

The Occurrence of Thallium in Minerals in Japan

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Introduction

Thallium is one of the geochemically high dispersive elements.⁽¹⁾ Some minerals containing thallium as their principal constituent are known to be secondary minerals and very rare.⁽²⁾ Besides its occurrence in these minerals, thallium is sometimes found concentrated in an intermixture of copper,⁽³⁾ iron⁽⁴⁾ and zinc⁽⁵⁾ sulfide ores. Thus, the flue-dust and chamber muds in refineries or sulfuric acid factories processing these ores are rather important as a technical source of thallium as studied by many workers.

Prof. K. Kimura and Y. Koyama⁽⁶⁾ have investigated the thallium content in about eighty minerals in Japan by their semi-quantitative spectroscopic method. The author together with the above had hoped to investigate further the occurrence of thallium in these minerals and ores. Results of about 30 samples spectroscopically tested by the above method proposed by the two workers and the results of some which were chemically determined by the authors' method by using hexammine cobalti-trichloride as precipitant⁽⁷⁾ to thallium, will be reported here.

Experimental

Spectroscopic Test Thallium has been spectroscopically determined by the following table proposed by the two workers.

Experimental Conditions Spectrograph: E 2 Type Spectrograph, Adam Hilger Co. Ltd., London. Electrode: Electrolyzed copper rod (diameter 3 mm.). Diameter of hole into which the sample is inserted is 1 mm. and depths, 3 to 4 mm.

Current: Gradually increased up to 7 amperes during the first 30 seconds, maintaining 7 amperes for 40 seconds.

(1) Nordenskiöld, *Lieb. Ann.*, **145** 127 (1868); V. M. Goldschmidt, *Zeit. Kryst. Min.*, **30**, 272 (1898); Kréhlík, *Zeit. Kryst. Min.*, **51**, 379 (1912)

(2) Gmelin, *Handbuch der anorganische Chemie* 8 (1939)

(3) A. Lamy, *Lieb. Ann.*, **124**, 218 (1862); T. U. Phipson, *Compt. rend.*, **78**, 563 (1874); W. I. Vernadsky, *Bl. Acad. Petersb.*, (6) **4**, 1139 (1910)

(4) W. Crooks, *J. Chem. Soc.*, **17**, 115 (1864); W. N. Hartley and H. Ramage, *J. Chem. Soc. Ind.*, **71**, 540 (1897); I. Noddack, *Angew. Chem.*, **49**, 835 (1936)

(5) W. T. Roesper, *Ann. J. Sci.*, (2) **35**, 421 (1863); F. Wöhler, *Lieb. Ann.*, **142**, 263 (1867); Y. Murakami, *This Bulletin*, in press.

(6) K. Kimura and Y. Koyama, *J. Chem. Soc. Japan*, **57**, 1190 (1936)

(7) Y. Murakami, *This Bulletin*, in press.

Dry plate: Process, panchromatic, Fuji Photo-graph Ind. Co. Ltd., Japan.

Developing: Developed at 3 min., 18°C with a special developer for the process plate above mentioned.

Table 1.

Relation between thallium content and intensity of its spectrum line*				
Wave length Å	Thallium content (%)			
	1	0.1	0.01	0.001
3775.7	s	s	s	w
3229.8	w	—	—	—
2921.5	w · w	—	—	—
2918.3	s	w	w · w	—
2826.2	w · w	—	—	—
2710.7	?	—	—	—
2709.3	w · w	—	—	—
2379.6	w	—	—	—

* Cited from the report by K. Kimura and Y. Koyama (*J. Chem. Soc. Japan*, **57**, 1190 (1936))

Analytical Test Some of these samples spectroscopically found abundant in thallium were analyzed chemically. The sample about 10 g. powdered (100 mesh), dried at 105°C and made into a solution with the acid mixture was then determined closely following the author's method.

Experimental results

Analytical results are shown in Table 2.

Conclusion

By comparing the spectroscopical with the analytical results, it may be stated that the method proposed by Prof. K. Kimura *et al* can be utilized as a rapid and good method of the determination of thallium. The author's method in testing ores is also satisfactory, being distinctive in that it is hazardless and speedy, a condition not known in any other method of the past.

V. M. Goldschmidt⁽⁸⁾ had classified thallium as a chalkophile element, and it had been stated by Berg⁽⁹⁾ that thallium occurs in zinc-blende and iron sulfide ore, concentrated from the hydrothermal rest-solution in geochemical crystallization. Though a large number of the sample has not as yet been tested, the same results have been obtained, being distinctively so with markasite and pyrite. But in copper sulfide ore, thallium is either not found at all or else found in a very small amount.

(8) V. M. Goldschmidt, *Videnskapselsk. Skr. Nr. 3*, 55 (1923)

(9) G. Berg, "Das Vorkommen der chemischen Element auf der Erde," 262, Leipzig (1932)

Table 2
Thallium content in minerals

Sample	Occurrence	Line detected	Content		Other constituent (in order of intensity)
			Spectroscopically	Chemically	
1. Markasite	Mori, Yamagata Pref.	3775.72(s) 2918.32(w)	0.1 %	0.085 %	Fe, Si, Al.
2. Markasite	Tomimoto Yamagata Pref.	—	—	—	Fe, Si.
3. Enarzite	Shimokita Oage, Aomori Pref.	3775.72(s) 2918.32(w)	0.1	0.056	Fe, Si.
4. Markasite No. 1	Shimokita Oage, Aomori Pref.	3775.72(s) 2918.32(w)	0.1	—	Fe, Bi, Pb, As, Mn.
5. No. 2	"	3775.72(W.W)	0.1 to 0.01	—	Pb, Fe.
6. No. 3	"	3775.72(s) 2918.32(?)	<0.1	—	Pb, Fe, As.
7. No. 4	"	3775.72(s) 2918.32(?)	<0.1	—	Fe, Si.
8. Pyrite	Ochiaizawa bed, Hanaoka, Akita Pref.	not tested	—	0.007	
9. Black ore	Nishikanon bed, Hanaoka, Akita Pref.	not tested	—	0.001	
10. Markasite	Kamiyama bed, Hanaoka, Akita Pref.	not tested	—	0.125	
11. Zinc blend	Yunohanazawa, Akita Pref.	3775.72 2918.32(w)	0.1 to 0.01	0.070	Zn, Si, Pb.
12. Copper ore No. 1	Doyashiki Hanaoka, Akita Pref.	not tested	—	0.005	
13. No. 2 concentrates	"	not tested	—	0.024	
14. No. 3	"	not tested	—	0.003	
15. Markasite (in brown coal)	Agi, Gifu Pref.	—	—	—	Fe, Si, Mg.
16. Black ore	Owani, Aomori Pref.	—	—	—	Zn, Pb, Mg.
17. Covelin	Masutomi, Yamana-shi Pref.	3775.72(?)	<0.001	—	Cu, Si.
18. Markasite	"	—	—	—	Fe, Si.
19. Enarzite	"	—	—	—	Cu, As.
20. Ruzonite	"	—	—	—	Cu, Sb, As, Sn.
21. Pyrite	Nishikanon bed, Hanaoka, Akita Pref.	not tested	—	0.007	
22. Bismuth ore	Togane, Gifu Pref.	3775.72(?)	<0.001	—	Bi, Mo, Ca, Pb, Al, W, Sn.
23. Markasite	Masutomi, Yamanashi Pref.	3775.72 2918.32(w.w)	0.1	not tested	Fe, Si.
24. Zinc blend No. 1	Okurazawa, Akita Pref.	3775.72(w.w)	0.001	—	Zn, Si, Na, Pb, Al.
25. No. 2	"	3375.72(w.w)	0.001	—	Zn, Si, Na, Pb, Al.
26. Bismuthinite	Ebisu, Gifu Pref.	—	—	—	
27. Bithmuth ore	Hohen, Yamaguchi Pref.	—	—	—	Fe, Si, Mg.
28. Nature Bismuth	Ebisu, Gifu Pref.	3775.72(w) 2918.32(w)	0.1 to 0.001	not tested	Bi, Al, Mo, W, Sn, Zn, Si, Ag, As.
29. Lead ore No. 1	Taishu (Akusuidani); Nagasaki Pref.	—	—	—	Fe, Si, Pb, Mg.
30. No. 2	Taishu(Sasu bed No.6); Nagasaki Pref.	3775.72(?)	0.001	—	Fe, Zn, Pb, Mg.

Thallium in natural bismuth and its ore could not be found in Ebisu mine formerly reported by Prof. K. Kimura and K. Koyama as a source of abundant thallium in zinc-blende and others. On the contrary it is remarkable that these samples abundant in thallium have been found in the Northeastern

District (Tohoku-Chiho) of Japan.

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Modified Colorimetric Determination of Copper with Sodium Diethyldithiocarbamate in the Presence of Hydroxylamine

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Introduction

Sodium diethyldithiocarbamate was at first used by Callan and Henderson⁽¹⁾ in the colorimetric determination of a small amount of copper. He was followed by several workers who had studied this colorimetric determination, and among them Conn *et al.*⁽²⁾ made a special study of the various colorimetric determinations of copper being used up to that period. He pointed out the experimental defect of each method of determination and recommended the use of the sodium diethyldithiocarbamate method as the most accurate. This method is to be followed after isolating the copper with hydrogen sulphide to avoid interference from other elements usually present in the sample to be tested. He reported that hydrogen sulfide separation is superior to the tedious and time-consuming electrolytic separation recommended by Grendel.⁽³⁾ Yet unfortunately it was also reported unsatisfactory.⁽⁴⁾

Upon these results Sylvester and Lampitt⁽⁵⁾ attempted the colorimetric determination of copper in milk with this same reagent after having extracted the copper with chloroform as dithizonate. But Nydahl⁽⁶⁾ proposed the same method as Sylvester and Lampitt in determining copper in fats, using carbon tetrachloride in place of chloroform as an extractant. Thus this reagent, producing an intense golden yellow coloration when put into contact with any amount of copper in the solution, has been used as highly sensitive reagent in the determination of minute quantities of the element.

However it has one drawback in colorimetry in that, when extracted with some other organic solvents, it does not vary in degrees of coloration in direct proportion to the amount of copper present. To solve this difficulty

organic solvents such as ether,⁽⁷⁾ chloroform,⁽⁸⁾ carbon tetrachloride,⁽⁸⁾ amyl alcohol⁽⁹⁾ and isoamyl alcohol⁽¹⁰⁾ were proposed but none were satisfactory.

Such being the case, color comparison must be undertaken by a series of standard solutions treated in the same way or by the use of a Lovibond tintometer at the loss of accuracy and sensitivity of the reagent. But McFarlane⁽⁹⁾ reported that the use of a Dubosque colorimeter would, to some extent, produce color variations proportional to the amount present. Of course that is when the copper is extracted with amyl alcohol. However, unfortunately the results obtained by some workers could,⁽¹⁰⁾⁽¹¹⁾ not prove this statement. Naturally the degree of coloration in the original aqueous solution strictly conforms with the Lambert-Beers' law as it does in the case of amyl alcohol and carbon tetrachloride solution being used as an extractant, provided that the specially made filter⁽¹²⁾ is used. The use of such a filter, however, is not generally possible. On the other hand Nydahl explained in his report that his method in practice agrees with the law if shaken successively two or three hundreds times with carbon tetrachloride. However, the best accuracy cannot be expected. Though a highly sensitive reagent is used for the determination, this drawback is unavoidable being probably due to the difficulty of transferring the colored products completely into solvents.

This defect was, however, finally abolished by the application of a new method tried by the author using carbon tetrachloride as an extractant in the presence of hydroxylamine. The object of this report will therefore be to give some details on this new method.

Procedure Discussed

Color reaction Though sodium diethyl-

(1) T. Callan and J.A.R. Henderson, *Analyst*, **54**, 650 (1929)

(2) L.W. Conn, A.H. Johnson, H.A. Trebler and V. Karprenko, *Ind. Eng. Chem. Anal. Ed.*, **7**, 15 (1935); R.W. Thatcher, *J. Am. Chem. Soc.*, **55**, 4524 (1933)

(3) F. Grendel, *Phrm. Weekblad.*, **67**, 913, 1343 (1930); *Z. Anal. Chem.*, **97**, 47 (1934)

(4) Walker, *J. Assoc. Offici. Agr. Chem.*, **13**, 426 (1930)

(5) N.D. Sylvester and L.H. Lampitt, *Analyst*, **60**, 377 (1935)

(6) F. Nydahl, *Z. Anal. Chem.*, **116**, 315 (1939)

(7) S.L. Tompsett, *Biochem. J.*, **29**, 480 (1929)

(8) L.A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932)

(9) McFarlane, *Biochem. J.*, **26**, 1022 (1932); *Z. Anal. Chem.*, **101**, 71 (1935)

(10) E.J. Caulson, *J. Assoc. Offici. Agr. Chem.*, **20**, 178 (1937)

(11) D.L. Drabkin, *J. Assoc. Offici. Agr. Chem.*, **21**, 202 (1938); L.A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932); c.f. O.B. Winter, *J. Assoc. Offici. Agr. Chem.*, **19**, 359 (1936)

(12) D.L. Drabkin, sec foot-note (11)

dithiocarbamate is not exclusively active with copper, but reacts with such metals as Bi, Fe, Mn, Ni, Co, Cr, forming colored complexes and with Zn, Pb, Hg, Cd, Sb, Sn and Al becoming turbid, it nevertheless has been used for copper determination because of its high sensitivity. It is therefore necessary that copper be preliminarily separated from other metals to obtain the best results. After a comparative study of preliminary separation of copper, the author decided upon the use of dithizone in the basic solution containing some citrate after the Sandells' direction, details of which will be reported in the last communications. With the use of dithizone in carbon tetrachloride and the acid treatment with 0.01 N hydrochloric acid some of these interfering metals are avoided, for Sb, Sn, Al and Cr, do not react with dithizone and Pb, Zn and Cd perfectly separate into the acid solution being isolated from copper by treating the dithizonates with 0.01 N hydrochloric acid. The amount of Fe and Mn in this case is extremely small owing to the addition of citrate which prevents its reaction with dithizone. Even should they be present, 50 p.p.m. of each are permissible in a small amount of copper as 1 to 3 p.p.m.⁽⁵⁾ Coloration with some other metals was studied, and E_T was calculated from the results, meaning the extinction coefficient of 1 cm. of the solution when 1 γ of the element present in 1 ml. of the solution is measured. (Table 1)

of hydroxylamine. Sylvester *et al* reported that 50 p.p.m. each of Co or Ni are permissible with 0.2 to 2.7 p.p.m. copper determination. It is evident from these results that serious interference is far from being encountered, because the amount of these elements in living plants are usually one hundredth to thousandths of the amount of copper.⁽¹⁴⁾

Likewise it is generally unnecessary to consider the interference of bismuth because of its rarity in biological matter and its lower sensitivity. Thus from the above study of interferences from other metals in copper determination, it can be concluded that the application of this color reaction to copper in biological matter can be successfully undertaken without serious interference.

Hydroxylamine in the extraction The degree of coloration into the aqueous solution is strictly proportional to the amount of copper present, but not when extracted with some organic solvents. It is thought that the rate of transference of colored matter into organic solvents is so small that complete transference is impossible. Thereupon this color reaction has not been widely used though superior in such respects as simplicity, high sensitivity and speed. To overcome these defects Haddok and Evers⁽⁸⁾ recommended that extraction be repeated until the solution becomes colorless. Yet this process, it is said by many workers, is not in conformity with the Lambert-Beers' law. Only

Table 1

Sensitivity of some elements to sodium diethyldithiocarbamate

Ions	Cu	Mn	Co	Ni	Bi	Zn	Pb	Fe	Ti
E_T	0.201	0.0000	0.0168	0.0081	0.0018	0.0040	0.0001	0.0007	0.0000
Color-reaction	Golden yellow	Pink (unstable)	Dull green	Greenish yellow	Yellow (precipitated)	White turbidity	White turbidity	Deep brown (precipitated)	Yellowish white turbidity

E_T was obtained in carbon tetrachloride solution extracted at pH 10.5 and the color reaction (in third column) means the coloration in the water solution when a considerable amount of the element is present.

These results indicated that the reagent is ultimately most sensitive to copper and that interference from other metals is generally negligible even though the acid treatment might not have been the best. If the coloration is produced at pH higher than 10.5, as much as 5 mg. Zn is permissible in 10 γ copper determination as it can be thought $Zn(NH_3)_4^{++}$ forms with slightly excess ammonia. Therefore it is possible to determine copper in the presence of a considerable amount of Zn. But in this case, it is safer to make a color comparison immediately as it tends to become turbid on standing. It is easy to prevent the turbidity by lead with the addition of thiourea and in this case the extraction of the copper compound is easily made without the addition

McFarlane reported that it conforms to the law when extracted with amyl alcohol though the range of concentration proportional to the degree of coloration is somewhat narrow. Nydahl added that this would conform with the law if shaken vigorously about three hundred times for each extraction, but accurate results cannot be expected in this case.

The addition of hydroxylamine in the process of extraction newly tried by the author clearly solves this difficult problem. By its addition in making the extraction with carbon tetrachloride it conforms accurately with the law and brings about the best results by a short

(14) F. Honcamp, "Handbuch der Pflanzenernährung und Düngenlehre", I. 261, Leipzig (1931)

shaking for 20 seconds. The addition of hydroxylamine had been found useful in several cases when tested with solvents which had been proposed. Yet among them carbon tetrachloride is the most advantageous owing to its larger density, lower solubility and lower vapor pressure which are properties convenient for practical use.

and for ineffectiveness on the stability of the coloration. The smaller the pH of the aqueous phase the more necessary is the repetition of the extractive operation.

Though the effective period of the sodium diethyldithiocarbamate solution was reported to be one week or at the most two weeks,⁽¹⁵⁾ it was found that it could be effective for a

Table 2
Stability of the coloration in carbon tetrachloride
Extinction Coefficient

Time(min.)	0	30	60	80	100	180	24 hrs.
10.05 γ Cu ^(a)	0.384	0.380	0.376	0.370	0.373	0.370	0.362
10.05 Cu ^(b)	0.452	0.436	0.414	—	0.409	0.404	0.401
20.10 Cu ^(a)	0.755	0.750	—	—	—	0.743	0.735

(a) extracted at pH 10.5 after adding 2 ml. of 4 % hydroxylamine and the final volume, 25 ml.

(b) the same condition as (a) except the addition of 6 ml. of 4 % hydroxylamine.

Another advantage is that it has no ill effect on the stability of the coloration, at the same time preventing any change in coloration.

It was found that no appreciable decrease was noticed after 24 hours standing. Yet the stability decreases slightly upon increasing the amount of hydroxylamine added, though its efficiency for extraction increases. For this therefore 2 ml. of 4 % hydroxylamine solution was found most satisfactory. Further advantage of its addition is found in diminishing the pinkish coloration due to the presence of manganese, if a little excess of ammonia than the recommended is added.

month if used in the presence of hydroxylamine and stored in an amber colored bottle.

Accuracy and reproducibility The addition of hydroxylamine has increased the sensitivity of the reagent as the extraction can be completely carried out. The results obtained on the various concentrations of copper standard solution will be shown in Table 5, indicating that it holds closely to the Lambert-Beers' law therefore rendering the color comparison much more simple.

These results have found that the range of error lies within 5 % according to the amounts of copper (5 γ to 20 γ) in 25 ml. carbon

Relation between the amounts of hydroxylamine and the stability of the coloration					
4 % hydroxylamine added (ml.)		2	4	6	8
Extinction	0 min.	0.384	0.406	0.452	0.509
Coefficient	30 min.	0.380	0.396	0.436	0.459

Table 4
Efficiency of extraction at various pH (copper present 11.00 γ)

pH	3.0	6.7	7.2	8.6	9.7	10.5	10.9	11.5
Extinction Coefficient	0.430	0.440	0.457	0.451	0.454	0.464	0.434	0.414
Copper found (γ)	10.70	10.95	11.37	11.22	11.29	11.54	10.75	10.30

The extraction must be done under great precaution so that the separated carbon tetrachloride be free from droplets of aqueous solution during the procedure of drawing off from the separatory funnel, which brings about futile oxidation of the reagent in extracted solution. Oxidation of the reagent develops a certain cloudiness.

It was found that pH 7.2 to 10.5 was the the most suitable pH for speedy extraction

tetrachloride solution. But, whenever possible, the copper range selected should not be less than 0.2 p.p.m. in order to obtain greatest accuracy.

In practical use a blank test should be frequently made on all material used. In this case when cells of 50 mm. thickness were used the readings correspond to 0.9 γ copper. When its method is compared with the extractive

(15) J. Grant and A. Mezgy, *Analyst*, **61**, 401 (1936)

Table 5
Accuracy and conformability to the law

Copper present (γ)	Accuracy		Diff. (γ)	Conformability	
	Extinction Coefficient (50 mm. thickness)	Copper found (γ)		Extinction Coefficient (average)	$E\gamma$ (Calculated)
2.01	0.081	2.02	+0.01	0.081	0.203
5.03	0.197	4.90	-0.13		
	0.193	4.80	-0.23		
	0.208	5.17	+0.14	0.201	0.201
	0.191	4.75	-0.28		
	0.215	5.35	+0.32		
10.05	0.392	9.83	-0.22		
	0.396	9.95	-0.10		
	0.386	9.60	-0.45	0.401	0.201
	0.401	9.98	-0.07		
	0.408	10.14	+0.09		
20.10	0.422	10.50	+0.45		
	0.820	20.40	+0.30		
	0.800	19.90	-0.20	0.801	0.203

titration or mixed colored method with dithizone,⁽¹³⁾ both tedious and requiring skillful operation and a considerable blank factor (owing to the color of the reagent itself), the new method is speedier and more accurate owing to its complete extraction of copper by the addition of hydroxylamine.

Reagent and Apparatus

Apparatus Separatory funnel: Approximately 30 ml. capacity. Silica dish or platinum dish; These apparatus should be free from copper by washing with distilled nitric acid.

Reagent Water; Redistilled in glass apparatus. Hydrochloric acid (1:1): It is preferable to use freshly distilled hydrochloric acid showing constant boiling point. Ammonia saturated: Saturate redistilled water with ammonia gas generating from ammonia aqua on heating by the addition sodium hydroxide. Sodium diethyldithiocarbamate, 0.1 per cent solution; Dissolve 0.5 g. of the reagent in 500 ml. of redistilled water, stored preferably in amber colored bottle. Hydroxylamine, 4 per cent solution; Dissolve 4 g. of its hydrochloride salt in 100 ml. of redistilled water. Carbon tetrachloride: Shake with one tenth of its volume of concentrated sulfuric acid and then wash with redistilled water to remove the latter. After that purify by distillation in usual way.

Procedure

The aliquot portion of the solution containing copper is treated as follows: If copper was concentrated with organic reagent such as dithizone it should be ignited to destroy all organic matter in silica or platinum dish. Then add 1 ml. of hydrochloric acid (1:1) and by means of a glass rod over the interior of the dish so that all the cupric oxide will be dissolved. At this point if copper is less than approximately 10 γ hardly any color is noticeable. Add 10 ml. of water, transfer into the separatory funnel and rinse thoroughly

with some water. Thus the solution to be tested is ready for the extraction.

Make the solution alkaline with ammonia to litmus paper and add the excess of 0.2 ml. of ammonia solution. Next add 2 ml. of 4 per cent hydroxylamine solution and 10 ml. of 0.1 per cent sodium diethyldithiocarbamate solution in the order named. It becomes instantly golden yellow due to the copper. Shake vigorously with 7 ml. of carbon tetrachloride and draw it off into a 25 ml. volumetric flask after leaving it to settle. Leave a few drops of the carbon tetrachloride to prevent mixing of the aqueous solution and rinse the stem of the funnel with 2 ml. of carbon tetrachloride. In this extraction the stem should be perfectly dried. Then shake again in the same manner as before. Usually two shakings is sufficient to entirely extract the colored matter. Then fill to the mark with carbon tetrachloride and measure the extinction coefficient with Pulfrich photometer using S 43 filter (434 m μ). If the final volume is reduced to less than 25 ml., then less than 5 γ of copper can be determined with fair results.

Conclusion

The addition of hydroxylamine proposed by the author has removed entirely all defects in the determination of copper with sodium diethyldithiocarbamate as pointed out by previous workers.

Its use has given satisfactory results superior to other methods in the following respects: (a) Speedy and complete extraction of copper diethyldithiocarbamate complex with carbon tetrachloride, (b) Normal effect on the stability of coloration and the effective period of the reagent remarkably increased and (c) increase of accuracy in color comparison by complete

(13) E.B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **9**, 464 (1937)

extraction of the colored matter so that it conforms with Lambert-Beers's law.

By the adoption of this method, copper can be determined in a short while after bringing the sample into solution. The experiments already related have proved that it is one of the most accurate methods in comparison with other methods which have been used. At the present time when the role played by copper in biological matter is given greater attention this new method will fulfill its mission in being of invaluable importance

in this respect. A new colorimetric method of copper in biological matter adapting both the dithizone extraction and this new method will be reported in the near future by the author.

The author wishes to express his appreciation to Prof. Kenjiro Kimura for his many valuable suggestions and never-failing encouragement throughout this investigation.

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Étude sur la précipitation de la protéine par les sels complexes métalliques II Précipitation de la protéine par les sels complexes du chrome, du fer, de l'argent, et du platine

par Réinosouké Hara

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Il existe depuis longtemps beaucoup d'études sur la réaction entre la protéine et le sel inorganique. Certains sels minéraux, comme le phosphotangstate, l'acide hydroferrocyanique, et l'acide métaphosphorique, peuvent précipiter la protéine en solution acide, mais le sel métallique peut la précipiter en solution neutre ou faiblement alcaline. S.E. Michael⁽¹⁾ a classé tous les sels complexes métalliques en deux, complexes cationiques et complexes anioniques, et il a aussi démontré que le sel cationique est capable de précipiter la protéine au domaine plus alcalin que le point isoélectrique et le complexe anionique précipite au domaine acide. Comme les sels complexes du cobalt sont exposés dans mon dernier mémoire,⁽²⁾ j'ai fait la précipitation de la protéine, et montré que la protéine et le sel complexe peuvent stoechiométriquement réagir, c'est-à-dire, la protéine et le sel complexe forment un composé défini. La protéine est chimiquement un composé qui se combine avec l'acide aminé en donnant un certain type de la liaison, et le corps principal de cette réaction doit être cet acide aminé. H. Ley⁽³⁾ a déjà donné une formule d'un

complexe interne
$$\begin{array}{c} \text{OC} \text{---} \text{O} \\ | \\ \text{H}_2\text{C} \text{---} \text{H}_2\text{N} \end{array} \text{---} \text{Cu} 1/2 \text{ au glyco-}$$

col-cuivre, et après, P. Pfeiffer⁽⁴⁾ a préparé des composés d'addition qui ont une composition défini entre divers sels neutres et des acides aminés comme $\text{LiCl} \cdot \text{CH}_2\text{---NH}_2 \cdot \text{COOH} \cdot \text{H}_2\text{O}$. Il

a aussi montré leur constitution $\text{X} [\text{H}_3\text{N}^+ \text{---} \text{COO}^-] \text{M}^+$, et donne le nom "*amphisalze*" à ces composés. En employant des sels complexes du chrome, du fer, de l'argent, et du platine dans ce présent mémoire, je vais comparer ce résultat au cas des sels complexes cobaltiques déjà publiés dans mon dernier compte-rendu. Les sels complexes utilisés sont des complexes du chrome, et du platine, des complexes cationiques. Des complexes du chrome, du l'argent, et du fer sont encore employés comme des complexes anioniques. Les conditions d'expérience sont identiques aux cas présentés dans le mémoire précédent. Les solutions de tampon employées sont $\text{NH}_4\text{OH} \text{---} \text{NH}_4\text{Cl}$ à 1/10 N et $(\text{HOOC})_2(\text{CHOH})_2 \text{---} (\text{NaOOC})_2(\text{CHOH})_2$ à 1/10 N, montrent les pH 8.8 et 2.

Détermination de la concentration du sel complexe qui est capable de précipiter la protéine En prenant la solution de la protéine à 0.5 %, on les a dissous dans le tampon (pH 8.8 ou 2), ensuite on a ajouté 1 cc. de la solution de diverses concentrations du sel complexe à 1 cc. de chaque solution. On en a examiné les résultats de précipitation après 30 minutes, le résultat est montré dans la table 1 en indiquant "≡" la précipitation parfaite, "#, +" la précipitation imparfaite, "±" la louche (pas claire) et "—" pas de précipité.

Les complexes cationiques du chrome, du platine ne peuvent pas toujours précipiter la protéine comme ceux du cobalt, tandis que les sels complexes anioniques du chrome, du fer, et de l'argent le font très remarquablement. L'albumine d'oeuf n'est presque jamais pré-

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(4) P. Pfeiffer et J.V. Modelski, *Z. physiol. chem.*, **81**, 329 (1912), **85**, 1 (1913)

Table 1

sel complexe	caséine	insuline	albumine d'oeuf	gélatine	pH
$[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ (<i>cis</i>)	—	—	—	—	8.8
$[\text{Cr}(\text{en})_2(\text{SCN})_2]\text{SCN}\cdot 2\text{H}_2\text{O}$ (<i>trans</i>)	—	—	—	—	"
$[\text{Cr}(\text{NH}_3)_2\text{SCN}](\text{SCN})_2$	+	+	—	—	"
$[\text{Cr}(\text{en})_3]\text{Cl}_3\cdot 3\text{H}_2\text{O}$	++	++	±	—	"
$[\text{Cr}(\text{Co}\cdot\text{NH}_2\cdot\text{NH}_2)_6]\text{Cl}_3\cdot 3\text{H}_2\text{O}$	+++	+++	+++	±	"
$[(\text{en})_2\text{Cr} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix} \text{Cr}(\text{en})_2]\text{Cl}_4\cdot 2\text{H}_2\text{O}$	+++	+++	+	—	"
$[\text{Cr} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix} \text{Cr}(\text{en})_2]_3\text{Cl}_6\cdot 6\text{H}_2\text{O}$	+++	+++	+	—	"
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	—	—	—	—	"
$[\text{Pt}(\text{en})_2]\text{Cl}_2$	—	—	—	—	"
$[\text{Pt}(\text{S}\cdot\text{C}\cdot\text{NH}_2\cdot\text{NH}_2)_4]\text{Cl}_2$	—	—	—	—	"
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (<i>α-cis</i>)	—	—	—	—	8.8 et 2
$\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\cdot\text{H}_2\text{O}$ (sel Reinécké)	+++	+++	+++	+	2
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$	+++	+++	+++	+	"
$\text{K}_3[\text{Cr}(\text{SCN})_6]\cdot 4\text{H}_2\text{O}$	+++	+++	+++	+	"
$(\text{NH}_4)_4[(\text{C}_2\text{O}_4)_2\text{Cr} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix} \text{Cr}(\text{C}_2\text{O}_4)_2]$	+++	+++	+++	+	"
$\text{K}[\text{Ag}(\text{CN})_2]$	+++	+++	+++	+	"
$\text{K}_3[\text{Fe}(\text{CN})_6]$	+++	+++	+++	+	"
(prussiate rouge de potasse)					
$\text{K}_4[\text{Fe}(\text{CN})_6]$	+++	+++	+++	+	"
(prussiate jaune de potasse)					

cipitée par les sels complexes cationiques, excepte un complexe d'urée $[\text{Cr}(\text{urée})_6]\text{Cl}_3$, la gélatine ne l'est guère non plus. Les complexes cationiques du platine ne peuvent pas précipiter même la caséine. Le complexe chromique d'urée peut très remarquablement précipiter la protéine.

a) *Précipitation de la protéine par les sels complexes cationiques* Les complexes cationiques du chrome et du platine ont été utilisés et ces sels, excepte $[\text{Cr}(\text{urée})_6]\text{Cl}_3$, ne peuvent pas toujours précipiter la protéine, et les complexes du platine employés, ne sont pas capables de précipiter même la caséine et l'insuline.

Aucune protéine n'est précipitée par le complexe chromique de la valence +I comme le sel cobaltique, et le sel complexe qui n'a pas de charge électrique tel que $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ne précipite jamais la protéine, tandis que le complexe d'urée peut considérablement précipiter la protéine. La concentration du complexe cationique qui est nécessaire pour la précipitation est montrée ci-dessous.

b) *Précipitation de la protéine par les sels complexes anioniques* J'ai employé les complexes du chrome, du fer, et d'argent, qui peuvent parfaitement précipiter la protéine de même que dans le cas du complexe cobaltique.

Table 2

sel complexe	protéine	concentration qui est nécessaire pour la précipitation (mol)	pH
$[\text{Cr}(\text{NH}_3)_2\text{SCN}](\text{SCN})_2$	caséine	1/60	8.8
$[\text{Cr}(\text{en})_3]\text{Cl}_3\cdot 3\text{H}_2\text{O}$	"	1/30 — 1/300	"
$[\text{Cr}(\text{CO}\cdot\text{NH}_2\cdot\text{NH}_2)_6]\text{Cl}_3\cdot 3\text{H}_2\text{O}$	"	1/20 — 1/1000	"
$[(\text{en})_2\text{Cr} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix} \text{Cr}(\text{en})_2]\text{Cl}_4\cdot 2\text{H}_2\text{O}$	"	1/100 — 1/1000	"
$[\text{Cr} \begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix} \text{Cr}(\text{en})_2]_3\text{Cl}_6\cdot 6\text{H}_2\text{O}$	"	1/100 — 1/3000	"

Table 3

sel complexe	protéine	concentration qui est nécessaire pour la précipitation (mol)		pH
$\text{NH}_4[\text{Cr}(\text{NH}_3)_5(\text{SCN})_4] \cdot \text{H}_2\text{O}$	caséine	1/30	1/60	2
"	albumine d'oeuf	1/30	1/60	"
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	caséine	1/10	1/300	"
"	albumine d'oeuf	1/10	1/350	"
$\text{K}_3[\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$	caséine	1/10	1/300	"
"	albumine d'oeuf	1/10	1/300	"
$(\text{NH}_4)_4[(\text{C}_2\text{O}_4)_2\text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr}(\text{C}_2\text{O}_4)_2]$	caséine	1/20	1/500	"
"	albumine d'oeuf	1/20	1/700	"
$\text{K}[\text{Ag}(\text{CN})_2]$	caséine	1/20	1/100	"
"	albumine d'oeuf	1/20	1/80	"
$\text{K}_3[\text{Fe}(\text{CN})_6]$	caséine	1/10	1/300	"
"	albumine d'oeuf	1/10	1/350	"
$\text{K}_4[\text{Fe}(\text{CN})_6]$	caséine	1/10	1/600	"
"	albumine d'oeuf	1/10	1/600	"

Le domaine de la concentration du sel complexe pour la précipitation est comme suit.

Calcul de l'équivalent de l'ion complexe combiné avec 1 g. de protéine La protéine est précipitée par les complexes, séparée par centrifugation en la lavant cinq fois par l'eau, et on peut sécher dans l'exsiccateur. Le dosage du chrome a été fait comme suit : en prenant 20-30 g de la protéine précipitée, en la décomposant par l'acide azotique fumant, en la neutralisant par l'ammoniaque, et en y ajoutant le peroxyde du sodium pour oxyder le sel chromique en chromate, j'ai colorimétriquement fait le dosage du chrome. Pour le dosage du fer, on a traité la protéine précipitée par l'acide azotique fumant, et s'il y a quelque chose d'insoluble, on y ajoute l'acide hydrochlorique, on chauffe au bain-marie pour dissoudre le composé insoluble et on réduit par le chlorure stanneux, puis on peut en faire le titrage par KMnO_4 à 1/100N. Pour le dosage de l'argent, en décomposant la protéine précipitée par l'acide azotique fumant, en la diluant avec l'eau et en y ajoutant l'acide hydrochlorique,

on peut peser gravimétriquement l'argent comme chlorure. Pour ce dosage du chrome, du fer, et de l'argent, on a d'abord calculé la quantité de l'ion complexe combinée avec 1 g. de protéine, et déterminé l'équivalent de son ion complexe.

a) *Equivalents des ions complexes des sels complexes cationiques* Les équivalents des ions complexes cationiques sont montrés dans la table 4.

Quant à la caséine, les équivalents des complexes cationiques du chrome présentent généralement des résultats concordants, en indiquant approximativement $90-100 \times 10^{-5}$, mais les complexes cobaltiques montrent individuellement des valeurs assez variables. Mais, la valence +2, comme $[\text{Cr}(\text{NH}_3)_5\text{SCN}](\text{SCN})_2$, m'apparaît qu'assez petite. L'équivalent de $[\text{Cr}(\text{urée})_6]\text{Cl}_3$ donne 63×10^{-5} en albumine d'oeuf qui est plus élevé que dans le cas du complexe cobaltique.

b) *Equivalents des ions complexes des sels complexes anioniques* Quant aux sels complexes anioniques, leurs équivalents restent constants

Table 4

protéine (solution à 0.5 %)	sel complexe	concentration de la solution du sel complexe (mol)	Cr % dans la protéine précipitée	ion complexe (%)	équivalent de l'ion complexe combiné avec 1 g. de la pro- téine $\times 10^{-5}$
caséine	$[\text{Cr}(\text{NH}_3)_5\text{SCN}](\text{SCN})_2$	1/30	1.75 1.64	6.56 6.15	72 67
:	$[\text{Cr en}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	1/50	1.50 1.38	6.69 6.16	93 85
:	$[\text{Cr}(\text{Co} \cdot \text{NH}_2 \cdot \text{NH}_2)_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	1/50	1.52 1.48	12.04 11.73	100 97
:	$[\text{en}_2\text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr en}_2]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$	1/100	2.30 2.27	8.36 8.25	97 95
:	$[\text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr en}_2]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$	1/250	3.12 3.14	10.05 10.11	100 101
albumine d'oeuf	$[\text{Cr}(\text{Co} \cdot \text{NH}_2 \cdot \text{NH}_2)_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	1/20	1.04 0.97	8.24 7.69	65 61

Table 5

protéine (solution à 0.5 %)	sel complexe	concentration de la solution du sel complexe (mol)	Cr, Ag, Fe % dans la protéine précipitée	ion complexe (%)	équivalent de l'ion complexe combiné avec 1g. de la pro- téine $\times 10^{-3}$
caséine	$\text{NH}_4 [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4] \cdot \text{H}_2\text{O}$	1/20	3.69 3.75	22.57 22.93	91 95
"	$\text{K}_3 [\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	1/40	1.48 1.40	8.99 8.51	94 88
"	$\text{K}_3 [\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$	1/40	1.47 1.50	11.31 11.54	96 98
"	$(\text{NH}_4)_4 \left[(\text{C}_2\text{O}_4)_2 \text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr} (\text{C}_2\text{O}_4)_2 \right]$	1/80	2.31 2.27	10.88 10.70	100 98
"	$\text{K} [\text{Ag}(\text{CN})_2]$	1/20	7.74 8.00	11.47 11.85	81 84
"	$\text{K}_3 [\text{Fe}(\text{CN})_6]$	1/40	1.61 1.75	6.10 6.62	92 105
"	$\text{K}_4 [\text{Fe}(\text{CN})_6]$	1/80	1.27 1.18	4.81 4.47	96 88
albumine d'oeuf	$\text{NH}_4 [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4] \cdot \text{H}_2\text{O}$	1/20	2.98 2.71	18.22 16.58	70 63
"	$\text{K}_3 [\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	1/40	1.23 1.18	7.47 7.17	77 73
"	$\text{K}_3 [\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$	1/40	1.14 1.10	8.77 8.46	72 69
"	$(\text{NH}_4)_4 \left[(\text{C}_2\text{O}_4)_2 \text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr} (\text{C}_2\text{O}_4)_2 \right]$	1/80	1.90 1.84	8.95 8.67	80 77
"	$\text{K} [\text{Ag}(\text{CN})_2]$	1/20	6.25 5.78	9.26 8.56	64 59
"	$\text{K}_3 [\text{Fe}(\text{CN})_6]$	1/40	1.25 1.18	4.73 4.47	70 66
"	$\text{K}_4 [\text{Fe}(\text{CN})_6]$	1/80	1.10 1.04	4.16 3.94	82 77

indépendamment de l'espèce et de la valence des complexes, et s'accordent suffisamment avec les valeurs données par les complexes anioniques du cobalt. Les équivalents des complexes anioniques ont montré ci-dessous.

Conclusion (1) La précipitation de la protéine par les sels complexes cationiques du chrome est imparfaite comme ceux du cobalt, tandis que les complexes anioniques du chrome, du fer, et de l'argent donnent une précipitation parfaite.

(2) Les complexes cationiques du chrome ne peuvent pas toujours précipiter la protéine, et ceux de la valence +1 ne peuvent jamais précipiter aucune protéine.

(3) Les complexes cationiques du platine ne peuvent pas non plus précipiter la protéine.

(4) Le sel complexe qui n'a pas de charge électrique, tel que $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ne peut jamais précipiter la protéine.

(5) Le complexe d'urée de chrome montre une grande capacité de précipitation sur la protéine, mais on ne comprend pas si ce caractère doit sa forme à la liaison dans son radical complexe.

(6) Les équivalents calculés de la quantité du métal dans la protéine précipitée ne sont pas déterminés au cas des complexes cationiques du chrome à cause de la précipitation

imparfaite, mais, cette variation est moindre que celle montrée par le complexe cobaltique.

(7) Les équivalents des sels complexes anioniques du chrome, du fer, et de l'argent ne sont pas différents les uns des autres, s'accordant suffisamment avec le cas du cobalt, et en générale ils restent constants, indépendamment de l'espèce et la valence des complexes.

(8) L'équivalent du complexe d'urée du chrome par rapport à l'albumine d'oeuf est plus élevée que celui donné par le complexe cobaltique.

(9) De ces résultats obtenus, on peut conclure que la protéine et le sel complexe réagissent stoechiométriquement, et les sels complexes cationiques du chrome, à l'exception de complexe d'urée du chrome, ne donnent pas de précipitation parfaite en ne montrant pas l'équivalent maximum de l'ion complexe combiné avec 1g de protéine. On peut cependant obtenir la précipitation parfaite et l'équivalent maximum par les complexes anioniques du chrome, du fer, et de l'argent. Le complexe d'urée du chrome est aussi parfaitement capable de précipiter la protéine et montré son équivalent maximum.

Les présentes recherches ont été menées à bien grâce à l'aimable indication de M. le

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A New Method of the Graphical Representation of a Quarternary System on a Plane Surface*

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Introduction To represent the phase equilibrium of a quaternary system under constant temperature and pressure, a regular tetrahedron or generally a three-dimensional space figure may be employed. When such a model is considered to be placed on a plane which intersects with the three axes at equal angles, it forms, so to speak, a pyramid with three faces. For the representation of the system on a plane surface, the projection of the model on the base of the pyramid has been employed usually. The projection is orthogonal (perpendicular), or clinographical (perspective) from the zenith of the pyramid.⁽¹⁾⁽²⁾ However, to express the three coordinates of a space figure on a plane surface, one projection is obviously insufficient, and a numerical table or an additional figure is necessary to supplement it. Moreover, for the representation of these projections, a triangular section-paper must be used and, consequently, the treatment of the figure is rather troublesome.

Since the phase rule of a quarternary system is particularly important to treat sea water systematically*** or to establish the sea-salt industry,⁽³⁾ a convenient new method of representing the system on a plane surface will be

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*** A comprehensive review of the literature on the equilibria of the system of sea-salts has been made by D'Ans in (1). While main salt components of sea water are chlorides and sulphates of sodium, potassium and magnesium, owing to the predominance of NaCl, deposition of the other salts takes place always in the coexistence of it; and, under these circumstances, the system can be treated as a quaternary system consisting of three salts or radicals, and water.

(1) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Berlin (1933)

(2) W.C. Blasdale, "Equilibria in Saturated Salt Solutions," New York (1927).

(3) Cf., Y. Tanaka, *J. Japanese Chemistry (Kagaku-no-Ryoiki)*, **8**, 224 (1949)

proposed in the present report, and, by the use of this method, the crystallization processes in the system will be solved quite generally.

New Method Proposed. The method of the graphical representation proposed here is, as shown in Fig. 1, to project the three-dimensional space model of the system, axes of which intersect each other at right angles, orthogonally on two of the axial planes (i.e., on the surfaces of the pyramid). The two projections correspond to the plan and the elevation of the model. The composition of the system will be expressed, as usual, in terms of the absolute number of equivalents of the solutes per 1000 mols of the solvent.* Fig. 1

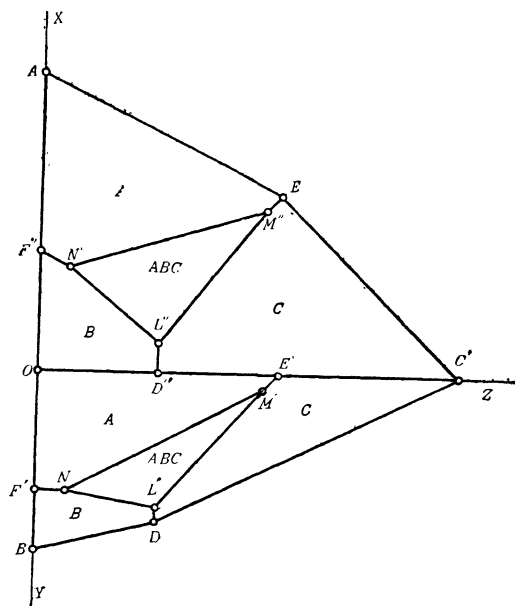


Fig. 1

is the projection of an ideal system, with three salt components and water, on the axial planes YOZ and XOZ . There exist four solid

* For the system of sea-salts, it is convenient to take K^+ , Mg^{++} and SO_4^{--} as unite equivalents.

phases **A, B, C** and **ABC** in this example.*

The two projections of the present figure represent the isothermal of the system completely. The three coordinates of a point can be known immediately from the figure; and, as the coordination is rectangular, the drawing and reading of the figure are very easy by the use of common section-paper. As will be shown later, the graphical solution of the crystallization processes can be executed quite conveniently. Only it is advisable to select the planes of projection according to the system or to the object of the study. Reciprocal salt pairs can also be expressed completely by the present figure. Two cations and one anion or the converse are taken as the salt components, a part of the space being left without use.

Mathematical Solution of the Crystallization Processes Such cases as only a single solid phase is concerned are not yet completely discussed in the four-component system consisting of three salts and water, while the deposition of two or three solid phases at the same time has already been treated extensively. Therefore, before treating the crystallization processes graphically, general solution of the above problem will be made.

An isothermal process, in which the composition of the solution changes according to the water content of the system due to the concentration or the dilution and, at the same time, according to the elimination or the addition of a certain solid phase, may represent the case quite generally. The deposition of a solid phase by the isothermal evaporation of a solution corresponds to this case, and the polythermal changes can also be treated by this procedure.

A unit amount of a mixture, x_p , y_p and z_p mols of the salt component **A, B** and **C**, respectively, per 1000 mols of H_2O , which is not necessarily in equilibrium and in which solid phases may be included, is taken as a starting substance. The point corresponding to this composition will be mentioned as *P*. It is considered that the system undergoes the above-mentioned process and reaches an equilibrium at a certain point, *Q*. The solid phase concerned will be taken as $A_nB_iC_j \cdot mH_2O$, and let the composition of the solution at *Q* be x , y and z mols of the components per 1000 mols of H_2O . Then,

$$x_p = hn + wx, \quad y_p = in + wy \quad \text{and} \quad z_p = jn + wz$$

$$\dots\dots\dots(1)$$

where 1000 w is the water content in mol of the solution of *Q*, and n is the amount of the compound subtracted from the system in mol

* The figure has been chosen so that all the saturation surfaces are plane.

up to that time.* Since, in the present process, the composition of the solution may be altered from the point *P* along this plane, the plane will be mentioned as the composition plane.

Now, when the solid phase exists at *Q*, as the system is considered to be in equilibrium, *Q* should lie at the same time on the saturation surface of the compound. Therefore, *Q* is to lie on the intersecting line between the composition plane and the saturation surface, and, if they do not cross each other practically, the compound does not appear as a solid phase. This line is the crystallization path from *P* with regard to the solid phase in question.

Generally, the saturation surface of a compound is by no means plane. However, when it is assumed as such, a point on this plane can be expressed as

$$x/a + y/b + z/c = 1 \dots\dots\dots(2)$$

where a , b and c are the length of the three axes OX , OY and OZ at which they intersect with the saturation plane.** Then the crystallization path in question can be obtained from (1) and (2) as a straight line. Thus the path has been determined mathematically quite in general. When a third condition is defined, special points on the path can also be determined.

Application of the New Method on the Graphical Solution Now, the above mentioned process will be followed graphically by using the present figure. At first, the intersection of a plane saturation surface (or generally a plane) with the plane of projection will be considered. The trace of the saturation surface of the compound **ABC** in Fig. 1, *LMN*, on the plane XOZ will be taken for illustration. As shown in Fig. 2, let the line *MN* cross with XOZ at t , and t' be its projection on YOZ . Then, since t' should lie on OZ , the point can be found from the figure at once, and consequently, t is easily obtainable. The same is for w' and w , and the trace can be represented by the line *tw*. Similarly, *LMN* intersects with YOZ on uv , and accordingly, the intersecting points of this plane with the axes OX , OY and OZ (a , b and c) are determined immediately.

The determination of the trace of a composition plane on the axial planes is more simple. For example, the trace of this plane on XOZ is expressed, from (1), as

* According to the concentration or the dilution, $w < 1$ or > 1 ; and since $n > 0$ by the elimination, $n < 0$ by the addition. As h , i and j are simple integers and frequently some of them become 0, the equations are simplified for practical instances.

** According to the orientation of the plane, a , b and c may have negative values.

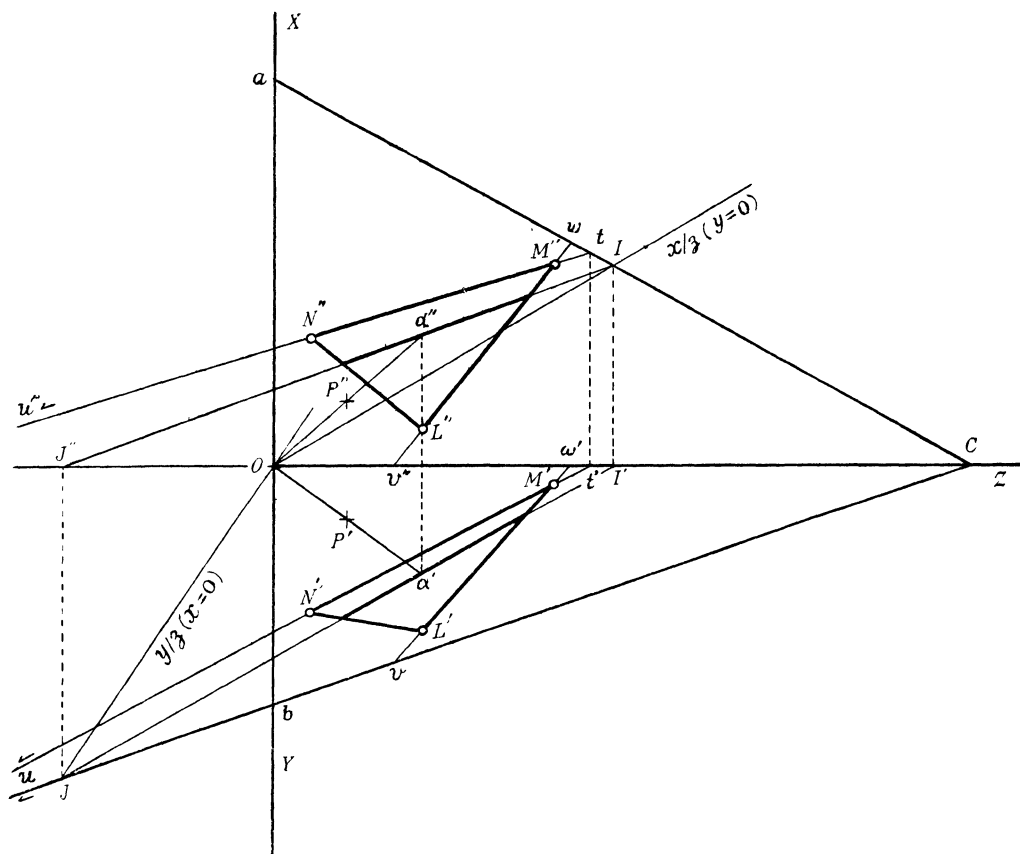


Fig. 2.

$$x/z = (jx_p - hz_p) / (iz_p - jy_p),$$

because $y=0$ on this plane. For the compound **ABC**, as $h=i=j=1$, it becomes

$$x/z = (x_p - y_p) / (z_p - y_p).$$

The line is shown in Fig. 2, and it crosses with ac at I , and similarly the trace on YOZ crosses with bc at J . Then, IJ represents the intersecting line between the saturation plane and the composition plane; it is the crystallization path. In the figure, the path is shown as its projections, IJ'' and $I'J$.

Curved saturation surfaces may be treated by assuming that a limited part of them is plane. Special points on the path can also be obtained easily, and the behavior of crystallization on the boundary of the saturation surface has, as already mentioned, been discussed extensively. The present method may particularly be suitable for the treatment of these instances.* The details will be published elsewhere.

Summary

A new method of representing the phase equilibrium of a quarternary system under a constant temperature and pressure on a plane surface has been proposed. The method is to project the three-dimensional space model of the system, axes of which intersect each other at right angles, orthogonally on two of the axial planes. The two projections can represent the complete state of the system, and the treatment of the figure is quite simple and convenient.

The crystallization processes in such a quarternary system have been solved mathematically quite in general, and the application of the present method of graphical representation on the solution of the processes has been illustrated.

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* For instance, on concentrating the solution with the composition at P , **A** begins to deposit at α in Fig. 2.

A Contribution to the Equilibrium of the System of Sea Salts at 110°C*

By YASUO TANAKA, SHOZO TAKASAGO and TAKASHI KOMATSU

(Received June 21, 1949)

Introduction It is expected from the phase diagram of the system of sea salts at 110°C obtained by D'Ans⁽¹⁾ that, on concentrating the bittern at higher temperatures, the majority of sulfate radicals should easily be removed as kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, together with NaCl, leaving chlorides of potassium and magnesium in the mother liquor. In practice, however, a difficulty lies in the formation of a muddy precipitate, called "earthy sulfate" or "high-temperature crystal," at this stage.⁽²⁾ This precipitate contains a certain potassium salt; its treatment is difficult, and its formation causes the loss of potassium.

In this respect, since the above-mentioned isothermal contains rough estimations in certain respects and, particularly, as seen from Table 1, the points *K* and *X* of D'Ans are too far from the observed values, further experiments are desirable. Another problem to be considered in this connection is the pheno-

menon of supersaturation. Since sulfates especially kieserite, are liable to be supersaturated in the system of sea salts⁽³⁾ and, further, actual bittern has a colloidal nature, containing inorganic and organic suspensions, the influence of supersaturation in both pure and actual solutions must be clarified.

In the present report, the determination of the point *K* and a preliminary experiment concerning the point *X* in the system of sea salts at 110°C have been made with pure substances, supersaturation being taken into consideration. The summary of the results has also been shown in Table 1.

Materials and Experimental Procedure. The materials used were the products of E. Merk. Sodium- and magnesium chlorides were used after recrystallization. From their analyses, all the materials were regarded as sufficiently pure with definite waters of crystallization.

The apparatus adopted for the experiment was similar to what was used by Tschugäff and

Table 1

Pt*	Literature	Temp. (°C)	Na_2Cl_2 (mol/1000)	K_2Cl_2 (mol/1000)	MgCl_2 (mol H_2O)	MgSO_4 (mol H_2O)	Solid phases
<i>I</i>	Leimbach ⁽⁴⁾	100	16	—	26	10	NaCl, Vant., Löw.
	D'Ans ⁽¹⁾	110	34	—	27	11	
<i>I, K</i>	D'Ans ⁽¹⁾	111	33.5	—	27.5	10.5	Löw.+Vant.→Kies. (+NaCl)
<i>K</i>	Leimbach ⁽⁴⁾	100	16	—	49	11	NaCl, Löw., Kies.
	Maeda ⁽⁵⁾	105	21.298	—	44.08	11.32	
	D'Ans ⁽¹⁾	110	33.0	—	28	11	
	Tanaka	"	17.5	—	49.5	13.5	
<i>X</i>	Leimbach ⁽⁴⁾	105	26.8	9.1	31.45	11.86	NaCl, Löw., Kies., Lang.
	Tanaka	110	20	12	41	8	Löw.+Vant.→Kies.
<i>X, V***</i>	D'Ans ⁽¹⁾	108	26.5	29.6	14.0	16.0	(+Lang.+NaCl)
<i>V</i>	"	110	26.1	30.2	14.3	15.7	NaCl, Vant., Löw., Lang.

* Notions are followed after D'Ans. However, the point *Y* of him is denoted here as *X*, because the point has been expressed him by as *X* below 83°. Below 83°, *X* is the coexisting point of NaCl, kieserite, langbeinite and kainite.

** The values of D'Ans are estimated, and the others are observed ones.

*** According to the diagram of D'Ans, since this transition takes place at 108°, löweite does no more coexist with langbeinite at 110°. A new bivariant point, NaCl, Vant., Kies. and Löw., must be given at this temperature, although the point is abridged in his diagram.

* Phase-Rule Studies on the Sea-Salt Industry. II. Presented at the meeting of the Kinki-Section of the Chemical Society of Japan at Kyoto on May 7, 1949.

(1) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Berlin (1933)

(2) Cf., T. Nishimura, *J. Soc. Chem. Ind. Japan*, **20**, 384, 587 (1917); **22**, 255 (1919); S. Oka, *J. Electrochem. (Japan)*, **11**, 186 (1943)

(3) Cf., for instance, H.L. Robson, *J. Am. Chem. Soc.*, **49**, 2772 (1927); V.G. Kuznetsow, *Bull. acad. sci., U.R.S.S., Classe sci. math. nat., Ser. Chim.* **1937**, 385

(4) G. Leimbach, *Mitt. K.F.A.*, **4**, 11 (1925); G. Leimbach and A. Pfeifferberger, *Caliche*, **11**, 428 (1930)

(5) T. Maeda, *J. Soc. Chem. Ind., Japan*, **23**, 573, 954 (1920). It is regrettable Maeda's research is neglected by D'Ans. D'Ans seems to have extrapolated these two points chiefly from the data at lower temperatures.

