the rest. Here we find that the general tendency is for the radium content to increase with the rise in their orifice temperature.

We shall next take the ten springs of the Yamada group, the radium contents of which are plotted as ordinates and their orifice temperature as abscissae, resulting in Fig. 10. Since the three springs, Nos. 32-34, lie some distance away from the others, these three are again separated from this group, so that in each group the points lie nearly close to a straight line. There is again a tendency for the radium content to increase with the



The numerals against the black circle are the hot spring numbers in the Table 11.

Fig. 10. Relation between the Ra-content and the orifice temperature of the springs of the Yamada group.

rise in their orifice temperature, which results correspond well with the solubility of radium salts in water.

Relation between the radium content and the pH value of spring waters. As will be seen from Table 11, the pH value of the waters of the Yamada group is somewhat lower than that of the Misasa group, while the radium content of the former is higher than that of the latter, which may be due to differences in the geological formations through which the waters pass. It is also worthy of note that the pH value of Spring No. 34 differs from the others in the same group, besides having a lower radium content than the others.

Radium discharge. The radium discharge is calculated for each spring from its radium content and daily flow of water, the result of which is given in Table 11. The radium brought up by a group of springs in this district amounts to about 1 milligram per year.

VI. Thermal Springs of Itō, Sizuoka Prefecture. The water samples of the Itō Thermal Springs were obtained in September, 1937, by the Itō Hot Spring Owners' Association. The orifice temperature and the pH value of these springs were measured by Kuroda in December, 1939, with results as shown in Table 12.

Table 12. Thermal springs of Itō.

No.	Spring	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	pH (Kuro- da)	No.*	l:m:n
1	Yukawa, Yukawa-no-yu (Komoti-yu)	44.0	0.16	7.8	145	6:58:35
2	„ Private bath (T. Ōkawa)	41.9	0.04	8.2	140	4:51:46
3	Matubara, Matubara-no-yu (Ō-yu)	42.0	0.16	8.0	117	5:54:41
4	„ Tennen-yu	43.7	0.19	8.0	118	6:58:36
5	„ Tōkyō-kwan-no-yu	52.0	0.04	8.0	129	3:63:34
6	„ Masuya-ryokwan-no-yu	48.0	0.51	7.5	112	45:43:12
7	„ Daitō-kwan-no-yu	45.7	0.17	7.5	—	—
8	„ Private bath (K. Iizima)	40.5	0.27	7.3	93	25:41:34
9	„ Hōsen-kwan-no-yu	42.0	0.39	7.5	83	27:49:24
10	Kusumi, Private bath (S. Naruto)	38.0	0.14	7.4	28	11:48:42
11	„ Tennen-yu	44.3	0.11	8.0	32	7:25:67
12	„ Enpanrō-no-yu	47.7	0.09	7.5	39	10:47:43
13	„ Arai-kwan-no-yu	40.5	0.26	7.4	6	21:30:50
14	Oka, Yōki-kwan-no-yu	51.0	0.18	8.0	178	2:90:9
15	„ Tōkai-kwan-no-yu	51.2	0.17	7.9	155	6:86:8
16	„ Private bath (K. Satō)	52.3	0.27	8.1	—	—
17	„ „ (M. Aoki)	52.8	0.20	8.0	159	0:95:5
18	„ „ (T. Suzuki)	44.8	0.28	7.6	151	10:68:22
19	„ „ (Wakatuki)	45.0	0.25	7.1	149	3:61:36
20	Kamata, Private bath (Toyosima)	51.0	0.08	8.0	210	0:76:24

* Numbers correspond to those used in the preceding paper by T. Fukutomi.⁽²⁶⁾

After investigating the physical and chemical properties of the water of 207 of the thermal springs in the town of Itō and its neighbourhood, T. Fukutomi and Z. Huzii⁽²⁶⁾ concluded as follows:

There is no doubt of the existence in the town of Itō and neighbourhood of 3 primary springs of entirely different character, namely, the one (B) characterized by high temperature, small amounts of chemical constituents, and the other (A), differing from the preceding in its relatively low temperature, moderate quantity of chloride, sulphate, calcium, and the last one (C), the cold underground water. The primary hot spring A is a weak common salt spring, its orifice temperature being 47.4°C and the total amount of chemical constituents 6.6 g./l. The fact that springs containing a large quantity of this primary spring water are all located at the seaside, indicates some relation between the water of this primary spring and sea water. The primary hot spring B is a simple thermal, its orifice temperature being 54.8°C and the total amount of chemical constituents 0.085 g./l. The cold underground water has a temperature of 28°C, the total amount of its chemical constituents being 0.02 g./l. The percentage ratio 1:m:n in the mixing of three primary springs A, B and C in each spring water, as calculated by T. Fukutomi and Z. Huzii, is shown in Table 12.

Assuming now the radium content of the underground water to be 0.0×10^{-12} g. Ra./l. and the percentage ratio 1:m:n of each sample of water taken for radium determination to be as that given by Fukutomi, the writer calculated the radium content of the primary hot springs A and B from the data in Table 12 and obtained the following results.

Primary hot springs A contains 0.9×10^{-12} g. and B 0.2×10^{-12} g. of radium per liter of water.

Table 13.

Primary hot spring	Temp. of spring °C	Total chemical constituents g./l.	Radium content g./l. $\times 10^{12}$
A	47.4	6.6	0.9
B	54.8	0.085	0.2
C (underground) water	28	0.02	0.0

Table 13 shows a general tendency for the radium content to increase with increasing amounts of the chemical constituents.

The writer next calculated the radium content of each spring water from their percentage ratio 1:m:n, in the mixing of the 3 primary springs A, B and C, and their radium contents, with results as shown in Table 14, which calculated values agree fairly well with the observed values in each sample. This result, therefore, supports the theory of Fukutomi and Huzii.

(26) T. Fukutomi and Z. Huzii, *Bull. Earthq. Res. Inst.*, **15** (1937), 506.

Table 14. Comparison of the calculated and observed values for radium content of spring waters.

No.	Radium content g./l. $\times 10^{12}$		No.	Radium content g./l. $\times 10^{12}$	
	Calculated	Observed		Calculated	Observed
1	0.2	0.16	11	0.1	0.11
2	0.1	0.04	12	0.2	0.09
3	0.2	0.16	13	0.3	0.26
4	0.2	0.19	14	0.2	0.18
5	0.2	0.04	15	0.2	0.17
6	0.6	0.51	17	0.2	0.20
8	0.3	0.27	18	0.2	0.28
9	0.3	0.39	19	0.2	0.25
10	0.2	0.14	20	0.2	0.08

VII. Thermal and Mineral Springs of Arima, Hyōgo Prefecture. The spring waters from Arima were sampled by Y. Nemoto in November, 1936. The radium content of these waters are shown in Table 15, which also gives the total evaporated residue determined by him.

The next sampling was made by K. Yamasaki in August, 1939, the results of which are shown in Table 16. Their total residues were determined by Kurorda.

The geographical distribution of these springs is shown in Figs. 11 and 12, from which distribution the four springs in Arima are regarded as one group. The radium contents of these springs are plotted against their

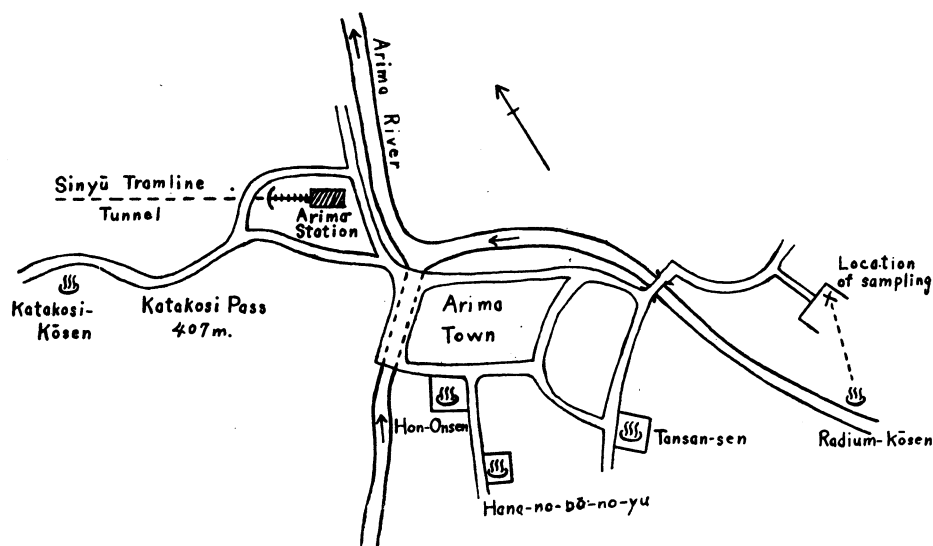


Fig. 11. Distribution of the Arima thermal and mineral springs. I.

Table 15. Thermal and mineral springs of Arima.

(Sampled November, 1936)

No.	Spring	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./l. (Y. Nemoto)	Flow of water hl./day (Y. Nemoto)	Radium discharge 10^{-3} g. (mg.)/year
1	Arima, Hon-Onsen	—	71.29	18.43	1263	3.286
2	„ Hana-no-bō-no-yu	37.6	68.50	20.23	270	0.875
5	Arino, Katakosi-Kōsen	—	90.82	16.08	4	0.013
6	„ Yakendo-Kōsen	20.0	57.53	9.57	130	0.273

Table 16. Thermal and mineral springs of Arima.

(Sampled August, 1939)

No.	Spring	Temp. of spring °C	Temp. of air °C	Radium content g./l. $\times 10^{12}$	Total residue g./l. (K. Kuroda)
1	Arima, Hon-Onsen	43.0	22.0	64.97	16.75
2	„ Hanano-bō-no-yu	34.5	22.0	47.08	17.38
3	„ Tansan-sen	16.0	22.0	0.76	
4	„ Radium-Kōsen*	27.5	22.0	12.68	
5	Arino, Katakosi-Kōsen	21.0	26.0	111.05	23.63
6	„ Yakendo-Kōsen	22.0	28.5	61.57	10.91

* Since the source of this spring was buried in the ground by a flood in July of 1938, water conveyed from the spring by means of a bamboo conduit pipe was sampled at Tanaka's villa, situated approximately 100 meters distance from the source. (V. Fig. 11)

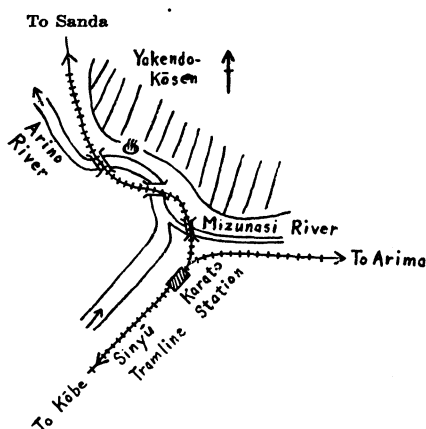


Fig. 12. Arima mineral springs. II.

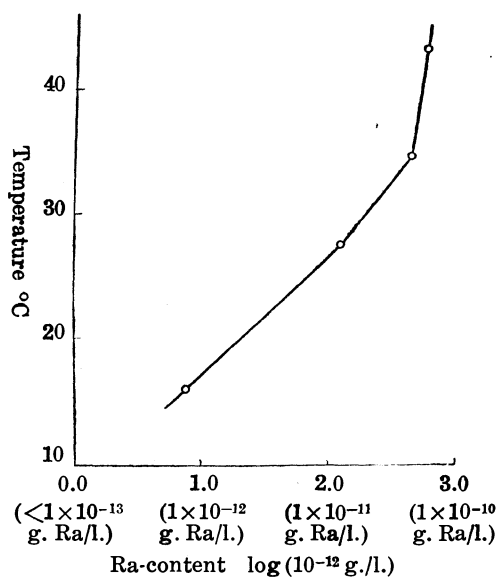


Fig. 13. Relation between the Ra-content and the orifice temperature of the Arima thermal and mineral springs.

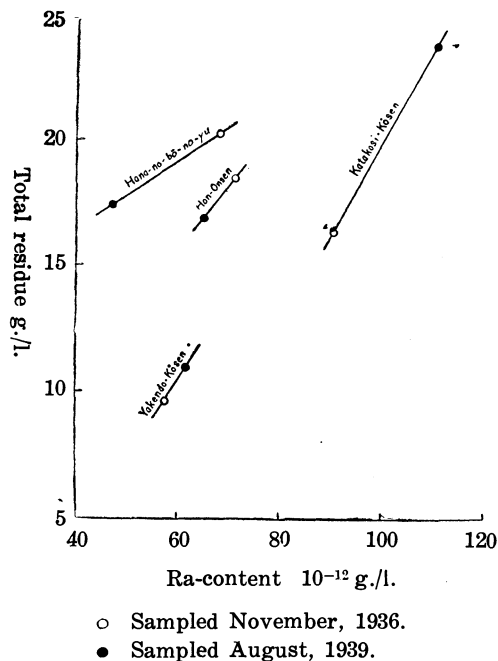


Fig. 14. Relation between the differences in the Ra-content and the amount of total residue in the Arima thermal and mineral springs.

orifice temperature in Fig. 13. The relation between them appears to be simple linear.

Considering then the difference in the radium content of the four springs between the first and second determinations, it is interesting to note that, as will be seen from Tables 15 and 16, the differences run parallel to that of the amounts of total solid matter (V. Fig. 14).

From the daily flow of water measured by Nemoto in November, 1936, and their radium concentration, the radium discharge of the four springs was calculated, with results as given in Table 15. Since the springs of Arima Hon-Onsen have considerably high radium concentration and the flow of water is abundant, the quantity of radium brought up by this single spring to the surface of the earth amounts

to more than 3 mg. per year.

VIII. Hot Springs of Beppu, Ōita Prefecture. The water samples of Beppu Hot Springs for radium determination were drawn in August and September, 1937, by the city office of Beppu. The orifice temperatures of these springs were measured at the time of sampling, with results as shown in Table 17. For some of them the *pH* value was determined by the Beppu Geophysical Research Laboratory⁽²⁷⁾ in November, 1927, and in February, 1928, the results of which are also given in this table for reference.

The geographical distribution of these 41 springs is shown in Fig. 15. According to S. Suzuki,⁽²⁸⁾ the hot springs of Beppu are, from their geographical and geological distributions, divided into three groups. The first is the group of the hot springs of Beppu, Kwankwaizi and Horita, the second that of Kamegawa, Kannawa and Myōban, and the third that of the hot springs in the basin of Yuhuin.

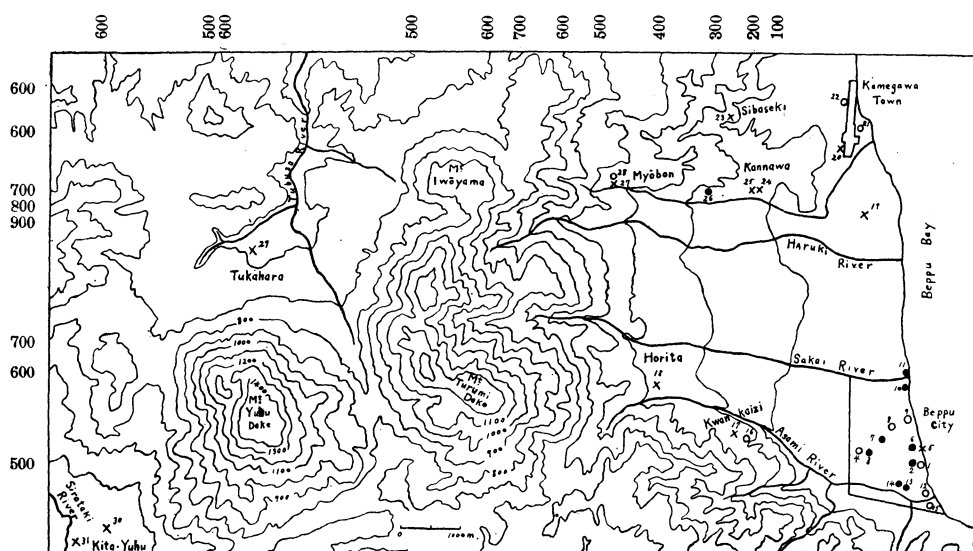
As will be seen from Table 17, the springs of the first group, which are all very weak acidic or very weak alkaline, show a somewhat high radium content compared with that of other groups, that of the second group, excluding the springs at Kamegawa, which are all strongly acidic

(27) *Repts. Beppu Geophys. Research Lab.*, **1** (1937), 78.

(28) S. Suzuki, *Repts. Beppu Geophys. Research Lab.*, **1** (1937), 6.

and usually contain small quantities of radium, and that of the third which shows the lowest radium concentration.

The fact that in each group of springs, their radium contents appear to bear no general relation to their orifice temperature, is believed to be due to other yet unknown factors.



- Hot spring containing more than 3×10^{-13} g. Ra/l.
- Hot spring containing $1 \sim 3 \times 10^{-13}$ g. Ra/l.
- × Hot spring containing less than 1×10^{-13} g. Ra/l.

1. Reityō-sen	Beppu	15. Hamawaki-Onsen	Beppu
2. Kotobuki-Onsen	„	16. Sira-yu	Kwankaizi
Yanagi-Onsen	„	17. Kwankaizi-Onsen	„
Kusunoki-Onsen	„	18. Horita-Onsen	Horita
3. Hurō-sen	„	19. Bōtyō-sen	Kita-isigaki
4. Ta-no-yu	„	20. Si-no-yu	Kamegawa
5. Kaigan-suna-yu	„	21. Kiyō-sen	„
6. Takegawara-Onsen	„	22. Hamada-Onsen	„
Umezono-Onsen	„	23. Sibaseki-Onsen	Sibaseki
7. Kitamati-Onsen	„	24. Netu-no-yu	Kannawa
8. Kaimonzi-Kōen-Onsen	„	25. Sibū-yu	„
9. Yumimatu-Onsen	„	26. Umi-zigoku	„
10. Matogahama-Onsen	„	27. Zizō-Onsen	Myōban
11. Yumigahama-Onsen	„	28. Kakuzyu-sen	„
12. Hinode-Onsen	„	Yakusi-Onsen	„
13. Syōzyu-sen	„	29. Tukahara-Onsen	Tukahara
14. Nagesi-Onsen	„	30. Yunotubo-Onsen	Yuhuin
Kamiya-Onsen	„	31. Otomaru-Onsen	„

Fig. 15. Geographical distribution of the amount of radium in the Beppu hot springs.

Table 17. Hot springs of Beppu.

No.	Location	Spring	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Reaction pH	Chemical classification
Group I						
1	Beppu	Reityō-sen	60.0	0.22	Very weak alkaline	Simple
2	„	Kotobuki-Onsen	46.5	0.18	Weakly acidic	„
3	„	Yanagi-Onsen	49.5	0.64	Very weak alkaline	„
4	„	Kusunoki-Onsen	44.5	0.39	Very weak acidic	„
5	„	Hurō-sen	59.0	0.32	Weakly acidic	Iron carbonate
6	„	Ta-no-yu A	57.0	0.18	„	Simple
7	„	„ B	43.0	0.15	„	„
8	„	Kaigan-suna-yu	58.5	0.04	Weakly acidic	Iron carbonate
9	„	Takegawara-Onsen	64.5	0.74	„	„
10	„	Umezono-Onsen	61.5	0.75	Very weak alkaline	Simple
11	„	Kitamati-Onsen	55.0	0.30	„	„
12	„	Kaimonzi-Kōen-Onsen	62.0	0.25	Very weak alkaline	Simple
13	„	Matogahama-Onsen	49.5	0.76	„	„
14	„	Yumimatu-Onsen	62.0	0.25	„	Alkaline
15	„	Yumigahama-Onsen	49.0	0.59	„	„
16	„	Unsenzi-Onsen	51.0	0.21	„	„
17	„	Hinode-Onsen	50.5	0.17	Very weak alkaline	Simple
18	„	Syōzyu-sen	47.0	0.48	„	„
19	„	Nagesi-Onsen	52.5	0.72	Very weak alkaline	Simple
20	„	Kamiya-Onsen	51.0	0.11	„	Simple carbon dioxated
21	„	Hamawaki-Onsen	46.5	0.14	Very weak alkaline	Common salt
22	Kwankaizi	Sira-yu	43.0	0.22	„	„
23	„	Kwankaizi-Onsen	55.5	0.00	7.4	Simple carbon dioxated
24	Horita	Horita-Onsen	81.0	0.09	7.6	Sulphur
Group II						
25	Kita-isigaki	Bōtyō-sen	63.0	0.00	„	„
26	Kamegawa	Si-no-yu	54.0	0.00	Very weak alkaline	Weak common salt
27	„	Kiyō-sen	56.8	0.11	Weakly acidic	„
28	„	Hamada-Onsen	80.5	0.24	Neutral	Carbonated
29	„	Gomusō-Onsen	45.0	0.04	„	„
30	„	Suzi-yu	58.0	0.00	„	„
31	Sibaseki	Sibaseki-Onsen	67.0	0.00	3.2	Iron carbonate
32	Kannawa	Netu-no-yu	48.0	0.00	5.2	Simple
33	„	Sibu-yu	91.0	0.00	Acidic	Acid vitriol

Table 17.—(Concluded)

No.	Location	Spring	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Reaction pH	Chemical classification
34	Kannawa	Umi-zigoku	90.5	0.54	1.6	Muriated acid vitriol
35	Myōban	Zizō-Onsen	60.0	0.00	Strong acidic	Sulphurated acid
36	„	Kakuzyu-sen	70.0	0.27	„	„
37	„	Yakusi-Onsen	87.0	0.27	„	Acid alum vitriol
Group III						
38	Yuhuin	Tanakaiti-Onsen	58.0	0.00		Simple
39	„	Yunotubo-Onsen	58.0	0.09		„
40	„	Otomaru-Onsen		0.06		
41	Tukahara	Tukahara-Onsen	48.0	0.00		

IX. Relation between the Radium and the Radon Contents of Spring Waters. In this study, samples of water from 477 different mineral springs were tested for radium concentration. Some of them have been also measured for radon content by the present writer and other investigators. The radium and radon contents of these springs are shown in Table 18, arranged in the order of their radon contents.

The radon content of the mineral waters at Masutomi in Yamanashi Prefecture; Kasio, Itozawa and Tadati in Nagano Prefecture; and Ena, Itigaku, Yogarasu, Naegi and Kasagi in Gifu Prefecture, were measured by the writer by means of the IM Fontactoscope. The data of the other springs were obtained by R. Ishizu, Y. Kinugasa, H. Kibezaki⁽¹⁾; S. Matuura⁽²⁹⁾ of the Kyūsyū Imperial University; K. Siratori⁽³⁰⁾ of the Tōhoku Imperial University; Y. Hattori⁽³¹⁾ of the Tokyo Imperial Hygienic Laboratory and others.

Although the radon contents obtained by the writer were measured from the same sample that was used for radium determination, in the other cases some time elapsed between the date when the waters were tested for radon content and that when the samples were drawn for radium determination. Since the radon concentration may vary more or less with lapse of time, the old measurements are likely to differ from what they are today, although we shall not be very far out in estimating approximately the rough values for the radon content of each sample from these data.

According to Carl Genser⁽³²⁾, the radioactive natural waters are divided into three types.

(1) The Radium-salt-water type, containing radium and radon in their radioactive equilibrium proportions (e.g. Heidelberg).

(2) The Radium-emanation-water type, containing no dissolved

(29) S. Matuura, I. Iwasaki and R. Hukusima, *J. Chem. Soc. Japan*, **61**(1940), 225.

(30) K. Siratori, *Science Repts. Tōhoku Imp. Univ.*, **16** (1925).

(31) Y. Hattori, *Bull. Imp. Hygienic Lab.*, **52** (1939), 141.

(32) C. Genser, *Z. deutsch. geol. Gesell.* **1933**, 482.

Table 18. Relation between the radium and the radon contents of spring waters.

No.*	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	Radon per liter of water			
					in 10^{-10} curies	in Mache's units	Examined by	Date
346	Radium-Kōsen No. 2	Ikeda	Simane	19.46	5384	1479	S. Matuura	Oct. 1939
175	Wadegawara No. 2	Masutomi	Yamanasi	11.62	4889	1343	T. Nakai	Oct. 1936
174	„ No. 1	„	„	6.76	2139	588	„	„
183	Kuridaira No. 1	„	„	0.77	2097	576	„	„
169	Ōsiba	„	„	2.68	1318	362	„	„
187	Kuridaira No. 3	„	„	6.56	1290	355	„	Apr. 1937
180	Nibuzawa	„	„	6.22	1203	330	„	Oct. 1936
184	Kuridaira No. 1. B.	„	„	0.73	1108	304	„	„
247	Radium-Kōsen	Ena	Gihu	0.0	808	222	„	May 1936
186	Yunokubo No. 1	Masutomi	Yamanasi	7.56	736	202	„	Oct. 1936
345	Radium-Kōsen No. 1	Ikeda	Simane	36.43	721	198	S. Matuura	Oct. 1939
181	Sio-no-sawa-tugane-yu	Masutomi	Yamanasi	1.33	701	193	T. Nakai	Oct. 1936
315	Yamadaku-no-yu	Misasa	Tottori	3.65	613	169	Y. Hattori	Oct. 1935
170	Ginsentō-huru-yu	Masutomi	Yamanasi	9.39	556	153	T. Nakai	Oct. 1936
298	Ryōyōzyo-gensen	Misasa	Tottori	2.89	473	130	Y. Hattori	Oct. 1935
273	Radium-Kōsen	Arima	Hyōgo	12.68	440	121	R. Nomitu of the Imp. Univ. of Kyōto	Sept. 1931
171	Ginsentō-kami-no-yu	Masutomi	Yamanasi	7.35	378	104	T. Nakai	Oct. 1936
308	Seitō-kwan-no-yu	Misasa	Tottori	0.14	311	85.6	Y. Hattori	Oct. 1935
291	Hanaya-no-yu	„	„	0.85	271	74.4	„	„
304	Aburaya-soto-yu	„	„	0.21	236	64.7	K. Shiratori	Aug. 1925
297	Akazakiya-no-yu	„	„	5.25	194	53.4	Y. Hattori	Oct. 1935

* Numbers correspond to those used in Table 3.

Table 18.—(Continued)

No.*	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	Radon per liter of water			
					in 10^{-10} curies	in Mache's units	Examined by	Date
131	Spring No. 1	Murasugi	Niigata	0.51	180	49.6	Y. Kinugasa.	Aug. 1914
302	Eirakuan-no-yu	Misasa	Tottori	0.37	177	48.8	Y. Hattori	Oct. 1935
132	Spring No. 2	Murasugi	Niigata	0.04	177	48.6	Y. Kinugasa	Aug. 1914
312	Tennen-gankutu- no-yu No. 1	Misasa	Tottori	10.06	156	42.9	Y. Hattori	Oct. 1935
173	Ginsentō-simo-no-yu	Masutomi	Yamanasi	3.42	153	42.2	T. Nakai	Oct. 1936
133	Spring No. 3	Murasugi	Niigata	0.04	147	40.3	Y. Kinugasa	Aug. 1914
326	Tama-no-yu	Sekigane	Tottori	0.10	141	38.6	Y. Hattori	Sept. 1935
348	Yugakai-Onsen No. 2	Yugakai	Simane	30.57	140	38.5	S. Matuura	Oct. 1939
289	Private bath (M. Yamamoto)	Misasa	Tottori	0.25	132	36.3	K. Shiratori	Aug. 1925
299	Iwa-yu (Otoko-yu)	„	„	2.95	131	36.0	R. Ishizu	Mar. 1914
347	Yugakai-Onsen No. 1	Yugakai	Simane	35.06	128	35.3	S. Matuura	Oct. 1939
300	Iwa-yu (Onna-yu)	Misasa	Tottori	3.61	126	34.5	Y. Hattori	Oct. 1935
284	Seirei-no-yu	Katimi	„	0.23	122	33.6	„	Mar. 1937
321	Kabu-yu	Sekigane	„	0.11	121	33.1	„	Sept. 1935
323	Kame-no-yu	„	„	0.14	120	33.0	„	„
322	Kami-no-yu	„	„	0.13	113	31.1	„	„
306	Kiya-kazoku-yu	Misasa	„	3.72	103	28.4	R. Ishizu	Mar. 1914
288	Otyaya-no-yu	„	„	0.28	102	27.9	„	Feb. 1914
194	Totikubo No. 1	Masutomi	Yamanasi	32.62	93.2	25.6	T. Nakai	Oct. 1936
58	Mamegara-hudō-no-yu	Sirakawa	Hukusima	1.27	89.2	24.5	Ishikawa Middle school	Nov. 1930
292	Nakaya-no-yu	Misasa	Tottori	0.90	89.2	24.5	R. Ishizu	Mar. 1914
293	Bun-aburaya-no-yu	„	„	2.24	89.2	24.5	„	„

252	Syō-no-yu	Kasagi	Gihu	0.0	70.0	19.3	T. Nakai	May 1936
305	Iwasaki-no-yu No. 2	Misasa	Tottori	2.81	70.0	19.3	Y. Hattori	Oct. 1935
303	Aburaya-uti-yu	"	"	0.89	69.9	19.2	R. Ishizu	Mar. 1914
176	Hattōdaira No. 1	Masutomi	Yamanasi	0.11	63.7	17.5	T. Nakai	Oct. 1936
248	Itigaku-Kōsen	Itigaku	Gihu	0.0	60.1	16.5	"	May 1936
251	Sika-no-yu	Kasagi	"	0.0	59.6	16.4	"	"
198	Yuzawa No. 1	Masutomi	Yamanasi	71.81	58.4	16.1	"	Apr. 1937
296	Saiki-honkwan-no-yu	Misasa	Tottori	2.37	57.9	15.9	K. Shiratori	Aug. 1925
294	Hasizuya-no-yu	"	"	1.00	56.4	15.5	R. Ishizu	Mar. 1914
309	Iwasaki-no-yu No. 1	"	"	0.37	54.7	15.1	Y. Hattori	Oct. 1935
295	Yakusidō-no-yu	"	"	3.82	52.7	14.5	"	"
325	Tokiwa-no-yu	Sekigane	"	0.28	46.2	12.7	"	Sept. 1935
59	Moto-yu No. 1	Bobata	Hukusima	0.11	43.5	12.0	S. Hanzawa	Sept. 1914
172	Ginsentō-naka-no-yu	Masutomi	Yamanasi	0.43	42.0	11.6	T. Nakai	Oct. 1936
290	Naka-no-yu	Misasa	Tottori	0.35	40.0	11.0	R. Ishizu	Feb. 1914
182	Gantō-hunsen	Masutomi	Yamanasi	2.46	39.5	10.9	T. Nakai	Oct. 1936
250	Kitatani-no-izumi	Naegi	Gihu	0.0	37.9	10.4	"	May 1936
287	Kabu-yu	Misasa	Tottori	1.14	37.1	10.2	R. Ishizu	Feb. 1914
179	Higasiobi-no-izumi	Masutomi	Yamanasi	35.65	32.4	8.90	T. Nakai	Oct. 1936
286	Nakataya-no-yu	Katimi	Tottori	0.73	31.2	8.57	R. Ishizu	Feb. 1914
167	Itozawa-no-izumi	Itozawa	Nagano	0.0	29.4	8.00	T. Nakai	May 1936
285	Sagi-no-yu	Katimi	Tottori	1.93	29.0	7.98	Y. Hattori	Mar. 1937
185	Kuridaira-tennen-buro	Masutomi	Yamanasi	26.05	27.1	7.40	T. Nakai	Oct. 1936
191	Tuganerō-kasikiri-no-yu	"	"	23.95	23.7	6.50	"	Apr. 1937
193	Umamiti-zawa	"	"	4.93	23.3	6.40	"	Oct. 1936
208	Wada-matuba-Kōsen	"	"	82.66	22.2	6.10	"	Apr. 1937
280	Suzukiya-no-yu	Hamamura	Tottori	1.63	19.5	5.35	R. Ishizu	Feb. 1914
188	Tuganerō No. 1	Masutomi	Yamanasi	64.53	17.8	4.90	T. Nakai	Oct. 1936
55	Moto-yu	Kasi	Hukusima	0.53	16.7	4.59	Y. Kinugasa	Nov. 1913

Table 18.—(Continued)

No.*	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	Radon per liter of water			
					in 10^{-10} curies	in Mache's units	Examined by	Date
366	Yōzyō-yu	Dōgō	Ehime	0.03	16.1	4.42	H. Kibezaki	July 1913
189	Tuganerō No. 2	Masutomi	Yamanashi	29.39	14.6	4.00	T. Nakai	Oct. 1936
365	Kami-no-yu	Dōgo	Ehime	0.08	14.5	3.98	H. Kibezaki	July 1913
206	Siobuti-no-yu	Masutomi	Yamanashi	11.06	14.2	3.90	T. Nakai	Oct. 1936
281	Tabakoya-no-yu	Hamamura	Tottori	2.40	14.2	3.89	R. Ishizu	Feb. 1914
57	Yuzin-no-yu	Kasi	Hukushima	0.75	12.3	3.38	Y. Kinugasa	Nov. 1913
195	Kinsentō	Masutomi	Yamanashi	29.30	12.0	3.30	T. Nakai	Oct. 1936
168	Siogasawa-Kōsen	Tadati	Nagano	0.0	11.9	3.28	„	Nov. 1936
154	Zinbara-ryokwan-no-yu	Awara	Hukui	0.56	11.7	3.21	Y. Kinugasa	Dec. 1913
327	Yōzyō-kwan-no-yu	Tōgō	Tottori	0.84	11.2	3.07	R. Ishizu	Feb. 1914
56	Tengu-no-yu	Kasi	Hukushima	0.41	10.4	2.86	Y. Kinugasa	Nov. 1913
344	Koyabara-Onsen	Koyabara	Simane	6.15	8.88	2.44	S. Matuura	Oct. 1939
211	Simo-no-daira-no-yu	Masutomi	Yamanashi	13.00	8.37	2.30	T. Nakai	Apr. 1937
164	Me-no-yu	Asama	Nagano	0.06	8.26	2.27	Y. Kinugasa	Aug. 1914
8	Toyotomi-Onsen	Toyotomi	Hokkaidō	10.10	8.08	2.22	Hokkaidō Ind. Research Lab.	July 1934
275	Yakendo-Kōsen	Arima	Hyōgo	57.53	8.01	2.20	Y. Nemoto	Nov. 1936
279	Simo-no-yu	Yosioka	Tottori	0.61	7.72	2.12	Y. Hattori	Feb. 1937
108	Yubiso-no-yu No. 2	Yubiso	Gumma	0.30	7.17	1.97	M. Komori	Apr. 1913

243	Seko-no-yu	Yugasima	Sizuoka	0.10	7.03	1.93	Y. Kinugasa	Mar. 1913
283	Kyōdō-yu	Hamamura	Tottori	0.60	6.92	1.90	R. Ishizu	Feb. 1914
209	Siōzawa-kuromori-Kōsen	Masutomi	Yamanashi	11.57	6.55	1.80	T. Nakai	Apr. 1937
272	Tansan-sen	Arima	Hyōgo	0.76	6.34	1.75	H. Kibezaki	May 1913
359	Kawa-no-yu	Tawarayama	Yamaguchi	0.00	6.21	1.71	"	Aug. 1914
207	Nakazima-no-izumi	Masutomi	Yamanashi	2.94	6.19	1.70	T. Nakai	Apr. 1937
204	Siokawa-asai-no-yu	"	"	1.20	5.46	1.50	"	"
210	Siōzawa-kuromori-yosino-kwan	"	"	0.00	4.37	1.20	"	"
249	Yogarasu-Kōsen	Yogarasu	Gifu	0.0	3.93	1.08	"	May 1936
38	Kyōdō-yokuzuyō-no-yu	Atumi	Yamagata	0.58	3.68	1.01	H. Kakehi Phys. Institute of Tōhoku Imp. Univ.	June 1914
53	Tansan-sen	Naruko	Miyagi	0.06	3.64	1.00	T. Nakai	Apr. 1937
212	Kamase-hudō-no-yu	Masutomi	Yamanashi	0.00	3.64	1.00	"	Apr. 1937
373	Hunagoya-Kōsen	Hunagoya	Hukuoka	0.00	3.43	0.94	H. Kibezaki	Aug. 1914
351	Sin-sagi-no-yu	Yunogō	Okayama	0.50	3.09	0.85	R. Ishizu	July 1913
350	Sagi-no-yu	"	"	0.62	3.06	0.84	"	Mar. 1914
277	Iwai-Onsen	Iwai	Tottori	0.56	2.87	0.79	Y. Hattori	Dec. 1937
276	Kyū-Onsen	Takarazuka	Hyōgo	26.46	2.66	0.73	Osaka Imp. Hyg. Lab.	Sept. 1913
87	Nomi-yu	Ikao	Gumma	0.00	2.44	0.67	Y. Kinugasa	Nov. 1913
90	Ohaguro-no-yu	"	"	0.09	1.86	0.51	"	"
260	Kosi-no-yu No. 1	Katuura	Wakayama	0.19	1.53	0.42	T. Iwasaki and K. Kuroda	Nov. 1939
205	Siokawa-nisida-no-yu	Masutomi	Yamanashi	0.0	1.46	0.40	T. Nakai	Apr. 1937
92	Ōseki-no-yu	Ikao	Gumma	0.00	1.35	0.37	Y. Kinugasa	Nov. 1913

Table 18.—(Concluded)

No.*	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	Radon per liter of water			
					in 10 ⁻¹⁰ curies	in Mache's units	Examined by	Date
340	Ameya-ryokwan-no-yu	Usio	Simane	0.06	1.19	0.33	R. Ishizu	Mar. 1914
401	Kiyō-sen	Kamegawa	Ōita	0.11	1.16	0.32	"	Oct. 1913
405	Sibaseki-Onsen	"	"	0.00	1.13	0.31	"	"
235	Ō-yu	Yosina	Sizuoka	0.10	1.09	0.30	Y. Kinugasa	Mar. 1913
217	Matubara-no-yu	Itō	"	0.16	1.06	0.29	R. Ishizu	Feb. 1913
160	Yamasio-Kōsen	Kasio	Nagano	18.5	0.93	0.26	T. Nakai	May 1936
342	Moto-yu	Sigaku	Simane	1.02	0.93	0.26	S. Matuura	Oct. 1939
270	Hon-Onsen	Arima	Hyōgo	71.29	0.92	0.25	H. Kibezaki	May 1913
98	Sirahata-no-yu	Kusatu	Gumma	0.16	0.80	0.22	R. Ishizu	Apr. 1913
400	Si-no-yu	Kamegawa	Ōita	0.00	0.80	0.22	"	Oct. 1913
379	Hurō-sen	Beppu	"	0.32	0.66	0.18	H. Kibezaki	Mar. 1913
94	Tiyo-no-yu	Kusatu	Gumma	0.10	0.62	0.17	R. Ishizu	Apr. 1913
97	Netu-no-yu	"	"	0.15	0.58	0.16	"	"
244	Kidati-no-yu	Yugasima	Sizuoka	0.30	0.55	0.15	Y. Kinugasa	Mar. 1913
96	Zizō-no-yu	Kusatu	Gumma	0.01	0.51	0.14	R. Ishizu	Apr. 1913
93	Wasi-no-yu	"	"	0.05	0.47	0.13	"	"
409	Zizō-Onsen	Myōban	Ōita	0.00	0.47	0.13	"	Oct. 1913
253	Iwō-sen	Gero	Gihu	0.00	0.44	0.12	Tokyo Imp. Hyg. Lab.	Nov. 1934
402	Hamada-Onsen	Kamegawa	Ōita	0.24	0.40	0.11	R. Ishizu	Oct. 1913
254	Yunosima-Onsen	Gero	Gihu	0.00	0.36	0.10	Tokyo Imp. Hyg. Lab.	Sept. 1934
130	Senami-Onsen	Senami	Niigata	0.11	0.22	0.06	Y. Kinugasa	Aug. 1914
397	Kwankaizi-Onsen	Kwankaizi	Ōita	0.00	0.07	0.02	H. Kibezaki	Mar. 1913

radium, only gaseous emanation (most of the famous radioactive springs in Germany belong to this type).