Chlopin⁽⁶⁾ and by Maeda.⁽⁵⁾ The principle of the method is to maintain the system without evaporation at constant temperature and, at the same time, to stir the system by boiling the solution with a reflux condenser under a proper reduced pressure.* Portions of the solution were taken out for analysis by means of a pipette fitted with a filter of cotton wool. The determinations of the solid phase were omitted.

The analyses were carried out after the usual analysis of the bittern.⁽⁷⁾ Chloride ion was determined volumetrically by the Vorhard's method, sulfate and magnesium by the usual gravimetric methods and potassium gravimetrically as $\text{NaK}_2\text{Co}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$. Sodium was estimated by the difference.** The results were expressed as mols of radicals per 1000 mols of water.

The System, $\text{MgCl}_2\text{-MgSO}_4\text{-H}_2\text{O}$ To know the general conception of the crystallization velocity of kieserite at higher temperatures, this two-salt system was studied at first. The experiments were carried out under various conditions, and the solutions were analysed from time to time. The results are arranged in Table 2.

Table 2

Expt. No.	Time (hr.)	Mg (mol/1000)	Cl_2 (mol/1000)	SO_4 (mol/1000)	Initial conditions and remarks
1	5	86.2	73.3	12.6	No precipitate at room temp. It was formed after heating 3.5 hrs.
	7.5	83.5	73.7	9.8	
	12.5	81.9	74.7	7.2	
	15	81.6	74.6	7.0	
2	2.5	74.5	65.9	8.6	With some precipitate at room temp. (The sample in 1 was used after dilution.)
	4.5	75.7	67.3	7.3 ₅	
	6	75.6	68.2	7.3 ₅	
3	1	125.4	121.7	3.6 ₅	An excess of MgSO_4 was presented at room temp.
	2	125.8	122.1	3.7	
	4	125.9	122.3	3.6	
4	2	84.9	73.8	11.1	With a slight precipitate at room temp.
	4	83.4	74.4	9.0	
	6	84.4	75.9	8.5	
5	1	113.1	107.3	5.8	The solution was concentrated by boiling, and the measurement was commenced after some precip. was observed.
	2	116.6	111.1	5.5	
	4	119.1	115.0	4.1	
	6	120.6	116.7	3.9	
6	2	70.4	58.3	12.1	As in 5.
	4	68.4	57.9	10.5	
	6	69.2	58.9	10.3	
7	2	84.5	73.9	10.6	Some $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was added at high temp. It was once dissolved, and the precip. was observed again after 0.5 hr.
	4	83.1	73.5	9.6	
	6	83.2	74.4	8.8	

* In the present case, as the solutions boil at 110° under a pressure not so far from 1 atm., the effect of pressure on the solubility may be neglected.

** In the case of the partial system, $\text{MgCl}_2\text{-MgSO}_4\text{-H}_2\text{O}$, magnesium was also estimated by the difference, because its direct determination was not so accurate when it existed in large quantities.

(6) L.A. Tschugäff and W. Chlopin, *Z. anorg. Chem.*, **86**, 154 (1914)

(7) Cf., N. Naito and T. Mizuno, "Method of Inorganic Analyses and Tests," Dairen (1944)

Our results agree rather better with those of Maeda at 105°C⁽⁵⁾ than with Campbell's at 100°C,⁽⁸⁾ and the solid phase may be regarded as consisting always of kieserite. The discontinuity, which is observed in Campbell's result and is considered by him as the transition point from kieserite to anhydrous MgSO_4 , is never seen in the results of the others. His data, particularly those near the transition point of him, seem to be too high.

As for the crystallization velocity, it may be concluded from the results that the formation of the nuclei of kieserite is very difficult, and, when they are once formed to a certain amount, further crystallization takes place smoothly and the system reaches to an equilibrium within several hours.

Determination of the point K in the System, $\text{NaCl-MgSO}_4\text{-MgCl}_2\text{-H}_2\text{O}$ As the general tendency of the crystallization velocity in the system of sea salts at higher temperatures could be seen from the above experiment, the present experiments were executed under the following procedure: a mixture with a certain composition, nearly saturated or with a precipitate, was concentrated step by step by boiling, and for each step the solution was analysed after keeping the system at 110°C for 5 hours. The results are shown in Table 3 and Fig. 1.* Considering from the composition of the start-

Table 3

Expt. Ser. No.	Na_2 (mol/1000)	Mg (mol/1000)	Cl_2 (mol/1000)	SO_4 (mol/1000)	Total salts (mol/1000)	Solid phases
A —	(25	50	60	15	75)	(initial composition)
11	23.3	54.3	64.9	12.7	77.6	NaCl , Löw.
12	20.5	58.5	65.9	13.1	79.0	" "
13	15.4	66.3	68.2	13.5	81.7	" "
14	10.9	73.0	70.1	13.8	83.9	(metastable)
15	11.7	68.0	69.5	10.2	79.7	(metastable)
						NaCl , Löw., Kies. (not in equil.)
B —	(14	54	35	33	68)	(initial composition)
16	9.4	70.2	54.4	25.2	79.6	Löw., Kies.
17	15.1	64.9	62.9	17.1	80.0	" "
18	19.3	60.9	71.1	9.0 ₅	80.2	" "
						(metastable)
C —	(16	53	53	16	69)	(initial composition)
19	16.7	62.9	65.8	13.7 ₅	79.6	Löw. (near K-point)
20	14.7	64.5	71.6	7.6	79.2	NaCl , Kies
21	11.8	69.3	75.5	5.6	81.1	" "
D 22	9.7	75.0	79.2	5.5	84.7	NaCl , Kies.
23	5.2	87.4	89.5	3.1	92.6	" "
24	0.4	109.0	107.1	2.3	109.4	" "
25	0.1	119.0	117.4	1.7	119.1	" "

* As for the graphical representation of the system used here, see I of this report (this Bulletin, **23**, 11 (1950))

(8) A.N. Campbell, K.W. Downes and C.S. Samis, *J. Am. Chem. Soc.*, **56**, 2507 (1934)

ing mixtures, these solutions are well explained as being in contact with the solid phases described in the table, respectively.

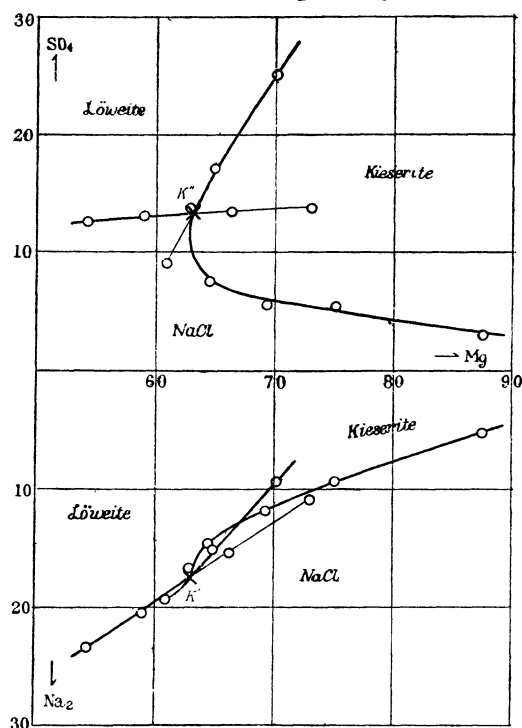


Fig. 1

In the figure, three boundary curves cross each other quite well at one point, and so it can be regarded as the point *K*. The fact that the curves of series A and B extend beyond this point may be explained as due to the existence of meta-stable equilibrium owing to the difficulty of transformation of the crystals once deposited, or to the phenomenon of supersaturation. The composition of the point is near to

Na₂ 17.5, Mg 63, Cl₂ 67 and SO₄ 13.5 mols per 1000 mols of H₂O.

To compare the result with the data in Table 1, our result coincides quite well with that of Leimbach at 100°C. Maeda's result at 105°C also lies not so far from them. The magnesium content of the point by D'Ans is obviously too small. Consequently, the point *K* of D'Ans at 110°C should be revised, and löweite should have a considerably larger field of existence at higher temperatures.

Preliminary Experiment on the System, NaCl-KCl-MgSO₄-MgCl₂-H₂O The solubility determinations in the five component system of sea salts, particularly those of the boundary curve between the points *X* and *R* at 110°C have been undertaken. Although the experiment is not yet completed, it is concluded at least that the potassium contents of the results are smaller and the magnesium contents are larger, particularly in the vicinity of the point *X*, than what are expected from the diagram of D'Ans. The point *X* seems to lie at about

Na₂ 20, K₂ 12, Mg 49, Cl₂ 73 and SO₄ 8 mols per 1000 mols of H₂O, and the point agrees pretty well with that of Leimbach at 105°C (cf., Table 1). The point *X* of D'Ans, too, seems to be revised, and langbeinite may have a larger field.

However, even if the point *X* lies where it is found in the present result, the crystallization path in concentrating sea water at higher temperatures is to pass through the kieserite field as well, and there is no possibility of depositing langbeinite or other salts on the way. Extensive studies in this concern is desirable, and, at the same time, supersaturation in the actual evaporation of the bittern must be examined carefully.

Summary

1. The solubility of magnesium sulfate in magnesium chloride solution at 110°C has been studied with a special reference to the crystallization velocity. In this system, it seems that the formation of the nuclei of kieserite is very difficult, and, when they are once formed, further crystallization takes place smoothly.

2. In the system, NaCl-MgSO₄-MgCl₂-H₂O, at 110°C, it has been found that the point *K* lies at about

Na₂ 17.5, Mg 63, Cl₂ 67 and SO₄ 13.5 mols per 1000 mols of H₂O. The content of magnesium is much larger than what has been estimated by D'Ans, and, accordingly, the löweite field of him should be enlarged.

3. Preliminary experiment on the five component system of sea salts at 110°C has shown that langbeinite may have a larger field than expected from the diagram of D'Ans.

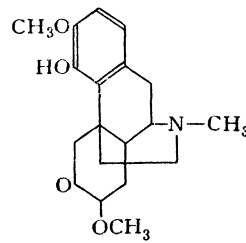
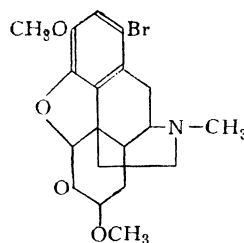
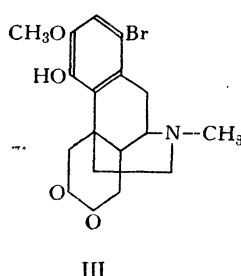
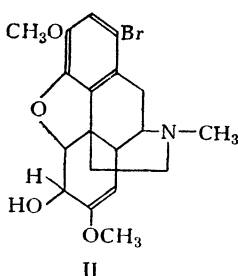
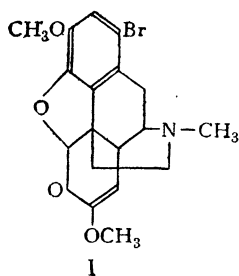
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On the Reduction of 1-Bromo-sinomenine*

By Kakuji GOTO, Tatsuo ARAI and Tetsuro KONO

(Received July 16, 1949)

By the catalytic reduction of 1-bromo-sinomenine (I) in weakly acidic solution, as well as by the sodium-amalgam reduction, its oxide ring is invariably opened and we obtain a mixture of alkali-soluble bases, which is almost inseparable into pure components. However, by the reduction with aluminium isopropylate we obtained a base of m. p. 171°C , to which we give the constitution II and which we will call 1-bromo-sinomenine-alcohol from the following reasons:



(1) The base of m. p. 171°C is insoluble in 2% caustic soda and gives no ferric chloride reaction.

(2) By benzoylation, it gives a monobenzoyle derivative, but it is not reacted by diazomethane.

(3) It contains two original methoxyl groups, one of which is exceedingly hydrolysable with dilute acid (enol methoxyl).

(4) It gives 1-bromo-diacetyl-sinomenol, namely, 1-bromo-3, 7-dimethoxy-4, 6-diacetoxy-phenanthrene, on acetolysis.

The substance of m. p. 171° may be, therefore, an optical antipode of hypothetical 1-bromo-7-methoxy-codeine, for it contains the morphine skeleton and all its functional groups, but superfluous bromine and enol-methoxyl at the same time.

A very remarkable property of this substance is the ease, with which it is converted into 1-bromo-sinomeninone (III). For instance, when the substance of m. p. 171° was dissolved in 2% hydrochloric acid at room temperature and when the solution was immediately made alkaline with sodium carbonate, we obtained 1-bromo-sinomeninone in 64% yield. It seems that the mere dissolution of the substance in a dilute mineral acid effects this deep-seated transformation.

Now, we find several cases of hydrolytical

opening of oxide-ring in the chemistry of the morphine group as in the molecular rearrangement of thebaine into thebenine or of morphine into apomorphine. In both cases, a stronger acid (14% or fuming) and a higher temperature (100° or 130°) are necessary. Only in the conversion of β -chlorcodide into β -ethyl-thiocodide, the opening of oxide-ring is effected by 5/2 N caustic soda at the boiling temperature (after Small).

The above-mentioned property of this substance led us to some confusion at the earlier stage of investigation. We supposed at first the substance of m. p. 171° had the constitution IV, namely 1-bromo-dihydrosinomenine, on the ground that the substance of this constitution could never be obtained by the bromination of

dihydrosinomenine (V), but we always got 1-bromo-sinomeninone (III) instead.⁽¹⁾ We suspected that this might have been due to the easy decomposition of preformed IV into the more stable III.

If it is the case, then the substance of m. p. 171° formed by the reduction, may be decomposed into III by a slight shock, namely by the dilute hydrochloric acid. It may be strange that the ketonic group remains intact, while the double linkage is reduced by Meerwein-Ponndorf's method. But Lund⁽²⁾ gives an instance where ketonic group and α, β -double bond were reduced simultaneously.

In this respect, we applied the above reduction method to sinomenine and 1-bromo-sinomenine, with the results that both these substances were very difficultly reduced on their ketonic group. We recovered some unchanged

* Studies on Sinomenine, Part LXII. Parts LIX and LX, Acta Phytochimica. XV, 183, 187 (1949)

(1) *Ann.*, **489**, 94 (1931)

(2) *Ber.*, **70**, 1520 (1937)

substances, but could not isolate reduced bases in crystalline state.

Catalytic reduction of 1-bromo-sinomenine in pyridine solution, using PtO_2 as catalyst, was more fruitful. It gave the substance of m. p. 171° and 1-bromo-dihydrosinomenine, each in a 10-20% yield. This indicates that in some molecules the ketonic group only and in others the double bond as well as the oxide-ring are reduced. However, in sinomenine and 1-bromo-sinomenine the reduction goes on in a somewhat different way. For, we obtained from the former dihydrosinomenine and dihydrosinomeninol, and from the latter, 1-bromo-dihydrosinomenine. Thus the oxide-ring seems to play an important part in the catalytic reduction as well as in the Meerwein-Ponndorf's reduction.

The production of the substance of m. p. 171° in the above catalytic reduction seems to have decided the constitution of this substance in favor of formula II. But the last decision was given by the reformation of 1-bromo-sinomenine by the oxidation of the substance of m. p. 171° by Pshorr's method. The latter gave on the oxidation with chromic acid as well as with potassium permanganate, the starting material, 1-bromo-sinomenine, in tolerable yield, viz. 40% resp. 20%.

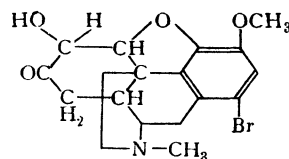
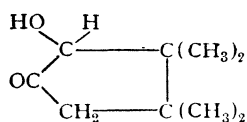
The constitution being thus settled, a problem still remains, why then 1-bromo-sinomenine alcohol is so unstable towards dilute mineral acid. We do not think that the $\text{C}_{(7)}$ -situated ketonic group is so efficient as to make the oxide-ring open by such mild treatment. For, we prepare 1-bromo-sinomenine-ketone by heating 1-bromo-sinomenine in 10% hydrochloric acid solution for one hour at 100° .⁽³⁾ The fission of oxide-ring may be, therefore, brought about perhaps by one of the following causes.

(1) The $\text{C}_{(6)}$ -situated alcohol group may cooperate with $\text{C}_{(7)}$ -situated ketonic group to open the oxide-ring. The newly introduced alcoholic group may converge to one ketonic group in $\text{C}_{(6)}$ to be able to conjugate the ketonic group in $\text{C}_{(7)}$. The drawback of this supposition is that we have no similarly constituted morphine alkaloids, and therefore have met with no analogical transformation.

(2) The second theory is based on α -ketol-rearrangement and recurs to the above hypothetical 1-bromo-dihydrosinomenine (IV). If the $\text{C}_{(6)}$ -alcoholic and $\text{C}_{(7)}$ -ketonic group, produced by the hydrolysis of the enol methoxyl, interchanged the position by α -ketol-rearrangement, then the supposed very unstable base IV might be produced, and this may be instantly transformed into 1-bromo-sinomeninone, owing to its supposed instability.

This transformation, caused by such mild

reagent, might at first seem very strange, but the investigation of Ingold and Shoppee⁽⁴⁾ on the tautomerism of 1-hydroxy-2, 2, 3, 3-tetramethyl-cyclopentanone-5 seems to throw some light on the above view.



Naturally, there may be some deep difference in the behaviour of 5-membered and 6-membered rings, yet the similarity of the constitution of these two substance is more than apparent. If, by the α -ketol rearrangement, the $\text{C}_{(6)}$ -ketonic and $\text{C}_{(7)}$ -alcoholic base is produced from 1-bromo-sinomenine-alcohol even in a minute quantity and transformed into more stable 1-bromo-sinomeninone, then the reaction, as it is not reversible, may largely proceed in this direction.

The fact that we always obtain 7-hydroxy-derivative only in the catalytic reduction of sinomeninone, an α -diketone, may indicate that the equilibrium is strongly in favor of 7-hydroxy-6-keto-derivative than the reversed one.

Experimental

(1) Preparation of 1-bromo-sinomenine alcohol

A. With aluminium isopropylate The apparatus was constructed after H. Lund.⁽²⁾ One and half gram of aluminium-isopropylate was dissolved in 20 cc. isopropyl alcohol and 2g. of 1-bromo-sinomenine was added. The reduction was carried out on a steam bath and was complete after two or three hours, during which 50 cc. isopropyl alcohol were added in drops. Then the solvent was distilled over and the residue was treated with 11% cold caustic soda solution so as to dissolve the aluminium hydroxide almost completely. The alkaline solution was then shaken with ether four times. When the dried ether was distilled away, 1-bromo-sinomenine alcohol crystallized out in stout prisms. The crystallisation can be accelerated with addition of alcohol. M. p. 171° . Yield 40-60%. Recrystallization from methanol, alcohol or acetone did not raise the melting point. The substance showed no coloring with ferric chloride in methanol solution.

Analysis Found: C, 56.17; H, 5.422; N, 3.374; CH_3O , 14.93%. Calc. for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{NBr}$ (408): C, 55.88; H, 5.39; N, 3.431; CH_3O , 15.20%. Sp. rotation. 0.2055g. subst. was dissolved into 10 c.c. methanol.

$\alpha = +1.10^\circ$ $[\alpha]_D^{10} = 1.10/2.055 \times 100 = +53.530^\circ$. Mol. weight after Rast. Camphor, 3.274, 3.834, 3.460 mg.; subst., 0.195, 0.336, 0.358 mg. $\Delta = 6.0^\circ, 8.5^\circ, 10.6^\circ$ Mol. weight = 379, 412, 390

(3) This Bulletin, 5, 165 (1930)

(4) Shoppee, *J. Chem. Soc.*, 1928, 1667

Methiodide Prepared in methanol solution and recrystallized from water. M. p. 232-233°. Analysis. Found: C, 43.52; H, 4.504; I, 23.01%. Calc. for $C_{20}H_{25}O_4NBrI$: C, 43.64; H, 4.54; I, 23.08%.

Once, when the methanol solution was boiled, we obtained the methiodide of 1-bromo-sinomeninone (m. p. 245-246°), instead of that of the original substance. This might be due to the liberation of hydroiodic acid during the reaction. (compare (2))

Monobenzoyl ester 0.5g. of 1-bromo-sinomenine alcohol was dissolved in 1 cc. pyridine and benzoyl chloride (1 mol) was added under cooling. The mixture was then set aside overnight and the benzoylated substance was precipitated with water. The precipitate was then collected and recrystallized from the mixture of alcohol and acetone. M. p. 194.5°. The yield was ca. 70%. The analysis coincides well with the calculation for monobenzoyl-compound. (Found: C, 61.15; H, 4.89%. Calc. for $C_{26}H_{23}O_5NBr$: C, 60.94; H, 5.08%)

The ester was hydrolysed to the original substance (m. p. 171°), when boiled with sodium carbonate in pyridine.

B. Reduction of 1-bromo-sinomenine with PtO_2+H_2 in pyridine solution One gram of 1-bromo-sinomenine was dissolved in 20 cc. of pyridine and 0.05g. PtO_2 was added. In shaking the flask in the hydrogen atmosphere at 1 atm. and 26-27°, ca. 100 cc. hydrogen was absorbed in three hours and the reaction came almost to a standstill. As the pyridine alone had absorbed ca. 40 cc. hydrogen in a blank test, the net volume of hydrogen absorbed amounted to 56.5 cc. (at N. T. P.), corresponding to one molecular equivalent (calc. 55 cc.). The platinum black was then filtered off and the solution was concentrated in vacuum. The residue was dissolved in 5% acetic acid and filtered quickly. The filtrate was made alkaline with 11% caustic soda solution and was shaken four times with ether. The treatment of the ethereal residue was done as described under (A), and 1-bromo-sinomenine alcohol (m. p. 171°) was obtained in 10-20% yield. The m. p. was unaltered by admixture with the specimen prepared by the aluminium isopropylate method.

When the above mentioned caustic soda solution was saturated with carbon dioxide and extracted with chloroform, a substance which melts at 216° was obtained. The melting point was, however, raised to 235°, when recrystallized from chloroform and alcohol. The yield was 10-20%.

It gave a green color with ferric chloride and formed a semicarbazone of m. p. 250-256° and methiodide of m. p. 224° (dec.). These facts indicate that we have here 1-bromo-dihydrosinomenine.⁽⁵⁾

(2) Rearrangement of 1-bromo-sinomenine alcohol into 1-bromo-sinomeninone

This was effected under various concentration of hydrochloric acid with varying yields. The best yield was described in the theoretical part. Dilute acetic acid seems to effect this change very slowly, or not at all. (compare (4)).

(3) Acetolysis of 1-Bromo-sinomenine alcohol

0.7g. of the substance was boiled with 0.7g. of

sodium acetate and 7cc. of acetic anhydride for eight hours. After the solution was concentrated to a syrup in vacuum, a quantity of water was added, the precipitate was collected (ca. 0.7g.) and recrystallized from glacial acetic acid. M. p. 186° (also, the mixed melting point with 1-bromo-diacetyl-sinomenol of different origin).

Analysis. Found: C, 55.71; H, 3.921; CH_3O , 13.90%. Calc. for $C_{20}H_{17}O_6Br$: C, 55.43; H, 3.92; CH_3O , 14.31%.

(4) Catalytic reduction of 1-bromo-sinomenine alcohol

By the catalytic reduction of 1-bromo-sinomenine alcohol with $Pd-SO_4Ba$ as catalyst in a weakly acidic (hydrochloric or acetic) solution, we obtained (a) sinomeninone, when only one mol of hydrogen was absorbed, and (b) α - and β -dihydrosinomeninones, when two mols of hydrogen was utilized. Sinomeninone was identified with its melting point (151°, when dried over P_2O_5 in vacuo at 100°), with melting point of the iodo-methylate (M. p. 265°), with elemental analysis, with methoxyl determination (two, one from crystal methanol) as well as with its decomposition into 3-methoxyl-4,6-acetoxyl-phenanthrene. It is clear that the weak acidity of the solution first converted the substance into bromo-sinomeninone and the debromination followed.

α - and β -Dihydrosinomeninone are only the further reduction product of the sinomeninone. The remarkable fact here is that the 2% acetic acid effected the conversion of the substance into the 1-bromo-sinomeninone in this case. Seeing that the time elapsed in this reduction amounted to more than 24 hours and that the debromination necessarily gave rise to some hydrobromic acid, the above change does not seem to be exceptional.

(5) Reduction of some other sinomenine derivatives with aluminium isopropylate

The experimental condition was the same as was given in ((1) A). The results are summarized as follows:

(i) Sinomenine (4g.) Starting material was recovered more than 50%. No other crystalline substance was isolated from mother liquor.

(ii) 1-Bromosinomenine hydrochloride (6g.) Starting substance was recovered in 10%, besides a small amount of a substance of m. p. 216°, which was not further examined.

(iii) (+)-1-Bromo-dihydro-codeinone (4.4g.) Four grams of non-phenolic base (m. p. 188°) was obtained, but not investigated further.

(iv) 1-Bromo-sinomeninone Reduction took seven hours. Ether took up almost nothing from the caustic alkali solution. Chloroform extraction from soda alkaline solution, gave 2.3g. of mixed bases. Acetylation of this mixture gave a minute quantity of a substance of m. p. 184°. This melting point coincides with that of triacetate of 1-bromo-tetrahydro-sinomeninone prepared for comparison.⁽⁶⁾ The mixed melting point was also unaltered. This proves that in 1-bromo-sinomeninone, its both ketonic groups were reduced by aluminium isopropylate in a small degree.

(6) K. Goto and T. Arai, This Bulletin, 17, 116 (1942)

(5) This Bulletin, 4, 197 (1929)

(6) Catalytic reduction of sinomenine and 1-bromo-sinomenine with $\text{PtO}_2 + \text{H}_2$ in pyridine solution

Conducted as given in (1) B).

(i) Sinomenine (1g.) was reduced with PtO_2 (0.2g.) in 20cc. pyridine. Temperature 25-26°. It took 2-5 hours to absorb 120cc. hydrogen (calc. 136cc. for 2H_2). Yield: dihydro-sinomeninol (F. 160-162°) in 60%.⁽⁷⁾

(ii) When only 0.05g. PtO_2 was used in the same experiment, one mol of hydrogen was absorbed in three hours. Yield: dihydro-sinomenine (m. p. 198°) in 50-60%. Also, it was identified as oxime (m. p. 212-213°).

(iii) 1-Bromo-sinomenine (1g.) was reduced in the same condition as in (ii). One mol of hydrogen was absorbed in three hours. Yield: 1-bromo-dihydro-sinomenine (m. p. 235°) in 20-30%. Its semicarbazone showed the correct melting point 248-250°.

The reduction seems thus largely to depend upon the quantity of the catalyst used. When the catalyst was used in a small quantity, the reduction stopped after the hydrogenation of the double linkage, while in larger quantity the ketonic group is reduced to alcoholic also. This is a direct contradiction to the reduction of 1-bromo-sinomenine, in which the ketonic group is reduced in prior to the double linkage. This may be due to the influence of the oxide-ring. We have already met with the similar phenomenon in the aluminium isopropylate reduction (compare (5)).

(7) Oxidation of 1-bromo-sinomenine alcohol to 1-bromo-sinomenine

A. With CrO_3 . 0.1g. CrO_3 was dissolved in 10 cc. of acetone. One third of this solution was dropped slowly into 10cc. of acetone solution containing 0.2g. of 1-bromo-sinomenine alcohol, at room temperature. The brown precipitate was

filtered off and the filtrate was concentrated until crystals separated. The crystals (m. p. 180-200°) were dissolved in chloroform and the solution was washed with dilute caustic soda. To the concentrated chloroform solution, a large quantity of alcohol was added to make 1-bromo-sinomenine crystallize out. M. p. 214°, also admixture with 1-bromo-sinomenine prepared by bromination method. Yield 40%. Analysis. Found: C, 55.86; H, 5.13; N, 3.20%. Calc. for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{NBr}$: C, 56.11; H, 4.93; N, 3.45%.

B. With KMnO_4 . 1-Bromo-sinomenine alcohol (0.2g.) was dissolved in acetone (10cc.) and KMnO_4 (0.08g.) was added little by little during 1.5 hours. MnO_2 was filtered off, and the solution was concentrated. Dilute caustic soda was added and 1-bromo-sinomenine was extracted three times with chloroform. The purification was carried out as above, but the melting point was somewhat lower (210°). The base was therefore turned into its methiodide, which showed the correct melting point 211° (also the mixed melting point). Yield of the base 20%.

The 1-bromo-sinomenine alcohol was not, however, acted by H_2O_2 in acetic acid or by NaOBr in a mild condition.

Our thanks are due to Miss Yoshiko Suzuki of our laboratory (Agricultural Department), who helped us in carrying out some of the micro-analyses in this work.

The cost of this work was partly defrayed by the Science Research Fund, given by the Educational Ministry for which we thank here heartily.

*Agricultural Department, the University of Tokyo
and the Kitasato Institute.*

(7) K. Goto and S. Mitsui, This Bulletin, 5, 282 (1930)

Absorption of Nitrogen by Zirconium and Iron

By Shizuo FUJIWARA

(Received August 19, 1949)

Zirconium is one of the elements which are said to have good effect of denitrogen, deoxygen, etc., when added in steel. It is used, also, as a getter in the vacuum-tube. These are owing to its great affinity to metalloid atoms.

It is the object of the present papers to investigate in detail the characteristics of the nitrides formation of zirconium, ferro-zirconium and pure iron, which will make a contribution to the problems concerned to the use of this element.

Experimental

The increase of the weight of the samples (zirconium-metal, ferro-zirconium and pure

iron) which was resulted from the progress of the nitrogen absorption with the samples, was measured.

The dish containing the sample was hanged vertically with a spring balance and the whole was settled in a tube. All of the equipments, the dish, the spring balance and the tube, were made of fused silica. The stream of the purified nitrogen was sent into the tube which was heated in an electric furnace.

As the sample absorbed nitrogen at some temperature, the balance stretched and the stretched length was measured with the telescope of the cathetometre, and then temperature was gradually raised. Increase of 1 mg. in weight corresponded to 0.628 ± 0.002 mm. of

the stretched length, Δl .

Results

Samples Zr-metal: amorphous, black powder made in Japan.

Fe-Zr: " "

Iron: powder of reduced iron made by Kahlbaum Co.

In Table 1 the compositions of the samples are given.

Table 1

Sample	Zr cont. (total %)	Zr % (as carbides)	Zr % (as oxides)
Zr-metal No. 114	94.0	4.9	6.0
103	84.0	49.3	—
131	96.7	7.3	21.2
133	96.5	3.9	29.9
Fe-Zr	40	28.1	0.4
	44	29.9	3.1

Experiments Expt. No. 1—Zr-metal No. 114. Sample taken: 100.5 mg. The reaction between Zr and nitrogen began in the range of 265°-290°C and then continued linearly as the temperature was raised and the time passed. The temperature was raised up to 1000°C during 6 hours. (Table 2).

Table 2

Expt. No. 1			Expt. No. 2		
T°C	t min.	Δl mm. ($\times 1/100$)	T°C	t min.	Δl mm. ($\times 1/100$)
265	85	0	470	120	0
290	96	25	520	130	20
400	199	235	620	186	85
450	240	350	"	220	205
520	250	390	"	260	465
650	298	515	700	265	490
760	323	589	760	275	565
870	330	679	850	281	620
920	365	870	940	290	640
1020	368	919	950	310	740

Expt. No. 3			Expt. No. 4		
T°C	t min.	Δl mm. ($\times 1/100$)	T°C	t min.	Δl mm. ($\times 1/100$)
100	10	0	250	67	0
400	35	75	280	77	35
"	100	100	300	164	175
"	295	340	"	307	315
"	518	765	"	407	425
600	559	780	500	542	555
770	576	740	800	557	585
730	616	"	850	602	620
880	626	720	900	610	605
900	636	690	"	620	595
940	645	725	"	627	585
910	655	750	1030	632	595
900	677	780	"	662	625
"	685	710			
"	725	"			
950	733	750			
1010	744	750			

T°C temperature where the experiment was carried out

t min. ...the time since the start of the experiment

Δl mm....stretching of the spring balance

Expt. No. 2—Zr-metal No. 103. Sample taken

: 109.0 mg. It is strange that the beginning-temperature of the reaction lies between 470°C and 520°C and differs from those of the other samples (No. 114, 131, 133) which react at 265°-290°C.

This would be due to the special condition of the sample, because, while all the other samples were produced through reduction with carbon or sodium metal, the present one was made by alumino-thermit method and would have been affected by aluminium in some way.⁽¹⁾

Expt. No. 3—Zr-metal No. 131. Sample taken: 111.5 mg. In this case, the decomposition occurred at 600°C and the decrease of the weight of the sample was observed. This decreasing tendency continued up to 900°C. Just above 900°C, the length of the spring balance once increased and then the decreasing tendency began again (Table 2).

Similar decreasing tendency at 900°C was also observed in the case of the sample, Zr-metal No. 133, in Expt. No. 4.

The present author has found by chemical analysis that the decomposition or the transformation of carbides into nitrides occur at 700°C and 900°C in the researches concerning the metalloid compounds of zirconium and hafnium.⁽²⁾ The results found here seem to correspond to that phenomenon.

Expt. No. 4—Zr-metal No. 133. Sample taken: 76.6 mg.

Expt. No. 5—Fe-Zr No. 44. Sample taken: 115.2 mg.

Expt. No. 6—Fe-Zr No. 40. Sample taken: 131.1 mg.

The most distinctive character of the Fe-Zr that makes it different from Zr-metal is the temperature where the absorption of nitro-

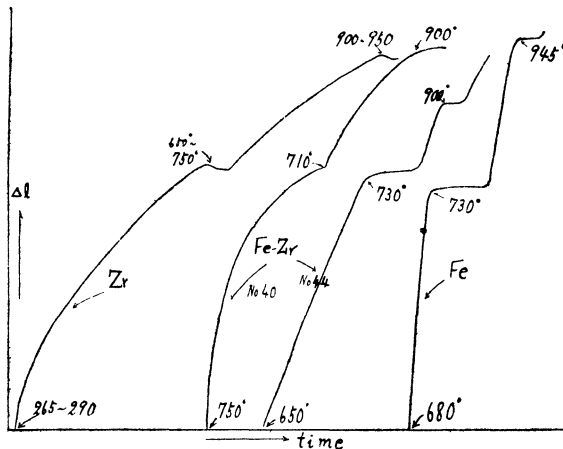


Fig. 1

(1) Aluminium begins to absorb nitrogen at 600°~700°C. (K. Iwase, *Sci. paper. Tohoku Univ.*, 15, 531 (1926))

(2) S. Fujiwara, *J. Chem. Soc. Japan*, in press.

gen begins; it is $650^{\circ}\sim 750^{\circ}\text{C}$ which is far higher than $265^{\circ}\sim 290^{\circ}\text{C}$, at which Zr-metal begins to absorb nitrogen.

Moreover, in this case the absorption curve shows the breaks at 700°C and 900°C as shown in Fig. 1.

It must be emphasized that these temperatures where the absorption begins and the breaks occur exactly coincide to those for the pure metal of iron except that the curvature for Fe-Zr is greater and the figure of the absorption curve for iron is rather steep.

Expt. No. 7—Pure Iron. Sample taken: 163.0 mg. In the earlier stages of heating, the weight of the sample decreases as seen in Table 3. It would be due to the desorption of the moisture contained in the sample.

Table 3

Expt. No. 5			Expt. No. 6			Expt. No. 7		
T °C	t min.	Δl mm. ($\times 1/100$)	T °C	t min.	Δl mm. ($\times 1/100$)	T °C	t min.	Δl mm. ($\times 1/100$)
630	165	0	700	114	0	200	16	-185
550	172	15	"	131	130	"	44	-215
700	191	65	"	170	215	250	50	-255
"	220	165	710	191	230	300	55	"
740	245	185	"	222	250	"	76	"
730	258	245	910	235	275	670	133	0
"	290	"	"	250	295	680	144	20
820	308	"	"	275	325	730	169	347
960	330	310	920	302	370	"	179	372
970	345	"	920	310	"	"	184	"
"	353	"	"	320	"	"	219	"
"	368	345				800	226	372
"	380	360				940	244	457
						945	254	492
						"	259	517
						"	274	"
						"	284	"
						"	294	542

The absorption of nitrogen begins at about 650°C and then the weight of the sample increases rapidly. The absorption goes on straight up to 730°C , where the increasing tendency of the weight stops and the equilibrium comes.

After this equilibrium is passed, the rapid increase in the weight of the sample begins again and then comes the equilibrium at 945°C . These circumstances are shown in Fig. 1.

The nitrides formation of the γ -iron in the

range of 620° and 700°C has been found only by K. Iwase⁽¹⁾ among many workers. The results of the present author that the absorption begins at 650°C and the equilibrium is obtained at 730°C seem to coincide to those of K. Iwase.

Conclusion

The characteristic temperatures are summarized in Table 4 and in Fig. 1. Fe-Zr and

Table 4

	Zr-metal	Fe-Zr	Iron
Temp. where N_2 absorption begins	265 ~ 290	650 ~ 750	650
Temp. where 1st equilibrium begins	600 ~ 700	730	730
Temp. where 2nd equilibrium begins	900 ~ 950	900 ~ 960	945

iron coincide exactly both in the beginning temperature and the equilibrium temperature. These features may be attributed to the nitrogen absorption by α - and the γ -iron. The effect of zirconium in Fe-Zr may be seen in the gentle slope of the absorption curve for Fe-Zr No. 40, but it is not so distinct.

As zirconium has great affinity to the metalloid atoms, it begins to absorb nitrogen at as early as 260°C . Two breaks are observed in the absorption curve of Expt. No. 3 (Sample 131) and one in Expt. No. 4 (Sample 133). These breaks would represent some equilibrium, but the reactions occurring here would be different from those for pure iron and Fe-Zr, and as it could be found in the former case, the decrease of the weight was due to the decomposition of the samples.

The absorption curve goes on linearly with the rise of temperature in the case of Zr metal and is far less steep than those for iron and Fe-Zr. It may be concluded from all these results that the nitrogen absorption of the former is different from the latter.

The author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance and encouragement.

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On the Anomalous Melting Point and the Decomposition of Acetyl-salicylic Acid

By Yojiro TSUZUKI and Masako SAWADA

(Received September 2, 1949)

In Beilstein's Handbook Vol. X (1927) it is described that Bayer's aspirin is different in some respects from most preparations of acetyl-salicylic acid, namely, it has a crystalline form of plates, and shows a high melting point of 137°, while others are needles and usually melt at 135°. Some pharmacists,⁽¹⁾ having made comparative studies on a number of samples of acetyl-salicylic acid produced in France, Germany and in our country, came to the conclusion that our domestic products are not inferior to the imported ones. It was also shown⁽²⁾ that the crystals of various domestic products consist of plates like those of Bayer's aspirin, although some difference is observed in crystalline habit according to makers, but, unfortunately, there lacks any description on their melting points.

Melting point Some papers have already been published⁽³⁾ on the examination how the melting point of acetyl-salicylic acid varies with the solvents used for recrystallization, but the melting points described by them were always below 134°. With a view to reinvestigate this question, we have made recrystallization from various solvents and measured the melting points of the products.

The recrystallization was carried out by evaporating the solvents slowly at lower temperatures. The crystals separated out were usually plates like Bayer's aspirin, but sometimes there appeared prismatic crystals. The melting point was determined by putting a capillary tube with the sample suddenly in a bath heated up to 130° and by elevating the temperature of the bath at a rate of 4° per minute. The results are presented in Table 1, which shows that the melting point, being in most cases nearly 135°, reaches as high as 137°, when acetyl-salicylic acid is recrystallized from a hydrophobic solvent such as chloroform. Thus it may safely be concluded that Bayer's aspirin is not a special chemical substance in melting point nor in crystalline form.

Table 1

Solvent	m. p. (corr.)	Solvent	m. p. (corr.)
Chloroform	136.3-137.4	Ethyl alcohol	135.1
Dioxan	135.7	Methyl alcohol	132.6-133.6
Acetic anhydride	135.7	Water	131.6
Ether	135.6		

(1) H. Suzuki, I. Keimatsu and K. Ito, *Chem. Abstr.*, **29**, 5429 (1935)

Decomposition It has already been recognized that acetyl-salicylic acid undergoes decomposition before it reaches its melting point, but the extent of thermal decomposition has never been measured. Hence we have measured the quantity of salicylic acid set free by thermal decomposition⁽⁴⁾ of acetyl-salicylic acid, employing a newly devised colorimetric method of determining salicylic acid, since none of the known methods⁽⁵⁾ is found quite suitable for our purpose.

The standard solution of our new method is made by adding 0.5 cc. of a 12 per cent aqueous solution of ferric chloride hexahydrate to 20 cc. of a 0.06 per cent methanol solution of salicylic acid containing 1 g. of acetyl-salicylic acid, whereby a brown color with a violet tint is developed, and compared by a 0.001 mol/l.

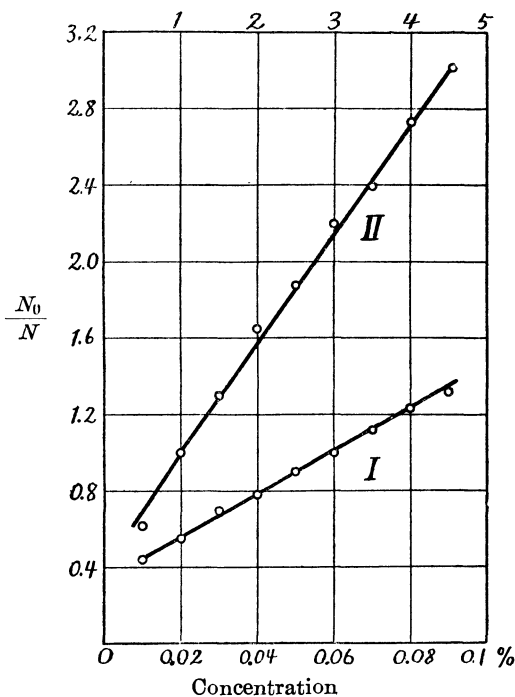


Fig. 1

(2) S. Watanabe and A. Watanabe, *Proc. Imp. Acad. Japan.*, **11**, 379 (1935)

(3) Capelli, *Pharm. Ztg.*, **65**, 800 (1920); K. Suda and H. Ogakureyama, *J. Pharm. Soc. Japan*, No. 481, 241 (1922) (in Japanese); Putnam, *Ind. Eng. Chem.*, **16**, 778 (1924)

(4) This expression is not quite right, the decomposition is rather hydrolysis due to moisture.

(5) Allport, "Colorimetric Analysis", p. 162 London (1947)

Duboscq colorimeter with a series of solutions of various concentrations prepared in a similar way. It has thus been found that a linear relationship exists between the concentration of salicylic acid and the ratio of the lengths of the two solutions, N_0/N , N_0 being that of the standard (I in Fig. 1). In Table 2 are shown the results of experiments made at 110° with 1 g. of acetyl-salicylic acid.

Table 2
Decomposition of acetyl-salicylic acid.

Time min.	N_0/N	Conc. %	Decomposition %	Lowering of melting point	
				obs.	calc.
5	0.613	0.025	0.65	1	0.48
15	0.672	0.031	0.79	4	0.57
25	0.925	0.053	1.38	4	1.02
35	1.093	0.068	1.77	5	1.30

In Table 3 are shown the results of measurements made at 128°. In this case 0.2 g. of acetyl-salicylic acid was used. After heating at this temperature for a definite length of time it was dissolved in 20 cc. methanol and 0.5 cc. of a 1/2 mol aqueous solution of ferric chloride was added to it. By comparing this solution colorimetrically with the standard made from a 1/1000 mol methanol solution of salicylic acid and the iron reagent, the quantity of free salicylic acid was determined by means of a relation previously established between N_0/N and concentration of salicylic acid (II in Fig. 1).⁽⁶⁾

Table 3
Decomposition of acetyl-salicylic acid at 128°

Time min.	N_0/N	Conc. 10 ³ mol/l.	Decomposition %	Lowering of melting point (°C)	
				obs.	calc.
5	0.719	0.60	1.08	2	0.79
15	1.825	2.45	4.41	13.5	3.23
25	2.23	3.25	5.81	20.5	4.22

Lowering of melting point The difference in melting point between the original acetyl-salicylic acid and the heated is shown in the column (obs.) of the lowering of melting point in Tables 2 and 3. It is seen from this column that the melting point naturally falls with the duration of heating as well as with the elevation of temperature. We have calculated the lowering of melting point from the data of decomposition on the assumption that the depression is caused by the decomposition of acetyl-salicylic acid. For this purpose we measured the molecular depression of acetyl-salicylic acid by using adipic acid, salicylic acid and hydroquinone as solutes. The results of measurements are shown in Table 4.

The calculated values of lowering of melting point shown in Tables 2 and 3 were obtained

(6) The line I is related with the lower ordinate, the line II with the upper. The concentration is expressed in different measures, so as to fit the lines into a diagram.

from the data of decomposition by using 6.6 as the mean value of molecular depression. The observed values, as may be seen, are always incomparably larger than the calculated. Hence it seems to us that the abnormal depression of melting point of acetyl-salicylic acid is not solely due to the dissolution of both salicylic and acetic acids formed by its thermal decomposition.

Table 4
Molecular depression of acetyl-salicylic acid.

Solute	Conc. %	Depression	Molecular depression
Adipic acid	15	6.66	6.48
"	30	13.33	6.49
Salicylic acid	13.8	6.50	6.50
"	27.6	12.75	6.38
Hydroquinone	11	6.75	6.75
"	22	14.00	7.00

Mean 6.6

Anomalous melting point Such an anomalous behavior in melting point is observed not only in acetyl-salicylic acid, but also in its *p*-isomer, namely, *p*-acetoxy-benzoic acid. As the melting point of this compound is variously recorded in the literature, we have examined it with some materials obtained by recrystallizing from various solvents such as ether, acetic anhydride, ethyl alcohol, methanol, dilute alcohol, and water, and have found it to lie between 186° and 188°. The discrepancy, though much smaller than in acetyl-salicylic acid, is yet clearly seen. A sample of *p*-acetoxy-benzoic acid, once melted, shows a depression by 2° to 3°. By repeating this process fifteen times, we have realized that the melting point can be lowered finally even to 165°. This depression is undoubtedly associated with thermal decomposition of *p*-acetoxy-benzoic acid. While on the contrary, both free salicylic and free *p*-hydroxy-benzoic acids show no sign of this phenomenon. Their melting points are quite definite, exhibiting no tendency of lowering, even if repeatedly melted.

Thus it was confirmed that the lowering of melting point is exclusively due to the instability of their acetyl derivatives.

We have in the next place made comparison in stability between the *o*- and *p*-compounds, since it appears to us that acetyl-salicylic acid is more liable to decomposition than its *p*-isomer. According to the measurements of Anschütz and Motschmann⁽⁷⁾ the velocity constants of hydrolysis of acetyl-salicylic acid in water at 100° is 0.14701 ($t=30$ min.), while that of the *p*-isomer is 0.05975. We have also found that the saponification velocity constants of *o*- and *p*-acetoxy-benzoates in boiling dilute alcohol are respectively 0.015 and 0.0015 ($t=$ min.). Thus it is clear that *p*-acetate is far

(7) Ann., 392, 116 (1912)

resistent to decomposition than acetyl-salicylic acid. Besides, in harmony with this fact, a wide difference is observed between the velocities of formation of the two acetyl derivatives, viz., it takes more than three hours to obtain the *p*-compound by boiling a mixture of hydroxy-benzoic acid and acetic anhydride,

whereas it takes only one hour with acetyl-salicylic acid. Thus it is evident that acetyl-salicylic acid is more easily formed and more liable to be decomposed.

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Analytical Chemistry by Means of Organic Compounds XIV

Electrolytic Reduction of Organic Reagents at the Dropping Mercury Cathode and Its Application to Amperometric Titrations — 8-Hydroxyquinoline* (1)

By Masayoshi ISHIBASHI and Taitiro FUJINAGA

(Received September, 13, 1949)

Many organic compounds are reducible at the dropping mercury electrode, so the organic reagents which precipitate metal ions are very useful in the amperometric titrations. Kolthoff and his coworkers have been greatly instrumental in developing these titrations.⁽¹⁾ In the meantime, we also introduced this titration method and described some examples of our works⁽²⁾ in which organic reagents were applied to it.

In the present paper, the behavior of electrolytic reduction of 8-hydroxyquinoline at the dropping mercury electrode is discussed and in the subsequent paper, the amperometric titration of magnesium, copper etc. with that reagent will be introduced.

Experimental

Chemicals and Apparatus Used Oxine (8-hydroxyquinoline) made by Takeda Chemicals Co. was twice steam-distilled and dissolved in pure dilute ethyl alcohol. Magnesium carbonate, ferric nitrate and zinc sulfate were Merk or Kahlbaum's "zur Analyse". The c. p. copper sulfate was twice recrystallized. They were all examined in their purity by the polarographic method. Buffer solutions from pH=2.2 to 12.0 were Kolthoff, Vleeshouwer's.⁽³⁾ pH=1.0 and pH=13.0 were 0.1 N hydrochloric acid and sodium hydroxide respectively. The polarograph used is a Heyrovsky-Shikata type made by Yanagimoto Co., Kyoto.

Polarographic Behavior of Oxine Polarograms of oxine in various pH solutions are shown

grams of oxine in various pH solutions are shown

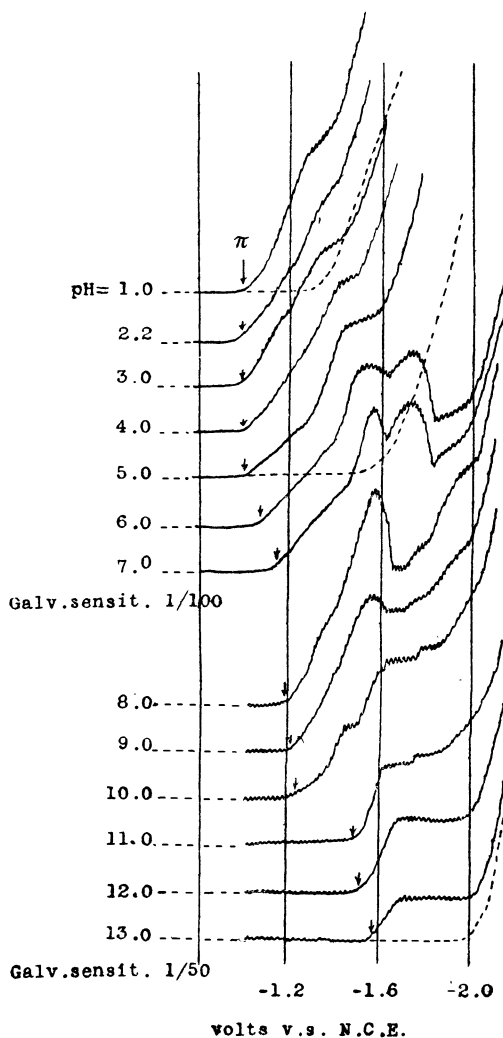


Fig. 1
Polarograms of oxine in various pH solutions

* Presented at the annual meeting of the Chemical Society of Japan in 1948 and the annual meeting of the Research Institute of Chemistry, Kyoto University in 1947.

(1) I. M. Kolthoff *et al.*, *J. Amer. Chem. Soc.*, **61**, 3402 (1939). *ibid.*, **62**, 211, 3332, etc. (1940)

(2) M. Ishibashi and T. Fujinaga, "Polarography in Inorganic Analysis" in "The Review of Analytical Chemistry (in Japanese)" Vol. 2 Kyoritsu-sha publ. Co., Tokyo (1944)

(3) I. M. Kolthoff, "Acid-base Indicators", Macmillan Co. (1937)

in Fig. 1. These solutions have the composition of 10^{-3} M-oxine, 10^{-2} M-KCl and some tylose, except buffer agents. For the amperometric purpose, the polarograms of oxine in 1 N-NH₄OH, NH₄Cl and 1 N-CH₃COOH, CH₃COONa are researched (Fig. 2). Current-voltage curve of copper sulfate in 1 N-NH₄OH, NH₄Cl by using the platinum rotating electrode are also shown in Fig. 3.

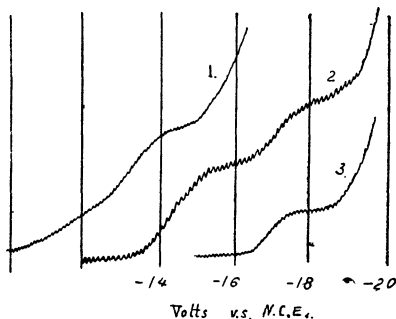


Fig. 2

Polarograms of oxine in some buffer solutions

Curve 1: 1 N- CH₃COOH, CH₃COONa

Curve 2: 1 N- NH₄OH, NH₄Cl

Curve 3: 0.1 N- NaOH

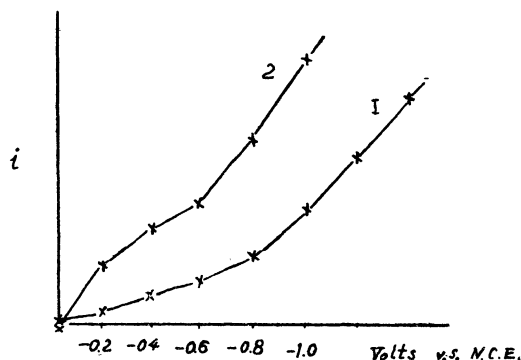


Fig. 3

Current-voltage curve using the rotating Pt electrode

Curve 1: 1 N- NH₄OH, NH₄Cl

Curve 2: 1 ml. of 0.001 N-CuSO₄ was added to the above solution.

Experimental Results

In the reversible polarographic wave, the equation is given as

$$E = E^{1/2} - \frac{RT}{nF} \ln \frac{i}{(i_a - i)}$$

where E is the electrode potential of the dropping electrode, $E^{1/2}$ is the half-wave potential of the wave, i is the reduction current at E volts and i_a is the diffusion current of the reducible ion. Then the plots of $\log i/(i_a - i)$ against E will show the inclination of $0.058/n$ at 18°C. Fig. 4 shows the above analysis of the wave of oxine at pH=11.0 and it also shows that the reduction is reversible and that $n=1$, so oxine will be reduced in the alkaline medium as follows.



which is analogous to meriquinone formation.

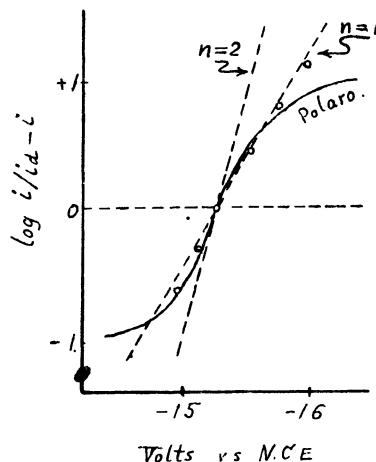


Fig. 4

Analysis of the polarographic wave of oxine at pH=11.0

With decreasing pH, the reduction becomes complicated and irreversible, so each polarogram becomes to produce characteristic maximum respectively whose behavior is analogous to quinoline⁽⁴⁾ and so the reduction current of oxine is chiefly due to the quinoline nucleus. The addition of tylose suppresses the maximum but could not eliminate it even in its higher concentration.

In the acidic medium the reduction is also irreversible and the plots of $\log i/i_a - i$ against E does not give straight line and in these medium the deposition of hydrogen seems to be catalytically urged, comparing with the blank wave (the dotted curves in Fig. 1).

The relation of pH to the reduction potential of oxine π are shown in Fig. 5, where π is not the half-wave potential, but the potential at which 45° tangent touches the curve. Assuming

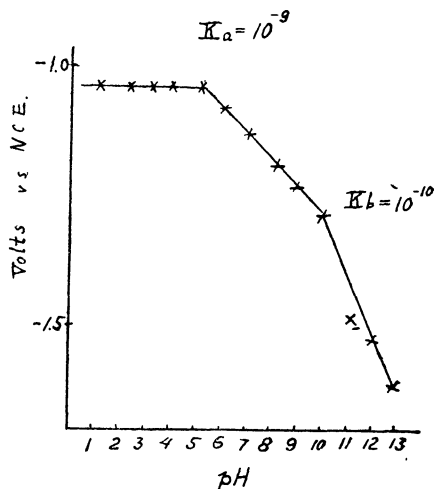


Fig. 5

Relation of the reduction potential π to pH

(4) I. Tachi and H. Kabai, *J. Electrochem. Association Japan*, **3**, 1 (1935)

the π to be the parallel value to the standard reduction potential, the bending points will be the position of $\text{pH}=\text{pK}_a$ and $\text{pH}=\text{pK}_b$ respectively and it becomes $\text{K}_a=10^{-9}$ and $\text{K}_b=10^{-10}$. These dissociation constants coincide with Kolthoff's data.⁽⁵⁾

In ammoniacal solution, the diffusion current of the first wave of oxine is reached at $E_c=-1.60$ volts v. s. normal calomel electrode and at this potential the diffusion current of oxine is proportional to its concentration. In 0.1 N-NaOH, the same condition is found at $E_c=-1.80$ volts v.s. N.C.E. In acetic acid acetate medium, the short diffusion current range is found at $E_c=-1.40$ volts and the diffusion current of oxine is proportional to its concentration only in the limited concentration range.

These medium were used in the amperometric titration of magnesium, copper, etc. with

oxine and it will be discussed in the subsequent paper.

Using the platinum rotating micro-electrode,⁽⁶⁾ the oxine was not reduced before the hydrogen deposition even in the ammoniacal solution, but the copper was reduced (see Fig. 3).

Summary

The behavior of electrolytic reduction of oxine at the dropping mercury electrode was discussed. The reduction of oxine in alkaline medium is simple and reversible at the electrode and the possibilities of amperometric titrations with oxine in these mediums were researched.

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(5) I. M. Kolthoff, *Chem. Weekbl.*, **24**, 606 (1927)

(6) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem. Anal. Ed.*, **18**, 161 (1946)

Analytical Chemistry by Means of Organic Compounds XV

Electrolytic Reduction of Organic Reagents at the Dropping Mercury Cathode and its Application to Amperometric Titrations—8-Hydroxyquinoline (2)

By Masayoshi ISHIBASHI and Taitiro FUJINAGA

(Received September 13, 1949)

In the previous paper, the behavior of electrolytic reduction of oxine were investigated and it was seen that the waves of oxine were well-defined in ammoniacal and alkaline medium and ill-defined in acidic medium. These were applicable to the amperometric titration of magnesium, copper, zinc and iron.

Experimental

Titration was carried out with the apparatus shown in Fig. 1. The manipulation of the titration was as follows. A measured volume (usually 20 ml.) of the standard sample solution in the proper medium was introduced into the cell and hydrogen gas was passed through for thirty minutes. The proper e. m. f. was applied to the cell and the current was measured. Alcoholic oxine solution was added successively with a microburette. After each addition the content of the cell was mixed by passing hydrogen gas for half a minute and the current was recorded after it became constant (after one or two minutes). In all cases the values of the current, corrected for the volume change, were plotted against the amount of reagent added. A small ordinary beaker was used as a titration cell, which was not closed when the concentration of metals was larger than about 10^{-3} M. However it was necessary to keep on stirring by hydrogen gas, except the case of measurement.

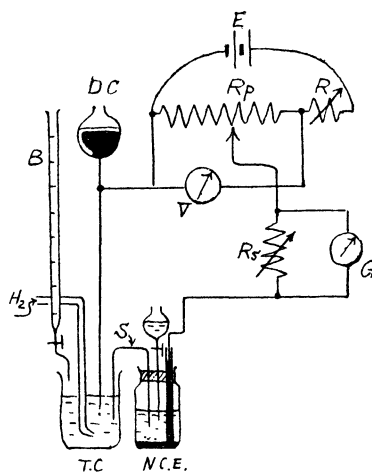


Fig. 1

Apparatus of amperometric titration

- E*: accumulator
- R_p*: potentiometer
- R*: variolhm
- V*: voltmeter
- G*: galvanometer
- R_s*: shunt of galvanometer
- D.C.*: dropping mercury electrode
- T.C.*: titration cell
- N.C.E.*: normal calomel electrode
- B*: burette
- S*: salt bridge

Titration of Magnesium From the preliminary experiments, it was decided to carry out the titration of magnesium in a medium of ammonium chloride and ammonia. With the normal calomel electrode as anode, the applied e. m. f. was -1.60 V., so the first wave of oxine was used in the titration. In this medium the proportionality of diffusion current of oxine to its concentration was satisfactory (see Fig. 2). Results obtained in the titration of magnesium

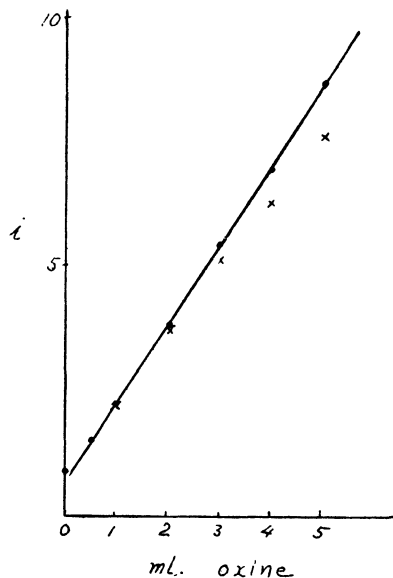


Fig. 2
The proportionality of diffusion current of oxine to its concentration
× observed values
• corrected values

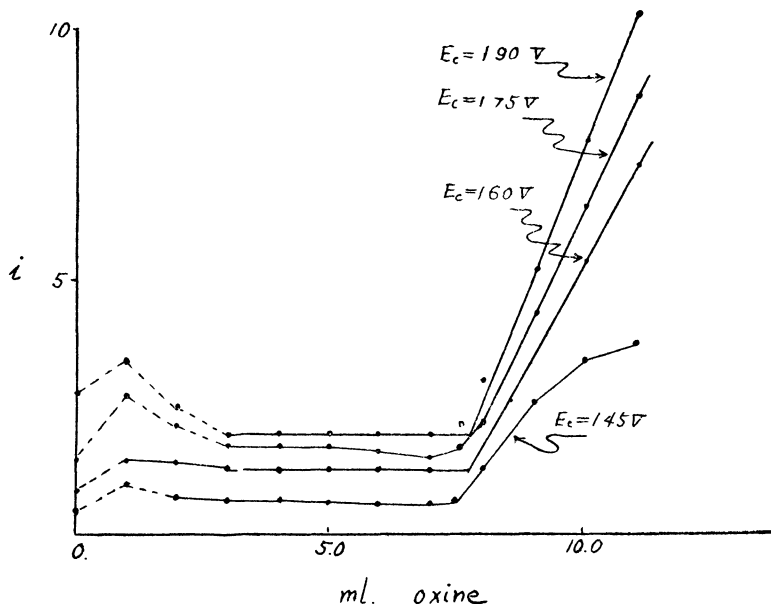


Fig. 3
Titration of magnesium in sea-water with oxine at various applied potentials

solutions are given in Table 1. Reverse titration was also agreeable. Calcium, when its amount was very small did not interfere with the titration. When its amount was large, high results were found. However, if ammonium oxalate was added in excess, the correct result was obtained, when separation of calcium oxalate was not necessary before the titration.

Application of this titration to the analysis of magnesium in aluminium alloy, brine and sea-water were successful (Table 2). Aluminium alloy was dissolved in sodium hydroxide and the residue was dissolved in hydrochloric acid and ammonium hydroxide solution was added in excess. Then hydrogen sulfide was bubbled to precipitate other heavy elements and titrated with oxine without separating the precipitate. These sulfides did not interfere with the titration at this applied potential. Brine contains little calcium. Sea water contains calcium about 0.4 g. per litre, while calcium oxinate is slightly soluble when ammonium salts is present,⁽¹⁾ and by the salt effect of supporting electrolyte and sea-water, the direct titration was possible without adding ammonium oxalate.

Table 1
Titration of magnesium with oxine

No.	Mg used mg.	Ca added mg.	Oxine used ml.	Factor of oxine	Mg found mg.	Error %
1	4.30	0	6.38	0.672	4.287	-0.3
2	6.45	0	9.75	0.672	6.431	-0.3
3	8.60	0	12.77	0.672	8.581	-0.2
4	6.08	0	9.00	0.672	6.048	-0.5
5	4.30	20	6.35	0.672	4.267	-0.7
6	4.30	40	6.35	0.672	4.267	-0.7

* No. 1, 2 and 3 are mean value of several titrations.

* No. 4 is reverse titration (oxine was titrated with magnesium).

* In No. 5 and 6, ammonium oxalate was added in excess before titration.

These samples were gravimetrically analysed as magnesium pyrophosphate. In this case calcium in sea water was eliminated as calcium oxalate. Sea water used was collected near Suma in the bay of Osaka and its chlorinity was 15.74. The magnesium content obtained in this experiment showed very good coincidence with that calculated from the Wattenberg's

(1) R. Berg, *Z. anal. Chem.*, **71**, 23 (1927)

data⁽²⁾ (Table 3).

Sample No. taken	Oxine used ml.	Factor of oxine	Mg found		Error %
			(Ampero.) mg.	(Gravi.) mg.	
1. Al-alloy					
998.lmg.	7.30	0.680	4.964	4.742	+4.0
1006.lmg	7.05	0.680	4.794	4.778	+0.3
2. Brine					
0.20 ml.	28.30	0.672	19.02	19.05	-0.2
0.10 ml.	14.10	0.672	9.48	9.53	-0.5
3. Sea water					
5.00 ml.	8.05	0.680	5.474	5.456	+0.3
5.00 ml.	8.00	0.680	5.440	5.456	-0.3
5.00 ml.*	8.00	0.680	5.440	5.456	-0.3

* Calcium was precipitated as calcium oxalate.

Mg in kg. of sea-water (by Wattenberg)	Mg in ml. of sea-water (calc. from Wattenberg)	Mg in ml. of sea-water (Ampero. titr.)	Error
Cl=19.00 % g.	Cl=15.74 % mg.	Cl=15.74 % mg.	%
1.280	1.086	1.0882	0.2

Titration of Iron, Zinc and Copper and Their Differential Titrations Ferric oxinate is quantitatively precipitated from the tartrate solution,⁽¹⁾ but this was not applicable for the titration, because the precipitation is

complete only when the excess reagent is added. However we found that ferric iron dissolved in excess of ammonium carbonate reacts stoichiometrically with oxine and this medium is applicable for the titration. Copper was titrated in a medium of ammonium chloride-ammonia at $E_c = -1.60$ V. and sodium acetate-acetic acid at $E_c = -1.40$ V. and also titrated in ammoniacal medium using the rotating platinum wire electrode at $E_c = -0.40$ V. See Fig. 4. Zinc was titrated in the same medium as copper and in 0.1 N-sodium hydroxide at $E_c = -1.80$ V. The reduction of oxine in acidic medium is irreversible and the diffusion current of oxine is only proportional to its concentration in the small concentration range. Therefore, after passing the end point, it is difficult to get a straight line any more.

Next, it was attempted to titrate iron, zinc and copper, differentially when they are present altogether. Sample should be divided into three parts. To the first part we added ammonium carbonate in excess until precipitate of basic carbonate redissolved and titrated at $E_c = -1.60$ V (A cc.). To the second part ammonium chloride and ammonia were added to precipitate ferric hydroxide and the solution was titrated at $E_c = -1.60$ V (B cc.). To the last part, after heating to boiling, sodium hydroxide was added to precipitate copper and iron and the titration was carried out at $E_c = -1.80$ V after cooling the solution (C cc.).

Then the concentration of each component will be calculated from the next equations:

$$[\text{Fe}] = X(A-B)$$

$$[\text{Cu}] = X(B-C)$$

$$[\text{Zn}] = X C$$

In these equations X is the normality of oxine solution. This work, however, is only the preliminary one and the error was about 5% in the determination of zinc and copper. Results are shown in Fig. 5 and Table 4.

Summary

Magnesium was directly titrated by the amperometric method. The accuracy was 0.7% or better with 10^{-3} M concentration of magnesium. Its application to the analysis of alloy, brine and sea-water were studied. The interference of calcium and its elimination are described.

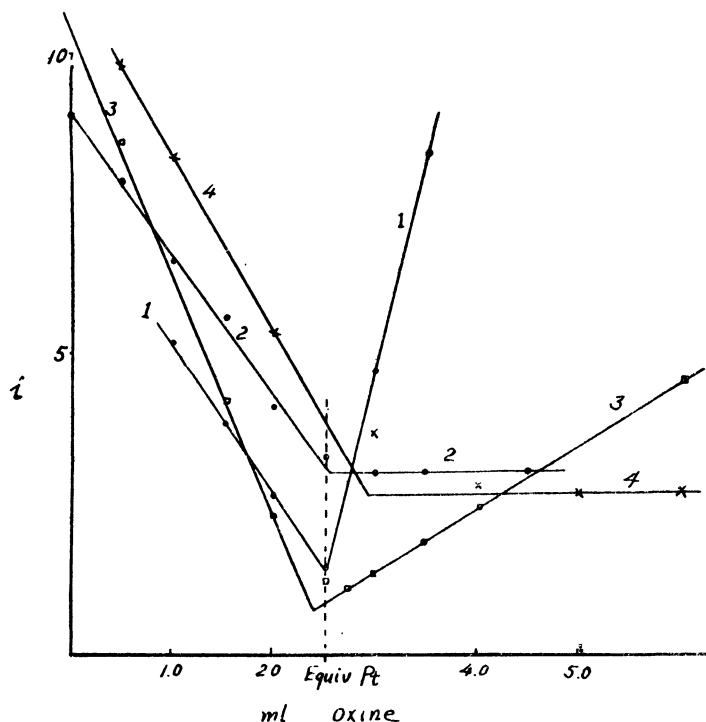


Fig. 4

Titration of copper with oxine

Curve 1 : No. 2 in Table 4 Curve 2 : No. 5 in Table 4
Curve 3 : No. 3 in Table 4 Curve 4 : No. 4 in Table 4
(Pt electrode at $E_c = -0.4$ V)

(2) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**, 46 (1938)

Table 4
Titration of copp, zinc and iron

No.	Metal taken mg.	Medium	Oxine used mg.	Conc. of oxine N	Metal found mg.	Error %
1.	3.369 Cu	Amm. chl.	5.00	0.0211	3.353	- 0.4
2.	1.685 Cu	Amm. chl.	2.48	0.0211	1.663	- 0.3
3.	0.1685 Cu	Amm. chl.	2.42	0.00211	0.1622	- 3.2
4.	0.0337 Cu	Amm. chl.	2.90	0.000422	0.0388	+15.04
5.	1.685 Cu	Amm. chl.	2.48	0.0211	1.663	- 1.3
6.	1.685 Cu	Acet. ac.	2.50	0.0211	1.676	- 0.5
7.	1.798 Zn	Amm. chl.	2.60	0.0211	1.793	- 0.3
8.	1.798 Zn	Acet. ac.	2.59	0.0211	1.791	- 0.4
9.	1.798 Zn	Sod. hyd.	2.60	0.0211	1.793	- 0.3
10.	1.033 Fe	Amm. carb.	2.64	0.0211	1.042	+ 0.9
11.	1.685 Cu } 1.798 Zn }	Amm. chl.	5.12	0.0211		+ 0.0
12.	1.685 Cu } 1.798 Zn }					
13.	1.033 Fe } 1.685 Cu } 1.798 Zn }	Amm. carb.	7.75	0.0211		+ 0.01

* In No. 5, the rotating platinum electrode was used.

* In No. 12, copper was precipitated as cupric oxide.

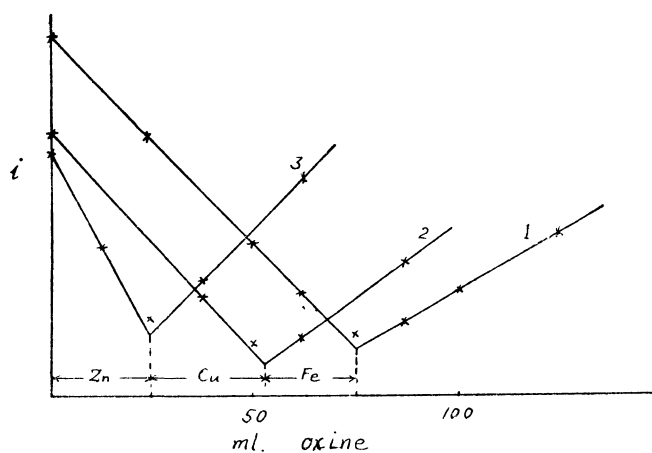


Fig. 5

Titration of mixture of iron,
zinc and copper with oxine

Curve 1: in 2 N-(NH₄)₂CO₃

Curve 2: in 1 N-NH₄OH, NH₄Cl

Curve 3: in 0.1 N-NaOH

Iron, zinc and copper were also titrated with oxine and their differential titration was investigated.

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Heats of Transition of Hexachloroethane

By Syûzô SEKI and Masanobu MOMOTANI

(Received September 13, 1949)

It is known that the crystalline hexachloroethane has three modifications; triclinic, monoclinic and cubic. The transition points are 45°C (triclinic~monoclinic) and 72°C (monoclinic~cubic), respectively. X-ray investigations of these transition phenomena have been already undertaken by Finback⁽¹⁾ and West,⁽²⁾ of whom the former concluded that in the cubic modification the molecules as a whole are in the rotational motion in a rough sense.

In connection with the structural investigations, Nitta and one of the authors⁽³⁾ had several years ago measured the vapor pressures

of this substance and found that the entropy change at 72°C is greater than that change at the melting point. This result suggests that the cubic modification of this substance may be a sort of the so-called plastic crystals.⁽⁴⁾

On the other hand, the transition point at 45°C was not found from our vapor pressure curves. Nelson⁽⁵⁾ had already measured the vapor pressures below 72°C, but he could not

(3) I. Nitta, S. Seki, *J. Chem. Soc. Japan*, **62**, 581, (1941)

(4) According to the recent investigation by Aston and Pace, in the case of hexafluoroethane also the entropy change at transition point is greater than that at melting point. *J. Am. Chem. Soc.*, **70**, 566 (1948)

(5) Nelson, *Ind. Eng. Chem.*, **22**, 227 (1930)

(1) C. Finback, *Tids. Kjem. Bergvesen.*, **17**, No. 9 (1937)

(2) C. D. West, *Z. Krist.*, **88**, 195 (1934)

also find the transition at this temperature.

Recently, Ivin and Dainton⁽⁶⁾ have reported the measurement of vapor pressure of hexachloroethane without finding the lower transition point. From the accuracy of their apparatus they estimated that the enthalpy change at this transition point may be smaller than 700 cal./mol. Their data on vapor pressures are somewhat lower than our values, but much better agreement with ours than with that of Nelson when compared. It is also found from their results that the heat of transition at 72°C amounts to 1.9 ± 0.3 kcal./mol., which is in good agreement with our data, 2.07 kcal./mol.

It is now very desirable to determine the heat of transition at 45°C by the direct specific

heat measurement. For this purpose and also as a part of our thermochemical investigation of plastic crystals, we have constructed a conduction calorimeter and measured the specific heats of this crystal. The details of experimental procedures may be described elsewhere. The obtained specific heat curves are represented in the accompanying figure and a part of the specific heats as well as heats of transition are indicated in Tables 1 and 2.

Table 2

	$t^\circ\text{C}$	ΔH cal./mol.	ΔS e. u.	ΔV cc./kg.
Transition	45.0	613 ^c	1.93 ^c	9.7
Transition	71.4	1965 ^c (1900 $\pm$ 300 ^a)	5.70 ^c	28.0
Melting	185	2330 ^d (2070 ^b)	5.50 ^d	—

a. K. J. Ivin, F. S. Dainton⁽⁶⁾

b. I. Nitta, S. Seki⁽³⁾

c. This research

d. Van der Lee

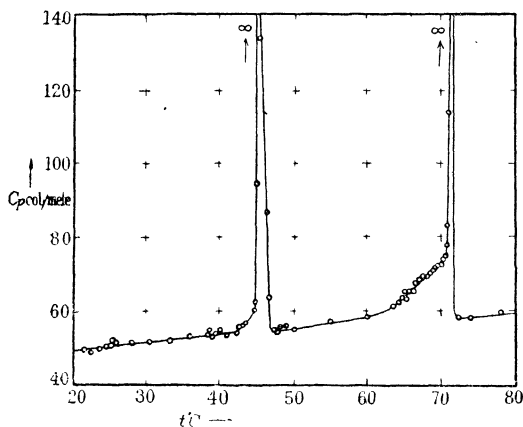


Fig. 1

Table 1
Specific heat of hexachloroethane

$t^\circ\text{C}$	C_p cal./mol	$t^\circ\text{C}$	C_p cal./mol	$t^\circ\text{C}$	C_p cal./mol
22.25	48.9	45.80	110.7	67.47	68.8
23.45	49.7	43.05	95.9	68.18	68.6
24.55	51.5	46.55	86.5	68.48	69.3
25.35	52.1	46.75	63.0	68.85	69.1
35.95	52.9	47.45	54.8	69.09	70.9
37.85	53.4	47.70	54.2	69.45	71.0
38.51	54.8	47.95	55.3	69.90	71.7
39.35	53.3	48.55	55.9	70.14	73.3
41.12	53.0	48.95	55.0	70.50	74.2
42.90	55.7	50.00	54.7	70.63	77.2
43.25	56.4	55.05	55.7	70.85	82.6
44.58	59.9	60.0	57.7		
44.75*	62.0	63.60	60.5	transition	
45.40*	94.2	64.25	61.3	70.99	113.2
45.55*	328.7	64.65	63.0	71.02	175.3
		65.00	64.3	71.07	501.3
transition		65.35	62.0	71.50	307.9
45.00	253.9	65.70	64.4	72.70	57.1
45.15	213.8	66.05	64.4	73.80	57.3
45.25	173.8	66.40	66.9	78.00	58.7
45.40	133.5	67.10	67.7		

* superheating

(6) K. J. Ivin, F. S. Dainton, *Trans. Faraday Soc.*, **43**, 32 (1947)

Since the transition at 45°C was found frequently to be superheated, we have measured the specific heat as slowly as possible (0.1°/minute) to avoid this. The observed magnitude of heat of transition at 45°C (613 cal./mol.) is in good agreement with that expected from the vapor pressure measurement by Ivin and Dainton and also by us. As shown in the figure, the upper transition is accompanied by the preceding gradual increase of specific heat. The heat of transition at 72°C (1.965 cal./mol) obtained by this direct method is also consistent with the data from the vapor pressure measurements.

In the table, the volume changes at transition points are also presented. We can see a very good parallelism between the entropy and the volume changes at these transition points.

For the theoretical treatment of the transition energies from the point of view of structural chemistry, it is necessary to determine the crystal structure more accurately. For this purpose, the X-ray analyses of these three modifications are now going on in this laboratory by other members and for the cubic form a model of molecular motions more precise than that of Hassel is gained. The discussion of the mechanism of the transitions may be postponed, to bring this investigation to completion.

In conclusion, the authors wish to express their sincere thanks to prof. Nitta for his kind guidance throughout this work. This study was helped by the Research Grant given by the Ministry of Education.

Department of Chemistry, Faculty of
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Studies on the Ammoniacal Copper Solutions I The Reaction Order of the Reduction by Carbon Monoxide and a Correction for the Escaping Carbon Monoxide

By Minoru HIRATA

(Received September 14, 1949)

It is a well-known fact that ammoniacal solutions of cuprous compounds absorb readily carbon monoxide.⁽¹⁾ Such solutions are used in determining carbon monoxide in gas analysis and for the purification of material gases in the ammonia manufacturing industry to remove carbon monoxide.

For the latter purpose, solutions containing both cuprous and cupric compounds are used circulating. In this case the absorbed carbon monoxide reduces cupric compounds in copper solutions and prevents the solutions from the increase of cupric compounds content which would be caused by the oxygen in material gases.

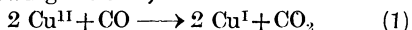
Hainsworth and Titus,⁽²⁾ Larson and Teithworth,⁽³⁾ Gump and Ernst⁽⁴⁾ and Möller⁽⁵⁾ studied on those solutions, but in spite of the importance of the reducing action of carbon monoxide the kinetics of the reduction were hitherto scarcely investigated. The present author has aimed to make clear this problem.

The compositions of the original copper solutions employed in the studies are shown in Table 1.

Table 1 (g./100 cc.)				
Cu ^I	Cu ^{II}	NH ₃	HCOOH	CO ₂
8-15	1-5	8-16	2-10	6-13

Theoretical

It is verified that two mols of cupric copper are reduced by one mol of carbon monoxide and at the same time produce one mol of carbon dioxide. Though it is difficult to show the actual details of the reaction definitely, these experimental facts may be expressed by the following scheme,



Here, Cu^{II} and Cu^I express the cupric and cuprous compounds respectively, whose chemical formulas have not yet been definitely determined.

According to the author's experiments, the reaction velocity of the reduction is proportional to each concentration of cupric copper and the absorbed carbon monoxide. Hence

(1) Condamine, *Compt. rend.*, **179**, 691 (1925); Moser u. Hanika, *Z. anal. Chem.*, **67**, 448 (1926); D. R. P., 289694 (1914)

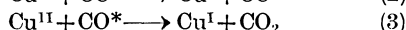
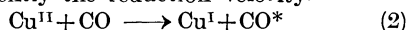
(2) *J. Am. Chem. Soc.*, **43**, 1 (1921)

(3) *J. Am. Chem. Soc.*, **44**, 2878 (1922)

(4) *Ind. Eng. Chem.*, **22**, 382 (1930)

(5) *Z. anorg. allgem. Chem.*, **224**, 113 (1935); *ibid.*, **224**, 130 (1935)

remembering the stoichiometric relation expressed by (1), it may be considered that the reduction occurs in two stages; the reaction of the first stage (2) which proceeds far slowly in comparison with the second stage (3) decides consequently the reduction velocity.



The author assumed that in the reaction of the first stage carbon monoxide is converted into an unstable intermediate state which has lost a half of its reducing power and this substance causes immediately the further reduction in the second stage. Though the nature of the intermediate state of carbon monoxide is not clear, it should correspond electronically to CO⁺ and so is described by CO* in the present paper. The results of reactions (2) and (3) coincide stoichiometrically with that of the reaction (1).

Let the initial concentrations of Cu^{II} and carbon monoxide be represented by *a* and *b* respectively, and let the concentration increase of Cu^I after time *θ* by *x*. The following two expressions may be given for the reduction velocity according to the above-mentioned reduction mechanism (1), and (2) and (3) respectively,

$$\frac{dx}{d\theta} = k^{\text{III}}(a-x)^2 \left(b - \frac{x}{2}\right) \quad (4)$$

and

$$\frac{dx}{d\theta} = k(a-x) \left(b - \frac{x}{2}\right), \quad (5)$$

where *k*^{III} and *k* are the velocity constants respectively.

From the author's experiments, it has been known that *k* is nearly constant independently of the lapse of time, while *k*^{III} increases with it. Namely the reduction is of the second order.

In almost all of actual reactions, some of the absorbed carbon monoxide escape unreacted from solutions, therefore in such cases equation (5) should be corrected as follows,

$$\frac{dx}{d\theta} = k(a-x) \left(b - \frac{x}{2} - v\right), \quad (6)$$

where *v* is the concentration of the escaped carbon monoxide during the time *θ*.

If it is assumed that the escaping velocity of the gas is proportional to its average concentration in the solution at that time,

$$\frac{dv}{d\theta} = k' \left(b - \frac{x}{2} - v\right) \quad (7)$$

is obtained, where k' is a constant characteristic of the reduction which we name the "exhalation coefficient".

When $b - \frac{x}{2} \gg v$, equation (7) should be strictly true.

From equations (6) and (7),

$$\frac{dv}{dx} = \frac{k'}{k} \cdot \frac{1}{a-x} \quad (8)$$

is obtained. Integrating equation (8),

$$v = -\frac{k'}{k} \ln(a-x) + \beta_1 \quad (9)$$

is obtained, where β_1 is an integration constant. At the initial state, $x=0$ and $v=0$, therefore,

$$\beta_1 = \frac{k'}{k} \ln a \quad (10)$$

Inserting equation (10) into (9),

$$v = \frac{k'}{k} \ln \frac{a}{a-x} \quad (11)$$

If the value of v corresponding to any value of $a-x$ is known, that of $\frac{k'}{k}$ can be found out. Consequently the value of v against any arbitrary value of $a-x$ can be calculated.

By raising the temperature after the reduction is almost finished, the value of $a-x$ at the practical completion of reduction $(a-x)_{\theta=\infty}$ is obtained. On the other hand, the value of v at that time $v_{\theta=\infty}$ is found out as the difference between the quantity of the carbon monoxide initially absorbed and the quantity expended in the reduction.

Then, from equation (11),

$$\frac{k'}{k} = \frac{v_{\theta=\infty}}{\ln \frac{a}{(a-x)_{\theta=\infty}}} \quad (12)$$

is obtained.

From equations (11) and (12), v is written as follows:

$$v = \frac{v_{\theta=\infty}}{\ln \frac{a}{(a-x)_{\theta=\infty}}} \ln \frac{a}{a-x} \quad (13)$$

In practical calculation, the cupric copper concentration $a-x$ with the lapse of time θ was observed, from which the $(a-x)-\theta$ curve

was plotted. This curve was utilized for correcting the value of $a-x$ against θ , and this was necessary on account of the instability of copper solution.

Practically, velocity constants were numerically calculated instead of integrating equations (4), (5) or (6); for instance, equation (14) was adopted instead of equation (6),

$$\frac{x_i - x_{i-1}}{\theta_i - \theta_{i-1}} = \frac{1}{2} k \left(a - \frac{x_i + x_{i-1}}{2} \right) \left(2b - \frac{x_i + x_{i-1}}{2} - 2v_i \right) \quad (14)$$

$i-1$ and i mean the successive numbers of measurements, and v_i is the value expressed by equation (15),

$$v_i = \frac{k'}{k} \ln \frac{a}{\left(a - \frac{x_i + x_{i-1}}{2} \right)} \quad (15)$$

Experimental

Experiments were made as follows; 70.0 cc. of copper solution was taken, and it was allowed to absorb a certain quantity of carbon monoxide. Then this solution was portioned 5.00 cc. each into several test tubes. The surface of the copper solution was always covered with liquid paraffin to prevent the evaporation of the solution, the loss of ammonia and carbon dioxide by escaping, and the oxidation of cuprous compounds by air.

The test tubes were dipped into a thermostat of the accuracy of $\pm 0.1^\circ\text{C}$, and the change of the cupric copper concentrations with the time elapsed was observed. It required 3 to 5 minutes for the contents of the test tubes to reach a certain temperature after dipping into the bath. At the end of the experiment, the last test tube was dipped into a water bath of 75°C for the period of 30 minutes to complete the reduction. In most cases, reduction was practically completed before the latter treatment was carried out. It was confirmed that the evaporation and the loss of copper solution and its spontaneous oxidation by diffusion of air would scarcely take place throughout the experiment.

The order of the reaction The two examples in which carbon monoxide scarcely escaped unreacted from the solutions are quoted in Tables 2 and 3. The small quantities of the escaped carbon monoxide were neglected, and k^{III} and k calculated using equations (4) and (5) are given.

Table 2

No. of measurement i	Time θ_i min.	$\theta_i - \theta_{i-1}$ min.	Cu ^{II} -conc. obs. g.mol/l.	Cu ^{II} -conc. $a-x_i$ corr. g.mol/l.
0	0	—	0.508	0.508
1	5	5	0.453	0.453
2	10	5	0.423	0.419
3	15	5	0.388	0.393
4	20	5	0.374	0.374
5	30	10	0.345	0.345
6	50	20	0.310	0.310
7	90	40	0.280	0.280
8	150	60	0.275	0.275
9	300	150	0.275	0.275
10	∞	—	0.275	0.275

R. 61

$x_i - x_{i-1}$ g.mol/l.	$\frac{x_i + x_{i-1}}{2}$ g.mol/l.	k^{III} g.mol/l. min.	k g.mol/l. min.
—	—	—	—
0.055	0.028	(0.458)	(0.220)
0.034	0.072	0.439	0.190
0.026	0.102	0.470	0.191
0.019	0.125	0.467	0.179
0.029	0.149	0.516	0.181
0.035	0.181	0.595	0.195
0.030	0.213	0.750	0.221
—	—	—	—
—	—	—	—
—	—	—	—

Initial concentration of CO : 0.1181 g.mol/l.

Reaction rate of CO : 98.7% Temperature of experiment : 50.0°C

Table 3 R. 64

No. of measure- ment i	Time θ_i min.	$\theta_i - \theta_{i-1}$ min.	Cu ^{II} -conc. obs. g.mol/l.	Cu ^{II} -conc. $\alpha - x_i$ corr. g.mol/l.	$x_i - x_{i-1}$ g.mol/l.	$\frac{x_i + x_{i-1}}{2}$ g.mol/l.	k^{III} g.mol/l. min.	k g.mol/l. min.
0	0	—	0.512	0.512	—	—	—	—
1	5	5	0.462	0.462	0.050	0.025	(0.391)	(0.190)
2	10	5	0.434	0.429	0.033	0.067	0.383	0.170
3	15	5	0.404	0.403	0.026	0.096	0.414	0.172
4	20	5	0.379	0.382	0.021	0.120	0.452	0.177
5	30	10	0.349	0.352	0.030	0.145	0.464	0.170
6	50	20	0.316	0.316	0.036	0.178	0.512	0.171
7	90	40	0.287	0.287	0.029	0.211	0.552	0.161
8	150	60	0.275	0.275	—	—	—	—
9	300	150	0.275	0.275	—	—	—	—
10	∞	—	0.275	0.275	—	—	—	—

Initial concentration of CO : 0.1204 g.mol/l.

Reaction rate of CO : 98.5%

Temperature of experiment : 50.0°C

Now it is clear from the tables that k is constant independently of the time elapsed, while k^{III} increases with it and so the reducing reactions are of the second order.

The correction for the escaping carbon monoxide The results of the experiments where the escaping of carbon monoxide seemed pretty high, are given in Tables 5 and 6. In the last columns k calculated from equation (14) are tabulated. We

can see that k calculated in such a way is constant enough through the whole course of each experiment. The compositions of the copper solutions used in the experiments are shown in Table 4.

Table 4

No. of experi- ment	Total Cu g.mol/l.	NH ₃ g.mol/l.	HCOOH g.mol/l.	CO ₂ g.mol/l.
R. 20	1.02	5.12	0.36	1.60
R. 70	0.30	1.04	0.10	0.31

Table 5 R. 20

No. of measure- ment i	Time θ_i min.	$\theta_i - \theta_{i-1}$ min.	Cu ^{II} -conc. obs. g.mol/l.	Cu ^{II} -conc. $\alpha - x_i$ corr. g.mol/l.	$2 v_i$ g.mol/l.	$x_i - x_{i-1}$ g.mol/l.	$\frac{x_i + x_{i-1}}{2}$ g.mol/l.	k
0	0	—	0.463	0.463	0	—	—	—
1	2	2	0.448	0.448	0.001	0.015	0.008	(0.193)
2	5	3	0.443	0.439	0.002	0.009	0.020	0.0858
3	8	3	0.432	0.431	0.002	0.008	0.028	0.0818
4	13	5	0.421	0.419	0.003	0.012	0.038	0.0812
5	20	7	0.407	0.405	0.004	0.014	0.051	0.0777
6	30	10	0.387	0.388	0.006	0.017	0.067	0.0803
7	50	20	0.366	0.362	0.008	0.026	0.088	0.0846
8	90	40	0.330	0.330	0.011	0.032	0.117	0.0889
9	150	60	0.310	0.310	0.014	0.020	0.143	(0.0907)
10	300	150	0.305	0.305	—	—	—	—
11	∞	—	0.300	0.300	0.017	—	—	—

Initial concentration of CO : 0.0898 g.mol/l.

Reaction rate of CO : 90.8%

Temperature of experiment : 50.0°C

Table 6. R 70

No. of measure- ment i	Time θ_i min.	$\theta_i - \theta_{i-1}$ min.	Cu ^{II} -conc. obs. g.mol/l.	Cu ^{II} -conc. $\alpha - x_i$ corr. g.mol/l.	$2 v_i$ g.mol/l.	$x_i - x_{i-1}$ g.mol/l.	$\frac{x_i + x_{i-1}}{2}$ g.mol/l.	k
0	0	—	0.102	0.102	0	—	—	—
1	5	5	0.093	0.093	0.001	0.009	0.005	(1.032)
2	10	5	0.086	0.087	0.003	0.003	0.012	0.987
3	15	5	0.083	0.083	0.004	0.004	0.017	0.896
4	20	5	0.077	0.080	0.005	0.003	0.021	0.924
5	30	10	0.077	0.076	0.006	0.0045	0.024	0.962
6	50	20	0.072	0.071	0.007	0.0045	0.029	(1.027)
7	90	40	0.068	0.068	—	—	—	—
8	150	60	0.068	0.068	—	—	—	—
9	300	150	0.077	0.068	—	—	—	—
10	∞	—	0.077	0.063	0.008	—	—	—

Initial concentration of CO : 0.0212 g.mol/l.

Reaction rate of CO : 80.3%

Temperature of experiment : 50.0°C

These facts seem to prove the above-mentioned assumption, equation (7), which was made for the calculation to correct the effect of the escaping carbon monoxide to be quite appropriate.

Summary

1. It is experimentally verified that the reduction of cupric copper by the carbon monoxide absorbed in the copper solution is a reaction of the second order.

2. In the calculation of the velocity constant for the reduction, it is found that the correction made for the carbon monoxide escaping unreacted, under the assumption that the escaping velocity of the carbon monoxide is proportional to its concentration in the solution at that time, is appropriate.

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LETTER

1, 2-Bis-(*p*-hydroxyphenyl)-1, 2-bis-(methylthio)-ethane, An Estrogenic Sulfur Analog of Hexestrol⁽¹⁾

By Yoshiyuki URUSHIBARA
and Michinori ŌKI

(Received April 17, 1950)

In the programme of the survey of the possible estrogenic activity of hexestrol and stilbestrol analogs in which the members constituting the molecular skeletons of the well-established synthetic estrogens are replaced with other atoms or groups without altering the molecular shapes significantly, the discovery of a potent estrogen in 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-dimethoxy-ethane, $\text{HOC}_6\text{H}_4\text{CH}(\text{OCH}_3)\text{CH}(\text{OCH}_3)\text{C}_6\text{H}_4\text{OH}$, an oxygen analog of hexestrol,⁽²⁾ has naturally allured the authors to the synthesis of the corresponding sulfur analog, namely, 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-bis-(methylthio)-ethane, $\text{HOC}_6\text{H}_4\text{CH}(\text{SCH}_3)\text{CH}(\text{SCH}_3)\text{C}_6\text{H}_4\text{OH}$.

The dibromide, m. p. 213-4°, from diacetoxy-stilbene was heated with methylthio-magnesium iodide, prepared by digesting sulfur with a Grignard reagent of methyl magnesium iodide or by passing methyl mercaptan into a Grignard reagent of ethyl magnesium iodide. The products were recrystallized from ethyl acetate. 1, 2-Bis-(*p*-acetoxyphenyl)-1, 2-bis-(methylthio)-ethane, $\text{CH}_3\text{COOC}_6\text{H}_4\text{CH}(\text{SCH}_3)\text{CH}(\text{SCH}_3)\text{C}_6\text{H}_4\text{OCOCH}_3$, was obtained in poor yields (10% or less of the theory) from the less soluble fractions. It melts at 118-9°, is soluble in

methanol, acetone, acetic acid, and ethyl acetate, difficultly soluble in benzene and in chloroform, and almost insoluble in petroleum ether. Found: S, 16.86%; molecular weight, 374. Calculated for $\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}_2$: S, 16.43%; molecular weight, 390.

The authors owe a more successful synthesis of 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-bis-(methylthio)-ethane to I. W. Ruderman and E. M. Fettes⁽³⁾ who have recorded a new preparation of thio-ethers. *p,p'*-Dihydroxy-hydrobenzoin (1.5 g.), $\text{HOC}_6\text{H}_4\text{CHOHCHOHC}_6\text{H}_4\text{OH}$, m. p. 219°, prepared by reducing *p*-hydroxy-benzaldehyde with sodium amalgam, was suspended in glacial acetic acid (75 cc.), methyl mercaptan (4 cc.) was added, and dry hydrogen chloride was passed into the mixture for two hours while methyl mercaptan (1 cc.) was added every quarter to make up for possible losses. The mixture was left to stand under a stopper for a couple of days. The crystalline deposits, and the crystals resulting in two or three days from the oil precipitated on pouring the mother liquor into water, were recrystallized from methanol-water. The substance thus obtained forms colorless needles, and on heating it melts at 193.5-5°, solidifies instantly, and then decomposes gradually and totally at 255°. Such a melting behaviour was not affected by recrystallization from pure methanol, acetone-water, or glacial acetic acid. Yield, 1.2 g. (65% of the theory). Found: S, 21.17%; molecular weight, 310. Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2$: S, 20.93%; molecular weight, 306. The compound is easily soluble in methanol, acetone, and ether, sparingly soluble in benzene and in chloroform, almost insoluble in petroleum ether, and slightly soluble in boiling water. It precipitated a crystalline addition compound with mercuric chloride in saturated aqueous solution. Such a behaviour unlike a mercaptol

(1) A brief account was read by T. Takahashi before the annual meeting of the Chemical Society of Japan in Kyoto on April 2, 1950.

(2) Y. Urushibara and T. Takahashi, this Bulletin, **23**, No. 2 (1950), in press.

(3) *J. Am. Chem. Soc.*, **71**, 2264 (1949)

excludes a¹ structure of the mercaptol of dihydroxy-desoxybenzoin, $\text{HOC}_6\text{H}_4\text{CH}_2\text{COC}_6\text{H}_4\text{OH}$, which might result from the dihydroxyhydrobenzoin. Further, acetylation with acetic anhydride and pyridine gave the same diacetate as obtained from diacetoxystilbene dibromide and methylthio-magnesium iodide.

In vagina smear test with ovariectomized mice 20 gammas of the free phenolic substance injected subcutaneously in two portions in oil

solution produced oestrus in 67 percent, and 40 gammas in 100 percent, of the animals.

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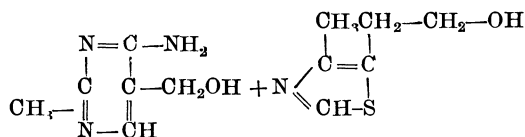
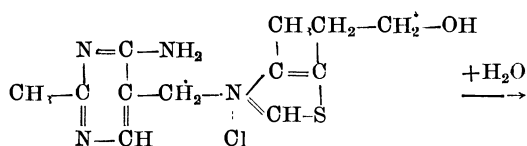
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On the Specificity of Aneurinase

By Kiku MURATA

(Received September 14, 1949)

Aneurinase, which decomposes aneurin, has been found in shell-fishes by Fujita⁽¹⁾ and in fishes by Sealock.⁽²⁾ The mode of the enzymatic decomposition has been studied by Fujita,³⁽⁴⁾⁽⁵⁾ Yamasaki⁽⁶⁾ and also by Woolley.⁽⁷⁾ According to their results aneurin is splitted into pyrimidine and thiazole as follows;



To study the more precise mechanism of the action of aneurinase against aneurin, it is desirable to have some knowledge on the specificity of the enzyme in relation to the chemical constitution of the substrate. The author has, therefore, studied on the action of aneurinase on various aneurin analogues as described below, and the results are summarised in Table 1.

Table 1

Expt. No.	Substrate		Decomposition by Enz.
	Name	Structure	
1, 2	4-methyl-5-β-hydroxyethyl-N-[(2'-methyl-4'-hydroxy-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride (I)	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2 \\ \\ \text{N}=\text{C}-\text{OH} \\ \quad \\ \text{CH}_2-\text{C}-\text{C}-\text{CH}_2-\text{N} \\ \quad \quad \\ \text{N}-\text{CH} \quad \text{Cl} \quad \text{C}=\text{C} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}-\text{S} \end{array} \cdot \text{HCl}$	-
3	4-methyl-5-β-hydroxyethyl-N-[(2'-methyl-4'-aminomethyl-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride (II)	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2 \\ \\ \text{N}=\text{C}-\text{NH}\cdot\text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_2-\text{N} \\ \quad \quad \\ \text{N}-\text{CH} \quad \text{Cl} \quad \text{C}=\text{C} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}-\text{S} \end{array} \cdot \text{HCl}$	-
4, 5, 6	4-methyl-5-β-hydroxyethyl-N-[(2'-hydroxymethyl-4'-amino-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride (III)	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2 \\ \\ \text{N}=\text{C}-\text{NH}_2 \\ \quad \\ \text{HOCH}_2-\text{C}-\text{C}-\text{CH}_2-\text{N} \\ \quad \quad \\ \text{N}-\text{CH} \quad \text{Cl} \quad \text{C}=\text{C} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}-\text{S} \end{array} \cdot \text{HCl}$	+
7, 8	4-methyl-5-β-hydroxyethyl-N-[(2'-ethyl-4'-amino-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride (IV)	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2 \\ \\ \text{N}=\text{C}-\text{NH}_2 \\ \quad \\ \text{C}_2\text{H}_5-\text{C}-\text{C}-\text{CH}_2-\text{N} \\ \quad \quad \\ \text{N}-\text{CH} \quad \text{Cl} \quad \text{C}=\text{C} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}-\text{S} \end{array} \cdot \text{HCl}$	+

(1) Fujita and Numata, *J. Biochem. Soc. Japan*, **17**, 156 (1943); **18**, 63 (1944).

(2) Sealock, *J. Am. Chem. Soc.*, **65**, 935 (1943).

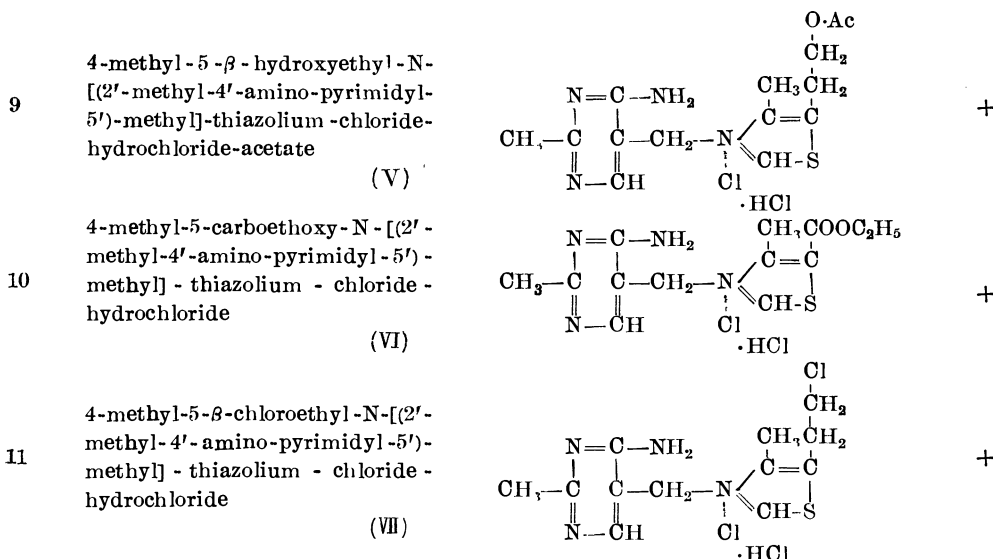
(3) Fujita and Numata, *J. Biochem. Soc. Japan*, **18**, 327 (1944).

(4) Fujita, Description of the 14th meeting on special committee of V. B₁, (1947).

(5) Fujita and Hasegawa, Description of the 29th meeting on special committee of V. B₁, (1948).

(6) Yamasaki, *J. Jap. Soc. Food and Nutr.*, **1**, 8 (1948).

(7) Woolley, unpublished (it is introduced on *Ann. Review of Biochem.* (1944)).



From Table 1 it is clear that the side chain of the thiazole nucleus and some substitution at position 2 on the pyrimidine nucleus have no effect but the amino group at position 4 of the latter is absolutely necessary* for the hydrolytic decomposition of aneurin by aneurinase.

It may be presumed that aneurin splits into the pyrimidine and thiazole residues after the protein part of aneurinase has been joined to the amino group on the pyrimidine nucleus in the aneurin molecule. According to Woolley,⁽⁷⁾ in the isolation of the thiazole and pyrimidine residues from the decomposition products by the action of aneurinase, the separation of the thiazole residue is followed by the detachment of the pyrimidine residue and the velocity of the detachment of the latter depends upon what species of shell-fish was used in the preparation of the enzyme. Reasons for this are, however, to be left in the future study; there may be some relation between the amino group in the pyrimidine nucleus and the enzyme action.

Experimental

Preparation of the Crude Extract of the Enzyme.—The meat and juice removed from shells were weighed together and triturated with addition of the sand. An equal quantity of *N*/10 sodium bisphosphate was added to it and the mixture was kept on standing over-night and centrifuged for 10 minutes. The clear supernatant liquid thus obtained was used as the crude enzyme extract.

Test for Enzymatic Activity.—The enzyme extract was mixed with an equal volume or a slightly excess of buffer solution of sodium acetate (*pH* 6.1) and a unit quantity of aneurin was added as shown in Table 2. After one hour at 60°, the reaction mixture was filtered and the

content of aneurin remained in the filtrate was determined by the method of diazo or thiochrome. It was then possible to calculate the amount of aneurin decomposed by the ferment by subtracting the amount of aneurin remaining in the filtrate from what has been added originally.

Table 2

Reaction condition	Volume of enzyme extract, cc.	Substrate (V, B ₁ analogues added), γ /cc.	Volume of buffer solution, cc.	Volume of 2 <i>N</i> hydrochloric acid, cc.
1	6	200 γ /2 cc.	11.5	0.5
2	3	100 γ /1 cc.	6.0	—
3	10	150 γ /1.5 cc.	18.0	0.5
4	2	10 γ /1 cc.	2.0	—
5	24	120 γ /1.2 cc.	22.8	—
6	22	110 γ /1.1 cc.	20.9	—
7	20	300 γ /3 cc.	36.5	0.5
8	2	10 γ /1 cc.	17.0	—

The Main and Blank Tests.—Equal volumes of the enzyme extract were put in two round bottom flasks of about 100 cc. in volume, which are attached to reflux condensers through a ground glass joint. The one, to be used as a blank test, was boiled gently over the asbestos pad for three minutes to inactivate the enzyme. The rest of the operations was the same for the both tests. A unit quantity of the buffer and a substrate under consideration were added to each and warmed to 60° for one hour. At the end of the reaction, water droplets condensed at the neck of the flasks and the lower part of the condensers were mixed well with the reaction mixtures in order to keep the concentration constant. They were then filtered and the filtrates were subjected separately for the aneurin determination.

The determination of aneurin was made by the usual methods, the diazo and thiochrome, except in the cases of substrate (VI) and (VII), where the determinations were done in the alkaline solution because the thiochrome of these compounds were difficult to dissolve in isobutanol.

Since the value obtained by the main test indicates percentage of aneurin recovered, it is then

* Those compounds which do not possess the free amino group and undergo splitting with difficulty can be made to decompose with addition of an equal amount of V. B₁.

Table 3

Expt. No	Reaction condition	Test	Substrate	Aneurin content, τ /cc.	Diazo method				Thiochrome method					
					Enzyme extract, cc.	Substrate (calculated) (aneurin), τ	Aneurin recovered, τ	Recovery, %	Decomposition, %	Enzyme extract, cc.	Substrate (calculated) (aneurin), τ	Aneurin recovered, τ	Recovery, %	Decomposition, %
1	1	Enz. act.	—	10	5	50	14.9	—	70.4	—	—	—	—	
		Main	(I)	"	"	"	41.5	—	3.1	T. R. negative	—	—	—	
		Blank		"	"	"	42.8	85.6	—					
		Blank		"	"	"	33.2	—	0.3					
2	3	Enz. act.	—	5	10	50	13.3	—	70.3	0.4	2.0	0.04	—	98.0
		Main	(I)	"	"	"	41.6	—	4.2	T. R. negative	—	—	—	
		Blank		"	"	"	43.4	86.8	—					
		Blank		"	"	"	—	—	—					
3	3	Enz. act.	—	5	10	50	6.8	—	86.4	—	—	—	—	—
		Main	(II)	"	"	"	32.7	—	0	T. R. negative	—	—	—	
		Blank		"	"	"	32.7	65.4	—					
		Blank		"	"	"	—	—	—					
4	3	Enz. act.	—	5	—	—	—	—	—	0.4	2.0	0	—	100.0
		Main	(III)	"	10	50	2.3	—	95.2	—	—	—	—	
		Blank		"	"	"	47.6	95.2	—	—	—	—	—	
		Blank		"	"	"	—	—	—	—	—	—	—	—
5	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0.01	—	98.0
		Main	(III)	2.5	20	50	5.0	—	84.4	0.4	1.0	0.16	—	69.3
		Blank		"	"	"	32.1	64.2	—	0.2	0.5	0.52	104.0	—
		Blank		"	"	"	—	—	—	—	—	—	—	—
6	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0	—	100.0
		Main	(III)	2.5	20	50	0	—	100.0	0.4	1.0	0	—	100.0
		Blank		"	"	"	48.1	96.2	—	0.2	0.5	0.53	106.0	—
		Blank		"	"	"	—	—	—	—	—	—	—	—
7	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0	—	100.0
		Main	(IV)	2.5	18	45	0	—	100.0	0.4	1.0	0	—	100.0
		Blank		"	"	"	46.7	104.0	—	0.2	0.5	0.49	98.0	—
		Blank		"	"	"	—	—	—	—	—	—	—	—
8	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0	—	100.0
		Main	(IV)	5	10	50	10.0	—	81.7	0.2	1.0	0.18	—	64.0
		Blank		"	"	"	54.4	103.0	—	0.1	0.5	0.50	100.0	—
		Blank		"	"	"	—	—	—	—	—	—	—	—
9	4	Enz. act.	—	2	—	—	—	—	—	0.2	0.4	0	—	100.0
		Main	(V)	2.5	20	50	0	—	100.0	0.4	1.0	0	—	100.0
		Blank		"	"	"	40.0	80.0	—	0.2	0.5	0.52	104.0	—
		Blank		"	"	"	—	—	—	—	—	—	—	—
10	8	Enz. act.	—	0.5	—	—	—	—	—	2.0	1.0	0	—	100.0
		Main	(VI)	"	—	—	—	—	—	2.0	1.0	0	—	100.0
		Blank		"	—	—	—	—	—	1.0	0.5	0.52	104.0	—
		Blank		"	—	—	—	—	—	—	—	—	—	—
11	8	Enz. act.	—	0.5	—	—	—	—	—	2.0	1.0	0	—	100.0
		Main	(VII)	"	—	—	—	—	—	2.0	1.0	0.01	—	99.0
		Blank		"	—	—	—	—	—	1.0	0.5	0.60	120.0	—
		Blank		"	—	—	—	—	—	2.0	1.0	—	—	100.0
Blank	"	—	—	—	—	—	—	1.0	0.5	0.48	96.0	—		

possible to calculate its decomposition percentage. The blank test shows percentage of recovery of aneurin added originally, this value was compared with that obtained by the main test. These results are shown in detail in Table 3.

Conclusion

The experimental results show that the free amino group in the pyrimidine ring of aneurin molecule is essential for the decomposition of aneurin by aneurinase, but other groups in the pyrimidine or the thiazole nuclei have little influence on this hydrolytic decomposition.

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Synthetic Mica Research*

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Introduction

Research in the production of synthetic mica was initiated in 1938 in response to the need of a local supply of high-grade mica. Experimental work was begun in January 1939 and directed originally to find compositions which crystallized easily. It was necessary to determine the temperatures of crystallization of mica in order to proceed with the work. The temperatures and velocities of crystallization were measured. Experiments to obtain large crystals were continued simultaneously with the above measurements. The corrosion of crucibles by the melt became more serious as the charge of melting increased and the rate of cooling decreased. Suitable crucibles for the synthetic work were investigated.

Temperatures of Crystallization and the Velocities of Crystallization of Synthetic Mica

The theoretical chemical formula of the fluor-

phlogopite is $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$ or $0.5 \text{ K}_2\text{O}$, 2.0 MgO , 1.0 MgF_2 , $0.5 \text{ Al}_2\text{O}_3$, 3.0 SiO_2 . If the ratio of MgO to MgF_2 in the formula is varied, subsequent compositions can be represented by points in the three component system of phlogopite-orthoclase-magnesium fluoride.⁽¹⁾ By replacing the orthoclase with other silicates and the magnesium fluoride with other fluorides, various compositions are represented by points in three component systems.

Systems used in representing the various compositions are:

POM	phlogopite-orthoclase-magnesium fluoride ⁽²⁾
P(K6S)M	phlogopite-($0.5\text{K}_2\text{O}$, 3SiO_2)-magnesium fluoride ⁽³⁾
P(KS)M	phlogopite-(K_2O , SiO_2)-magnesium fluoride ⁽³⁾
POA	phlogopite-orthoclase-aluminium-fluoride ⁽⁴⁾
PO(Ks)	phlogopite-orthoclase-potassium silicofluoride ⁽⁴⁾

Table 1

Exptl. designation	Chemical composition, mol					Constitution			Temp. of crystn. °C.
	K_2O	MgO	Al_2O_3	SiO_2	MgF_2	Phlogopite	Orthoclase	MgF_2	
POM 1	0.50	2.00	0.50	3.00	1.00	1.0	—	—	1361
POM 2	0.51	1.88	0.50	3.00	1.13	0.790	0.051	0.159	1348
POM 3	0.50	1.58	0.50	3.00	1.42	0.488	0.129	0.383	1307
POM 4	0.50	2.06	0.50	3.00	0.94	0.797	0.051	0.152 (MgO)	1332
POM 5	0.50	2.00	0.50	3.00	2.03	0.48	—	0.52	1329
POM 6	0.50	1.75	0.50	3.00	1.70	0.48	0.07	0.45	1322
POM 7	0.50	1.30	0.50	3.00	1.00	0.48	0.36	0.26	1317
POM 8	0.50	0.96	0.50	3.00	0.48	0.48	0.52	—	1356
P(K6S)M 1	0.50	1.58	0.40	3.00	1.40	0.50	$0.5 \text{ K}_2\text{O}$, 0.3 SiO_2	0.375	1323
P(KS)M 1	0.69	1.85	0.46	3.00	1.60	0.50	K_2O , SiO_2	0.375	1296
P(KS)M 2	0.53	1.98	0.48	3.00	1.19	0.80	0.05	0.15	1340
POA 1	0.50	3.00	0.17	3.00	0.69	1.00	—	AlF_3	1362
POA 2	0.50	2.40	0.23	3.00	1.13	0.50	0.125	0.375	1333
POKs 1	0.26	2.63	0.54	3.00	0.43	0.50	0.125	$\frac{1}{2} \text{ K}_2\text{SiF}_6$	1309
PKs 1	0.19	3.37	0.56	3.00	0.75	0.50	—	0.50	1320
PKs 2	0.19	3.37	0.56	3.00	0.47	0.80	—	0.20	1355
POKa 1	0.10	2.40	0.25	3.00	0.47	0.50	0.125	$\frac{1}{2} \text{ K}_2\text{AlF}_6$	1300
PKa 1	—	3.00	0.33	3.00	0.67	0.50	—	0.50	1315
PKa 2	—	3.00	0.33	3.00	0.42	0.80	—	0.20	1350

* This paper is an abstract of the summary of the work published on *Kogyo Kagaku Zasshi* (The Journal of the Society of Chemical Industry, Japan or The Journal of the Chemical Society of Japan, Industrial Chemistry Section) from 1943 to 1948 and *Kogyo Butsuri Kagaku* (Industrial Physical Chemistry), 1948, No. 1, 108-119, and 1949, No. 2, 179-203.