(3) The Radium-emanation-water type, containing radium-salts in which the amount of dissolved radium is less than that required for radioactive equilibrium with the radon that is present in this water (e.g. Oberschlema, Brambach, Kreuznach, etc.).

The hot springs of Arima Hon-Onsen show a radium content of 0.71×10^{-10} g. per liter of water and a radon content of 0.92×10^{-10} curie per liter. The radium is almost in radioactive equilibrium with radon, but since the radon content of this spring was determined in 1913 and the radium content in 1936, there is more than a twenty years interval between the two determinations, with the result that it may be unsafe to compare such data. Assuming, however, that its radon content did not vary much during this interval of time, this spring would belong to the Radium-salt-water type.

The Ena spring contains 8.08×10^{-10} curie of radon per liter, although no dissolved radium can be detected in this water. This spring is a typical Radium-emanation-water.

As will be seen from Table 18, in almost every case the amount of radium in the spring waters was found to be much less than that required for radioactive equilibrium with the radon that is present in them. Even in the water from the Wadamatuba spring in Masutomi, which shows the highest radium content,⁽³³⁾ the radon content was found to be 22.2×10^{-10} curie and the amount of radium found was 0.83×10^{-10} g. per liter of water, showing that the radon in the water is about 27 times greater than that which the radium present in the water is able to produce. In other words, the permanent activity of this water is only 4 per cent of its temporary activity.

Thus all the radioactive natural waters in Japan, with only one exception, belong to the class of Radium-emanation-water or Radium-emanation-water with radium-salt, which shows that although a part of the radon in the water of mineral springs is formed directly from their parent radium dissolved in them, the greater part of them might have been extracted independently of the radium from the rocks where the waters originate and through which they pass. The difference between the amount of radon and that of radium in natural waters may be due to the difference between the solubility of gaseous radon in water and that of the radium salts.

The correlation between the radium and radon contents is shown in Fig. 16, in which the radium contents of the spring waters that were examined by the writer are plotted against their radon contents. Here we see that spring waters of high radium content do not always show a high radon content, while those of high radon concentration do not always contain a large amount of radium. The amounts of radium and of radon in spring waters do not always run parallel with each other. For example, the waters of the Wadamatuba spring in Masutomi, which shows the

(33) Although the Katakosi spring in Arima and the Matu-no-yu in Tamatukuri show higher radium content than this spring, they have never been tested for radon.

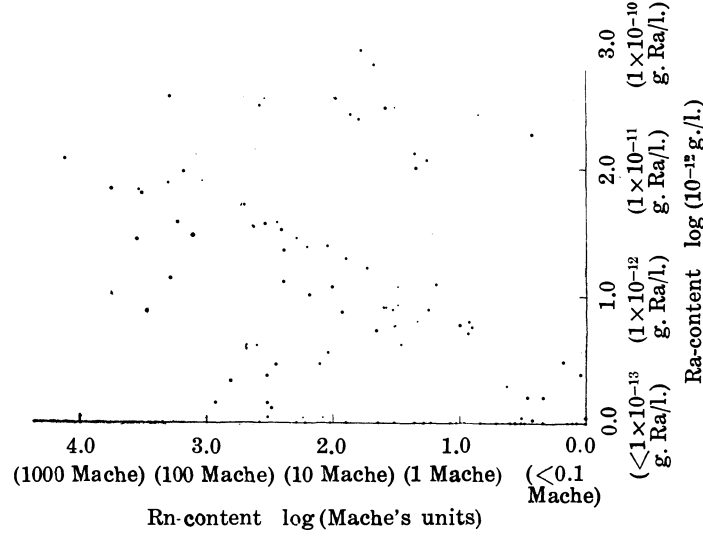


Fig. 16. Relation between the Ra-content and the Rn-content of Japanese mineral springs.

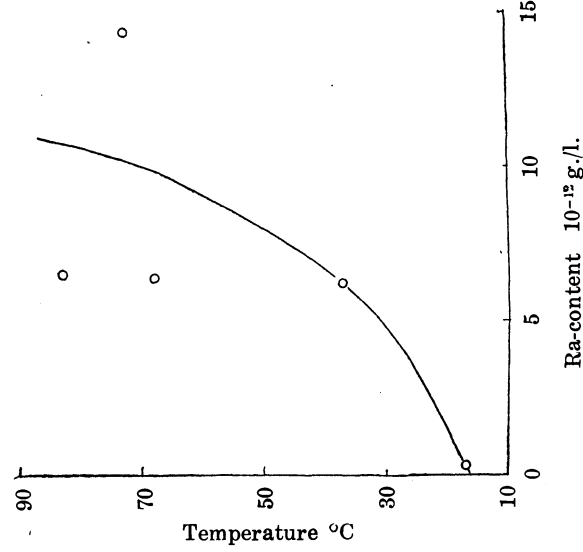


Fig. 17. Relation between the Ra-content and the orifice temperature of the Matunoyama hot springs.

highest radium content of 82.66×10^{-12} g. per liter of water, contain only 6.1 Mache's units of radon, while the waters of Ikeda spring No. 2 and that of Wadegawara No. 2, both show an unusually high concentration of radon, do not contain so much radium as the others, which shows, as already stated, that radon from spring waters does not originate in dissolved radium alone, but also from other sources.

X. Relation between the Radium Content and the Orifice Temperature of Mineral Springs. We shall now take some groups of springs and study the relation between their radium content and their orifice temperature.

The correlation between the radium content and the orifice temperature of the Masutomi springs in Yamana Prefecture, that of the Misasa springs in Tottori Prefecture, and that of the Arima springs in Hyōgo Prefecture, has been shown in the preceding figures (V. Table 10, Figs. 9, 10, 14). In Figs. 17-21, the radium content of the spring waters is plotted against their orifice temperature for the Matunoyama springs in Niigata Prefecture; Katuura in Wakayama Prefecture; Hamamura (including Kati-mi) in Tottori Prefecture; and Ikeda and Yugakai in Simane Prefecture.

As will be seen from these figures, there seems

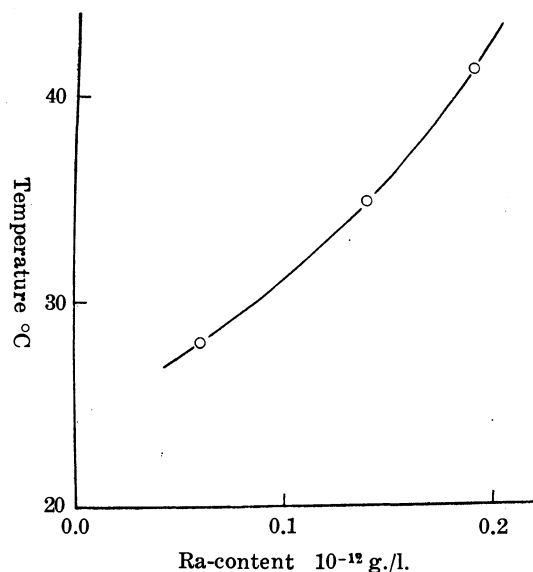


Fig. 18. Relation between the Ra-content and the orifice temperature of the Katuura thermal springs.

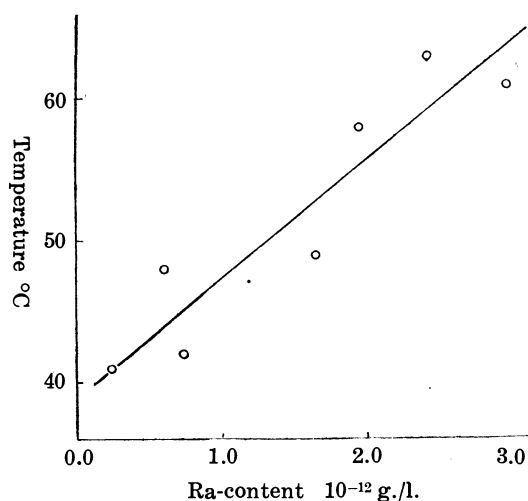


Fig. 19. Relation between the Ra-content and the orifice temperature of the Hama-mura (Katimi) hot springs.

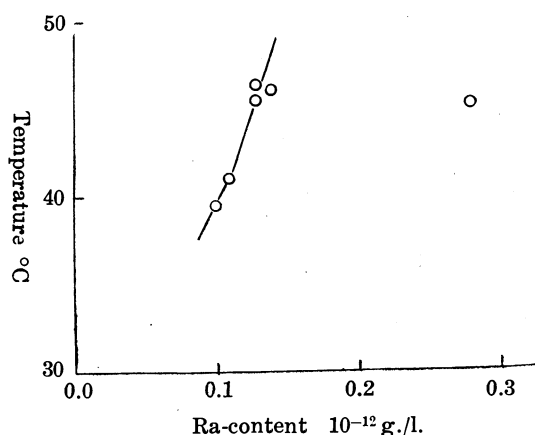


Fig. 20. Relation between the Ra-content and the orifice temperature of the Sekigane hot springs.

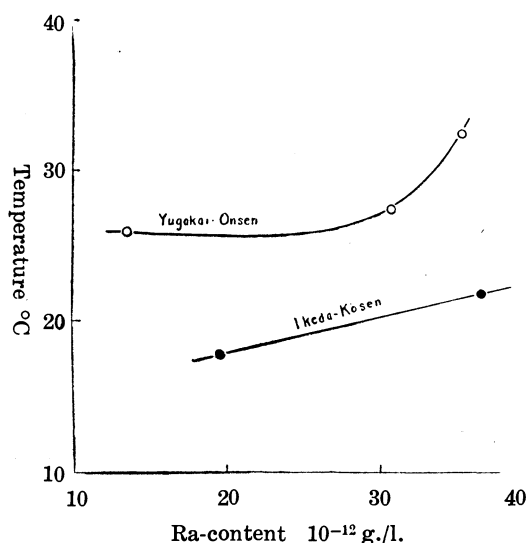


Fig. 21. Relation between the Ra-content and the orifice temperature of the Yugakai thermal springs and the Ikeda mineral springs.

to be a linear relation between them, the radium content increasing with rise in orifice temperature in almost every group, which may be explained by the difference in the solubility of radium by temperature, assuming that the radium contained in spring waters comes mostly from rocks where the waters originate and through which they pass.

As stated in the previous chapter, however, in the case of the Beppu springs in Oita Prefecture, no such correlation exists between their radium contents and orifice temperature. It may be affected by other unknown factors more pronounced than that of temperature.

XI. Relation between the Radium Content and the Chemical Qualities of Spring Waters. *Chemical classification of mineral springs and their radium contents.* According to the system arranged by the Pharmaceutical Society of Japan, the mineral springs are classified as below.

1. Simple cold.	2. Simple.
3. Simple carbondioxated.	4. Earthy carbondioxated.
5. Alkaline.	6. Common salt.
7. Bitter.	8. Iron carbonate.
9. Vitriol.	10. Alum.
11. Alum vitriol.	12. Acid.
13. Sulphur.	

In Table 19, the mineral springs are arranged according to their chemical composition.

Chemical analyses of these mineral springs were made by the Imperial Hygienic Laboratories of Tokyo and Ōsaka.⁽³⁴⁾ The data of the springs starred were obtained by the Hygienic Laboratories of the respective Prefectures.

Although some of these data are old, it is believed that the main chemical constituents of the springs do not vary much so far as no great changes occur at their origins, so that we may presume from these results the chemical classification to which any water sample taken for radium determination belongs to. The total evaporated residues of these waters and those of some of their essential chemical constituents are also given in this table for reference.

As will be seen from this table, almost all the simple cold springs contain no radium. The simple thermals also show a low radium content, being lower than 1×10^{-12} g. radium per liter of water, excluding the waters at Yakusidō-no-yu in Misasa, which is a radioactive spring containing 14.50 Mache units of radon. Thus the simple springs in which the quantity of dissolved solid constituents is less than 1 gram per kilogram, are all poor in radium. As will be described in the next section, there appears to be a linear relation between the radium content of spring waters and their total solid constituents, with the result that spring waters containing small quantities of solid matter are usually poor in radium.

All sulphur springs show comparatively low radium content. It is well known that sulphur springs are closely related to volcanos and it is also evident from numerous measurements that volcanic rocks are generally very poor in radium compared with other igneous rocks, such as granite, etc., from all which one naturally expects sulphur springs to be poor in radium.

(34) A Table of Composition of Mineral Waters in Japan, Bull. Imp. Hygienic Lab., **34** (1929); **54** (1940) and other reports of the Imperial Hygienic Laboratories.

Table 19. Mineral springs arranged according to chemical composition.

1. Simple cold springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	Radio-activity	Mache's units
76	Naka-no-yu*	Yokomuki	Hukusima	24.0	0.00	0.64	Radioactive	40.3
133	Spring No. 3*	Murasugi	Niigata	13.5	0.04			
167	Itozawa-no-izumi*	Itozawa	Nagano	13.0	0.0			
168	Siogasawa-Kōsen	Tadati	"	12.0	0.0		Radioactive	22.2
247	Radium-Kōsen	Ena	Gihu	13.1	0.0	0.12		
248	Itigaku-Kōsen*	Itigaku	"	12.1	0.0			
249	Yogarasu-Kōsen*	Yogarasu	"	14.0	0.0		Radioactive	16.5
250	Kitatani-no-izumi*	Naegi	"	12.3	0.0			

2. Simple thermals.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	Radio-activity	Mache's units
19	Tuta-Onsen*	Tuta	Aomori		0.24			
25	Yuze-Onsen*	Yuze	Akita		0.00			
44	Ō-yu*	Aone	Miyagi	54.0	0.55	0.54		
55	Moto-yu	Kasi	Hukusima	51.0	0.53			
56	Tengu-no-yu	"	"	48.5	0.41			
57	Yuzin-no-yu	"	"	50.0	0.75			
66	Private bath* (K. Hasimoto)	Iwasiro-atami	"		0.05	0.39		

** Numbers correspond to those used in Table 3.

Table 19.—(Continued)

2. Simple thermals. (Concluded)

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	Radio- activity	Mache's units
68	Private bath* (M. Ōgosi)	Iwasiro-atami	Hukusima	35.0	0.08	0.38		
79	Moto-yu	Kawazi	Totigi	46.0	0.10	0.33		
105	Minakami-Onsen	Minakami	Gumma	40.0	0.49	0.42		
107	Yubiso-Onsen No. 1	Yubiso	"	50.0	0.00			
108	" No. 2	"	"	66.0	0.30	0.55		
123	Ubako-no-yu	Ubako	Kanagawa	39.7	0.05	0.65		
131	Spring No. 1*	Murasugi	Niigata	25.6	0.51	0.35	Radioactive	49.6
132	" No. 2*	"	"	26.0	0.04		"	48.6
164	Me-no-yu	Asama	Nagano	36.5	0.06	0.44		
165	Higasiyama-Onsen*	Higasiyama	"	42.0	0.08			
215	Yukawa-no-yu	Itō	Sizuoka	44.0	0.16	0.92		
217	Matubara-no-yu	"	"	42.0	0.16	0.98		
236	Moto-yu	Yosina	"	39.0	0.06	0.48		
239	Hōsen-Onsen	"	"	47.5	0.02	0.65		
241	Kan-no-yu	"	"	51.0	0.00	0.82		
295	Yakusidō-no-yu	Misasa	Tottori	74.5	3.82	0.86	Radioactive	14.5
309	Iwasaki-no-yu No. 1	"	"	54.5	0.37	0.64	"	15.1
322	Kami-no-yu	Sekigane	"	46.3	0.13	0.50	"	31.1
323	Kame-no-yu	"	"	46.0	0.14	0.58	"	33.0
325	Tokiwa-no-yu	"	"	45.3	0.28	0.65	"	12.7
326	Tama-no-yu	"	"	39.5	0.10	0.69	"	38.6
327	Yōzyō-kwan-no-yu	Tōgō	"	50.0	0.84	0.93		
354	Mizuno-ryokwan-no-yu*	Yuda	Yamaguti		0.22			
358	Mati-no-yu	Tawarayama	"	40.0	0.00	0.18		
359	Kawa-no-yu	"	"	40.0	0.00	0.18		
360	Syō-no-yu	"	"	38.0	0.00	0.19		

365	Kami-no-yu*	Dōgo	Ehime	46.8	0.08	0.78	
366	Yōzyō-yu*	"	"	45.4	0.03	0.83	
367	Donkōbori-no-yu*	"	"		0.03		
371	Spring No. 2*	Musasi	Hukuoka		0.17		
375	Reityō-sen*	Beppu	Ōita	60.0	0.22	0.97	
376	Kotobuki-Onsen*	"	"	46.5	0.18	1.35	
377	Yanagi-Onsen*	"	"	49.5	0.64	0.72	
378	Kusunoki-Onsen*	"	"	44.5	0.39	0.89	
380	Ta-no-yu A*	"	"	57.0	0.18	0.70	
381	" B*	"	"	43.0	0.15		
384	Umezono-Onsen*	"	"	61.5	0.75	1.00	
386	Kaimonzi-Kōen-Onsen*	"	"	62.0	0.25	1.17	
387	Matogahama-Onsen*	"	"	49.5	0.76	1.62	
391	Hinode-Onsen*	"	"	50.5	0.17	0.77	
393	Nagesi-Onsen*	"	"	52.5	0.72		
406	Netu-no-yu*	Kannawa	"	48.0	0.00	0.42	
436	Tokyoya-no-yu	Takeo	Saga	52.0	0.89		
437	Huruyu-Onsen*	Huruyu	"		0.05		
477	Kamii-kwan-no-yu	On-yō	Korea	46.0	0.00	0.21	

3. Simple carbondioxated springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	Free CO ₂ g./Kg.	
53	Tansan-sen	Naruko	Miyagi	39.0	0.06			
272	Tansan-sen*	Arima	Hyōgo	16.0	0.76			
394	Kamiya-Onsen*	Beppu	Ōita	51.0	0.11	0.72		
397	Kwankaizi-Onsen*	Kwankaizi	"	55.5	0.00	0.77	0.59	
441	Moto-yu-Onsen*	Yunoura	Kumamoto	45.0	0.04	0.32	0.05	
470	Ramune-Onsen No. 1*	Ramune	Kagosima		0.20	2.45	1.22	
471	" No. 2*	"	"		0.18	1.08	1.62	

Table 19.—(Continued)

4. Earthy carbondioxated springs.

5. Alkaline springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	Free CO ₂ g./Kg.	NaCl g./Kg.
a. Alkaline springs.								
262	Yukawarō-no-yu*	Yukawa	Wakayama	40.2	0.10			
263	Kawayu-Onsen*	Kawayu	„	56.0	2.53			
267	Kami-no-yu*	Ryūzin	„	48.0	0.57			
268	Simo-no-yu*	„	„		0.15			
269	Tomiya-ryokwan-no-yu*	Yumura	Hyōgo	88.0	0.79			
312	Tennen-gankutu-no-yu No. 1	Misasa	Tottori	79.5	10.06	2.27		
369	Nibuzawa-Kōsen	Nibuzawa	Ehime		0.14			
388	Yumimatu-Onsen*	Beppu	Ōita	62.0	0.25			
b. Alkaline carbondioxated spring.								
444	Iwa-no-yu-Onsen*	Yunoura	Kumamoto	45.0	0.06	0.35	0.79	
c. Alkaline muriated springs.								
7	Ponyu-Onsen	Ponyu	Hokkaidō	37.0	0.00	1.87		0.57
264	Reimei-no-yu*	Yuzaki	Wakayama	57.3	8.44			
443	Hukamizu-Onsen*	Yunoura	Kumamoto	42.0	0.02	0.36		

6. Common salt springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	NaCl g./Kg.
a. Weak common salt springs.							
125	Mamane-no-yu	Yugawara	Kanagawa	75.0	0.00	2.00	1.22
126	Simo-no-yu	"	"	63.0	0.10	1.99	1.20
130	Senami-Onsen	Senami	Niigata	100.0	0.11	4.19	3.37
183	Kuridaira No. 1	Masutomi	Yamanashi	22.0	0.77	3.62	1.40
184	" No. 1. B.	"	"	17.0	0.73	2.32	
298	Ryōyōzyo-gensen	Misasa	Tottori	72.0	2.89	1.31	0.61
300	Iwa-yu (Onna-yu)	"	"	68.0	3.61	1.23	0.57
305	Iwasaki-no-yu No. 2	"	"	68.0	2.81	1.16	0.71
342	Moto-yu*	Sigaku	Simane	45.0	1.02	3.14	1.52
395	Hamawaki-Onsen*	Beppu	Oita	46.5	0.14		3.13
400	Si-no-yu	Kamegawa	"	54.0	0.00	1.22	0.68
401	Kiyō-sen*	"	"	56.8	0.11	2.65	
416	Ō-yu*	Yunohira	"	92.0	0.24	1.58	0.89
417	Hana-no-yu-Onsen*	"	"	78.0	0.19	1.58	0.97
b. Simple common salt spring.							
c. Concentrated common salt springs.							
160	Yamasio-Kōsen	Kasio	Nagano	12.1	18.5	29.45	26.81
270	Hon-Ōsen	Arima	Hyōgo	43.0	71.29	18.43	
d. Carbondioxated common salt springs.							
146	Nagae-Kōsen*	Nagae	Toyama	21.0	0.42	2.32	1.01
345	Radium-Kōsen No. 1	Ikeda	Simane	21.7	36.43	9.83	5.60

Table 19.—(Continued)

6. Common salt springs. (Concluded)

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	NaCl g./Kg.	SO ₄ " g./Kg.
d. Carbondioxated common salt springs. (Concluded)								
346	Radium-Kōsen No. 2*	Ikeda	Simane	17.7	19.46			
476	Yuno-o-Onsen*	Yuno-o	Kagosima	74.0	1.53	2.27	0.58	
e. Alkaline common salt springs								
8	Toyotomi-Onsen	Toyotomi	Hokkaidō	43.5	10.10	11.70	9.82	
102	Alkali-sen	Isobe	Gumma	15.5	15.53	26.91	21.35	
347	Yugakai-Onsen No. 1	Yugakai	Simane	32.3	35.06	10.35	6.66	
440	Gozen-no-yu*	Hinaku	Kumamoto	48.0	0.08	0.70	0.37	
445	Kotobuki-Onsen*	Yunoura	„	41.0	0.02	0.67	0.42	
f. Saline common salt springs.								
40	Kamasaki-no-yu	Kamasaki	Miyagi	47.0	1.00	5.19	2.47	1.37
41	Mogamiya-no-yu	„	„	38.5	1.37	5.03	2.41	
42	Kimuraya-no-kyū-yu	„	„	39.0	3.03	5.15	2.42	1.37
43	Kimuraya-no-sin-yu	„	„		2.58	5.14	2.42	1.35
77*	Iwasakiya-no-yu	Ōsio	Hukusima		3.72	4.56	2.88	0.52
g. Earth-muriated common salt springs.								
26	Onogawa-Onsen	Onogawa	Yamagata	76.0	8.37	5.67	3.90	
27	Kyokuato-gensen	Akayu	„	62.0	0.09			
28	Matusima-kwan-no-yu	„	„	54.0	0.09			
129	Monkawa-Onsen	Monkawa	Kanagawa	45.0	0.41	21.97	15.84	

134	Netu-no-yu	Matunoyama	Niigata	68.0	6.43	15.08	8.68	
135	Hii-no-yu	"	"	83.0	6.49	13.87	7.93	
136	Kagami-no-yu	"	"	72.5	14.30	15.50	7.97	
147	Gotairan-no-yu	Wakura	Isikawa	82.0	6.04	21.00	11.41	
148	Moto-yu*	"	"		5.89			
149	Sin-yu*	"	"		4.83			
271	Hana-no-bō-no-yu	Arima	Hyōgo	37.6	68.50	20.23		
274	Katakosi-Kōsen	"	"	21.0	111.05	23.63		
350	Sagi-no-yu	Yunogō	Okayama	38.0	0.62	2.27	1.18	
351	Sin-sagi-no-yu	"	"	37.7	0.50	2.25	1.17	
448	Mura-no-yu-Onsen*	Ibusuki	Kagosima	65.0	0.89	5.11	3.34	
449	Yaziga-yu-Onsen*	"	"	56.0	0.55	4.08	2.74	
h. Earthy common salt springs.								
174	Wadegawara No. 1	Masutomi	Yamanasi	18.0	6.76	3.25		
175	" No. 2	"	"	19.5	11.62	7.12		
180	Nibuzawa	"	"	24.0	6.22	7.25	4.98	
181	Sio-no-sawa-tugane-yu	"	"	20.0	1.33	4.89	5.29	
194	Totikubo No. 1	"	"	27.0	32.62	9.42		
195	Kinsentō*	"	"	31.0	29.30	7.49	3.51	
i. Sulphated common salt springs								
38	Kyōdō-yokuzyō-no-yu	Atumi	Yamagata		0.58	3.51	2.35	0.57
128	Moti-no-yu	Yugawara	Kanagawa	59.0	0.28	2.28	1.29	0.49
154	Zinbara-ryokwan-no-yu	Awara	Hukui	76.0	0.56	10.03	5.90	0.39
156	Hatu-yu	Sibu	Nagano	73.5	0.08			
157	Ō-yu No. 1	"	"	77.0	0.11	1.21	0.53	0.37
158	" No. 2	"	"		0.03			

Table 19.—(Continued)

7. Bitter springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	SO ₄ '' g./Kg.
a. Bitter springs.							
438	Spring No. 1*	Tosita	Kumamoto		0.04		
439	„ No. 2*	„	„		0.10		
b Saline bitter springs.							
22	Usi-no-yu*	Yumoto	Iwate		0.08	1.44	
153	Yamasiro-Onsen*	Yamasiro	Isikawa	66.0	0.13		
235	Ō-yu	Yosina	Sizuoka	50.0	0.10	1.24	0.64
245	Sagasawa-Onsen	Sagasawa	„	58.0	0.21	1.62	0.78
340	Ameya-ryokwan-no-yu*	Usio	Simane	43.0	0.06	1.10	
c. Sulphated bitter springs.							
15	Sin-yu*	Sinyu	Aomori	60.0	0.05	1.64	
34	Gensen*	Akakura	Yamagata	65.0	0.12		
47	Kawara-no-yu*	Sakunami	Miyagi	54.0	0.21		
106	Tanikawa-Onsen	Tanikawa	Gumma	62.0	0.10	1.02	0.49
109	Asahi-no-yu	Hōsi	„	44.0	0.00	1.20	0.72
112	Sarugakyō-Onsen	Yuzima	„	59.0	0.55	1.79	
277	Iwai-Onsen	Iwai	Tottori	51.0	0.56	1.22	0.96
285	Sagi-no-yu	Katimi	„	58.0	1.93	0.98	0.41
d. Earthy sulphated bitter springs.							
87	Nomi-yu	Ikao	Gumma	44.0	0.00	1.16	0.29
88	Spring No. 2	„	„	49.0	0.00	1.08	0.21
90	Ohaguro-no-yu	„	„	50.0	0.09	1.46	0.32
91	Hukiage-no-yu	„	„	41.0	0.00	1.65	0.39

92	Oseki-no-yu	Ikao	Gumma	47.0	0.00	1.03	0.27
104	Yuhara-Onsen	Yuhara	„	55.0	0.09	1.47	0.57
e. Muriated saline bitter springs.							
280	Suzukiya-no-yu	Hamamura	Tottori	49.0	1.63	1.07	
286	Nakataya-no-yu	Katimi	„	42.0	0.73	1.36	0.46
f. Muriated sulphated bitter springs.							
127	Hirokawara-no-yu*	Yugawara	Kanagawa	68.0	0.05	4.79	
284	Seirei-no-yu	Hamamura	Tottori	41.0	0.23	1.64	0.63

8. Iron carbonate springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	NaCl g./Kg.	CO ₂ g./Kg.
a. Iron carbonate springs.								
379	Hurō-sen*	Beppu	Oita	59.0	0.32	0.80		
382	Kaigan-suna-yu*	„	„	58.5	0.04	0.99		
383	Takegawara-Onsen*	„	„	64.5	0.74	0.97		
405	Sibaseki-Onsen*	Kamegawa	„	67.0	0.00	1.59		
b. Earthy iron carbonate spring.								
89	Spring No. 3	Ikao	Gumma	47.5	0.06	0.82		
c. Iron carbonate common salt springs.								
143	Moto-yu	Seki	Niigata	41.0	0.09	1.06	0.98	
344	Koyabara-Onsen*	Koyabara	Simane	38.3	6.15	8.03	3.91	
450	Misuzi-no-yu*	Ibusuki	Kagosima	58.0	0.51	3.69	2.36	

Table 19.—(Continued)

8. Iron carbonate springs. (Concluded)

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	NaCl g./Kg.	CO ₂ g./Kg.
d. Iron carbondioxated common salt spring.								
276	Kyū-Onsen	Takarazuka	Hyōgo	18.5	26.46	18.80	15.26	
e. Iron carbondioxated springs.								
257	Yosino-Onsen	Yosino	Nara		0.43	0.83		1.38
373	Hunagoya-Kōsen No. 2*	Hunagoya	Hukuoka	22.0	0.00	0.36		1.69
434	Nagaiki-no-yu*	Nagayu	Ōita	42.0	0.58	2.70		2.55

9. Vitriol springs.

10. Alum springs.

11. Alum vitriol springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.		
72	Spring No. 1*	Wasikura	Hukusima	50.0	0.00			

12. Acid springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	H ₂ SO ₄ (free) g./Kg.	HCl (free) g./Kg.	H ₂ S g./Kg.
a. Acid springs.									
6	Kawayu-Onsen*	Kawayu	Hokkaidō		0.00				
11	Netu-no-yu*	Sukayu	Aomori	50.0	0.32	1.09	0.10		
12	Hie-no-yu*	„	„	48.0	0.15	0.95	0.13		

93 407	Wasi-no-yu Sibu-yu*	Kusatu Kannawa	b. Acid vitriol springs.				4.09 1.71	0.08
			Gumma Oita	60.0 91.0	0.05 0.00			
98	Sirahata-no-yu	Kusatu	c. Acid alum vitriol spring.				2.51	
			Gumma	61.0	0.16			
408	Umi-zigoku	Kannawa	d. Muriated acid alum vitriol spring.				3.51	0.22
			Oita	90.5	0.54			
24	Okama-no-yu*	Tamagawa	e. Sulphureted acid springs.					
75	Numaziri-Onsen	Numaziri	Akita		0.60			
86	Sika-no-yu	Nasu	Hukusima	63.0	0.84	1.94	0.17	0.13
409	Zizō-Onsen*	Myōban	Totigi	76.0	0.55	2.14	1.07	0.04
410	Kakuzyu-sen*	"	Oita	60.0	0.00	1.02	0.59	0.01
			"	70.0	0.27	5.88	2.21	0.002
33	Kawara-no-yu*	Takayu	f. Sulphureted acid alum vitriol spring.				4.02	1.68
			Yamagata	42.0	0.23			

13. Sulphur springs.

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	H ₂ S g./Kg.
a. Sulphur springs.							
59	Moto-yu No. 1*	Bobata	Hukusima	14.0	0.11	0.18	
150	Hōsi-no-yu*	Awazu	Isikawa	64.0	0.21	2.35	0.02
251	Sika-no-yu*	Kasagi	Gihu	15.1	0.0		
253	Iwō-sen	Gero	"	52.0	0.00	0.32	0.002
254	Yunosima-Onsen*	"	"	65.0	0.00		
370	Spring No. 1*	Musasi	Hukuoka		0.15		
398	Horita-Onsen*	Horita	Oita	81.0	0.09	0.36	0.01

Table 19.—(Concluded)

13. Sulphur springs.. (Concluded)

No.**	Spring	Location	Prefecture	Temp. of spring °C	Radium content g./l. $\times 10^{12}$	Total residue g./Kg.	H ₂ S g./Kg.
b. Hydrogen sulphide springs.							
21	Hanamaki-Onsen	Hanamaki	Iwate	72.0	0.00	0.96	0.002
141	Myōkō-Onsen*	Myōkō	Niigata	60.0	0.24		
145	Moto-yu*	Tubame	„		0.00		
266	Sin-tubaki-no-yu*	Tubaki	Wakayama	33.5	0.26	0.39	0.05
454	Kabusiki-Onsen*	Kabusiki	Kagosima	52.0	0.00	0.36	0.04
455	Private bath* (K. Huzita)	Miyanozyō	„	52.0	0.06	0.39	0.002
466	Hayasida-Onsen*	Kirisima- Eino-o	„	71.0	0.39		
c. Alkaline sulphur springs.							
138	Tamago-no-yu*	Matunoyama	Niigata	17.0	0.29		
259	Kowase-no-yu*	Katuura	Wakayama	28.0	0.06		
260	Kosi-no-yu No. 1*	„	„	41.5	0.19		
261	Obatakeyama-no-yu*	„	„	35.0	0.13		
d. Muriated sulphur springs.							
20	Nanasigure-Kōsen	Nanasigure	Iwate		0.60	13.33	0.01
38	Kyōdōyokuzyō-no-yu	Atumi	Yamagata		0.58	3.51	
159	Yamada-Onsen*	Yamada	Nagano	60.0	0.25	4.75	
290	Naka-no-yu	Misasa	Tottori	66.0	0.35	1.24	0.002
e. Earthy sulphur spring.							
85	Kakkō-Onsen*	Nasu	Totigi	60.0	0.00	1.79	0.02

We shall next consider springs containing comparatively large amounts of sulphate ions, such as bitter, alum, vitriol and acid springs, some of which show a fairly high radium content. As for the relation between the radium and sulphate ions in mineral waters, I. D. Kurbatov,⁽²⁾ who studied a number of salt waters from the petroleum district in North Caucasus, Russia, reported that the amount of sulphate ions in the water is not an indicator of the presence or absence of radium and its isotopes and that brines of unusually high radium concentration contain also some sulphate ions. According to the analyses of S. Gōda, brines from Tzeliutsing in Szechwan, China, notwithstanding its unusually high radium content of 2.5×10^{-10} g. per liter of water, contains 0.147% of sulphate ions. Table 20 gives the amount of sulphate ions⁽³⁴⁾ in some Japanese springs containing fairly large quantities of radium. As will be seen from this table, springs with high radium content are not always poor in sulphate ions.

Finally, common salt springs are generally rich in radium, especially spring waters containing a large quantity of sodium chloride, all of which, with a few exceptions, show high radium concentration. This cannot be easily explained, because the origin of the sodium chloride in spring waters is not yet clearly understood.

Relation between the radium content and the quantities of dissolved solid constituents of spring waters. The radium content and the quantities of dissolved solid constituents in spring waters were shown in Tables 7, 11, 16, 19.

Table 20. Sulphate ion content of spring waters of high radium content.

No.*	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	SO ₄ " g./Kg.
8	Toyotomi-Onsen	Toyotomi	Hokkaidō	10.10	0.001
26	Onogawa-Onsen	Onogawa	Yamagata	8.37	0.093
40	Kamasaki-no-yu	Kamasaki	Miyagi	1.00	1.371
42	Kimuraya-no-kyū-yu	"	"	3.03	1.374
43	Kimuraya-no-sin-yu	"	"	2.58	1.348
77	Iwasakiya-no-yu	Osio	Hukusima	3.72	0.516
102	Alkali-sen	Isobe	Gumma	15.53	0.000
134	Netu-no-yu	Matunoyama	Niigata	6.43	0.094
136	Kagami-no-yu	"	"	14.30	0.241
147	Gotairan-no-yu	Wakura	Isikawa	6.04	0.191
160	Yamasio-Kōsen	Kasio	Nagano	18.5	0.000
180	Nibuzawa	Masutomi	Yamanasi	6.22	0.470
181	Sio-no-sawa-tugane-yu	"	"	1.33	0.472
276	Kyū-Onsen	Takarazuka	Hyōgo	26.46	0.000
285	Sagi-no-yu	Katimi	Tottori	1.93	0.408
298	Ryōyōzyo-gensen	Misasa	"	2.89	0.092
347	Yugakai-Onsen No. 1	Yugakai	Simane	35.06	0.442

* Numbers correspond to those used in Table 3.

Although the amount of total evaporated residues determined by Okauti, Nemoto and Kuroda were obtained for the same samples that were used for radium determination, the other data obtained by the Tokyo and Ōsaka Imperial Hygienic Laboratories and the Hygienic Laboratories of the various Prefectures, are all old results. We can presume, however, from these data the approximate quantities of dissolved solid constituents

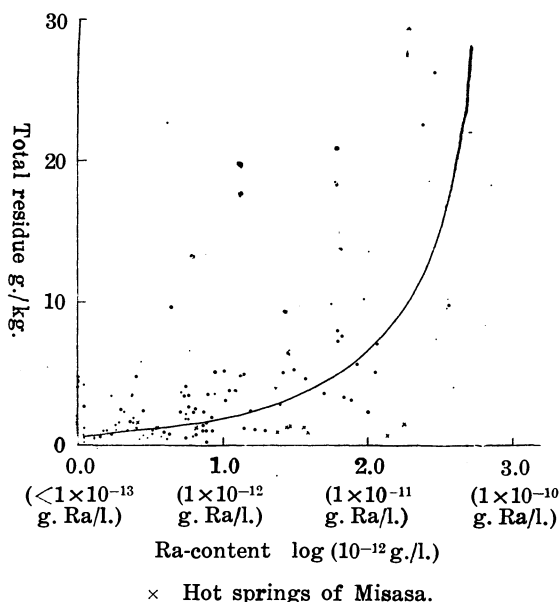


Fig. 22. Relation between the Ra-content and the amount of total residue of Japanese springs.

however, notable that the waters at Misasa have a high radium content notwithstanding the small quantities of dissolved solid constituents.

Relation between the radium content and the pH value of spring waters. The radium content and the pH value of spring waters are given in Table 21, arranged according to their pH values, which latter were determined by Kuroda⁽³⁵⁾ and the writer from the samples that were used for radium determination with the colorimetric method. Some old results obtained by Hattori,⁽³¹⁾ the Beppu Geophysics Research Laboratory⁽²⁷⁾ and the Imperial Hygienic Laboratory of Tokyo⁽³⁶⁾ are given in the table for reference. Besides these data, the chemical reactions of spring waters of comparatively high radium content, are shown in Table 22.

As shown in these tables, all spring waters of high radium content seem to belong to the weak acidic, neutral or weak alkaline waters, while the strong acidic and the strong alkaline waters show a fairly low radium content.

In the case of strong acidic spring waters, it may be presumed that

(35) These unpublished data are reported here by permission of Mr. K. Kuroda, for which courtesy the writer tenders his sincere thanks.

(36) Reports of the Imperial Hygienic Laboratory of Tokyo.

acidic gases, derived from magma very deep in the earth, ascend in the state of vapour and reach the superficial crustal layer, where some of it turn liquid owing to the effect of underground water and then gush out to the surface of the earth. Should they pass through the rocks as solution from the beginning, the waters might act on the rocks with the result that the waters would lose their strong acidity. Assuming then that the largest part of the radium contained in spring waters comes from the rocks where the waters originate and through which they pass, as stated in the previous section, the above fact that strong acidic spring waters show a fairly low radium content is easily understood.

As to the strong alkaline spring waters, the strong alkalinity is due to many reasons, so that the low radium concentration of strong alkaline spring waters can not be explained simply.

Table 21. The radium content and the pH value of spring waters.

No.†	Spring	Location	[Prefecture	Radium content g./l. $\times 10^{12}$	pH
98	Sirahata-no-yu	Kusatu	Gumma	0.16	1.55†
408	Umi-zigoku	Kannawa	Oita	0.54	1.6**
124	Yoemon-no-yu	Yunohana-zawa	Kanagawa	0.17	2.3*
	Kōbō-no-yu	"	"	0.19*	2.8*
	Gongen-no-yu	"	"	0.13*	2.9*
405	Sibaseki-Onsen	Kamegawa	Oita	0.00	3.2**
123	Ubako-no-yu	Ubako	Kanagawa	0.05	3.3†
	Huezuka-no-yu	Yunohana-zawa	"	0.00*	3.5*
88	Spring No. 2	Ikao	Gumma	0.00	5.2***
406	Netu-no-yu	Kannawa	Oita	0.00	5.2**
91	Hukiage-no-yu	Ikao	"	0.00	5.4***
87	Nomi-yu	"	"	0.00	5.6***
92	Ōseki-no-yu	"	"	0.00	5.6***
343	Abura-yu	Sigaku	Simane	0.80	5.9
183	Kuridaira No. 1	Masutomi	Yamanasi	0.77	6.0*
342	Moto-yu	Sigaku	Simane	1.02	6.0
345	Radium-Kōsen No. 1	Ikeda	"	36.43	6.0
89	Spring No. 3	Ikao	Gumma	0.06	6.1***
344	Koyabara-Onsen	Koyabara	Simane	6.15	6.1
90	Ohaguro-no-yu	Ikao	Gumma	0.09	6.2***
175	Wadegawara No. 2	Masutomi	Yamanasi	11.62	6.2*
316	Kōyōen-no-yu	Misasa	Tottori	16.06	6.2
346	Radium-Kōsen No. 2	Ikeda	Simane	19.46	6.2
348	Yugakai-Onsen No. 2	Yugakai	"	30.57	6.2
349	" No. 3	"	"	13.45	6.2
179	Higasiobi-no-izumi	Masutomi	Yamanasi	35.65	6.3*

† Numbers correspond to those used in Table 3.

‡ Determined by the Imperial Hygienic Laboratory of Tokyo.

* Determined by Kuroda.

** Determined by the Beppu Geophysics Research Laboratory.

*** Determined by Hattori.

Table 21. — (Continued)

No.†	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	pH
194	Totikubo No. 1	Masutomi	Yamanasi	32.62	6.3*
195	Kinsentō	"	"	29.30	6.3*
313	Tennen-gankutu-no-yu No. 2	Misasa	Tottori	7.11	6.3
317	Sinsen-ryō-no-yu	"	"	2.12	6.3
169	Osiba	Masutomi	Yamanasi	2.68	6.4*
185	Kuridaira-tennenburo	"	"	26.05	6.4*
188	Tuganerō No. 1	"	"	64.53	6.4*
189	" No. 2	"	"	29.39	6.4*
208	Wada-matuba-Kōsen	"	"	82.66	6.4*
312	Tennen-gankutu-no-yu	Misasa	Tottori	10.06	6.4
318	Misasa-kwan-no-yu	"	"	15.01	6.4
347	Yugakai-Onsen No. 1	Yugakai	Simane	35.06	6.4
170	Ginsentō-huru-yu	Masutomi	Yamanasi	9.39	6.5*
171	Ginsentō-kami-no-yu	"	"	7.35	6.5*
174	Wadegawara No. 1	"	"	6.76	6.5*
311	Onsen-hotel-no-yu	Misasa	Tottori	13.48	6.5
314	Ōhasi-ryokwan-soto-yu	"	"	15.95	6.6
315	Yamadaku-no-yu	"	"	3.65	6.6
172	Ginsentō-naka-no-yu	Masutomi	Yamanasi	0.43	6.7*
289	Private bath (M. Yamamoto)	Misasa	Tottori	0.25	6.7
291	Hanaya-no-yu	"	"	0.85	6.8
292	Nakaya-no-yu	"	"	0.90	6.8
298	Ryōyōzyo-gensen	"	"	2.89	6.8
299	Iwa-yu (Otoko-yu)	"	"	2.95	6.8
304	Aburaya-soto-yu	"	"	0.21	6.8
307	Haikyū-zyo-no-yu	"	"	2.32	6.8
319	Okayamaidai-ryōyōzyo- no-yu	"	"	17.67	6.8
287	Kabu-yu	"	"	1.14	6.9
288	Otyaya-no-yu	"	"	0.28	6.9
294	Hasizuya-no-yu	"	"	1.00	6.9
300	Iwa-yu (Onna-yu)	"	"	3.61	6.9
301	Iwa-yu (Makura-yu)	"	"	2.90	6.9
303	Aburaya-uti-yu	"	"	0.89	6.9
134	Netu-no-yu	Matunoyama	Niigata	6.43	7.0*
290	Naka-no-yu	Misasa	Tottori	0.35	7.0
293	Bun-aburaya-no-yu	"	"	2.24	7.0
297	Akazakiya-no-yu	"	"	5.25	7.0
306	Kiya-kazoku-yu	"	"	3.72	7.0
308	Seitō-kwan-no-yu	"	"	0.14	7.0
104	Spring No. 1	Minakami	Gumma	0.09	7.05†

Table 21.—(Continued)

No.†	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	pH
135	Hii-no-yu	Matunoyama	Niigata	6.49	7.1*
233	Private bath (Wakatuki)	Itō	Sizuoka	0.25	7.1*
286	Nakataya-no-yu	Katimi	Tottori	0.73	7.1
302	Eirakuan-no-yu	Misasa	„	0.37	7.1
309	Iwasaki-no-yu No. 1	„	„	0.37	7.1
21	Hanamaki-Onsen	Hanamaki	Iwate	0.00	7.15‡
137	Usagiguti-Onsen	Matunoyama	Niigata	6.17	7.2*
136	Kagami-no-yu	„	„	14.30	7.2*
295	Yakusidō-no-yu	Misasa	Tottori	3.82	7.2
305	Iwasaki-no-yu No. 2	„	„	2.81	7.2
310	Bansuirō-no-yu	„	„	0.26	7.2
277	Iwai-Onsen	Iwai	„	0.56	7.25***
222	Private bath (K. Iizima)	Itō	Sizuoka	0.27	7.3*
281	Tabakoya-no-yu	Hamamura	Tottori	2.40	7.3
284	Seirei-no-yu	Katimi	„	0.23	7.3
224	Private bath (S. Naruto)	Itō	Sizuoka	0.14	7.4*
227	Arai-kwan-no-yu	„	„	0.26	7.4*
264	Reimei-no-yu	Yuzaki	Wakayama	8.44	7.4*
285	Sagi-no-yu	Katimi	Tottori	1.93	7.4
320	Gunzihogoin-ryōyōzyo- no-yu	Misasa	„	0.64	7.4
321	Kabu-yu	Sekigane	„	0.11	7.4
324	Turu-no-yu	„	„	0.13	7.4
397	Kwankaizi-Onsen	Kwankaizi	Ōita	0.00	7.4**
279	Simo-no-yu	Yosioka	Tottori	0.61	7.45***
129	Monkawa-Onsen	Monkawa	Kanagawa	0.41	7.5‡
220	Masuya-ryokwan-no-yu	Itō	Sizuoka	0.51	7.5*
221	Daitō-kwan-no-yu	„	„	0.17	7.5*
223	Hōsen-kwan-no-yu	„	„	0.39	7.5*
226	Enpanrō-no-yu	„	„	0.09	7.5*
296	Saiki-honkwan-no-yu	Misasa	Tottori	2.37	7.5
322	Kami-no-yu	Sekigane	„	0.13	7.5
323	Kame-no-yu	„	„	0.14	7.5
326	Tama-no-yu	„	„	0.10	7.5
107	Yubiso-no-yu No. 1	Yubiso	Gumma	0.00	7.5‡
105	Spring No. 2	Minakami	„	0.49	7.6‡
138	Tamago-no-yu	Matunoyama	Niigata	0.29	7.6*
232	Private bath (T. Suzuki)	Itō	Sizuoka	0.28	7.6*
325	Tokiwa-no-yu	Sekigane	Tottori	0.28	7.6
398	Horita-Onsen	Beppu	Ōita	0.09	7.6*
215	Yukawa-no-yu	Itō	Sizuoka	0.16	7.8*
236	Moto-yu	Yosina	„	0.06	7.8‡
229	Tōkai-kwan-no-yu	„	„	0.17	7.9*

Table 21. — (Concluded)

No.†	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	pH
267	Kami-no-yu	Ryūzin	Wakayama	0.57	7.9*
217	Matubara-no-yu	Itō	Sizuoka	0.16	8.0*
218	Tennen-yu (Matubara)	„	„	0.19	8.0*
219	Tōkyō-kwan-no-yu	„	„	0.04	8.0*
225	Tennen-yu (Kusumi)	„	„	0.11	8.0*
228	Yōki-kwan-no-yu	„	„	0.18	8.0*
231	Private bath (M. Aoki)	„	„	0.20	8.0*
234	„ (Toyosima)	„	„	0.08	8.0*
230	„ (K. Satō)	„	„	0.27	8.1*
216	„ (T. Ōkawa)	„	„	0.04	8.2*
108	Yubiso-no-yu No. 2	Yubiso	„	0.30	8.45†
109	Asahi-no-yu	Hōsi	„	0.00	8.45†
260	Kosi-no-yu No. 1	Katuura	Wakayama	0.19	8.6*
259	Kowase-no-yu	„	„	0.06	9.1*
261	Obatakeyama-no-yu	„	„	0.13	9.1*
262	Yukawarō-no-yu	Yukawa	„	0.10	9.2*
266	Sin-tubaki-no-yu	Tubaki	„	0.26	9.2*

Table 22. Chemical reactions of spring waters of high radium content.

No.*	Spring	Location	Prefecture	Radium content g./l. $\times 10^{12}$	Reaction
8	Toyotomi-Onsen	Toyotomi	Hokkaidō	10.10	Very weak alkaline
40	Kamasaki-no-yu	Kamasaki	Miyagi	1.00	„
42	Kimuraya-no-kyū-yu	„	„	3.03	„
43	Kimuraya-no-sin-yu	„	„	2.58	Neutral
77	Iwasakiya-no-yu	Ōsio	Hukusima	3.72	„
102	Alkali-sen	Isobe	Gumma	15.53	Very weak alkaline
147	Gotairan-no-yu	Wakura	Isikawa	6.04	„
160	Yamasio-Kōsen	Kasio	Nagano	18.5	„
276	Kyū-Onsen	Takarazuka	Hyōgo	26.46	Acidic

* Numbers correspond to those used in Table 3.

XII. Radium Content of Brines from Oil Fields. *Brines from oil fields.* The radium content of brines from the oil fields in Akita and Niigata Prefectures and that from the natural gas field with indications of oil, in Tiba Prefecture, is shown in Table 23. The results of chemical

analysis of K. Hosino⁽³⁷⁾ of the Tokyo Imperial Industrial Research Institute are also shown in this table, where the composition is given in molar ratio, taking sodium as 100. The last column shows, for reference, the absolute concentration of the sodium (gram per liter) in each brine.

On the origin of the brine in oil fields, several theories have so far been published by a number of investigators.⁽³⁸⁾ Hunt,⁽³⁹⁾ in 1875, before any other investigator, suggested, from the fact that the brine water from Ontario has an unusually high content of calcium chloride and magnesium chloride, that it comes from ancient sea water that was embedded simultaneously with the formation of the petroleum deposit. In 1905, Lane⁽⁴⁰⁾ extended this idea more generally and published a well-known theory called the connate or fossil water theory, according to which the brine from an oil field is nothing else but the ancient sea water separated from its surroundings at the time of deposition of the sedimentary rocks, and now held fast in deeply buried rocks. On the other hand, the opinions of Washburne⁽⁴¹⁾ and Richardson⁽⁴²⁾ differ somewhat in that their belief is that the salts contained in brine water did not originate from sea water as the forementioned investigators believed, but from some other salts derived from readily soluble basic magmas or salt deposits. These opinions, however, do not seem to be adequate for Japan, where geological conditions differ from those in other countries. It may therefore be mentioned here that the acceptable theories at present are those which are based on sea water as the origin, which, however, differs in the details.

With the assumption that Japanese brine waters have been derived from ancient sea waters, the radium content of these brines is compared with that of sea waters (V. Table 24). As will be seen from Tables 23 and 24, the former is much higher than the latter, some of these brine samples showing an unusually high radium content compared with spring waters. Is it to be considered that it is entirely due to radium dissolved out from contiguous soft rocks?

Comparing now the composition of sea waters and that of Japanese brines, marked similarities are found between them in the ratios of sodium, potassium, calcium and bromine, but much smaller quantities are observed in the magnesium and sulphate and much larger quantities in the iodine in the case of brine. As to the small content of sulphate in the brine from the oil fields, which is true not only for Japan but also for any other countries, many explanations have been offered by investigators, abroad, such as Höfner,⁽⁴³⁾ Rogers,⁽⁴⁴⁾ Palmer,⁽⁴⁵⁾ Mills and

(37) These unpublished data are reported here by permission of Mr. K. Hosino, to whom the author desires to express his sincere thanks for his courtesy.

(38) T. Ishikawa and T. Baba, this Bulletin, **53** (1932), 362.

(39) T. S. Hunt, *Chemical and Geological Essays*, Boston, (1875), 117.

(40) A. C. Lane, *J. Geol.*, **14** (1905), 221; *Geol. Soc. Am. Bull.*, **19** (1908), 501.

(41) C. H. Washburne, *Am. Inst. Eng. Trans.*, **48** (1904), 687.

(42) G. B. Richardson, *Econ. Geol.*, **12** (1917), 37.

(43) H. V. Höfner, *Das Erdöl*, II (1909), 28.

(44) G. S. Rogers, *U. S. Geol. Surv. Bull.*, (1917), 653; *U. S. Geol. Surv., Prof. Paper*, (1919), 117.

(45) C. Palmer, *Econ. Geol.*, (1924), No. 7.

Table 23. Radium content and chemical composition of Japanese brines.

No.	Oil field (Natural gas field)	Prefecture	No. of the petroleum well	Radium content g./l. $\times 10^{12}$	Total solid matter* g./Kg.	Composition of water*								
						Na	K	Ca	Mg	Cl	SO ₄	Br	I	Na g./Kg.
1	Omonogawa	Akita	1	11.05	21.45	100	1.42	0.62	0.26	56.2	0.00	0.11	0.04	12.77
2	„	„	25	7.14	24.87	100	1.33	0.23	0.13	51.0	0.00	0.08	0.04	14.83
3	Araya	„	1	10.02	22.44	100	1.40	0.46	0.65	54.3	0.00	0.08	0.02	13.14
4	Aburaden	„	1	7.02	24.11	100	1.33	0.44	0.71	55.2	0.00	0.09	0.03	14.41
5	Oguni	Niigata	R 32	0.0	14.68	100	0.00	0.29	1.54	77.9	0.02	0.10	0.04	5.51
6	Oguti	„	R 97	0.0	11.11	100	0.00	0.23	1.84	17.9	0.03	0.13	0.03	4.06
7	Ōmo	„	R 4	12.8	29.17	100	1.36	0.16	0.15	105.8	0.00	0.16	0.04	10.46
8	Ōguti	„	C 1	1.10	2.45	100	4.26	5.02	0.83	57.4	0.00	0.09	0.00	1.24
9	Yoita	„		0.04	9.37	100	1.13	0.50	1.98	108.2	0.03	0.27	0.01	3.43
10	Takamati	„	R 36	2.2	15.69	100	0.00	0.54	0.22	85.2	0.02	0.22	0.04	5.75
11	Iriwada	„	R 5	1.5	22.91	100	0.00	3.81	0.56	115.2	0.01	0.21	0.06	7.94
12	Nagamine	„	C 93	0.0	35.19	100	0.00	3.65	6.15	76.8	0.00	0.30	0.06	11.05
13	Okano	„	R 1 (78 m.)	2.47	18.59	100	0.15	10.84	2.42	109.1	0.17	0.43	0.08	5.63
14	„	„	R 1 (108 m.)	2.84	23.35	100	0.00	9.60	4.48	138.8	0.02	0.38	0.10	6.96
15	Ōtaki	Tiba		0.0	12.45	100	1.05	0.63	2.14	72.2	0.03	0.19	5.20	4.48

* Analysed by K. Hosino.

Wells,⁽⁴⁶⁾ and Bastin.⁽⁴⁷⁾ Little attention, however, has hitherto been given to the comparatively small content of mangesium in the brine. Recently, T. Ishikawa and T. Baba,⁽³⁸⁾ after studying the compositions of Japanese brine and that of fish blood, especially from the marked similarity in their ratios of sodium, potassium, magnesium and iodine, suggested that the origin of the brine from oil fields is the body fluids of these fishes whose oils have been known to most plausibly explain the origin of petroleum.

From the high concentration of radium in ocean-bottom sediments, R. D. Evans, A. F. Kip and E. G. Moberg,⁽⁵⁷⁾ after studying the radium content of marine life, concluded that it must be partly due to biochemical processes, namely, that various forms of marine life have radium concentrated in their bodies, die and settle to the bottom.

These two theories contribute vitally important suggestions to the fact that brine waters have comparatively high radium content. At the

Table 24. Radium content of ocean water as reported by various observers.

Author and Date	General Locality	Radium content g./l. $\times 10^{12}$	Author and Date	General Locality	Radium content g./l. $\times 10^{12}$
Eve ⁽⁴⁸⁾ (1907)	N. Atlantic	0.6	Wright, Heise ⁽⁵⁴⁾ (1918)	South China Sea	0.1-0.2
Joly ⁽⁴⁹⁾ (1908)	Ireland	11.2-34.6*	Devaputra, Thompson, Utterback ⁽⁵⁵⁾ (1932)	Pacific Atlantic	3.3-6.9* 38-47*
	Mediterranean	11.5-28.2*	Evans ⁽⁵⁶⁾ (1934)	Pacific Atlantic	0.03
	Arabia	27.8*		Pacific	0.15
Eve ⁽⁵⁰⁾ (1909)	N. Atlantic	0.47-1.50	Evans, Kip, Moberg ⁽⁵⁷⁾ (1937)	Pacific	0.02-0.06
Joly ⁽⁵¹⁾ (1909)	Atlantic	8-17*	Föyu, Karlik, Petterson, Rona ⁽⁵⁸⁾ (1939)	Baltic Sea	0.03-0.2
	Mediterranean	2-14*	S. Göda ⁽⁵⁹⁾ (1939)	Sweden	
	Black Sea	7*		Yellow Sea	0.04-0.15
	Indian Ocean	4-7*		East China Sea	
Satterly ⁽⁵²⁾ (1911)	S.E. England	0.2-1.6		South China Sea	
Lloyd ⁽⁵³⁾ (1915)	Gulf of Mexico	1.7			

* According to Evans,⁽⁵⁷⁾ the high radium concentration of sea water obtained by Joly and Devaputra is owing to experimental errors.

- (46) V. R. Mills and R. C. Wells, U. S. Geol. Surv. Bull., (1919), No. 693.
 (47) E. S. Bastin, *Bull. Am. Assoc. Petr. Geologists*, **10** (1926), No. 12.
 (48) A. S. Eve, *Phil. Mag.*, (6), **13** (1907), 248.
 (49) J. Joly, *Phil. Mag.*, (6), **15** (1908), 385.
 (50) A. S. Eve, *Phil. Mag.*, (6), **18** (1909), 18.
 (51) J. Joly, *Phil. Mag.*, (6), **18** (1909), 396.
 (52) J. Satterly, *Proc. Cambridge Phil. Soc.*, **16** (1910-12), 360.
 (53) S. J. Lloyd, *Am. J. Sci.*, **39** (1915), 580.
 (54) J. R. Wright and G. W. Heise, *Philippine J. Sci.*, **13A** (1918), 49.
 (55) D. Devaputra, T. G. Thompson, C. L. Utterback, *J. conseil intern. exploration mer*, **7** (1932), 358; *C. A.* **29** (1935), 2076.
 (56) R. D. Evans, *Phys. Res.*, **46** (1934), 328.
 (57) R. D. Evans, A. F. Kip and E. G. Moberg, *Am. J. Sci.*, **36** (1938), 241.
 (58) E. Föyu, B. Karlik, H. Petterson and E. Rona, *Nature*, **143** (1939), 276.
 (59) S. Göda, *Bull. Shanghai Natural Sci. Research*, **9** (1939), 111.

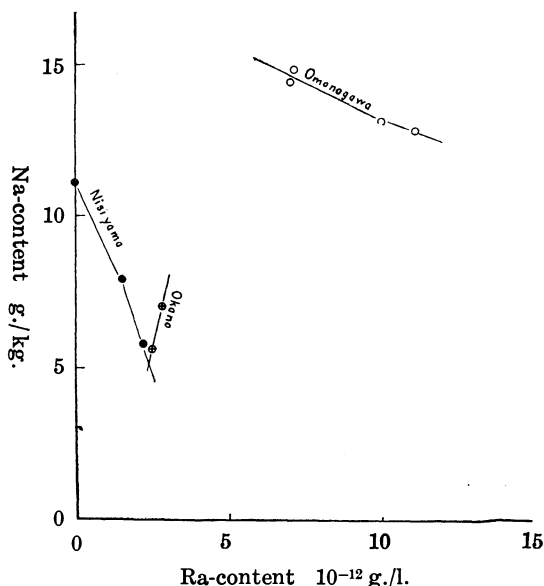


Fig. 23. Relation between the Ra-content and the Na-content of brines.

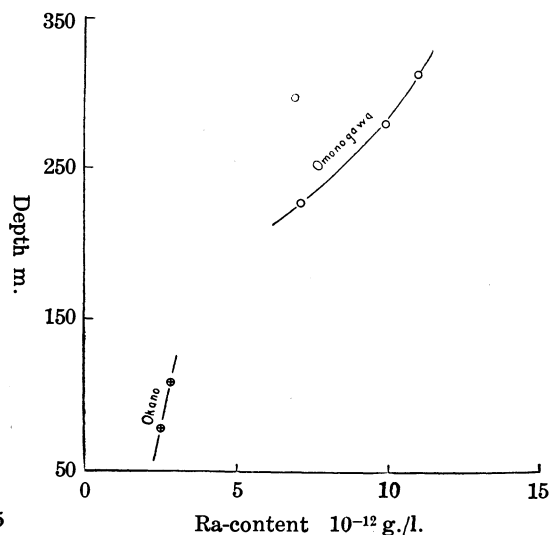


Fig. 24. Relation between the Ra-content of brine waters from the petroleum well and the depth of the well. I.

same time, we may naturally assume that the presence of a certain part of the radium content is due to radium dissolved from contiguous soft rocks.

The radium content of brine waters from oil fields in other countries has been determined by a number of investigators, all of which show high values, especially brines from the oil fields in Caucasus, Russia; that from

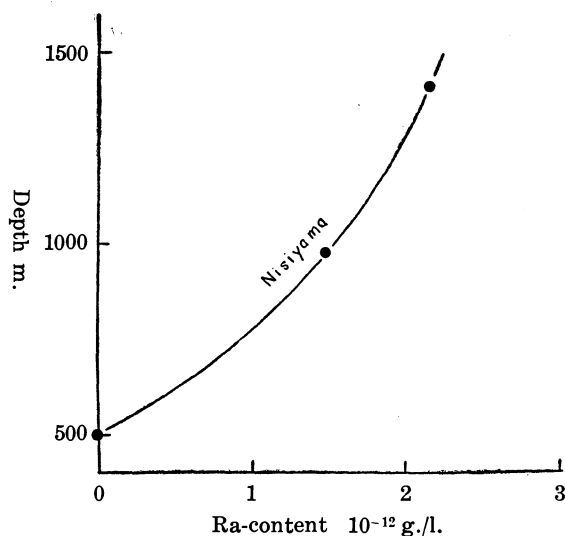


Fig. 25. Relation between the Ra-content of brine waters from the petroleum well and the depth of the well. II.

Tzeliutzing in Szechwan, China, having an extraordinary high content of radium, as described in a previous chapter. Although it is not certain whether the origin of brines from oil fields in other countries is the same as that in Japan, it is an interesting fact in connection with the high radium content of Japanese brines.

S. Gōda,⁽⁶⁾ after studying the radium content as well as the other chemical constituents of brine waters from Tzeliutzing in Szechwan, China, reported that the radium contents of brines decreased with the increase of their sodium contents. We shall now compare the brines from

a number of petroleum wells which are situated close together (V. Table 25). In Fig. 23 their radium content is plotted against their sodium content. As may be seen from this figure, there appears to be a distinct relationship between it and S. Gōda's findings. In Figs. 24 and 25 the correlation between their radium contents and the depths at which the brine samples were drawn is shown. So far as the present results are concerned, there seems to be a linear relation between them also.

Table 25.

No.*	Oil-field •	Petroleum well		Radium content g./l. $\times 10^{12}$	Na g./Kg.
		No.	Depth m.		
I. Omonogawa series (Akita Prefecture)					
1	Omonogawa	1	310	11.05	12.27
2	„	25	226	7.14	14.83
3	Araya	1	278	10.02	13.14
4	Aburaden	1	297	7.02	14.41
II. Nisiyama series (Niigata Prefecture)					
10	Takamati	R 36	1399	2.2	5.75
11	Iriwada	R 5	971	1.5	7.94
12	Nagamine	C 93	502	0.0	11.05
III. Okano series** (Niigata Prefecture)					
13	Okano	R 1	78	2.47	5.63
14	„	„	108	2.84	6.96

* Numbers correspond to those used in Table 23.

** These two brine samples were drawn from different depths of the same well.

Hot springs from oil fields. Hot springs often gush out from oil fields. According to the investigations by Y. Chitani,⁽⁶⁰⁾ the hot springs of Toyotomi in Hokkaidō; Tomine, Asahikawa, Yumoto in Akita Prefecture; Hanezawa, Mogami in Yamagata Prefecture; and Senami, Tukioka and Matunoyama in Niigata Prefecture, belong to this kind of hot springs. Geologically, they usually gush out from a fairly definite stratum (for example the Lower Neogene series), all of which are alkaline common salt springs, their chemical composition being nearly constant.

Of these the hot springs of Toyotomi in Hokkaidō; and Matunoyama and Senami in Niigata Prefecture, have been determined for their radium content, the results of which are given in Table 26. The chemical composition of these spring waters, analysed by the Tokyo Imperial Hygienic Laboratory,⁽³⁴⁾ are also given in this table for reference in the same way as in Table 23.

(60) Y. Chitani, *J. Geography*, **40** (1928), 626, 698; **41** (1929), 45, 141.

Table 26. Radium content and chemical composition of hot springs from oil fields.

No.	Spring	Prefecture	Radium content g./l. $\times 10^{12}$	Total solid matter g./Kg.	Composition of water								
					Na	K	Ca	Mg	Cl	SO ₄	Br	I	Na g./Kg.
1	Toyotomi-Onsen	Hokkaidō	10.10	11.70	100	0.84	1.18	0.75	90.9	0.01	0.05	0.05	4.35
2	Senami-Onsen	Niigata	0.11	4.19	100	3.47	5.71	0.02	103.3	4.97			1.33
3	Matunoyama-Onsen	„	14.30, 7.16, 6.49, 6.43 6.17, 2.62, 0.29										

Table 27. Radium content and chemical composition of mineral waters of the brine type.

No.	Spring	Prefecture	Radium content g./l. $\times 10^{12}$	Total solid matter g./Kg.	Composition of water								
					Na	K	Ca	Mg	Cl	SO ₄	Br	I	Na g./Kg.
1	Kasio-Kōsen	Nagano	18.5	29.45	100	0.83	3.25	0.66	108.9	trace	0.04	trace	10.55
2	Sionoha-Onsen	Nara	5.52										

As will be seen from this table, the hot springs of Toyotomi and Matunoyama have a fairly high radium content. The radium content of the Senami hot springs is very low; according to Chitani,⁽⁶⁰⁾ since a large quantity of sea water is supplied continuously to this spring, the low radium concentration of this spring may be owing to mixing with sea water, which is very poor in radium.

Thus all hot springs from oil fields show comparatively high radium concentration. Although their origins are not yet clearly understood, it is an interesting fact in connection with the high radium content of brine waters from oil fields.

Mineral waters of brine type. According to T. Ishikawa and T. Baba,⁽³⁸⁾ the mineral waters of Kasio in Nagano Prefecture, belong to the mineral waters of brine type. The composition of this water is shown in Table 27 in the same way as before. Though no petroleum has yet been obtained at Kasio, it is on the famous Itoizawa-Sizuoka fault line, along which may exist an extension of the great petroleum zone of northern Japan.

The origin of the mineral waters at Sionoha in Nara Prefecture, is also believed to be connate water, the same as that of the mineral waters at Kasio, although its composition is not yet clearly known.

The radium content of these two mineral waters is shown in Table 27, from which it is also significant that they all show comparatively high radium content, the same as in the brine waters from oil fields.

XIII. Radium Content of Sinter Deposits from Mineral Springs. Some of the mineral springs, especially the earthy carbonioxated ones, produce abundant sinter deposits at the source and on the creek bed on which they flow, as well as in the conduits and at the baths.

On account of the lowering in pressure and temperature of spring water after gushing out from the ground, a part of the calcium bicarbonate that is held in solution loses its carbonic acid and forms a neutral carbonate which settles as a deposit. At the same time other mineral constituents that are dissolved in the spring waters also deposit as the result of physical and chemical reactions.

Since the sinter deposits from mineral springs consist mainly of calcium carbonate, besides calcium sulphate, ferric oxide, manganese dioxide, etc., if the waters contain radium, it should be absorbed by the calcium carbonate, calcium sulphate, ferric oxide and manganese dioxide into the sinter deposits.⁽⁶¹⁾

The sinter deposits from mineral springs rich in radium, such as the Masutomi Mineral Springs in Yamanashi Prefecture, and the Ikeda Mineral Springs and the Yugakai Hot Springs in Simane Prefecture, were tested for radium. The sample from the Ikeda Mineral Springs, which was obtained at the source of Spring No. 1, consists mainly of calcium carbonate, colored brown by ferric hydroxide. That from the Yugakai Hot Springs is a mixture of sinter deposits obtained at the sources of Springs Nos. 1-3. It is also colored brown. These two samples were obtained in August, 1939. The samples from the Masutomi Mineral

(61) Refer to next chapter.