(1) Tokiti Noda and Sachio Sugiyama, *Journ. Soc. Chem. Ind., Japan*, **46**, 921 (1943), *Suppl. Bind.*, 193 B (in English).

(2) T. Noda and S. Sugiyama, *ibid.*, **46**, 1082 (1943), *Suppl. Bind.*, 225 B; **47**, 320 (1944).

(3) T. Noda and S. Sugiyama, *ibid.*, **47**, 623 (1944).

(4) T. Noda and S. Sugiyama, *ibid.*, **47**, 625 (1944).

P(Ks)	phlogopite-potassium silicofluoride ⁽⁵⁾
POKa	phlogopite-orthoclase- potassium aluminofluoride ⁽⁶⁾
PKa	phlogopite-potassium aluminofluoride ⁽⁶⁾

The "quenching" method was used for the measurement. Raw materials used were chemically pure silicon oxide, magnesium oxide, aluminium oxide, magnesium oxide, potassium carbonate and fluorides. The mixture of a definite proportion of these raw materials was enclosed in a small platinum tube and suspended with a platinum wire in a platinum ribbon resistance furnace and heated to $1420^{\circ}\sim 1430^{\circ}$. After completely melted, the specimen was cooled to a desired temperature and maintained at the temperature for one hour or more and quenched. The experimental results are shown in Table 1. Temperature of crystallization means the temperature where mica crystals begin to appear.

In general, good results were obtained with compositions which contained large concentrations of phlogopite. In POM group, POM2 gave the best result. As the melt of orthoclase has a high viscosity and solidifies into hard glass, its presence in large amounts is not favorable. Melts of P(K6S)M and P(KS)M compositions gave softer and better splitting mica than POM compositions. Better results were obtained with phlogopite-fluoride two-component compositions. Among various fluorides tested, potassium silicofluoride gave the best result and magnesium fluoride the next.

The velocity of crystallization of several compositions was measured by the same method as the measurement of the temperature of crystallization. Specimens maintained at a definite supercooled temperature for various periods were quenched. The velocity was calculated from the largest dimension of produced crystals. The results are shown in Table 2.

Table 2

Specimen	Temp. of crystn. °C.	Degree of su- percol- ling °C.	Max. velocity of crystn. mm./min.	Approx. no. of nuclei, no./3 mm ² .
POM 3	1307	6	0.12	—
POM 2	1348	3	0.08	one to several
		6	0.16	10 to 30
		10	0.47	several tens
		20	0.40	many
P(KS)M 1	1296	3	0.13	—
P(KS)M 2	1340	3	0.10	4 to 8
		6	0.18	20 to 40
		10	0.59	many

The velocity of crystallization increases to a maximum point and then begins to decrease, as the degree of supercooling increases. The

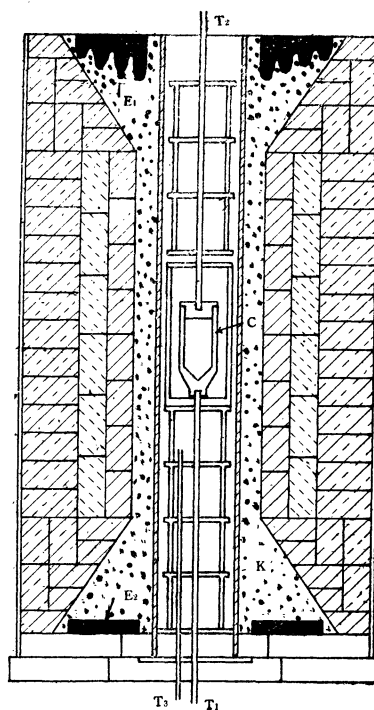
(5) S. Sugiyama, *Journ. Soc. Chem. Ind., Japan*, 48, 14 (1945).

(6) S. Sugiyama, *ibid.*, 48, 15 (1945).

number of nuclei increases rapidly with the degree of supercooling. Therefore, it is desirable to maintain a minimum degree of supercooling with sacrifice of the velocity, in order to produce as large crystals as possible in a given space.

Experiments on the Formation of Large Crystals

A large number of the experiments were performed in a small scale with a platinum resistance furnace and in a somewhat larger scale with a cryptol resistance furnace of about 1kg. capacity. A large variety of compositions were tested, but the formation of large crystals resulted with the compositions in the neighborhood of POM 2. From PKs 2 easily splitting mica crystals were produced. Sometimes, calcined silica, alumina, and magnesia were mixed with potassium carbonate and heated to about 900° to drive off carbon dioxide. The heated mass was powdered and mixed with magnesium fluoride, pressed and filled in the crucible. In other cases, calcined oxides, potassium carbonate and magnesium fluoride were mixed and pressed without the preliminary heating. The filled crucible was covered with a lid and put in a larger grog crucible. The space between the two crucible was filled with granulated grog. The assembled crucible was set in the proper position of the furnace. A general section of the furnace is shown in the figure. The crucible was heated slowly to about 900° and from 900° to $1420\sim 1450^{\circ}$ as



Vertical section of the cryptol resistance furnace: T₁, T₂, T₃, thermocouple; C, graphite crucible; E₁, E₂, iron electrode; K, cryptol.

quickly as possible to avoid the loss of fluorine. When the charge in the crucible was melted completely, it was cooled to $1400^{\circ}\sim 1380^{\circ}$ and from that temperature to 1300° slowly at the rate of $2\sim 3^{\circ}$ per hour. After passing this temperature

range, the current was cut off. After the furnace was cooled down, the crucible was taken out. The temperature of the charge was measured by thermocouples continuously and by an optical pyrometer frequently.

Three methods were tested to start the crystallization from one point.

(a) The upper part of the melt was kept at higher temperature, so that nuclei would be formed at the cone-shaped bottom and grow upward. This method was used most frequently. It was somewhat difficult to control the temperature gradient as desired with the cryptol furnace.

(b) An inner graphite crucible, whose horizontal section was triangular or fan-shaped, was placed in the melting crucible. The inner crucible had a small hole at the corner of the bottom. When the melt was cooled, the part between the inner and the outer crucibles solidified first. The peeped crystal from the small hole of the inner bottom might have become a starting point for crystallization of the inner melt. Comparatively large crystals were formed in the small inner space.

(c) A platinum plate attached on a water-cooled brass pipe was dipped in the melt. Crystals attached rapidly on the plate. The plate was then raised very slowly, as a single crystal grew vertically downward.

Although the latter two methods were tried but not many times, they seemed to be promising.

Originally, high aluminous grog crucibles were used. With longer contact with the melt, these crucibles were attacked seriously. Various kinds

from aluminous or grog crucible reacted with the melt and precipitated magnesium spinel. Spinel was very stable in the melt. Several compositions of the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system were tested for corrosion. Specimens of spinel accompanying small amount of periclase and forsterite were very stable. Good sintered specimens of mullite or forsterite-periclase resisted sufficiently good, too.⁽⁷⁾⁽⁸⁾

Properties of Synthetic Mica

The chemical composition and the optical properties of synthetic mica are shown in Table 3.⁽⁹⁾

The synthetic mica is stable at high temperatures up to 1100° and begins to decompose at 1200° by liberating small amounts of gas.⁽¹⁰⁾⁽¹¹⁾ The liberated gas contained silicium tetrafluoride in large amounts.⁽¹¹⁾

Preparation of Various Kinds of Mica by Isomorphous Substitution

Various kinds of mica were prepared by substituting the tetrahedral aluminum, octahedral magnesium and cubo-octahedral potassium of phlogopite by their crystal chemical equivalent elements.

A. Substitution of Tetrahedral Aluminium

(a). **Boron-phlogopite.**⁽¹²⁾—The mixture of 0.50 K_2O , 1.50 MgO , 1.50 MgF_2 , 0.50 B_2O_3 , 0.05 Al_2O_3 , 3.00 SiO_2 melted clearly at 1250° and

Table 3

Specimen	Chemical composition						Optical properties					Chemical formula
	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	F	Total	Refractive Index				Optical angle, 2 E	
	%	%	%	%	%	%	α	β	γ	γ-α		
1	42.01	16.84	26.61	8.66	5.70	99.81	1.522	1.553	1.554	0.029	19°	$\left\{ \begin{array}{l} (\text{O}_{0.7}\text{F}_{1.3})\text{K}_{0.5}\text{Mg}_{2.8}\text{Al}_{0.4} \\ (\text{Al}_{1.0}\text{Si}_{9.0}\text{O}_{10.0}) \\ (\text{O}_{0.6}\text{F}_{1.4})\text{K}_{0.5}\text{Mg}_{2.7}\text{Al}_{0.4} \\ (\text{Al}_{1.2}\text{Si}_{8.8}\text{O}_{10.0}) \\ (\text{O}_{0.6}\text{F}_{1.4})\text{K}_{0.5}\text{Mg}_{2.9}\text{Al}_{0.3} \\ (\text{Al}_{0.9}\text{Si}_{9.1}\text{O}_{10.0}) \end{array} \right\}$
2	40.73	18.50	25.41	9.20	6.03	99.87	1.544	1.564	1.566	0.029	20°	
3	43.44	13.90	26.95	9.68	6.16	100.12	1.513	1.539	1.540	0.027	22°	

Table 4

	Chemical composition						Chemical formula	Optical properties					Specific gravity
	SiO ₂	B ₂ O ₃	Al ₂ O ₃	MgO	MgF ₂	K ₂ O		α	β	γ	$\gamma-\alpha$	2E	
	%	%	%	%	%	%							
(1)	43.5	9.4	2.7	21.1	14.3	11.1	$\left\{ \begin{array}{l} (\text{F}_{1.80}\text{O}_{0.19})\text{K}_{0.9}\text{Mg}_{2.97}\text{Al}_{0.10} \\ (\text{Al}_{0.10}\text{B}_{1.07}\text{Si}_{2.86}\text{O}_{10.00}) \end{array} \right\}$	1.506	1.526	1.529	0.020	13°	2.730
(2)	43.4	9.8	1.5	19.8	15.2	11.2	$\left\{ \begin{array}{l} (\text{F}_{1.95}\text{O}_{0.05})\text{K}_{0.95}\text{Mg}_{2.94}\text{Al}_{0.10} \\ (\text{B}_{1.12}\text{Si}_{2.68}\text{O}_{10.00}) \end{array} \right\}$	1.505	1.521	1.522	0.017	27°	2.731
(2')								1.501	1.526	1.518	(calc.)		

(1) melted in grog crucible, (2) melted in platinum crucible, (2') calculated⁽¹³⁾

of crucibles obtained in the market were tested. Sintered alumina crucible resisted very well, but it was not used because of its high cost. In a large number of experiments, artificial graphite crucibles were used. They can be used repeatedly, since the solidified mass separates easily from the crucible. But graphite makes a reducing atmosphere in the crucible and changes the composition of the melt more easily than neutral atmosphere. This reducing atmosphere colors the mica block gray, therefore it is desirable to operate in neutral or oxidizing atmosphere.

It was observed that aluminium oxide came

(7) T. Noda and Masao Konno, *Journ. Ceramic Soc., Japan*, **57**, 25 (1949).

(8) T. Noda and Kiyoshi Mori, *ibid.*, **57**, 104 (1949).

(9) T. Noda and S. Sugiyama, *Journ. Soc. Chem. Ind., Japan*, **46**, 760 (1943), Suppl. Bind., 162 B.

(10) T. Noda and Koichi Aoki, *ibid.*, **51**, 7 (1948).

(11) T. Noda and Toru Matsushita, *ibid.*, **51**, 83 (1948).

(12) T. Noda, Nobutoshi Daimon and Hitoshi Toyoda, *ibid.*, **47**, 449 (1944).

(13) T. Noda and Daimon, *Journ. Electrochem. Soc., Japan*, **14**, 125 (1946).

began to crystallize at 1150° . The chemical compositions and the optical properties of the produced mica crystals are as shown in Table 4.

(b). **Zinc-mica.**⁽¹⁴⁾—To the mixture of 0.50 K_2O , 1.50 MgO , 1.50 MgF_2 , 0.50 ZnO , 0.05 Al_2O_3 , 3.50 SiO_2 was added excess ZnO to cover the loss by evaporation. The mixture was melted in a grog crucible and cooled. Comparatively good mica crystals separated out. The chemical composition of the mica is:

SiO_2 , 41.58%; ZnO , 7.03%; Al_2O_3 , 9.06%,

MgO , 17.83%; MgF_2 , 14.11%; K_2O , 10.75%.

The chemical formula is $F_{2.0}K_{1.0}Mg_{2.9}Zn_{0.2}(Zn_{0.2}Al_{0.8}Si_{3.0}O_{10.0})$.

(c). **Beryllium-mica.**⁽¹⁴⁾—The mixture of 0.50 K_2O , 1.90 MgO , 1.10 MgF_2 , 0.50 BeO , 0.05 Al_2O_3 , 3.00 SiO_2 melted at about 1350° . Mica crystals separated by cooling.

(d). **Iron-mica.**⁽¹⁴⁾—The mixture of 0.50 K_2O , 1.50 MgO , 1.50 MgF_2 , 0.50 Fe_2O_3 , 0.05 Al_2O_3 , 3.00 SiO_2 crystallized out black to brown mica.

B. Substitution of Cubo-octahedral Potassium⁽¹⁵⁾

(a). **Sodium-mica.**—The mixture of 0.50 Na_2O , 1.50 MgO , 1.50 MgF_2 , 0.50 Al_2O_3 , 3.00 SiO_2 melted at about 1325° . Mica crystals obtained were small.

(b). **Calcium-mica.**—The mixture of 0.50 CaO , 1.50 MgO , 1.50 MgF_2 , 0.50 Al_2O_3 , 3.00 SiO_2 melted at about 1200° . Rapid cooling resulted glass. By slow cooling, minute mica crystals were obtained.

(c). **Strontium-mica.**—The mixture of 0.50 SrO , 1.50 MgO , 1.50 MgF_2 , 0.50 Al_2O_3 , 3.00 SiO_2 melted at about 1450° . Small mica crystals

were obtained.

(d). **Barium-mica.**—The mixture of 0.50 BaO , 1.50 MgO , 1.50 MgF_2 , 0.50 Al_2O_3 , 3.00 SiO_2 melted at about 1400° . Mica crystals obtained were large, but brittle and difficultly splitting. The mixture of 1.00 BaO , 1.50 MgO , 1.50 MgF_2 , 1.00 B_2O_3 , 2.00 SiO_2 melted at about 1200° . By rapid cooling glass formed, by slow cooling, small mica crystals crystallized.

C. Substitution of Octahedral Magnesium and Preparation of Colored Mica⁽¹⁶⁾

The following mixtures shown in Table 5 produced mica crystals. (The temperature of melting by reaction and the colors of the produced mica crystals are also listed).

Table 5

Cemical composition of mixtute	Temp. of melting $^{\circ}C$.	Color of mica
0.5 K_2SiF_6 , 1.5 MgO , 1.5 MnO_2 , 0.5 Al_2O_3 , 2.5 SiO_2	1350	brown
0.5 K_2SiF_6 , 1.5 MgO , 1.5 FeO , 0.5 Al_2O_3 , 2.5 SiO_2	1350	brack
0.5 K_2SiF_6 , 2.75 MgO , 0.25 $NiCO_3$, 0.5 Al_2O_3 , 2.5 SiO_2	1400	{yellowish green
0.5 K_2SiF_6 , 2.75 MgO , 0.08 Co_3O_4 , 0.5 Al_2O_3 , 2.5 SiO_2	1400	pink -
0.5 K_2SiF_6 , 2.75 MgO , 0.09 Cr_2O_3 , 0.5 Al_2O_3 , 2.5 SiO_2	1400	yellow
0.5 K_2SiF_6 , 2.75 MgO , 0.125 NH_4VO_4 , 0.5 Al_2O_3 , 2.5 SiO_2	1400	
0.5 K_2SiF_6 , 2.0 MgO , 1/3 Co_3O_4 , 0.5 B_2O_3 , 2.5 SiO_2	1200	blue
0.5 K_2O , 2 LiF , TiO_2 , 0.5 B_2O_3 , 3 SiO_2	1100	{faint pink
BaF_2 , 2 MgO , 0.5 Li_2CO_3 , 0.5 B_2O_3 , 3 SiO_2	1100	white
SrF_2 , 2 MgO , 0.5 Li_2CO_3 , 0.5 B_2O_3 , 3 SiO_2		white
CaF_2 , 2 MgO , 0.5 Li_2CO_3 , 0.5 B_2O_3 , 3 SiO_2		white

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(14) T. Noda and N. Daimon, *Journ. Soc. Chem. Ind., Japan*, **49**, 125 (1946).

(15) T. Noda, N. Daimon and Utai Songkram, *Journ. Ceram. Soc., Japan*, **52**, 95 (1944).

On the Properties of Water Surface in Contact with Various Vapors*

By Toshio IKEDA and Tokurô OZAKI

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The Experimental Procedure and the Results.—The surface tension of water in various vapors was measured by the drop-volume method. The experimental equipment is shown in Fig. 1. The thick capillary polished flat at one end, where the water drop hangs, was joined to a burette filled of distilled water by a thick rubber tube for vacuum use, and to

the middle of the tube a screw cock was attached in order to control the rate of dropping. The capillary end is held air-tight in the thick glass globe by a large couthouc cork through which a glass tube is reserved for sending the air saturated with the vapor to be investigated into the glass globe, and the pressure in the globe may easily be regulated by a pump.

After sending the air saturated with the vapor into the glass globe for about 5 min., the dropping of water is started at the constant rate. From the observations of fifty drops we

* "International Critical Table" IV, 436; Landolt-Börnstein, "Phys.-chem. Tabellen" Bd. I, 208, 243 (1923); Erg. Bd. I, 149, 154 (1927); 154, 168 (1931).

obtain the mean volume of an water drop, v_{cc} , and the average life of one drop, τ .

The behaviors at 20° are shown in Fig. 2-a and -b. As it is seen there, the surface tension of water is affected markedly by the sort of vapor in contact, which are arranged in increasing order, that is : in air < benzyl chloride < carbon bisulfide < *n*-hexane, carbon tetrachloride < benzene < ethylene dichloride < chloroform < iso-

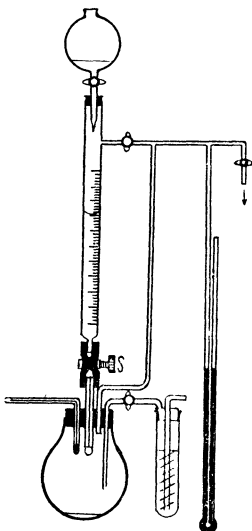
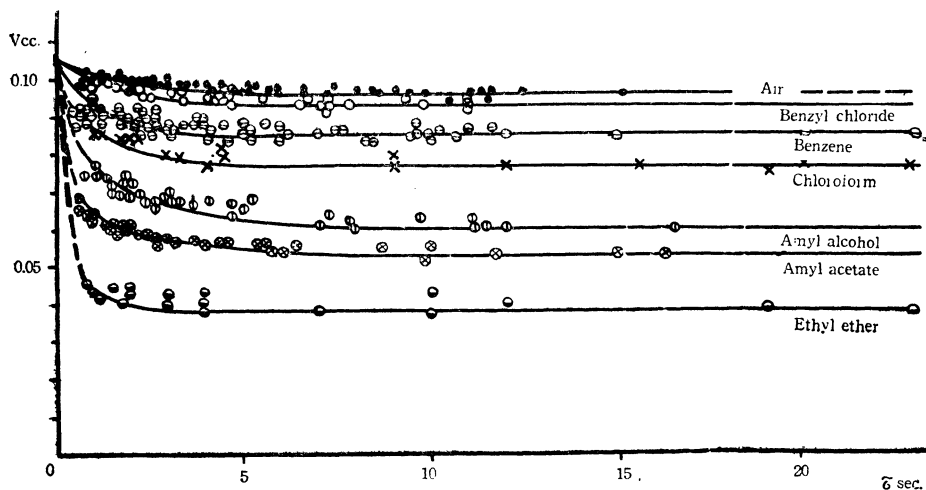
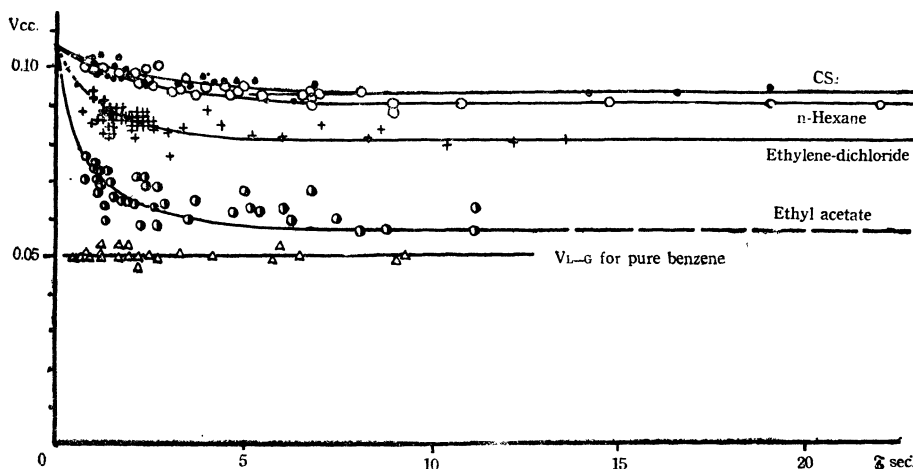


Fig. 1.

amyl alcohol < ethyl acetate < isoamyl acetate < ethyl ether.

The "Ageing" of the Water Surface and its Mechanism.—As is seen in Fig. 2, the water surface developed afresh has its maximum value of surface tension which diminishes to the equilibrium value with time, about 6 seconds in general. Therefore, the aging period of the water surface must be about 6 seconds, which is extremely short as compared with that of solution which demands more than 30 min. or even several hours. In other words, the time demanded to attain the adsorption equilibrium of vapor on the water surface is extremely short as compared with that of the solute in solution. This may be ascribed to the fact that the movement of the molecules in gas phase is by far free as compared with that in solution.

The Vapor-Water Interfacial Tension and the Relation to "Antonoff's Rule".—The surface tension of water (W)-drop in vapor

Fig. 2 a.— v_{W-G} , Drop volume of water in vapor.Fig. 2 b.— v_{W-G} , Drop volume of water in vapor.

(G), γ_{W-G} , is calculated by the formula

$$\gamma_{W-G} = \frac{v \cdot \rho \cdot g}{2\pi ar} \quad (1)$$

(taking the contact angle of water for zero) where v is the volume of a water-drop, ρ the density of water, g the acceleration of gravity, r the outer radius of capillary used and a is a correcting constant to be determined by experiment. In our experiment, $r=0.338$ cm., $a=0.610$. The results are shown in Table 1 where v_s (column 2) is the observed volume of one drop in the constant region after its ageing period, about 6 sec., γ_{Z-G} is the surface tension of the "pure" organic liquid in contact with

where W' and L' denote the phase W and L saturated with each other, and A the air in contact with W' or L' . Since the three phases W' , L' and A are in equilibrium, and since just the surface layer of water-drop in contact with the vapor of L is assumed to be saturated with L , so that we may put $\gamma_{W-G}=\gamma_{W'-A}$. And since the surface tension of organic liquids are not affected exceedingly by whether they are wet or dry,⁽¹⁾ the law (2) may be reduced to the "Antonoff's rule" itself.

As regards the lower membered acetic esters and alcohols, the relation may be expressed as follows:

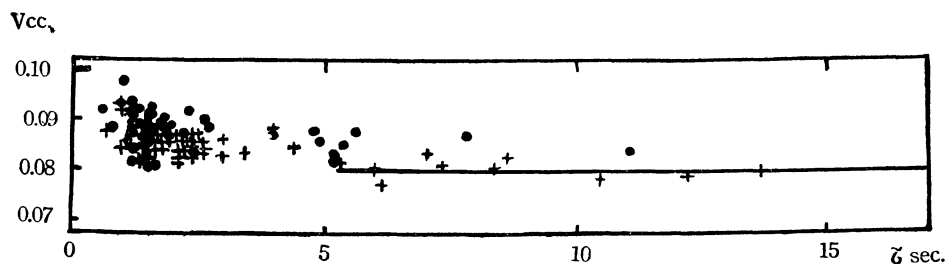


Fig. 3.—The effect of pressure on v_{W-G} (G =ethylene dichloride): + under ordinary pressure, ● under 10~15 cm.Hg.

air (with its vapor G), and $\gamma_{W'-L'}$ is the interfacial tension at the interface of water-liquid saturated with each other.

Table 1 (20°C.)

Name of G or L.	v_s , cc.	γ_{W-G} dyne /cm.	γ_{L-G} dyne /cm.	$\gamma_{W'-L'}$ dyne /cm.	$\gamma_{W'-L'} + \gamma_{L-G}$ dyne /cm.
Air	0.096	72.6	—	—	—
Benzyl chloride	0.093	70.5	39.9*	30.5	70.4
Carbon bisulfide	0.092	69.5	33.58	49.3	82.88
<i>n</i> -Hexane	0.090	68.0	17.34	50.96	68.30
Carbon tetra- chloride }	0.090	68.0	25.68	43.6	69.28
Benzene }	0.085	64.2	28.88	34.96	63.84
Ethylene dichloride }	0.080	60.5	31.1	29.2** (60.3)	
Chloroform	0.076	57.5	26.0	31.8	57.8
iso-Amyl alcohol	0.060	45.5	23.8	5.0	28.8
Ethyl acetate	0.056	42.5	23.6	6.7	30.3
iso-Amyl acetate	0.053	40.0	24.08	10.8	34.88
Ethyl ether	0.038	28.5	17.10	10.7	27.8

* Observed by capillary height method.

** This value was estimated from $\gamma_{W'-L'}=37.2$ dyne/cm. for ethylene dibromide at 20°. In many cases, the value of $\gamma_{W'-L'}$ for aliphatic halogenide decreases by about 8 dynes on replacing the bromine atom by chlorine.

Comparing the columns 3 and 6, we shall see the excellent agreements between them except carbon bisulfide, alcohols, acetic esters. These agreements can not be considered accidental. Thus we may take the following rule

$$\gamma_{W-G} = \gamma_{W'-L'} + \gamma_{L-G} \quad (2)$$

Using similar expression, the "Antonoff's rule" is expressed in

$$\gamma_{W-A} = \gamma_{W'-L'} + \gamma_{L'-A}, \quad (3)$$

$$\gamma_{W-G} > \gamma_{W'-L'} + \gamma_{L-G} \quad (4)$$

On the other hand, the relation for carbon bisulfide is

$$\gamma_{W-G} < \gamma_{W'-L'} + \gamma_{L-G} \quad (5)$$

The Effects of Pressure.—On decreasing the vapor pressure, the increase in the surface tension of water, γ_{W-G} , so that in v , might be expected owing to diminishing the attraction of molecules of vapor outside on the surface molecules of water. The observations were made about ethylene dichloride under reduced pressure of the system down to 10 cm.Hg, which corresponds to 0.8 cm.Hg in partial pressure. The increase of v by 0.004 cc. was found with difficulty even at $\tau < 6$ sec., but the prolongation of the ageing period up to 10 seconds, which was 6 sec. under ordinary pressure, so that the effect of pressure on v , if any, must appear under sufficient low pressure.

Summary

The surface tension of water in various vapors were measured by the drop-volume method. As a result of the experiment, it was found that the "Antonoff's rule" holds good with some exceptions. In any vapors, a remarkable, but short ageing of water surface was found, which was 6 seconds in general, and which is prolonged by reduced pressure.

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(1) W.D. Harkins, "The 6th Colloid Symposium Monograph," 17 (1928).

Separation of a Small Amount of Titanium from Iron by Ion-Exchange Resin

By Yukichi YOSHINO and Masuo KOJIMA

(Received December 10, 1949)

Introduction

In determining a small amount of titanium, the colorimetric method with hydrogen peroxide⁽¹⁾ has been most commonly used. But, if a sample contains much iron, the color of ferric ion intensifies that of the test solution.

W.F. Hillebrand⁽²⁾ says that 0.1 g. of Fe_2O_3 in 100 cc. of solution corresponds to 0.02 per cent TiO_2 in the same volume of solution.

To avoid this interference, various devices have been offered. For example, the addition of the same amount of iron to the standard solution⁽³⁾ is the simplest method. In the case when iron content is very high, however, this method would prove ineffective in determining titanium. P. Faber⁽⁴⁾ recommended the addition of phosphoric acid to both the standard and the test solution in order to neutralize the effect of iron. However, since phosphoric acid weakens the yellow tint to some extent, the use of this method is not always desirable when the amount of titanium is very small.

For accurate analysis, therefore, separation of titanium from iron before the color development seems to be the most desirable. For such a purpose, the separation of iron as ferrous sulfide in presence of tartaric acid⁽⁵⁾ has been in the most common use. For the satisfactory employment of this method, however, the double precipitation of ferrous sulfide is necessary, because a part of titanium is apt to coprecipitate with it. Moreover, the tartaric acid must be completely decomposed before development of the color.

The authors have studied the method of separation of both elements using an ion-exchange resin and found that even a large amount of iron could be removed as ferricyanide complex ion as described in the following.

Experimental

Apparatus and Reagent.—The cation-exchanger used was one of commercial phenolsulfonic acid polymers and between 30 and 70 mesh of size. Five or ten grams of the resin were conveniently equipped in a 50 cc. burette. The standard solu-

(1) A. Weller, *Ber.*, **15**, 2592 (1882).

(2) W.F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 160 (1919).

(3) W.A. Noyes, *Journ. Anal. App. Chem.*, **5**, 39 (1891).

(4) P. Faber, *Chem. Zeit.*, **31**, 263 (1906).

(5) R. Fresenius, *Z. anal. Chem.*, **1**, 69 (1862).

tion of ferric ion was prepared from Merck's ferric sesquichloride and that of titanium from Kahlbaum's titanium dioxide after bisulfate fusion.

Determination Method of Titanium.—In the experiment, the standard solutions of both ions were mixed together in various proportions, then following two ways of treatment were studied.

Method 1.—On treating the sample solution, in which iron concentration is rather high, with 50 per cent potassium or sodium cyanide solution, the iron is converted into both ferricyanide complex ion and ferric hydroxide precipitate, while titanium coprecipitates quantitatively as white titanium hydroxide owing to the excess of alkali cyanide. The precipitates are filtered off and dissolved with dilute sulfuric acid. This is diluted with water and passed through the column of resin previously saturated with hydrogen ion. Then, the resin is washed with about 200 cc. of 2*N*-KCN solution at the rate of 1 cc. per minute or less. The adsorbed iron is gradually eluted out as ferricyanide complex, while titanium remains without change. After washing the column thoroughly with water, adsorbed titanium is eluted with from 100 to 200 cc. of 10 per cent sulfuric acid. The aliquot portions of the eluent are used for colorimetric determinations of titanium as well as remaining iron. The results are shown in Table 1.

Table 1

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	{Ti++++	0.12	0.12	0
	{Fe+++	50.2	2.3	—
2	{Ti++++	0.68	0.68	0
	{Fe+++	67.2	0.3	—

If the concentration of iron is relatively low, all the iron is apparently converted into complex ion by previous treatment with the excess of concentrated potassium cyanide solution while titanium forms the precipitate. In such a case, a little dilute sulfuric acid just enough to dissolve the precipitate is added very cautiously and the solution is passed through the column of resin. After elution with 10 per cent sulfuric acid, titanium is determined as before. Table 2 shows the results of such experiments.

Table 2

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	{Ti++++	0.48	0.45	-0.03
	{Fe+++	0.88	trace	—
2	{Ti++++	0.68	0.66	-0.02
	{Fe+++	0.88	trace	—

Method 2.—Various mixed solution of iron and titanium are passed through the resin

without any previous treatment. The adsorbed iron is eluted out with from 300 to 500 cc. of 2*N*-NaCN solution as slowly as 1 cc. per minute or less. The elution and determination of titanium are conducted as described above. The results are listed in Table 3.

Table 3

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	{Ti ⁺⁺⁺⁺	0.68	0.66	-0.02
	{Fe ⁺⁺⁺	0.88	0.08	—
2	{Ti ⁺⁺⁺⁺	0.68	0.71	+0.03
	{Fe ⁺⁺⁺	8.78	0.16	—
3	{Ti ⁺⁺⁺⁺	0.68	0.68	0
	{Fe ⁺⁺⁺	67.2	0.25	—

The results obtained by both Methods 1 and 2 seem to be satisfactory for the colorimetric determination of a small amount of titanium in a sample rich in iron.

Determination of Titanium in Limonite.—As an example of practical application of the method, the titanium content in the limonite from Asahida mine, Kumamoto Pref., Kyushu is determined. The spectroscopic analysis of the sample showed the presence of the following minor constituents.

Al, Be, Ca, K, Li, Mg, Mn, Na, Si, Ti, V.

Of these, the content of vanadium was previously determined by E. B. Sandell's colorimetric method⁽⁶⁾ and obtained the value of 0.012 per cent as V. The iron content was 74.51 per cent as Fe₂O₃. Therefore, the test solution was prepared according to the following procedure. About 1 gram of the powdered sample was weighed and fused with sodium carbonate and the fused mass was leached with water. The residue was dissolved in a small volume of hot 10 per cent sulfuric acid and diluted to 250 cc., of which 50 cc. was used for titanium determination according to the Method 1.

To make sure, we took another portion of the

(6) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 5, 336 (1936).

test solution and separated iron as ferrous sulfide by the ordinary hydrogen sulfide method and determined titanium colorimetrically. The results of both experiments were in good agreement as indicated in Table 4.

Table 4

Method of Separation		Titanium Content, % TiO ₂
Resin	method	0.207
H ₂ S	method	0.197

Discussion

As cation exchange resin is not resistant enough against alkaline solution, its repeated use will result in the decrease of exchange capacity and will not be desirable. By reason of that, Method 1 which requires less alkali cyanide solution as an eluting agent seems to be more preferable to Method 2 in case of a sample rich in iron.

Summary

Separation of a small amount of titanium from iron with cation exchange resin was studied using alkali cyanide solution as eluting agent of iron. Successful results were obtained even in case of high iron concentration. This method enables us to remove the interfering effect of the iron on titanium colorimetry with hydrogen peroxide.

As an example of practical application, this method was tried in determining the titanium content of a limonite. The result agreed with that of the ordinary method of separation.

The authors, hereby, wish to express their hearty thanks to Prof. Eiiti Minami at the University of Tokyo for his kind guidance and encouragement. And authors also appreciate Messrs. M. Honda, H. Kakihana and M. Tanaka's advices, which proved to be of tremendous help in performing these studies.

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Studies on Foams. IV. The Effect of Electrolyte on the Foam Formation of Congo Red Solution

By Masayuki NAKAGAKI

(Received December 12, 1949)

The foams may be classified into two groups, namely hydrophobic or less stable foam and hydrophilic or more stable foam. The less stable foam is obtained by the aqueous solutions of alcohols, fatty acids and electrolytes and it has shorter foam duration than 30 seconds. The more stable foam is obtained by soaps, dyes, proteins and various detergents. According to O. Bartsch⁽¹⁾ the less stable foam behaves

like the negatively charged hydrophobic colloid and easily unstabilized by the addition of electrolyte, while the more stable foam hardly affected by the electrolyte. The present author considers, however, that such a conclusion is not quite correct, especially in the case of the more stable foam. In order to study on this problem the foam formation of congo red solution in the existence of electrolytes has been measured.

(1) O. Bartsch, *Kolloid-Beih.*, **20**, 1 (1925).

The foam formation was determined by the shaking test. Twenty cubic centimeters of solution was taken into a test tube of 40 cc. in capacity and 1.8 cm. in diameter, providing a glass stopper. This was shaken up and down for 30 seconds at the rate of 3 times per second and at the amplitude of 25 cm. Soon after the shaking, the height of the foam zone becomes maximum (usually less than 5 seconds). The height of the maximum foam zone A_m is read, which is taken as a measure of foaminess of the solution. The foam, then, gradually collapses untill at last a part of free liquid surface appears. Let the time required for the appearance of free liquid surface be t , which is taken as the measure of the foam duration. The change of the height of foam zone with time is also recorded. The strength of foam, τ , is calculated as the reciprocal of the collapsing velocity of foam zone for the initial 30 seconds, thus,

$$\tau = \frac{30}{A_m - A_{30}} \left(\frac{\text{sec.}}{\text{cm.}} \right) \quad \text{for } t > 30 \text{ sec.}$$

where A_{30} denotes the foam height read at 30 seconds after the the maximum height of foam zone is attained.

The stock solution of dye has been prepared in the following manner. Four grams of congo red (Merck's sample) was boiled with distilled water for several minutes and then adjusted accurately to one litre in volume after cooling. Just before the measurement, this solution was diluted with distilled water or some electrolyte solution untill the concentration of dye became 3.20 grams per litre. In order to avoid the effect of aging of solution, measurements have been undertaken just at one week after the preparation of the stock solution.

The general feature of the change of foam formation of congo red solution by the addition of sodium chloride is shown in Fig. 1. A prominent maximum is found in the curve of the foam duration at relatively low concentration of electrolyte, and also a maximum is seen in the curve of foam strength, while no maximum is observed in the curve of the foaminess. It is usually said that the foaminess and foam duration or foam strength of a solution are independent of each other. As an example the solutions of saponin and *n*-butyl alcohol are often cited, the former produces a more stable but less voluminous foam than the latter. This example, however, is not suitable in this case, for the foam stability of saponin solution may be due to some special reason, such as the formation of an insoluble film. In fact, foaminess and foam duration change, in most cases, similarly with each other, by the change of concentration. This is valid as far as the viscosity of solution is not extremely large, as discussed in the previous paper⁽²⁾ on

the less stable foams. This does not seem, however, to be true for the finely dispersed, long lasting foam.

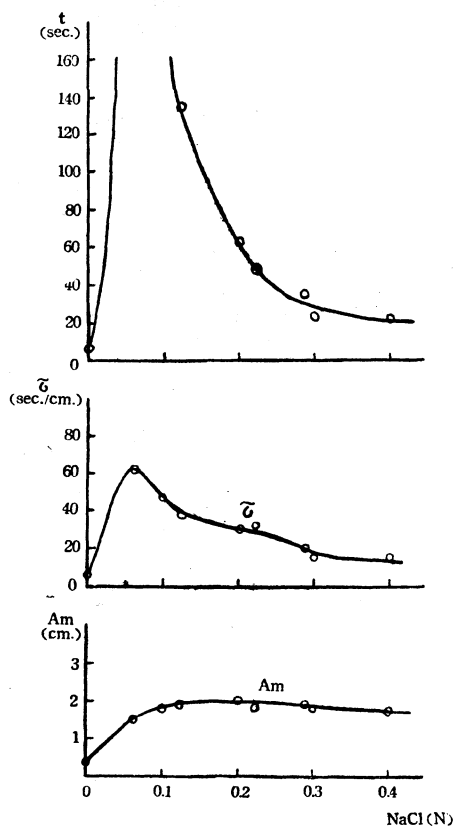


Fig. 1.—The effect of NaCl on the foam formation of congo red solution.

Such a steep maximum in foam duration of 3.20 g./l. congo red solution is also found by the addition of NaNO_3 , NaOH , HCl , and BaCl_2 . It is notable that a good peptization agent NaOH , a strong precipitation agent BaCl_2 , and an acid HCl behave in the same manner as NaCl and NaNO_3 , though the concentration for the maximum of foam duration is different from each other. As it is well known, acid precipitates blue congo acid from the solution of congo red. The concentrations of these electrolytes at the maximum point of foam strength are shown in Table 1.

One plausible explanation of the maximum of foam formation may be the peptization of dye particles by the electrolyte. Wo. Ostwald⁽³⁾ and R. Tanaka⁽⁴⁾ found the phenomenon that the congo acid is peptized by the addition of small amount of electrolyte. W. Schramek and E. Götze⁽⁵⁾ stated from diffusion data, and T. H. Morton⁽⁶⁾ from ultra-filtration experiments,

(3) Wo. Ostwald, *Ber.*, **62**, 1194 (1929).

(4) R. Tanaka, *Kolloid-Z.*, **54**, 156 (1931).

(5) W. Schramek and E. Götze, *Kolloid-Beih.*, **34**, 218 (1932).

(6) T. H. Morton, *Trans. Faraday Soc.*, **31**, 262 (1935).

(2) M. Nakagaki, *This Bulletin*, **21**, 30 (1948).

that the particle size of dye became minimum by the addition of small amount of electrolyte. C. Robinson,⁽⁷⁾ E. Valkó⁽⁸⁾ and S. M. Neale,⁽⁹⁾ however, recognized no minimum point on their curves of particle size to concentration of added electrolyte. The same conclusion was obtained by the present author. It will be reported in another paper. After all, peptization may be an action to disperse a precipitated mass into colloidal particles, scarcely affecting the size of particles already dispersed in sol state.

In spite of little change of particle size, the foam formation shows a steep maximum with the addition of the small amount of electrolyte. This is explained by the idea presented in the preceding paper,⁽¹⁰⁾ that the foam formation is mainly predominated by the separately dispersed ions rather than the portion of dye dispersed in colloidal aggregates, and that the surface chemical properties of dye ions are determined by the balance of its hydrophilic and hydrophobic character. The addition of electrolyte decreases the affinity of the polar part of dye ions to solvent, and this results in the increase of the surface activity of solute. In fact, the specific surface tension to water measured by du Nouy's tensiometer for 3.20 g./l. of congo red solution decreases from 0.98 for

pure dyestuff solution to 0.96 for solution containing 0.48 *N* of sodium chloride. The increase of surface activity, from which the increase of foam formation is explained, is regarded as a presage of salting out. When the concentration of electrolyte is further increased, the affinity of polar group of dye ion to solvent becomes weaker, till the dye ions coagulate and precipitate from the solution. The decrease of foam duration may be related to this process. The coagulation value will have a certain connection with the electrolyte concentration of maximum foam strength, as a measure of the ability of electrolyte to enfeeble the affinity between dye and solvent.

The coagulation value of 2.00 g./l. congo red solution has been measured, and the result is cited in Table 1. Since the coagulation of congo red is a "Slow Coagulation," the coagulation value is varied with time, and coagulation is observed in fairly dilute solution of electrolyte after a long time. In this report, the coagulation value is defined as the minimum concentration of electrolyte necessary to make solution turbid after 24 hours. Comparing the concentration of electrolyte for maximum foam strength with the coagulation value, the general drift coincides with one another.

Summary

The changes of foaming power of the solution of congo red by the addition of electrolytes have been estimated. There is a prominent maximum in the foam duration by the change of the concentration of electrolyte, while no such maximum is seen in the foaminess. The electrolyte concentration, at which the foam strength becomes maximum, and the coagulation value changes in the same trend from an electrolyte to the other. This is accounted for the fact that the affinity of polar part of dye ion to solvent is weakened by the addition of electrolyte.

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Table 1
Maximum Foam Formation and Coagulation Value.

Electro-lyte	Concn. of electrolyte for max. foam strength, <i>N</i> *	Coagulation value**, <i>N</i> .
NaOH	0.17	0.73
NaNO ₃	0.11	1.07
NaCl	0.062	0.71
BaCl ₂	0.0043	0.0056
HCl	0.0028	0.0043

* Concentration of congo red is 3.20 g./l.

** Concentration of congo red is 2.00 g./l.

(7) C. Robinson, *Proc. Roy. Soc. (London)*, **A148**, 681 (1935); *Trans. Faraday Soc.*, **31**, 277 (1935).

(8) E. Valkó, *Trans. Faraday Soc.*, **31**, 231, 278, (1935).

(9) S. M. Neale, *Trans. Faraday Soc.*, **31**, 282 (1935).

(10) M. Nakagaki, *This Bulletin*, **22**, 200 (1949).

The Chlorination of Ethylene in Alcohol

By Kazuo SATAKE and Takeo KANEKO

(Received December 12, 1949)

It is well known that the chlorination of ethylene in aqueous solution yields ethylene chlorohydrine and dichloride. About the reactions, there are number of investigations, espe-

cially about the factor which is likely to determine the ratio of two additions, between ethylene and hypochlorous acid on the one hand, and between ethylene and chlorine on

On the other hand, hydrogen chloride produced during the ethoxy- and chlorine-addition, inhibited this addition selectively and the more the reaction proceeded, the greater the ratio of the dichloride-formation became. When the concentration of chloride ion in the solution reached to 1/2 *N*, the formation of chloroether decreased remarkably and scarcely stopped till it became 2 *N*. The ether was obtained as main product only in the case of large excess of alcohol. (See Table 2.)

presence of a considerable amount of sulfuric acid showed no effect to the ratio of both additions, though some polymerisation of ethylene occurred by the acid. Acetic acid was the same, except that some other products (probably ethylene chlorohydrine acetate) were formed. So this apparent inhibition of ethoxy- and chlorine-addition was mainly due to chloride ion in the solution, and the effect of hydrogen ion was not so great.

In the presence of suitable chloride ion-

combining substances such as Ag^+ or Pb^{++} , the ratio of chlorohydrine ether in the reaction mixtures increased greatly. Alkaline, which neutralized the hydrogen ion produced during the reaction, did not increase the chlorohydrine ether formation, but inhibited both additions at various degrees, as long as the concentration of chloride ion did not change by the effect of the cation. In these cases, the ac-

cumulation of insoluble chloride or the presence of insoluble neutralizing agent as ferric hydroxide seemed to affect adversely for the dissolving of the reacting gases into the solution. The adverse effects followed in the order: $\text{Fe}(\text{OH})_3 \gg \text{KCl}, \text{NaCl} > \text{NH}_4\text{Cl}, \text{Ca}(\text{OH})_2$.

Table 2
The Effect of the Ratio of Reactants

Ethanol, mol	Chlorine,		Ethylene,		Yield of dichloride, %	Yield of chloroether, %	Final concn. of Cl
	mol	ml./ min.	mol	ml./ min.			
3.0	2.5	85	5.5	185	58	28	2.3
4.0	2.0	90	4.0	180	44	40	1.8
5.0	1.8	95	3.8	200	37	46	1.6
7.5	2.5	95	5.0	150	34	49	1.4
4.0	1.2	85	2.2	155	35	50	1.3
4.0	1.0	—	1.7	—	29	53	1.2
8.0	1.0	—	2.1	—	25	59	1.0
2.0	2.0	80	—	—	73	12	2.5
10.0	0.5	—	1.0	170	8	76	0.8

At 10°, yields were based upon the amount of chlorine introduced.

When the sufficient amounts of hydrogen or ammonium chloride were added to the solution at the beginning of the chlorination, no chlorohydrine ether was formed, though chlorine and ethylene reacted rapidly, giving ethylene dichloride as the sole product. While the pre-

Table 3

The Effect of Many Substances

Addition of	Yield of dichloride, %	Yield of chloroether, %	Remarks
2 <i>N</i> -HCl	96	0	Addition-velocity increased.
<i>N</i> /2-HCl	88	6	
<i>N</i> /2-NH ₄ Cl	78	11	
Ammonia* (a)	0	48	Large amount of acetaldehyde was formed.
" (b)	14	40	
" (c)	30	54	
NaOH(equiv. to Cl)	2	25	
Ca(OH) ₂ (")	26	45	
Fe(OH) ₃ (")	0	18	
ZnO (")	25	59	Ethylene was scarcely adsorbed. ZnCl ₂ produced, catalyzed.
MgO (")	27	53	
PbO (")	{ 10	68	A nitro-ester was formed?
	8	74	
AgNO ₃ (")	0	50	
Pb(NO ₃) ₂ (")	6	62	
Pb(CH ₃ COO) ₂ (")	17	56	An acetate was formed. Large amount of ethylene chlorohydrine and ββ'-dichloroethyl ether were produced. Adsorption of ethylene was very rapid. The velocity of additions increased.
30% Water	31	25	
Active carbon 1 g.	41	57	
HgCl ₂ 1 g.	39	54	
AlCl ₃ 1 g.	38	53	
FeCl ₃ 1 g.	40	52	
Urea 1 g.	30	57	Other chloro-compounds were formed. Some coloration occurred, with polymerisation of ethylene.
5 g.	31	65	
10 g.	27	68	
30 g.	18	69	
<i>N</i> -Acetic acid	35	50	
<i>N</i> -Sulfuric acid	33	43	

At 10°, ethyl alcohol 4.0 moles, chlorine 1.0 mole, ethylene 1.5 to 2.0 moles. The yield was based on the amount of chlorine introduced. * Ammonia was continuously introduced as gas; (a) large excess, (b) to maintain neutral, (c) slight acidic. The others were added at the beginning of the reaction.

34.02, 33.84. Calculated: 32.65.

The distillation residue was dissolved in ether, and the ether solution was washed with solution of sodium carbonate and water, then dried with calcium chloride. After the removal of the solvent by distillation on a water-bath, the remaining oil was redistilled.

$\beta\beta'$ -Dichloro-diethylether b. p. 170°-173° (uncorr.) d (15°) 1.228, n (D, 20°) 1.457. Cl % found: 46.52, 47.36. Calculated: 48.86.

The approximate estimation of the ratio of dichloride and chloroether in the reaction mixtures could be done by the difference of the specific gravities between the two, if the amount of dichloroether was less than few per cent.

When the chlorination was done above 10°, some amounts of acetaldehyde was detected in the trap

and the fore-run fraction (below 40°) of the upper aqueous layer. It was identified as p-nitro-phenylhydrazone (m. p. 128°), dimedone derivative (m. p. 139°-140°) and semicarbazone (m. p. 163°).

A number of substance shown in Table 3, except ammonia, were divided into very fine powder and added to alcohol in some portion during the introduction of gases. Ammonia was added through a flowmeter from the gas inlet tube with ethylene.

Properties of chlorohydrine ether as synthetic material or solvent are now on study.

In conclusion, the authors wish to express their thanks to Prof. Shiro Akabori, who gave many valuable advices and encouragements.

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1, 2-Bis-(*p*-hydroxyphenyl)-1, 2-dialkoxy-ethanes, Estrogenic Oxygen Analogs of Hexestrol⁽¹⁾

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E. C. Dodds, L. Goldberg, W. Lawson, and R. Robinson⁽²⁾ pointed out a close structural resemblance of diethyl-stilbestrol, $\text{HOC}_6\text{H}_4\text{-C}(\text{C}_2\text{H}_5)=\text{C}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_4\text{OH}$, just then prepared by them, to estrone or estradiol. Hexestrol, $\text{HOC}_6\text{H}_4\text{CH}(\text{C}_2\text{H}_5)\text{CH}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_4\text{OH}$, another strong synthetic estrogen, is expected to bear a much closer structural resemblance to the natural estrogens, because it is a meso-form and the groups around carbon atoms 8 and 9 of the natural estrogens are arranged also in a "meso-form". This has been demonstrated by X-ray investigations.⁽³⁾ The stereoisomerides, *d*-, *l*-, and racemic forms, of hexestrol have been reported to possess very weak potencies.⁽³⁾

The structural resemblance causing the development of similar physiological properties may be given by the union of two principal features, namely, a resemblance in the shapes of the molecular skeletons and the presence of the same functional groups at the corresponding positions of the similar-shaped skeletons. As for the skeleton, the replacement of the members constituting it with different atoms or groups may cause no radical change in the physiological action, unless the shape is altered significantly and unless an appearance of a new physiological action is associated with the replacement. Thus, the authors are interested in

possible estrogenic activity of hexestrol analogs in which oxygen atom or the imino-group replaces one or both of the methylene groups or nitrogen atom one or both of the central methine groups.

One of such compounds is 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-dimethoxy-ethane, $\text{HOC}_6\text{H}_4\text{-CH}(\text{OCH}_3)\text{CH}(\text{OCH}_3)\text{C}_6\text{H}_4\text{OH}$. It was already prepared by Th. Zincke and S. Münch.⁽⁴⁾ They described a higher and a lower melting stereoisomerides without determining their configurations. The present authors presumed the higher melting compound to be the meso-form, and prepared it by the following improved method:

Bromine was added to diacetoxy-stilbene, $\text{CH}_3\text{COOC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OCOCH}_3$, obtained by the acetylation of dihydroxy-stilbene, $\text{HO-C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{OH}$, and the resulting dibromide, $\text{CH}_3\text{COOC}_6\text{H}_4\text{CHBrCHBrC}_6\text{H}_4\text{OCOCH}_3$, was treated with an excess of sodium methoxide in methanol at room temperature. After left to stand overnight, the reaction mixture was poured into water, and acidified with hydrochloric acid. The precipitated substance was recrystallized from dilute methanol. The product thus obtained showed the melting point 220–222°, while Zincke and Münch gave 219–221°.

The minimum dose to produce typical oestrus in ovariectomized mice by subcutaneous injections in two portions in oil solution was found 0.5 gamma, and showed 5 percent activity of hexestrol evaluated by the same method.

(1) Preliminary note was published in the *Chemistry and Chemical Industry (Kagaku to Kogyo)*, **2**, No. 2, 34 (1949).

(2) *Nature*, **141**, 247 (1938).

(3) C. H. Carlisle and D. Crowfoot, *J. Chem. Soc.*, **1941**, 6; also cf. U. v. Solmssen, *Chem. Rev.*, **37**, 481 (1945).

(4) *Ann.*, **335**, 157 (1904).

Considering that the simple dihydroxy-dibenzyl, $\text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$, shows only a very weak activity, the minimum active dose being as much as 100 mg. in rats, the two methoxy groups proved really quite effective in imitating the molecular shape of hexestrol, and thus it has been indicated that the methylene groups in the ethyl groups of hexestrol can be replaced with oxygen atoms without causing any fundamental change in the physiological properties. Further, the strong activity has demonstrated that the configuration of the compound used is in fact a meso-form.

The corresponding diethoxy-compound, 1,2-bis-(*p*-hydroxyphenyl)-1,2-diethoxy-ethane, $\text{HOC}_6\text{H}_4\text{CH}(\text{OC}_2\text{H}_5)\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{OH}$, was newly synthesized by a similar method using sodium ethoxide in ethanol instead of sodium methoxide in methanol. It forms colorless needles when recrystallized from dilute ethanol, melts at $212.5\text{--}214.5^\circ$, and shows similar solubilities in various solvents to the methoxy-compound. As expected, it showed a far smaller potency than the methoxy-compound, the minimum active dose being 10 gammas.

A nitrogen analog of hexestrol dimethyl ether,

ethyl-*p*-methoxyphenyl-(1-*p*-methoxyphenyl-propyl)-amine, $\text{CH}_3\text{OC}_6\text{H}_4\text{N}(\text{C}_2\text{H}_5)\text{CH}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_4\text{OCH}_3$, m.p. 63.5° , has been prepared. It developed incomplete but distinct durable oestrus. A more detailed account will soon appear.⁽⁵⁾ In this connection, it may be added that J. B. Niederl and M. I. Dexter⁽⁶⁾ have found blood-pressure lowering, but no oestrus producing, action in 1,2-bis-(*p*-hydroxyphenyl)-1,2-di-(methylamino)-ethane, $\text{HOC}_6\text{H}_4\text{CH}(\text{NHCH}_3)\text{CH}(\text{NHCH}_3)\text{C}_6\text{H}_4\text{OH}$. In the present authors' opinion, however, it must be determined whether the compound is really a meso-form or not before concluding estrogenic inactivity of the nitrogen analog of hexestrol represented by the above formula.

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the University of Tokyo, Tokyo*

(5) A preliminary note was presented by Y. Nomura at the annual meeting of the Chemical Society of Japan on April 3, 1949.

(6) *J. Am. Chem. Soc.*, **70**, 3071 (1948).

Calculations of the Energy Levels of Cyclooctatetraene (C_8H_8)

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(Received October 21, 1949)

1. Introduction

The cyclooctatetraene molecule has already been treated by Hückel⁽¹⁾ according to the molecular orbital method. But as its molecular structure was not known at the time, he treated its molecule as plane and suggested the possibility of its substance to be paramagnetic.

Lately, by R. C. Pink and A. R. Ubbelohde⁽²⁾ and also by the members of our laboratory⁽³⁾ it is found experimentally that the substance is not paramagnetic but diamagnetic* like many other organic substances and also that its molecule has no resultant spin in the ground state. The purpose of the present paper is to calculate the energy levels of the molecule from the stand-point of the Heitler-London-Slater-Pauling

method,⁽⁴⁾⁽⁵⁾⁽⁶⁾ assuming different structures (D_{2d} and D_{4d}) proposed by different investigators and from different experimental grounds, and also to show which structure is in better agreement with the experimental results of magnetic susceptibility, absorption spectra and thermochemical data.

The structure of cyclooctatetraene, though investigated by several physico-chemical methods, but has not yet been decided. Until now, as a result of investigation, the structures of C_8H_8 , "Crown Form"⁽⁷⁾⁽⁸⁾⁽⁹⁾ (D_4 , or D_{4d}) and "Tub Form" (D_{2d})⁽¹⁰⁾⁽¹¹⁾⁽¹²⁾ are reported. (Fig. 1).

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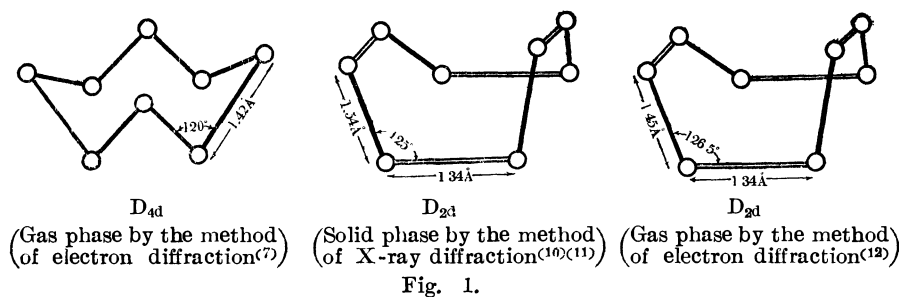
(12) K. Hedberg and V. Schomaker, Annual Meeting of Am. Chem. Soc., (1949).

* The molar magnetic susceptibility was found in our laboratory to be -55.3×10^{-6} , independent of the temperature between 20° and 80°.

(1) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(2) R. C. Pink and A. R. Ubbelohde, *Nature*, **160**, 502 (1947); *Trans. Faraday Soc.*, **44**, 708-16 (1948); *Chem. Abst.*, No. 7 (Apr. 10), (1949).

(3) S. Shida and S. Fujii, Scientific Meeting of Tokyo Institute of Technology (August 1949).



First, in calculating the energy levels of C_8H_8 as the symmetry of D_{2d} , a molecule of C_8H_8 is treated as follows: Each carbon atom has one π -electron whose density cloud is a dumbbell with its axis perpendicular to the plane of the σ -bonds (approximately sp^2 -bonds). It is assumed that the interaction of the π -electron and the σ -electron is small.

2. Calculation of Singlet States

All the possible structures will be described first. They are linearly independent, namely, the canonical sets for cyclooctatetraene; the two Kekule structures (Ψ^1, Ψ^2), the eight Dewar I structures ($\Psi^3, \Psi^5, \dots, \Psi^{10}$) and the four Dewar II structures ($\Psi^{11}, \Psi^{12}, \Psi^{13}, \Psi^{14}$) exist. These are shown in Fig. 2. For instance, two Kekule structures for benzene have identical energy, but those for cyclooctatetraene (D_{2d}) have not. This arises from the fact that the exchange integral is divided into two.

$\Psi^k (k=1, 2, 3, \dots, 14)$, wave function attached to the each structure k of the canonical set, is

$$\Psi^k = \frac{1}{2^4(8!)^{\frac{1}{2}}} \sum_p (-1)^p P \psi_1(1) \psi_2(2) (\alpha_1 \beta_2 - \beta_1 \alpha_2) \times \psi_3(3) \psi_4(4) (\alpha_3 \beta_4 - \beta_3 \alpha_4) \times \dots (1)$$

The energy levels are given by solving the secular equation

$$\det || \Psi^j | H - W | \Psi^k || = 0 \quad \dots (2)$$

$$(\Psi^j | H - W | \Psi^k) = U_{jk} (Q - W) + V_{jk} \alpha + W_{jk} \alpha' \quad \dots (3)$$

$$Q = \int \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \psi_5(5) \psi_6(6) \psi_7(7) \psi_8(8) H \tilde{\psi}_1(1) \tilde{\psi}_2(2) \tilde{\psi}_3(3) \tilde{\psi}_4(4) \tilde{\psi}_5(5) \tilde{\psi}_6(6) \tilde{\psi}_7(7) \tilde{\psi}_8(8) d\tau \quad \dots (4)$$

$$\alpha = \int \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \psi_5(5) \psi_6(6) \psi_7(7) \psi_8(8) H \tilde{\psi}_1(2) \tilde{\psi}_2(1) \tilde{\psi}_3(3) \tilde{\psi}_4(4) \tilde{\psi}_5(5) \tilde{\psi}_6(6) \tilde{\psi}_7(7) \tilde{\psi}_8(8) d\tau \quad \dots (5)$$

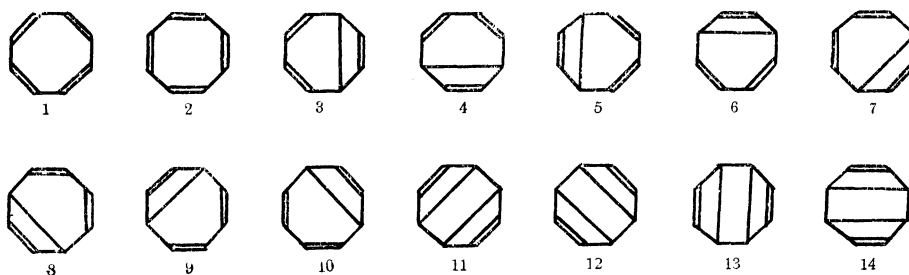


Fig. 2.—1~2, Kekule structures; 3~10, Dewar I structures; 11~14, Dewar II structures.

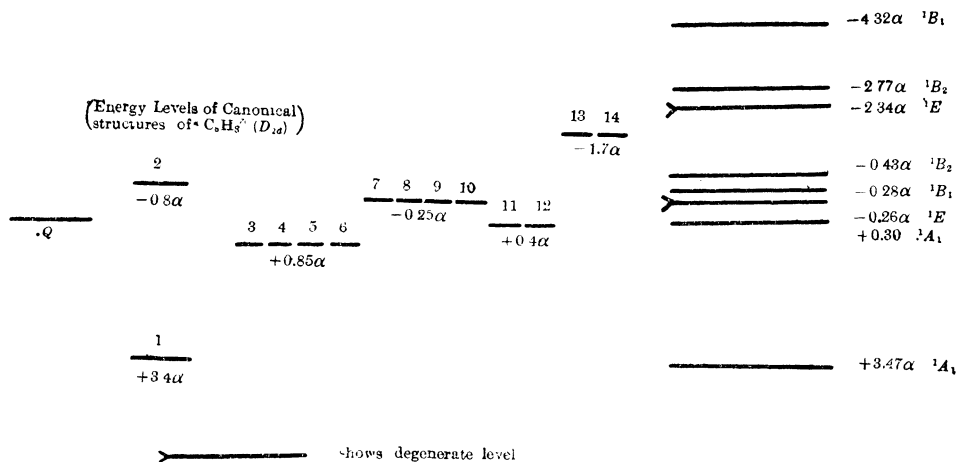


Fig. 3.—Energy levels of singlet states, except four $^1A_1$ levels (in the case of $\alpha' = 0.3\alpha$).

Table 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 {	$\frac{8}{16}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$
	$-\frac{16}{16}\alpha'$	$+\frac{4}{4}\alpha'$	$-\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{8}{8}\alpha'$	$-\frac{8}{8}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$
2 {	$\frac{1}{4}\alpha$	$\frac{8}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{16}\alpha$
	$+\frac{4}{4}\alpha'$	$-\frac{16}{16}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{8}{8}\alpha'$	$-\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{8}{8}\alpha'$	$-\frac{8}{8}\alpha'$	$-\frac{8}{8}\alpha'$
3 {	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$
	$-\frac{2}{2}\alpha'$	$+\frac{8}{8}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$
4 {	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$
	$-\frac{2}{2}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$
5 {	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{2}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$
	$-\frac{2}{2}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$
6 {	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{8}{8}\alpha$	$\frac{4}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$
	$-\frac{2}{2}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$
7 {	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$
	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$
8 {	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$
	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$
9 {	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$
	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$
10 {	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{8}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$
	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$
11 {	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$
	$-\frac{8}{8}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$-\frac{16}{16}\alpha'$	$-\frac{16}{16}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$
12 {	$\frac{4}{16}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{2}{2}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{8}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$
	$-\frac{8}{8}\alpha'$	$+\frac{8}{8}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$-\frac{16}{16}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$
13 {	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{8}{8}\alpha$	$\frac{2}{8}\alpha$
	$+\frac{2}{2}\alpha'$	$-\frac{8}{8}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$-\frac{16}{16}\alpha'$	$-\frac{2}{2}\alpha'$
14 {	$\frac{2}{8}\alpha$	$\frac{4}{16}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{4}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{2}{8}\alpha$	$\frac{1}{4}\alpha$	$\frac{1}{4}\alpha$	$\frac{2}{8}\alpha$	$\frac{8}{8}\alpha$
	$+\frac{2}{2}\alpha'$	$-\frac{8}{8}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{2}{2}\alpha'$	$+\frac{4}{4}\alpha'$	$+\frac{4}{4}\alpha'$	$-\frac{16}{16}\alpha'$	$-\frac{2}{2}\alpha'$

Notation $\frac{8}{16}\alpha - \frac{16}{16}\alpha' = 8(Q-W) + (32\alpha - 16\alpha')$

$$\alpha' = \int \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \psi_5(5) \psi_6(6) \psi_7(7) \psi_8(8) H \tilde{\psi}_1(1) \tilde{\psi}_2(2) \tilde{\psi}_3(3) \tilde{\psi}_4(4) \tilde{\psi}_5(5) \tilde{\psi}_6(6) \tilde{\psi}_7(7) \tilde{\psi}_8(8) \dots (6)$$

U_{jk} , V_{jk} , W_{jk} is determined by Pauling's island method.

Then the Kekule I structure has an energy lowering of $(4\alpha - 2\alpha')$, whereas the Kekule II structure has an energy lowering of $(4\alpha' - 2\alpha)$. The Kekule II structure has a higher energy than the Kekule I structure $\alpha' < \alpha$ as explained in Section 5.

The determinant evaluated for cyclooctatetraene (fourteen canonical structures) is shown in Table 1.

Factorizing the secular determinant by a linear combination of the canonical structures, the energy levels of the singlet states of C_8H_8 (D_{2d}) are obtained.

In the next problem, the symmetry of the levels may be found by the group theory.

3. Selection Rules

The symmetry of the fourteen levels may be found from the characters of the reducible representation on the basis of the fourteen structures.

If the symmetry of C_8H_8 is D_{2d} , its character is as shown in Table 2.

	Table 2				
$V_d = D_{2d}$	E	C_2	$2C_4 = 2S_4$	$2C'_2$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	1	-1	1	-1
$B_2(z)$	1	1	-1	-1	1
$E(x \pm iy)$	2	-2	0	0	0

The characters of the symmetry operations in the reducible representation Γ for C_8H_8 are shown in Table 3.

	Table 3				
	E	C_2	$2C_4 = 2S_4$	$2C'_2$	$2\sigma_d$
Γ	14	6	2	6	6

The reducible representation Γ is broken into its irreducible parts $\Gamma = \sum a_i \Gamma_i$ by means of the character tables (Tables 2 and 3), namely

$$\Gamma = 6A_1 + 2B_1 + 2B_2 + 2E \quad \dots (7)$$

These irreducible representations correspond to the fourteen energy levels of singlet state. The selection rule for transitions between $^1A_1$ and all the other energy levels will be discussed by the group theory.

$$\begin{cases} P_z & A_1 B_2 A_1, A_1 B_2 B_1, A_1 B_2 E \\ P_{x,y} & A_1 E A_1, A_1 E B_1, A_1 E B_2 \end{cases}$$

The transitions from ground state to the excited levels are forbidden for reduced form does not contain A_1 .

$$\begin{cases} P_z & A_1 B_2 B_2 = A_1 \\ P_{x,y} & A_1 E E = A_1 + A_2 + B_1 + B_2 \end{cases}$$

The transitions from ground state to the B_2 , E levels are allowed.

The transitions from $^1A_1$ to $^1B_2$ and ^1E are allowed. In this point C_8H_8 is different from benzene for the transition from the ground state of benzene to the excited state is forbidden so far as the polar terms are neglected. In the following chapter the result of calculation, by which the singlet ground state was found out to be more stable than the triplet ground state, will be described.

4. Calculation of Triplet States

The triplet states of cyclooctatetraene are calculated by analogous method to that in the case of the singlet states.

The canonical set is composed of twenty eight structures. But the energy of triplet ground state is approximately the lowest of those, calculated from the only eight canonical structures in the case of D_{2d} , because the remaining twenty canonical structures have higher energies than the former.

The eight canonical structures are shown in Fig. 4 and the secular determinant is given in Table 4.

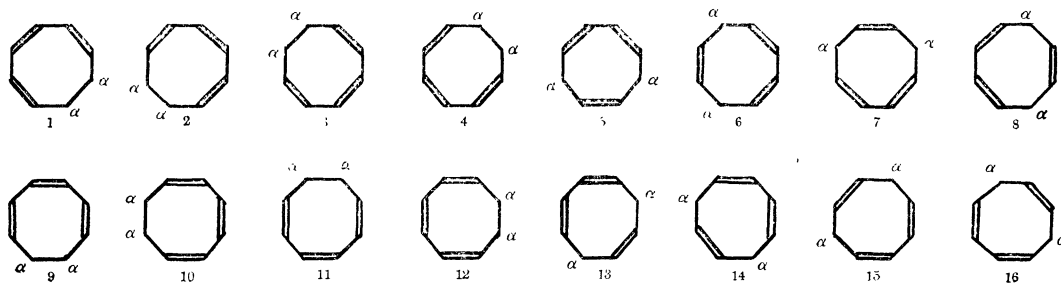


Fig. 4.—Upper eight canonical structures are used for the triplet states of D_{2d} and all of sixteen canonical structures for the triplet states of D_{4d} .

Table 4

	1	2	3	4	5	6	7	8
1	$8/16\alpha - 16\alpha'$	$0/4\alpha'$	0/0	$0/4\alpha'$	$4/8\alpha - 2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha - 2\alpha'$
2	$0/4\alpha'$	$8/16\alpha - 16\alpha'$	$0/4\alpha'$	0/0	$4/8\alpha - 2\alpha'$	$4/8\alpha - 2\alpha'$	$0/2\alpha'$	$0/2\alpha'$
3	0/0	$0/4\alpha'$	$8/16\alpha - 16\alpha'$	$0/4\alpha'$	$0/2\alpha'$	$4/8\alpha - 2\alpha'$	$4/8\alpha - 2\alpha'$	$0/2\alpha'$
4	$0/4\alpha'$	0/0	$0/4\alpha'$	$8/16\alpha - 16\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha - 2\alpha'$	$4/8\alpha - 2\alpha'$
5	$4/8\alpha - 2\alpha'$	$4/8\alpha - 2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$8/8\alpha - 4\alpha'$	$2/4\alpha + 2\alpha'$	$0/2\alpha'$	$2/4\alpha + 2\alpha'$
6	$0/2\alpha'$	$4/8\alpha - 2\alpha'$	$4/8\alpha - 2\alpha'$	$0/2\alpha'$	$2/4\alpha + 2\alpha'$	$8/8\alpha - 4\alpha'$	$2/4\alpha + 2\alpha'$	$0/2\alpha'$
7	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha - 2\alpha'$	$4/8\alpha - 2\alpha'$	$0/2\alpha'$	$2/4\alpha + 2\alpha'$	$8/8\alpha - 4\alpha'$	$2/4\alpha + 2\alpha'$
8	$4/8\alpha - 2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha - 2\alpha'$	$2/4\alpha + 2\alpha'$	$0/2\alpha'$	$2/4\alpha + 2\alpha'$	$8/8\alpha - 4\alpha'$

The secular determinant is factorized by linear combination of eight canonical structures like the singlet states. The same parameter, α , appeared as it did in the energy of the singlet states. The energy of the triplet ground state calculated is -1.84α (if $\alpha' = 0.2\alpha$) or -1.76α (if $\alpha' = 0.3\alpha$). Therefore, it is expected from the H-L-S-P method that C_8H_8 is diamagnetic.*

5. Energy Levels and Resonance Energy

The energy levels of singlet states of C_8H_8 , except four $^1A_1$ levels in each case of $\alpha' = 0.2\alpha$, 0.25α , 0.3α , 0.35α , are given in Table 5. The reason why the values of α' are selected as above will be shown in section 7.

The two Kekule structures have not the same energy and the higher Kekule structure scarcely affects the ground state. Then the lower Kekule structure, the four lower Dewar I structures and the two lower Dewar II structures greatly contribute to the energy of the ground

Table 5
The Energy Levels of Singlet States of C_8H_8 Except Four $^1A_1$ Levels.

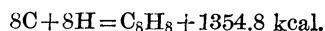
	$\alpha' = 0.2\alpha$	$\alpha' = 0.25$	$\alpha' = 0.3\alpha$	$\alpha' = 0.35\alpha$
$^1B_1$	-4.21α	-4.27α	-4.32α	-4.38α
$^1B_2$	-2.48α	-2.62α	-2.77α	-2.92α
^1E	-2.22α	-2.28α	-2.34α	-2.41α
$^1B_2$	-0.32α	-0.38α	-0.43α	-0.48α
$^1B_1$	-0.19α	-0.23α	-0.28α	-0.32α
^1E	-0.18α	-0.22α	-0.26α	-0.29α
$^1A_1$	0.10α	0.20α	0.30α	0.40α
$^1A_1$	3.63α	3.55α	3.47α	3.40α

state.

In order to determine the value of the splitting up of the energy levels, it is necessary to find the numerical values of α , α' . The two

methods of finding these values are as follows: first, experimentally from thermochemical data, secondly, theoretically by the $2p\pi$ hydrogen-like functions.

The heat of formation is calculated from recent data.⁽¹³⁾



The values of bond energy obtained from recent data⁽¹⁴⁾ are as follows:

$$\left. \begin{array}{l} C-C = 60.3 \text{ kcal.} \\ C-C = 102.9 \text{ kcal.} \\ C-H = 87.15 \text{ kcal.} \end{array} \right\} \rightarrow \left\{ \begin{array}{l} \text{therefore the heat} \\ \text{of formation of} \\ C_8H_8 = 1350 \text{ kcal.} \end{array} \right.$$

This difference, 4.8 kcal, may be taken as the experimental resonance energy which is about 11% ~ 13% of that for benzene. (Benzene, $\alpha = -1.55$ ⁽¹⁵⁾ or -1.92 e.v.⁽¹⁶⁾)

(13) E.J. Prosen, W.H. Johnson and F.D. Rossini, *J. Am. Chem. Soc.*, **69**, 2068 (1947).

(14) J. L. Cotrell and L. E. Sutton, *J. Chem. Phys.*, **15**, 685 (1947).

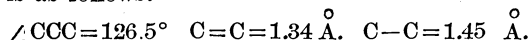
(15) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 365 (1933).

(16) G. B. Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 152 (1936).

* The results calculated by the G-M-S method also suggest us that $C_8H_8(D_{2d})$ is diamagnetic. This calculation will be published.

But it is necessary to examine critically the resonance energy of this experimental data. The structure of C_8H_8 is not plane, therefore, the steric hindrance demands considerations. Namely, the steric influences between CH and CH, and that of the bond energy of $C=C$ must be taken into considerations.

Next we shall calculate by the $2p\pi$ hydrogen-like functions. The structure of cyclooctatetraene proposed by Hedberg and Schomaker⁽¹²⁾ is as follows:



The eigenfunctions are:

$$\Psi_{\pi}(r, \theta, \varphi) = \sqrt{\frac{Z^6}{32\pi}} e^{-Zr/2} r \sin\theta \cos\varphi \dots (8)$$

The effective nuclear charge Z was chosen to be $Z=3.18$, a value which was obtained by Zener.⁽¹⁷⁾

Although Griffing⁽¹⁸⁾ calculated the value of α for benzene, it was known that this approximate calculation would not give the correct absolute value. Then, the value of α' is calculated on the assumption that the exchange integral depends on the overlap of $2p\pi$ function, as this value depends on approximately the angle between $2p\pi$ functions at the neighboring carbon nuclei and $\alpha'=0.3\alpha$ is obtained. Then energy levels are calculated using various value of α' (0.20α , 0.25α , 0.30α , 0.35α). The resonance energy is calculated by use of $\alpha=1.5$ e.v. This value of α is obtained with regard to the exchange integral of benzene and the effect of geometrical form of cyclooctatetraene upon the strength of binding in comparison with that of benzene. But the exact value of α must be obtained in future from the detailed experimental data.

Table 6

	$\alpha'=0.2\alpha$	$\alpha'=0.25\alpha$	$\alpha'=0.30\alpha$	$\alpha'=0.35\alpha$
Ground state	3.63 α	3.55 α	3.47 α	3.40 α
Kekule I	3.60 α	3.50 α	3.40 α	3.30 α
Resonance energy	$\begin{cases} 0.03\alpha \\ 1.04 \text{ kcal.} \end{cases}$	$\begin{cases} 0.05\alpha \\ 1.73 \text{ kcal.} \end{cases}$	$\begin{cases} 0.07\alpha \\ 2.42 \text{ kcal.} \end{cases}$	$\begin{cases} 0.10\alpha \\ 3.46 \text{ kcal.} \end{cases}$

The larger the exchange integral α' , the larger the resonance energy grows, as mentioned above.

6. Absorption Spectrum

The absorption spectrum of cyclooctatetraene⁽¹⁹⁾ is shown in Fig. 5.

In our judgment about the value of ϵ , the shoulder of the absorption band 2800 Å. is the forbidden transition. Hence this absorption band may be the ${}^1A_1 \rightarrow {}^1A_1$ transition calcu-

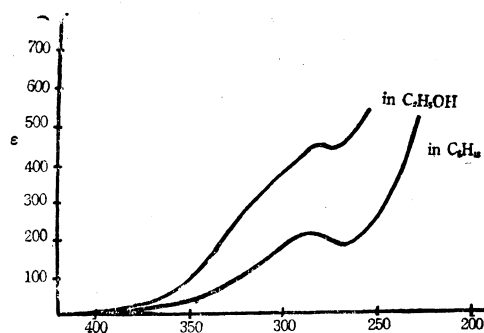


Fig. 5.

lated by the H-L-S-P method.* The absorption band below 2000 Å. which is now investigated, is supposed to be the allowed transition ${}^1A_1 \rightarrow {}^1E$. The wave lengths of each transition calculated by the H-L-S-P method is shown in Table 7.

Table 7

	$\alpha'=0.2\alpha$	$\alpha'=0.25\alpha$	$\alpha'=0.30\alpha$	$\alpha'=0.35\alpha$
${}^1A_1 \rightarrow {}^1A_1$	3.53 α	3.35 α	3.17 α	3.00 α
Wave length	2330 Å.	2460 Å.	2600 Å.	2740 Å.
${}^1A_1 \rightarrow {}^1E$	3.81 α	3.77 α	3.73 α	3.69 α
Wave length	2160 Å.	2180 Å.	2210 Å.	2230 Å.

7. In the Case of D_{4d}

The experimental results that the structure of cyclooctatetraene may be "Crown Form" (D_{4d}) are reported by O. Bastiaisen, O. Hassel and A. Langseth⁽⁷⁾ (electron diffraction), and so the energy levels of C_8H_8 is calculated to have the symmetry of D_{4d} by the H-L-S-P method. The procedure of calculation is similar to that in the case of D_{2d} .

In the symmetry D_{2d} there are two different exchange integrals α and α' , but in D_{4d} $\alpha=\alpha'$, so the energies of two Kekule structures are identical. Then the determinant of C_8H_8 (D_{4d}) is obtained by putting $\alpha=\alpha'$ in the determinant of D_{2d} . The energy levels of singlet states of C_8H_8 (D_{4d}) are obtained after calculating the above determinant, and the symmetry of the levels is decided from the group theory, and the transition only from ${}^1A_1$ to the symmetry ${}^1E_1$ is allowed. The results are shown in Fig. 9.

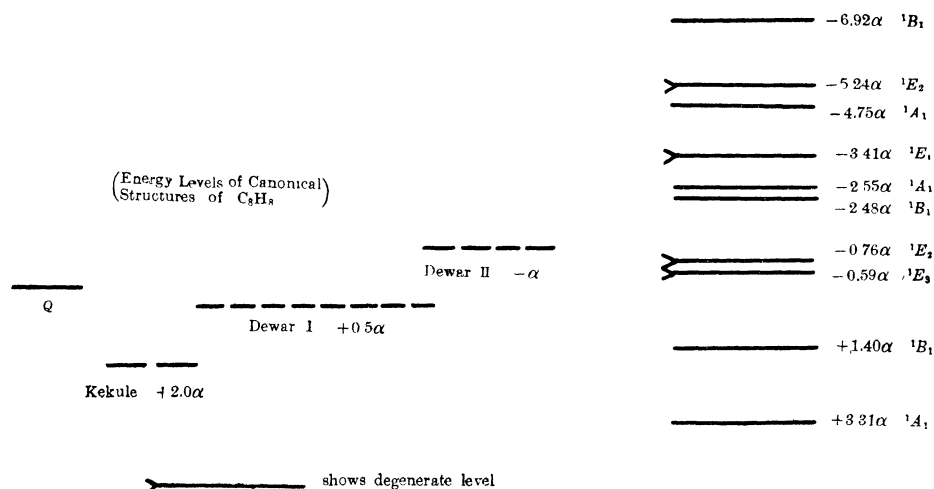
For the purpose of obtaining the energy of the triplet ground state the calculation is made using sixteen canonical structures, excepting

* We obtain that ${}^1A_2$ level is lower than ${}^1A_1$ level calculating by the G-M-S method, and the calculation by the H-L-S-P method including polar terms produces ${}^1A_2$ level, where the value of ${}^1A_2$ level cannot be calculated because the new Coulomb integral and exchange integral are not known exactly. So we cannot decide whether 2800 Å. band is the ${}^1A_1 \rightarrow {}^1A_1$ transition or the ${}^1A_1 \rightarrow {}^1A_2$ transition.

(17) C. Zener, *Phys. Rev.*, **36**, 51 (1930).

(18) V. Griffing, *J. Chem. Phys.*, **15**, 421 (1947).

(19) S. Miyakawa, unpublished.

Fig. 6.—Energy levels of singlet states in the case of D_{4d} .

the twelve structures which have higher energies in twenty eight structures, and get 2.24α as the energy of the triplet ground state. The energy of the singlet ground state (3.31α) is lower than that of the triplet ground state (2.24α). The singlet state $^1A_1$ is, therefore, the ground state of cyclooctatetraene, and it is expected to be diamagnetic from the standpoint of the H-L-S-P method.

The resonance energy for C_8H_8 (D_{4d}) is as following. The singlet ground state ($^1A_1$) has the energy 3.31α , (Fig. 6) whereas one Kekule structure which is the structure of the lowest energy, has an energy of 2.0α . The difference, 1.31α , between the energy of the ground state and that of the Kekule structure is resonance energy.⁽²⁰⁾ The resonance energy for C_8H_8 is experimentally 4.8 kcal. (§ 5), then $1.31\alpha=4.8$ kcal, and we obtain $\alpha=3.66$ kcal. And, theoretically, the values of α in each case of various angles between carbons are calculated, on the assumption that the Hamiltonian of C_8H_8 is approximately the same as that C_6H_6 and the exchange integral depends on the overlap of $2p\pi$ function as this value depends on approximately the angle between $2p\pi$ func-

tions at the neighboring carbon nuclei (Table 8). The value of α which is calculated from the absorption spectrum is different from that obtained from the thermochemical data and the numerical calculation. If the structure of cyclooctatetraene is D_{4d} , $\angle CCC$ angle may be greater than 120° ⁽⁸⁾, because in case of 120° the resonance energy is so small that cyclooctatetraene cannot exist stable. $\angle CCC$ of cyclooctatetraene forms the angle that is unstabilized by the steric hindrance and stabilized by the resonance energy balance.

So far the interaction only between neighboring atoms has been considered. But if cyclooctatetraene is D_{4d} and α is small, the interaction between the second neighboring atoms is not neglected. In respect to this point a further investigation is going on.

Summary

The energy levels of cyclooctatetraene as D_{2d} and D_{4d} were calculated by the H-L-S-P method. Then we showed that the ground state of C_8H_8 (D_{2d} and D_{4d}) may be diamagnetic. The resonance energy of C_8H_8 (D_{2d} and D_{4d}) is about several kilocalories (about ten per cent of that of benzene) from thermochemical data and numerical calculation. The wave length of absorption spectra calculated assuming D_{2d} is in better agreement with the experimental result than that calculated assuming D_{4d} .

The authors wish to express their appreciation to Professor Mikio Tamura at Kyoto University for some very helpful correspondence and discussion. The helpful suggestions of Kazuo Niira, Seikyo Mizushima and Saburo Nakamura are gratefully acknowledged.

(20) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934). Resonance Energy $=1.29\alpha$.

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Table 8

$\angle CCC$	$2p\pi \sim 2p\pi$ angle	α	
		e. V.	kcal.
120°	80°	-5.31×10^{-2}	- 1.22
121°	78°	-7.61×10^{-2}	- 1.75
122°	75.8°	-1.06×10^{-1}	- 2.44
123°	73.4°	-1.45×10^{-1}	- 3.34
124°	71.5°	-1.77×10^{-1}	- 4.08
125°	68°	-2.48×10^{-1}	- 5.72
126°	65°	-3.17×10^{-1}	- 7.31
127°	61.2°	-3.68×10^{-1}	- 8.48
128°	58.3°	-4.89×10^{-1}	-11.27

Viscosities of the Solutions of Polyvinyl Acetate in Acetone-Water Mixtures*

By Koshiro YOSHIOKA

(Received December 26, 1949)

The viscosities of the solutions of high molecular substances have been studied by many authors recently. It is generally said that the specific viscosity of the dilute solutions of flexible linear macromolecular substance is high in "good" solvents and low in "poor" solvents. Especially in the case of the solution in a mixture of "solvent" and "nonsolvent," the specific viscosity decreases gradually when the proportion of "nonsolvent" increases.⁽¹⁾ There appears a maximum in the specific viscosity of the solutions of polyvinyl acetate in methanol-water mixtures, which has been observed by Matsumoto.⁽²⁾ In the present report, the results of the viscosity measurements on the dilute solutions of polyvinyl acetate in acetone-water mixtures, will be described.

Experimental

Polyvinyl Acetate.—The sample of polyvinyl acetate made by Dai-Nippon Celluloid Company has been used in the experiments. Insoluble polymer was removed from the sample by dissolving it in acetone and filtering carefully. After filtration the polymer was precipitated from the acetone solution by pouring it slowly into water, and the precipitated polymer was dried in vacuum. The same stock sample was used throughout the experiment. The osmotic molecular weight of the present sample was determined to be 155,000 by Endo.⁽³⁾

Acetone.—Ordinary material was boiled with potassium permanganate for some hours and then distilled with the addition of potassium carbonate. The distillate was dehydrated over calcium chloride and fractionated.

Solutions.—Solutions were prepared by dissolving polyvinyl acetate in acetone-water mixtures of varying proportions. The composition of the solvent varied from pure acetone to 25 vol.-% of water. The concentration was determined by evaporating the solution to dryness and expressed in grams of polymer per 100 cc. of solution.

Viscosity Measurement.—Viscosities were measured at $20 \pm 0.02^\circ$ in the ordinary manner, by means of an Ostwald type capillary viscometer. The relative viscosities (η_r) were calculated ac-

cording to the following formula⁽⁴⁾

$$\eta_r = \frac{t}{t_0} \frac{d}{d_0} \left\{ 1 + \frac{V d_0}{8 \pi l \eta_0 t_0} \left(1 - \frac{t_0^2}{t^2} \right) \right\}, \quad (1)$$

where t_0 and t are the efflux times of solvent and solution respectively; d_0 and d are the corresponding densities; V is the volume of the "measuring bulb" in a viscometer; l is the length of the capillary; η_0 is the absolute viscosity of solvent. In equation (1), the term in brackets represents the kinetic energy correction, which amounted to about 1.3% in the worst case.

Results and Discussion

The resulting data are plotted in Fig. 1 as the specific viscosity ($\eta_{sp} = \eta_r - 1$)-concentration (c) ratio against the concentration, with vary-

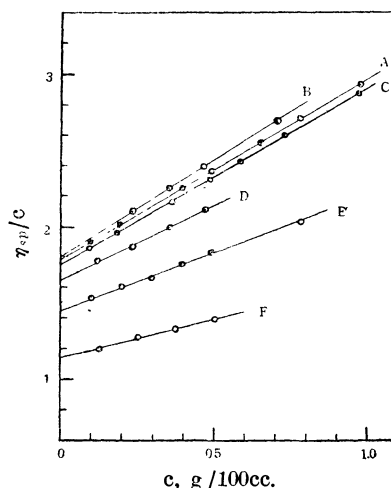


Fig. 1.—Specific viscosities of solutions of polyvinyl acetate in acetone-water mixtures at 20° . (A) Pure acetone; (B) Water 4.76%; (C) Water 10%; (D) Water 15.38%; (E) Water 20%; (F) Water 25%.

ing proportions of water. As is clear from Fig. 1, the concentration dependence of specific viscosity is well expressed by the following equation in low concentration range

$$\eta_{sp}/c = [\eta] + Kc, \quad (2)$$

where $[\eta]$ and K are constants. $[\eta]$ is the limiting value of η_{sp}/c at infinite dilution and usually called intrinsic viscosity. Equation (2) may also be expressed as follows

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c, \quad (3)$$

where $k = K/[\eta]^2$ and is a dimensionless number.

$[\eta]$ and K are calculated by the method of least squares and given as function of solvent composition in Table 1, Fig. 2 and Fig. 3. In Table 1 is also given the value of k .

(4) R.H. Wagner, *Anal. Chem.*, **20**, 155, (1948).

* Read before the annual meeting of the Society on April 1, 1949.

(1) T. Alfrey, A. Bartovics and H. Mark, *J. Am. Chem. Soc.*, **64**, 1557, (1942); T. Alfrey, *J. Colloid Sci.*, **2**, 99, (1947).

(2) S. Matsumoto, *The Chemistry of High Polymer (Kobunshi Kagaku)*, **6**, 179, (1949).

(3) K. Endo, *J. Chem. Soc., Japan*, **71**, 232, (1950).

Table 1
Viscosities of Solutions of Polyvinyl Acetate in
Acetone-Water Mixtures at 20°

Compn. of solvent (Vol. % of water)	$[\eta]$	K	k
0 (pure acetone)	1.785	1.184	0.37
4.76	1.800	1.273	0.39
10.00	1.746	1.171	0.38
15.38	1.654	0.967	0.35
20.00	1.454	0.746	0.35
25.00	1.140	0.505	0.39

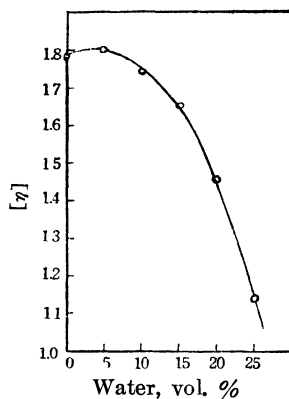


Fig. 2.—Effect of solvent composition on $[\eta]$.

For solvents containing up to about 10% water, the change of the intrinsic viscosity is small, and even a slight maximum is observed. From this experimental fact, it is supposed that the extension of polyvinyl acetate molecule in acetone is not appreciably changed by the addition of a small amount of water, in spite of its nature as typical nonsolvent. A similar result was obtained by Endo⁽³⁾ from his osmotic measurements on the same system.

With a larger content of water, the intrinsic

viscosity decreases as usual.

It is to be noted that k does not vary appreciably (i.e. 0.35~0.39) as the amount of water increases, in spite of the remarkable change of K . Recently, Saito⁽⁴⁾ and Ishihara⁽⁵⁾ calculated theoretically the concentration dependence of specific viscosity, and found that $k=0.4$ as first approximation for spherical particles. This value is close upon the experimental data obtained by the present author.

Summary

Viscosities of the dilute solutions of polyvinyl acetate have been measured in acetone-water mixtures of varying proportions. The experimental results are well expressed by the following equation

$$\eta_{sp}/c = [\eta] + k[\eta]^2c.$$

The intrinsic viscosity ($[\eta]$) shows a slight maximum at about 5% of water content, and decreases gradually for larger content of water. The value of k is close upon 0.4 and does not vary appreciably.

The author expresses his sincere thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The expense of this work has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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

(5) N. Saito, Lecture at the special meeting of the Physical Society of Japan, on May 1, 1949.

(6) A. Ishihara, Lecture at the special meeting of the Physical Society of Japan, on October 23, 1949.

Fluorometric Microdetermination of Uranium. I. Fluorescent Material for the Determination

By Masaki NAKANISHI

(Received December 27, 1949)

Introduction

Hexavalent compounds of uranium, the uranyl salts, have peculiar fluorescent property. Their fluorescence is observed by irradiating either the crystal or the solution with the ultraviolet light. This phenomenon is utilized to detect or determine a small amount of uranium in analytical chemistry, and has found its use in the microdetermination of the element.⁽¹⁾ On the other hand, however, another

type of fluorometric method is possible, in which uranium is brought into an activator of some solid solution (so-called fluorescent material), and this method will be treated in this paper.

The activating action of uranium on fluorescent materials in solid solution state was widely studied by E.L. Nichols and M.K. Slattery.⁽²⁾⁽³⁾⁽⁴⁾ They found that sodium fluoride

(2) E.L. Nichols and M.K. Slattery, *J. Opt. Soc. Am.*, **12**, 449 (1926).

(3) M.K. Slattery, *J. Opt. Soc. Am.*, **19**, 175 (1929).

(4) M.K. Slattery, *Proc. Nat. Acad. Sci.*, **14**, 777 (1928).

(1) C.W. Sill and H.E. Peterson, *Anal. Chem.*, **19**, 646 (1947).

and lithium fluoride, activated by the addition of a small amount of uranium, show bright luminescence of yellow and green hue respectively in the ultraviolet light, the brightness of which exceeds that of solid uranyl salts under the same excitation.

For the detection of a minute quantity of uranium, J. Papish and L.E. Hoag,⁽⁵⁾ and then F. Hernegger⁽⁶⁾ recommended the fluorescence method, in which the fluorescent material, formed with sodium fluoride as a ground material and uranium as an activator, is used.

Afterwards F. Hernegger and B. Karlik⁽⁷⁾ developed this method into the microdetermination of uranium.

In connection with the geochemical researches on radioactive elements, which have been pursued more than ten years in this laboratory, the writer examined the details of this fluorescence method and confirmed it to be available, especially for geochemical purposes, for which the determination of less than one millionth gram of uranium was required.

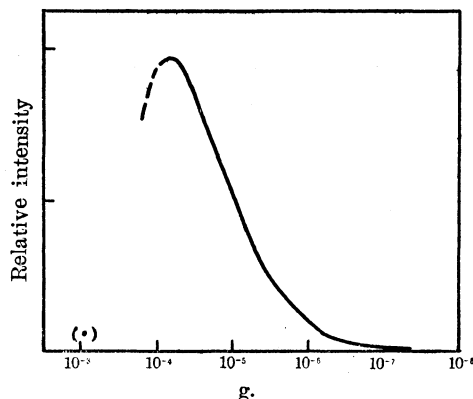
Even in comparison with the radioactivity measurement method,⁽⁸⁾ which has been hitherto most sensitive for radioactive elements, this fluorescence method is more delicate, so far as uranium is concerned, on account of the feeble radioactivity of uranium.

Fluorescent material of sodium fluoride activated by uranium shows a vivid yellow fluorescence, when irradiated with rays of the ultraviolet region. The intensity of the fluorescence varies remarkably according to the uranium content of the fluorescent material, and by the present treatment no more than 10^{-9} gram of uranium is necessary to produce the noticeable fluorescence.

Fluorescent Material of Sodium Fluoride Containing Uranium

Relation between Uranium Content and Fluorescence Intensity.—Some different quantities of uranium were mixed in aqueous solution with about 20 mg. of sodium fluoride. After drying, fluorescent beads were prepared by fusing the residue on a platinum loop, the procedure of which will be detailed in the following papers. Fluorescence of each bead caused by the excitation of ultraviolet rays was investigated regarding its luminescence intensity by the photographic spectrophotometry. Fig. 1 shows the results: the ordinate (intensity) is drawn to an arbitrary scale, the abscissa shows the amount of uranium con-

tained in about 20 mg. of sodium fluoride. As is seen in Fig. 1, the maximum intensity is reached at about 5×10^{-5} g. of uranium in a bead. In the photographic experiment concerned, the time of exposure was too short to catch an image corresponding to 10^{-8} g. of uranium. By visual observation, however,



Amount of uranium in 20 mg. NaF bead

Fig. 1.—Fluorescence intensity.

fluorescence due to 10^{-8} g. of uranium is still bright, and as uranium content decreases from 10^{-8} g., the fluorescence becomes rapidly fainter and finally almost vanishes at about 10^{-9} g. Pure sodium fluoride presents no fluorescent phenomenon.

In case a bead contains 10^{-4} g. of uranium or more, it is supersaturated with regard to uranium, and the excessive uranium compound interferes with the proper formation of fluorescent material, the intensity of which depends much upon the experimental conditions. Therefore the fluorescence intensity of 10^{-3} g. of uranium indicated in Fig. 1 is no more than an example.

If we consider the narrow region of uranium content, the fluorescence intensity is reasonably regarded to be linear to the uranium content between about 10^{-5} and 10^{-9} g. On this base lies the microdetermination method of uranium, and its favorable range of application extends from 10^{-5} to 10^{-8} g. of uranium.

Fluorescence Band Spectrum.—Like many other fluorescent and phosphorescent substances, this fluorescent material has some emission bands. To obtain the quantitative spectral energy distribution of the luminescence, the photographic spectrophotometry⁽⁹⁾ was applied here again.

As an intensity scale, the tungsten filament lamp was used. Its brightness was reduced to some different extents, and the corresponding spectra were photographed on a plate, together with the spectrum of the fluorescence in question. The time of exposure was the same for

(5) J. Papish and L.E. Hoag, *Proc. Nat. Acad. Sci.*, **13**, 726, (1927).

(6) F. Hernegger, *Anz. Akad. Wiss. Wien*, **70**, 15, (1933).

(7) F. Hernegger and B. Karlik, *Sitz. Akad. Wiss. Wien, Abt. IIa*, **144**, 217, (1935).

(8) Wm. D. Urry, *Am. J. Sci.*, **239**, 191, (1941).

(9) H.B. Dorgelo, *Phys. Z.*, **26**, 756, (1925).

each spectrum. The work was made at room temperature, and an ordinary panchromatic plate was employed. The bead of sodium fluoride contained 10^{-4} g. of uranium, nearly the optimum proportion to form the fluorescent material. A filtered mercury vapour lamp of high pressure was employed to excite the bead, where the effective ultraviolet light extended from 2480 to 3660 Å. Then followed the determination of blackness of the photographic image corresponding to these spectra with the microphotometer, and next the calculation of spectral energy distribution relative to the standard lamp, and at last correction for inequality of the standard lamp through the spectral region. Spectral energy distribution of the fluorescence thus obtained is graphically shown in Fig. 2. The fluorescence bands cover the region from 5300 to 6150 Å of wave length. It is obviously seen in Fig. 2 that the

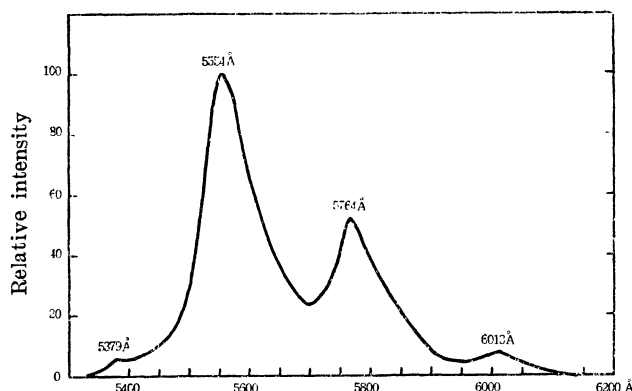


Fig. 2.—Fluorescence band spectrum

fluorescence includes four distinct partial bands, in which two are remarkably strong. Relative intensity of these four band maxima are tabulated.⁽¹⁰⁾

Wave length in Å	Relative intensity	Hygroscopic Ten- dency.—The prepared
5379	5.8	fluorescent material is
5554	100	slightly hygroscopic.
5764	51.8	The disc-like bead of
6013	7.6	this material on a pla-

tinum loop is often dewed with water from atmospheric moisture in wet weather. The fluorescence intensity of the bedewed bead becomes less intense especially for the smaller uranium content. Even after drying and re-fusion, it does not reveal its proper intensity. In most cases this treatment makes the fluorescence more intense, because it means prolonging the time of fusion, or in other words increased loss of ground material, sodium fluoride, by evaporation. Therefore the fluorescent

(10) As for the wave length of band maxima, Nicho's and Slattery (*ibid.*) reported at 534, 557, 577, 606, 634 $m\mu$, and HERNEGGER and KARLIK (*ibid.*) at 555, 577, 602, 626 $m\mu$. For the fine structure at the liquid air temperature, see (3).

beads of both sample and standard must be prepared immediately before the comparison in the same way. And if it is required to reserve the beads, they should be kept in a desiccator.

Interfering Substances.—We can enumerate many examples of the fluorescent material which is remarkably affected by a small amount of impurities; but the fluorescent material applied to the uranium determination is fortunately less affected by other impurities.

The interferences by other impurities will be generally examined on the analytical-chemical side.

Niobium and zinc are reckoned to be the only elements, except uranium, which act as activator for sodium fluoride. They produce luminescence of clearer green and orange hue respectively and less intense. But it is usually unnecessary to pay particular attention to

niobium, because it is only a very minor contamination of ordinary samples, but special mineralogical or metallurgical ones, and furthermore is easily separated from uranium by the chemical procedures. Almost the same applies to zinc. Although we can not neglect the influence of zinc, inasmuch as it is a relatively abundant element, it is eliminated by any proper chemical treatment.

Impurities which form luminescent substances with uranium are to be removed too. These impurities include fluorides of other alkali metals and calcium, strontium chloride, borax, microcosmic salt, sodium phosphate, etc.⁽³⁾ Generally their fluorescence is not so bright as that of sodium fluoride. It depends also upon the purification of sodium fluoride and careful manipulation to prevent this kind of interference.

Next in order is reference to the interferences of heavy metals. For example, iron is most likely to contaminate and severely reduces the intensity of fluorescence by the probable absorption of ultraviolet light. Manganese colors the bead green, but has almost no influence on the fluorescence. Thorium, if more than 10^{-5} g. of the element is mixed in the bead of about 20 mg. weight containing 10^{-8} g. of uranium, gives a somewhat orange color to the bead, but reduces only a little the fluorescence intensity. Generally speaking, heavy metals can hardly disturb the test, if they are removed by any means to an imponderable trace comparable with the present amount of uranium.

Some earths, e.g. silica, titania, form complex fluorides with sodium fluoride which do not take the place of sodium fluoride in the

luminescence test, but their influence can be prevented, too, by treating with more sodium fluoride.

Then insoluble matters, *e.g.* alumina, often cover the effective surface of the bead, if they remain much in the bead after fusion, which diminish or extinguish the luminescence to a greater extent. These difficulties are avoided in practical cases by ordinary chemical treatments, the details of which will be mentioned in the succeeding papers. After all, it is concluded that every kind of contamination is undesirable, but it interferes little if its quantity is as small as that of the uranium.

Summary

As the most sensitive method for the determination of uranium, the fluorescence method is recommended. Fluorescent material of so-

dium fluoride containing a small amount of uranium (10^{-4} to 10^{-9} g. per 20 mg. of sodium fluoride) was investigated in this paper from several sides.

Relation between fluorescence intensity and uranium content is described, and the fluorescence band spectrum was studied by spectrophotometry, regarding its spectral energy distribution.

Various interfering factors to this method were examined too, especially as to its analytical application.

In conclusion, the writer wishes to express his hearty thanks to Prof. K. Kimura, to whom he is much indebted for the continual stimulation and the kind guidances.

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Selective Catalysis. The Catalytic Reaction between Acetylene and Hydrogen

By Kenzi TAMARU

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Many investigations have already been made on the hydrogenation of acetylene.⁽¹⁾⁻⁽¹²⁾ Most of them, however, deal with the products of hydrogenation by the flow method, no attention being paid on the kinetics of reaction. Generally speaking, when acetylene and hydrogen react on a hydrogenation catalyst, there occur three kinds of reactions simultaneously, that is

- 1) $C_2H_2 + H_2 = C_2H_4$
- 2) $C_2H_4 + H_2 = C_2H_6$
- 3) $nC_2H_2 + mH_2 = C_{2n}H_{2(n+m)}$

These reactions are considered as proceeding at

- (1) Paal and Hoenninger, *Ber.*, **48**, 275 (1915).
- (2) Ross, Culbertson and Parsons, *J. Ind. Eng. Chem.*, **13**, 775 (1921).
- (3) Morris and Reyerson, *J. Phys. Chem.*, **31**, 1332 (1927).
- (4) Johnson, *Brit. Pat.*, 294, 787 (1927).
- (5) Yoshikawa, *Bull. Chem. Soc., Japan*, **7**, 201 (1932).
- (6) Ackermann, *Brennstoff-Chem.*, **18**, 357 (1937).
- (7) Fischer and Knorr, *Z. Elektrochem.*, **43**, 608 (1937).
- (8) A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **61**, 3396 (1939).
- (9) Cremer, Knorr and Plieniger, *Z. Elektrochem.*, **47**, 737 (1941).
- (10) Sheridan, *J. Chem. Soc.*, **1944**, 378; *ibid.*, **1945**, 133, 301, 305, 470.
- (11) Kwan, *J. Phys. Chem. Res. Inst., Tokyo*, **23**, 205 (1944).
- (12) Yamanaka, *J. Phys. Chem. Res. Inst., Tokyo*, **25**, 329, 481 (1949).

various rates according to the reaction conditions and the state of the catalyst. The reason for the remarkable change of the reaction velocities is not well clarified yet. Some interesting results were obtained by Kwan⁽¹¹⁾ and Farkas⁽⁸⁾ on nickel and platinum catalysts respectively. The plausible explanations, however, on the selective action of the catalysts have not been obtained. In the present report some results of the experiments are described on the kinetics of the reactions between acetylene and hydrogen using palladium alumina as catalyst.

Experimental Procedure

The acetylene gas was generated from calcium carbide and water, and purified by the usual method.* Hydrogen was obtained by the electrolysis of water. Palladium alumina catalyst (1:100) was prepared by Sano's method⁽¹³⁾ from palladium chloride solution. The alumina used was the sample made for the purpose of chromatography by Nippon Aluminium Co.

The experiments were undertaken by the usual static method, the volume of the reaction vessel being about 120 cc. The reacting gas was taken out by a Toepler pump and analysed. The analysis of acetylene and ethylene was carried out according to the method of Treadwell⁽¹⁴⁾ modified by Fujio.⁽¹⁵⁾ Acetylene, ethylene and heavy

* Refer Vanino's "Präparativen Chemie"

(13) Sano, *J. Chem. Soc., Japan*, **58**, 393 (1937).

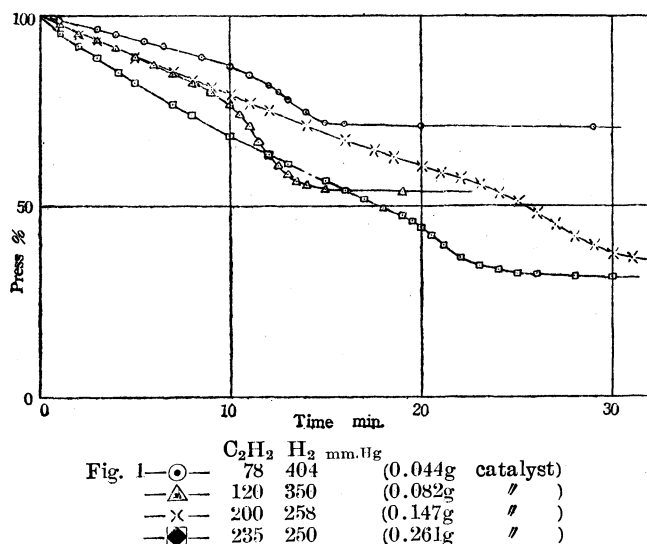
(14) Treadwell, *Helv. Chim. Acta*, **2**, 601 (1919).

(15) Fujio and Shirai, *Experimental Reports of Japanese Naval Institute of Fuel*, **4**, No. 4, 47.

hydrocarbons were determined by absorption with the solution of mercuric cyanide, mercuric nitrate and fuming sulfuric acid respectively. After the removal of the above gases, hydrogen and saturated hydrocarbons were estimated by the explosion method using oxygen gas.

Experimental Results

The results of experiments at 30° are shown in Fig. 1, the abscissa of which being pressure and the ordinate time. In the course of reaction it was observed that the rate of hydrogenation increased rapidly at a certain stage. An example of the change of composition with time is shown in Fig. 2. In this figure the



solid line shows the total gas pressure, and the dotted lines show the partial pressures of the component gases. It can be seen, from Fig. 2, that the hydrogenation of acetylene proceeds in two distinct stages. At first all acetylene is hydrogenated or polymerized, and after that ethylene is hydrogenated to ethane. The start of the second stage is indicated by a sudden increase in the rate of hydrogenation.

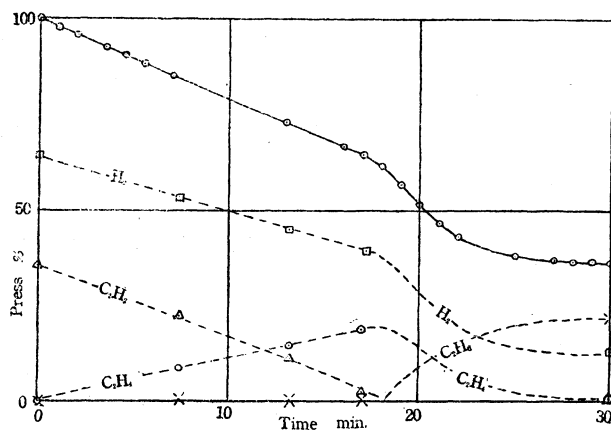


Fig. 2.— C_2H_2 182 mm.Hg + H_2 332 mm.Hg, Pd-Alumina catalyst 0.105 g. at 30°.

The sudden drop of the gas pressure corresponds to the moment when all acetylene has been used up.

The initial velocity of hydrogenation is proportional to the amount of the catalyst used. The dependence of the reaction products on the initial composition is shown in Fig. 3, the ordinate of which shows the final pressure relative to the initial one, and the abscissa the initial content of acetylene. The initial pressures of gas range from 450 to 500 mm. Hg. The solid line shows the dependence of the total gas pressure of the reaction product on the initial composition, and the dotted lines

the final content of hydrogen, ethylene, ethane or acetylene. The broken line indicates the ratio of final non-polymerized acetylene to the initial one, taking in the ordinate the ratio in percentage of acetylene. The chain line expresses the values of the velocity constant calculated from each experiment. The way of calculation of the velocity constant will be given later. Fig. 3 shows that if the initial content of acetylene is approximately 41% or 51%, the reaction products are wholly ethane or ethylene respectively, and that the polymerized portion of, acetylene increases with the initial content of acetylene.

The hydrogenation of ethylene which occurred in the last half of the reaction, is faster than the formation of ethylene at 30°, but as the reaction temperature is raised, the difference in the rates of the two reactions grows smaller till the former in turn becomes slower than the latter. An example of the experiment at 74° is shown in Fig. 4. It is to be noticed that at higher temperature the formation of ethane proceeds appreciably while acetylene is being hydrogenated.

From these results the energy of activation for the hydrogenation of acetylene is calculated to be 12 kilocalories. This figure is somewhat higher than the energy of activation for the hydrogenation of ethylene, which has been determined to be 9 kilocalories in the same catalyst and at the same temperature range.

Discussion

The feature of the hydrogenation of acetylene on palladium alumina catalyst at room temperature is that the hydrogenation takes place in two distinct steps. At the first step the acetylene is converted into the ethylene and the

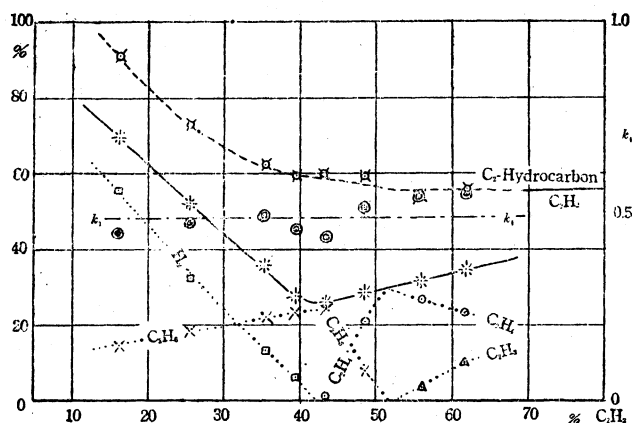
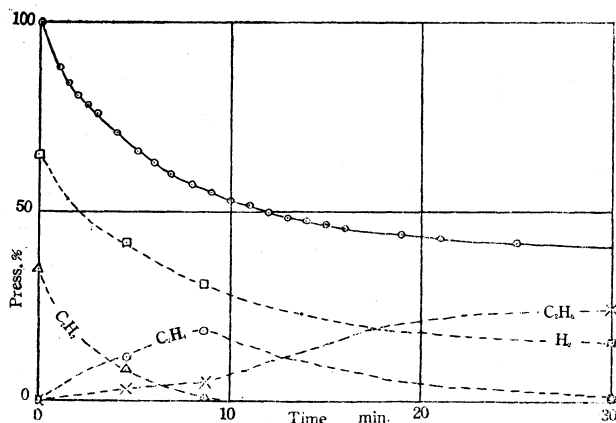


Fig. 3.

Fig. 4.— C_2H_2 182 mm. Hg + H_2 331 mm. Hg Pd-Alumina 0.025 g.

polymers, and at the second step the ethylene is hydrogenated to ethane. The second reaction proceeds after all acetylene has been used up.

The author considers that the selective hydrogenation may be due to the difference of the adsorbability of acetylene and ethylene on the catalyst, and not to the difference of the velocity of the hydrogenation reaction. The dependence of the rate of hydrogenation on the pressure of acetylene and hydrogen can readily be explained by the strong adsorption of acetylene on the catalyst. The velocity of the first stage of hydrogenation of acetylene may be expressed by the following equation, which is analogous to the one given by Cremer,⁽⁹⁾

$$-\frac{dP}{dt} = \frac{k_1 P_{\text{H}_2}}{1 + b P_{\text{C}_2\text{H}_2}},$$

where P denotes the pressure of gas, t the time and, b and k_1 the constants. The velocity constant k_1 calculated from the initial velocities by using the value $b = 0.0031$ is given in Fig. 3, the pressure being expressed in mm. Hg and the time in minutes. However, as the polymers produced in the first stage cover the surface of the catalyst, some corrections must

be applied for the retarding action in the calculation. The second stage of the reaction, the hydrogenation of ethylene, can be treated approximately as a first-order reaction.

At high reaction temperature, the first stage becomes faster than the second one, the activation energy of the former being greater than that of the latter. In this case the ethane formation is observed during the first stage. This suggests the fact that the adsorption of acetylene decreases at the raised temperature and the ethane formation can, consequently, proceed on the uncovered surface of the catalyst.

Considered from the results of the present experiments, it will be expected that the yield of ethylene by the flow method can be increased with the decrease of acetylene content in the initial reactant, by controlling the various reaction conditions, and that the reaction product can be wholly ethylene or ethane by making properly the initial composition.

Summary

1) The catalytic hydrogenation of acetylene was investigated by Pd-Alumina under various conditions.