Springs are called "radium-fossil", which were deposited from mineral waters by the same mechanism as just mentioned, increasing gradually in size and compactness during a long interval of time. They also consist mainly of calcium carbonate, being colored a light yellow by ferric hydroxide. The samples were drawn in October, 1936.

The results of these determinations are given in Table 28. As might be expected, they all show an extraordinary high radium content, the sinter deposits obtained at the source of the springs being especially rich in radium.

Table 28. Radium content of sinter deposits from mineral springs.

Spring	Location	Radium content of water g./l. $\times 10^{12}$	Radium content of deposit g./g. $\times 10^{12}$
Radium Kōsen No. 1	Ikeda	36.43	872
Yugakai Onsen No. 1	Yugakai	35.06	202
„ No. 2		30.57	
„ No. 3		13.45	
Tuganerō-simo-no-yu	Masutomi	25.05	175
Higasiobi-no-izumi	„	35.65	19.2
Siokawara	„		18.4
Ginsentō-huru-yu	„	9.39	9.6
Kuridaira No. 3 (Kozizimeki)	„	6.56	8.8

XIV. Extraction of Radium from Mineral Waters. The extraction of radium from mineral waters containing radium was studied for the following purposes: first, to investigate a technique for separating radium from natural waters containing large amounts of it, without the necessity of using a large quantity of reagents, and, secondly, from the geochemical point of view, in order to make clear the process of migration and concentration of radium by natural waters.

For the purpose of this experiment the following method was adopted:

First, as "a carrier of radium", solutions of various metallic salts were added to the water sample. Then by adding suitable precipitants into this solution, these metals were precipitated from them, when the radium in the solution is separated from them, being precipitated with or adsorbed by these precipitates, and concentrated in them.

As "a carrier of radium" for adding to the water sample, such metals as manganese, iron, barium, calcium and strontium were used for the following reasons: first, the radium content of the sediments from the spring waters or that of the ocean-bottom sediments are closely related to the amount of manganese or iron in them; second, since metallic radium belongs to the group of alkali-earths, its salts closely resemble those of barium. Besides these metals, aluminium, chromium, copper, zinc and bismuth were also used in this experiment.

Methods. As water samples for these experiments, the mineral waters from the spring of Arima Hon-Onsen, containing 71.29×10^{-12} g. Ra/l., that of Wadamatuba-Kōsen at Masutomi, containing 82.66×10^{-12} g. Ra/l. and that of Tuganerō-no-yu No. 1 at Masutomi, containing 64.53×10^{-12} g. Ra/l. were used. We also used waters of much higher radium content made by concentrating these spring waters.

Since the sediments in mineral waters contain fairly large quantities of radium, these sediments were dissolved by adding a few c.c. of hydrochloric acid to the water. As the sediments consist mainly of calcium carbonate, they are dissolved almost completely with hydrochloric acid. The insoluble residue is then filtered off and the filtrate thus obtained used as standard solution.

To 500 c.c. of this solution is added a solution of salts of such metals⁽⁶²⁾ as manganese, iron, barium, calcium, strontium, aluminium, chromium, copper, zinc and bismuth, and these metallic salts are precipitated from the water by the methods shown below. The precipitates thus obtained are filtered off and dissolved by the methods shown below.

Methods of experiment. 1) MnO_2 : A solution of manganese chloride is added to the standard solution. By treating it with sodium hydroxide and hydrogen peroxide, manganese is precipitated as manganous acid. The precipitate is filtered off and dissolved in hydrochloric acid.

2) MnS : A solution of manganese chloride is added to the standard solution. After adding ammonium chloride and ammonia, the solution is boiled, after which hydrogen sulphide is passed through it. The precipitate of manganous sulphide is filtered off and dissolved in hydrochloric acid.

3) $\text{Fe}(\text{OH})_3$: A solution of ferric oxide is added to the standard solution. By adding ammonium chloride and ammonia, iron is precipitated as its hydroxide. The precipitate is filtered off and dissolved in hydrochloric acid.

4) $\text{Al}(\text{OH})_3$, 5) $\text{Cr}(\text{OH})_3$, 6) $\text{Bi}(\text{OH})_3$: Solutions of aluminium sulphate, chromium sulphate and bismuth nitrate are in turn added to the standard solution. Aluminium, chromium and bismuth are precipitated as their hydroxides. The precipitates are filtered off and dissolved in hydrochloric acid.

7) BaSO_4 , 8) SrSO_4 : After adding a few c.c. of sulphuric acid, solutions of barium chloride and strontium chloride are added in turn to the standard solution. The precipitates of barium sulphate and chromium sulphate are filtered off, ignited and fused with a carbonate mixture. (a) The fused mass is leached with distilled water to dissolve the sodium sulphate. (b) The insoluble residues of barium carbonate and strontium carbonate are dissolved in hydrochloric acid.

9) BaCO_3 : Barium chloride solution is added to the standard solution, and the latter heated to boiling. After rendering it alkaline with ammonia, a solution of ammonium carbonate is added slowly. The precipitate of barium carbonate is filtered off and dissolved in hydrochloric acid.

The mineral waters of Tuganerō-no-yu, however, hold a fairly large concentration of sulphate ions, so that when it is used as standard solution, barium sulphate is precipitated by addition of barium chloride. Ammonium carbonate is added to this solution, when the barium ion remaining in solution is precipitated as barium carbonate. The precipitate is filtered and (a) barium carbonate is dissolved in hydrochloric acid, (b) the insoluble residue of barium sulphate being dissolved by the same treatment as in (7).

10) CaCO_3 , 11) SrCO_3 : Solutions of calcium chloride and strontium chloride are added to the standard solution and calcium carbonate and strontium carbonate precipitated by the same treatment as in (9), and then filtered off and dissolved in hydrochloric acid.

12) CuS : A solution of cupric chloride is added to the standard solution.

(62) These reagents were ascertained by blank tests to contain no radium.

After making the solution acidic with hydrochloric acid, hydrogen sulphide is passed through it and cupric sulphide is precipitated, which is filtered off and dissolved in aqua regia.

13) ZnS : A solution of zinc chloride is added to the standard solution. After rendering the solution alkaline with ammonia, hydrogen sulphide is passed through it and zinc sulphide is precipitated, which is filtered off and dissolved in hydrochloric acid.

14) Fe(OH)_3 , etc. in standard solution: By adding ammonium chloride and ammonia to the standard solution (the mineral waters of Arima Hon-Onsen), the iron, aluminium, etc. present in them are precipitated as mixtures of their hydroxides, which are filtered off and dissolved in hydrochloric acid.

The resulting solution, containing all the radium adsorbed by the precipitate, is put into a curie bottle and sealed. The radium content of this solution is determined by the method described in the previous section. By comparing this result with that of the standard solution, it is possible to calculate the proportion of radium in the standard solution that has been separated from it with the precipitate.

At first, 1 g. of each metallic salt (weight of cation) was added to the standard solution as the radium carrier, while for such metals as manganese, iron, barium, calcium and strontium, which adsorb especially large quantities of radium, the amounts of these metallic salts to be added to the solution were varied from 0.01 g. to 1 g. (weight of cation).

Results. The results of the experiments when 1 g. (weight of cation) of each metallic salt has been added in the standard solution as "radium carrier" are shown in Table 29. When iron, aluminium, chromium, bismuth or manganese are precipitated from the standard solution as their hydroxides, a small quantity of iron, aluminium, etc. that are held in the standard solution are also precipitated with them, whence it is presumed that the results include the amount of radium precipitated along with the precipitates of iron, aluminium, etc. from the standard solution.

For such metals as manganese, iron, calcium, strontium and barium, which show results of 100% or nearly so in Table 29, the quantities of these metallic salts to be added to the standard solution were varied from 0.01 g. to 1 g. (weight of cation). The results are given in Table 30.

Finally it would be interesting to know whether or not the result when the precipitate of iron is added to that of manganese or calcium is the sum of the two results. The results of this experiment are shown in Table 31.

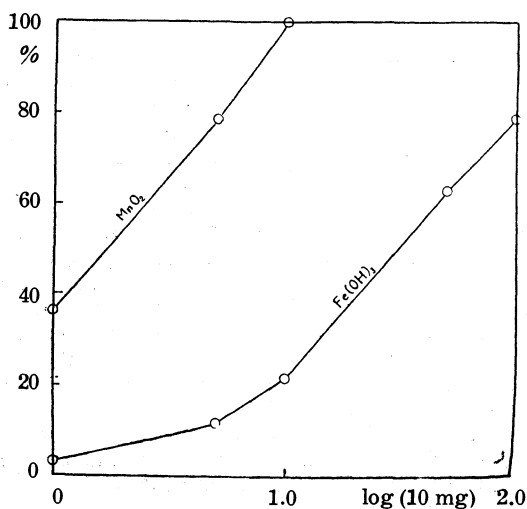


Fig. 26. Relation between the quantity of the radium carrier and the percentage of radium adsorbed from the water.

Discussions. 1) As will be seen from Table 30, the quantity of radium that is extracted from the solutions seems to increase with increase in the quantity of the precipitate caused by the carrier. If, in order to ascertain more exactly the relation between these two quantities, the points are plotted on a diagram with the logarithm of the quantity of the radium carrier to be added as abscissae and the percentage of radium adsorbed from the water as ordinates, we obtain Fig. 26, in which the points lie fairly close to that of a straight line.

2) As seen in Table 29 and Table 30, the best results were obtained when sulphates and carbonates of barium, calcium and strontium were used as carrier.

It is generally considered that radioactive cations are adsorbed by precipitates containing anions that form insoluble compounds with the former, and that when both these compounds containing the same anion

Table 29.

Carrier	Standard solution	Quantity of radium in standard solution 10^{-12} g.	Quantity of radium in precipitate 10^{-12} g.	Per cent of radium adsorbed from the water %
1) MnO_2	B_2	76.2	76.2	100.0
2) MnS	B_2	76.2	0.0	0.0
3) $\text{Fe}(\text{OH})_3$	B_1	44.7	35.2	78.7
4) $\text{Al}(\text{OH})_3$	B_2	76.2	7.2	9.5
5) $\text{Cr}(\text{OH})_3$	B_2	76.2	52.5	68.9
6) $\text{Bi}(\text{OH})_3$	B_2	76.2	3.4	4.5
7) BaSO_4				93.7
(a) Na_2SO_4	A	35.0	0.0	{ 0.0
(b) BaCO_3	A	35.0	32.8	
8) SrSO_4				92.0
(a) Na_2SO_4	A	35.0	0.0	{ 0.0
(b) SrCO_3	A	35.0	32.2	
9) BaCO_3	B_2	76.2	76.2	100.0
10) CaCO_3	B_2	76.2	76.2	100.0
11) SrCO_3	B_2	76.2	76.2	100.0
12) CuS	A	35.0	4.9	14.0
13) ZnS	A	35.0	23.8	68.0
14) $\text{Fe}(\text{OH})_3$ etc. in standard solution (Arima Hon-Onsen)	A	35.0	1.8	5.1
Standard solution :				
A 35.0×10^{-12} g. Ra/500 c.c.		Arima Hon-Onsen		
B_1 44.7×10^{-12} g. Ra/500 c.c.		Wadamatuba-Kōsen (concentrated)		
B_2 76.2×10^{-12} g. Ra/500 c.c.		,, (concentrated)		
C 42.2×10^{-12} g. Ra/500 c.c.		Tuganerō-no-yu No. 1 (concentrated)		

Table 30.

Quantity of radium carrier (weight of cation)	Standard solution	Quantity of radium in standard solution 10^{-12} g.	Quantity of radium in precipitate 10^{-12} g.	Per cent of radium adsorbed from the water %
I. MnO_2				
1) 0.01 g.	B_2	76.2	27.6	36.2
2) 0.05 g.	B_2	76.2	59.9	78.6
3) 0.10 g.	B_2	76.2	76.0	$99.7 \div 100$
4) 0.50 g.	B_2	76.2	76.2	100.0
5) 1.00 g.	B_2	76.2	76.2	100.0
II. $\text{Fe}(\text{OH})_3$				
1) 0.01 g.	B_1	44.7	1.5	3.4
2) 0.05 g.	B_1	44.7	5.1	11.4
3) 0.10 g.	B_1	44.7	9.5	21.3
4) 0.50 g.	B_1	44.7	28.0	62.6
5) 1.00 g.	B_1	44.7	35.2	78.7
III. CaCO_3				
1) 0.01 g.	C	42.2	37.6	89.1
2) 0.05 g.	C	42.2	38.6	91.5
3) 0.10 g.	C	42.2	39.4	93.4
4) 0.50 g.	C	42.2	42.2	100.0
5) 1.00 g.	C	42.2	42.2	100.0
IV. SrCO_3				
1) 0.01 g.	C	42.2	37.6	89.1
2) 0.05 g.	C	42.2	41.2	97.6
3) 0.10 g.	C	42.2	41.2	97.6
4) 0.50 g.	C	42.2	42.2	100.0
5) 1.00 g.	C	42.2	42.2	100.0
V. BaCO_3				
1) 0.01 g.				91.5
(a) CO_3''	C	42.2	38.6	{ 91.5
(b) SO_4''				{ none
2) 0.05 g.				96.2
(a) CO_3''	C	42.2	4.6	{ 10.9
(b) SO_4''	C	42.2	36.0	{ 85.3
3) 0.10 g.				$100.5 \div 100$
(a) CO_3''	C	42.2	1.6	{ 3.8
(b) SO_4''	C	42.2	40.8	{ 96.7
4) 0.50 g.				$100.9 \div 100$
(a) CO_3''	C	42.2	3.6	{ 8.5
(b) SO_4''	C	42.2	39.0	{ 92.4
5) 1.00 g.				$99.5 \div 100$
(a) CO_3''	C	42.2	18.4	{ 43.6
(b) SO_4''	C	42.2	23.6	{ 55.9

Table 31.

Quantity of radium carrier (weight of cation)	Standard solution	Quantity of radium in standard solution 10^{-12} g.	Quantity of radium in precipitate 10^{-12} g.	Per cent of radium adsorbed from the water	
				Observed %	Calculated %
I. $\text{MnO}_2 + \text{Fe}(\text{OH})_3$					
1. Mn 0.01 g. + Fe 0.1 g.	B ₁	44.7	36.1	80.8	36.2 + 21.3 = 57.5
2. Mn 0.01 g. + Fe 0.05 g.	C	42.2	28.2	66.8	36.2 + 11.4 = 47.6
II. $\text{CaCO}_3 + \text{Fe}(\text{OH})_3$					
Ca 0.01 g. + Fe 0.01 g.	C	42.2	42.2	100.0	89.1 + 3.4 = 92.5

* Calculated from the results in Table 30.

are isomorphous, their coprecipitating reactions are promoted. The present results support well this conclusion.

It is also well known that the method of coprecipitating radium by barium sulphate has been used from olden times when radium was extracted from uranium minerals, such as pitchblende and carnotite.

3) From the geochemical point of view, it is noteworthy that the quantity of radium precipitated along with (perhaps adsorbed by) the precipitate of manganese and iron is very large.

I. D. Kurbatov,⁽²⁾ after studying the sediments deposited from spring waters at Pyatigorsk, Russia, reported that the quantity of radium in a deposit depends not upon the sulphate ions contained in the sediment, but on the quantity of ferric and manganese oxides in it. These sediments, which consist mainly of calcium carbonate, are colored a light yellow to brown by ferric hydroxide according to the amount of ferric hydroxide present. The quantity of radium in the deposit depends upon the amount of ferric oxide, as shown by the following data (Table 32) given in terms of gram per 100 g. of sediment.

Table 32.

	Deposit 1.	Deposit 2.	Deposit 3.	Deposit 4.
Ra	3×10^{-10} g.	10×10^{-10} g.	59×10^{-10} g.	111×10^{-10} g.
Fe_2O_3	0.05	0.18	1.07	1.83

The present results given in Tables 29–31, agree well with these facts. The results in Table 31 show that when the precipitate of iron is added to that of calcium carbonate and manganese dioxide, the quantity of radium adsorbed by these precipitates increases remarkably.

As to the relation between radium and manganese or iron in the ocean-bottom sediments, C. S. Piggot⁽⁶³⁾ reported that the oceanic manganese concretions show an extraordinary high radium content. L. M.

Kurbatov⁽⁶⁴⁾ also found two manganese concretions from the Pacific Ocean containing a marked high radium content of 1.47 and 0.48×10^{-10} g. per g. More recently, H. Hamaguti⁽⁶⁵⁾ upon determining the radium, manganese and iron contents of deep-sea deposits from the Pacific Ocean, reported that the radium content increases with increasing manganese or iron content, which facts may be explained by the mechanism just mentioned.

4) From the present experiments, it has become possible to separate radium from natural waters without the necessity of using a large quantity of reagents. If, therefore, a mineral spring containing a sufficiently large quantity of radium is found in a country poor in radium ores as in Japan, it may be possible to extract it profitably. Much to our regret, however, so far as the present results are concerned, the natural waters in Japan are also poor in radium, so that for the present, we shall have to leave this problem merely as a suggestion, and wait until a natural water with sufficient radium concentration can be found.

In conclusion, the writer wishes to express his hearty thanks to Professor K. Kimura of the Tokyo Imperial University for kind advices and suggestions received during the course of this work, and also to Dr. F. Kodera, Director of the Tokyo Imperial Industrial Research Institute and Mr. T. Nishimura, Chief of the first department of the Institute, for their kind guidance and for permission to publish this report. He is also indebted to Mr. K. Yamasaki and Mr. K. Kuroda of the Tokyo Imperial University, Mr. K. Hosino and Mr. Y. Nemoto of the Tokyo Imperial Industrial Research Institute, and to the Hot Spring Society of Japan for their wholehearted assistance in collecting the water samples used in this study. A part of the cost of this investigation was defrayed from grants given to Prof. K. Kimura by the Nippon Gakusyutu Sinkōkwai (the Japan Society for the Promotion of Scientific Research) and by the Hattori Hōkōkwai Foundation to which also the writer wishes to record his thanks.

*Tokyo Imperial Industrial Research Institute,
Shibuyaku, Tokyo.*

(63) C. S. Piggot, *Am. J. Sci.*, **25** (1933), 229.

(64) L. M. Kurbatov, *Am. J. Sci.*, **33** (1937), 147.

(65) H. Hamaguti, *J. Chem. Soc. Japan*, **59** (1938), 171, 675; **61** (1940), 67.

Absorption Spectra of Co-ordination Compounds. IV. Ethylenediamine Cobaltic Complexes.

By Hisao KUROYA and Ryutaro TSUCHIDA.

(Received September 12, 1940.)

Introduction. I. On Absorption Bands: In the previous papers,⁽¹⁾⁽²⁾⁽³⁾ one of the authors discussed on the origins of the selective absorption bands, which complex salts show in the near infra-red, the visible and the near ultra-violet regions of the spectrum, concluding as follows:

(a) The first absorption band: This may be attributed to electron transitions in an unsaturated transition shell of the central ion. Accordingly, if the central ion belongs to a group of typical elements, this band does not appear, because such an ion has no unsaturated transition shell. Again we should not expect this band, when the central ion, even if this belongs to a group of transition elements, has an electronic configuration of the pseudo-inert-gas or inert-gas type. An example for the former case is potassium mercuric iodide, $K_2[HgI_4]$ ⁽⁴⁾, and one for the latter potassium chromate, $K_2[CrO_4]$ ⁽⁵⁾.

The first absorption bands are found almost always in the visible region. Luther and others⁽⁵⁾ discussed on the relation between the stability and the colour of complex salts. We can not determine, however, the stability of complex salt by its colour or by the position of its first absorption band, the band owing its origin to electrons of the central ion alone and not to co-ordination electrons combining the central atom to the ligands.

(b) The second absorption band: This may be explained as due to a kind of incomplete dissociation of the complex radical by irradiation. Showing the excited states of the co-ordination electrons, therefore, this band may be considered as giving the measure of stability of complex salts or co-ordination compounds in a wider sense.

(c) The third absorption band: This appears, when (i) a pair or pairs of negative ligands are situated in trans-positions to each other in octahedral or square complex radicals, e.g., $[Co(NH_3)_4Cl_2]^{(1)}+$ ⁽⁶⁾ and $[Co(NH_3)_4(NO_2)_2]^{(1)+}$ ⁽⁷⁾ or $[Ni(CN)_4]^{--}$ ⁽⁸⁾, and (ii) two or more negative ligands are co-ordinated around the central ion in tetrahedral complex radicals such as chromate ion, CrO_4^{--} ⁽⁹⁾.

(1) R. Tsuchida, this Bulletin, **13** (1938), 388.

(2) R. Tsuchida, *ibid.*, **13** (1938), 436.

(3) R. Tsuchida, *ibid.*, **13** (1938), 471.

(4) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 733; S. Kashimoto, R. Tsuchida, *ibid.*, **60** (1939), 347.

(5) R. Luther, A. Nikolopoulos, *Z. physik. Chem.*, **82** (1913), 361.

(6) R. Tsuchida, this Bulletin, **11** (1936), 721.

(7) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

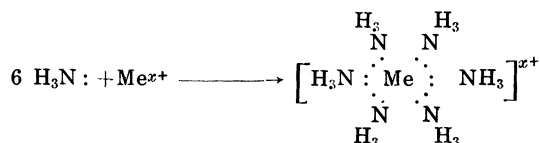
(8) H. Kuroya, R. Tsuchida, *ibid.*, **61** (1940), 597.

(d) The special absorption band: This band found in special cases is due to absorption band proper to the ligand itself⁽³⁾, or to a new strongly absorbing centre⁽²⁾ which has been formed by co-ordination of the particular ligand.

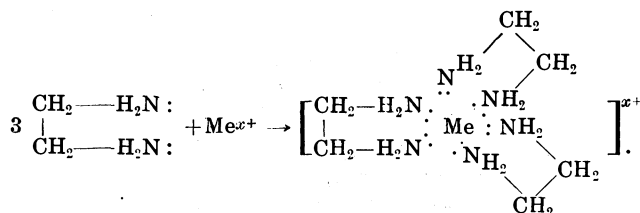
These conclusions have been reached by one of the authors after a series of experimental works and the results have been carefully developed to explain absorption spectra of various compounds, inorganic and organic.

II. On Ethylenediamine Complex Salts: It is a well-known fact that the complex salt of ethylenediamine, which can be regarded as a substitution product of the corresponding ammine complex, is much more stable than the ammine salt, although their colours are similar to each other. For example, praseo-cobalti-salt $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{(3)}\text{X}$ is decomposed faster in aqueous solutions than the corresponding ethylenediamine salt $[\text{Co en}_2\text{Cl}_2]^{(3)}\text{X}$. Of the two possible isomers of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{X}_3$ only cis-diaquo-salt is known, whereas in the more stable diaquo-ethylenediamine-compounds both the cis- and the trans-forms have been obtained.

Ammonia forms ammine complexes, being co-ordinated around the central atoms by its lone pair of electrons, and such an interpretation can be adopted also for the formation of ethylenediamine complexes: thus



and



The similarity between properties of ammine salts and those of the corresponding ethylenediamine complexes may thus be understood.

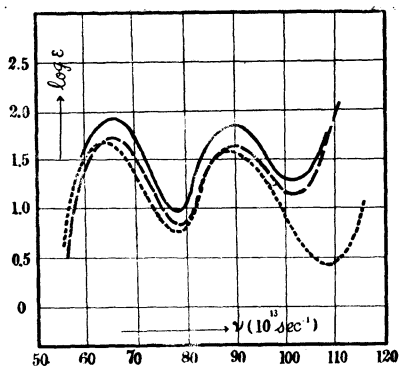
According to the postulates proposed by the authors, however, we can expect a shift of the second absorption band of ethylenediamine complex towards the more spectrally stable direction, or in other words, the shorter wave-lengths, compared with the less stable ammine salt.

For the purpose of confirming this point of view, the authors have prepared fourteen ethylenediamine complex salts and investigated their absorption spectra, comparing them with those of the corresponding ammine salts, which had been measured in this laboratory. In this paper the results of these experiments are dealt with, and the bearings of the observations on the problem of configuration or chemical combination will be discussed.

Experimental Results and Discussions. The experimental results are summarized in Table 1, while the absorption curves thus obtained are shown in Fig. 1-12 together with those of the corresponding ammine complexes for the purpose of comparison.

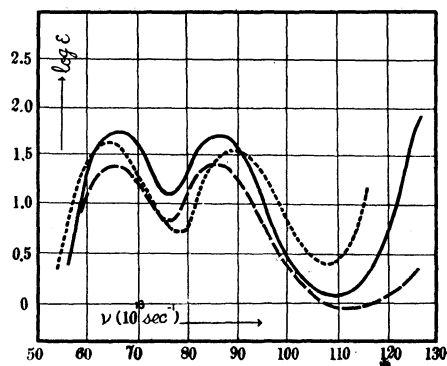
Table 1.

Complex salt	First band		Second band		Third band		Special band	
	$\nu_1(10^{13})$	$\log \epsilon$	$\nu_2(10^{13})$	$\log \epsilon$	$\nu_3(10^{13})$	$\log \epsilon$	$\nu_s(10^{13})$	$\log \epsilon$
$[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$	63.2	1.66	88.8	1.58				
$[\text{Co en}_2 (\text{NH}_3)_2 \text{Cl}] \text{Br}_3$	64.8	1.72	89.2	1.62				
$[\text{Co en}_3] \text{Br}_3$	64.6	1.88	89.2	1.81				
$[\text{Cr}(\text{NH}_3)_6] \text{Cl}_3$	65.0	1.44	85.4	1.45				
$[\text{Cr en}_3] \text{Cl}_3$	66.0	1.78	85.6	1.75				
$[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$	58.0	1.65	83.1	1.66				
$[\text{Co en}_2 \text{NH}_3 \text{Cl}] \text{Cl}_2$	58.0	1.76	83.0	1.76				
$[\text{Co py}_4 \text{NH}_3 \text{Cl}] \text{Cl}_2$	56.8	1.95	82.6	1.93				
$[\text{Co}(\text{NH}_3)_4 (\text{NO}_2)_2 \text{Cl}] \text{Cl}$	67.9	2.32	87.0	3.54	119.6	4.08	?	?
$[\text{Co en}_2 (\text{NO}_2)_2 \text{Cl}] \text{NO}_3$	69.9	2.20	88.6	3.44	120.4	4.37	?	?
$[\text{Co}(\text{NH}_3)_4 (\text{NO}_2)_2 \text{Cl}] \text{Cl}$	65.5	1.99	91.2	3.10			?	?
$[\text{Co en}_2 (\text{NO}_2)_2 \text{Cl}] \text{NO}_3$	69.0	2.10	92.8	3.68			?	?
$[\text{Co}(\text{NH}_3)_4 \text{Cl} \cdot \text{NO}_2] \text{Cl}$	63.2	1.87	88.8	3.13	123.0	4.07	(80.4)	(2.42)
$[\text{Co en}_2 \text{Cl} \cdot \text{NO}_2] \text{Cl}$	68.8	2.00	89.6	3.37	124.2	4.35	(79.6)	(2.22)
$[\text{Co en}_2 \text{Cl} \cdot \text{NCS}] \text{Cl}$	59.6	2.18	(88.4)	(2.75)			?	?
$[\text{Co en}_2 \text{Cl} \cdot \text{NCS}] \text{Br}$	54.0	2.10	(86.8)	(2.93)	110.4	3.43	92.5	3.36
$[\text{Co en}_2 \text{NO}_2 \cdot \text{NCS}] \text{Cl}$	64.8	2.34	?	?			?	?
$[\text{Co en}_2 \text{NO}_2 \cdot \text{NCS}] \text{NCS}$	65.3	2.30	?	?	?	?	?	?
$[\text{Co}(\text{NH}_3)_4 \text{CO}_3] \text{Cl}$	57.4	2.03	82.8	2.02				
$[\text{Co en}_2 \text{CO}_3] \text{Cl}$	58.6	2.08	83.6	2.04				
$[\text{Co}(\text{NH}_3)_4 \text{C}_2\text{O}_4] \text{Cl}$	59.0	1.78	83.4	1.78				
$[\text{Co en}_2 \text{C}_2\text{O}_4] \text{Br}$	60.0	1.96	84.2	2.10				
$[\text{Co} \{ \text{OH} \rangle \text{Co}(\text{NH}_3)_4 \}_3] \text{Cl}_6$	60.8	2.28	?	?			99.2	3.84
$[\text{Co} \{ \text{OH} \rangle \text{Co en}_2 \}_3] (\text{NO}_3)_6$	61.2	2.44	?	?			99.0	3.82
$[(\text{NH}_3)_4 \text{Co} \{ \text{OH} \rangle \text{Co}(\text{NH}_3)_4] \text{Cl}_4$	57.0	2.28	79.2	2.40			107.4	3.34
$\alpha\text{-}[\text{Co}(\text{glycine})_3]$	56.8	1.98	81.0	2.16				



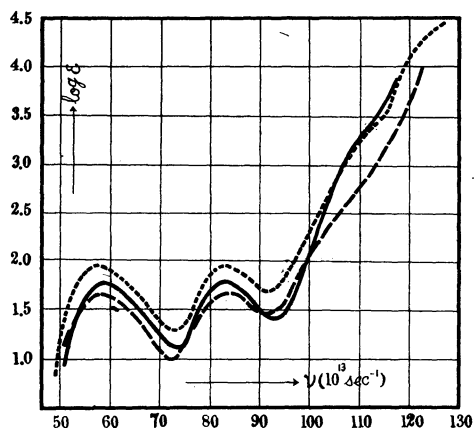
- (1) ——— $[\text{Co en}_3]\text{Br}_3$
 (2) - - - $[\text{Co en}_2(\text{NH}_3)_2\text{Cl}_6]\text{Br}_3$
 (3) - · - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Fig. 1.



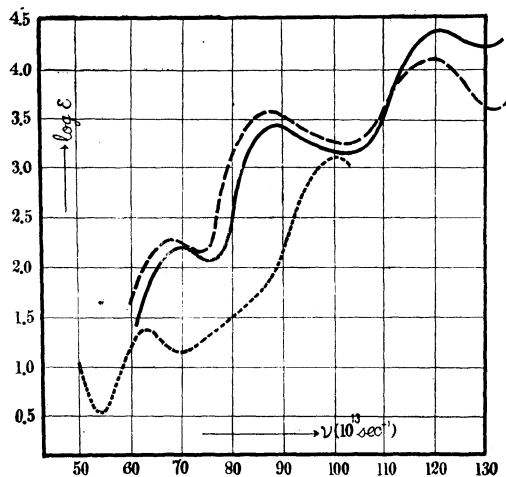
- (1) ——— $[\text{Cr en}_3]\text{Cl}_3$
 (2) - - - $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
 (3) - · - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Fig. 2.



- (1) ——— $[\text{Co en}_2\text{NH}_3\text{Cl}_2\text{Cl}_2]$
 (2) - - - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (3) - · - $[\text{Co py}_4\text{NH}_3\text{Cl}]\text{Cl}_2$

Fig. 3.



- (1) ——— $[\text{Co en}_2(\text{NO}_2)_2\text{Cl}_6]\text{NO}_3$
 (2) - - - $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2\text{Cl}_6]\text{Cl}$
 (3) - · - $[\text{Co en}_2\text{Cl}_2\text{Cl}_6]\text{Cl}$

Fig. 4.

There can be found distinct shifts of both the first, the second, and even the third absorption band in most cases towards the shorter wavelengths in ethylenediammine compounds compared with the corresponding ammine salts. In a few cases, these bands have frequencies equal to those of the corresponding ammine salts. It is also noteworthy that in nearly all the ethylenediammine salts, their extinction coefficients are larger than those of the ammine salts.

Now, when we compare the absorption spectra of $[\text{Co en}_3]\text{Br}_3$ and less stable $[\text{Cr en}_3]\text{Cl}_3$, it can be found that the first absorption band

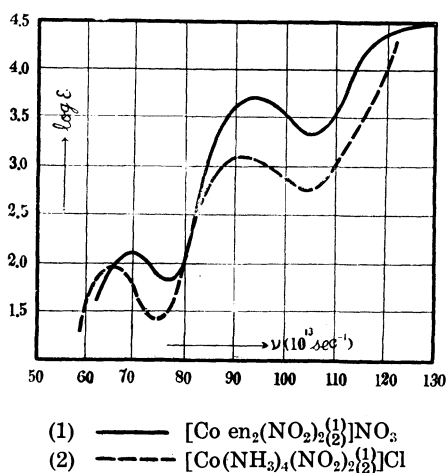


Fig. 5.

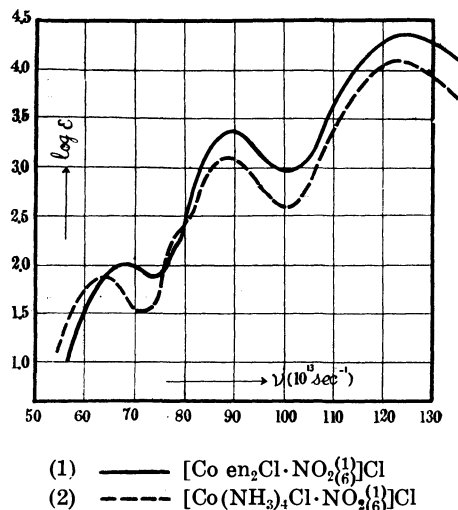


Fig. 6.

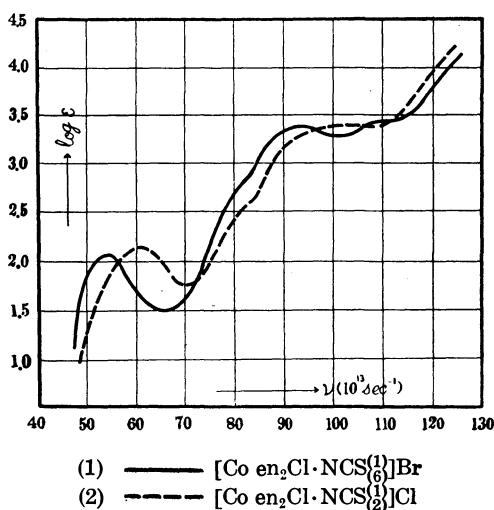


Fig. 7.

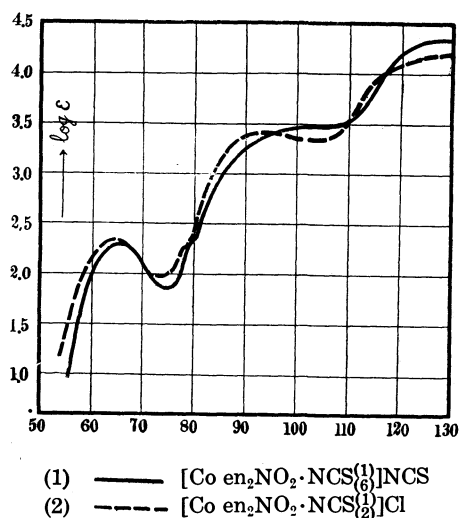


Fig. 8.

of the Cr^{III}-salt has shorter wave-lengths, while the second band of the Co^{III}-salt is, on the contrary to the first band, more hypsochromic than the Cr^{III}-salt. Similar relation can be seen for [Co(NH₃)₆]Cl₃ and [Cr(NH₃)₆]Cl₃. Such positions of the bands may be regarded as a proof of the validity of the author's hypothesis stated above, that the second absorption band is a scale for the stability of co-ordination compound, while the first absorption band is unqualified to be so. It is an important fact that the luteo-Co^{III}-salts are, despite of their more intense colours, not inferior in the stability to the luteo-Cr^{III}-salts, in agreement with the order of their second absorption bands.

In the following, the individual cases will be described.

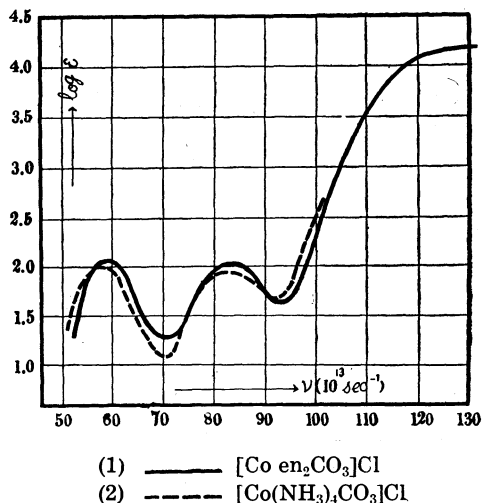


Fig. 9.

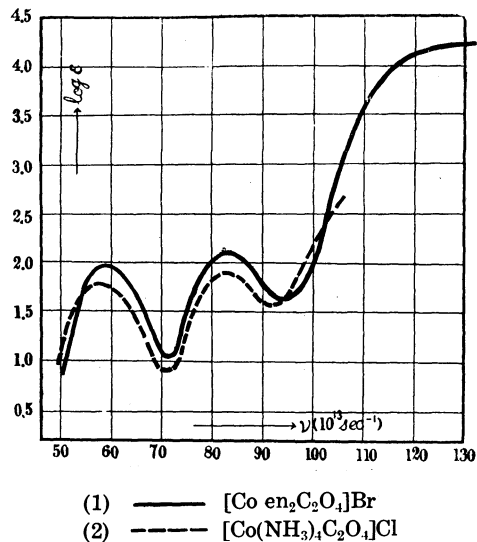


Fig. 10.

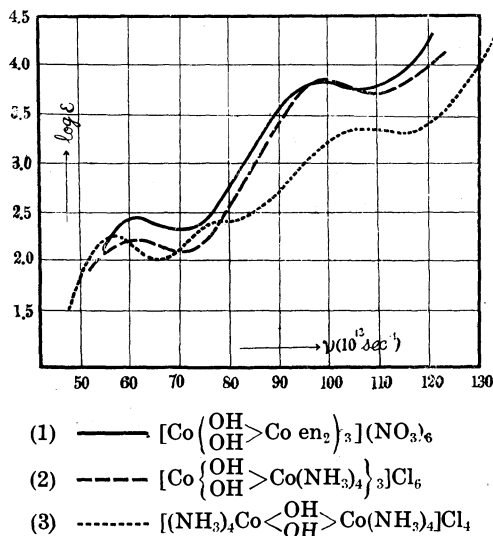


Fig. 11.

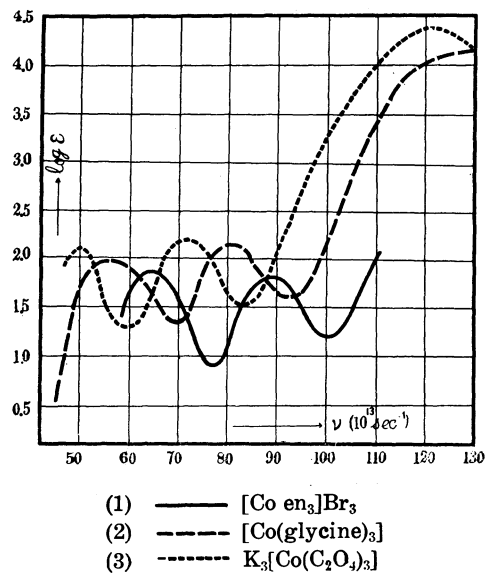


Fig. 12.

(i) Luteo-salts: Showing the absorption bands of the almost identical frequency, the stabilities of [Co(NH₃)₆]Cl₃, [Co en₂(NH₃)₂]₂Br₃ and [Co en₃]Br₃ are equal to each other. The case is also similar in the luteo-Cr^{III}-salts.

(ii) Purpureo-salts: Three salts, [Co(NH₃)₅Cl]Cl₂, [Co en₂NH₃Cl]₂ and [Co py₄NH₃Cl]Cl₂, are of the almost identical colour, and in fact, the first and the second bands of them lie in practically the same positions respectively. With regard to the configuration of the tetrapyridine salt, there are two possible cases, namely cases of cis- and trans-

configurations, concerning the positions of NH_3 -molecule and Cl -ion. It is difficult, however, to decide whether this salt has *cis*- or *trans*-configuration, only from the absorption spectrum. In the present state, the *cis*-form is more probable, because this salt can be prepared by interaction of aqueous ammonia with $[\text{Co py}_4\text{Cl}_2]\text{Cl}$, which, according to A. Werner⁽⁹⁾, has its Cl -ions in *trans*-positions, and, therefore, by entirely the same procedure as in the preparation of $[\text{Co en}_2\text{NH}_3\text{Cl}_2^{(1)}]\text{Cl}_2$ from the praseo-salt $[\text{Co en}_2\text{Cl}_2^{(1)}]\text{Cl}$.

(iii) Croceo-salts: It will be found that the third absorption band of the ethylenediamine salt can be observed distinctly in the region of $\nu=120-130$, overlapping with the special band due to the co-ordinated ethylenediamine molecules, while the ammine croceo-salt is well known to be an example for the salt having the third absorption band. By comparing the absorption curves of both the salts, we can see that every member of the three bands is much more stabilized by the remarkable shift towards the shorter wave-lengths in the ethylenediamine compound, compared with the ammine salt.

It will be added, moreover, that the special absorption band due to the co-ordinated nitro-radicals⁽¹⁰⁾ could not be distinguished from the second band.

(iv) Flavo-salts: Comparing the absorption of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^{(1)}]\text{Cl}$ and $[\text{Co en}_2(\text{NO}_2)_2^{(1)}]\text{NO}_3$, we can observe shifts of both the first and the second band to the side of shorter wave-lengths in the latter.

A hump of the absorption curve of the ethylenediamine salt in the region of $\nu=120-130$ is attributed to the selective absorption proper to the co-ordinated ethylenediamine molecules, and the third absorption band due to *trans*-negative radicals is naturally out of question here.

(v) 1,6-Chloro-nitro-salts: $[\text{Co en}_2\text{Cl.NO}_2^{(1)}]\text{Cl}$ has been proved to have the third band in the present work, while the third band of the corresponding ammine salt had been reported previously⁽¹¹⁾. The special absorption bands proper to the nitro-radicals are illustrated here; they can be seen approximately at $\nu=80$. Regarding the relative positions, the bands of the ethylenediamine salt seem more hypsochromic.

(vi) Chloro-rhodanato-salts: Of the two possible isomers, *cis*- and *trans*-form, the latter ought to have a third band, because of co-ordination of the negative ligands in *trans*-positions. A small band at $\nu=110.4$ may be assigned to it. On the other hand, one special band due to the co-ordinated rhodanato-radical is to be expected for each of them, and then inflection of their absorption curves in the middle between $\nu=80$ and 90 can be explained as the results of overlapping of the special bands upon the second bands.

It is regrettable that there do not exist the ammine salts corresponding to either of the two isomers of $[\text{Co en}_2\text{Cl.NCS}]\text{X}$.

For the interesting problem, which of the two isomers is more stable, no answer can be given from the spectra alone, as their second bands are unable to be determined.

(9) A. Werner, R. Feenstra, *Ber.*, **39** (1906), 1538.

(10) H. Kuroya, R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 1142.

(11) R. Tsuchida, S. Kashimoto, this Bulletin, **11** (1936), 785.

(vii) Nitro-rhodanato-salts: In these, there will be expected several absorption bands, namely, the first, the second, and the special bands due to the co-ordinated nitro- und rhodanato-radicals in the case of cis-form, and moreover, in addition to them, the third absorption band in the case of trans-form. In reality, however, only the first bands can be distinguished in the both isomers, surely because of complex superposition of these bands.

(viii) Tetrammine-carbonato- and -oxalato-salts: It can be seen obviously from Figs. 8 and 9 that the ethylenediamine compound is more stable in every set of carbonato- and oxalato-salts, for the bands, especially the second, are more hypsochromic in the ethylenediamine compounds.

(ix) Hexol-salts: With regard to the first bands only, which are distinct in both the ammine and the ethylenediamine salt, the latter is more hypsochromic than the former. The second bands, however, could not be discriminated due to their complex configurations.

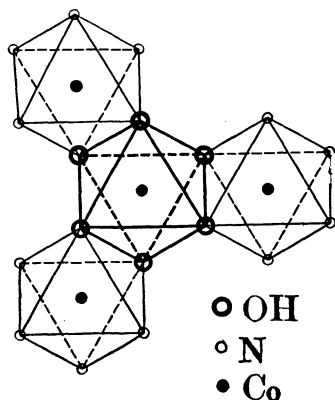


Fig. 13. Configuration of hexol-salt.

At the beginning of the present work, we expected the existence of a third absorption band in hexol-salts, because OH-radicals as many as six are co-ordinated around the innermost Co-atom, forming thus three pairs of trans-anions. The bands having their absorptive maxima nearly at $\nu=99$, however, should not be considered as the expected third bands, for there is a similar band in the absorption curve of the diol-salt, which is not at all qualified to possess its third band. Such being the case, the absence of the third absorption band of hexol-salts seemed to be difficult to explain at first sight. The lack of the third band in hexol-salts, however, may be understood by comparing them with aquo-complex salts; the OH-radical in hexol salts are quite similar to the OH_2 -molecule in aquo-

salts, with regard to the co-ordinative behaviour of the O-atom which has three ligands, two hydrogen atoms and one metallic ion in the aquo-salts and one hydrogen atom and two metallic ions in hexol-salts.

In addition, a few words may be said of the questionable bands at $\nu \approx 99$; the present authors would like to explain these as being due to co-ordination of the ligands around the central O-atoms, because Prof. Tsumaki⁽¹²⁾ had shown previously the appearances of similar bands in some of organic complex salts.

(x) α -[Co(glycine)₃] (violet form): Two forms are theoretically possible for cobaltic triglycine: cis-cis- and cis-trans-form (Fig. 14). In fact, Ley and Winkler⁽¹³⁾ had prepared these two isomers. A question, however, is left unsolved, which of the two isomers, violet α - or red β -form, is to be a cis-cis-, and the other a cis-trans-form. Attempting to solve this problem, the present authors have measured the absorption of the

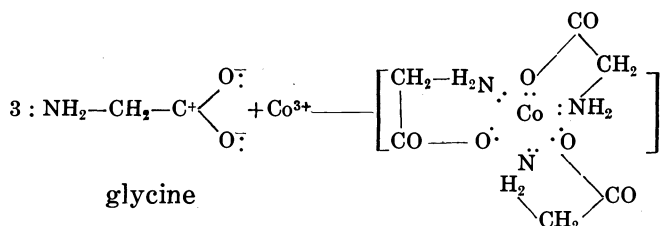
(12) R. Tsuchida, T. Tsumaki, this Bulletin, **13** (1938), 527.

(13) H. Ley, H. Winkler, *Ber.*, **42** (1909), 3900.

violet form only, the red form being unavailable for measurements because of its insolubility in water. Now, were the violet form a cis-trans-form, its absorption curve would show a third band on account of the carboxyl radicals distributed in trans-positions.

In the present work, however, no band was detected, which might be described as the third band. This may be considered as a favorable proof for the cis-cis-configuration.

It is well known that a molecule of α -amino acid can co-ordinate itself to an ion of heavy metals, e.g., Cu^{++} , Co^{3+} , etc., in order to form the so-called "inner complex", which is usually insoluble in water. Co-ordination must take place through the agency of its lone pairs of electrons, which belong to the NH_2 -radical and the oxygen atoms of carboxyl radical; thus:



Accordingly, apart from the configuration referred to above, it may be reasonable to consider, that cobaltic triglycine is intermediate between $[\text{Co en}_3]^{3+}$ and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$, concerning the modes of co-ordinative combinations.

Hereupon, it is desirable to compare the absorption spectra of those salts. In Table 2, the frequencies, at which they show the maximum ϵ -values respectively, are tabulated, and their absorption curves are arranged side by side in Fig. 12.

Table 2.

Complex Salt	First band ν_1 (10^{13})	Second band ν_2 (10^{13})	Third band ν_3 (10^{13})
$[\text{Co en}_3]\text{Br}_3$	64.6	88.2	—
$[\text{Co}(\text{glycine})_3]$	56.8	81.0	—
$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]^{(14)}$	49.6	71.0	122.4

As can be seen from the table as well as the figure, the triglycine compound in question lies intermediate between the other two, offering

(14) S. Kashimoto, M. Kobayashi, this Bulletin, 12 (1937), 350.

an obvious proof for the supposition that the chemical combination through a N-Co-bond might be stronger than that through a O-Co-bond.

Conclusion. By summarizing the results obtained above, it is confirmed decisively a hypothesis of the authors, that the second absorption band may be attributed to co-ordination electrons combining the central atom to the ligands, and, therefore, the stability of the co-ordination compound may be measured by its second absorption band, because the second band of ammine complex is, in general, more bathochromic than that of the corresponding ethylenediamine salt which is practically much more stable.

Then, it must come into question, why the ethylenediamine complexes are more stable in these ways. If a linkage of N-C-C-N of an ethylenediamine molecule is supposed to be on a plane, a simple calculation indicates the N-N-distance as equal to $2.5\text{\AA}$., assuming the atomic radius $R_N=0.7$ and $R_C=0.77\text{\AA}$.⁽¹⁵⁾, while, on an assumption of $R_{Co}=1.22\text{\AA}$.⁽¹⁵⁾ and the angle N-Co-N= 90° , N-N must have the value $2.7\text{\AA}$.

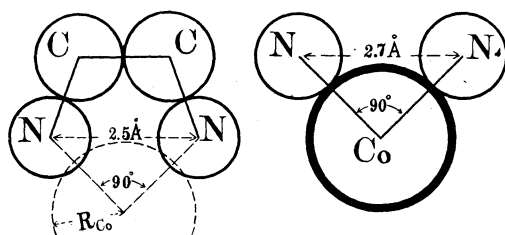


Fig. 15.

An ethylenediamine molecule, therefore, can be easily co-ordinated to a central cobalt atom, if a little distortion would be permitted around its bonds. According to P. Trunel's measurement⁽¹⁶⁾ of dipole moment, there are completely free rotations around the C-C- and C-N-bond in an ethylenediamine molecule. Under this circumstance, the co-ordinating procedure will be

very smooth and steady⁽¹⁷⁾.

In addition to this condition, the both ends of ethylenediamine molecule are bonded to the central atom, making thus the combination in the co-ordination sphere much more poor in chances of its being broken out than in ammine complex, in which every member of the co-ordinated NH_3 -molecules is singly bonded to the central atom.

Experimental. (1) Diethylenediamine cobaltic complexes: Prepared by the methods of A. Werner⁽¹⁸⁾ by the processes shown in Table 3.

(2) $[\text{Co en}_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$ (Luteo-cobaltic-salt): This salt can be synthesized by use of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and ethylenediamine with facility, but also will be obtained in a comparatively good yield as a by-product, when the praseo-salt $[\text{Co en}_2\text{Cl}_2]\text{Cl}$, which is a starting substance of the diethylenediamine series, is prepared. The authors' method of separation from a mixture of the luteo- and the praseo-salt is given in Table 4.

(15) L. Pauling, "The Nature of the Chemical Bond", 2nd Ed., 164 and 182, New York (1940).

(16) P. Trunel, *Compt. rend.*, **203** (1936), 563.

(17) Cf. J. P. Mathieu, *Bull. soc. chim.*, **5** (1938), 749.

(18) A. Werner, *Ann.*, **386** (1912), 1.

Table 3.

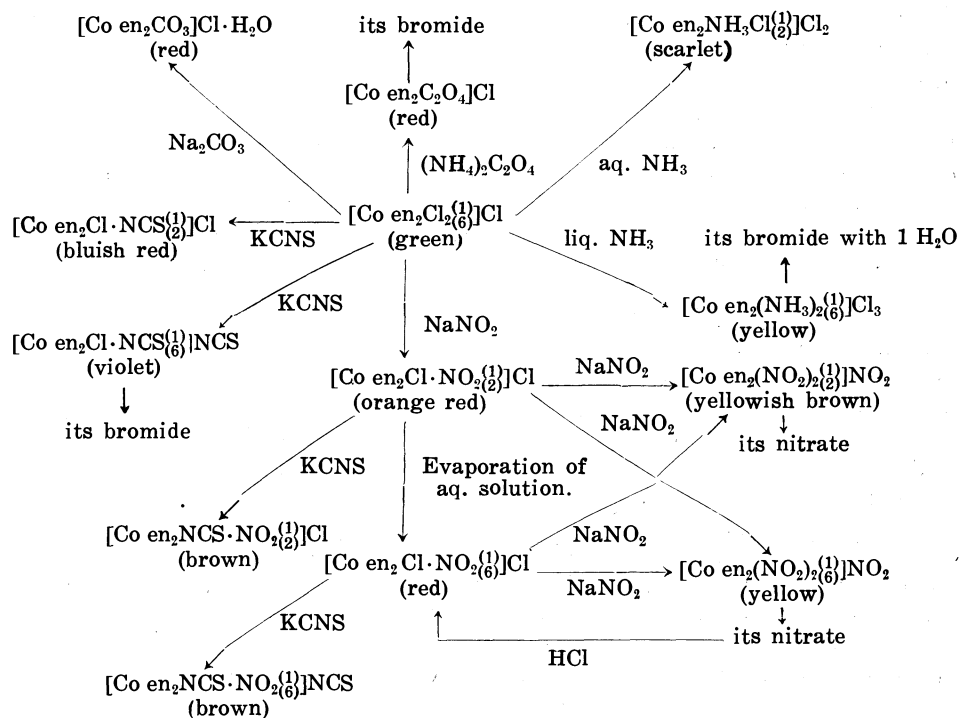
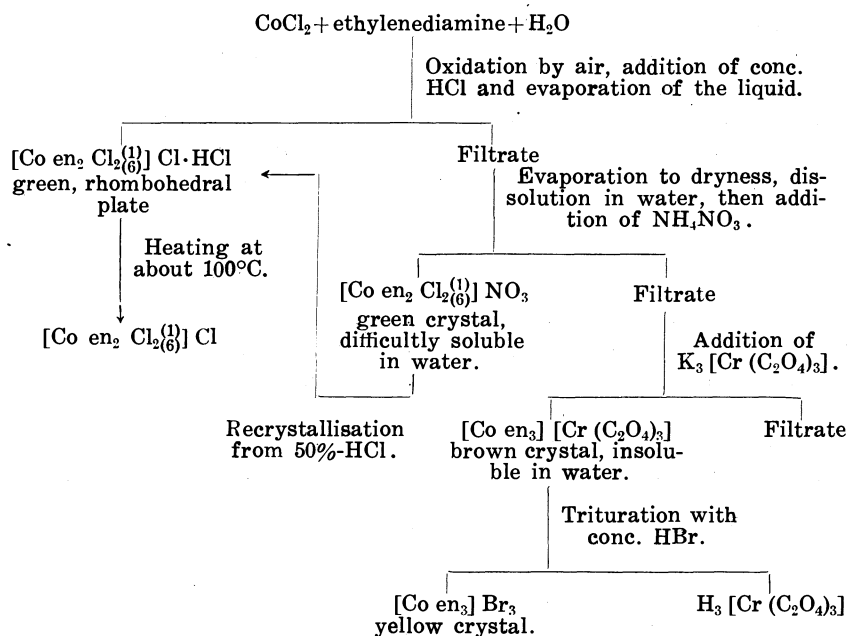


Table 4.



(3) $[\text{Cr en}_3]\text{Cl}_3 \cdot 3.5\text{H}_2\text{O}$ (Luteo-chromic-salt): Pfeiffer⁽¹⁹⁾ had prepared this salt, using ethylenediamine hydrate and partially dehydrated, grey-coloured chrome alum. The authors followed his method. Both the luteo-Cr-salt and the luteo-Co-salt are yellow, the former being lighter in hue.

(4) $[\text{Co py}_4\text{NH}_3\text{Cl}]\text{Cl}_2$: This can be obtained, being derived from $[\text{Co py}_4\text{Cl}_2]\text{Cl}$, which was originally synthesized by A. Werner⁽⁹⁾ by oxidising a cold solution of cobaltous chloride in pyridine with chlorine; the tetrapyridine salt, the colour of which is bluish green, is triturated with small quantity of aqueous ammonia, then the chloro-ammine salt may be formed immediately, causing a colour change from green to violet-red.

(5) $[\text{Co}\left\{\begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} > \text{Co}(\text{NH}_3)_4 \right\}_3]\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ (Hexol-salt): According to the method given by Werner⁽²⁰⁾, tetrammine chloro-aquo-cobaltic sulphate, $[\text{Co}(\text{NH}_3)_4\text{Cl} \cdot \text{H}_2\text{O}]\text{SO}_4$, was dissolved in a closed vessel containing 10% aqueous ammonia solution, and, after several hours, there was found the aimed, difficulty soluble hexol-sulphate, forming flat, scale-like and almost black crystals. This sulphate was then converted into its chloride by use of barium chloride.

(6) $[\text{Co}\left\{\begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} > \text{Co en}_2 \right\}_3](\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$ (Ethylenediamine hexol-salt): Prepared by the method of Werner⁽²¹⁾, who obtained this hexol-salt by oxidation of a solution containing cobaltous nitrate and ethylenediamine in an airy place. This salt is considerably richer in brownish colour than the corresponding ammine-hexol.

(7) $[(\text{NH}_3)_4\text{Co} < \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} > \text{Co}(\text{NH}_3)_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ (Diol-salt: The sulphate was prepared by the method of Werner⁽²²⁾, a dehydration of tetrammine hydroxo-aquo-cobaltic sulphate, $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O} \cdot \text{OH}]\text{SO}_4$, at temperatures between 100 and 110°, and this diol-sulphate was converted into its chloride by use of barium chloride.

(8) $\alpha\text{-}[\text{Co}(\text{glycine})_3] \cdot 2\text{H}_2\text{O}$ (violet form): Cobaltic hydroxide, $\text{Co}(\text{OH})_3$, and pure glycine were together boiled in aqueous solution for several hours, according to the method of Ley and Winkler⁽¹³⁾. One modification thus formed, the red β -form, being insoluble in water, the liquid was filtered off and from this could be crystallised the violet α -salt.

Summary.

1. Absorption spectra of a number of ethylenediamine cobaltic complex salts have been observed. Generally speaking, their absorption bands, especially the second, are more hypsochromic than those of the corresponding ammine salts.

2. The results have proved that the author's hypothesis on the absorption spectra holds good for the ethylenediamine complex salts.

(19) P. Pfeiffer, *Ber.*, **37** (1904), 4277.

(20) A. Werner *Ber.*, **47** (1914), 3087; S. M. Jörgensen, *Z. anorg. Chem.*, **16** (1898), 186.

(21) A. Werner, *Ber.*, **40** (1907), 2119.

(22) A. Werner, *ibid.*, **40** (1907), 4437.

3. Examples of the third absorption bands have been found in the diethylenediamine cobaltic complexes of known configurations.

4. A new method of separating $[\text{Co en}_3]^{3+}$ and $[\text{Co en}_2\text{Cl}_2]^{+}_{(6)}$ has been devised.

*Department of Chemistry, Faculty, of Science,
Osaka Imperial University.*

Copper, Lead, and Zinc Content of the Hot Springs of Japan.

By Kazuo KURODA.

(Received September 25, 1940.)

The occurrence of copper in a large number of hot springs of Japan has been found spectroscopically by K. Kimura⁽¹⁾ and in the present work a method for the determination of the minute quantities of copper in the large amounts of iron was studied and the method was applied to the determination of the element in a number of mineral springs of Japan. The copper, lead, and zinc content of some weak alkaline hot springs were also estimated by Fischer's method⁽²⁾.

I. Determination of the Minute Quantities of Copper in the Mineral Springs. Add nitric acid to a 500 c.c. portion of the mineral water and boil to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) to slight excess and 5 c.c. of saturated ammonium carbonate solution. Warm and filter. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1) and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with dilute nitric acid and evaporate to dryness.

Dissolve the residue in nitric acid, adjust to pH 3 and titrate with the carbon tetrachloride solution of dithizone. The orange yellow colour of the carbon tetrachloride layer indicates the presence of silver. The silver is removed until the carbon tetrachloride layer turns to reddish violet. The carbon tetrachloride solution of dithizone is added with small portions until it remains green when vigorously shaken for several minutes. The amount of copper is obtained from the volume of the carbon tetrachloride solution of dithizone used to extract the reddish violet dithizone complex of copper. Each c.c. of the dithizone solution corresponded to 2.5 γ of copper.

(1) Not yet published.

(2) H. Fisher, *Angew. Chem.*, **47** (1934), 685; **50** (1937), 919. etc.

II. Copper Content of Some Mineral Springs of Japan.

The results from the quantitative determination of the minute traces of copper in some mineral springs of Japan is shown in Table 1. The iron content of some of these mineral springs was determined gravimetrically or by Mellor's colorimetric method, and the atomic ratio of copper to iron in the mineral springs was calculated (Table 2).

Table 1. Copper Content of Some Mineral Springs of Japan.

No.	Mineral spring	Prefecture	Temperature (°C)	pH	Copper Content	
					(γ/l.)	% (total residue.)
1	Kinbu	Yamanasi	—	—	68000	0.15
2	Kinkei	Totigi	10.0	2.4	1033	0.050
3	Daruma-Zigoku, Yunohanzawa, Hakone.	Kanagawa	93.0	2.0	163	0.0081
4	Hon-Onsen, Arima	Hyōgo	—	—	140	0.00084
5	Kinkei No. 2	Totigi	8.7	2.9	140	—
6	Yoemon-Yu, Yunohanzawa, Hakone.	Kanagawa	87.8	2.2	90	0.0053
7	Yagendo, Arima.	Hyōgo	—	—	38	0.00035
8	Iron spring No. 1, Sinyu, Sukayu.	Aomori	—	—	12	—
9	Iron spring No. 2, Sinyu, Sukayu.	Aomori	—	—	10	—
10	Gongen-Yu, Yunohanzawa, Hakone.	Kanagawa	51.0	2.5	10	0.0010
11	Cold spring near Kinkei.	Totigi	6.0	6.5	6	—

Table 2. Atomic Ratio of Copper to Iron.

No.	Mineral Spring	Iron Content (g./l.)	Atomic Ratio of Copper to Iron. (Cu : Fe)
1	Kinbu	10.416	1 : 174
2	Kinkei	0.177	1 : 196
3	Daruma-Zigoku	0.016	1 : 112
4	Hon-Onsen	0.030	1 : 242
5	Kinkei No. 2	—	—
6	Yoemon-Yu	0.157	1 : 1980
7	Yagendo	—	—
8	Iron Spring No. 1	0.00015	1 : 14
9	Iron Spring No. 2	—	—
10	Gongen-Yu	0.0068	1 : 777
11	Cold Spring near Kinkei	—	—

III. Copper, Lead, and Zinc Content of a Number of Weak Alkaline Hot Springs of Japan. The copper, lead, and zinc content of a number of weak alkaline hot springs in Japan were estimated by the colorimetric method. For the determination of lead, the colorimetric method which was described in the previous paper⁽³⁾ was used. For the colorimetric determination of zinc, H. Fisher and G. Leopoldi's method⁽⁴⁾ was adopted. The results of the experiments are shown in Table 3. Copper was detected in three samples (out of twelve samples), and lead in two samples (out of twelve samples). The traces of zinc were always found in these hot springs. The average zinc content of twelve samples was 13 γ per litre.

Table 3. Copper, Lead, and Zinc Content of Some Hot Springs of Japan.

No.	Hot Spring	Prefecture	Temperature (°C)	pH	Cu	Pb (mg/l.)	Zn
1	Itō No. 3	Sizuoka	42.0	8.0	0.000	0.033	0.009
2	Itō No. 4	„	42.0	8.0	0.003	0.000	0.016
3	Itō No. 8	„	40.5	7.3	0.003	0.002	0.008
4	Itō No. 10	„	38.0	7.4	0.002	0.000	0.010
5	Itō No. 13	„	40.5	7.4	0.000	0.000	0.008
6	Moto-Yu, Kawazi	Totigi	43.0	7.7	0.000	0.000	0.009
7	Komoti-Yu, Kawazi	„	43.0	7.7	0.000	0.000	0.021
8	Iwa-no-Yu, Kawazi	„	42.5	7.7	0.000	0.000	0.027
9	Yakusi-Yu, Kawazi	„	43.0	7.7	0.000	0.000	0.024
10	Hudō-no-Yu, Kawazi	„	40.2	7.7	0.000	0.000	0.025
11	River Water, Ozikagawa, Kawazi	„	15.5	7.1	0.000	0.002	0.036
12	Takara-no-Yu, Kinugawa	„	55.5	8.0	0.000	0.000	0.012
13	Senami	Niigata	100.3	8.7	0.000	0.000	0.010
14	Sea Water, Itō	Sizuoka	—	—	0.009	0.004	0.006
15	Sea Water, Senami	Niigata	—	—	0.010	0.001	0.008

Summary.

(1) A method for the determination of the minute quantities of copper in the mineral springs was studied.

(2) Copper, lead, and zinc content of a number of hot springs of Japan were estimated.

The author expresses his hearty thanks to Prof. Kenjiro 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.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

(3) K. Kuroda, this Bulletin, **15** (1940), 153.

(4) H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107** (1936), 241.

The Addition of Hydrogen Bromide to Cholesteryl Bromide and the Oxygen Effect.

By Yoshiyuki URUSHIBARA, Keiiti NAMBU, and Toshio ANDO.

(Received September 26, 1940.)

The addition of hydrogen bromide to allyl bromide and to undecenoic acid (in toluene) follows the Markownikoff rule⁽¹⁾ in the absence of oxygen and peroxides and gives the normal products, 1,2-dibromopropane and 10-bromoundecanoic acid respectively, in a nearly pure state. The presence of a minute quantity of oxygen in the reacting mixtures causes a reversal of the direction of addition, the abnormal products, 1,3-dibromopropane and 11-bromoundecanoic acid respectively, being formed as the main products. The oxygen effect on the addition of hydrogen bromide has been observed also with many other ethenoid compounds.⁽²⁾ Further, isostilbene has been found to isomerize to stilbene in the presence of hydrogen bromide and oxygen, but not in the presence of either one of them⁽³⁾.

One (Y.U.) of the authors and O. Simamura investigated the action of the mixture of hydrogen bromide and oxygen on allyl bromide and on stilbene⁽⁴⁾. The former gave water, free bromine, 1,2,3-tribromopropane, and a peroxide, probably dibromoisopropyl peroxide, besides 1,3-dibromopropane, the main product. The latter yielded stilbene dibromide as the main product, which was accompanied by small amounts of a peroxide and free bromine. From these results they postulated a mechanism of the oxygen effect.

Until recently all the examples of addition reactions showing explicitly the oxygen effect were of the addition of hydrogen bromide to terminal double bonds, and ethenoid compounds such as isoundecenoic acid^{(5) (6)}, isoundecenol⁽⁶⁾, and *cis*- and *trans*-pentene-(2)⁽⁷⁾, which belong to the type $\text{CH}_3\text{-CH=CH-CH}_2\text{-R}$ with a well-balanced non-terminal ethylene group, gave equal parts of isomeric addition products irrespective of the conditions of addition, thus making the detection of the oxygen effect impossible. Recently it was demonstrated that trimethylethylene⁽⁸⁾ and 2-bromobutene-(2)⁽⁹⁾, both with unbalanced non-terminal ethylene groups, are

(1) W. B. Markownikoff, *Ann.*, **153** (1870), 256.

(2) For reviews of works on the oxygen effect compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461; *Ann. Rep.*, **1939**, 219.

(3) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507; **13** (1938), 566.

(4) Y. Urushibara and O. Simamura, *ibid.*, **14** (1939), 323. Compare also O. Simamura, *ibid.*, **15** (1940), 292.

(5) P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108.

(6) E. P. Abraham, E. L. R. Mowat, and J. C. Smith, *ibid.*, **1937**, 948.

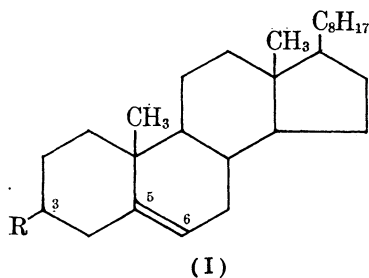
(7) M. S. Kharasch, C. Walling, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1559.

(8) C. Walling, M. S. Kharasch, and F. R. Mayo, *ibid.*, **61** (1939), 2693; A. Michael and N. Weiner, *J. Org. Chem.*, **4** (1939), 531.

(9) C. Walling, M. S. Kharasch, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1711.

subject to the oxygen effect when they add hydrogen bromide. The present paper describes the addition of hydrogen bromide to cholesteryl bromide as another example of the hydrogen bromide addition to a non-terminal double bond subject to the oxygen effect.

In cholesterol and other cholestene-(5) derivatives represented by formula I the ethylene group is much unbalanced and carbon atom 5 is sterically much hindered compared with carbon atom 6. Hence, it can be anticipated that the normal addition of hydrogen bromide will produce one isomeride in a predominating proportion while in the presence of oxygen the abnormal addition will yield the other isomeride as the main product, stereoisomerism being disregarded.



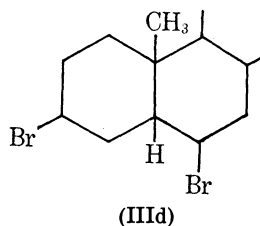
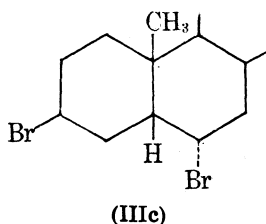
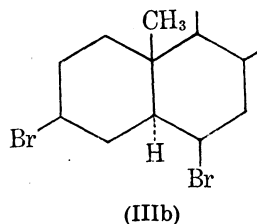
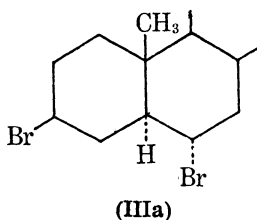
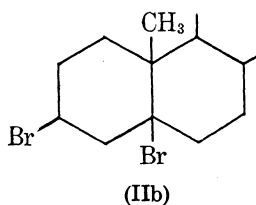
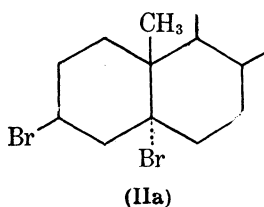
- (Ia) R = OH
- (Ib) R = Br
- (Ic) R = Cl
- (Id) R = H
- (Ie) R = CH₃CO₂

On treatment with hydrogen bromide, however, cholesterol (Ia) is liable to substitution of a bromine atom for the hydroxyl group⁽¹⁰⁾, and further it has been shown by Ashton and Smith⁽¹¹⁾ that undecenol, the alcohol corresponding to undecenoic acid, fails to yield an abnormal product under strongly oxidant conditions because of the counter-effect of the hydroxyl group. Cholesteryl halides and cholestene (Id) may be free from such possible difficulties. Thus cholesteryl bromide (Ib) was used for the present investigation, because it is more easily obtainable than cholestene and better suited for the investigation of hydrogen bromide addition than cholesteryl chloride (Ic).

The mechanism of the hydrogen bromide addition as represented in the previous paper⁽⁴⁾ requires the hydrogen atom to add to carbon 6 and the bromine atom to carbon 5 in the normal addition, and in the abnormal addition, if it occurs, the direction of addition of hydrogen bromide to be reversed. Then two stereoisomeric products (IIa and IIb) are possible in the normal addition, because carbon atom 5 becomes asymmetric, and four (IIIa, IIIb, IIIc, and IIId) are possible in the abnormal addition owing to the asymmetry of both carbon atoms 5 and 6. All the possible isomerides, however, may not be obtained in practice. If only one product is obtained in each case, the direction of addition of hydrogen bromide may well be inferred from the examples of simpler ethenoid compounds, but the stereochemical configuration of each product has to be determined.

(10) The action of hydrogen chloride on cholesterol yields 3,5-dichlorocholestane besides cholesterol hydrochloride, J. Mauthner, *Monatsh.*, **27** (1906), 305.

(11) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 1308.



The addition of hydrogen bromide to the cholesterol derivatives represented by formula I has never been studied. Recently Pirrone⁽¹²⁾ treated cholesterol with hydrobromic acid in alcoholic solution and obtained an isomeride of cholesterol with small amounts of two substances melting at 120° and 104–105° respectively, which have not been characterized.

There have been many investigations on the addition of hydrogen chloride to cholesterol derivatives. Mauthner⁽¹³⁾ obtained a hydrochloride melting at 154–155° from cholesterol and hydrogen chloride. The conversion of it into allocholesterol⁽¹⁴⁾ (IVa) shows that the chlorine atom is situated at carbon atom 5. Fazi⁽¹⁵⁾ obtained several products from the action of hydrogen chloride on cholesterol, but none have been sufficiently characterized. It seems that he doubts the homogeneity of Mauthner's hydrochloride. By the catalytic reduction of cholesterol dichloride Décombe and Rabinowitch⁽¹⁶⁾ obtained a chlorocholestanol, to which they suggested a constitution of 6-chlorocholestanol. It appears that Fazi attributed the same constitution to one of his products⁽¹⁷⁾.