2) The hydrogenation of acetylene proceeds in two distinct steps. The first step consists of the reduction and polymerization of acetylene, and the second step the reduction of ethylene to ethane. The second reaction starts after all of the acetylene is reduced to ethylene, and is indicated by a sudden increase in the rate of hydrogenation.

3) The results indicate that acetylene is strongly adsorbed on the surface of the catalyst and the inhibition of the hydrogenation by acetylene is pronounced.

4) It was found that the final products of the hydrogenation can be made wholly into ethylene or ethane and that the highest yield of ethylene is obtained possibly, when acetylene content is small, by avoiding the polymerization of acetylene.

The author expresses his sincere thanks to Prof. J. Sameshima and Dr. H. Akamatsu for their kind guidance and encouragement throughout this work.

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On the Viscosity of the Uranium Hexafluoride

By Kunihiro KIGOSHI

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The viscosity and Sutherland's constant of the uranium hexafluoride were measured with the Maxwell type viscosimeter. The sample of the uranium hexafluoride was obtained by the reaction of fluorine gas on the uranium carbide, and the fluoride obtained was purified by the sublimations under the room temperature repeated several times. The first two sublimation processes were carried out through the dehydration tube which was charged with resublimed phosphorus pentoxide. The purified sample became colorless and clear crystals having a vapor pressure expressed by the following formula,

$$\log P_{\text{UF}_6}(\text{mm.Hg}) = 10.023 - 2486/T + 0.0012 T, \quad (1)$$

where T is absolute temperature. The measurements of vapor pressure were performed by a static method at the temperature interval between 0° and 34.6° .

Apparatus

An oscillating-disk viscosimeter⁽¹⁾ with gold plated copper disks was used. An oscillating disk having a diameter of 30 mm. and thickness of 2 mm. was placed between two fixed disks. The distance between inner surfaces of the two fixed disks was 3 mm. The oscillating disk was adjusted to a place at the middle of these disks, and the distances which separate the oscillating disk and upper and lower fixed disks were kept equal 1.0 mm. The oscillating disk was suspended by platinum wire, of which the length about 20 cm. and diameter 0.05 mm. A thick copper wire of about 5 cm. length was used for the connection of the platinum wire and the oscillating disk. At the top of this copper wire a small mirror was cemented. These metal works were contained in the quartz glass tube with a quartz glass window. All these apparatus were immersed in a thermostat. Amplitudes of successive oscillations were observed by means of a telescope with cross hair, with the aid of an illuminated scale.

Method of the Determination of Viscosity

The fundamental equation for the oscillating-disk viscosity apparatus is

$$\eta = (\lambda - \kappa) / Kt, \quad (2)$$

where η =viscosity, λ =logarithmic decrement, κ =logarithmic decrement caused by wire and mirror, t =period of one oscillation, in seconds, and K =the apparatus constant. The correction

for end effect and slipping coefficient at the metal surfaces can be neglected in this case.⁽²⁾ We can obtain the logarithmic decrement λ with the following formula,

$$\ln(a_\nu - b_\nu) - \ln(a_{\nu+n} - b_{\nu+n}) = n\lambda\phi \quad (3),$$

where a_ν and b_ν are the successive observations of the amplitudes of left and right sides of an oscillation. Suffixes of ν and $\nu+n$ mean the observations about the ν - and $\nu+n$ -th oscillations respectively. The period of one oscillation t ($=16.03$ sec. in this apparatus) was constant throughout the observations, then the equation (2) may be written as follows,

$$\eta = H(\lambda - \kappa), \quad (3')$$

where H is an apparatus constant. The constant κ and H were obtained from the following observations.

A main part of the logarithmic decrement κ is derived from the energy losses in platinum wire. The friction of mirror has a small contribution on κ ⁽²⁾ therefore we may neglect it and take κ as a wire constant. To obtain the wire constant the logarithmic decrement was measured under the high vacuum. A series of six observations of a_ν and b_ν with $n=30$ were performed in each determination. The average of κ was 0.000728 and each value agreed to within 1 per cent. The apparatus constant H was determined by logarithmic decrement with air at temperature 15.2° . The averaged value was $\lambda=0.010667$. When we take the viscosity of air as $\eta=179.62 \mu$ poises,⁽³⁾ the constant H may be derived as $H=\eta/(\lambda-\kappa)=18073 \times 10^{-6}$.

To check the apparatus, the viscosity of hydrogen was measured at temperature 12.9° . The observed value was $\eta=86.7 \mu$ poises, which agreed well with published values.⁽³⁾ There was no great change in apparatus constant with temperature variation, since the measurements with air at temperature 40.5° and 15.2° gave probable value of Sutherland's constants for air. The observed values of λ was 0.011321 at temperature 40.5° , and Sutherland's constant $S=104$ was obtained from these values. Hydrogen used in this experiment was obtained by electrolysis and purified through heated tube filled with platinized asbestos and a trap cooled with liquid oxygen. Dry air was purified through concentrated sodium hydroxide solution and a trap cooled with liquid oxygen.

(2) G. E. MacWood, *Physica*, **V**, No. 5, 374, 763 (1938).

(1) B. P. Sutherland and O. Maass, *Can. J. Research*, **6**, 428 (1932); E. Kanda, *J. Chem. Soc. Japan*, **58**, 804 (1937).

(3) H. L. Lohnston and K. E. McCloskey, *J. Phys. Chem.*, **44**, 1053 (1940).

The observations using these gases were performed under an atmospheric pressure.

Viscosity of the Uranium Hexafluoride

Preliminarily, highly evacuated apparatus was filled with uranium hexafluoride by sublimation from the container of UF_6 crystals. The viscosities were measured at approximate 10° intervals from 14.5° to 44.7° . The observed values of λ and η are shown in Table 1. The sample for the observations at the temperature 14.5° was filled by the sublimation under 8° . For the observations at the temperature higher than 20° , the sample was sublimed at 18° . Therefore in each case the pressure of uranium hexafluoride in apparatus was 33 mm.Hg and 68 mm.Hg respectively. The measurements of logarithmic decrements taking the series of

Table 1

$t^\circ\text{C.}$	λ	μ poises (obs.)	μ poises (calc.)
14.5	0.00973	162.7×10^{-6}	162.4×10^{-6}
26.3	0.01013	169.9 "	170.1 "
35.2	0.01045	175.7 "	176.0 "
44.7	0.01083	182.5 "	182.2 "

eleven observations of a_ν and b_ν with $n=5$ (e. g. $\nu=10, 15, 20 \dots 70$) agreed to within 0.2 per cent.

The Sutherland's formula,

$$\eta = CT^{3/2}/(T+S) \quad (4)$$

can be fitted to the observed values using the following numerical constants:

$$C = 28.44 \times 10^{-6}, \quad S = 566.8$$

The calculated values from these expression are shown in Table 1.

By the use of the following formula,

$$C = \frac{5}{16 \sigma^2} \left(\frac{km}{\pi} \right)^{1/2}, \quad (5)$$

where k = Boltzmann constant, σ = molecular diameter, m = mass of the molecule, we can obtain the molecular diameter of uranium hexafluoride.

$$\sigma = 4.20 \text{ \AA.}$$

When we assume that the observed viscosities are proportional to T^s , then $s=1.16$ in this case. The rigidity ν of the molecule given by $s=1/2+2/(\nu-1)$ is obtained for uranium hexafluoride as $\nu=4.03$.

Summary

On the uranium hexafluoride obtained by the reaction between fluorine and uranium carbide, the viscosity was measured between 14.5° and 44.7° . The purification of uranium hexafluoride was performed by several repeated sublimation. The oscillating-disk viscosimeter was used in this experiments and its apparatus constant was obtained by the observation of the apparatus filled with air. The molecular diameter of uranium hexafluoride was determined from the Sutherland's constant, and the rigidity of the molecule was also obtained from the observed values.

The studies on uranium hexafluoride have been performed during February, 1945 at Dr. Nishina's Laboratory of the Institute of Physical and Chemical Research in Tokyo. The author wishes to express his hearty thanks to Dr. Nishina for his valuable advice.

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J. Sameshima.

Professor Jitsusaburo Sameshima

Professor Jitsusaburo Sameshima, who celebrates his sixtieth birthday this year, on July 3rd, was born in 1890 in the city of Osaka. He graduated from the Chemistry Department of Tokyo Imperial University in 1914. In this university he devoted himself to the research work on physical chemistry under the guidance of Professor Kikunae Ikeda. In the spring of 1918, during the 1st World War, he was sent abroad as a research scholar of the government. He worked in the laboratory of Professor T. W. Richards at Harvard University, U. S. A., where he was influenced by the great master of exact chemical experiments. While he was in Europe he studied under Professor F. G. Donnan in London, Professor J. Perrin in Paris and Professor H. K. Onnes in Leiden.

On his return home in 1921, he was appointed to an assistant professor and in the following year to a professor of Tohoku Imperial University in Sendai. In March 1923, he became Professor of Physical Chemistry in Tokyo Imperial University. Since then he has held this position continuously for twenty seven years. From 1939 to March 1950 he was Director of the Chemical Institute of Faculty of Science, the University of Tokyo.

Professor Sameshima's work on physical chemistry is chiefly connected with the theory of solution, properties of gas, sorption of gas by solid, and surface and colloid chemistry. The papers on the vapor pressure of binary solutions were published in 1918 in the Journal of American Chemical Society. These papers are often referred in the college text-books of physical chemistry. The separation of gas mixtures by atmolysis, i. e., the diffusion through porous plate, drew his attention and an equation was derived on the efficiency of separation in 1923. Needless to say that this phenomenon has an important meaning in the isotopic separation. He, then, carried out a series of measurements on the sorption of gases

on solid matters. He proposed the opinion that the taking of gases by charcoal is the phenomenon of sorption in the interstices of carbon atoms and he obtained the equations of the velocity of sorption. He studied the sorption of gases by zeolite and other minerals. His work on surface and colloid chemistry includes the problems on viscosity, protecting colloid, surface pressure, foam etc. He devised a simple method of measuring the friction coefficient and obtained some interesting results on the surface chemistry. He published several books on chemistry, among which the "Experimental Method of Physical Chemistry" is most widely known in Japan.

His connection with the Chemical Society of Japan is worth mentioning. He is the actual founder of this "Bulletin." The Chemical Society of Japan had only one publication printed in the Japanese language when he became the professor of Tokyo Imperial University. In Japan there was no regularly issued publication on chemistry printed in any European languages. Professor Sameshima eagerly insisted on the utmost necessity of internationalizing Japanese chemical publication. Thus, by his effort, the "Bulletin of the Chemical Society of Japan" started as a monthly journal in January 1926. All the editorial and distribution business were done almost by himself alone. More than four hundred copies were distributed throughout the world mostly without charge. This was certainly a big service and contribution of the Chemical Society of Japan to the learning circles of the world. His editorship continued from 1926 to 1930. In 1935 he was elected President of the Society.

Professor Sameshima, enjoying his excellent health, is devoting his full time to the advancement of chemistry in Japan.

July 1950

The Editor

On the Adsorption of Carbon Monoxide on Platinum Catalyst

By Takao KWAN

(Received November 11, 1949)

For elucidating the mechanism of contact catalysis it is necessary to have the information on the adsorbed state of the reactant. As regard to that of hydrogen on the metallic catalysts the conclusive evidence has been obtained by many workers for the existence of hydrogen atoms on the surface of catalyst. As to the adsorbed state of the other reactants, only a few data are available even with such simple molecule as carbon monoxide or carbon dioxide.

Among these, carbon monoxide might be one of the most interesting reactant both from the fundamental and industrial points of view, because it yields by hydrogenation, and, notwithstanding the simple structure, it has such a variety of product at various conditions of the reaction as those of Fischer-Tropsch synthesis for hydrogenation, methanol synthesis etc.

With regard to the former reaction Kodama and co-workers⁽¹⁾ proposed from the kinetic investigation that carbide was formed by the dissociation of carbon monoxide into carbon and oxygen atom in contradiction to Craxford.⁽²⁾

According to Beeck and co-workers⁽³⁾ who observed the relative amount of adsorption of various gases to that of carbon monoxide on nickel film found that the latter is twice as large as that of hydrogen, suggesting that carbon monoxide molecule as well as the dissociated hydrogen atom occupies one adsorption site on the surface or that carbon monoxide is adsorbed without dissociation.

The present author has previously investigated the adsorption of hydrogen on reduced nickel, cobalt and platinum and concluded, having recourse to the statistical mechanical method, that each of metal atoms on the surface of catalyst is equally capable of adsorbing a dissociated hydrogen atom.⁽⁴⁾ Extending the latter conclusion it may be assumed that every metal atom at the catalyst surface behaves physically identical even in the case of carbon monoxide adsorption.

On the basis of the assumption the adsorbed state of carbon monoxide on platinum catalyst is investigated in the present work by the similar method by determining the adsorption isotherm with special precaution for the thermodynamical equilibrium.

Materials and Experimental Procedure

Carbon monoxide.—Carbon monoxide was prepared by dropping formic acid from a dropping funnel into an evacuated flask containing concentrated sulfuric acid at 90°–100° and passed through a trap immersed in liquid air and then stored in a reservoir which was beforehand highly evacuated.

Platinum black.—0.93 gram of platinum black once used for the hydrogen adsorption was used here again.

The apparatus and the procedure for measurement of the adsorption was quite the same as those described in the foregoing paper.⁽⁴⁾

Experimental Result

Measured quantity of carbon monoxide was admitted into the reaction vessel containing the platinum catalyst and maintained at a desired temperature. Although the adsorption rate was fairly rapid as in the case of hydrogen, the equilibrium pressure was determined about 20 hours after admission by approaching both from desorption and adsorption sides similarly as in the previous case. Typical result is shown in Fig. 1 by the plots of the observed pressure against time elapsed along with occasionally varied temperature shown by annexed figures.

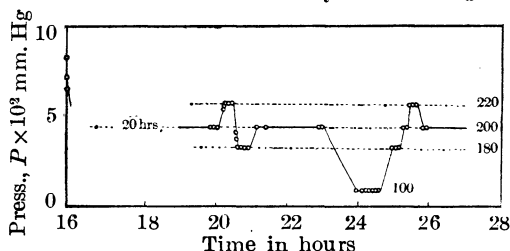


Fig. 1.—Reversibility of carbon monoxide adsorption on platinum catalyst.

After the equilibrium was thus attained and appropriate pressure read off additional portions of carbon monoxide were admitted successively into the reaction vessel and the corresponding equilibrium pressure were similarly determined in each case. The reversibility of the adsorption was assured over the whole range of adsorbed quantity although this was not the case with nickel or cobalt or iron at

(1) Matsumura, Kodama and Tarama, *J. Ind. Chem. Soc. Japan*, **42**, 42 (1940).

(2) Craxford, *Trans. Far. Soc.*, **35**, 946 (1939).

(3) Beeck, Smith and Wheeler, *Proc. Roy. Soc.*, **177**, 64 (1940).

(4) Kwan and Izu, "Catalyst", **4**, 22; 44 (1948).
Kwan, *Jour. Res. Inst. Catalysis, Hokkaido Univ.*, Vol. 1, No. 2, 81 (1949).

a lower adsorbed quantity.⁽⁵⁾

Calculating now the adsorbed quantity from the equilibrium pressure and the known quantity of admitted gas, adsorption isotherms were worked out at 180°, 200°, 220°, 280° and 300° and at pressures lower than 1 mm. Hg. The result is shown in Fig. 2.

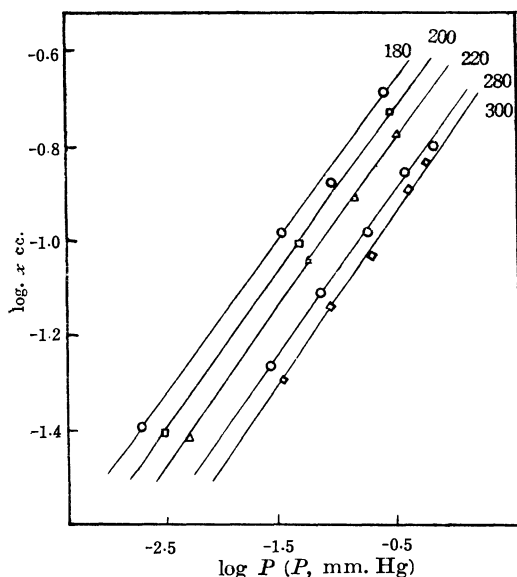


Fig. 2.—Adsorption isotherm of carbon monoxide on platinum black.

The observed isotherms were found to be expressed by the Freundlich's adsorption formulae as that,

$$x = CP^{1/n}, \quad n = 2.7$$

where x is the adsorbed quantity and P the equilibrium pressure.

It was already reported that carbon monoxide decomposed readily into carbon and carbon dioxide in the presence of metallic catalysts,⁽⁵⁾ but it has not taken place in the present case as shown by the following control experiment.

The U-tube connected directly to the reaction vessel and immersed into liquid air during the adsorption measurement was now dipped into an alcohol bath cooled at -80° . No pressure increase above that due to the relevant thermal expansion was observed, and it showed that the evolution of carbon dioxide and hence the appropriate decomposition may be practically ignored in the present case.

Differential heat of adsorption $\Delta\epsilon$ was derived from the usual expression,

$$\Delta\epsilon = RT^2 \left(\frac{\partial \log P}{\partial T} \right)_x$$

(5) Kwan and Izu, "Catalyst", 5, 43 (1949).

separately from the isotherms at 280° and 300° on one hand and from those at 180°, 200° and 220° on the other hand inasmuch as the catalyst was treated with hydrogen at 350° between the observation of the former group of isotherms and that of the latter one and such procedure is known liable by experience to disturb the reproducibility of the catalyst's activity. The results are shown in Table 1.

Table 1
Heat of Adsorption of Carbon Monoxide on Platinum Catalyst (kcal./mole)

From	x in cc.		
	0.039	0.063	0.100
isotherms at			
200° and 300°	11	11	10
180°, 200° and 220°	11	11	10

As shown in Table 1 $\Delta\epsilon$ is affected neither by the temperature range at which it is determined nor by x within the experimental error.

Statistical Mechanical Treatment

Adsorption isotherm of diatomic molecule δ formed by atoms δ_1 and δ_2 is statistical mechanically derived introducing a set of function p , q and θ due to Horiuti⁽⁶⁾ as follows:

$$\frac{\theta}{1-\theta} = \frac{q^{\delta(a)}}{p^{\delta(a)}} \quad (1.2)$$

$$\frac{\theta}{1-2\theta} = \frac{q^{\delta_1(a)}}{p^{\delta_1(a)}} = \frac{q^{\delta_2(a)}}{p^{\delta_2(a)}} \quad (1.2)$$

where $\delta(a)$ denotes the molecule δ , $\delta_1(a)$ and $\delta_2(a)$ dissociated atoms respectively at the adsorbed state.

At adsorption equilibrium we have that,

$$p^\delta = p^{\delta(a)} \quad (2.1)$$

$$\text{or } p^\delta = p^{\delta_1(a)} p^{\delta_2(a)} \quad (2.2)$$

respectively for the case when δ is undissociated at the adsorbed state. In the former case we have from Eqs. (1.1) and (2.1) as that,

$$\frac{\theta}{1-\theta} = \frac{q^{\delta(a)}}{p^\delta} \quad (3.1)$$

and in the latter as that,

$$\left(\frac{\theta}{1-2\theta} \right)^2 = \frac{q^{\delta_1(a)} q^{\delta_2(a)}}{p^\delta} \quad (3.2)$$

Since p^δ is however denoted from its definition as that,

$$p = \frac{Q^\delta}{N^\delta} = \frac{kTQ^\delta}{P} \quad (4)$$

where P is the pressure and Q the partition function, Eqs. (3.1) and (3.2) are now expressed respectively as that,

(6) Horiuti, *J. Res. Inst. Catalysis*, Vol 1, No. 1, 8 (1948).

(7) The θ must be equal because of the stoichiometrical relation for δ_1 and δ_2 .

$$\frac{\theta}{1-\theta} = \frac{q^{\delta(a)}P}{kTQ^\delta} \quad (5.1)$$

$$\left(\frac{\theta}{1-2\theta}\right)^2 = \frac{q^{\delta_1(a)}q^{\delta_2(a)}P}{kTQ^\delta} \quad (5.2)$$

Eqs. (5.1) and (5.2) are further transformed in a suitable form for calculation respectively as that,

$$\frac{\theta}{1-\theta} = q^{\delta(a)} e^{T \frac{\partial \log q^{\delta(a)}}{\partial T}} \frac{P}{Q_0^\delta} e^{\frac{\Delta E}{RT}} \quad (6.1)$$

$$\left(\frac{\theta}{1-2\theta}\right)^2 = q^{\delta_1(a)}q^{\delta_2(a)} e^{T \frac{\partial \log q^{\delta_1(a)}q^{\delta_2(a)}}{\partial T}} \times \frac{P}{Q_0^\delta} e^{\frac{\Delta E}{RT}} \quad (6.2)$$

where

$$Q_0^\delta = kT \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 I kT}{s h^2} \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} e^{\frac{7}{2}}$$

h ; Planck constant,

k ; Boltzman constant,

s ; symmetry number,

m , I and ν ; mass, moment of inertia and fundamental frequency of gaseous molecule δ .

$q^{\delta(a)}$, $q^{\delta_1(a)}$ and $q^{\delta_2(a)}$; function particular to the adsorbed state of $\delta(a)$, $\delta_1(a)$ and $\delta_2(a)$ denoted as $q^{\delta_1(a)} = \prod (I - e^{-\frac{h\nu_i}{kT}})^{-1}$

$$e^{-\frac{\epsilon_0 + \frac{1}{2}h\nu_i}{kT}}$$

etc. where ν_i 's are frequency of normal vibration at the adsorbed state.

Taking now $\delta \equiv \text{CO}$ and assuming $h\nu \gg kT$ in q 's and hence

$$q^{\delta(a)} e^{T \frac{\partial \log q^{\delta(a)}}{\partial T}} = 1, \quad q^{\delta_1(a)}q^{\delta_2(a)} e^{T \frac{\partial \log q^{\delta_1(a)}q^{\delta_2(a)}}{\partial T}} = 1$$

the calculation of the covered fraction of the surface $\theta_{\text{calc.}}$ was carried out at 300° and at pressures 0.01 and 0.1 mm. Hg using the observed heat of adsorption 11 kcal. mole and the following molecular constants of carbon monoxide molecule respectively for Eqs. (6.1) and (6.2).

$$I = 14.37 \times 10^{-40} \text{ g. cm.}^2 \text{ (8)}$$

$$\nu = 2168.89 \text{ cm.}^{-1} \text{ (8)}$$

On the other hand the covered fraction of the surface $\theta_{\text{obs.}}$ was determined from the adsorbed quantity and the surface area of the catalyst, assuming that every platinum atom on the surface was equally capable of adsorbing carbon or oxygen atom.

The particle size of platinum black estimated by the observation of the diffuseness of the Debye-Scherrer pattern of the electron diffraction was found, as mentioned in the previous paper⁽⁴⁾, appreciably smaller than that given by B.E.T. method, although, in the case of nickel, the particle size estimated by either of the methods was found satisfactorily coincident with each other. Without inquiring into the above discrepancy $\theta_{\text{obs.}}$ was calculated on the basis of $280 \times 10^4 \text{ cm.}^2/\text{g.}$ or the particle size 10 Å, due to the electron diffraction method as well as of $14 \times 10^4 \text{ cm.}^2/\text{g.}$ due to B.E.T. method assuming that 10^{15} Pt atoms per square centimeter are capable of adsorbing each one carbon or oxygen atom. The results are shown together with those given by statistical mechanical calculation in Table 2.

Table 2

The Relation between the Equilibrium Pressure P and the Covered Fraction $\theta_{\text{obs.}}$ or $\theta_{\text{calc.}}$
 $T = 300^\circ \text{ C.}$, $\Delta E = 11 \text{ kcal./mole.}$

θ	Remark	Equil. press. (mm.Hg)	
		0.01	0.1
$\theta_{\text{calc.}}$	$\text{CO} \rightleftharpoons \text{CO (a)}$	10^{-12}	10^{-11}
	$\text{CO} \rightleftharpoons \text{C (a)} + \text{O (a)}$	10^{-6}	3×10^{-6}
$\theta_{\text{obs.}}$	Electron diffraction	3×10^{-4}	7×10^{-4}
	B.E.T.	6×10^{-3}	10^{-2}

As seen from Table 2, the assumption of adsorbed state of CO(a) fails in accounting for the experimental result, whereas the assumption of the dissociated state into C(a) and O(a) gives the calculated values which are somewhat in accord with the observed values. In the case of undissociated adsorption, different values should be obtained for $\theta_{\text{obs.}}$, according as carbon monoxide occupies one or two Pt atoms, but the fact gives little modification to the above conclusion.

Conclusion is that carbon monoxide is adsorbed on platinum, being dissociated into carbon and oxygen atom.

The present author wishes to express his sincere thanks to the Director of the Institute, J. Horiuti, for his kind and valuable direction on this work. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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(8) Sponer, "Molekulspektren", Berlin 1936.

Rate of Hydrogen Adsorption on Reduced Copper

By Takao KWAN

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As reported hitherto the adsorption of gas on metallic catalysts at ordinary or higher temperature is in most cases very rapid initially but slows down at later stage as referred to "secondary adsorption".

This effect is frequently attributed to some physical process, such as the diffusion of gas along grain boundaries or solution into the lattice which governs observed rate⁽¹⁾ at the stage. But the rate may equally be reduced by some other causes, for instance, the repulsion between the adsorbed atoms or traces of impurities contaminating the surface, or the heterogeneity of the surface, i. e., some surface of lower rate of adsorption. The present author actually observed⁽²⁾ that in the case of reduced nickel the rate of adsorption was considerably influenced by traces of impurities such as the vapor of tap grease or of remaining oxide which could actually be removed by continuous reduction for a long period at relatively high temperature.

Copper powder, used for the adsorption of hydrogen revealing the above mentioned features of adsorption process, has usually been prepared by alternative oxydation and reduction⁽³⁾ at the temperature lower than 200°: it is hence doubtful if the reduction were complete or not.

The latter question is further amplified by the experimental results that the adsorbed quantity of hydrogen per unit weight of the catalyst is exceptionally small, compared with that of other metals, in spite of exceptionally large heat of adsorption even exceeding 30kcal./mole⁽⁴⁾ which would definitely favor the opposite effect as inferred from the consideration from the standpoint of statistical mechanics in the foregoing work.

In consequence the adsorption of hydrogen on copper is observed giving special stress on the complete reduction of the adsorbent; the result is that on the contrary to the existing data as described below an exceptionally large quantity of hydrogen is adsorbed with a rate

proportional to hydrogen pressure without any slow stage at the later part as mentioned above.

Experimental Procedure and Materials

The apparatus and the procedure for measurement of adsorption is quite the same as reported in the previous paper.⁽²⁾

Copper.—Copper carbonate of "Kojima Co." was heated at 450° for 65 hours and two grams of resulting oxide were reduced at 400° under several cm.Hg hydrogen pressure.

Hydrogen pressure decreased within first few hours but no more during the following one week. Throughout the latter period the catalyst was kept at the condition of reduction as described above but it was occasionally evacuated and supplied with fresh hydrogen several times.

Five grams of "Kahlbaum's reduced copper, extra fine" was similarly reduced as well as another sample for the adsorption measurement.

In any case, copper was kept from grease or mercury vapor by means of liquid air trap, directly attached to the reaction vessel. Copper thus prepared was evacuated at 400° for one hour before use.

Hydrogen.—Electrolytic hydrogen was passed over platinized asbestos at 300° and then through a liquid air trap to remove the water vapor.

Experimental Results

Measured quantity of hydrogen gas was admitted into the reaction vessel containing the copper catalyst, evacuated beforehand as described above and maintained at any desired temperature.

The rate of adsorption was found considerably small even at the initial stage; for the pressure decrease it took two or three days below 300° to become measurable by McLeod gauge. The rate of hydrogen adsorption on Kojima's copper as well as on Kahlbaums observed at 400°, 350° and 300° is shown in Table 1 and Figure.

Table 1
Rate of Hydrogen Adsorption on
Kojima's Copper

$T = 300^{\circ}\text{C.}$		$P_0 = 1.38 \times 10^{-1} \text{ mm.Hg}$
$t, \text{hr.}$	$P \times 10^{-1} \text{ mm.Hg}$	$k, \text{mm.Hg/hr.}$
4	1.34	0.0012
21	1.20	0.00126
43	1.03	0.00127
66	0.89	0.00125
	mean	0.00125

(1) Ward, *Proc. Roy. Soc.*, **133**, 506 (1931); Melville and Redéal, *Proc. Roy. Soc.*, **153**, 77 (1936); Iijima, *Sc. Pap. I. P. C. R. Tokyo*, **22**, 285 (1933); Morozov, *Trans. Far. Soc.*, **31**, 659 (1935).

(2) Kwan, *Journal of the Research Inst. for Catalysis*, Vol 1, No. 2, 81 (1949).

(3) Ward, *Proc. Roy. Soc.*, **113**, 506 (1931); Melville and Redéal, *ibid.*, **153**, 77 (1936); Beebe, Low, Wildner and Goldwasser, *J. Am. Chem. Soc.*, **57**, 2527 (1935).

(4) Ward, *Proc. Roy. Soc.*, **133**, 506 (1931).

$T=350^{\circ}\text{C.}$ $P_0=1.6 \times 10^{-1}$ mm.Hg		
t , hr.	$P \times 10^{-1}$ mm.Hg	k , mm.Hg/hr.
4	1.43	0.0053
18	0.91	0.0059
27	0.68	0.0059
40	0.50	0.0055
45	0.45	0.0053
60	0.22	0.0056
mean		0.0056

$T=400^{\circ}\text{C.}$ $P_0=1.46 \times 10^{-1}$ mm.Hg		
t , hr.	$P \times 10^{-1}$ mm.Hg	k , mm.Hg/hr.
4	0.97	0.0193
17	0.73	0.0185
23	0.29	0.022
28	0.11	0.022
66	0.07	0.021
mean		0.020

Table 2

Rate of Hydrogen Adsorption on Kahlbaum's Copper

$T=350^{\circ}\text{C.}$ $P_0=6.26 \times 10^{-1}$ mm.Hg		
t , hr.	$P \times 10^{-1}$ mm.Hg	k , mm.Hg/hr.
14	4.50	0.0044
30	3.06	0.0044
38	2.50	0.0045
66	1.24	0.0046
mean		0.00447

$T=400^{\circ}\text{C.}$ $P_0=5.90 \times 10^{-1}$ mm.Hg		
t , hr.	$P \times 10^{-1}$ mm.Hg	k , mm.Hg/hr.
18	1.4	0.015
24	1.0	0.014
41	0.19	0.016
45	0.12	0.016
51	0.058	0.016
mean		0.0155

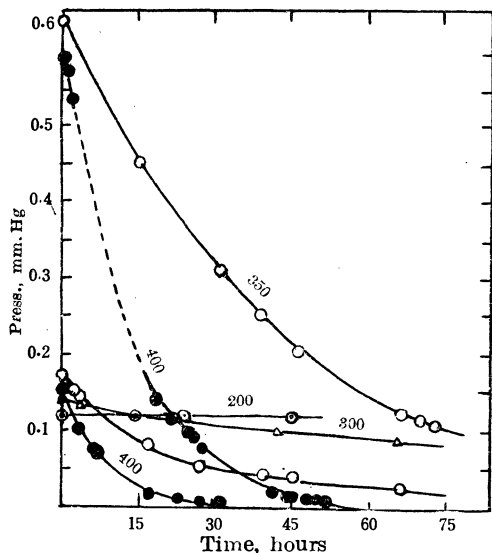


Fig.—Rate of hydrogen adsorption.

The first column of the table shows the time measured from the admission and the second one the pressure at the moment. P_0 is the initial pressure calculated from the knowledge of the admitted amount of gas and from that

of the whole space preliminarily determined without catalyst.

The third column shows constant k calculated from the observed data according to the expression,

$$k = \frac{1}{t} \log \frac{P_0}{P}$$

derived from the proportionality of the adsorption rate to the momentary pressure, ignoring the minute equilibrium pressure ($< 10^{-3}$ mm.Hg at 400°) finitely attained, compared with the working pressure $10^{-1} \sim 10^{-2}$ mm.Hg. The assumed proportionality is verified satisfactorily by the constancy of k .

It was shown that the measured pressure decrease was practically due to the adsorption and the solution of hydrogen into the bulk of the copper was negligible as calculated on the basis of the solubility data due to Sieverts⁽⁴⁾.

From the rate constant at the different temperatures the heat of activation E was calculated according to the usual expression that,

$$E = RT^2 \frac{d \log k}{d T} = 20 \text{ kcal./mole.}$$

As regards to the adsorption equilibrium the following may be inferred from the observation although the direct measurement has not been carried out.

Adsorbed quantity for unit weight of copper, which was calculated from the initial pressure and the lowest pressure attained at 400° shown in Table 2 and the volume of the apparatus, is about 0.1 cc. N.T.P. per gram which gives the lower limit of adsorbed quantity at the condition, whereas the lowest observed pressure gives the upper limit to the equilibrium pressure. This figure of adsorbed quantity is however exceedingly larger than any existing data,^{(1),(3)} regardless of the higher temperature and the lower pressure in the present measurement, which favors the lower degree of adsorption.

On the other hand the surface area of the copper powder employed was observed by B. E. T. method, being found to be so small as almost within experimental error. Estimating from the latter the upper limit of the surface area and assuming that each hydrogen molecule occupied two copper atoms the lower limit of the covered fraction θ of the surface was calculated from the above lower limit of adsorption at 0.2.

From the upper limit of equilibrium pressure and the lower limit of θ at 400° , the lower limit of the heat of adsorption may be calculated according to the statistical-mechanical expression Eq. (17) in the foregoing report that

(5) Sieverts, *Z. phys. Chem.*, **60**, 129 (1927). Pressure decrease as calculated by the data is only about 10^{-4} mm.Hg at the temperature 400° and at the pressure 10^{-1} mm.Hg.

$\Delta\epsilon > 35$ kcal./mole.

This figure is extremely larger than any data hitherto reported but it is in accord with that 47 kcal.⁶⁾ derived from spectroscopic data for dissociation energy of CuH.

In conclusion, the present author wishes to express his sincere thanks to the Director of the Institute, J. Horiuti, for his kind and

valuable direction given to this work. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

(6) Sponer, "Molekulspektren," Berlin (1935).

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Chromium Content of Volcanic Rocks

By Tomitaro ISHIMORI

(Received November 18, 1949)

The chromium contents of volcanic rocks of both Japan and Manchuria were determined, and it was clarified that many of the Japanese basalts contain considerably smaller amounts of chromium compared with those of the Manchurian basalts.

The chromium contents of several rock-forming minerals as well as the distribution of the element among them were also studied.

Method for the Determination of Chromium.—For the determination of chromium, Sandell's colorimetric method⁽¹⁾ was adopted. Preliminary experiments were carried out in detail to examine the accuracy of the method.

Results Obtained.—In order to study the geochemistry of chromium in Japanese volcanic rocks, the chromium contents of 27 basaltic rocks, 30 andesites, 13 dacites and 11 liparites (including 3 obsidians) were determined. Fourteen basalts from Manchuria, one specimen of German basalt occurred near Göttingen, 3 granites from Japan and 3 composite samples of shales²⁾ were also analyzed and the results were compared with those of Japanese volcanic rocks.

Number of specimens containing less than 0.0005, 0.0005 to 0.001, 0.001 to 0.005, 0.005 to 0.01 and more than 0.01 % Cr_2O_3 in each rock-types are shown in Table 1.

Eleven rock-forming minerals which were carefully separated from rocks were studied. The results are given in Table 2, together with the data obtained by E. Traeger.³⁾

Geochemical Discussions. A. The Relation between Chromium and Silica Contents of Rocks.—As indicated in Table 1, the

Group of samples	less than 0.0005%	0.0005~0.001 %	0.001~0.005%	0.005~0.01 %	more than 0.01%
Japanese basaltic rocks	2	2	4	11	8
Japanese andesites	7	3	13	5	2
Japanese dacites	3	3	7	0	0
Japanese liparites	11	0	0	0	0
Manchurian basalts	0	1	0	0	13
German basalts	0	0	0	0	1
Japanese granites	2	1	0	0	0
Composite sample of shales	0	0	0	1	2

chromium content in volcanic rocks varies in very wide range. The chromium contents for the series of plutonic rocks given by V. M. Goldschmidt⁽⁴⁾ are as follows:

Peridotite	0.50 % Cr_2O_3
Gabbro	0.05
Diorite	0.01
Granite	0.0003
Nepheline syenite	0.0001

In the present study the analogous relations are again recognized. Although it is recognizable that some basalts contain very little chromium, the element is generally concentrated in basic rocks, and we find the tendency that the chromium content decreases as the acidity of rocks increases, and in the group of liparites all specimens contain only traces of chromium.

In some basalts which showed higher chromium content, such as olivine basalt, Shodoshima, picotites and other proper minerals of

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

(2) These composite samples were prepared by Dr. Noll and Prof. E. Minami. cf. *Nachrichten von Gesellschaft wiss. Göttingen, math-phys. Klass. Fachgr. IV.* **14**, 155 (1935).

(3) E. Traeger, *Chemie der Erde*, **9**, 3286 (1935).

(4) V. M. Goldschmidt, *J. Chem. Soc.* **1937**, 662.

Table 2

Location	Sepd. form	Oliv.	Pyroxene				Hor.	Mag.	Plag.
			Au.	En.	Cr-dio.	pig.			
Nishigatake (Saga Pref.)	basalt	0.048	0.44						
Hitotumegata		0.008							
East Manch.	olivine nodules	0.019		0.41	0.81				
Hakone	hyperth. andesite								none
Haruna	andesite						0.0009		
Formosa	andesite						0.0027		
Hakone	allivalite	0.009							none
Oshima (Izu)	An-ei lava					0.005		0.017	
Asama			0.04						
Oshima (Izu)	dolerite							0.0027	
Aziro (Izu)	olivine-eucrite	0.001							
Values given by Traeger		0.02~ 0.2	0.02~ 0.2	1~3			0.02~ 0.2		

Figures are given in % Cr_2O_3 .

chromium were detected by petrographers. The wide variation in chromium content seems to be closely connected with both the formation and the separation of these proper minerals in the course of magmatic fractional crystallization.

B. Comparison of Japanese Basalts with those of Manchurian.—With one exception of leucocratic basalt (0.0005 % Cr_2O_3), all of the Manchurian basalts contain more than 0.01 % Cr_2O_3 . Therefore the mean value of them is about three times that of Japanese basalts.

German basalt that occurred near Göttingen shows nearly the same value as the mean value of Manchurian basalts.

G. v. Hevesy, A. Merkel and K. Wuerstlin⁽⁵⁾ gave 0.053 % Cr for the composite sample of igneous rocks, and their data are several times the mean value of Manchurian basalts.

C. Distribution of Chromium among Rock-forming Minerals.—As Table 2 shows,

(5) G. v. Hevesy, A. Merkel and K. Wuerstlin, *Z. anorg. allgem. Chem.* **219**, 192 (1934).

mafic minerals are much more enriched with chromium than plagioclases. Among the mafic minerals, it seems that the chromium is concentrated in the order of pyroxene, olivine and hornblende.

D. It is remarkable that the composite samples of shales contain 0.0095 to 0.013 % Cr_2O_3 . This value is almost the same as those of Japanese basaltic rocks.

The author wishes to express his hearty thanks to Prof. Iwaji Iwasaki for his kind guidance. He also expresses his appreciation to Prof. Eiichi Minami, Dr. Hisashi Kuno and Mr. Yohachiro Okamoto, who were kind enough to send him many samples.

The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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New Pterins (Xanthopterin-B, Leucopterin-B and a 6-Dehydroxy-leucopterin⁽¹⁾ Derivative) Obtained from *Bombyx mori* (Silk Worm)

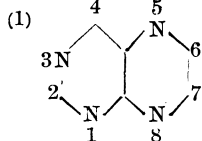
By Yoshimasa HIRATA*, Koji NAKANISHI* and Hideo KIKKAWA**

(Received December 10, 1949)

According to Kikkawa⁽²⁾ and others, the

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(According to
the Ring Index)

various pigments of *Bombyx mori* (riboflavin of the Malpighian tubes, urochrome, the eye-, epidermis-, egg- and red-excrement pigments) are derived from tryptophan through the common precursor, +chromogen. +Chromogen corresponds to the so-called cn^+ substance⁽³⁾⁽⁴⁾

(2) H. Kikkawa, *Kagaku*, **19**, 414 (1949).

(3) G. W. Beadle *Genetics*, **22**, 587 (1937).

(4) B. Ephrussi, *Am. Nat.*, **72**, 5 (1938).

suffix B coming from Bombyx. The extraction was carried out in the dark to avoid photolysis. The ether-treated and denatured tissues, after being extracted with 350 cc. of 2 *N* hydrochloric acid, were submitted to the

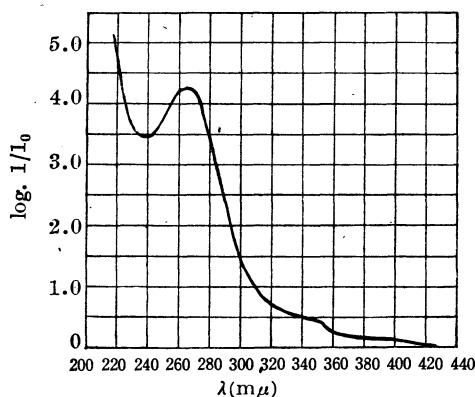


Fig. 2.—Ultraviolet absorption spectrum of xanthopterin-B (in 0.1 *N* NaOH). Since the substance was unobtainable in a crystalline state, the concentration of the solution was obscure and thus the extinction coefficient could not be calculated.

procedure previously stated when uric acid and leucopterin-B were obtained. The hydrochloric acid solution was extracted from the filtrate with 100 cc. phenol and re-extracted with 100 cc. water by means of the addition of ether. The aqueous solution was evaporated when a minute amount of yellow powder (xanthopterin-B) resulted. Xanthopterin-B was soluble in water, acid, alkali and phenol, and insoluble in ether. The ultraviolet absorption spectrum in 0.1 *N* sodium hydroxide (Fig. 2) has a band at 265 *mμ* and a shoulder at about 350 *mμ*, which is not identical with xanthopterin. Photolysis is described in the previous paper⁽¹¹⁾. The Folin-Denis' reaction was slightly positive. It is to be noted that both leucopterin-B and xanthopterin-B are reduced reversibly by sodium hydrosulfite into a non-fluorescent leuco-derivative, which suggested the possibilities of these pterins to play a vitamin B₁ and B₂-like role in the oxidation-reduction system of living cells, similar to those observed in the case of xanthopterin⁽¹²⁾ and fluoresceyanin⁽¹³⁾ (or ichtyopterin).

Paper Chromatography of the Pterins.—(Table 2). The method described by Good and

Table 2

One-dimensional Paper Chromatography of Various Extracts and Pterins

Name of substance	Leucopt.	Decompd. product of xantho. B	Decompd. product of xantho.	Leuco. B	Xantho.	Xantho. B
Color of fluorescence	pale-blue	bright-blue	blue	purple	sky-blue	yellowgreen
R _f value	0.12	0.26	0.30	0.33	0.41	0.50
Silk worm						
normal	+			+		
"lem"	+			+		+
"lem" (photolysis)	+	+		+		
"odd"	+			+		
Butterfly						
<i>Pieris rapae</i>	+			+		
<i>crucivora</i> B						
<i>Eurema laeta</i> B	+			+	+	+
<i>Eurema laeta</i> B (photolysis)	+	+		+	+	
Xanthopterin			+		+	
Ichtyopterin or fluoresceyanin (<i>Cyprinus carpio</i> L)				+		
Pyrrol-chrome (<i>Rana nigromaculata</i>)		0.24 (light blue)		+	0.40 (blue)	0.47 (blue)

* The R_f values merely coincided with leucopterin-B but the substances were not identical.

(12) W. Koschura and H. Haug, *Z. physiol. Chem.*, **259**, 97 (1939).

(13) R. G. Busnel, F. Chauchard, H. Mazone, M. Pesson and M. Polonovski, *Compt. rend. Soc. Biol.*, **137**, 594 (1943).

(14) P. M. Good and A. W. Johnson, *Nature*, **163**, 31 (1949).

(15) Partridge, *Biochem. J.*, **42**, 238 (1943).

Johnson⁽¹⁴⁾ was employed, using the butyl alcohol-acetic acid mixture of Partridge,⁽¹⁵⁾ and characteristic fluorescence for location of the individual pterins. The following general method was employed for preparing the samples: the denatured tissues were extracted with boiling water, ammonium sulfate added, the

precipitate discarded, pigment extracted into liquid phenol and returned to water by the addition of ether. In case of silk-worms, the separated pure pigments were employed as well. The scales of a carp (*Cyprinus carpio* L.) were used as an ichtyopterin⁽¹⁶⁾ (or fluoresceyanin⁽¹⁷⁾) source. Xanthopterin was received from Dr. E. L. Rickes, Merck and Co., Inc., and pyrrol-chrome⁽¹⁸⁾ from Dr. T. Goda, the University of Tokyo, to which we are greatly thankful.

Though ichtyopterin (fluoresceyanin) and leucopter-B possessed the same R_f values (0.33), the two differed with respect to ultraviolet absorption spectrum and the change of fluorescence accompanying the change in pH (mentioned below). The purple fluorescent pigment found in Pierids seemed to be identical with ichtyopterin (from R_f value and fluorescence behavior).

Pyrrol-chrome⁽¹⁸⁾, a fluorescent and reducing material obtained from the dorsal skin of the frog, *Rana nigromaculata*, gave a similar spot besides three other spots. The chemical nature of pyrrol-chrome is obscure, but this fact indicated the possibility of some relationship with the other pterins.

As stated by Becker and Schöpf⁽¹⁹⁾, and Good and Johnson,⁽¹⁴⁾ the nature of the blue spot at 0.30 is obscure. When a 0.1 N sodium hydroxide solution was dropped on this spot, the fluorescence changed into a greenish tone, whilst that of the spots at 0.26 and 0.33 faded out under similar treatments: this indicated in a simple manner, the unidentity of these spots.

Fluorescence. (a) **Leucopter-B.**—The fluorescence was the strongest at pH 4-8 (Table 3). mediums and in acetic acid.

Table 3

Fluorescence of Leucopter-B and Ichtyopterin				
	pH 1.6 (HCl)	pH 2.8 (AcOH)	pH 9.6 (NH ₄ OH)	pH 12.6 (NaOH)
Leucopter-B	feeble	purple	purple-blue	blue
Ichtyopterin*	feeble	purple	purple-blue	pale-blue

* The purple fluorescent substance in the extracts of *Pierids* also behaved similar to ichtyopterin.

The change of fluorescence observed for the purple fluorescent material in pyrrol-chrome was rather akin to ichtyopterin than to leucopter-B.

(b) **Xanthopterin-B.**—It behaved similar to xanthopterin, in acidic, alkaline and neutral

With the mutant "od", the fluorescence of the extracts as well as the spot on the paper chromatogram were feeble, and the amount of uric acid also very small. These explain the transparency of the skin of this mutant.

A Crystalline 6-Dehydroxy-leucopter-B⁽¹⁾ Derivative.—We had unfortunately missed to record the exact species of this characteristic silk-worm, which at first seemed to belong to the normal white types, and were thus unable to obtain this material for the second time, in spite of many repeated extraction procedures. Thus its presence suggested the possible existence of white mutants which are passed over due to their similar external aspects.

The boiling water extract of 50 larvae was acidified and cooled when crystals (uric acid) and white powder were obtained. The white powder was boiled with 2N hydrochloric acid, dissolved and the solution cooled, upon which a considerable amount of colorless plates precipitated. This was recrystallized from the same solvent and the following natures were observed. The solid crystal (decomposition point: over 270°) had a purple fluorescence, and formed yellow sodium and ammonium salts, the solution possessing a green or light bluish fluorescence. The yellow alkali solution (0.1%) faded out into a colorless solution when left for a day. It gave a positive murexide test, and Folin-Denis' reaction, and dissolved in fuming hydroiodic acid with the precipitation of iodine.

On dilution of the solution, the iodine was reduced and the pterin reprecipitated. These natures were identical with those described for isoxanthopterin but the ultra-violet absorption spectrum (Fig. 3) was not identical, the max-

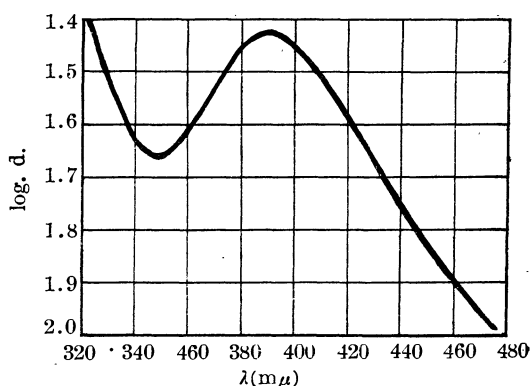


Fig. 3.—Ultraviolet absorption spectrum of the 6-dehydroxy-leucopter-B derivative (in 0.1 N NaOH). d: length of tube concentration: 0.1%

imum being located at 390 mμ, as compared with the values 252 mμ and 340 mμ for isoxanthopterin⁽¹⁶⁾. But the behavior with hydroiodic acid indicated this pterin to be a derivative of 6-dehydroxy-leucopter-B⁽¹⁾. The sus-

(16) R. Hüttel and G. Sprengling, *Ann.* **554**, 69 (1943).

(17) M. Polonovski, R. G. Busnel and M. Pesson, *Compt. rend. Acad. Sci.*, **217**, 163 (1943).

(18) T. Goda, *J. Fac. Sci., Imp. Univ. Tokyo*, Section IV, **5**, 305 (1941).

(19) Becker and Schöpf, *Ann.*, **524**, 49, 124 (1936).

pension in acetic anhydride was clarified by the addition of sulfuric acid, which demonstrated the presence of a hydroxyl group.

Summary.—Chemical researches on the epidermis pigments of a normal type (China 108) and mutants ("lem" and "od") of *Bombyx mori* have been carried out in order to elucidate the tryptophan metabolism. Besides uric acid as its calcium salt (which was commonly distributed), the following three new pterins were obtained from the respective races:

- (a) Normal type: leucopterin-B, leucopterin.
- (b) Mutant "lem": leucopterin-B, xanthopter-in-B and leucopterin.
- (c) Mutant "od": leucopterin-B, leucopterin.
- (d) Unidentified white race: 6-dehydroxy-leucopterin derivative.

Leucopterin-B and ichtyopter-in, xanthopter-in-B and xanthopter-in, the 6-dehydroxy-leucopter-in derivative and isoxanthopter-in, respectively, showed many superficial similarities but differed in their ultraviolet absorption spectrum

and several other natures. The pterin nature of the epidermis pigments being established, we have acquired a new information related to tryptophan metabolism and +chromogen.

In conclusion the authors wish to acknowledge their indebtedness to Prof. F. Egami for his advices and encouragements given in the course of this work and Prof. K. Yamasaki and Mr. K. Sone for the measurement of the ultraviolet absorption spectrum. We also gratefully acknowledge the precious gifts from Drs. E.L. Rickes and T. Goda. The advices given by Dr. T. Hama, the University of Tokyo, have also benefited us a great deal. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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On the Phase Transition of Pentaerythritol

By Sadao HOSHINO and Seizo NAGASAKI

(Received December 21, 1949)

Introduction

It is well known that the crystal of pentaerythritol, $C(CH_2OH)_4$, shows a phase transition accompanying a change of the lattice form at about 180° . The crystal structures of low and high temperature modifications of this crystal have been determined by Nitta and Watanabe,⁽¹⁾ and others.⁽²⁾ According to their reports the tetragonal form at room temperatures has a layer structure and in each layer molecules are bound by hydrogen bonds with each other, while in the cubic form at above 180° oxygen atoms in the molecule take statistical positions.

Since the nature of the phase transition of pentaerythritol and the accompanying changes in intermolecular and atomic binding will largely depend on the existence of hydrogen bond, it seems of interest to know the thermal behavior of this substance at the transitional range. We performed, therefore, specific heat measurements for this crystal. There are, however, some difficulties in the experimentation with this crystal. First, the complete purification of the specimen is very difficult, so that we

can not expect to obtain accurate experimental data corresponding to that of the pure substance. Furthermore, the heat measurement is considerably disturbed by the fact that this crystal holds a very large transition energy and a high sublimation pressure. On account of these obstructions we could not obtain accurate data, but the obtained result as described below may be sufficient to show the general trend of the phenomenon.

Measurement of the Specific Heat, and Calculations of the Heat of Transition and of Fusion, and the Corresponding Entropy Change

We used the apparatus which has been reported by Takagi and one of the authors.⁽³⁾ The sample for the specific heat measurement was put into a vessel made of pyrex (Fig. 1). The heat given to the specimen was generally in the range of $1/100 \sim 1.5/100$ cal./g.sec., and the velocity of temperature rise, at the range corresponding to the normal specific heat, was about $40 \sim 60$ sec./deg. The weight of specimens was in the order of 10 g.

Fig. 2 shows the "specific heat-temperature curve". The anomaly at about 180° corre-

(1) I. Nitta and T. Watanabe, *Nature*, **140**, 365, (1937); This Bulletin, **63**, 28-35, (1938).

(2) F. J. Llewellyn, E. G. Cox and T. H. Goodwin, *J. Chem. Soc.*, **1937**, 883.

(3) S. Nagasaki and Y. Takagi, *J. Appl. Phys. Jap.*, **17**, No. 5, 104 (1948).

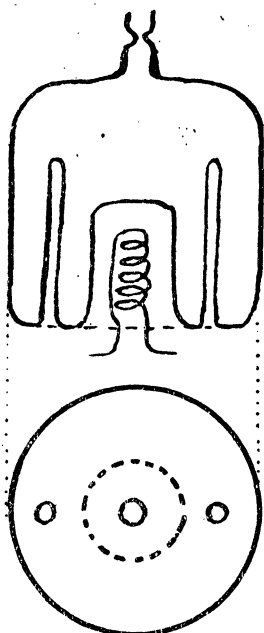


Fig. 1.— Glass vessel.

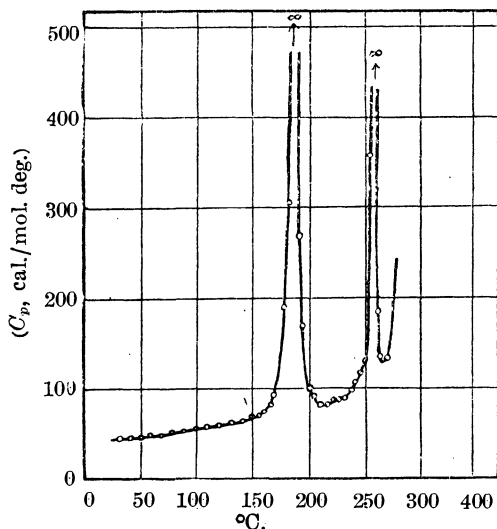
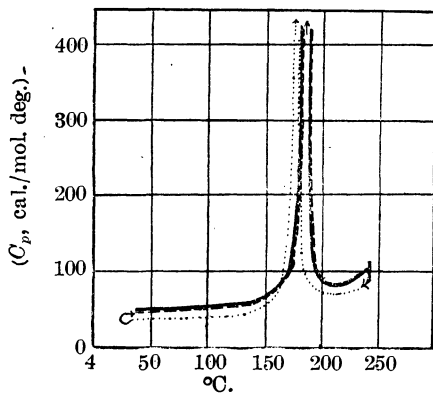
Fig. 2.— C_p -Temperature curve.

Fig. 3.

sponds to the transition of the crystal form from a tetragonal structure to a cubic one; and a peak at about 260° corresponds to melting. Above the melting temperature the curve rises again, owing to the vaporization of the substance. In order to avoid the influence of the sublimation of the specimen, we also performed the measurement with the sample sealed in the vessel. These results are shown in Figs. 3, 4. In these diagrams the

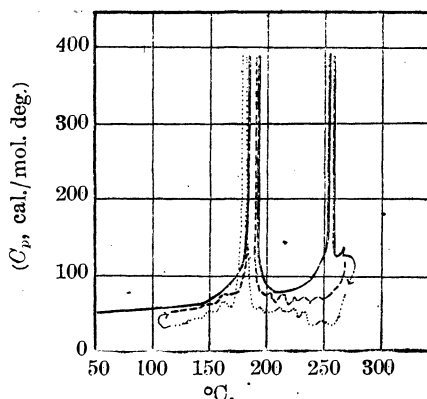


Fig. 4.

dotted lines showing the cooling curves are indicated by an arbitrary scale. The broken lines are the reheating curves. In Fig. 4, it should be noted that in cooling and reheating processes there does not appear the latent heat of crystallization, or that of fusion. From these curves we calculated the heat of transition and of fusion, and the corresponding entropy changes, which are shown in Table 1.

Table 1

	a	b
Transition point	184°C.	184°C.
$\Delta E_{\text{trans.}}$	8.4 kcal./mole	6.2 kcal./mole
$\Delta S_{\text{trans.}}$	8.5 R	6.5 R
Melting point	256°C.	—
$\Delta E_{\text{melt.}}$	1.3 kcal./mole	—
$\Delta S_{\text{melt.}}$	1.3 R	—

ΔE —energy change

ΔS —entropy change

a: data from the normal curve

b: from the anomalous reheating curve

Measurement of the Heat of Sublimation

In Fig. 2 we see that above the melting point the curve shows an anomalous rise. This phenomenon may be due to the vaporization of the sample. A direct measurement of the heat of vaporization is also possible by the method similar to the specific heat measurement, if we use a vessel of a copper block as indicated Fig. 5, and fill the upper cavity of the vessel with the sample.

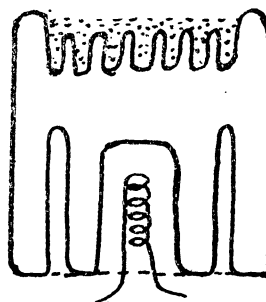


Fig. 5.— Copper vessel.

The vapor, evaporated from the sample at above 260° , is exhausted little by little by use of a vacuum pump. Obtained result is given in Fig. 6. In this figure the dotted line corresponds to the contribution due to the

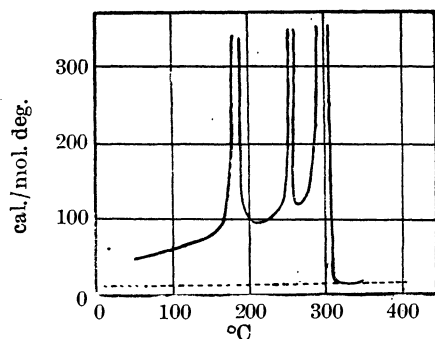


Fig. 6

copper vessel. The heat of vaporization can be estimated by the procedure of the calculation, just the same as that of the heat of transition. A mean value of the several measurements is about 22 kcal./mole. Using this value, the heat of transition and the heat of fusion, we can estimate the heat of sublimation of this crystal in the state of low or high temperature modification.

Now we will offer a discussion of the obtained results in the last section.

Discussion of the Results

By Fig. 2 and Table 1a, we know the general nature of the specific heat curve and the values of the energy and entropy changes corresponding to the respective phase changes. We shall first discuss the heat of lattice transition and of fusion. Though the transition energy, owing to the change of crystal form, is large in value compared with that of many other substances, it is still too small to destroy all the hydrogen bonds existing in this crystal, because the bond energy of $O-H\cdots O$ is about 6.2 kcal./mole⁽⁴⁾ for methyl or ethyl alcohol, and pentaerythritol includes four hydrogen bonds in one molecule. This fact seems to mean that all of OH radicals in the high temperature cubic modification are not "rotating" freely. This conclusion has been confirmed by X-ray analysis.⁽¹⁾ It is also noted that the transition energy is several times greater than the heat of fusion, which is probably indicative of the fact that the crystal structure of the cubic form somewhat resembles the structure of the liquid state.

The great value of transition energy seems to mean that the phase transition of this crystal is related to the breaking of some hydrogen bonds. The observed value 8.4 kcal./mole agrees with the energy required to cut one hydrogen bond per molecule. We can expect, therefore, that pentaerythritol is containing some free OH radicals, not only in the liquid state but also in the high temperature

crystal form. According to the result of the crystal analysis, the hydrogen bonds are arranged in two-dimensional layers in the structure of low temperature form. On the other hand, in the high temperature form, which is the cubic crystal, the three axial directions are equivalent to each other, so that the hydrogen bonds should form a three dimensional network. From the above consideration we can assume that in the high temperature cubic form there are only three hydrogen bonds per molecule, which are statistically arranged in a three dimensional way. We may also expect the behavior of the hydrogen bond in the liquid state to be similar to that in the cubic crystal form.

To ascertain the above conclusion, some experiments, such as the measurement of infrared absorption and observation of Raman effect, may be performed. Especially, the X-ray investigation of the diffuse scattering by using a single crystal of this substance may be important. However there are some difficulties in the experiment, since this crystal has a large thermal expansion coefficient, and therefore we can not easily obtain the single crystal of the high temperature form.

In the preceding section we stated that the heat of sublimation at room temperatures can be estimated as the total sum of the heat of transition, fusion and vaporization. The value obtained by this procedure is about 32 kcal./mole, and it is considered to contain the energy required to destroy all the hydrogen bonds. If we estimate this energy by using a value obtained from the other simple alcohol,⁽⁴⁾ it is about 25 kcal./mole. The difference of these values may be due to the contribution of the van der Waals energy of lattice. According to the latest publication⁽⁵⁾ the heat of sublimation of this crystal, determined by the method of vapor pressure measurement, is 31.4 ± 0.2 kcal./mole at 120° , and it is in harmony with the result of our direct measurement.

We observed a fact difficult to explain well. Namely, when we cool the sample from above the melting temperature, the cooling curve (dotted line in Fig. 4) shows no clear latent heat of crystallization. The reheating curve (broken line) is also similar to this, and the transition energy calculated from the latter curve is exceedingly smaller than that from the normal curve (Table 1b). That is to say, the substance, which has once been heated above the melting temperature, does not completely return to the initial state when it cools. This peculiarity may be explained by the consideration that the sample polymerizes partly,

(4) L. Pauling, "Nature of the Chemical Bond," p. 304.

(5) I. Nitta, S. Seki and K. Suzuki, unpublished yet, reported at the Meeting of the Chemical Society of Japan held at Osaka on 19th Nov. 1949.

or it becomes glassy. However, it is necessary to make a deeper study, in order to give a conclusive explanation for this point.

In conclusion we wish to express our sincere thanks to Prof. I. Nitta, who kindly gave us the sample, and to M. Momodani for his valuable advice. This investigation was done throughout under the kind guidance of Prof.

Y. Takagi, to whom the authors express also their best thanks. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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On the Positions of the Hydrogen Atoms in the Crystal Structure of Muscovite, as Revealed by the Infra-Red Absorption Study

By Masamichi TSUBOI

(Received December 24, 1949)

Introduction

While studying the near infra-red absorptions of proteins and related substances mounted on thin cleavage pieces of muscovite, the writer's attention was called to the facts that muscovite shows a sharp and strong absorption band at the wave-length 2.75μ , which was later ascertained to be due to the OH groups in its crystal structure, and that the intensity of this band varies with the direction of the ray in the crystal. In view of the significance of these facts as clue to the positions, hitherto unknown, of the H atoms in muscovite, the writer proceeded to examine in detail how the absorption intensity of the 2.75μ band varies with the direction of the electric vector of the light that passes through a muscovite crystal. In this paper the results of these experiments are given.

Sample

The sample of muscovite examined is from Tanokami-Yama, Siga Prefecture, and has the following optical constants for D-light: $\alpha=1.559$, $\beta=1.593$, $\gamma=1.598$, $2V=41^\circ$. From this a colorless, transparent cleavage piece, $3\text{ cm.} \times 3\text{ cm.}$ in size, of uniform thickness (about 18μ) was taken for observation. Its crystallographic orientation was determined from the X-ray oscillation photograph (Mo $K\alpha$) by Mr. H. Mori, through the kindness of Prof. T. Ito, of the Mineralogical Institute, Tokyo University.

Experimental Procedure

The infra-red absorption measurements were made by means of a reflection monochromator with a 60° prism of quartz, in conjunction with the thermocouple and galvanometer system. The infra-red radiation from a heated nichrom wire was reflected by a selenium mirror at the angle of 68° to be polarized,⁽¹⁾ and was passed through

the sample, set on a universally rotatable stage with graded circles for reading the angles of rotation.

Absorption Band of Muscovite at 2.75μ

The percent transmissions of the sample of muscovite were first observed for the light ranging from 2.6 to 3.5μ in wave-length, and the results shown in Fig. 1, A were obtained.

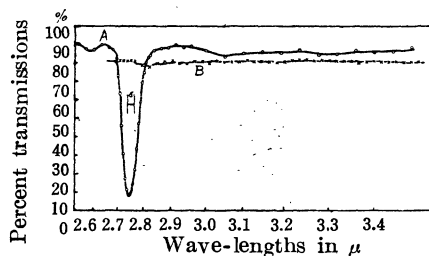


Fig. 1.—A: Percent transmissions of muscovite, 0.018 mm. thick. B: Percent transmissions of artificial mica, 0.3 mm. thick. s: Effective slit width.

Similar observations were made of a cleavage piece, 0.3 mm. thick, of an artificial mica⁽²⁾ in which F or O substitutes OH in natural muscovite, with the results shown in Fig. 1, B. As may be seen in these figures, while the cleavage piece of natural muscovite, as thin as 18μ , shows a sharp and strong absorption band at 2.75μ , the thicker cleavage piece of the OH-free artificial mica shows none. From these observations the band at 2.75μ may be assigned

(1947)), the efficiency of this setting as a polarizer was judged from the fact that the transmission at 2900 cm.^{-1} of a sample of succinic acid, put in the path of the reflected light, increased from 1% to 72% as it was rotated through 90° from the position at which the c axis is parallel to the plane of the selenium mirror.

(2) Prepared by Professor T. Noda ("Kôgyô Buturi-Kagaku," 1, 103 (1948); 2, 179 (1948)) and kindly placed at the writer's disposal.

(1) Following D. A. Crooks (*Nature*, 160, 17

with certainty to the fundamental O-H stretching vibration in crystal of muscovite.

Moreover the absorption band of muscovite is of the same character with that due to the free OH of alcohols in their dilute carbon tetrachloride solutions, in regards to the wave-length of the absorption maximum and the band width. This fact shows that the OH in muscovite is free from the hydrogen bonding, the O-H bond being almost unaffected by the surrounding atoms in the crystal.

Absorption Intensities in Different Directions of Muscovite

Now that it has become clear that the absorption band at 2.75μ of muscovite is due to the fundamental O-H stretching vibration, its intensity variation with the direction of the ray must give informations as to the orientations of the O-H bonds in the crystal structure. With the purpose of obtaining such informations, the linearly polarized radiation with the wave-length $2.75 \mu^{(3)}$ was passed through the sample of muscovite orientated in various directions, and the percent transmission in each direction was determined. In this experiment the electric vector of polarized light sent to the crystal was always orientated so that it was in the incident plane. The results obtained are shown in Tables 1 and 2 and in Figs. 2 and 3. Throughout this paper, the setting of the crystallographic axes of muscovite as proposed by W. W. Jackson and J. West⁽⁴⁾ is adopted.

Table 1
Observed Percent Transmissions (m)
of Light Sent Perpendicularly to the
Cleavage Plane

φ	$m, \%$
90°	43.6
80	44.4
70	45.5
60	47.3
50	49.2
40	51.0
30	52.9
20	53.5
10	54.5
0	55.0
-10	54.4
-20	53.7
-30	52.9
-40	51.5
-50	49.9
-60	47.8
-70	45.5
-80	44.4

φ is the azimuth of the electric vector for the incident light, measured with the crystallographic a axis. It is positive when measured counter-clockwise.

(3) The light used is not strictly monochromatic, but ranges in wave-length $2.69 \sim 2.81 \mu$, the effective slit width being 0.12μ , in which the total range of 2.75μ band is included.

(4) W. W. Jackson and J. West, *Z. Krist.*, **76**, 211 (1930); **85**, 160 (1933).

Table 2
Observed Percent Transmissions (m) of Light
Sent Obliquely to the Cleavage Plane

φ	θ	m	φ	θ	m	φ	θ	m
90°	50°	47.0%	30°	40°	50.0%	-30°	50°	50.5%
	40	46.2		30	50.1		40	50.1
	30	45.5		20	50.8		30	50.3
	20	44.4		10	51.3		20	50.6
	10	44.0		0	52.9		10	52.4
	0	43.6		-10	54.1		0	52.9
	-10	43.7		-20	56.4		-10	54.1
	-20	44.4		-30	57.6		-20	56.8
	-30	45.2		-40	61.1		-30	59.2
	-40	46.1					-40	62.0
60	40	49.4	0	50	51.4	-60	50	48.4
	30	48.0		40	52.0		40	47.6
	20	48.0		30	52.2		30	46.6
	10	47.9		20	52.4		20	45.9
	0	47.8		10	53.6		10	46.4
	-10	48.8		0	55.0		0	47.3
	-20	49.8		-10	57.0		-10	47.7
	-30	51.2		-20	60.1		-20	48.5
	-40	52.6		-30	64.5		-30	50.2
				-40	67.5		-40	52.6

φ is the azimuth of the incident plane, measured with the crystallographic a axis. It is positive when measured counter-clockwise. θ is the incident angle of the light. It is positive when measured to the front.

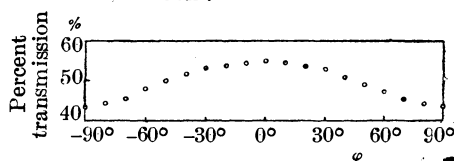


Fig. 2.—Observed percent transmissions of light sent perpendicularly to the cleavage plane of muscovite. As to the meaning of φ , see the note of Table 1.

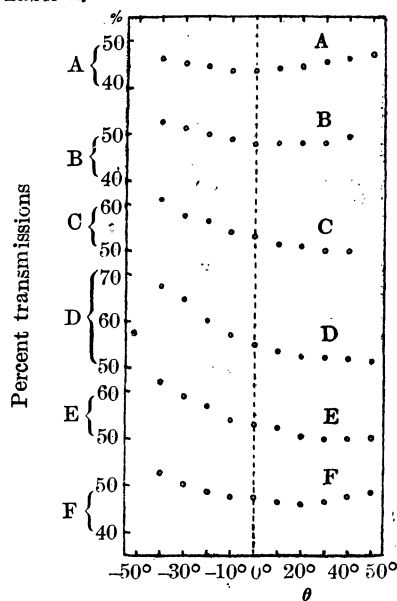


Fig. 3.—Observed percent transmissions of light sent obliquely to the cleavage plane of muscovite. A: $\varphi = 90^\circ$, B: $\varphi = 60^\circ$, C: $\varphi = 30^\circ$, D: $\varphi = 0^\circ$, E: $\varphi = -30^\circ$, F: $\varphi = -60^\circ$. As to the meanings of φ and θ , see the notes of Table 2.

In order to know how in the muscovite crystal the absorption coefficient is related to the

direction of the electric vector of the passing radiation, the absorption coefficient K in various directions were calculated from the data given above by the following equation, which is based on the Lambert's law:

$$K = \frac{1}{d \sec \chi} \log \left\{ (1 - r)^2 / \frac{I}{I_0} \right\},$$

where d is the thickness of the sample, χ the refracting angle, r the reflection coefficient at each boundary surface of the sample, and I/I_0 the transmittance. The results of the calculations are given in Table 3 and Fig. 4.

Table 3
Relative Absorption Coefficients (for 2.75μ radiation) in Different Directions in Muscovite (Expressed as $K_b = 1$.)

From the	φ			ψ		
	φ	ψ	K	φ	ψ	K
data in Table 1:	90°	24.0	0.93	60°	24.0	0.73
		18.5	0.95		18.5	0.75
		12.5	0.98		12.5	0.79
		6.3	1.00		6.3	0.81
		0	1.00		0	0.84
		-6.3	0.99		-6.3	0.84
		-12.5	0.98		-12.5	0.84
		-18.5	0.94		-18.5	0.85
		-24.0	0.93		-24.0	0.82
		-29.0	0.91			
(Of. remarks)						
	(5) below	30°	24.0	0°	24.0	0.37
			18.5		18.5	0.41
			12.5		12.5	0.49
			6.3		6.3	0.56
			0		0	0.61
			-6.3		-6.3	0.66
			-12.5		-12.5	0.70
			-18.5		-18.5	0.72
			-24.0		-24.0	0.74
		-30°	24.0	-60°	24.0	0.73
			18.5		18.5	0.78
			12.5		12.5	0.83
			6.3		6.3	0.85
			0		0	0.86
			-6.3		-6.3	0.90
			-12.5		-12.5	0.92
			-18.5		-18.5	0.90
			-24.0		-24.0	0.88
			-29.0		-29.0	0.86

K_a and K_b are the absorption coefficients of the passing radiations in muscovite whose electric vectors are parallel to the crystallographic axes a and b respectively. φ is the azimuth of the electric vector of the passing radiation in muscovite. It is positive when measured counter-clockwise, ψ is the angle which the electric vector makes with the cleavage plane. It is positive when measured upward.

Remarks:—In the course of calculating the values of K in Table 3 the following measures were taken:

(1) To find r and χ in the above equation and φ and ψ in the Table 3, the principal refractive indices, α , β and γ , of muscovite for the light of the wave-length 2.75μ must be known. These being unknown, the calculations were made on the assumption that $\alpha = \beta = \gamma = 1.58$. That this assumption does not affect seriously the final results

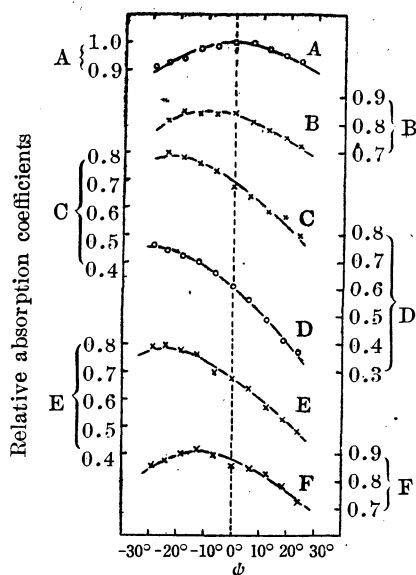


Fig. 4.—Relative absorption coefficients in different directions of muscovite. A: $\varphi = 90^\circ$, B: $\varphi = 60^\circ$, C: $\varphi = 30^\circ$, D: $\varphi = 0^\circ$, E: $\varphi = -30^\circ$, F: $\varphi = -60^\circ$. As to the meanings of φ and ψ see the notes of Table 3. The points marked with $\times$ represent the values of K , φ and ψ , obtained from calculations including the approximations as remarked in (6) in the text. Those marked with $\circ$ represent the values obtained without such approximations, the incident planes for the light here concerned containing either one of the crystallographic axes a and b .

aimed at, was ascertained by trials with other assumed values for α , β and γ , such as: (1) $\alpha = 1.526$, $\beta = 1.544$, $\gamma = 1.552$, (2) $\alpha = \beta = \gamma = 1.55$, (3) $\alpha = \beta = \gamma = 1.61$, etc., all of these trials having given the results not different qualitatively from one another.

(2) In the calculation of r , the absorption index κ (in the formula $n(1 - i\kappa)$ expressing the complex refractive index) was neglected, because κ of muscovite is about 0.006 for the light here used, as may be estimated from the Tables 1 and 2, and accordingly κ^2 is negligibly small compared with 1. The values of r were obtained by the Fresnel's formula concerning the reflection of light.

(3) As a test of the applicability of the Lambert's law to the present case, a spectroscopic observation was made of the 2.75μ absorption band of methanol in dilute carbon tetrachloride solution with the same slit width as that in the experiment with muscovite. This showed that the observed absorbance $\log I_0/I$ is not strictly proportional to the thickness d of the solution, but that the $\log I_0/I - d$ curve is somewhat convexly bent. The values of K in Table 3 are those corrected on the basis of this observation, assuming that the deviation of the observed values of $\log I_0/I$ from the Lambert's law is the same for the muscovite and for the methanol. These corrections, though added, are of little importance for the present purpose.

(4) It was not intended to obtain absolute values of K , for the accurate value of d was not known.

(5) The percent transmission, (m) of the light sent perpendicularly to the cleavage plane is given by

$$m = m_a \cos^2 \varphi + m_b \sin^2 \varphi,$$

where m_a and m_b denote the percent transmissions, respectively of the light with the electric vector parallel to the a axis and of the light with the electric vector parallel to the b axis, into which the incident light is divided after entering muscovite, and φ the angle which the direction of the electric vector of the incident light makes with the a axis. By substituting the values in Table 1 for m and φ in the above formula and by applying the method of least squares, the following values of m_a and m_b were obtained: $m_a = 55.2 \pm 0.1\%$, $m_b = 44.4 \pm 0.1\%$. From these the ratio of the absorption coefficients, K_a and K_b , were calculated as $K_a/K_b = 0.63$.

(6) The azimuths (φ) of the electric vectors within the crystal for the light sent obliquely to the cleavage plane were taken to be the same with those before entering the crystal, even in the case where the incident plane contains neither the crystallographic axis a nor b . Such approximations are considered to introduce no serious error to the results, because the retardation of the cleavage piece of muscovite for the light under consideration may probably be small compared with its wave-length.

In order to facilitate further discussions the writer here proposes to consider a surface of reference — “absorption coefficient—electric vector surface” or “ K - E surface”—which shows the variation of the absorption coefficient in different directions in a crystal. From a point within a crystal, lines are drawn in all directions representing those of the electric vectors of light, and each of these lines is cut so that its length may represent the absorption coefficient for the light concerned,

then the surface obtained by the ends of these lines is the K - E surface of the crystal. This is a surface with three extremity axes perpendicular to one another.⁽⁵⁾

The data given in Table 3 and Fig. 4 are indicative of the shape and the orientation of the K - E surface of the muscovite examined. The orientations and the relative lengths of the three extremity axes of the K - E surface are as follows:

(i) The greatest axis: parallel to the crystallographic axis b . Relative length=1.

(ii) The medium axis: orientated at $\varphi=0^\circ$, $\psi=-30^\circ$, i.e. at 30° from the crystallographic axis a in the acute angle β , in 010 plane.

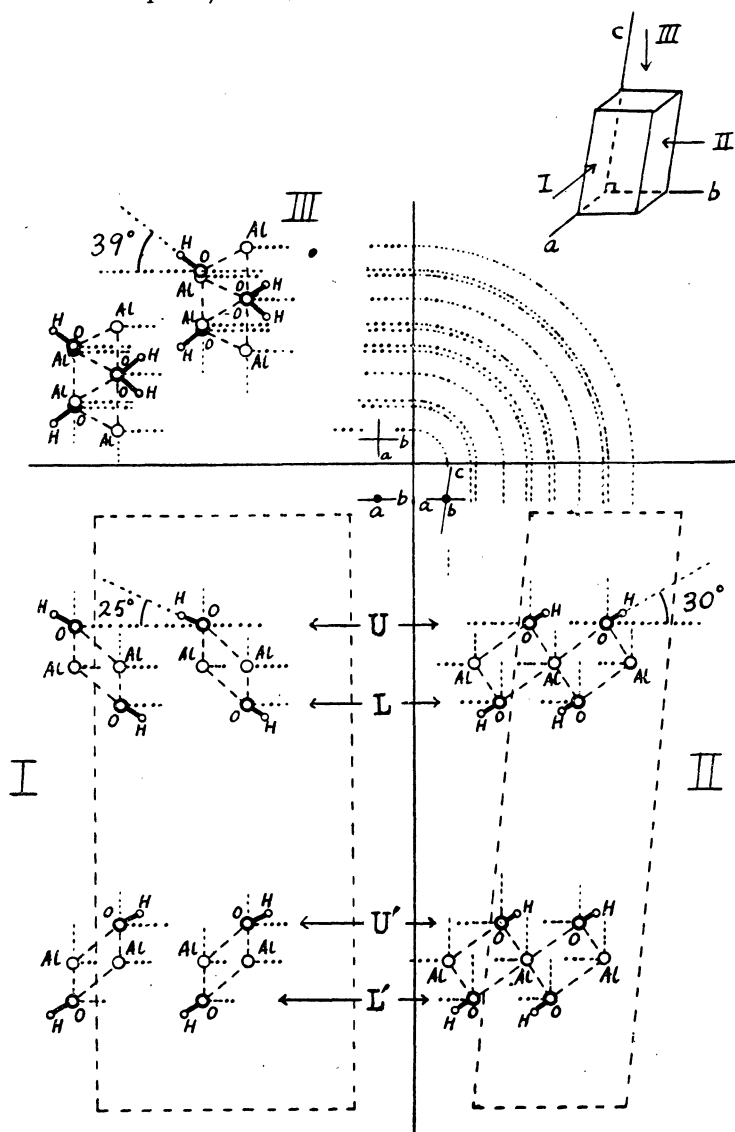


Fig. 5.—Orientations of the OH groups in the unit cell of muscovite. I: Projected on a plane normal to the a axis. II: Projected on 010. III: Projected on a cleavage plane.

(5) Details are to be published elsewhere.

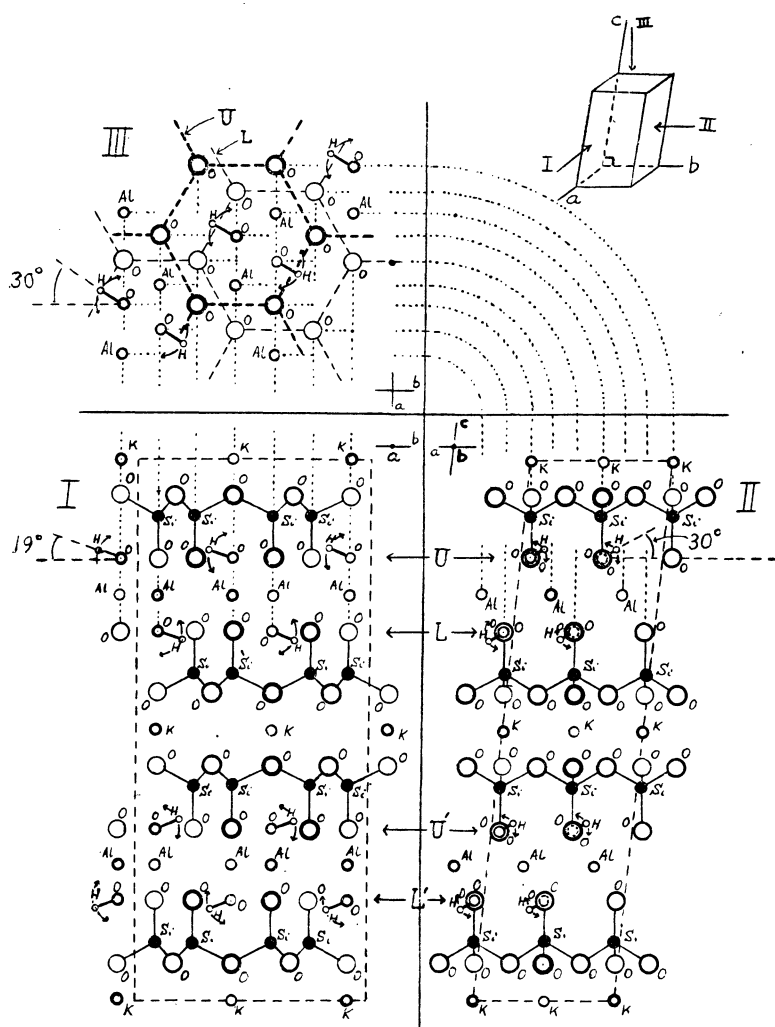


Fig. 6.—Crystal structure of muscovite. I: Projected on a plane normal to the a axis. II: Projected on 010. III: Projected on a cleavage plane.

Relative length $\doteq 0.8$.

(iii) The smallest axis: perpendicular to both of the greatest and the medium axes. Relative length is probably near to 0.

On the Position of the Hydrogen Atoms in Muscovite

The crystal structure of muscovite was studied by W.W. Jackson and J. West⁽⁴⁾ by the X-ray method. According to them, each unit cell of muscovite includes eight OH groups distributed in four sheets, U, L, U', and L' in Figs. 5 and 6, parallel to 001, between the Al layer and the Si_2O_5 layer. The positions of the H atoms of these OH groups can be con-
 jec-

tured from the data of the infra-red absorption of muscovite described in this paper.

In Table 4 and Fig. 5 are shown the orientations of the O-H bonds on the assumption that the H atoms take fixed positions, their vibration being neglected. Here, by φ and ψ are denoted respectively the azimuth and the angle with 001 of each of the O-H bonds, in a similar way as those of the electric vector in Table 3. These values of φ were determined so that $K_a/K_b = 0.63$, and ψ , so that the condition (ii) in the preceding section is satisfied. In Fig. 7 are given three principal sections of the theoretical K - E surface based on the calculations from the values of φ and ψ in Table 4. The points marked with $\circ$ represent the observed values of absorption coefficients. The coincidence of the theoretical and observed values of K is rather satisfactory.

It would seem inconceivable that φ 's for the O-H bonds in muscovite take such values

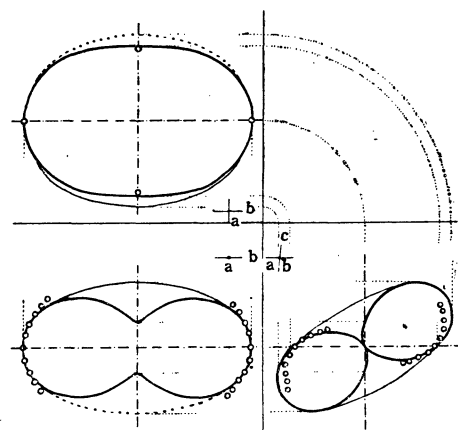


Fig. 7.—Three principal sections of the theoretical K - E surface, based on the orientations of the OH groups in Fig. 5. The points marked with $\circ$ represent the observed values of K .

Table 4

O-H's on the U sheet...	$\varphi = -129^\circ$, $\psi = 20^\circ$
" " " L "	$\varphi = 51^\circ$, $\psi = -20^\circ$
" " " U' "	$\varphi = 129^\circ$, $\psi = 20^\circ$
" " " L' "	$\varphi = -51^\circ$, $\psi = -20^\circ$

as -129° , 51° , 129° and -51° , in spite of the hexagonal arrangement of all the other neighbouring atoms. It would be more probable that the O-H bonds are orientated so that their azimuths (φ) are -120° , 60° , 120° and -60° . But then, the value of K_a/K_b should be 0.33 instead of 0.63, the observed value. This deviation, however, can be explained as due to the vibration of the H atoms around their equilibrium positions.

Taking all of what have been said above into consideration, the probable orientations of the O-H bonds at equilibrium in muscovite are as shown in Table 5 and Fig. 6. The values in Table 4 are interpreted as representing

Table 5

O-H's on the U sheet...	$\varphi = -120^\circ$	$\psi = 16.5^\circ$
" " L "	$\dots \varphi = 60^\circ$	$\psi = -16.5^\circ$
" " U' "	$\dots \varphi = 120^\circ$	$\psi = 16.5^\circ$
" " L' "	$\dots \varphi = -60^\circ$	$\psi = -16.5^\circ$

the apparent orientations of the O-H bonds at 30°C . (at which the present experiment was

carried on), resulted from the vibration of the H atoms around their equilibrium positions.

The writer wishes to express his sincere thanks to Professor San-ichiro Mizushima, Dr. Takehiko Simanouti and Mr. Kenji Kuratani for their kind guidance throughout this work. His thanks are also due to Professor Yonezo Morino and Professor Tokiti Noda for their placing the sample of artificial mica at the writer's disposal, to Professor Teiichi Ito and Mr. Hiroshi Mori for their kindness in determining the crystallographic orientation of the sample of muscovite used in this experiment, and to Professor Masazo Kiuchi for his advice as to certain optical treatments. The cost of this research has been partly defrayed from Grant in Aid for Scientific Research from the Ministry of Education, to which the writer's thanks are due.

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Rearrangement of *cis*-Caronic Acid to *trans*-Caronic Acid

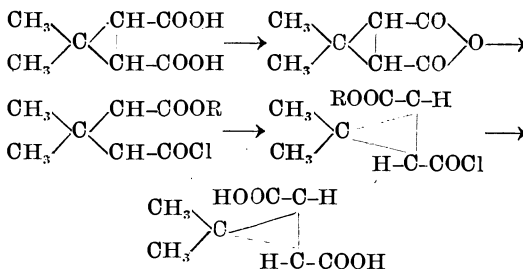
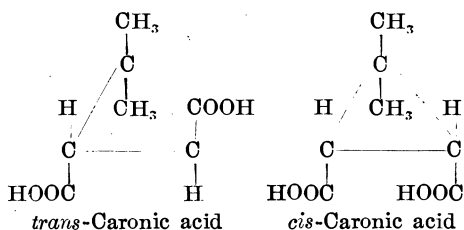
By Masanao MATSUI

(Received December 31, 1949)

There are many studies on the rearrangement from *cis*-compounds to *trans*-ones and *trans*-ones to *cis*-ones, but few can be found on the rearrangement of compounds which contain cyclopropane ring.

It has been known with caronic acid that its *trans* form rearranges to *cis* anhydride by heating the former with thrice its quantity of acetic anhydride at 220° in the sealed tube.⁽¹⁾

However, in the case of this caronic acid, as the two carboxyl groups are free, they may form the stable anhydride, and the rearrangement may not result. Therefore, it may be the matter of course that the *cis*-acid rearranges to *trans*-acid when it is heated after being converted to half ester which can not become intramolecular anhydride.



However, in any report it can not be discovered that the *cis*-acid rearranges to the *trans*-one. Like in the case of geometric isomerism of unsaturated compounds, the *trans*-acid would be more stable than the *cis*-one and the rearrangement of *cis* $\rightarrow$ *trans* would take place.

When the writer studied on caronic acid for other purpose, it was found that when isoamyl ester chloride of *cis*-caronic acid is heated, it rearranges to *trans*-acid as shown above. In the case of free *cis*-caronic acid, however, even if there was water enough to prevent free acid to convert its anhydride, the rearrangement from *cis* to *trans* did not perform, when the

(1) Perkin and Thorpe, *J. Chem. Soc.*, **75**, 52.

mixture of water and free *cis*-acid was heated at 200° for seven hours in a sealed tube.

It is interesting that the conversion occurs only in the case of the half ester acid chloride.

Experimental

***cis*-Caronic Anhydride.**—*trans*-Caronic acid (m.p. 212°, 1 part), totally synthesized, is heated with acetic anhydride (3 parts) at 220° in a sealed tube for six hours. Then it was distilled and the distillate boiling at *ca.* 143° (20 mm.) was collected. It crystallized soon. It was recrystallized from dry ether and showed m.p. 56°. Boiled with water, *cis*-caronic acid, m.p. 174°, was obtained.

Isoamyl Hydrogen *cis*-Caronate.—Twenty grams of caronic anhydride, 13 g. of isoamyl alcohol and 15 g. of benzene were mixed and the mixture was refluxed on a water-bath for three hours. After cooling, it was extracted with 10 % sodium carbonate solution. After the extract was washed with ether, it was acidified with hydrochloric acid. Separating oil was extracted with ether. The ether extract was washed with water and dried on the anhydrous sodium sulfate. After removal of the solvent from the ether solution, the remaining oil was distilled. The half ester was collected at 165–170° (10 mm.) as colorless viscous oil. Saponified with alkali, *cis*-caronic acid was obtained.

From Isoamyl Hydrogen *cis*-Caronate to

***trans*-Caronic Acid.**—Five grams of the half ester above described was added to 20 cc. of petroleum ether and next 3 g. of thionyl chloride was added drop by drop under cooling with ice and was left stand over night. Then it was warmed on a water-bath for half an hour. The petroleum ether and excess of thionyl chloride were removed under reduced pressure on a water-bath and crude isoamyl ester chloride of *cis*-acid was obtained. This was heated at 200° on an oil-bath for three hours. After cooling, water was added and, boiled for three hours and the reaction mixture was saponified. Then it was extracted with ether. The ether solution was dried on anhydrous sodium sulfate. After removal of the solvent from the ether solution the remaining oil was distilled under reduced pressure and the distillate, which boiled until the temperature of the bath rose to 220° at 10 mm., was discarded. The remainder crystallized on cooling. It was recrystallized from water and showed m.p. 212°. The test of the melting point, when mixed with *trans*-caronic acid, did not cause the depression of the melting point.

The writer wishes to acknowledge his indebtedness to Professor Ryuzaburo Nodzu for his valuable advices and also he desires to thank Mr. Susumu Hirase for his assistance.

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On the Refractive Power of the Lower valent Al Ion (Al^+ or Al^{++}) in the Crystal

By Goro YAMAGUCHI

(Received February 19, 1950)

Introduction.—The author found out the spinel crystal with lower valent Al ion in the ingot of abrasive fused alumina, which was made by the special method and its properties were reported in the previous papers.⁽¹⁾ Valency of such Al ion seems mono or di; mono is more probable because unpaired electron does not exist. This spinel crystal are explained as that two Mg ions of normal spinel (MgAl_2O_4) are substituted by Al^+ ion and Al^{+++} ion (or two Al^{++} ions). The properties of this spinel crystal are as follows;

Color; colorless

Refractive index; 1.78

Density; 3.72

Crystal structure; spinel $a_0 = 7.97\text{\AA}$.

Chemical composition (as normal oxide);

Al_2O_3 99.65%, MgO 4.91%, total 104.56%

Probable formula; $(0.412 \text{ Al}^+, 0.412 \text{ Al}^{+++},$

$0.176 \text{ Mg}) \text{ O} \cdot \text{Al}_2\text{O}_3$

In these values, especially high refractive index of the new spinel crystal are found. This phenomenon would depend on the high polarizability of the lower valent Al ion. In this paper, the calculation of the ionic

1) G. YAMAGUCHI, *J. Electrochem. Assoc. Japan*, **14**, 106 (1946); *J. Ceram. Assoc. Japan*, **55**, 42 (1947).

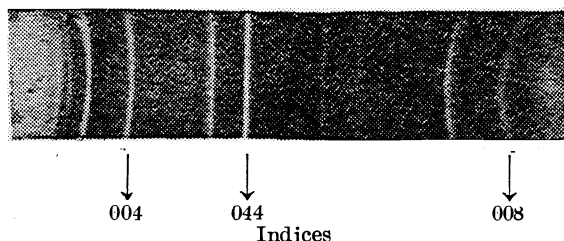


Fig. 1.—X-ray powder photograph of the new spinel crystal by Fe K ray.

refraction of the lower valent Al ion is attempted.

Calculation of the Ionic Refraction of Oxygen Ion in the Normal Spinel Structure.

—In this calculation the following values are used ;

Formula weight of spinel, M_{SP} ; 142.26

Density of spinel, D_{SP} ; 3.578⁽²⁾

Refractive index of spinel, N_{SP}^{++} ; 1.719⁽²⁾

Ionic refraction of Mg^{++} , R_{Mg}^{++} ; 0.26⁽³⁾

Ionic refraction of Al^{+++} , R_{Al}^{+++} ; 0.17

By introducing these values into Lorentz-Lorentz formula,

$$(N^2 - 1)M/(N^2 + 2)D = R$$

$R_{SP} = 15.69$ is obtained, where R_{SP} is formula refraction of spinel. Now R_{SP} is the sum of R_{Mg}^{++} , $2R_{Al}^{+++}$, and $4R_{O}^{--}$, then 3.77 is obtained as the value of ionic refraction of oxygen ion in normal spinel (R_{O}^{--}).

Calculation of Ionic Refraction and Ionic Polarizability of Al Ion.—By introducing the refractive index, the formula weight and the density of the new spinel crystal into Lorentz-Lorentz formula, 16.28 is obtained as the value of formula refraction of the new spinel crystal with Al^+ ion. Now 16.28 is the sum of $0.176R_{Mg}^{++}$, $0.412R_{Al}^+$, $2.412R_{Al}^{+++}$ and $4R_{O}^{--}$, then 1.80 is obtained as the value of R_{Al}^+ .

And next, by the equation ;

$\alpha = 3R/4\pi N_O = 0.393 \times 10^{-24}R$, where α is

2) E. Rinne, *N. Jahrb. Min. (A)* **53**, 106 (1928).

3) I. NODA, *J. Electrochem. Assoc. Japan*, **14**, 124 (1946).

ionic polarizability, 0.727×10^{-24} is obtained as the value of ionic polarizability of Al^+ ion.

These values are ten times as large as that of normal Al^{+++} ion and situated between the values of Ca ion and of Sr ion.

Moreover by the similar calculation in case of Al^{++} ion instead of ($Al^+ + Al^{+++}$)/2, 0.98 is obtained as the value of ionic refraction of Al^{++} ion and 0.397×10^{-24} , as the value of ionic polarizability.

Conclusions.—The hypothesis that lower valent Al ion exists as Al^+ , is more probable and in such case the following values are obtained ;

Ionic refraction of Al^+ ; 1.80

Ionic polarizability of Al^+ ; 0.727×10^{-24} ,

But if the form of the ion is Al^{++} , the values are as follows ;

Ionic refraction of Al^{++} ; 0.98

Ionic polarizability of Al^{++} ; 0.397×10^{-24}

The results show the high polarizability of lower valent Al ion depending on loosely combined electron in M shell. Many other particular and interesting properties of the crystal will follow this fact. Now the problem is whether typical Al_3O_4 , namely $(0.5Al^+, 0.5Al^{+++})O \cdot Al_2O_3$, exists or not. Perhaps, at normal state, Al^+ ions are not so stable that Al_3O_4 could not able to exist, but if Mg ions are mixed in molten state, spinel structure with Mg ions is stabilized at solidifying time and so Al^+ ions existing in molten state go into spinel structure and stabilized.

A part of the cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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The Crystal Structure of Adipic Acid

By Sakutaro HIROKAWA

(Received April 10, 1950)

Introductoin

The X-ray investigation of normal chain dicarboxylic acids is very important in various respects. W.A. Caspari⁽¹⁾ reported preliminarily the results of his investigation on some dicarboxylic acids. These are listed in Table 1, in which are added the data on succinic acid given by H.J. Verweel and C.H. MacGillavry.⁽²⁾

Table 1					
Acids	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	β	Molecules in the unit cell
Succinic (C ₄)	5.10	8.88	7.61	133°37'	2
Adipic (C ₆)	10.27	5.16	10.02	137° 5'	2
Pimelic (C ₇)	9.93	4.82	22.12	130°40'	4
Suberic (C ₈)	10.12	5.06	12.58	135°	2
Azelaic (C ₉)	9.72	4.83	27.14	129°30'	4
Cebacic (C ₁₀)	10.05	4.96	15.02	133°50'	2
Brassylic (C ₁₃)	9.63	4.82	37.95	128°20'	4
Hexadecanedicarboxylic (C ₁₈)	9.76	4.92	25.10	131°10'	2

As for the series of even acids, the lengths of crystallographic axes *a* and *b* of succinic acid are considerably different from those of adipic and higher acids. The question thus arises how and why the crystal structure of succinic acid differs from that of adipic or other members of the series. On the other hand, as adipic acid is an important material for the synthesis of Nylon, it is also of interest to investigate this substance from the view point of highpolymer chemistry.

In 1941 T. Ohashi⁽³⁾ and the present author started the crystal analysis of polymethylenediamine adipates, the so-called Nylonsalts, together with that of adipic acid, but unfortunately the work was interrupted by the War. After the War, the present author took this problem up again and finished some time ago the work on the crystal structure of adipic acid. Although he found recently that the structure determination of this crystal had been completed by C.H. MacGillavry⁽⁴⁾ and also by J.M. Robertson,⁽⁵⁾ it will not be insignificant

to publish the results of the independent determination of the present author.

Crystallographic Data

According to the description by P. Groth,⁽⁶⁾ the crystal of adipic acid is monoclinic holohedral, and the values of axial ratio and axial angle are $a:b:c=1.9673:1:1.79$ (?), $\beta=137^\circ 5'$. This crystal is optically negative, and the axial plane is *b*(010).

Cleavages parallel to (110) and to (011) are perfect and so the fibre cleavage is observed along (001). Single crystals used in the present experiment were prepared from ethylacetate solution by slow evaporation. They were well-formed tablets parallel to (001) and prisms elongated in the direction of the *c*-axis. The external forms are shown in Fig. 1. Specimens were cut out of these crystals into suitable shape and size.

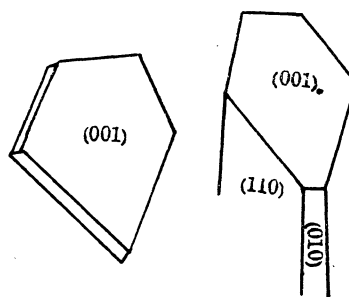


Fig. 1.—The external forms of crystals, smaller planes are not drawn.

From the Laue photographs taken parallel to (010) and perpendicular to (001) respectively, it was shown that the Laue symmetry was C_{2h} . The gnomonic projections of these photographs gave the following values; $a:b:c=1.95:1:1.93$, $\beta=137^\circ$.

From the Oscillation and Weissenberg photographs taken of *a*, *b* and *c*-axes respectively, it was found that the unit cell of adipic acid was monoclinic and was of the following dimensions:

$$a = 10.14 \pm 0.05 \text{ kX}, \quad b = 5.16 \pm 0.03 \text{ kX}, \\ c = 10.03 \pm 0.05 \text{ kX}, \quad \beta = 137^\circ.$$

The axial ratio calculated from these values

(1) W.A. Caspari, *Jour. Chem. Soc.*, **1926**, 3235.

(2) H.J. Verweel and C.H. MacGillavry, *Z. Krist.*, **102**, 60 (1939).

(3) T. Ohashi, *Annual Report of the Fibre Research, Osaka, Japan*, Vol. 4, (1942).

(4) C.H. MacGillavry, *Rec. trav. chim.*, **60**, 605 (1941).

(5) J.D. Morrison and J.M. Robertson, *Jour. Chem. Soc.*, **1949**, 987.

(6) P. Groth, "Chemische Krystallographie," Vol. III, 465.

is $a:b:c=1.964:1:1.945$. This is in good agreement with that obtained from the Laue photographs. Thus the values given by P. Groth may be concluded to be incorrect. On indexing all spectra of these photographs the following systematic absences were found; $(0k0)$ for $k=2n+1$, and $(h0l)$ for $h=2n+1$. All other types of spectra were found. Therefore, the space group of this crystal was concluded to be $P2_1/a-c^{52h}$.

The density measured by the flotation method using carbontetrachloride and ethanol was $\rho=1.357$ at 18°C . Accordingly the number of molecules in the unit cell was calculated to be $Z=2$.

Determination of Structure

There are four general positions $x, y, z; 1/2+x, 1/2-y, z; \bar{x}, \bar{y}, \bar{z}; 1/2-x, 1/2+y, z$, for the space group $P2_1/a$. These are shown in Fig. 2. However, in the present case, as the unit cell contains only two molecules, a molecule must either have a plane or a centre of symmetry. As the plane of symmetry can be elim-

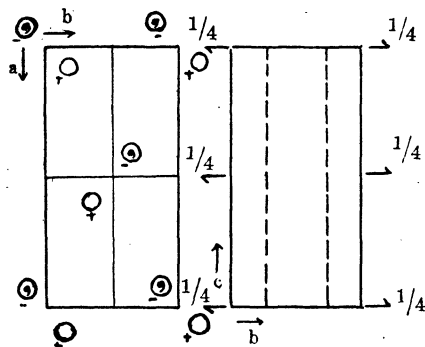


Fig. 2.—Symmetry of $P2_1/a$.

inated from the observed relative intensities of $(0k0)$ reflections, the molecule must have a centre of symmetry, which may be assumed to lie at the origin of the unit cell. Thus, neglecting all the hydrogen atoms as usual, five sets of parameters x, y, z are needed to be determined to fix the positions of carbon and oxygen atoms in the molecule; namely, three sets for C atoms and two for O's. Now it is preliminarily assumed, from the inspection of the size of the unit cell for the series of dicarboxylic acids given above, that (1) the molecule, neglecting hydrogen atoms is planar; (2) the carbon atoms in the molecule form a zig-zag chain; (3) the axis of the carbon chain orientates itself parallel or nearly parallel to the c -axis; (4) the bond distances are roughly $\text{C}-\text{C}=1.54 \text{ \AA}$, and $\text{C}-\text{O}=1.28 \text{ \AA}$; and finally (5) the bond angles are also roughly $\angle \text{CCC}=110^\circ$, $\angle \text{OCC}=120^\circ$, and $\angle \text{CCO}=120^\circ$. A rough model of the molecule thus assumed is shown in Fig. 3.

The line connecting a mid-point of the two

oxygen atoms at one end with that of the two

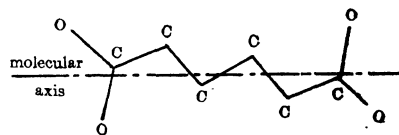


Fig. 3.

oxygen atoms at the other end is chosen for the molecular axis. Evidently this axis passes through the centre of symmetry. Since this axis and the plane of the carbon chain together fix a rectangular coordinate axes in the molecule, we can conveniently use the Eulerian angles to describe the orientation of the molecule in the unit cell.

Using these assumptions, the method of trial and error could lead to a possible approximate solution of parameter values for the atoms. The methods of the Patterson and the Fourier series were then applied to obtain more precise values of parameters.

These are shown in Figs. 4, 5 and 6. The final result of the determination is as follows;

	C_1	C_2	C_3	O_1	O_2
x	0.021	0.056	-0.021	-0.078	0.106
y	-0.090	-0.160	0.038	0.110	-0.240
z	0.329	0.210	0.054	0.290	0.479

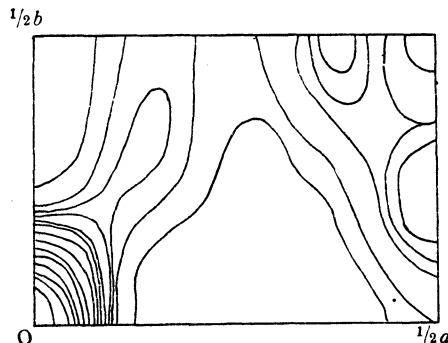


Fig. 4.— $P(x, y)$.

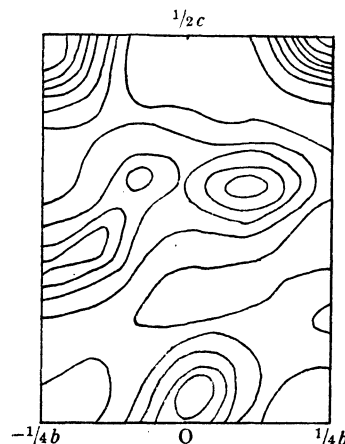
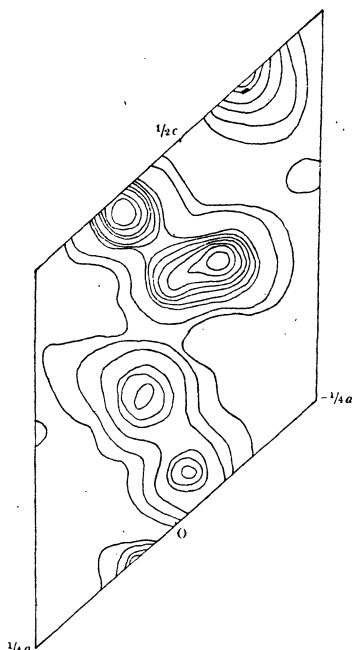


Fig. 5.— $\rho(y, z)$.

Table 2

<i>hkl</i>	$\sin \theta/\lambda$	$F_{calc.}$	$F_{obs.}$	<i>hkl</i>	$\sin \theta/\lambda$	$F_{calc.}$	$F_{obs.}$
001	0.071	-20	22	001	0.071	-20	22
20 $\bar{1}$	0.107	3	3	011	0.121	10	12
202	0.107	-13	9	002	0.135	-8	7
200	0.146	61	49	012	0.182	2	2
002	0.146	-7	6	020	0.193	-7	5
20 $\bar{3}$	0.149	29	15	021	0.211	22.5	21
40 $\bar{3}$	0.199	22	22	003	0.224	5	7
201	0.208	6	3	013	0.237	-6	2
402	0.211	-7	6	022	0.244	-8	7.5
20 $\bar{4}$	0.211	-18	17	004	0.297	17	17
404	0.218	-42	47	023	0.299	19	23
003	0.221	5	6	031	0.306	5	3
40 $\bar{1}$	0.244	18	16	014	0.312	14.5	15
40 $\bar{5}$	0.247	9	8	032	0.323	1	<2
202	0.256	-10	9	033	0.357	1	<2
20 $\bar{5}$	0.283	-5	4	024	0.360	-7.5	4
400	0.296	-2	4	005	0.374	13.5	16
004	0.297	17	17	015	0.375	-1	<2
60 $\bar{4}$	0.299	-16	16	040	0.388	-3	—
406	0.302	5	5	034	0.406	0	<2
60 $\bar{5}$	0.305	-2	3	025	0.410	1.5	—
60 $\bar{6}$	0.325	6	6	042	0.419	14	12
203	0.344	2	2	016	0.444	-1	<2
401	0.351	12	9	043	0.446	-7.5	6
20 $\bar{6}$	0.354	7	5	006	0.446	5	6
60 $\bar{7}$	0.354	-11	8	026	0.460	-2.5	3
407	0.364	-2	2	035	0.474	7	7
005	0.377	-14	13	052	0.514	3.5	2
60 $\bar{1}$	0.390	9	9	017	0.526	-3	2
60 $\bar{8}$	0.399	-4	4	027	0.540	3	3
804	0.406	6	6	008	0.593	4	3
80 $\bar{5}$	0.406	-10	10	018	0.601	-4	3
807	0.410	-6	5	028	0.602	0	—
204	0.413	13	10	110	0.062	55	45
402	0.416	-5	3	200	0.147	61	49
408	0.429	-16	15	210	0.175	-37	40
80 $\bar{8}$	0.432	5	3	020	0.194	-6	5.5
006	0.452	6	5	120	0.208	-15	12.5
609	0.457	0	—	310	0.244	17.5	17
80 $\bar{3}$	0.457	-9	5	220	0.244	6	4
809	0.458	-7	6	400	0.295	-2	4
403	0.478	5	6	320	0.295	-22	19
205	0.487	-5	3	130	0.300	-9	7
20 $\bar{8}$	0.494	-13	10	410	0.312	19	17
1007	0.500	4	2	230	0.325	-0.5	<2
100 $\bar{8}$	0.510	0	—	420	0.351	12	10
1006	0.510	-3	<2	330	0.364	1	<2
1049	0.517	-4	3	510	0.376	1	3
007	0.517	-2	2	040	0.388	-3	2
100 $\bar{5}$	0.530	-6	6	140	0.394	-2.5	2
80 $\bar{1}$	0.532	2	2	430	0.413	-6	6
404	0.545	0	—	240	0.413	-4.5	4
602	0.552	1	<2	520	0.414	-10	9
209	0.566	4	2	600	0.439	-6	2
100 $\bar{11}$	0.572	-3	3	340	0.439	-1	<2
60 $\bar{11}$	0.572	-4	2	610	0.449	-0.5	3
008	0.588	-3	4	530	0.466	4	<2
80 $\bar{12}$	0.604	-4	5	620	0.480	4.5	2.5
100 $\bar{12}$	0.604	0	2	440	0.485	-3	2
120 $\bar{8}$	0.608	-5	3	150	0.489	-4	2
120 $\bar{10}$	0.608	0	2	250	0.505	-2	<2
207	0.621	-2	<2	710	0.519	0	—
12011	0.621	2	2	540	0.525	-1	<2
120 $\bar{7}$	0.624	5	3	630	0.526	-6	5
40 $\bar{11}$	0.627	-2	<2	350	0.528	-2.5	<2
20 $\bar{10}$	0.634	0	3	720	0.544	-2	3
120 $\bar{6}$	0.634	-3	2				

Fig. 6. $\rho(x, z)$.

Discussion of the Structure

Using the obtained parameter values, the following interatomic distances and bond angles were calculated as follows:

$$\begin{aligned} C_3'-C_3 &= 1.54 \text{ \AA}, \\ \angle C_3' C_3 C_2 &= 110^\circ, \\ C_3-C_2 &= 1.52 \text{ \AA}, \\ \angle C_3 C_2 C_1 &= 115^\circ, \\ C_2-C_1 &= 1.48 \text{ \AA}, \\ \angle C_2 C_1 O_1 &= 126^\circ, \\ C_1-O_1 &= 1.28 \text{ \AA}, \\ \angle C_2 C_1 O_2 &= 110^\circ, \\ C_1-O_2 &= 1.31 \text{ \AA}, \\ \angle O_1 C_1 O_2 &= 124^\circ. \end{aligned}$$

The length of hydrogen bond is $O_1 \cdots O_2 = 2.63 \text{ \AA}$, and the shortest Van der Waals distance is $3.20 \text{ \AA}$ (between C_2 and O_2''). These are shown in Fig. 7.

As for the difference of lattice parameters of succinic acid crystal from others, it is only due to that of

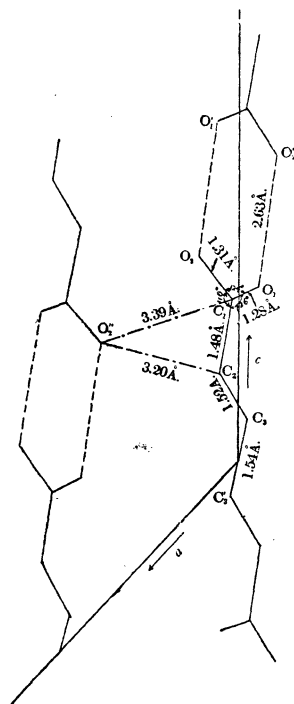


Fig. 7.

the packing of the molecular chains, each of which being similarly hydrogen-bonded.

The structure determined so far agrees approximately with that given by MacGillavry⁴⁾ and by Robertson.⁵⁾ However, there can be seen some difference with respect to C-O distances. These are listed in the following table.

	MacGillavry	Robertson	Hirokawa
C_1-O_2	1.38 Å	1.29 Å	1.31 Å
C_1-O_1	1.28	1.23	1.28

Thus, on one hand, the distance of C_1-O_2 obtained by the present author agrees more closely with that of Robertson, while, on the other hand, the distance of C_1-O_1 agrees better with that of MacGillavry.

It seems rather difficult to decide which of these come closest to the actual state of the structure of carboxylic radical in the crystal.

Summary

Oscillation and Weissenberg photographs using $\text{CuK}\alpha$ ($\lambda = 1.539 \text{ \AA}$) radiation show that the crystals of adipic acid are built upon a monoclinic unit cell having $a = 10.14 \text{ kX}$, $b = 5.16 \text{ kX}$, $c = 10.03 \text{ kX}$, and $\beta = 137^\circ$.

The space group is $C_{2h}^2 - P2_1/a$. This unit cell contains two molecules of $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$, the centres of the mass of the molecules being at $0, 0, 0$ and $1/2, 1/2, 0$ respectively. Positions of atoms in the unit cell are given by the following parameters; the carboxyl carbon (C_1), $x = 0.021$, $y = -0.090$, $z = 0.329$; α -methylenic carbon (C_2), $x = 0.056$, $y = -0.160$, $z = 0.210$; β -methylenic carbon (C_3), $x = -0.021$, $y = 0.038$, $z = 0.054$; oxygen I (O_1), $x = -0.078$, $y = 0.110$, $z = 0.290$; oxygen II (O_2), $x = 0.106$, $y = -0.240$, $z = 0.479$. The molecule is approximately planar and the plane of carboxyl radical is slightly twisted about the molecular axis.

The plane of zigzag carbon chain makes an angle about 40° to (010) and the molecules are linked with strong hydrogen bond along c -axis, and may be said to form a kind of chain lattice.

The author is indebted to Dr. Y. Go who suggested him to investigate this subject and to Prof. I. Nitta for his adequate suggestion and encouragement throughout this work. He also wishes to thank Mr. I. Taguchi for discussion of details.