(12) F. Pirrone, *Chem. Zentr.*, **111** (1940), I, 555.

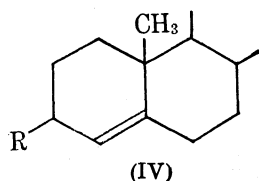
(13) J. Mauthner, *Monatsh.*, **27** (1906), 305.

(14) A. Windaus, *Ann.*, **453** (1927), 101; R. Schoenheimer and E. A. Evans, Jr., *J. Biol. Chem.*, **114** (1936), 567.

(15) R. de Fazi and L. de Fazi-Guerici, *Chem. Zentr.*, **103** (1932), I, 3302; R. de Fazi, *ibid.*, **109** (1938), II, 1781; R. de Fazi and F. Pirrone, *ibid.*, **111** (1940), I, 2652.

(16) J. Décombe and J. Rabinowitch, *Bull. soc. chim.*, [5], **6** (1939), 1510.

(17) *Idem*, *ibid.*, p. 1520.



(IVa) R = OH

(IVb) R = H

Mauthner⁽¹⁸⁾ showed the formation of two isomeric hydrochlorides from the addition of hydrogen chloride to cholestene, one of which he isolated in a pure state. As the both hydrochlorides were converted into the same pseudocholestene (IVb), they must be regarded as stereo-isomerides both with the chlorine atom at carbon atom 5. The isomeric 6-chlorocholestane was not formed from hydrogen chloride and cholestene but obtained from cholestanol-(6).⁽¹⁹⁾

From cholesteryl chloride and hydrogen chloride Mauthner⁽¹³⁾ obtained 3,5-dichlorocholestane as the only addition product. The same substance was formed by the action of hydrogen chloride on cholesterol⁽¹⁰⁾. The isomeric 3,6-dichlorocholestane was obtained by the action of phosphorus pentachloride on cholestanediol-(3,6)⁽²⁰⁾. On reduction with sodium and amyl alcohol 3,6-dichlorocholestane gave cholestane.

As summarized above, the addition of hydrogen chloride to cholesteryl chloride gives only one product, while the addition to cholestene and to cholesterol two or more. Thus cholesteryl bromide seemed to be the most suitable substance for the present purpose of studying the addition of hydrogen bromide and the oxygen effect.

The Action of Hydrogen Bromide on Cholesteryl Bromide under the Conditions Favourable for the Normal Addition. The action of hydrogen bromide on cholesteryl bromide in carbon tetrachloride with the addition of a small amount of catechol and the purification of the product gave a crystalline substance showing a melting point 101.5° (corr.), $[\alpha]_D + 5.36^\circ$, and a bromine content corresponding to the addition of a molecule of hydrogen bromide. The addition in the presence of ferric chloride which is known as an accelerating agent for the normal addition, and the addition in ethereal solution, yielded the same substance. Thus, it is evident that this hydrobromide is the normal product, the bromine atom being situated at carbon atom 5 (IIa or IIb).

The optical rotation affords a further evidence that the hydrobromide corresponds to the addition products of hydrogen chloride to cholesterol, cholestene, and cholesteryl chloride: According to Mauthner⁽²¹⁾ the laevo-rotation of these substances is converted into dextro-rotation by the addition of hydrogen chloride. Cholesteryl bromide is laevo-rotatory ($[\alpha]_D - 20.8^\circ$)⁽²²⁾, and the hydrobromide formed by the addition of hydrogen bromide under conditions mentioned above is dextro-rotatory. (The other hydrobromide described below is laevo-rotatory.)

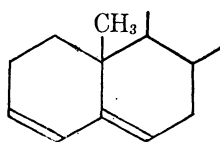
(18) J. Mauthner, *Monatsh.*, **28** (1907), 1113.

(19) O. Stange, *Z. physiol. Chem.*, **220** (1933), 34.

(20) A. Windaus, *Ber.*, **50** (1917), 133.

(21) J. Mauthner, *Monatsh.*, **27** (1906), 314, 421.

(22) J. H. Beynon, I. M. Heilbron, and F. S. Spring, *J. Chem. Soc.*, **1936**, 907.



(V)

The hydrobromide melting at 101.5° easily loses one or two molecules of hydrogen bromide: On boiling in acetone it gives cholesteryl bromide and on boiling in pyridine cholestadiene-(3,5) (V).

The Action of Hydrogen Bromide and Oxygen on Cholesteryl Bromide. The mixture of hydrogen bromide and oxygen was passed into a carbon tetrachloride solution of cholesteryl bromide, and the product was purified to a crystalline substance melting at 154° (corr.) and showing $[\alpha]_D -12.1^{\circ}$. Analysis showed it was another hydrobromide of cholesteryl bromide. Thus it has been found that oxygen exerts an effect on the addition to yield a hydrobromide different from the normal product formed without oxygen, and it is reasonable to assume that the direction of addition is reversed, so that the bromine atom adds to carbon atom 6 and the hydrogen atom to carbon atom 5 (IIIa, IIIb, IIIc, or IIId).

The hydrobromide melting at 154° is more stable than the other melting at 101.5° . It was not changed on boiling in acetone. However, attempts to substitute hydroxyl groups or hydrogen atoms for the both bromine atoms in this hydrobromide failed owing to the ease with which the added molecule of hydrogen bromide was split off under the conditions of the experiments, and nothing but the products from cholesteryl bromide were obtained: On boiling with potassium acetate in acetic acid it was transformed into cholesteryl acetate (Ie). On reduction with sodium and amyl alcohol the hydrobromide again lost hydrogen bromide and gave cholestene (Id). Thus it was impossible to obtain any information of the configuration about carbon atoms 5 and 6.

From the mother liquor of the hydrobromide melting at 154° another crystalline substance was obtained. Its bromine content corresponded to a dibromide of cholesteryl bromide, and on debromination with sodium iodide it gave cholesteryl bromide. As the substance was not obtained in a pure state and melted in a wide range of temperature ($84-127^{\circ}$), it could not exactly be determined whether or not it was identical with cholesteryl bromide dibromide (melting point 113°) formed from cholesteryl bromide and bromine.

The formation of the dibromide from cholesteryl bromide by the action of hydrogen bromide and oxygen corresponds to the formation of 1,2,3-tribromopropane and stilbene dibromide from allyl bromide and stilbene respectively by similar treatments.

Experimental.

Materials. Cholesteryl bromide was prepared by the action of phosphorus tribromide on cholesterol in benzene⁽²³⁾ and recrystallized twice from 99% ethanol, melting point 98° (uncorr.). Carbon tetrachloride was prepared by boiling a commercial product with an alkaline solution of potassium permanganate for 7 hours, drying over calcium chloride, and collecting the fraction distilling at $76.5-77^{\circ}$.

The Action of Hydrogen Bromide on Cholesteryl Bromide in Carbon Tetrachloride with the Addition of Catechol. Cholesteryl bromide (10 g.) was dissolved in carbon tetrachloride (30 c.c.), a small amount (0.4 g.) of catechol was added to the solution (catechol remained mostly undissolved), and dry hydrogen bromide was passed into the solution for 8 hours. The solution was washed with water several

(23) R. Kolm, *Monatsh.*, **33** (1912), 447.

times until the washing-water did not give a green colouration with ferric chloride, dried over anhydrous sodium sulphate, and evaporated at the temperature not exceeding 40°, when a yellowish oil remained. It was dissolved in ether (50 c.c.). On adding methanol to the ethereal solution a colourless crystalline precipitate separated out. The process of dissolving in ether and precipitating with methanol was repeated five times. The hydrobromide obtained in this way forms colourless fine needles melting at 101.5° (corr.). Found: Br,30.24. Calculated for $C_{27}H_{46}Br_2$: Br,30.12%. $[\alpha]_D^{26} = +5.36^\circ$ (11.2 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{26} = +0.06^\circ$).

The Action of Hydrogen Bromide on Cholesteryl Bromide in the Presence of Ferric Chloride. Hydrogen bromide was passed for 6 hours into a solution of cholesteryl bromide (11 g.) in carbon tetrachloride (60 c.c.) with the addition of ferric chloride hexahydrate (0.2 g.). The dark brown reaction mixture was washed with water to a light yellow solution, which was dried over anhydrous sodium sulphate and evaporated below 30°. The residue was dissolved in ether and precipitated with methanol. This process was repeated three times. Yield 4.5 g. Melting point 101° (corr.). No depression of the melting point in admixture with the above specimen of the hydrobromide.

The Action of Hydrogen Bromide on Cholesteryl Bromide in Ether. When hydrogen bromide was passed for 2 hours into a solution of cholesteryl bromide (10 g.) in ether (75 c.c.), the liquid separated into two layers. The crystals from the upper layer were dissolved in ether and precipitated with ethanol. This process was repeated four times. Yield 1 g. Needles melting at 101.5° (corr.). No depression of the melting point was observed in admixture with the specimen obtained in carbon tetrachloride in the presence of catechol. Found: Br,30.49. Calculated for $C_{27}H_{46}Br_2$: Br,30.12%.

The Action of Hydrogen Bromide and Oxygen on Cholesteryl Bromide in Carbon Tetrachloride. The mixture of hydrogen bromide and oxygen was passed for 3-7 hours into a solution of cholesteryl bromide (10 g.) in carbon tetrachloride (30 c.c.). The solution became first yellow and then wine-red. After diluting with an equal volume of carbon tetrachloride, the solution was washed with water, when it became light brown. The solution was then dried over anhydrous sodium sulphate and evaporated below 30°. The substance remained was dissolved in ether and precipitated with methanol. When the process of dissolving in ether and precipitating with methanol was repeated seven or eight times, the hydrobromide was obtained in colourless needles melting at 154° (corr.). Found: Br,29.65. Calculated for $C_{27}H_{46}Br_2$: Br,30.12%. $[\alpha]_D^{26} = -12.1^\circ$ (15.7 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{26} = -0.19^\circ$).

The hydrobromide was hardly affected on boiling in acetone for five hours.

On concentrating the mother liquor of the second recrystallization of the above hydrobromide an impure crystalline substance melting in the range of 84-127° (uncorr.) was obtained. It showed a composition of a dibromide of cholesteryl bromide. Found: Br,39.80. Calculated for $C_{27}H_{45}Br_3$: Br,39.34%. The melting point in admixture with the dibromide (melting point 113°, corr.) prepared by adding bromine to cholesteryl bromide was found 90-108° (uncorr.).

The Elimination of Hydrogen Bromide from the Hydrobromide Melting at 101.5°. The hydrobromide melting at 101.5° (0.5 g.) was boiled in pyridine (13-15 c.c.) for 12 hours, and the liquid was poured into water. The precipitated substance was extracted with ether. The ethereal solution was shaken with dilute sulphuric acid and water, dried over anhydrous sodium sulphate, and evaporated. On adding methanol to the oily residue a crystalline substance separated out. It was collected, dissolved in ether, and again precipitated with methanol. The substance thus obtained forms needles melting at 76° (corr.), contains no bromine, and gives a colouration changing through yellow and yellowish brown to red on adding 90% trichloroacetic acid to its chloroform solution. Thus the substance shows the properties of cholestadiene-(3,5).⁽²⁴⁾

(24) H. E. Staveland and W. Bergmann, *J. Org. Chem.*, **1** (1936), 567; J. C. Eck, R. L. Van Peursem, and E. W. Hollingsworth, *J. Am. Chem. Soc.*, **61** (1939), 172; I. M. Heilbron and F. S. Spring, *Biochem. J.*, **24** (1930), 133.

The hydrobromide (1 g.) was boiled in acetone (30 c.c.) for 5 hours. The crystalline substance separating out on cooling the acetone solution melted at 97° (corr.) and showed no depression of the melting point in admixture with cholesteryl bromide (mixed melting point 98°, corr.).

The Action of Potassium Acetate on the Hydrobromide Melting at 154°. The hydrobromide melting at 154° (1 g.) was boiled with anhydrous potassium acetate (20 g.) in glacial acetic acid (60 c.c.) for 10 hours. The acetic acid was neutralized with concentrated aqueous potassium hydroxide and the reaction product was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and evaporated in vacuum. The acetyl group was determined with the crude product: 0.328 g. of the substance was boiled with 20 c.c. of ca. 0.5 N alcoholic potash for 2 hours and the remaining alkali was titrated with 0.441 N hydrochloric acid, of which 22.68 c.c. was consumed, while in a blank test 20 c.c. of the alcoholic potash consumed 24.46 c.c. of the hydrochloric acid. (Found: CH_3CO , 10.30. Calculated for cholesteryl acetate, $\text{C}_{27}\text{H}_{45}\text{OCOCH}_3$: CH_3CO , 10.04%.

The product of the above saponification was extracted with ether. The substance obtained from the ethereal solution was recrystallized from methanol and identified with cholesterol by the melting point (148°, corr., mixed melting point 148.5°, corr.) and by the formation of the digitonide.

The Reduction of the Hydrobromide Melting at 154° with Sodium and Amyl Alcohol. The hydrobromide melting at 154° was reduced with sodium in amyl alcohol and the product was recrystallized several times from acetone to colourless small needles melting at 90.5–92° (corr.). It gave a yellow colouration with tetranitromethane. It was identified with cholestene: A mixture with an authentic specimen (melting point 90.5–92.5, corr.) melted at 90.5–92° (corr.).

The Debromination of the Dibromide from the Mother Liquor of the Hydrobromide Melting at 154°. The substance (0.2 g.) was dissolved in benzene (10 c.c.) and sodium iodide (2 g.) dissolved in ethanol (15 c.c.) was added. The mixture was heated on the water bath for 2 hours. The solvents were removed in vacuum and the residue was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and concentrated. The crystalline substance separating out on adding methanol was identified with cholesteryl bromide: It melted at 97–97.5° (corr.) alone and at 98° (corr.) in admixture with an authentic specimen.

Summary.

Hydrogen bromide was added to cholesteryl bromide in carbon tetrachloride. In the presence of catechol or ferric chloride a hydrobromide melting at 101.5° was obtained. Addition in ethereal solution gave the same product. Simultaneous action of oxygen yielded another hydrobromide melting at 154° and a substance with the composition of a dibromide of cholesteryl bromide. The direction of addition of hydrogen bromide is assumed to follow the examples of additions to simpler ethenoid compounds. The properties and the transformations of the hydrobromides are described. The both hydrobromides lose hydrogen bromide more or less easily.

The authors express their hearty thanks to the Department of Education and to the Imperial Academy for grants.

*Chemical Institute, Faculty of Science,
Imperial University of Tokyo.*

On the Nature of Foam. VII.⁽¹⁾ Foam Formation of Mixed Aqueous Solution of Saponin and Ethyl Alcohol.

By Tunetaka SASAKI.

(Received September 27, 1940.)

It is a problem of fundamental importance for the study of foam phenomena to clear the mechanism of its formation.

It has already been pointed out that it is reasonable to assume two factors to explain the mechanism of foam formation, namely, the stability of foam and foam producing power⁽²⁾. Though we cannot yet at present define these two quantities satisfactorily, they are briefly explained as follows. In ordinary cases, the stability of foam has relatively close relationship to a life of foam, for example, an aqueous solution of saponin or soap gives fairly stable foam on shaking which sometimes shows a life of several days, while in the case of solutions of alcohols or fatty acids, foam is unstable and short-living which last for only about thirty seconds. Foam is stabilized chiefly by the existence of plasticity or rigidity in foam film⁽³⁾, of saponin for example. Foam producing power, on the other hand, means the degree of easiness with which foam is produced. This factor is rather pronounced in solutions of alcohols and fatty acids. In practice, measurements carried out in properly dilute solutions of alcohol (butyl alcohol for example) and saponin shows that the foam volume⁽⁴⁾ of the former is larger although its life is shorter than those of the latter. Foam producing power is favoured by low surface tension and perhaps low viscosity, as in the case of aqueous solutions of surface active substances.

Now, there occurs a case where a considerable degree of foam formation is observed in dilute mixed solution of saponin and ethyl alcohol, even when foam cannot be produced in solutions which contain these solutes separately but in the same concentrations as in the mixed solution. Such a foam formation of mixed solution can be explained as the results of combined effects of stability due to saponin and foam producing power due to ethyl alcohol, either of which alone is not sufficient for the foam formation as in the cases of separate solutions.

Present paper describes the results and explanations of these and some other related phenomena.

Apparatus and Measurement. Measurements of the degree of foam formation were carried out with such mixed aqueous solutions of saponin

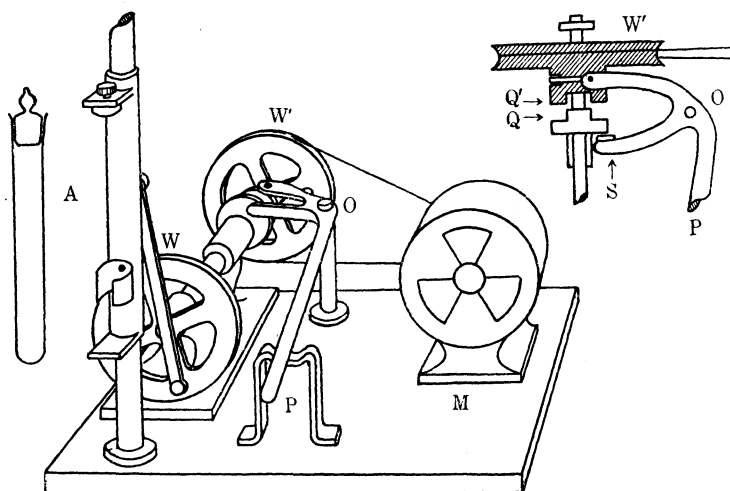
(1) The former reports are the followings: Sasaki, this Bulletin, 11 (1936), 797; 13(1938), 517; 13(1938), 669; 14(1939), 3; 14(1939), 63; 14(1939), 107; 14 (1939), 250.

(2) Sasaki, this Bulletin, 13 (1938), 517.

(3) Wilson and Ries, Colloid Symposium Monograph, 1 (1923), 145; Talmud, Suchowolskaja and Lubman, *Z. physik. Chem.*, A 151 (1930), 401.

(4) Volume of foam measured immediately after the stop of shaking is relatively in close relation to foam producing power.

and ethyl alcohol as they contain both solutes in a constant and varying concentration respectively.



- P —handle, rotatable around the point O.
 W —wheel with a crank.
 W'—wheel, connected to P and be able to slide on axis of W.
 S—brake acting on W.
 M —induction motor.
 A —test tube and its supporter.
 Q, Q'—projections belonging to W and W' respectively and acting as joint between them.

Fig. 1.

Foam was produced by shaking apparatus as shown in Fig. 1. In this Figure, by moving handle P rightwards, wheel W' shifts towards W to which it is connected by means of joint Q and Q'. Then, the test tube A containing liquid is made to vibrate by setting the motor M in motion. The vibration is interrupted by leftward movement of the handle P with resulting action of brake S upon W.

Conditions of measurement were the same as in the former report⁽⁵⁾, namely, 10 c.c. of solution for measurement is introduced in a well stoppered test tube (1.5 cm. in diameter and 15 cm. in length) and is shaken 50 times for 10 seconds with an amplitude of 12 cm. After shaking, following quantities are measured.

H_0 , height of foam zone (in cm.) produced immediately after the stop of shaking.

H_5 , height of foam zone in five minutes after shaking, in the case required.

L , Life of foam (in second).

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

Results of Measurement. The results of measurement were shown in Tables 1, 2 and Figs. 2-5. Concentration of saponin was in one case 0.009085 g./l. as in Table 1, Fig. 2 and Fig. 3, (system A) while in another case, it was 0.001820 g./l. as in Table 2, Fig. 4 and Fig. 5. (system B). These conditions were adopted as the critical concentration, namely, the former concentration of saponin in water corresponds to the heighest possible dilution at which solution still foams, while at latter concentration, aqueous solution of saponin foams no more. In Figs. 2-5, H_0 , H_5 and L are quantities referring to the mixed solution, and H_0' and L' are those referring to the solution of alcohol without saponin, for comparison.

Table 1.

Conc. of saponin (g./l.)	Conc. of alcohol (mol/l.)	H_0 (cm.)	H_5 (cm.)	L
0.009085	0	0.8	0	65.5 sec.
0.009085	0.0005143	0.7	0	25.5 sec.
0.009085	0.002572	0.8	0.5	>5 min.
0.009085	0.005143	1.2	0.8	>5 min.
0.009085	0.02571	2.3	1.7	>5 min.
0.009085	0.05143	3.1	2.2	>5 min.
0.009085	0.2571	4.8	3.4	ca. 2 hour
0.009085	0.5143	4.7	3.5	>5 min.
0.009085	0.7713	3.9	1.3	>5 min.
0.009085	1.029	4.4	0	17.6 sec.
0.009085	1.543	4.6	0	10.0 sec.
0.009085	17.13	0	0	0 sec.

Table 2.

Conc. of saponin (g./l.)	Conc. of alcohol (mol/l.)	H_0 (cm.)	L (sec.)	H_0' (cm.)	L' (sec.)
0.001820	0	0	0	0	0
0.001820	0.0005143	0.5	0	0	0
0.001820	0.002572	0.6	11.8	0	0
0.001820	0.005143	0.8	54.3	ca. 0.5	0
0.001820	0.02571	1.4	57.0	1	2.0
0.001820	0.05143	2.0	86.0	1.2	5.0
0.001820	0.2571	3.4	59.0	1.9	7.8
—	0.5143	—	—	1.8	7.6
0.001820	0.7714	3.2	12.0	—	—
—	1.029	—	—	3.1	7.5
0.001820	1.543	2.7	5.5	2.7	7.1
—	5.143	—	—	1.7	2
0.001820	17.13	0	0	0	0

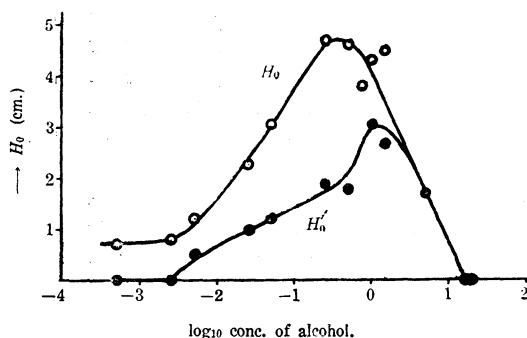


Fig. 2. Mixed solution of saponin and alcohol.
saponin = 0.009085 g./l

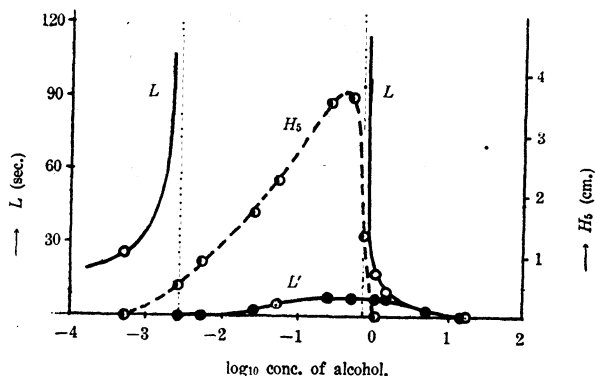


Fig. 3. Mixed solution of saponin and alcohol.
saponin = 0.009085 g./l.

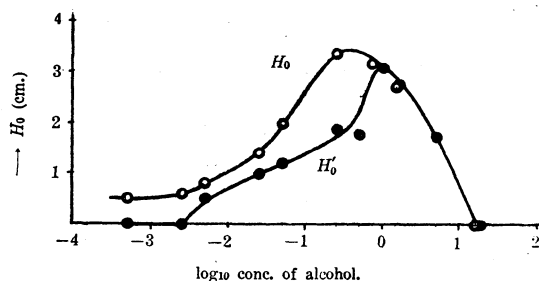


Fig. 4. Mixed solution of saponin and alcohol.
saponin = 0.001820 g./l.

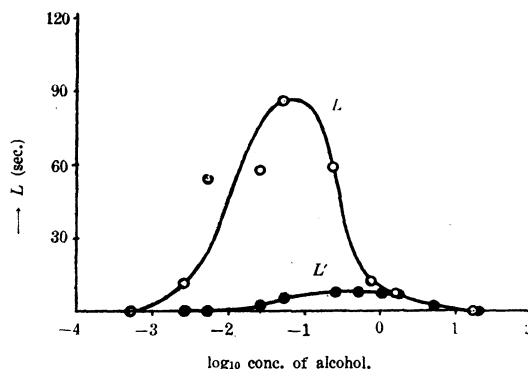


Fig. 5. Mixed solution of saponin and alcohol.
saponin = 0.001820 g./l.

It can be seen in Figs. 2 and 4, that diagrams of $H_0 \sim \text{conc.}$ and $H'_0 \sim \text{conc.}$ as a whole are analogous to each other. The foam height of mixed solution shows a magnitude which can be expected from that of corresponding alcohol solution, that is, the foam height of mixed solution is mainly determined by alcohol, and saponin shows only a little or no effect at all. When we observe, however, the relation between life of foam and concentration of alcohol in mixed solution as shown in Figs. 3 and 5, we find the followings. In the system A, foam life of saponin solution is increased in length from 65 seconds to more than 5 minutes by the addition of merely about 0.0026 mol/l. of alcohol. In the optimum case, foam lasting for about two hours can be obtained by the addition of 0.2571 mol/l. of alcohol. Foam life of solution containing alcohol alone, is also very small compared with that of mixed solutions as shown in Fig. 3. When foam life amounts to more than five minutes, the result of its measurement becomes uncertain. In such a case, foam height in five minutes after shaking is indicated instead of its life, for convenience. Foam life of the mixed solution is remarkably reduced by the addition of alcohol in excess (over concentration of 0.77 mol/l.). In the system B, the phenomena are

similar, though not so marked as in the system A. In this system, a mixed solution containing both 0.001820 g./l. of saponin and 0.005143 mol/l. of alcohol shows a foam life of 54 seconds, while solutions containing these amounts of solutes separately do not foam at all. ($L=0$). As a whole, foam life of saponin solution is fairly increased in length by the addition of alcohol within the region of concentration covering over from 0.0026 mol/l. to 0.77 mol/l. for both systems.

Discussion. Now, the explanation of the above phenomena is attempted.

(1) On the stand point of foam formation, saponin solution is marked for its stabilizing action, while foam producing power is characteristic for alcohol solution as described in the introduction of this paper. It is, therefore, reasonable to assume that the foam height of mixed solution which is perhaps closely related to foam producing power, is mainly determined by the properties of alcohol, and is not affected by the presence of saponin, because of its little foam producing power in such a dilution as in the present experiment. The remarkable increase in length of foam life of mixed solution, on the other hand, can be explained either as the stabilizing action of saponin for the foam formation of alcohol solution, or inversely, as the foam producing action of alcohol for saponin solution, that is, the action of alcohol to increase the degree of dispersion of saponin foam. Thus, the life of foam measured under these conditions is considered to be affected both by the foam producing and stabilizing action of solutes. In the region of such remarkable foam formation of the mixed solution, these two actions are attributed to saponin and alcohol respectively.

(2) In the region of mixed solutions, however, where the concentration of alcohol exceeds certain limit⁽⁶⁾, above two actions are exclusively determined by alcohol. This is especially pronounced in the case of the system B as shown in Figs. 4 and 5. Here, the life and height of foam measured in a mixed solution containing alcohol in concentration of more than 1.029 mol/l, shows the same value as in the corresponding alcohol solution without saponin. In such a case, properties of liquid films consisting foam are considered to be the same for both solutions, practically. The similar phenomena can also be observed in the system A, though a little less pronounced. These may be explained either from the preferential adsorption of alcohol in surface of foam film with an exclusion of saponin, or from dehydrating action of alcohol for saponin particles in foam film. Concerning to the former explanation, the possibility may be suggested for observing a state of preferential adsorption of a solute from a mixed solution by the measurement of properties exhibited by liquid films, such as the life and height of foam. As to the latter explanation, it is interesting, in this connection, to describe further the properties of foam as a disperse system.

(3) As a disperse system, foam can be considered to be a suspension or emulsion, the disperse phase of which is replaced by air or by the other gases, and so it is a kind of hydrosol in wider sense. Foam can, therefore, be divided also into two types, that is, hydrophilic and hydro-

(6) 1.543 mol/l and 1.029 mol/l. for systems A and B respectively.

pholic foams⁽⁷⁾, quite analogous to the hydrophilic and hydrophobic sols in the case of aqueous suspension⁽⁸⁾. Hydrophilic foam is relatively stable as produced in saponin or soap solution, and is insensitive for electrolyte. Hydrophobic foam, on the other hand, is unstable like that of alcohol or fatty acid solution, and is sensitive for electrolyte. Hydrophilic foam can also be rendered unstable by the addition of alcohol with resulting dehydration of foam film, just as in the case of hydrophilic sol. This is the case described in (2). But, just reverse to this phenomenon, we have also noticed the increase in length of the life of saponin foam by the addition of relatively small amount of alcohol as shown in the preceding section. We cannot, however, find the similar instance in aqueous suspension at all. This lack of analogy between foam and suspension is explained as follows.

In the case of aqueous suspension, effects of alcohol are measured in a system already dispersed preceding to the addition of alcohol, while in the case of foam, the same effects are observed in a system which is dispersed by shaking or by other means after the addition of alcohol. Therefore, in latter case, effects of alcohol during the process of dispersion and consequently upon the foam produced, must be considered in addition to those in the case of aqueous suspension. Accordingly, the phenomena can be explained if we take into account of the fact that the decrease in surface tension of saponin solution and some other effects which are produced by the addition of alcohol, favour a high degree of dispersion⁽⁹⁾.

The author wishes to express his hearty thanks to Nippon Gakuzyutu Sinkokwai (Japan Society for the Promotion of Scientific Research) for a grant.

Summary.

(1) The foam formation of mixed aqueous solution containing saponin in a constant amount and ethyl alcohol in varying concentration was studied. Life of the foam produced in aqueous solutions of saponin (concentrations being 0.009085 g./l. and 0.001820 g./l.) is remarkably increased in length by the addition of alcohol within the region of concentration covering over from 0.0026 mol/l. to 0.77 mol/l. Addition of alcohol in concentration exceeding 0.77 mol/l. again renders the foam unstable.

(2) Attempts were made to explain the mechanism of foam formation relating to the above phenomena.

(3) Foam and hydrosol were compared with respect to their properties as a disperse system, from which some resemblances as well as differences were pointed out between them.

*Chemical Institute, Faculty of Science
Kyushū Imperial University, Fukuoka.*

(7) The terms, "lyophile Schäume" and "lyophobe Schäume" were also introduced by Bartsch; see the footnote (8).

(8) Bartsch, *Kolloidchem. Beihefte*, 20 (1925), 1.

(9) In the case of emulsion, however, alcohol shows the effect similar to the case of this foam system. In such a case, alcohol is sometimes called "introfier"; see also, Holms, "Laboratory Manual of Colloid Chemistry", 3rd ed., 167, New York (1932).

On the Metallo-organic Compounds IX. Tris-trimethyltin oxonium halide, $((\text{CH}_3)_3\text{Sn})_3\text{OX}$.

By Taichi HARADA.

(Received September 30, 1940.)

Some time ago the present author⁽¹⁾ discussed on the formation of the compound having the empirical formula⁽²⁾ $((\text{CH}_3)_3\text{SnOH})_2\text{Sn}(\text{CH}_3)_3\text{X}$ which is formed by the action of sunlight upon trimethyltin halide containing tetramethyltin as an impurity. The mechanism of the formation of the compound in question is proposed as follows:

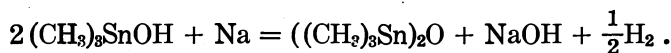
1. $2(\text{CH}_3)_3\text{SnX} \rightleftharpoons ((\text{CH}_3)_3\text{Sn})_2 + \text{X}_2$
2. $((\text{CH}_3)_3\text{Sn})_2 + \frac{1}{2}\text{O}_2 \longrightarrow ((\text{CH}_3)_3\text{Sn})_2\text{O}$
3. $\text{X}_2 + (\text{CH}_3)_4\text{Sn} \longrightarrow (\text{CH}_3)_3\text{SnX} + \text{CH}_3\text{X}$
4. $((\text{CH}_3)_3\text{Sn})_2\text{O} + (\text{CH}_3)_3\text{SnX} \longrightarrow ((\text{CH}_3)_3\text{Sn})_3\text{OX}.$

And then this tris-trimethyltin-oxonium halide readily combines with moisture in the solution and produces the crystalline compound in question.

The crystalline compounds are identical with the compounds formed between 2 molecular proportions of trimethyltin hydroxide and 1 molecular proportion of trimethyltin halides in moist benzene.

If the structures of the compounds were represented in the hydrate form $((\text{CH}_3)_3\text{Sn})_3\text{OX} \cdot \text{H}_2\text{O}$, then we might expect that the anhydrous form $((\text{CH}_3)_3\text{Sn})_3\text{OX}$ would be formed by the direct action of trimethyltin halides upon trimethyltin oxide. However, trimethyltin oxide has not been isolated until very recently. Of course before the isolation, it has been known as an amorphous powder, insoluble in water and all organic solvents, and to be formed by a slow oxidation of the trimethyltin free group in the air⁽³⁾⁽⁴⁾.

Therefore, the direct treatment of the oxide with trimethyltin halide to prepare the oxonium salt $((\text{CH}_3)_3\text{Sn})_3\text{OX}$ was not carried out. Of recent, the formation and the existence of the oxide as such have been held with doubt. The present author studied the preparation of trimethyltin oxide⁽⁵⁾ and isolated the oxide as a colourless liquid through the following reaction:



(1) T. Harada, this Bulletin, **2** (1927), 105.

(2) Kraus and T. Harada, *J. Am. Chem. Soc.*, **47** (1925), 2568.

(3) Kraus and Sessions, *ibid.*, **47** (1925), 2629.

(4) Kraus and Bullard, *ibid.*, **52** (1930), 4057.

(5) T. Harada, to be published shortly in *Sci. Papers Inst. Phys. Chem. Research* (Tokyo).

Trimethyltin oxide readily combines with trimethyltin halide directly or through the medium of a dry solvent to form the oxonium compound, $((\text{CH}_3)_3\text{Sn})_3\text{OX}$.

Recently Kraus and his student⁽⁴⁾ studied the structure of the complex compound, which might be written as $((\text{CH}_3)_3\text{Sn})_3\text{OX} + \text{H}_2\text{O}$ (A) or $((\text{CH}_3)_3\text{SnOH})_2\text{Sn}(\text{CH}_3)_3\text{X}$ (B), and investigated whether it is hydrated or not. They described that when the compound is treated with metallic sodium in liquid ammonia, an amount of hydrogen sufficient to correspond to the hydrate formula (A) is not produced. Certainly, the determination of the presence of water in question by the liquid ammonia method is one way of getting some notion regarding the structure of the complex compound since the constituent $(\text{CH}_3)_3\text{SnOH}$ in the formula (B) does not give an evolution of hydrogen⁽⁶⁾. When the experiment is carefully repeated with the iodide, no hydrogen but a small amount of a hydrocarbon is produced. However, this reason is not strong enough to reject the hydrate formula $((\text{CH}_3)_3\text{Sn})_3\text{OX} \cdot \text{H}_2\text{O}$, because if the compound dissociated or reacted with ammonia the amine complex of $(\text{CH}_3)_3\text{SnX}$ might be formed.

Then the oxide as soon as freed may react with the water and produces trimethyltin hydroxide⁽⁵⁾. If so one might expect that the solution will not give any evolution of hydrogen even though it is treated with 3 atomic proportions of sodium but will form trimethyltin, sodium



$((\text{CH}_3)_3\text{Sn})_3\text{OI}$ Crystals in
dry petroleum ether

hydroxide and sodium halide. It is true, however, that the water in the compound in question can not be removed without accompanying decomposition⁽¹⁾. It is also true that once the compound $((\text{CH}_3)_3\text{Sn})_3\text{OX}$ is dissolved in a moist solvent, the compound $((\text{CH}_3)_3\text{SnOH})_2\text{Sn}(\text{CH}_3)_3\text{X}$ is formed. Discussions and conclusions on the compounds of this type and related compounds will be presented in a subsequent paper.⁽⁷⁾

Experimental Part. $((\text{CH}_3)_3\text{Sn})_3\text{OI}$:—(A) The dry benzene (or petroleum ether) solution of trimethyltin oxide was treated with an excess of trimethyltin iodide. A crystalline precipitate (or crystals) was readily formed. The crystals were washed with dry petroleum ether to remove the iodide and subjected to dry air over P_2O_5 in a desiccator for a few minutes to evaporate the ether, and analyzed for the halogen. It melts at 94°C (uncor.) with slow decomposition.

Subs. 0.4054 g. AgI 0.1503 g. Calc. for $\text{C}_9\text{H}_{27}\text{OSn}_3\text{I}$; I, 20.01% Found: 20.04%.

(B) Trimethyltin oxide was treated directly with an excess of

(6) T. Harada, this Bulletin, 4 (1929), 266.

(7) T. Harada, to be published shortly in *Sci. Papers Inst. Phys. Chem. Research* (Tokyo).

trimethyltin iodide, and white powder-like crystals⁽⁸⁾ immediately formed with evolution of heat. In this experiment a trace of white insoluble dimethyltin oxide was also formed rendering the compound difficult to purify (free from the oxide) in the original state since the compound is sensitive to moisture when dissolved. The mixed precipitate, therefore, was washed with dry petroleum ether in order to remove the excess trimethyltin iodide and was then dissolved in moist benzene, filtered and finally crystallized as $((\text{CH}_3)_3\text{SnOH})_2\text{Sn}(\text{CH}_3)_3\text{I}$.

Subs. 0.2662 g. AgI 0.0945 g. Calc. for $\text{C}_9\text{H}_{29}\text{O}_2\text{Sn}_3\text{I}$; I, 19.43% Found: 19.20%.

Action of Na on the mixture $((\text{CH}_3)_3\text{Sn})_3\text{OI}$ and H_2O in liquid ammonia:— About 2.78 g. of $((\text{CH}_3)_3\text{Sn})_3\text{OI}$ was dissolved in liquid NH_3 and about 0.07 g. of H_2O was added to the solution. The mixture was then treated with an excess of Na giving a permanent light yellow coloration of $(\text{CH}_3)_3\text{SnNa}$. In this reaction no hydrogen but 7.5 c.c. of an unidentified hydrocarbon gas was produced; while Na if acting on the amount of water used should give 43.5 c.c. of H_2 at the standard condition.

Action of Na on $((\text{CH}_3)_3\text{SnOH})_2\text{Sn}(\text{CH}_3)_3\text{I}$ in liquid NH_3 :— (A) About 1.96 g. of the sample was dissolved in liquid ammonia and treated with about 0.5 g. of Na. In this experiment 8.6 c.c. of gas was obtained at the standard condition. The gas was not hydrogen but an unidentified hydrocarbon.

However, when this reduction was carried out with the iodide (1 mol proportion) and Na (1 atom proportion) in a relatively large amount of the solvent, a considerable amount of dimethyltin oxide⁽⁹⁾ containing trimethyltin hydroxide was obtained along with trimethyltin. The formation of dimethyltin oxide in this case is due to a decomposition of $(\text{CH}_3)_3\text{SnOH}$ by the long treatment with liquid NH_3 ; for the reason that even by simply streaming liquid ammonia upon $(\text{CH}_3)_3\text{SnOH}$ (in the absence of Na), a considerable amount of an unidentified hydrocarbon gas was shortly evolved leaving dimethyltin iodide.

$((\text{CH}_3)_3\text{Sn})_3\text{OBr}$:—This compound was prepared as was the corresponding iodide by treating trimethyltin oxide with an excess of trimethyltin bromide in dry petroleum ether; m.p. 88° (uncor.) with a slow decomposition.

Subs. 0.4671 g. AgBr 0.1453 g. Calc. for the formula: Br, 13.60% Found: 13.40%.

In this method, when trimethyltin chloride was used instead of the bromide a colourless liquid separated out simultaneous with the formation of a small amount of $(\text{CH}_3)_2\text{SnO}$.

(8) This was identical with the precipitate formed from the dry benzene solution of $(\text{CH}_3)_3\text{Sn}$ containing $(\text{CH}_3)_3\text{SnI}$ by oxidation in dry air (T. Harada, this Bulletin, **2** (1927), 105.).

(9) It was thought that it might be $((\text{CH}_3)_2\text{Sn})_2\text{O}$ in a previous experiment (T. Harada, this Bulletin, **2** (1927), 105.), for it appeared at that time to be the same substance obtained by a slow oxidation of $(\text{CH}_3)_3\text{Sn}$ in the air. (Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2629.)

Summary.

Tris-trimethyltin-oxonium halide $((\text{CH}_3)_3\text{Sn})_3\text{OX}$ has been prepared by the direct treatment (or in a dry solvent, for example, dry petroleum ether) of $((\text{CH}_3)_3\text{Sn})_2\text{O}$ with $(\text{CH}_3)_3\text{SnX}$ according to the equation:
 $((\text{CH}_3)_3\text{Sn})_2\text{O} + \text{Sn}(\text{CH}_3)_3\text{X} = ((\text{CH}_3)_3\text{Sn})_3\text{OX}.$

On the Aluminium Hydroxide Sol Prepared by Autoclave Treatment.

By Tominosuke KATSURAI and Tatsuyuki KITA.

(Received October 3, 1940.)

There are several methods for the preparation of aluminium hydroxide sol. However, nothing seems to have been said about the preparation by autoclave treatment. In this article we should like to give an account of this method.

Method. Gelatinous precipitate of aluminium hydroxide is obtained by adding ammonia, a little in excess, into a solution of AlCl_3 at room temperature under stirring. The precipitate is settled by centrifuging and the clear upper liquid is discarded. The precipitate is washed with water and subjected to centrifuging. This procedure is repeated three or four times until the upper liquid shows no coloration with phenolphthalein, but still shows a distinct reaction of chlorine with AgNO_3 . The upper liquid and the precipitate are thoroughly mixed and transferred to a beaker of fused quartz. The beaker is placed in an autoclave of steel. The autoclave is then heated at 190°C for one hour⁽¹⁾. After the autoclave has cooled down to the room temperature, the beaker is taken out, and we find a uniformly turbid sol in the beaker⁽²⁾.

The sol is stable and does not coagulate after standing over three weeks at room temperature. The sol remains stable for 4 or 5 days after the chlorine contained in it has been removed by dialysis. The dialysis was carried out against water, using a collodion bag, until the water shows no reaction of chlorine with AgNO_3 .

In preparing the sol, it is necessary to let a small quantity of chlorine remain in the precipitate of aluminium hydroxide. When the precipitate

(1) For details of experimental technique, Cf. T. Katsurai, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **35** (1939), 191.

(2) An example of preparation is as follows. We start by mixing 100 c.c. of 1N AlCl_3 and 150 c.c. of 1N NH_4OH . The concentration of the sol obtained is found, by chemical analysis, to be 1.0 g Al_2O_3 per 100 c.c. of the sol.

is washed completely free of chlorine, sol formation does not take place by the autoclave treatment (190°C –1 hr.). The precipitate remains unchanged at the bottom of the beaker.

This precipitate shows an amorphous pattern when it is studied by means of X-ray. In the experiment Mo $K\alpha$ -radiation was used, the experimental conditions being; filter= ZrO_2 , voltage= 45kV ., current= 7 mA ., time of exposure= 12 hr ., the distance between the capillary and the film= 50.1 mm .

Repeated autoclave treatment (190°C –1 hr.) of the precipitate, to which is added a small quantity of NH_4Cl , does not cause sol formation.

*The Institute of Physical and Chemical Research,
Komagome, Hongo, Tokyo.*

Quelques observations sur le symplexe, pseudoglobuline-lécithine dans le vitellus.

Par Koichi SATO.

(Reçu le 4 Octobre 1940.)

L'étude du symplexe de pseudoglobuline et lécithine présente un grand intérêt biologique et immunologique. Chick a formulé l'hypothèse que l'euglobuline est un complexe, pseudoglobuline-lécithine. Pirotsky et Modern⁽¹⁾ ont recherché si l'insolubilisation de la pseudoglobuline par l'action de la lécithine est un simple changement de degré de dispersion ou bien une véritable transformation chimique. Ils ont décidé immunologiquement que le complexe pseudoglobuline-lécithine se comporte comme la pseudo-globuline exempte d'euglobuline.

La méthode de la délipidation à peu près totale des protéides est celle de Hardy et Gardiner. Il nécessite l'emploi des appareils permettant de réaliser une longue série de lavage des protéides par l'alcool absolu à une température inférieure à -5°C . Ce lavage doit être suivi d'une série d'épuisement à l'éther. Macheboeuf et Tayeau⁽²⁾ ont réussi à trouver les méthodes permettant de délipider, sans dénaturation, par une solution d'oléate de sodium, de palmitate ou dibromstéarates de potassium ou de sodium.

J. Needham et J. R. Robinson⁽³⁾ ont préparé la livetine, pseudo-globuline de vitellus dont la description classique est celle de Kay et Marshall. Ils ont observé une réfraction double d'écoulement assez marquée, thixotropie et rhéopexie chez la livetine. D'après eux, la vitel-

(1) I. Pirotsky et F. Modern, *C. r. soc. Biol.*, **114** (1933), 387-389.

(2) M. A. Macheboeuf et F. Tayeau, *ibid.*, **129** (1938), 1181-1183, 1184-1186.

(3) J. Needham et J. R. Robinson, *ibid.*, **126** (1937), 163-165.

line elle-même ne donnait rien de ces effets, la vitellomucoïde (protéine précipitable par l'alcool après la récolte de la livetine) non plus.

Nous avons étudié si la vitelline est un symplexe, pseudoglobuline-lécithine, qu'on peut préparer sans dénaturation, et en même temps recherché si on peut produire le symplexe par l'addition de lécithine à livetine.

(1) *La séparation de la pseudoglobuline et la lécithine dans le vitellus.* Nous avons employé de diverses méthodes pour la séparation de pseudoglobuline. Les voici:

1°. On peut préparer livetine et lécithovitelline de vitellus d'après Kay et Marshall. On mélange le vitellus avec une solution de chlorure de soude (10 pour 100) et après l'extracton des substances lipidiques avec de l'éther, on précipite la lécithovitelline en soumettant la solution à la dialyse. La livetine précipite quand on porte la solution à la demi-saturation avec le sulfate d'ammonium. La lécithovitelline précipitée par dialyse est extraite avec de l'éther, et puis on l'agite fortement. Mais on ne peut plus voir aucun changement.

2°. On porte la solution (NaCl 10 pour 1000) de lécithovitelline à la demi-saturation avec le sulfate d'ammonium (pH 3.8). On introduit le précipité avec une grande quantité d'éther dans une bouteille, où on place des perles en verre, et on l'agite fortement. Après la répétition de ce traitement, on y verse cinq volumes d'eau et obtient une solution transparente, dont la lécithovitelline délipidée, c'est à dire, pseudoglobuline précipite à demi-saturation avec sulfate d'ammonium. Dans ce cas, une petite partie de protéine pourrait être dénaturée et précipitée.

3°. T. Mori⁽⁴⁾ a employé une solution diluée de chlorure de soude (1 pour 100) au lieu de sa solution concentrée (10 pour 100). Après précipitation avec le sulfate d'ammonium (ajoutant une petite quantité de l'acide chlorhydrique), on agite fortement le précipité dans une bouteille avec des perles en verre. Alors on obtient uniquement pseudoglobuline, livetine.

4°. La lécithovitelline peut être bien séparée par la méthode de Hardy et Gardiner.

5°. On ajoute de l'éther à la lécithovitelline précipitée par le sulfate d'ammonium et on l'expose aux ondes ultrasonores pendant 30 secondes, et puis on renouvelle l'éther et l'expose de nouveau pendant 30 secondes.⁽⁵⁾ On peut ainsi obtenir la pseudoglobuline.

6°. La lécithovitelline peut être délipidée avec l'éther à 40°C. Dans ce cas la dénaturation partielle est inévitable.

7°. On peut séparer par l'emploi de mélange de l'éther et le chloroforme ou bien de l'éther et l'alcool à la température basse.

(2) *Synthèse du symplexe de la livetine et la lécithine.*

Nous ajoutons en agitant fortement deux ou trois gouttes de solution étherique saturée de lécithine dans la solution de la livetine (1 pour 100).

(4) Nous remercions M. Takeshi Mori de l'institut de botanique de l'Université Impériale de Tokyo qui nous a prodigué des conseils judicieux.

(5) M. Nobuzo Narusé, l'assistant de SIOMI-Institut des recherches physiques et chimiques, a trouvé que cette méthode est applicable. Nous l'en remercions bien cordialement.

Au-dessus de pH 4 le symplexe livetine-lecithine précipite complètement, et au-dessous de pH 4 le symplexe est assez instable. En outre, chez la solution de chlorure de soude (10 pour 100), il paraît que le symplexe soit soluble au-dessus de pH 4; tandis qu'au-dessous de pH 4 il précipite comme lécithovitelline. Conséquemment, nous avons filtré la solution salée du symplexe au-dessus de pH 4 avec le papier et l'avons dialysé. Ainsi la précipitation en fut induite. Ce précipité se dissout dans la solution de chlorure de soude. Quand j'avais déjà écrit ce rapport, j'ai trouvé le travail de Hofer cité par J. A. Smith⁽⁶⁾. Les lécithine-protéines synthétiques ont été produits par Hofer en ajoutant la solution alcoolique de lécithine à l'albumine de la sérum.

L'union chimique entre la pseudoglobuline et la lécithine est séparable au-dessous de pH 4 à l'existence de sulfate d'ammonium par l'éther sous le traitement mécanique. Cette union est instable à l'alcool ou l'éther chauffé.

Malheureusement, il nous manque de méthode pour rechercher la mode d'union entre ces deux substances, et nous ne pouvons pas assurer si les deux pseudoglobuline, livetine et lécithovitelline délipidée sont égales.

Nous tenons à témoigner nos profonds remerciements à M. le Prof. Y. Go qui nous a donné toujours l'aide et l'encouragement.

*L'Institut des recherches de fibre,
L'Université Impériale d'Osaka.*

(6) J. A. B. Smith, *Annual Rev. of Biochem.*, **9** (1940), 110.

Absorptionsspektren von Metallkomplexsalzen des 2,2'-Dipyridyls. IV.⁽¹⁾

Von Kazuo YAMASAKI.

(Eingegangen am 1 Novembre 1940.)

In vorliegender Arbeit wird die spektrochemische Untersuchung der Eisenkomplexsalze des 2,2'-Dipyridyls und Cyans berichtet. Die untersuchten Komplexsalze sind: $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$, $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$, $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$, $[\text{Fe}(\text{CN})_6]\text{K}_4$ und $[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$, wobei *Dip* 2,2'-Dipyridyl bedeutet. Da nur das Salz $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$ in Wasser unlöslich ist, wurde seine Lichtabsorption in alkoholischer Lösung gemessen, während die der anderen Komplexsalze in wässrigen Lösungen beobachtet wurde. Die Absorptionskurven sind in Abb. 1 dargestellt, in denen die Logarithmen des molaren Extinktionskoeffizienten (ϵ) auf der Ordinate aufgetragen wurde.

(1) I Mitt., dies Bulletin, **12** (1937), 390; II Mitt., ebenda, **13** (1938), 538; III Mitt., ebenda, **15** (1940), 130.

Absorptionsbanden

Komplexsalz	$\lambda_{\max} (\log \epsilon_{\max}), \lambda \text{ in } m\mu.$			
	I	II	III	IV
$[\text{Fe}(\text{Dip})_3]\text{Cl}_2$ (2)	520 (3.85)	352 (3.79)	298+289 (4.78)	246 (4.40)
$[\text{Fe}(\text{Dip})_2(\text{CN})_2]$	570 (3.78)	372 (3.79)	300+291 (4.68)	247 (4.38)
$[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$	480 (3.37)	342 (3.56)	296 (4.38)	—
$[\text{Fe}(\text{CN})_6]\text{K}_4$	—	330 (2.3)*	—	—
$[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$	620 (2.25)	360 (3.2)*	300 (4.58)	—

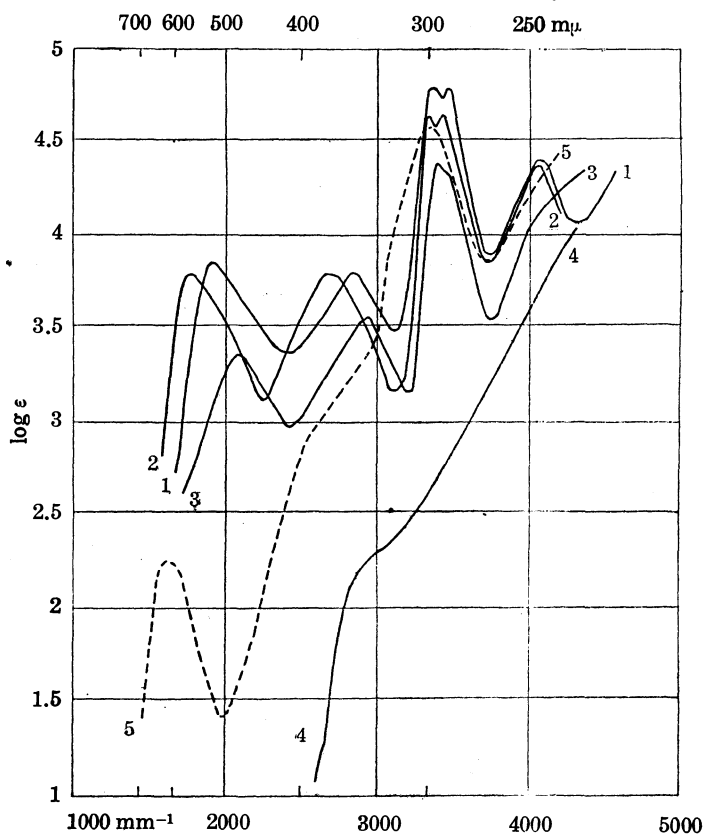


Abb. 1. Kurve 1: $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$, 2: $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$, 3: $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$.
4: $[\text{Fe}(\text{CN})_6]\text{K}_4$, 5: $[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$.

Alle diese Komplexsalze zeigen drei oder vier Absorptionsbanden. Wie schon in früheren Mitteilungen diskutiert, sind die dritte und vierte Banden bei ca. 295 und 246 $m\mu$ charakteristisch zur Dipyridyl-

(2) Die Lichtabsorption von $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$ ist fast gleich in Wasser wie in Alkohol. Die qualitativen Daten über seine Absorptionsbanden in alkoholischer Lösung, welche in der ersten Mitteilung von dieser Untersuchung berichtet wurden, werden hier durch die neuen quantitativen Daten ersetzt.

* Der Knick der Absorptionskurve.

molekül enthaltenden Komplexsalze, d.h. sie sind den koordinierten Dipyridylmoleküle zuzuschreiben. Diese Banden sind der Zahl der Dipyridylmoleküle im Komplexradikal abhängig, d.h. in $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$ und $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$ welche resp. drei und zwei Dipyridylmoleküle enthalten, spaltet sich die dritte Band bei $295\text{ m}\mu$ in zwei schmalen Banden und die vierte Band erscheint sich bei $246\text{ m}\mu$, während in $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$ welches nur ein Dipyridylmolekül in Liganden enthält, die Feinstruktur der dritten Band und die ganze vierte Band gleichzeitig verschwinden. Der ϵ -Wert der dritten Band ist zwar fast proportional der Zahl der koordinierten Dipyridylmoleküle im Komplexradikal wie folgt:

Komplexsalz	Zahl der Dipyridylmoleküle	$\log \epsilon$	Verhältnis der ϵ -Wert.
$[\text{Fe}(\text{Dip})_3]\text{Cl}_2$	3	4.78	2.5
$[\text{Fe}(\text{Dip})_2(\text{CN})_2]$	2	4.68	2.0
$[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$	1	4.38	1.0

Diese interessante Tatsache wurde früher von Tsuchida⁽³⁾ auch bei $[\text{Cr}(\text{NH}_3)_5\text{NCS}](\text{NCS})_2$, $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]\text{NH}_4$ und $[\text{Cr}(\text{NCS})_6]\text{K}_3$ beobachtet, und es wurde dabei bestätigt, dass der ϵ -Wert der eigentlichen Band des NCS-Radikals ebenfalls seinen Zahlen proportional ist.

Diese Substitution der Dipyridylmoleküle im Komplexradikal durch CN verursacht die regelmässige Verschiebung von Absorptionsbanden. Die Banden von $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$ befinden sich also im Spektralgebiet von längeren Wellenlänge als die des Salzes $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$; dagegen beobachtet man bei $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$ wiederum die Bandenverschiebung nach Violett, trotzdem die Zahl von CN-Radikal dabei weiter sich vermehrt. Bei dieser Verschiebung der Banden bleiben die Abstände derselben, d.h. $(\lambda_I - \lambda_{II})/(\lambda_{II} - \lambda_{III})$ immer unverändert:

$[\text{Fe}(\text{Dip})_3]\text{Cl}_2$	$(520-352)/(352-298) = 3.1$,
$[\text{Fe}(\text{Dip})_2(\text{CN})_2]$	$(570-372)/(372-300) = 2.8$,
$[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$	$(480-342)/(342-296) = 3.0$.

Die erste Band von $[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$ verschiebt sich nach Rot und ihre Extinktionskoeffizient ist erniedrigt im Vergleich mit $[\text{Fe}^{\text{II}}(\text{Dip})_3]\text{Cl}_2$. Die dritte Band des ersteren Salzes ist ebenfalls nach Rot verschoben und seine Absorptionskante deckt die zweite Band, die wie ersichtlich in der Abb. 1' einen Knick der Kurve darstellt.

Experimenteller Teil. Zur Messung der Lichtabsorption dienen das Nuttingsche Spektrophotometer und der Hilgerschen Quarzspektrograph mit rotierendem Sektor. Als Lichtquelle wurden die Eisen-Nickel Funken und die Wasserstofflampe benutzt.

$[\text{Fe}(\text{Dip})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$: Konzentrationen der benutzten Lösung: 1/8000, 1/40000 und 1/80000 Mol.

$[\text{Fe}(\text{Dip})_2(\text{CN})_2]$ und $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$ wurden nach den Angaben von Barbieri⁽⁴⁾ dargestellt. Durch Einwirkung einer berechneten

(3) R. Tsuchida, dies Bulletin, **13** (1938), 471.

(4) G. A. Barbieri, Atti Accad. Lincei, rendiconti, **20** (1934), 173.

Menge von KCN auf $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$, welche in möglichst wenig Wasser gelöst wurde, scheiden sich rotviolette Kristalle des $[\text{Fe}(\text{Dip})_2(\text{CN})_2] \cdot 3\text{H}_2\text{O}$ ab. Sie sind in Wasser unlöslich, aber leicht löslich in Alkohol mit rotvioletter Farbe. Um noch eine Dipyridylmolekül durch CN ersetzen zu lassen, wurden die Kristalle von $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$ mit der konzentrierten Lösung des KCN auf dem Wasserbad erwärmt. Durch Eindampfen der so entstandenen Lösung erhält man orangerote Kristalle von $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2 \cdot 3\text{H}_2\text{O}$. Diese Verbindung ist in Wasser löslich und wurde durch Umkristallisieren von beigemengten KCN befreit. Die Analysendaten dieser zwei Verbindungen stimmten gut mit den oben gegebenen Formeln überein. Die Konzentrationen der alkoholischen Lösung des $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$ sind 1/8000, 1/32000 und 1/40000 Mol, und die der wässrigen Lösung des $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$ sind 1/5000 und 1/40000 Mol.

$[\text{Fe}(\text{CN})_6]\text{K}_4 \cdot 3\text{H}_2\text{O}$: Das reinste käufliche Produkt wurde aus dem Wasser umkristallisiert. Da ihre wässrige Lösung durch Licht eine Zersetzung erleidet, so wurde die Lösung für Absorptionsmessung wiederholt während der Aufnahme erneuert. Die Konzentrationen der Lösung sind 1/10, 1/100 und 1/1000 Mol.

$[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$: Durch die Oxydation der wässrigen Lösung von $[\text{Fe}^{\text{II}}(\text{Dip})_3]\text{Cl}_2$ durch Chlorwasser wurde eine blaue Lösung von $[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$ gebildet⁽⁵⁾. Dieses Komplexsalz ist nur als eine Lösung bekannt und kann nicht im festen Zustand erhalten werden. Also wurde die chlorhaltige blaue Lösung ohne weitere Behandlung zur Messung benutzt. Da die Konzentration der $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$ -Lösung und ihre Mischungsverhältnisse mit dem Chlorwasser bekannt sind, kann die Konzentration des Ferrikomplexsalzes leicht berechnet werden. Die so berechneten Konzentrationen der benutzten Ferrikomplexsalzlösungen sind 1/3000, 1/4000 und 1/43000 Mol. Die möglichst geringe Menge des Chlorwassers⁽⁶⁾ wurde für die Oxydation der $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$ -Lösungen verwendet, weil das Chlorwasser seine eigene Absorptionsband bei 320 m μ , d.h. am Nahe der Banden des Ferrikomplexsalzes zeigt und die Messung der genannten Band dadurch stark gestört wird. Um diese Störung der von Chlorwasser verursachten Band völlig zu vermeiden wurde die wässrige Lösung welche die gleiche Menge von Chlorwasser wie die Ferrikomplexsalzlösung enthält hergestellt, und diese Lösung wurde als Kontrollflüssigkeit der Extinktionskoeffizientenmessung benutzt. Die blaue Lösung des Ferrikomplexsalzes ist unbeständig gegen Licht, also wurde die Lösung für die Absorptionsmessung während der Aufnahme auch wiederholt erneuert.

Zusammenfassung.

Die Absorptionsspektren von $[\text{Fe}(\text{Dip})_3]\text{Cl}_2$, $[\text{Fe}(\text{Dip})_2(\text{CN})_2]$, $[\text{Fe}(\text{Dip})(\text{CN})_4]\text{K}_2$, $[\text{Fe}(\text{CN})_6]\text{K}_4$ und $[\text{Fe}^{\text{III}}(\text{Dip})_3]\text{Cl}_3$ wurden untersucht. Der Ersatz der Dipyridylmoleküle im Komplexradikal durch CN

(5) F. Blau, *Monath.*, **19** (1898), 658.

(6) Das verwendete Chlorwasser enthält 0.33 g Cl/L.

verursacht die regelmässige Verschiebung der Absorptionsbanden. Der ϵ -Wert der eigentlichen Band der koordinierten Dipyridylmoleküle ist fast proportional seiner Zahl im Komplexradikal.

Es sei mir gestattet, Herrn Prof. Yuji Shibata für seine freundliche Anleitung und Ratschläge bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

*Chemisches Institut, Naturwissenschaftliche Fakultät
Kaiserliche Universität zu Tokyo.*

Studies on the Oiliness of Liquids. X. The Friction Coefficients of Mono- and Multi-molecular Layers.*

By Toshizo ISEMURA.

(Received November 22, 1940.)

In one of the preceding papers of this series, the static friction coefficients of glass surfaces on which monomolecular and multimolecular layers of some long chain fatty acids such as palmitic or oleic acid were deposited, had been reported⁽¹⁾. The friction coefficients of glass surfaces lubricated with such films are about one tenth of that of clean glass. These low friction coefficients were ascribed to the regular arrangement of the molecule. In the present experiment, the friction coefficients of some long chain compounds and cholesterol were measured and the effects of various conditions were also studied.

The friction coefficients were measured by the balance method. The experimental procedure and cleansing of the glass surfaces are quite the same as described in the former papers.⁽²⁾ The deposition of the monomolecular and multimolecular layers of such long chain compounds on the glass surface were conducted by Langmuir-Blodgett's technique.⁽³⁾ When no indication is made, tap water was used as the substrate water which was regulated its pH value to about 9 by the addition of a small quantity of ammonia. The results are summarized in Table 1. The piston oil used in the deposition of the film is also indicated in the table.

Acids show low friction coefficients, while alcohols show relatively high friction coefficients. Moreover, the values of friction coefficients of alcohols, and ester fluctuate considerably, especially in the cases of tetradecyl and cetyl alcohol. In the table, only the two extreme values were recorded. When the film of long chain acid such as stearic acid was deposited on the glass surface by withdrawal of the glass plate from the water covered with monomolecular film, water is entirely repelled from the glass surface. On the other hand, when the film of alcohol or ester was deposited in the same way, the glass plate was wetted by water. If the glass plate was withdrawn too slowly out of the water surface, the film may slip down from the plate on the water surface. By the withdrawal of the moderate speed the film was transferred on the glass with water and this was dried in desiccator by passing the current of dry air, and used for the friction measurement. By this procedure, the arrangement of the molecules in the deposited film may be irregular. This is a reason of the high friction coefficient and its fluctuation.

The friction coefficient of oleic acid is 0.20 when castor oil was used as the piston oil⁽¹⁾ and somewhat higher than that of elaidic acid. The

* IX, this Bulletin, 15 (1940), 288.

(1) H. Akamatu and J. Sameshima, this Bulletin, 11 (1936), 791.

(2) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, 11 (1936), 659.

(3) K. Blodgett, *J. Am. Chem. Soc.*, 57 (1935), 1007.

Table 1.

Clean glass: $\mu = 1.04$

Film substance	Piston oil	μ	μ Mean
Elaidic acid	Castor oil	0.10	0.12
		0.12	
		0.12	
		0.13	
		0.10	
		0.14	
		0.10	
		0.13	
		0.10	
Myristic acid	Castor oil	0.18	0.18
		0.20	
		0.14	
		0.22	
		0.18	
	Oleic acid	0.12 0.12	0.12
Linolic acid	Castor oil	0.11 0.15 0.10	0.12
	Oleic acid	0.13 0.09 0.11	0.11
Brassicidic acid	Castor oil	0.12	
	Oleic acid	0.11 0.10	0.11
Erucic acid	Castor oil	0.12 0.10 0.11 0.14	0.12
Cerotic acid	Castor oil	0.20 0.13 0.17 0.12	0.16
	Oleic acid	0.17 0.14 0.17	0.16
Triolein	Castor oil	0.20 0.18 0.16 0.17	0.18
Myricyl alcohol	Oleic acid	0.17 0.18 0.19 0.17 0.16	0.17

Table 1.—(Concluded)

Film substance	Piston oil	μ	μ Mean
Cholesterin	Castor oil	0.22 0.21 0.21	0.21
	Oleic acid	0.22 0.22	0.22
Tetradecyl alcohol	Castor oil	0.23~0.45	
	Oleic acid	0.19~0.47	
Cetyl alcohol	Castor oil	0.25~0.50	
	Oleic acid	0.18~0.52	
Octadecyl alcohol	Castor oil	0.18~0.34	
	Oleic acid	0.17~0.32	
Methyl palmitate	Castor oil	0.37~0.46	
	Oleic acid	0.32~0.46	

structure of the oleic acid is a cis-form while that of elaidic acid is a trans-form. Elaidic acid can be more closely packed than oleic acid. This fact may be a reason of the different friction coefficients of these two acids which have the same molecular formula. However, brassidic and erucic acid show almost the same friction coefficient. In the films of acids which are solid in ordinary temperature, the arrangement of the molecules is more regular than in that of liquid acids when the films are deposited in compressed state. This fact is a probable reason why oleic acid shows a relatively high friction coefficient. Cholesterin film shows the friction coefficient of the order of that of oleic acid.

In the former communication, it had been also reported that no further reduction of friction coefficient was observed by the increase of thickness of the film. However, in the present experiment it was found that the reduction of friction coefficient is caused definitely by the increase of the thickness of film. The friction coefficient diminishes gradually down to the penta- or heptamolecular layers, and then no further reduction could be recognised. Table 2 and Fig. 1 show the results. Oleic acid is only an exception. This is caused by the liquid nature of the substance in an ordinary temperature. When the number of layers are built up, assemblage of molecules in the film gains gradually the nature of liquid and the orientation of molecules in the film becomes somewhat more ir-

Table 2. μ of multimolecular layers.

Number of layers	Stearic acid	Oleic acid	Brassicidic acid	Erucic acid	Palmitic acid
1	0.12	0.14	0.11	0.12	0.10
3	0.09	0.12	0.08	0.08	0.09
5	0.06	0.14	0.07	0.08	0.07
7	0.06	0.15	0.08	—	0.06
9	0.06	0.17	0.08	—	0.06
11	—	—	—	—	0.06

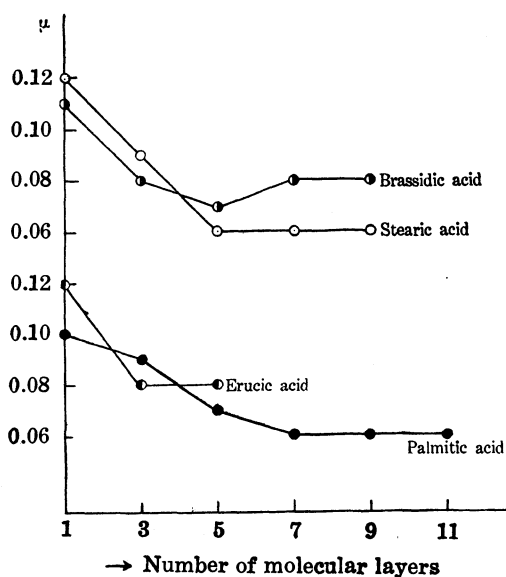


Fig. 1.

regular, so that the friction coefficient of oleic acid increases. Germer and Storks⁽⁴⁾ found by the examination of monomolecular and multimolecular layers with electron diffraction that on a clean metal surface molecules of the first layer stand with the axes of the hydrocarbon chains normal to the surface and the chains closely packed together laterally but irregularly arranged whereas in layers on top of the first, molecules of barium stearate or of stearic acid are regularly arranged. Accordingly, the fact that the friction coefficients of multimolecular layers being lower than that of monomolecular layers can be ascribed to more regular arrangement of the molecules in the film.

The effect of compression of the film by some piston oils of different spreading pressures during the deposition of film on the glass is also investigated. The results which were obtained by using oleic acid and castor oil as piston oil are shown partly in Table 1. The low pressure piston oils were prepared according to the indication of Norris and Taylor.⁽⁵⁾ The mixtures of various compositions of ethyl myristate and liquid paraffin which was specially purified for this purpose, were used. The spreading pressures were measured by Adam-Jessop's surface balance, and shown in Table 3. With these piston oils the effect of compression were studied. The results are shown in Table 4.

(4) Germer and Storks, *J. Chem. Phys.*, **6** (1938), 280.

(5) Norris and Taylor, *J. Chem. Soc.*, **1938**, 1719.

Table 3.

Piston oil	% of ethyl myristate	Spreading pressure (dyne/cm.)
No. 1	47.2	13.4
No. 2	32.8	10.5
No. 3	18.1	8.2
No. 4	10.1	5.1

Table 4.

Piston oil	Palmitic acid μ	Myristic acid μ
Oleic acid	0.10	0.12
Castor oil	0.11	0.18
No. 1	0.11	0.20
No. 2	0.12	0.18
No. 3	0.13	0.22
No. 4	0.13	0.21

From Table 1 and 4 we see that there occurs, generally, a small change in the values of friction coefficient by changing the piston oils of different spreading pressures. However, the value of μ increases definitely with the decrease of spreading pressure. Relatively large difference of μ was detected with myristic acid. Myristic acid makes an expanded film and the compressibility of the film is larger than the other substances which make the condensed film. In expanded film, molecules arrange rather irregularly even though the film is transferred on the glass plate in compressed state. Myristic acid film may be partly collapsed by the spreading pressure of oleic acid. The film of myristic acid which was deposited in compressed state by oleic acid could not be purely monomolecular.

Subsequently, the effect of the hydrogen ion concentration of the substrate water was investigated. The film transferred from acidic substrate has higher friction coefficient than that transferred from basic substrate. The results are shown in the second column of Table 5. The substrate was distilled water in which barium chloride and potassium bicarbonate were added in the concentration of 10^{-4} mol per litre, and the value of pH was regulated by the addition of ammonia. Stearic acid was used as an film substance. The glass plates on which stearic acid

Table 5.

pH	μ	μ'	% of the fractional conversion to neutral soap
6.50	0.19	0.56	48
6.75	0.16	0.60	54
6.93	0.17	0.54	58
7.39	0.15	0.49	67
8.18	0.12	0.36	80
9.00	0.12	0.24	89
9.26	0.12	0.23	91
9.38	0.12	0.22	92
9.69	0.11	0.16	93

film were deposited by Blodgett's method from the substrate water containing a small quantity of barium ion, were coated by a monomolecular layer consisting of a mixture of stearic acid and barium stearate. These plates were dipped in benzene for about 0.5~1 minute and after withdrawing the plate, the friction coefficients were reinvestigated. It was known that plate coated with the film from basic substrate had relatively low friction coefficient, while the plate coated with the film from acidic substrate had relatively high friction coefficient. According to Langmuir and Schaefer, the film of fatty acid contains metals if the substrate water contains some alkaline earth metals.⁽⁶⁾ The films formed by stearic acid are nearly pure neutral soap when the water is strongly alkaline, while they are of free acids when pH 3. The ratio of free acids and barium or calcium salts varies according to the values of pH. By dipping the plates coated with film in benzene, the free acids may be dissolved whereas the barium salts does not. So that, the friction coefficients of glass surfaces which were covered with the film from acidic substrate, increase considerably by dipping the plate in benzene. However, the plate covered with films from basic substrate show almost the same friction coefficients as before. In the intermediate range of pH the friction coefficients change with pH. The friction coefficients after dipping in benzene (μ') are shown in the third column of Table 5.

The ratio of barium stearate in the film can be calculated by the experimental formula of Langmuir and Schaefer⁽⁶⁾:

$$\log \frac{f}{f' - f} = -2.41 + 0.367 \cdot \text{pH}$$

where f denotes the fractional conversion to neutral soap and f' the limiting value of f for high values of pH and shown in the fourth column of the table. The friction coefficients decrease almost linear with the ratio of the fractional conversion to neutral soap. Fig. 2 shows the result.

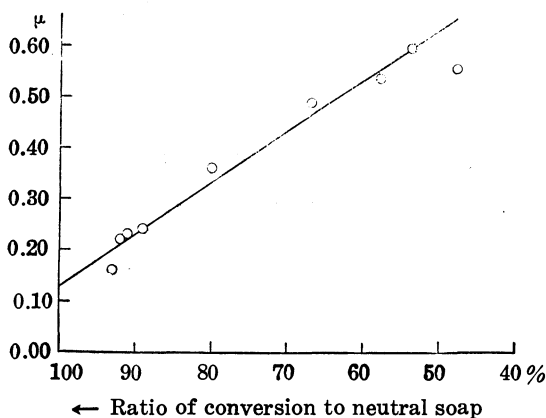


Fig. 2.

In the course of the present experiments, it was experienced that the stearic acid film spread on tap water can be transferred on glass plate more readily than that spread on distilled water only. The force-area relation of the film were studied with stearic acid both on tap water and distilled water using Adam-Jessop's surface balance. The force area curves obtained are reproduced in Fig. 3. It was found that the area occupied by a single molecule is 20.6 sq.

(6) Langmuir and Schasfer, *J. Am. Chem. Soc.*, **58** (1936), 284.

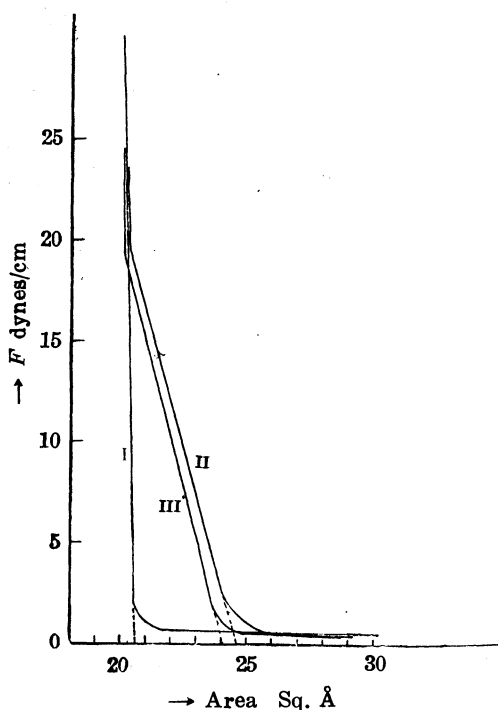


Fig. 3.

concentration of 0.05 mol per litre, area per single molecule was increased to 24.1 sq. Å. In Fig. 3, I shows the F-A curve of the stearic acid film on tap water, II that on fresh distilled water and III that on tap water added with ammonium oxalate.

In conclusion, the author expresses his hearty thanks to Prof. J. Sameshima for his kind guidance and encouragement throughout the present work. The expense for the experiments has been defrayed from the grant given to Prof. Sameshima by Nippon Gakujutu Sinkokai (Japan Society for the Promotion of Scientific Research), to which author's thanks are due. The author's acknowledgement is also due to Hattori Hokokai for a grant.

Summary.

(1) The static friction coefficients of glass surfaces covered with the mono- and multi-molecular layers of some long chain acids etc. have been measured.

(2) The friction coefficients of glass covered with monomolecular film of acids are about one tenth of that of clean glass. The friction coefficients of alcohols and esters are somewhat higher but fluctuate considerably.

(7) R. J. Myers and W. D. Harkins, *Nature*, **139** (1937), 368.

Å. on tap water and 24.6 sq. Å. on fresh distilled water. Molecules are more closely packed in the film on tap water than that on distilled water. Molecules in the film on tap water attract each other by lateral forces so that films are stabilised more firmly than the film on distilled water and transferred more readily. On the same reason the films might be deposited on glass plate more readily from basic substrate than from acidic substrate on which molecule occupies larger area.

The effect of the minute amount of metallic ion on the monomolecular films formed by the substance with acidic group was first indicated by Myres and Harkins⁽⁷⁾. The small limiting area of stearic acid on tap water may be ascribed to the effect of the presence of calcium ion in tap water. If ammonium oxalate was added to the tap water in the con-

(3) The friction coefficients of multimolecular layers decrease by the increase of their thickness until it becomes five or seven molecular layers, but shows no further reduction.

(4) The effect of compression during the deposition of the film was investigated. The film deposited in high compression state shows low friction coefficient.

(5) The film deposited from basic substrate shows lower friction coefficient than that deposited from acidic substrate.

(6) The force area relations of stearic acid monolayer have been studied on fresh distilled water, on tap water, and on tap water added with ammonium oxalate in relation to the transference of the film on the glass plate.

*Chemical Institute, Faculty of Science,
Tokyo Imperial University, Tokyo.*

Polymerisation of Tung Oil. III. Molecular Weights of Tung Oil and its Polymerides.

By Monzi TATIMORI.

(Received November 27, 1940.)

The determination of molecular weights of drying oils has the marked importance for the elucidation of polymerisation and oxidation mechanism. However, the results obtained are generally discrepant even with the standard methods. It has been generally known that the molecular weights of fatty oils determined by the cryoscopic method vary to a great extent with the solvent and concentration⁽¹⁾. As solvent camphor, benzene, nitrobenzene and others are generally used.

The molecular weight to be determined cryoscopically is calculated by the formula: $M=KC/\Delta T$, where K is the calculated depression of the freezing point due to 1 gram molecule of any solute in 100 g. of solution, C the concentration of solute in gram per 100 g. of solution, and ΔT , the observed depression of the freezing point. The molecular weight (which will hereafter be denoted briefly as M) calculated from the above formula is a linear function of concentration (C) in the range of dilute solution.

The true molecular weight corresponding to zero concentration is obtained by extrapolation. But in the case of benzene solution the molecular weight of fatty oils is not a linear function of concentration and the extrapolation to zero concentration is practically impossible.

(1) Normann, *Chem. Ztg.*, **31** (1907), 211; H. J. Backer, *Chem. Weekblad.*, **12** (1915), 1034; Morrel, *J. Oil Colour Chem. Assoc.*, **7** (1924), 146; Seaton and Sawyer, *J. Ind. Eng. Chem.*, **8** (1916), 490; Rhodes and Welz, *ibid.*, **19** (1927), 68.

Nevertheless the cryoscopic method with benzene is usually preferred, because the operations are easily practicable. J. S. Long and J. G. Smull⁽²⁾ reported about the oxidation and polymerisation mechanism of linseed oil, using the data of the apparent molecular weight of a constant concentration (molecular weight of 1 g. of oil in 25 c.c. of benzene).

In the study of polymerisation of tung oil, the author reported⁽³⁾ that the molecular weights of polymerised tung oils calculated from the specific viscosity of benzene solution, when the molecular weight was assumed to be proportional to the specific viscosity, were too great as compared with that inferred from the chemical commonsense. Therefore it is very important to ascertain the relation of molecular weight of polymerised tung oil and the concentration of solution, and to obtain the molecular weight at zero concentration.

Experimentals. Tung oil used was characterized as follows: density (15/15°C.) 0.9409, iodine value (Wijs' method) 166.8, refractive index (n_D^{20}) 1.5164. The polymerised tung oils were obtained by polymerising the raw tung oil at 220°C. and had the following refractive index.

Table 1. Refractive index of polymerised tung oils.

Sample	Polymerisation time (m.)	n_D^{20}
No. 0	Raw oil	1.5164
No. 1	0	1.5122
No. 2	20	1.5109
No. 3	40	1.5097
No. 4	50	1.5090
No. 5	60	1.5082

(1) *Camphor method.* The determination of molecular weight by the melting point depression of camphor was carried out as in the usual method.

For the sake of comparison, the molecular weight of pure oleic acid was measured and the value 290 (calculated molecular weight 284) was obtained. The molecular weight of the polymerised tung oils are shown in table 2.

Table 2. Molecular weights of polymerised tung oils.

Sample	Concentration (%)	Depression of m.p. (ΔT °C.)	Calculated molecular weight
No. 0	4.11	2.25	906
	4.14	2.33	881
	5.01	2.67	931
	5.50	2.80	979
	5.66	3.30	852
	6.17	3.75	810
			893
No. 1	3.35	1.50	1111
	3.68	1.65	1110
	4.77	2.10	1130
	9.97	4.68	(1055)
			1110

(2) J. S. Long and J. G. Smull, *J. Ind. Eng. Chem.*, **17** (1925), 138, 905.

(3) M. Tatimori, *this Bulletin*, **13** (1938), 142.

Table 2.—(Concluded)

Sample	Concentration (%)	Depression of m.p. (ΔT °C.)	Calculated molecular weight
No. 2	4.29	1.68	1269
	4.94	2.00	1230
	5.33	2.50	(1060)
	6.26	2.83	1100
	6.30	2.70	1160
			1220
No. 3	4.42	1.60	1374
	5.28	2.10	1254
	6.50	2.60	1240
	6.63	2.70	(1201)
			1380
No. 4	3.82	1.20	1593
	4.35	1.50	1444
	5.82	1.90	1523
	6.21	2.40	1314
	7.32	3.30	(1140)
			1550

The apparent molecular weight by the camphor method decreases as the concentration increases, but within the range of dilute solution the constant molecular weight is obtained.

(2) *Benzene method.* The molecular weight of oleic acid was measured and the value 565 was obtained. This is twice as much as the theoretical value. The molecular weights of polymerised tung oils are shown in Table 3.

Table 3. Molecular weights of polymerised tung oils.

Sample	Solvent (g.)	Solute (g.)	Concentration (%)	ΔT (°C)	$\frac{\Delta T}{C} \times 10^2$	M
No. 0	17.862	1.145	6.02	0.362	6.01	852
		1.558	8.02	0.530	6.60	795
		1.890	9.57	0.680	7.10	721
No. 1	17.862	0.635	3.44	0.120	3.50	1465
		0.990	5.25	0.200	3.81	1344
		1.521	7.85	0.330	4.21	1217
		2.093	10.49	0.520	4.96	1033
	13.400	2.117	13.64	0.765	5.61	913
		2.368	15.02	0.893	5.95	949
		2.695	16.74	1.035	6.18	817
		3.044	18.52	1.260	6.81	752
No. 2	17.862	1.100	5.80	0.180	3.10	1650
		1.475	7.63	0.259	3.39	1508
		1.820	9.25	0.370	4.00	1280
		2.567	12.56	0.570	4.53	1128
	13.400	1.636	10.88	0.455	4.18	1225
		1.859	12.18	0.588	4.83	1061
		2.209	14.16	0.770	5.44	942
		2.361	14.98	0.840	5.61	913

Table 3.—(Concluded)

Sample	Solvent (g.)	Solute (g.)	Concentration (%)	ΔT (°C)	$\frac{\Delta T}{C} \times 10^3$	M
No. 3	17.862	1.202	4.84	0.150	3.10	2152
		1.699	6.67	0.265	3.98	1678
		1.957	7.58	0.320	4.23	1580
		2.500	9.42	0.450	4.78	1396
		1.812	11.91	0.440	3.69	1387
	13.400	2.154	13.85	0.555	4.01	1278
		2.374	15.05	0.645	4.29	1195
		2.528	15.87	0.705	4.44	1153
No. 4	13.400	0.989	6.87	0.148	2.15	2376
		1.415	9.55	0.255	2.67	1916
		1.717	11.36	0.330	2.91	1751
		1.888	12.35	0.385	3.12	1642
No. 5	17.862	1.078	5.69	0.128	2.25	2277
		1.720	8.78	0.203	2.31	2215
		2.203	10.98	0.330	3.01	1703
		2.468	12.14	0.440	3.30	1554
		2.344	14.89	0.585	3.93	1303
	13.400	2.651	16.52	0.710	4.30	1191
		2.743	16.99	0.750	4.41	1159
		2.910	17.88	0.835	4.67	1097

The relations between the apparent molecular weight and the concentration are shown in Fig. 1.

It is noticed that the apparent molecular weight decreases rapidly with increasing concentration. These values, obtained by the camphor method, may be accepted as probable molecular weights. But, for the data obtained in the benzene solution the linear relation does not hold between the apparent molecular weight and the concentration, therefore it is impossible to extrapolate to the zero concentration.

A fundamental difficulty in the determination of molecular weights of polymerised tung oil lies in the following fact: in order to increase the accuracy of the measurement, the concentration of the solution must be increased; for this purpose the concentration in weight percent becomes too high, nevertheless the concentration in mol percent remains small, because the molecular weight of polymerised tung oil is very great. This difficulty becomes more eminent as the molecular weight of the solute increases. An abnormally great value for the mole-

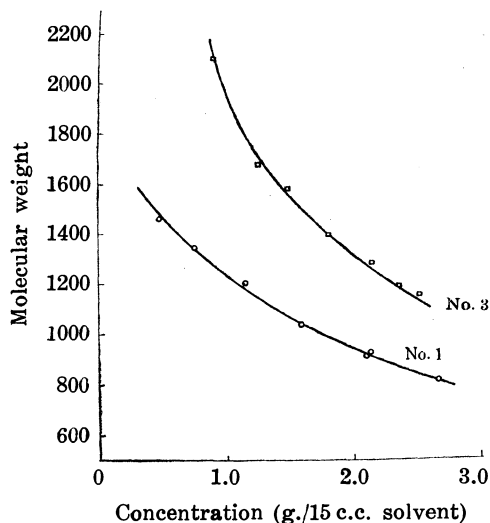


Fig. 1.

cular weight of polymerised tung oil in benzene solution was noticed by Gay⁽⁴⁾ and for which he obtained 4320.

This abnormality is probably due to an action between solute and solvent. In other solvents such great values are not obtained. The author carried out the molecular weight determination of another polymerised tung oil, using as solvent nitrobenzene, bromoform and ethylenebromide. With these solvents the linear function is held between the molecular weight and the concentration, and the values extrapolated to zero concentration are shown in Table 4.

Table 4.

Samples	Heating time at 206 °C. (m.)	n_D^{20}	Nitro- benzene	Bromoform	Ethylene bromide
No. 0	Raw oil	1.5193	800	800	830
1	0	1.5192	820	810	970
2	60	1.5171	960	1120	1160
3	120	1.5149	1320	1360	1420
4	180	1.5139	2095	1785	1940

Thus, reasonable values were obtained.

Gay reported that cyclohexane is an ideal solvent which displays no specific action on the solute. The author determined the molecular weight of raw tung oil in a purified cyclohexane and obtained the results shown in Table 5.

Contrary to other solvents the apparent molecular weight in cyclohexane increases with the increasing concentration and the value at zero concentration amounts to 970. This is a reasonable value for the molecular weight of commercial tung oil.

Discrepancies found between the theoretical value and the observed one may be explained by the mechanism of association of solute, solvation of solvent, association of solvent etc.

Table 5.

Sample (g.)	Melting point depression (ΔT °C.)	Molecular weight
0.3683	0.35	942
0.7721	0.70	1003
1.2168	1.09	1017
1.7161	1.49	1049

Table 6.

Sample	$\lim_{C \rightarrow 0} \Delta T/C$	$M_{C \rightarrow 0}$	M'
No. 0	4.35	1145	893
1	2.70	1845	1110
2	1.60	3110	1220
3	1.20	4150	1380
4	0.94	5030	1550
5	0.60	8300	—

(4) Gay, *Chemistry and Industry*, 1933, 70.

It is already known that some of high molecular compounds behave abnormally in the solution⁽⁵⁾. G. V. Schulz and his co-workers⁽⁶⁾ tried to obtain reasonable values for the molecular weight by the following formula, $M = RT / \lim_{C \rightarrow 0} (P/C)$, where P is the osmotic pressure and C the concentration.

In the case of benzene solution of polymerised tung oils the relation between $\Delta T/C$ and C may approximately be represented by a straight line. Thus the value of $\Delta T/C$ and molecular weight at zero concentration can be calculated as shown in Table 6.

In this table $M_{C \rightarrow 0}$ is the molecular weight calculated from $M_{C \rightarrow 0} = \frac{k}{100} \left(1 / \lim_{C \rightarrow 0} \frac{\Delta T}{C} \right)$, and M' the molecular weight determined by the freezing point depression of camphor. Further it is noticed that at the end of cooking the molecular weight of tung oil in benzene solution becomes very great, which coincides with the viscosity data⁽⁷⁾.

It is reasonable to think that this abnormality is due to the solvation of benzene. The relation between the molecular weight by camphor and benzene methods is shown in Fig. 2.

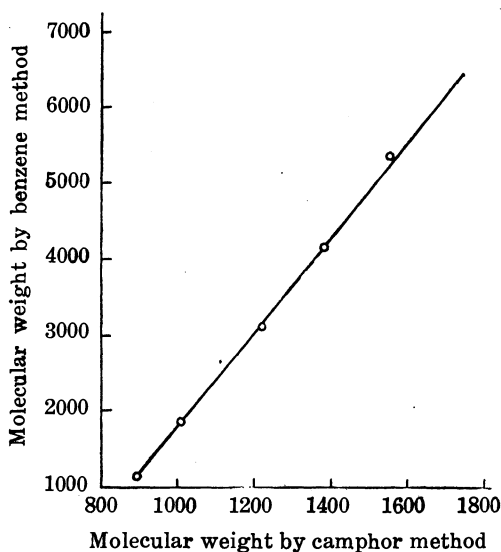


Fig. 2.

An approximate proportionality holds for them. The relations between the molecular weight by camphor method and refractive index, and also heating time of the oil are shown in Figs. 3 and 4.

(5) P. Stamberger and C. M. Blow, *Kautschuk*, **6** (1930), 22.

(6) G. V. Schulz, *Z. Phys. Chem. B*, **196** (1936), 317; G. V. Schulz and H. Staudinger, *Ber.*, **68** (1935), 2320; G. V. Schulz, *Z. angew. Chem.*, **49** (1936), 549.

(7) M. Tatimori, this Bulletin, **13** (1938), 142.

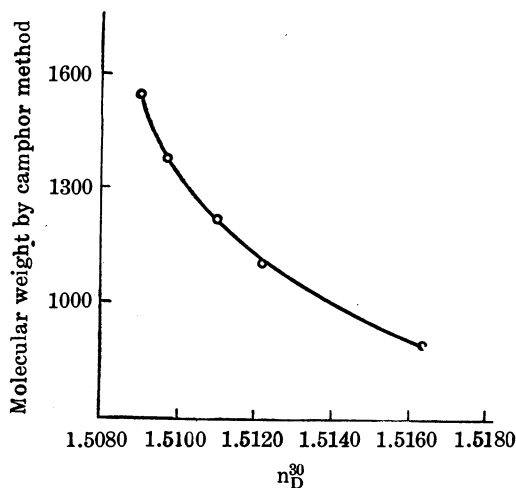


Fig. 3.

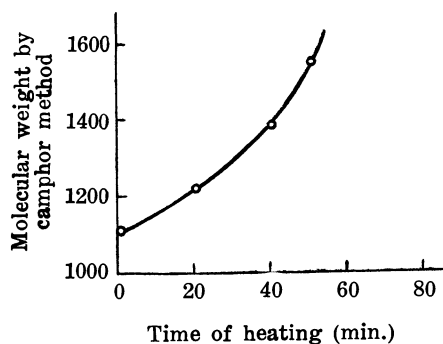


Fig. 4.

Summary.

The molecular weights of polymerised tung oils were measured in the solution of benzene, camphor, nitrobenzene, bromoform, ethylene bromide by the cryoscopic method.

By the camphor method reasonable molecular weights were obtained. But in benzene the molecular weight decreases rapidly with the increasing concentration. In nitrobenzene, ethylene bromide, bromoform the molecular weight behaves as linear function of concentration and the rate of decrease in molecular weight with increasing concentration is not so eminent as in benzene.

On the contrary in cyclohexane the molecular weight increases with the increasing concentration and reasonable values are obtained by extrapolation. The abnormality in benzene may be considered as the solvation action.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Mr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

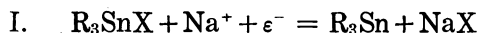
Laboratory of Hitachi Works, Hitachi Ltd.

On the Metallo-Organic Compounds. X. Electroisomerism in Triethyltin.

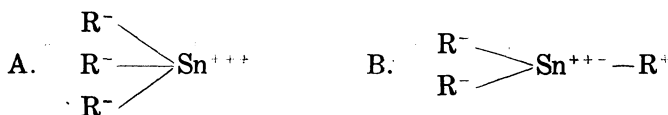
By Taichi HARADA.

(Received October 25, 1940.)

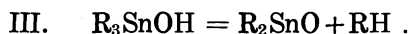
The triethyltin group may be prepared in various ways among which the two methods^{(1),(2)}—(1) the reduction of triethyltin halide⁽¹⁾, or the hydroxide and (2) the oxidation of sodium diethyl stannide or disodium tetraethyl stannide—are shown in equations I and II, respectively. The triethyltin group prepared by the reduction process I and the triethyltin group prepared by the oxidation process II are highly interesting as regards their properties; although of like appearance (their tin content, M.W. in naphthalene and benzene, and refractive index)⁽¹⁾ their rate of oxidation appears to differ markedly.



The electronic constitutions of the triethyltin groups thus obtained are represented, therefore, as follows:



It is expected from the electronic constitutions that the compound B would be more unstable than the compound A. Such constitutional isomers will be called "electroisomers" by the present author. The stability of the compounds can be determined by their degree of conversion into triethyltin hydroxide or into diethyltin oxide through the formation of triethyltin oxide (b.p. 158°, 15 mm., uncor.)⁽¹⁾ in the presene of oxygen and water. At present, under this condition the mechanism of the formation of diethyltin oxide is not known. However, perhaps it would conform with the following equation⁽³⁾



It cannot be strongly emphasized without further investigation from different points; however the existence of the so-called "electroisomers" is theoretically possible. Table 1, 2 and 3 (corresponding curves in Fig. 1.) illustrate the properties. The boiling points of both samples are approximately the same (152–154°, 17 mm (uncor.) for $(\text{C}_2\text{H}_5)_3\text{Sn}$ and 153–155°, 17 mm (uncor.) for $(\text{C}_2\text{H}_5)_2\text{SnC}_2\text{H}_5$).

(1) T. Harada, *Sc. Papers Inst. Phys. Chem. Research* (Tokyo), **35** (1939), 290.

(2) T. Harada, this Bulletin, **4** (1929), 266.

(3) T. Harada, *Sc. Papers Inst. Phys. Chem. Research* (Tokyo), **36** (1936), 501.

Table 1.

A. $(C_2H_5)_3Sn$ 0.4 g. Subs. in 75 c.c. of 75% alc.		B. $(C_2H_5)_2Sn$ C_2H_5 0.4 g. Subs. in 75 c.c. of 75% alc.
Days	pH	pH
0	6.0	6.2
1	6.6	7.2
3	7.6	7.7
4	7.7	7.7
5	$(C_2H_5)_2SnO = 0.08$ g.	$(C_2H_5)_2SnO = 0.19$ g.

Table 2.

A. $(C_2H_5)_3Sn$ 0.3 g. Subs. in 50 c.c. H_2O			B. $(C_2H_5)_2Sn$ C_2H_5 0.3 g. Subs. in 50 c.c. H_2O	
Days	c.c. of $\frac{1}{20}$ N HCl	pH	c.c. of $\frac{1}{20}$ N HCl	pH
0	0.10	6.9	0.20	7.0
1	0.20	7.1	0.40	7.2
2	0.30	7.2	0.50	7.4
3	0.40	7.3	0.60	7.4
4	0.45	7.4	0.70	7.5
6	0.50	7.4	0.75	7.6
	$(C_2H_5)_2SnO = 0.03$ g.		$(C_2H_5)_2SnO = 0.08$ g.	

Table 3.

A. $(C_2H_5)_3Sn$ 1.0 g. Subs. in 100 c.c. H_2O			B. $(C_2H_5)_2Sn$ C_2H_5 1.0 g. Subs. in 100 c.c. H_2O	
Days	c.c. of $\frac{1}{20}$ N HCl	pH	c.c. of $\frac{1}{20}$ N HCl	pH
0	0.05	6.7	0.05	6.8
1	0.08	6.8	0.10	7.0
2	0.15	7.0	0.20	7.1
4	0.20	7.1	0.35	7.2
6	0.25	7.2	0.45	7.4
8	0.30	7.3	0.55	7.5
11	0.40	7.4	0.65	7.5
14	0.50	7.5	0.75	7.6
16	0.55	7.5	0.75	7.6
18	0.60	7.5	0.75	7.6
21	0.65	7.6	0.80	7.6
24	0.70	7.6	0.80	7.6
29	0.70	7.6	0.80	7.6
	$(C_2H_5)_2SnO = 0.10$ g.		$(C_2H_5)_2SnO = 0.27$ g.	

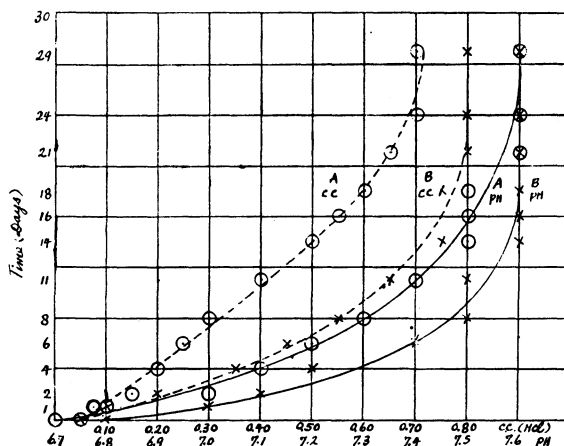


Fig. 1.

Experimental. One gram of sample A and B prepared by equations I and II respectively (and purified by distillation, and washing with alcohol and water)⁽¹⁾ were covered with 100 c.c. of water in Erlenmeyer flasks and agitated occasionally in a similar manner. One c.c. of each of the clear top aqueous solution was taken out and diluted with 10 c.c. of water, and finally was titrated with $\frac{1}{20}$ N HCl using methyl orange as indicator. Ten c.c. of the diluted solution were determined for pH simultaneously with phenol red as indicator. Insoluble $(C_2H_5)_2SnO$ on the other hand, was also formed by the above treatment. A similar experiment was also carried out with 0.4 g. of each of the sample but they were covered with 75 c.c. of 75% alcohol instead of water. The titration and the determination of pH were carried out similarly as above but for pH below 7.0, bromothymol blue was employed as indicator. In both cases, the total amount of diethyltin oxide precipitated from $(C_2H_5)_2SnC_2H_5$ was approximately three times that from $(C_2H_5)_3Sn$.

Summary.

The free triethyltin groups prepared by two methods, namely, the reduction of $(C_2H_5)_3SnX$ and the oxidation of $(C_2H_5)_2SnNa$ or $((C_2H_5)_2SnNa)_2$ appear to be identical. However, their rate of oxidation appears to differ markedly from one another. It is assumed that this is due to their electronic constitutional difference (electroisomeric) or in the methods of preparation.

The author wishes to express his appreciation to Dr. T. Suzuki for his kind advice during this investigation.

*The Institute of Physical and Chemical Research,
Komagome, Hongo, Tokyo.*

Antioxygenic Effects of Some Nitroso Compounds. An Interpretation of the Effects from the Point of View of Resonance.

By Yojiro TSUZUKI and Yukio KIMURA.

(Received November 30, 1940.)

It was shown by Carré and Peigné⁽¹⁾ that antioxygenic action seems to depend on the difference of the polarity of elements directly to antioxygenic substances. The authors have now examined several nitroso compounds for antioxygenic activity on the autoxidation of benzaldehyde exposed to atmospheric oxygen, since nitroso compounds have, in general, very large dipole moment. Their antioxygenic actions are, however, somewhat diverse. Some are very effective and some are not.⁽²⁾ Aliphatic nitroso compounds (such as nitroso-dimethylamine and nitroso-methylurethane) generally show no or very little retarding effect, while aromatic compounds show more or less strong activity.

Some examples of our experiments using nitrosobenzene, *p*-nitrosotoluene, *p*-chloro-, *p*-bromo- and *p*-iodo-nitrosobenzenes as antioxidants will be shown.

In a flask of 1370 c.c. volume, 5 c.c. freshly distilled benzaldehyde (5×10^{-2} mols) and the antioxidant (4×10^{-5} mols) are introduced. After standing for 24 hours the formed benzoic acid is titrated with alkali.

Antioxidant	Benzoic acid formed	Antioxidant	Benzoic acid formed
None	1.263 g.	<i>p</i> -Chloro-nitrosobenzene	0.074 g.
Nitrosobenzene	0.777 g.	<i>p</i> -Bromo-nitrosobenzene	0.069 g.
<i>p</i> -Nitrosotoluene	0.599 g.	<i>p</i> -Iodo-nitrosobenzene	0.018 g.

The experiments show that the order of the effects of the substituents is $I > Br > Cl > CH_3 > H$. This order is just coincident with the sequence of the *o,p*-directive forces of groups in aromatic substitution,⁽³⁾ which may be regarded as being determined by the electromeric effect of the radicals.⁽⁴⁾ The above results, therefore, indicates that the antioxygenic activity is likely to depend on the resonance of a nitroso compound, which is effected easily in the presence of conjugated double bonds as in the cases of aromatic nitroso compounds.

Nedzu Chemical Laboratory,
Musashi Higher School, Nakaarai Tokyo.

(1) P. Carré and L. Peigné, *Compt. rend.*, **208** (1939), 108.

(2) Among nitroso compounds the following ones have been already examined on the autoxidation of benzaldehyde with the results: nitroso-methylurethane is almost inactive, but *p*-nitroso-dimethyl-aniline is very active. C. Moureu, C. Dufraisse and M. Badoche, *Compt. rend.*, **183** (1926), 823.

(3) A. F. Holleman, *Chem. Rev.*, **1** (1925), 187.

(4) On the electromeric effect of the methyl group see E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, **1940**, 949.

Geochemische Untersuchungen der Vulkane in Japan. XXIV. Radongehalt von Mineralwasser in Masutomi.

Von Shinya OANA und Kazuo KURODA.

(Eingegangen am 22. November 1940.)

Bekanntlich gibt es in Masutomi, Kai-Provinz, stark radioaktive Mineralwasserquellen und die Untersuchung über ihren Radongehalt wurde schon früh im Jahre 1914 von R. Ishizu ausgeführt.⁽¹⁾ Neuerdings wurden die gleichartige Messungen von Radongehalt und weiter die Radiumbestimmung in dem genannten Mineralwasser von T. Nakai im Oktober, 1936 und im April, 1937 wiederum geleistet und berichtet.⁽²⁾

Wir haben gelegentlich der Studienreisen nach Masutomi im Juli, 1939 und im Oktober, 1940 die Radonbestimmungen derselben Quellen nochmals durchgeführt, um kennen zu lernen, ob der Radongehalt solcher Quellen mit den Zeiten etwaige Veränderung erleide oder nicht. Die Resultate unserer Messungen werden in Tabelle 1 angegeben.

Tabelle 1. Radongehalt von Mineralwasser in Masutomi.

	Namen der Quelle nach Nakai	Juli 1939			Oktober 1940		
		Radon in 1 L. Was- ser, in Mache- einheit	Temp. der Quelle °C.	pH- Wert	Radon in 1 L. Was- ser, in Mache- einheit	Temp. der Quelle °C.	pH- Wert
A ₁	Kinsentō	2.06	31.0	6.3	1.44	31.6	6.2
A ₂	Tuganerō No. 1	4.3	30.1	6.4	4.21	32.3	6.3
A ₃	„ No. 2	3.45	29.6	6.4	2.62	30.7	6.5
A ₄	Totikubo No. 1	16.1	28.0	6.3	4.24	27.5	6.3
A ₅	Hiuke-sui		14.7			13.5	6.0
B ₁	Nibuzawa		24.0			24.2	6.6
B ₂	Sio-no-sawa-tugane-yu		20.9			19.0	6.0
B ₃	Gantō-hunsen		26.0			16.5	6.2
B ₄	Kuridaira No. 1		21.2	6.0	638	22.3	5.9
B ₅	Kuridaira-tennen-buro		23.6	6.4	4.78	21.3	6.5
B ₆	Kuridaira No. 3	233	21.4		258	20.0	6.0
B ₇	Higasiobi-no-izumi	9.05	24.5	6.3	9.02	25.0	6.3
B ₈	Wadegawara No. 1		22.0	6.5	675	19.0	6.5
B ₉	„ No. 2	1090	20.5	6.2	1200	18.8	6.0
C ₁	Ginsentō-kami-no-yu		28.5	6.5	30.3	25.9	6.9
C ₂	Ginsentō-huru-yu		30.0	6.5	132	31.3	6.5

(1) R. Ishizu, "The Mineral Springs of Japan," 85, (1915).

(2) T. Nakai, dies Bulletin, 15 (1940), 363.

Tabelle 1.—(Fortsetzung)

	Namen der Quelle nach Nakai	Juli 1939			Oktober 1940		
		Radon in 1 L. Was- ser, in Mache- einheit	Temp. der Quelle °C.	pH- Wert	Radon in 1 L. Was- ser, in Mache- einheit	Temp. der Quelle °C.	pH- Wert
C ₃	Ginsentō-naka-no-yu		27.0	6.7	31.8	21.9	6.7
C ₄	Ginsentō-simo-no-yu				228	19.4	6.4
C ₅	Osiba		22.6	6.4	419	23.2	6.4
C ₆			29.1	6.6	17.2	22.0	6.5
D ₁			11.3	3.8		11.2	3.7
D ₂	Yuzawa No. 5		14.7	5.4		12.0	5.4
D ₃	„ No. 4		11.8	3.8		11.2	3.8
D ₄	„ , No. 3		11.9	4.0			
D ₅			14.1	4.0			
D ₆			14.4	5.8	2.64	14.0	5.6
D ₇	Yuzawa No. 1		17.8	6.0	2.76	18.0	5.6
D ₈			18.0	5.9			
D ₉			15.5	5.5			
D ₁₀			14.0	3.7			
D ₁₁			16.5	5.6			
D ₁₂			16.1	5.5			
E	Wada-matuba-Kōsen		11.5	6.4	3.48	12.5	6.5

Wir haben alle Mineralwasserquellen in Masutomi in 5 Gruppen geordnet, die in der Tabelle mit den Buchstaben A, B, C, D und E bezeichnet sind. Die angehängten Ziffern bedeuten die Stellen der Quellen, die in Reihenfolge nach der Höhe auf die Meeresfläche angeordnet sind. Die von T. Nakai gegebenen örtlichen Bezeichnungen⁽²⁾ sind in zweiter Reihe der Tabelle angegeben und sie beziehen sich auf unsere Zeichen in erster Reihe.

Was die Diskussion über jetzt von uns erhaltene Resultate anbelangt, so möchten wir sie bis zur folgenden Mitteilung, die bald zur Erscheinung kommen wird, hinhalten.

Es sei uns gestattet, Herrn Prof. Yuji 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 unseren herzlichen Dank auszusprechen.

*Chemisches Institut,
Naturwissenschaftliche Fakultät,
Kaiserliche Universität zu Tokyo.*