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Theory of Electrolytic Solution Computing Ion-Dipole Interaction

I. Dielectric Properties

By Masasi YASUMI

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The dielectric properties of electrolytic solutions have been treated theoretically based on the consideration of ion-dipole interaction. The magnitude of ion-dipole interaction have been calculated by assuming a suitable model for solution. Theoretical formulae for relaxation time, dielectric constant, and loss factor of electrolytic solution have been obtained. The formula in the limiting case of a dilute solution, is identical with that of Sack and Debye.

I. Introduction

The dielectric properties of electrolytic solution are different from those of pure solvent, though we neglect ion conductivity. The reason of this difference is based on (i) the interaction between ions and (ii) ion-dipole interaction. The magnitude of former effect was calculated quantitatively by Debye and Falkenhagen.⁽¹⁾ The latter effect was early pointed out by Mizushima,⁽²⁾ but quantitative calculation of this effect was difficult. The approximate methods of calculating this effect can be made in two different ways. (a) We consider a dipole located at the center of the dipole field, which affects the motions of ions. This method was developed by Oka.⁽³⁾ (b) We consider an ion as a center of ionic field which affects the motions of dipoles. Sack⁽⁴⁾ and Debye⁽⁵⁾ succeeded in calculating dielectric constant of dilute electrolytic solution from the latter point of view, but they could not calculate relaxation time and dielectric loss factor.

In the present paper we shall calculate dielectric constant, loss factor and relaxation time of strong electrolytic solution according to the method (b) which is, however, different from that of Sack and Debye.

When an electrolyte is dissolved into a polar solvent, the dipoles of the solvent will be arranged around an ion by the ionic field. If an external electric field is applied to this solution, motions of solvent dipoles will be different from those of pure solvent, owing to

the presence of the ionic field, which hinders the rotation of dipoles. Thus the motions of dipoles will become elastic, and the mean moment of a dipole will be reduced. At the same time, the mean relaxation time will be smaller.

Based on the following model, we shall treat this phenomena quantitatively.

II. Model and Hypotheses Used

(1) For the sake of convenience in calculation we assume the following model for a structure of solution. We consider a conducting shell of radius β_j with electric charge $-z_j e$ around an ion of radius α_j with electric charge $z_j e$, where z_j denotes valency of j -th ion, and $-e$, the electronic charge. Between an ion and a shell lie dipoles, and a solution is filled up by these shells.

If we assume this model for the solution, a dipole of solvent at the distance r from the center of an ion, has potential energy $-\mu z_j e / r^2$ from α_j to β_j , and when $r > \beta_j$, its value becomes zero suddenly. Here μ denotes effective moment, which depends on r , but as a first approximation we shall assume that it has a constant value.

(2) We shall further assume that the relaxation time of ionic atmosphere (Ionenwolke) has a different order of magnitude from that of dipole rotation; so that we may consider them separately.

(3) The resistance of media against dipole rotation will be assumed to obey Stokes' law of hydrodynamics, and the viscosity coefficient, which appears in Stokes' expression, has the same magnitude as that of macroscopic viscosity.

(4) The distribution function of dipoles f is assumed to be independent of r (distance from the center of an ion).

III. Fundamental Equation and its Solution

To know the change of relaxation time, dielectric constant and loss factor caused by the introduction of electrolyte into the solvent, we have to calculate the mean relaxation time, and the mean electric moment under the influence of ionic field when the external field is applied.

If f denotes the distribution function of

(1) Debye and Falkenhagen, *Physik. Z.*, **29**, 128, 402 (1928).

(2) S. Mizushima, *Jour. Chem. Soc. Japan*, **49**, 1 (1928).

(3) Syoten Oka, *Proc. Phy-Math. Soc. Japan*, **17**, 454 (1935).

(4) H. Sack, *Physik. Z.*, **28**, 199 (1927).

(5) P. Debye, "Polare Molekeln", Leipzig (1929).

dipoles in a shell in an external field, f satisfies the following equation.⁽⁶⁾

$$\frac{\partial f}{\partial t} = \frac{kT}{\rho} \Delta f + \frac{1}{\rho} \operatorname{div}(f \operatorname{grad} u) \quad (1)$$

where u denotes potential energy of a dipole;

$$u = u_0 + u_1 e^{i\omega t} \quad (2)$$

$$u_0 = -\frac{\mu e z_j}{r^2} \cos \vartheta \quad (3)$$

$$u_1 = -\mu F \cos \vartheta'. \quad (4)$$

In these equations u_0 is the potential energy of a dipole in the absence of the external field. ϑ is the angle between the axis of dipole and a line which joins the center of dipole with that of ion. u_1 is the potential energy due to an external field. ϑ' is the angle between the electric field vector and dipole axis. ρ denotes the resistance constant and is expressed as

$$\rho = 8\pi\eta a^3 \quad (5)$$

according to the assumption (3) of II. η is the viscosity coefficient, a , the radius of a sphere of dipole, ω , circular frequency, k the Boltzmann constant, T , the absolute temperature and t , the time.

By assumption (4) of II, Eq. (1) is to be solved on the condition of $r = \text{constant}$. The mean electric moment $\bar{\mu}_{jr}$ on the surface of shell $r = \text{constant}$ around j -th ion is evaluated according to the method developed by Kubo.⁽⁷⁾

The result obtained is as follows:

$$\bar{\mu}_{jr} = \frac{F e^{i\omega t}}{kT} \cdot \frac{\mu^2 R}{3} \frac{1}{1 + i\omega \bar{\tau}_{jr}} \quad (6)$$

where R represents the reduction factor

$$R = 1 - L^2(y) \quad (7)$$

$$y = \frac{\mu e z_j}{r^2 k T} \quad (8)$$

and L is the Langevin function. $\bar{\tau}_{jr}$ is the mean relaxation time on a shell $r = \text{constant}$ and has the following form:⁽⁸⁾

$$\bar{\tau}_{jr} = \frac{2}{2kT} R. \quad (9)$$

The mean relaxation time and mean electric moment of dipoles located in the said spheric shell are represented as follows:

$$\bar{\tau}_j = \frac{\rho}{2kT} \int_{\alpha_j}^{\beta_j} \{1 - L^2(y)\} \cdot 4\pi r^2 dr / \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr \quad (10)$$

$$\bar{\mu}_j = \gamma_j F e^{i\omega t} \quad (11)$$

where

$$\gamma_j = \frac{\mu^2}{3kT} \int_{\alpha_j}^{\beta_j} \frac{\{1 - L^2(y)\}}{1 + i\omega \bar{\tau}_{jr}} \cdot 4\pi r^2 dr / \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr. \quad (12)$$

The mean relaxation time and the mean electric moment (of whole solution) have the following forms:

$$\begin{aligned} \bar{\tau} &= \sum n_j (\beta_j^3 - \alpha_j^3) \bar{\tau}_j / \sum n_j (\beta_j^3 - \alpha_j^3) \\ \bar{\mu} &= F e^{i\omega t} \cdot \sum n_j (\beta_j^3 - \alpha_j^3) \gamma_j / \sum n_j (\beta_j^3 - \alpha_j^3) \\ &= F e^{i\omega t} \cdot \gamma. \end{aligned} \quad (14)$$

IV. Relaxation Time, Dielectric Constant and Loss Factor of Electrolytic Solution

A. Relaxation Time.—It can be seen from Eq. (9) that an electrolytic solution must have many relaxation times instead of one. However, to obtain a rough estimation, we can replace them by their mean value (Eq. (13)). Especially when we deal with dilute solution, the use of mean value will be a good approximation. This mean value is represented by Eq. (13). (see also Eq. (10)).

B. Dielectric Constant and Loss Factor.—Dielectric constant (complex) ϵ consists of two parts, the first part coming from solvent molecules and the second part from ions. We assume simply that ϵ is obtained by the addition of these two parts, i. e.

$$\epsilon = \epsilon_a + \epsilon_i \quad (15)$$

where ϵ_a is the part of solvent molecules and ϵ_i of ions. ϵ_i can be calculated by the Debye-Falkenhagen theory.⁽¹⁾⁽⁹⁾ (We do not write its formula explicitly.)

It seems to us that there is no satisfactory relation between ϵ_a and the mean electric moment $\bar{\mu}$ or γ , but we assume tentatively Clausius-Mosotti's hypothesis, i. e.,

$$\left\{ \frac{\epsilon_a - 1}{\epsilon_a + 2} - \frac{n^2 - 1}{n^2 + 2} \right\} V_0 - P_A = \frac{4\pi}{3} \gamma, \quad (16)$$

where γ is represented by Eq. (14). V_0 denotes molecular volume, P_A , atomic polarization, and n , refractive index of solution.

ϵ_a has real and imaginary parts,

$$\epsilon_a = \epsilon_a' - i\epsilon_a'' \quad (17)$$

Calculating γ from Eq. (14), we can obtain ϵ_a by the use of Eq. (16). The real part of

(6) Debye and Ramm, *Ann. Physik*, **28**, 28 (1937).

(7) Ryôgo Kubo, *Nippon Sôgaku-Buturigaku-kaisi*, **16**, 293 (1942).

(8) The dipoles on spherical shell $r = \text{constant}$ have many relaxation times, i. e., τ_{jr} 's instead of one, because the dipoles are affected by the ionic field.⁽⁶⁾⁽⁷⁾ However, these relaxation times are not so widely distributed⁽⁷⁾ that we can use their mean value $\bar{\tau}_{jr}$ without serious errors.

(9) H. Falkenhagen, "Electrolytes" Oxford University Press, London (1934).

ϵ_a (ϵ_a') denotes the dielectric constant and the imaginary part (ϵ_a''), the loss factor due to solvent molecules. If we know ϵ_a , we can calculate total dielectric constant (complex) ϵ from Eq. (15).

V. β_j

To evaluate ϵ_a , we must know γ_j . To calculate γ_j , we must know β_j . β_j may be called **effective screening radius**, and is generally dependent on temperature, solvents, solute, and the concentration of solution. We shall consider most possible forms of β_j .

A. Static Model.—As $\frac{4\pi}{3}\beta_j^3$ is the volume of afore-described sphere, $\sum \frac{4\pi}{3}\beta_j^3 n_j$ will be proportional to the volume apportioned to $\sum n_j$ ions, i.e., to the unit volume, when we adopt static model.

$$\frac{4\pi}{3} \sum n_j \beta_j^3 = K^3 \quad (18)$$

Here K represents a constant, which is independent of above-mentioned variables. Using this model we can derive the Sack-Debye formula⁽⁴⁾⁽⁵⁾ for dielectric constant of dilute solution. We shall discuss later this problem.

B. Dynamical or Statistical Model.—Considering thermal motions of ions, β_j should be dependent on temperature, electrolyte, solvent, and the concentration of solution. We assume that β_j is proportional to radius of ionic cloud $1/\kappa$, which appears in Debye-Hückel theory,⁽⁹⁾⁽¹⁰⁾ i.e.,

$$\beta_j = \frac{A}{\kappa} = A \left(\frac{\epsilon_0' kT}{4\pi e^2 \sum n_j z_j^2} \right)^{\frac{1}{2}} \quad (19)$$

where ϵ_0' is static dielectric constant of the solvent.

VI. Evaluation of Relaxation Time, Dielectric Constant and Loss Factor

A. Relaxation Time.—The mean relaxation time is represented by Eq. (13). The mean relaxation time of dipoles around j -th ion is represented by Eq. (10). The following is the formula rewritten:

$$\bar{\tau}_j = \tau_0 \int_{\alpha_j}^{\beta_j} \{1 - L^2(y)\} \cdot 4\pi r^2 dr \bigg/ \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr \quad (10)$$

$$\tau_0 = \rho / 2kT \quad (10')$$

To obtain the value of $\bar{\tau}_j$, it is necessary to calculate

$$\int_{\alpha_j}^{\beta_j} \{1 - L^2(y)\} \cdot 4\pi r dr. \quad (20)$$

The integration is difficult, but this value can be evaluated as follows. Divide the integration into three parts as follows:

$$\int_{\alpha_j}^{\beta_j} = \int_{\alpha_j}^{\frac{b_j}{2}} + \int_{\frac{b_j}{2}}^{\frac{3}{2}b_j} + \int_{\frac{3}{2}b_j}^{\beta_j} \quad (21)$$

where b_j is defined by Eq. (22).

$$b_j = z_j^{1/2} \left(\frac{\mu e}{kT} \right)^{1/2} \quad (22)$$

b_j is the value of r which makes $y = 1$, i.e., the distance at which the potential energy $\mu e z_j / r^2$ is equal to kT .

In the first term of the right hand side of Eq. (21), $L(y)$ can be replaced by $1 - 1/y$, for $(y)_{r=b_j/2} = 4$, $L(4) \doteq 1 - 1/4$. In the third term, we can replace $L(y)$ by $y/3$, for $(y)_{r=3b_j/2} = 4/9$, $L(4/9) = 0.1469 \doteq 1/3(4/9) = 0.1480$.

The second part can be transformed into the following form, according to the first mean value theorem of integration calculus.⁽¹¹⁾

$$\begin{aligned} & \int_{\frac{1}{2}b_j}^{\frac{3}{2}b_j} \{1 - L(y)\} 4\pi r^2 dr \\ &= \{1 - L^2(\xi)\} \int_{\frac{1}{2}b_j}^{\frac{3}{2}b_j} 4\pi r^2 dr \\ &= 4\pi \{1 - L^2(\xi)\} \cdot \frac{13}{12} b_j^3 \\ & \quad (4 > \xi > 4/9) \end{aligned}$$

The integral (21) can be rewritten as follows:

$$\begin{aligned} \int_{\alpha_j}^{\beta_j} \{1 - L^2(y)\} 4\pi r^2 dr &= 4\pi \left[\int_{\alpha_j}^{\frac{b_j}{2}} \frac{2r^4}{b_j^2} dr \right. \\ & \quad \left. + \frac{13}{12} \{1 - L^2(\xi)\} b_j^3 + \int_{\frac{3}{2}b_j}^{\beta_j} \left(1 - \frac{b_j^4}{9r^4}\right) r^2 dr \right] \\ &= 4\pi \left[\frac{1}{3} \beta_j^3 - \left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} b_j^3 \right. \\ & \quad \left. - \frac{2}{5} \frac{\alpha_j^5}{b_j^2} + \frac{1}{9} \frac{b_j^4}{\beta_j} \right] \\ &\doteq \frac{4\pi}{3} \left[\beta_j^3 - 3 \left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} b_j^3 \right. \\ & \quad \left. + \frac{1}{3} \frac{b_j^4}{\beta_j} \right] \quad (23) \end{aligned}$$

This formula holds only when $\beta_j > 3/2 b_j$ (i.e., solution not concentrated).

Here we neglected $2/5 (\alpha_j^5/b_j^2)$, considering it very small. Considering α_j^3 small as compared with β_j^3 , we can approximately rewrite Eq. (10) as follows.

(10) Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1928).

(11) See, Whitaker and Watson, "Modern Analysis," p. 65, 4th edition (1935).

$$\bar{\tau}_j \doteq \tau_0 \left[1 - 3 \left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \left(\frac{b_1}{\beta_j} \right)^3 + \frac{1}{3} \left(\frac{b_j}{\beta_j} \right)^4 \right] \quad (24)$$

Using Eqs. (22) and (18) or (19), $\bar{\tau}_j$ can be calculated, and $\bar{\tau}$ also. (by Eq. (13)).

B. Static Dielectric Constant ($\omega = 0$).—The static field is specified by the notation ∞ ($\lambda = \infty$).

$$\gamma_{j\infty} = \frac{\mu^2}{3kT} \int_{\alpha_j}^{\beta_j} \{1 - L^2(y)\} 4\pi r^2 dr \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr \quad (25)$$

This formula can be evaluated according to the same procedure as relaxation time.

$$\gamma_{j\infty} \doteq \frac{\mu^2}{3kT} \left[1 - 3 \left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \left(\frac{b_j}{\beta_j} \right)^3 + \frac{1}{3} \left(\frac{b_j}{\beta_j} \right)^4 \right] \quad (26)$$

Static dielectric constant $\epsilon_{d\infty}$ can be calculated from the following equation:

$$\left\{ \frac{\epsilon_{d\infty} - 1}{\epsilon_{d\infty} + 2} - \frac{n^2 - 1}{n^2 + 2} \right\} V_0 - P_A = \frac{4\pi}{3} \gamma_{\infty}, \quad (27)$$

where

$$\gamma_{\infty} \doteq \frac{\sum n_j \gamma_{j\infty} \beta_j^3}{\sum n_j \beta_j^3}. \quad (28)$$

For dilute solutions, we can derive limiting formula. By differentiation of Eq. (27) we can obtain

$$\begin{aligned} \Delta \epsilon_a &= \frac{4\pi}{3} \frac{(\epsilon_0' + 2)^2}{3V_0} \Delta \gamma_{\infty} \\ &\doteq - \frac{4\pi}{3} \frac{(\epsilon_0' + 2)^2}{3V_0} \frac{\mu^2}{3kT} \left[3 \left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \left(\frac{\sum n_j b_j^3}{\sum n_j \beta_j^3} \right) \right] \end{aligned} \quad (29)$$

where

$$n_j = \frac{Nc}{10^3} \nu_j \quad (30)$$

and N is Avogadro's number, c , concentration in mole per liter, and ν_j , number of j -th ions in electrolyte molecule.

Using static model, β_j is represented by Eq. (18). Eq. (29) is rewritten as follows.

$$\begin{aligned} \Delta \epsilon_a &= - \left(\frac{4\pi}{3} \cdot \frac{\mu^2}{3kT} \right) \left(\frac{(\epsilon_0' + 2)^2}{3V_0} \right) \left(\frac{4\pi}{3} \right) \\ &\quad \left[3 \left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \right] \left(\frac{\mu e}{kT} \right)^{\frac{3}{2}} \\ &\quad \left(\frac{Nc}{10^3 K^3} \right) \sum \nu_j z_j^{\frac{3}{2}} = -B \times c \sum \nu_j z_j^{\frac{3}{2}} \end{aligned} \quad (31)$$

B represents a constant independent of c , ν_j and z_j .

Sack and Debye derived an equation for the

dielectric constant of dilute electrolytic solution.⁽⁴⁾⁽⁵⁾

$$\epsilon_{d\infty} = \epsilon_0' (1 - B' c \sum \nu_j z_j^{\frac{3}{2}}). \quad (32)$$

Eq. (31) has a similar form as Eq. (32). They determined B' experimentally and obtained a value 3.3 at room temperature.⁽¹²⁾ If we put $K^3 = 2$ (all the spheres of radii β_j 's belonging to the ions of the same sign just fill up the whole solution), Eq. (31) can be rewritten at 20° as follows, ($\epsilon_0' = 80.1$, $V_0 = 18.05$, $\mu = 0.8168D$).⁽¹³⁾

$$\Delta \epsilon_{d\infty} = 2.64 \times 10^2 c \sum \nu_j z_j^{\frac{3}{2}}$$

or

$$\epsilon_{d\infty} = 80.1 \{ 1 - 3.3 c \sum \nu_j z_j^{\frac{3}{2}} \}. \quad (33)$$

The constant B' is found to be 3.3.⁽¹⁴⁾ This value agrees well with that of Sack and Debye 3.3 obtained experimentally, but this numerical agreement is rather fortuitous, since we have used so many hypotheses and simplifications.

Assuming dynamical model $\Delta \epsilon_{d\infty}$ is written as follows from Eqs. (29), (19) and (22).

$$\begin{aligned} \Delta \epsilon_{d\infty} &= - \frac{4\pi}{3} \cdot \frac{\mu^2}{3kT} \cdot \frac{(\epsilon_0' + 2)^2}{3V_0} \\ &\quad \frac{[3\{0.103 + \frac{13}{12} L^2(\xi)\}]}{A^3} \cdot \left(\frac{\mu e}{kT} \right)^{\frac{3}{2}} \\ &\quad \left(\frac{4\pi e^2}{\epsilon_0' kT} \right)^{\frac{3}{2}} N^{\frac{3}{2}} c^{\frac{3}{2}} \frac{\sum \nu_j z_j^{\frac{3}{2}}}{\sum \nu_j} \left(\sum \nu_j z_j^{\frac{3}{2}} \right)^{\frac{3}{2}} \\ &= -B'' c^{\frac{3}{2}} \frac{(\sum \nu_j z_j^{\frac{3}{2}})}{\sum \nu_j} \times \left(\sum \nu_j z_j^{\frac{3}{2}} \right)^{\frac{3}{2}} \end{aligned} \quad (34)$$

$\Delta \epsilon_{d\infty}$ is proportional to $c^{\frac{3}{2}}$.

For dilute solutions, experimental values of $\Delta \epsilon_{d\infty}$ are so inconsistent that we cannot see whether Eq. (31) or (34) is valid. We hope that reliable experimental values will appear in the near future.

C. Dielectric Constant and Loss Factor in Non-Static Case.—Dielectric constant and loss factor in non-static field ($\omega > 0$) are calculated from Eqs. (12), (14) and (16), but this calculation is very laborious though not impossible. For a rough estimation, there is a simpler method. We assume that an electrolytic solution has a single relaxation time which is represented by $\bar{\tau}$ (Eq. (13)). Then the complex dielectric constant is calculated by the following equation.

(12) There are many experimental values that are not represented by Eq. (32), cf. ref. (5).

(13) This value is obtained from the equation $\left(\frac{\epsilon_0' - 1}{\epsilon_0' + 2} - \frac{n^2 - 1}{n^2 + 2} \right) V_0 = \frac{4\pi}{3} \frac{\mu^2}{3kT}$. It is much smaller than that of gas.

(14) In order to obtain the value of B , we assume that $L^2(\xi) = \frac{1}{2} \{ L^2(4) + L^2(4/9) \} = 0.294$ in Eq. (31), so that the numerical value in Eq. (33) is rather ambiguous.

$$\left(\frac{\epsilon_a-1}{\epsilon_a+2}-\frac{n^2-1}{n^2+2}\right)V_0-P_A=\frac{4\pi}{3}\gamma_\infty\frac{1}{1+i\omega\bar{\tau}}. \quad (35)$$

γ_∞ and $\bar{\tau}$ are evaluated by Eqs. (26), (28), (13) and (24). A convenient method to calculate ϵ_a' and ϵ_a'' from $\bar{\tau}$ and γ_∞ is given by Debye.⁽⁵⁾

D. Dielectric Properties at Long Wave Length Region ($\omega\bar{\tau}\ll 1$).—In this case γ_j is represented approximately as follows. Divide γ_j into two parts, i. e.,

$$\gamma_j = \gamma_j' - i\gamma_j'' \quad (36)$$

$$\begin{aligned} \gamma_j' &= \frac{\mu^2}{3kT} \int_{\alpha_j}^{\beta_j} \frac{\{1-L^2(y)\}}{1+\omega^2\bar{\tau}_j^2} \cdot 4\pi r^2 dr \bigg/ \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr \\ &\doteq \frac{\mu^2}{3kT} \int_{\alpha_j}^{\beta_j} \{1-L^2(y)\} 4\pi r^2 dr \bigg/ \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr. \end{aligned} \quad (37)$$

This integration is evaluated already and is equal to $\gamma_{j,\infty}$ (Eq. (26)).

$$\gamma_j'' = \frac{\mu^2\omega\tau_0}{3kT} \int_{\alpha_j}^{\beta_j} \{1-L^2(y)\}^2 4\pi r^2 dr \bigg/ \int_{\alpha_j}^{\beta_j} 4\pi r^2 dr. \quad (38)$$

Eq. (38) can be evaluated by a similar procedure as in the case of $\gamma_{j,\infty}$, but writing out its formula here will be omitted.

E. Dielectric Properties at Short Wave Length Region ($\omega\bar{\tau}\gg 1$).—In this case $\gamma_j' \doteq 0$ and $\gamma_j'' \doteq (\mu^2/3kT) \times (1/\omega\tau_0)$. It means that in this region the properties of electrolytic solution are almost the same as those of pure solvent.

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New Colorimetric Determination of Copper in Biological Matters

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Introduction

Recently the presence of minute amounts of copper in biological matter is taken up as an interesting problem. Its determination has been conducted by various colorimetric methods, but among them the method with sodium diethyldithiocarbamate has been generally applied as the most suitable and the most sensitive since it was first used by Callan and Henderson.⁽¹⁾ However, this reagent often requires a preliminary separation of copper from other elements for procuring good results as it does not react alone with copper. Hence, for preliminary separation of copper, hydrogen sulfide separation,⁽²⁾ electrolytic separation⁽³⁾ and ammonium hydroxide separation method⁽¹⁾⁽⁴⁾ were proposed by many workers, but none of these methods became widely used as an approved method.

A better preliminary separation method of copper was therefore desired. Sylvester and

Lampitt⁽⁵⁾ attempted this problem by determining copper in milk after extracting it with dithizone and chloroform. At the same time Sandell⁽⁶⁾ determined copper by the mixed colored method or the extractive titration method with dithizone after preliminarily removing copper completely as dithizonates. This is proposed, however, for copper in silicate rocks. Nydahl⁽⁷⁾ used the same method as Sylvester and Lampitt in determining copper in fats using carbon tetrachloride in place of chloroform as an extractant.

Thus the preliminary separation of copper had been generally improved by the application of dithizone. Yet these can not be approved to be the best and the most accurate methods in colorimetric determination owing to their own drawback. The principal reason for this defect lies in the difficulty of transferring the colored products completely into the solvent. Consequently it does not conform with the Lambert-Beer's law and the color comparison must be done at the loss of accuracy and sensitivity of the reagent as pointed out by many

(1) T. Callan and J. A. R. Henderson, *Analyst*, **54**, 650 (1929).

(2) L. W. Conn, A. H. Johnson, H. A. Trebler and V. Karpenko, *Ind. Eng. Chem., Anal. Ed.*, **7**, 15 (1935); R. W. Thatcher, *J. Am. Chem. Soc.*, **55**, 4524 (1933).

(3) F. Grendel, *Pharm. Weekblad.*, **67**, 913, 1343 (1930); *Z. anal. Chem.*, **97**, 47 (1934).

(4) J. H. Hamence, *Trans. Faraday Soc.*, **30**, 299 (1934).

(5) N. D. Sylvester and L. H. Lampitt, *Analyst*, **60**, 377 (1935).

(6) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **9**, 464 (1937).

(7) F. Nydahl, *Z. anal. Chem.*, **116**, 315 (1939).

workers.⁽⁸⁾

The reaction of copper with the reagent was thoroughly studied by the author⁽⁹⁾ and above mentioned difficulty was solved by extracting copper diethyldithiocarbamate compound with carbon tetrachloride in the presence of hydroxylamine. As already reported in a former report, colorimetric determination of copper has become more accurate and speedy. Such being the case, when it was required to investigate the copper content in biological matters, dithizone was used for preliminary separation after studying those methods mentioned above and then copper was determined colorimetrically by applying a new method, the details of which are in the following.

Experiment

Decomposition.—McFarlane⁽¹⁰⁾ destroyed the biological matter in the sample by insertion in a muffle oven at 380° to 400° for 12 hours. Sylvester *et al.* and Winter⁽¹¹⁾ both recommended 500° to 550° in a silica dish with some sulfuric acid. The upper limit of temperature has not been set, but in this experiment it was performed in a silica dish at 400° to 450° in an electric furnace. The use of gas flame is undesirable owing to the greater possibilities of introducing impurities in the sample.

Nydahl recommended the wet-ashing method with nitric acid and perchloric acid in the presence of sulfuric acid after which the copper is to be determined in the resulting solution upon filtration of silica and calcium sulfate. It was noticed by the present author that the results are lower by this method especially in the presence of a large amount of silica, owing most probably to the occlusion in the silica. Such being the case, it is safer to remove the silica with hydrofluoric acid and perchloric acid and dissolve the residue in hydrochloric acid, when it is much abundant.

Isolation of Copper.—Though it cannot be said that sodium diethyldithiocarbamate is specifically reactive to copper alone comparing with other metals, it is highly sensitive to the element. It is, therefore, necessary that copper is preliminarily separated from other metals to obtain the best results. Generally there are many cases in which preliminary isolation with some reagents is undesirable as the reagent would impede the sensibility and the accuracy of the determination to follow. However such precautions are unnecessary in this case as the dithizone used to isolate copper is more sensitive than sodium diethyldithiocarbamate and moreover has spectroscopic sensitivity.

Some workers recommended isolation with hydrogen sulfide but this was found to be defective not as sensitive as had been reported: this defect was also recognized by the author. Thus dithizone was used to concentrate copper in the alkaline solution containing sodium citrate with a slight excess of ammonia (approximately pH 8.5) according to the Sandell's directions. The extraction in the alkaline solution as compared with the extraction in acid solution proposed by Hibbard⁽¹²⁾ was purposely tried with a view of simultaneously determining zinc and lead with copper. The determination of zinc and lead are being studied⁽¹³⁾. The presence of citrate is important in preventing the precipitation of iron hydroxide which absorbs some copper. Though some workers have denied such absorption,⁽¹⁴⁾ it has been reported and was also confirmed by the author. Higher pH than the cited is not desirable, as copper may be extracted in the enol form instead of keto form, resulting in failure to separate copper from lead and zinc in the next operation. This may be avoided by not adding too much ammonia and not shaking too long in the first extraction.

Under the conditions described already, the extraction of copper is completely accomplished with Pb, Zn, Ni, Co, Bi, Cd in part and sometimes Fe and Mn. When the carbon tetrachloride layer is shaken with hydrochloric acid solution (approximately 0.01 N) copper remains virtually unchanged in the carbon tetrachloride along with the greater part of Bi, Co and Ni. But Pb, Zn and Cd transfers into the aqueous phase. This treatment has already been recommended by several workers^{(6),(15)} as successful in separating copper from Pb and Zn.

Interference.—This reagent, though it has been widely used for copper determination, is not exclusively reactive with copper, but reacts with such metals as Bi, Fe, Mn, Ni, Co and Cr forming colored complexes and with Zn, Pb, Mg, Cd, Sb, Sn and Al becoming turbid. Under the conditions recommended, such metals as the majority of the elements mentioned above form dibizonates, but Sb, Sn, Ti, Al and Cr do not react with it.

Among the elements extracted as dithizonates, Zn, Pb and Cd separate perfectly into the acid solution being isolated from copper by the treatment with 0.01N hydrochloric acid. The amounts of Fe and Mn extracted are extremely small owing to the addition of citrate which prevents its reaction with dithizone.

Thus the interference due to the presence of the elements except for these above mentioned must be considered. But the interference due to Bi or Hg are practically not encountered because of their scarcity in biological matters, though there are a few exceptions. In a former report⁽⁹⁾ the sensitivity of Mn, Co, Ni, Bi, Zn, Pb, Fe and Ti were reported by the author and permissible amounts in determination were discussed. In practice

(8) Walker, *J. Assoc. Offici. Agr. Chem.*, **13**, 426 (1930); T. P. Hoar, *Analyst*, **62**, 36 (1937); D. L. Drabkin, *ibid.*, **21**, 203 (1938); O. B. Winter, *J. Assoc. Offici. Agr. Chem.*, **19**, 36 (1936); E. J. Coulson, *J. Assoc. Offici. Agr. Chem.*, **20**, 178 (1937).

(9) Y. Murakami, *This Bulletin*, **23**, 3 (1950).

(10) McFarlane, *Biochem. J.*, **29**, 480 (1929).

(11) O. B. Winter, *J. Assoc. Offici. Agr. Chem.*, **19**, 359 (1936).

(12) P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 615 (1938).

(13) Y. Murakami, *This Bulletin*, in press.

(14) L. A. Haddock and E. Evers, *Analyst*, **57**, 495 (1932).

(15) Y. Morita, *J. Chem. Soc. Japan*, in press.

cal use, no serious interference were found under the desirable conditions. It is not necessary to mention here the use of dithizone as its use was studied thoroughly by many successive workers and already proved to be the best.

Reagent and Apparatus.—Practical precautions regarding apparatus and some reagents were presented in a former report. Therefore some descriptions of reagent except them will be given here.

Perchloric acid, 70%, analytical grade. Hydrofluoric acid: it is best purified by distillation with platinum apparatus. Sodium citrate, 10% solution: Add 36g. of sodium hydroxide to 63g. of citric acid (monohydrate) and dilute to 1000 ml. On the recommendation by Sandell it can be purified. Dithizone, 0.01% solution. Ammonia, saturated. Hydrochloric acid (1:1). Hydrochloric acid 0.01 *N*. Sodium diethyldithiocarbamate, 0.1% solution. Hydroxylamine, 4% solution. Carbon tetrachloride. Separatory funnel, about 30 ml. capacity. Silica dish.

Procedure.—Weight 0.01g. to 0.015g. ash into a silica dish and add 10 to 15 ml. of hydrochloric acid (1:1). (If the sample is particularly abundant in silica, add 0.3 ml. of 70% perchloric acid and 1 ml. of hydrofluoric acid (1:1). Maintain the temperature constant till the dish becomes dull red. Continue heating until the solution was evaporated up and the excess of perchloric acid has been expelled). Then add 5 ml. of water to bring all soluble matter into solution by gentle heating. Repeat this procedure if necessary.

Next add 5 ml. of 10 per cent sodium citrate and add drops of saturated ammonia until the solution becomes alkaline to the litmus paper reaction and continue to add an excess of 0.2 ml. If the solution becomes noticeably turbid on the addition of ammonia, it is well to let it stand for a while before beginning the filtration. Filter the solution through a small filter paper of medium texture: transfer any residue in the dish to the paper and wash three or four times with 1 ml. portions of cold water containing a drop of ammonia and citrate solution. Transfer the filtered solution to a separatory funnel, and 5 ml. of 0.01 per cent dithizone solution and shake for 0.5 minute: if the carbon tetrachloride is not green at the end of this time, shake for more half a minute. Allow the carbon tetrachloride to settle and draw it off into another separatory funnel leaving a few drops in it to prevent loss of aqueous solution.

It is important that the separated carbon tetrachloride be free from droplets of aqueous solution. Iron so introduced will oxidized the reagent and became the cause of difficulties in the determination. Unless the separated carbon tetrachloride is distinctly green, showing that an excess of reagent is not present, add another 5 ml. portion of 0.01 per cent reagent to the aqueous solution and shake vigorously for 30 to 40 seconds. Draw it off and continue in this manner until the last 5 ml. of dithizone remains distinctly green after being shaken vigorously.

To separate copper add 10 ml. of 0.01 *N* hydrochloric acid to the combined extracts and shake vigorously for one minute. If the carbon tetrachloride remains red on shaking and does not

become greenish or purple, add sufficient dithizone solution to change the red to a bluish or purplish color which recombine copper liberated on this treatment. Draw off the carbon tetrachloride layer into another separatory funnel and shake vigorously for two minutes with 10 to 12 ml. of 0.01 *N* hydrochloric acid. Run the carbon tetrachloride into a silica dish, discarding the aqueous solution in which zinc, lead and others may be present. Evaporate the solvent on a waterbath till dry, add 3 or 4 drops of nitric acid (1:1) to moisten the residue.

Then evaporate and ignite gently to destroy all organic matter. To the cold dish add one ml. of hydrochloric acid (1:1) and rub the interior of the dish by means of a glass rod so that all the cupric oxide will be dissolved. Add 10 ml. of water, transfer into the separatory funnel and rinse thoroughly with some water. Make the solution alkaline with ammonia to litmus paper and add the excess of 0.2 ml. ammonia solution. Then add 2 ml. of 4 per cent hydroxylamine solution and next 10 ml. of 0.1 per cent sodium diethyldithiocarbamate solution. It becomes instantly golden yellow due to the copper. Shake vigorously with 7 ml. of carbon tetrachloride and draw it off into a 25 ml. volumetric flask after leaving it to settle. Leave a few drops of the carbon tetrachloride to prevent mixing of the aqueous solution and rinse the stem of funnel with 2 ml. of carbon tetrachloride. In this extraction the stem should be perfectly dried. Then shake again in the same manner as before. Usually two shakings are sufficient to extract completely the colored matter. Then fill to the mark with carbon tetrachloride and measure the extinction with Pulfrich Photometer using S 43 Filter (434m μ). If the final volume is reduced to less than 25 ml., then less than 5 γ of copper can be determined with fair results.

Accuracy and Reproducibility.—As reported already, the application of hydroxylamine has increased the sensitivity of the reagent because the extraction can be completely carried out and proved that it holds closely to the Lambert-Beer's law and the range of error lies within $\pm 5\%$ according to the amounts of copper (5 γ to 20 γ) in 25 ml. carbon tetrachloride solution. In this report, to examine the separation and extraction with dithizone, biological matters with known amounts of copper were tested as shown in Table 1, proving that this new method can be used as a sufficiently accurate and simple method for application.

Table 1
Reproducibility

	Sample	E*	Copper found, Content,	
			γ	%
Spinach	1.0037 g	0.320(a)	7.99	0.0080
		0.321	7.96	0.0079
Burdock	0.9521 g	0.698(b)	59.22	0.0603
		0.693	57.46	0.0603
Bone dust	0.8232 g	0.245(a)	6.11	0.0074
		0.257	6.39	0.0078

* E: Extinction coefficient

(a) When the cell of 50 mm. thickness was used (final volume 25 ml.).

(b) When the cell of 30 mm. thickness was used (final volume 50 ml.).

Results.—The copper content of some biological matter was determined closely following the new method proposed above (Table 2).

can be determined in two hours or less after bringing the sample into solution. The experiments already related has proved that it is

Table 2
Determination of Copper in Biological Matter

Sample	Ash, %	Ash taken, g.	E (50 mm.)	Cu found, r	Cu in ash, %	Remarks
Rice (Japan)	0.78	0.0328	0.064	1.58	0.0048	Saitama Prefecture (1943) uncleaned rice, 2nd class.
Rice (Burmese)	0.84	0.0444	0.426	10.60	0.0024	Basein Dist.(1943)
Spinach	16.99	0.1004	0.321	7.99	0.0080	Chiba Pref. March, 1943
Potato	1.93	0.0775	0.065	1.59	0.0021	Dehydrated, Saitama Prefecture June, 1943
Carrot	5.97	0.0121	0.294	7.30	0.0061	Dehydrated, Saitama Prefecture Autumn, 1943
Burdock	4.25	0.0952	0.693 ^(b)	58.34	0.0606	Dehydrated, Chiba Prefecture Autumn, 1943
Soy bean	4.38	0.0915	0.190	4.73	0.0052	Manchuria
Cabbage	6.02	0.0674	1.083	26.94	0.0400	Dehydrated
Fish meal	15.43	0.1015	0.181	4.50	0.0045	
Bone dust	55.43	0.0823	0.251	6.25	0.0076	
Bone dust	57.87	0.0670	0.180	4.48	0.0066	

Though a remarkable amount of copper was found in many of the samples, the above experiments were not performed for the purpose of obtaining results form such a study. The above was conducted strictly and quantitatively to determine the use for which this method is valid.

Summary

The new method for the determination of a minute amounts of copper in biological matters by extraction with dithizone and coloration with sodium diethyldithiocarbamate has been tested. By the adaption of this method, copper

one of the most accurate methods in comparison with other methods which have been used. As recent studies are throwing light upon the biological action of copper, a more accurate method for copper determination is sought by chemists and biologist interested in this problem. This new method will fulfil its mission in being of invaluable importance in this respect.

The author wishes to take this opportunity to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance and invaluable advices throughout this study.

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Studies on Foams. V. The Effect of Electrolytes on Triphenyl Methane Dye Solutions

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It is usually considered that a solution of alkaline nature, in general, produces much foams when it is shaken, while the acidic one does not foam. This is supposed to be due to the action of the minute quantity of soap produced by the saponification of acidic matters in dirt. For example, Goette⁽¹⁾ described that some oily dirt contains 31.4% of fatty

acids, the mean number of carbon atoms of which being 38. It may be considered that the solution containing organic amines will produce more stable foam in acidic solution than in alkaline one. From this standpoint, the effects of electrolytes on the foam formation of triphenyl methane dye solutions were studied. In the present experiments, the effects of sodium chloride, hydrochloric acid and sodium hydroxide on the foaming ability of

(1) E. K. Goette, *J. Colloid Sci.*, **4**, 459 (1949).

brilliant green and crystal violet solutions have been determined.

One gram of the each dye (Merck's sample) was dissolved in one litre of water, respectively. After keeping it on standing for one week, the electrolytes were added and the concentration of dye was adjusted to 0.8 g. per litre. The method of experiment has been described in the preceding report.⁽²⁾ Twenty cc. of solution was taken in a test tube of 40 cc. capacity, and shaken up and down for 300 seconds. The height of maximum foam zone, A_m , and the reciprocal of the mean velocity of foam collapse in the initial 30 seconds, τ , were determined. The foaming ability, F , of the solution is defined as the products of A_m and τ . Surface tension was measured by du Nouy's tensiometer and recorded as the specific surface tension relative to the solution containing the same concentration of electrolyte: γ/γ_s . Measurements were undertaken at the room temperature (27°). The results obtained for crystal violet are depicted in Fig. 1. An analogous curve is obtained for brilliant green.

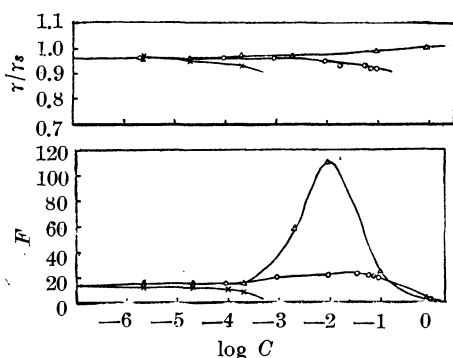


Fig. 1.—Crystal violet, O, NaCl; Δ , HCl; $\times$, NaOH

The surface tensions of the solutions of both dyes decrease by the addition of sodium chloride, while the foaming ability shows a maximum point at the concentration of 0.0356 *N* sodium chloride. In the cases of hydrochloric acid and sodium hydroxide, the surface tensions increase with the decrease of *pH* value, and the foaming abilities become maximum at 0.0917 *N* hydrochloric acid. The foam of the electrolyte solution is by far the less stable than that of the solution containing dye.

The dye, in general, is a colloidal electrolyte and forms micelles in its solution. This was suggested, for instance, by Pauli and Lang⁽³⁾ from the results of measurements of electrical conductivity. The dye micelles are considered to exist in an equilibrium with the single ions of dye in the solution. It has been reported

in the foregoing paper,⁽⁴⁾ that the foam formation of the solution is closely connected to the molecular structure of the dye molecules and its surface activity, and the foam formation is mainly influenced by the portion dispersed as single ion. This conclusion was obtained by the comparison of foam formation of dyes having various molecular structures. In order to explain, however, the variation of foam formation of one dye in detail, the displacement of equilibrium, (micelle) $\rightleftharpoons$ (ion) should also be taken into consideration.

The variations of foam formation and surface tension by electrolytes are accounted by the displacement of equilibrium and by the change of surface activity, as described in the preceding paper.⁽²⁾ The displacement of equilibrium by neutral electrolytes is understood as a preceding phenomenon of coagulation. These dyes precipitate at about 0.9 *N* of sodium chloride.

In order to account for the effects of acids and alkalis, both of the change of *pH* of solution and the structural change following to it should be taken into consideration. For example, the color change of congo red by the variation of *pH* was attributed by Wo. Ostwald⁽⁵⁾ to the change of particle size. Later, A. Hantzsch⁽⁶⁾ accounted it with the structural change of dye ion. The latter conception has been widely accepted. The change of structure, therefore, should be taken into account, when dye changes its color with the variation of *pH*. Such a structural change will affect the equilibrium between micelle and ion, and the foam formation will accordingly change.

The change of electrical charge and molecular structure of crystal violet have been discussed conclusively by Adams and Rosenstein⁽⁷⁾ by means of absorption spectra. According to them, dye ions having electrical charge 0, +1 + 2, + 3 and + 4 are colorless, violet, yellow, green and colorless, respectively. These ions coexist in chemical equilibrium in the solution. When *pH* of solution decreases, the mean value of electrical charge increases.

The surface activity of dye ion increases, as stated in the preceding paper,⁽²⁾ when the hydrophilic character becomes weaker or hydrophobic character becomes stronger. Since the radical having an electrical charge has the strong hydrophilic character, both of the hydrophilic property of ion and the surface tension of the solution increase when *pH* of solu-

(4) M. Nakagaki, this Bulletin, **22**, 200 (1949).

(5) Wo. Ostwald, *Kolloid-Z.*, **10**, 97; 132 (1912); **24**, 67 (1919).

(6) A. Hantzsch, *Kolloid-Z.*, **15**, 79 (1914); *Ber.*, **48**, 158 (1915).

(7) E. Q. Adams and Rosenstein, *J. Am. Chem. Soc.*, **36**, 1452 (1914).

(2) M. Nakagaki, this Bulletin, **23**, 47 (1950)

(3) W. Pauli and F. Lang, *Monatsh.*, **67**, 159 (1936).

tion becomes smaller. This conclusion coincides with the data cited in Fig. 1. The foam formation may be accounted under the consideration of the shift of equilibrium (micelle) $\rightleftharpoons$ (ion), and of the variation of surface activity of dye ion. The equilibrium displaces to ion side when the hydrophilic character of ion increases. Since the foam formation of solution is thought to be mainly contributed from the portion dispersed in single ion state, the foam formation will increase when *pH* of solution decreases and the hydrophilic character of ion increases. When *pH* of solution became small enough, the foam formation begins to decrease owing to the decrease of surface activity of dye ion. By these two factors, the foam formation becomes maximum at the concentration 0.00917 *N* of hydrochloric acid.

Analogous explanation will be valid also for soap solutions. The variations of foam formation with *pH* for sodium salts of palmitic, myristic, and lauric acid are measured by G. D. Miles and J. Ross.⁽⁸⁾ A maximum of foam

formation has been observed on alkaline side, in opposition to the case of crystal violet and brilliant green. This is reasonable, since soaps are sodium salts of fatty acids and dyes are hydrochlorides of organic amines.

Summary

Effects of sodium chloride, hydrochloric acid, and sodium hydroxide on the surface tension and foam formation of solutions of crystal violet and brilliant green were measured. By the addition of sodium chloride surface tension decreases and foam formation shows a maximum. In the cases of hydrochloric acid and sodium hydroxide, surface tension increases with the decrease of *pH* and foam formation shows a maximum at about *pH* = 2. These results were accounted by the change of surface activity of dye ion and the displacement of the equilibrium (micelle) $\rightleftharpoons$ (ion).

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

The Diffusion of Dye Solutions

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Numbers of method are known by which the particle size of colloid is determined. Among these, the measurement of the diffusion velocity is used especially for the colored solution, since the distribution of the concentration can easily be estimated by the colorimetry. Diffusion methods have already been described by R. Auerbach,⁽¹⁾ Wo. Ostwald and A. Quast,⁽²⁾ and K. Brass and K. Eisner.⁽³⁾ These methods, however, contain some ambiguity in the calculation of the diffusion coefficient. In the present report, the results of determination of the particle size of congo red solutions containing sodium chloride will be described by using the calculation method developed by the author.

The apparatus used is shown in Fig. 1 (a). M is the diffusion cell, made of a capillary tube, 10 cm. in length, 0.13 cm. in inner diameter and sealed at one end. S is a rubber stopper and D is another capillary tube which

was used to make flow out the excess of the solution in A. The experimental procedure is as follows. The diffusion cell, M, is filled with distilled water or some other solvent and then dipped upside-down into the dye solution, A, as shown in the figure. After about 24 hours, the cell is taken out and the diffused amount of dye is determined by the colorimetry. The standard solutions are prepared by diluting the original dye solution. A number of capillary tubes which have the same thickness with M are filled with the standard solutions. One of the tubes, N, is placed side by side with M as shown in Fig. 1 (b) and the colors are compared. The position of the color

of the same intensity in the tube M with the standard solution is found by this way. The distribution of the concentration of dye in the

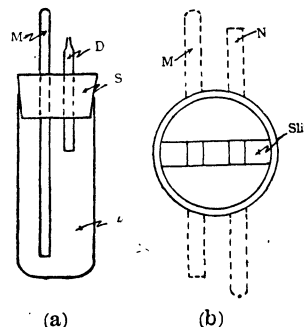


Fig. 1.

(1) R. Auerbach, *Kolloid-Z.*, **35**, 202 (1924); **37**, 379 (1925).

(2) Wo. Ostwald and A. Quast, *Kolloid-Z.*, **48**, 83 (1929); **51**, 273, 361 (1930).

(3) K. Brass and K. Eisner, *Kolloid-Beih.*, **37**, 56 (1933).

tube M is determined by using the standard solutions of various dilutions.

The relation between concentration c and the diffused distance x is expressed by Fick's equation

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2}, \quad (1)$$

where D_e is the apparent diffusion coefficient, and t the time. D_e is considered as a constant. This equation is solved under the initial and boundary conditions:

$$\left. \begin{array}{l} \text{at } t = 0 \text{ and } x > 0, \quad c = 0, \\ \text{and at } t \geq 0 \text{ and } x = 0, \quad c = c_0, \end{array} \right\} \quad (2)$$

and the result,

$$D_e = \frac{x^2}{t} \varphi(v), \quad (3)$$

$$\text{where} \quad v = c_0/c, \quad (4)$$

and $\varphi(v)$ is defined as follows:

$$\begin{aligned} 1/v &= c/c_0 \\ &= 1 - (2/\sqrt{\pi}) \int_0^{1/(2\sqrt{\varphi})} \exp(-\xi^2) d\xi. \end{aligned} \quad (5)$$

The value of $\varphi(v)$ has been calculated as a function of v by R. Fürth⁽⁴⁾ for $v \geq 2$. The value of $\varphi(v)$ for $v < 2$ was newly calculated and tabulated in Table 1, together with that of R. Fürth. It should be noticed that the value $\varphi = 3.80$ for $v = 1$ used by Wo. Ostwald and A. Quast⁽²⁾ and A. Nistler⁽⁵⁾ is entirely faulty.

An example of data obtained for congo red solution is given in Table 2. It is seen that the apparent diffusion coefficient D_e varies with the concentration at distance x . Referring to other data, it is seen that the apparent diffusion coefficient varies also with the concentration.

Table 1
The Value of $\varphi(v)$

v	$\varphi(v)$	v	$\varphi(v)$	v	$\varphi(v)$
1	∞	1.9	1.25	10	0.185
1.1	38.2	2	1.099	12	0.166
1.2	11.26	3	0.532	15	0.147
1.3	5.80	4	0.379	16	0.142
1.4	3.73	5	0.303	24	0.120
1.5	2.63	6	0.262	32	0.107
1.6	2.09	7	0.234	48	0.0931
1.7	1.71	8	0.212	64	0.0854
1.8	1.47	9	0.197		

Since the diffusion coefficient D is a function of concentration, Fick's equation should be written over again as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right). \quad (6)$$

(4) R. Fürth, *Phys. Z.*, **26**, 719 (1925); *Kolloid-Z.*, **41**, 300 (1927).

(5) A. Nistler, *Kolloid-Beih.*, **31**, 1 (1930).

Referring to the calculation of R. Fürth⁽⁴⁾ and using the initial and boundary conditions of Eq. (2), this is solved as

$$\frac{1}{v} = \frac{c}{c_0} = \frac{\int_{x/\sqrt{t}}^{\infty} (1/D) \exp\left\{-\int_0^{\lambda} (\lambda/2D) d\lambda\right\} d\lambda}{\int_0^{\infty} (1/D) \exp\left\{-\int_0^{\lambda} (\lambda/2D) d\lambda\right\} d\lambda}, \quad (7)$$

Table 2
Diffusion of Congo Red in Distilled Water

Concentration at distance, x	$\varphi(v)$	Distance diffused, x , cm.	Apparent diffusion coefficient, D_e , $10^{-6} \text{cm}^2/\text{sec.}$	Differential diffusion coefficient, D , $10^{-6} \text{cm}^2/\text{sec.}$
0.0231 44	0.0965	1.35	2.14	2.25
0.0253 40	0.100	1.32	2.12	2.25
0.0675 15	0.147	1.07	2.05	2.22
0.1012 10	0.185	0.94	1.99	2.22
0.1265 8	0.212	0.88	2.00	2.21
0.1519 6.8	0.240	0.83	2.01	2.20
0.2531 4	0.379	0.65	1.94	2.19
0.3374 3	0.532	0.52	1.76	2.16
0.5062 2	1.099	0.33	1.46	2.12
0.6327 1.6	2.09	0.23	1.34	2.10

Concentration of original solution: $c_0 = 1.012 \text{ g./l.}$
Temperature: $T = 25^\circ\text{C.}$

Time of diffusion: $t = 0.823 \times 10^5 \text{ sec.}$

$\alpha = 1.537$; $\beta = 0.277$; $D_0 = \alpha^2 = 2.36(10^{-6} \text{cm}^2/\text{sec.})$.

where D is considered as a function of a parameter λ . D is often called as "differential" diffusion coefficient. Now, this equation may be rewritten in the form:

$$D = -\frac{1}{2t} \cdot \frac{dx}{dc} \int_0^c x dc. \quad (8)$$

From the experiment described above, c is obtained as a function of x , and D can be calculated. Since the numerical calculation is, however, somewhat troublesome, some other device is desirable. One method may be to recalculate the apparent diffusion coefficient to differential diffusion coefficient. As shown in Fig. 2, where the data of Table 1 was plotted,

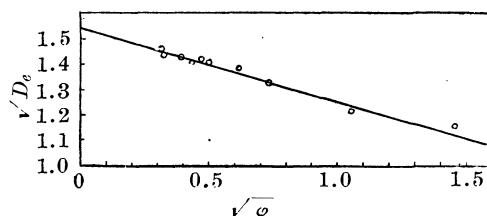


Fig. 2.

the empirical formula

$$\sqrt{D_e} = \alpha - \beta\sqrt{\varphi} \quad (9)$$

is approximately valid. Then, Eq. (8) be-

comes to

$$D = \alpha^2 \left\{ 1 - \frac{\sqrt{\pi}}{2} \frac{\beta}{\alpha} \frac{1}{v} \exp.(1/4 \varphi) \right\}. \quad (10)$$

The differential diffusion coefficient calculated from this equation decreases with the increase of the concentration at distance x , though it is not affected with the concentration of original solution. Such a variation of differential diffusion coefficient is usually thought to be due to the decrease of activity coefficient of solute with the increase of its concentration, and Einstein-Sutherland's equation

$$D = \frac{RT}{N \cdot 6\pi\eta r} \quad (11)$$

is valid only for the infinite dilution. In this equation, R is the gas constant, T is the absolute temperature, N is Avogadro's number, η is the viscosity of solvent, and r is the radius of the diffusing particles. The diffusion coefficient at infinite dilution D_0 is given by

$$D_0 = \alpha^2. \quad (12)$$

For congo red solution at 25°, the values for D_0 were found as: 2.46×10^{-6} cm.²/sec. for original concentration of 5.062 g./l., 2.45×10^{-6} cm.²/sec. for 3.037 g./l., 2.36×10^{-6} cm.²/sec. for 1.012 g./l., and the average 2.42×10^{-6} cm.²/sec. ($\pm 3\%$).

The effect of diffusion potential should be considered on the diffusion of colloidal electrolyte. When a colloidal electrolyte diffuses, counter ions go faster than colloidal ions, and diffusion potential is established. This accelerates the diffusion of colloidal ions. Extremely large diffusion coefficient is, therefore, obtained for entirely pure colloidal electrolyte in pure water. Such a diffusion potential can be eliminated if neutral salt, or "supporting electrolyte", is added in the diffusion column, as stated by G. S. Hartley and C. Robinson,⁽⁶⁾ C. Robinson,⁽⁷⁾ E. Valkó,⁽⁸⁾ and S. Lenher and J. E. Smith.⁽⁹⁾ But the addition of electrolyte may cause the aggregation of colloidal particles, so the estimation of particle size by diffusion is a delicate matter.

The diffusion coefficient of congo red solution in presence of sodium chloride was measured and the result is cited in Table 3, where D_0 is the differential diffusion coefficient at infinite dilution, and particle radius r is calculated from Eq. (11). Molecular weight M is cal-

culated from the equation

$$M = \frac{4}{3} \pi r^3 N d \quad (13)$$

where N is Avogadro's number and d is the density of the particle assumed to be $d = 1.5$. Dividing the molecular weight by the formula weight of congo red, 696, the degree of association is obtained. Diffusion data for pure congo red solution without sodium chloride, obtained by many investigators, are cited in Table 4. E. Valkó and C. Robinson used extremely purified congo red and conductivity water, so that very large diffusion coefficient was obtained, and other authors used usual distilled water and obtained somewhat smaller values, which coincide with that in Table 3. Referring to these data, it is supposed that the diffusion potential may be reduced by the existence of only a trace of electrolyte. From this standpoint, it can be supposed that the decrease of diffusion coefficient by the addition

Table 3

Particle Size of Congo Red (18°C.)

Concentration of NaCl, N	Diffusion coefficient, D_0 , 10^{-6} cm. ² /sec.	Particle radius, $\text{\AA}$.	Molecular weight, M	Degree of association
0	2.16	9.3	3100	4.5
0.1002	1.80	11.0	5100	7.3
0.2004	1.67	11.8	6300	9.1
0.3006	1.44	13.5	9300	13
0.4008	1.12	17.3	20000	29
0.5010	0.96	19.8	30000	43

Concentration of congo red in original solution is 3.202 g./l.

Table 4

Diffusion of Congo Red

Temperature, °C.	Diffusion coefficient, 10^{-6} cm. ² /sec.	Particle radius, $\text{\AA}$.	Observers
20	0.81~1.16	24.1 ~18.2	Wo. Ostwald and Quast ⁽²⁾
18	0.94~1.31	21.0 ~15.1	A. Nistler ⁽³⁾
6.9	0.78~1.26	18.3 ~11.3	Herzog and Polotzky ⁽¹⁰⁾
18	1.56~1.85	12.6 ~10.6	Fürth and Ullmann ⁽¹¹⁾
25	6.63~7.75	3.78~ 3.23	Valkó ⁽⁸⁾
20	5.67~5.68	3.74~ 3.73	Robinson ⁽⁷⁾

of sodium chloride may be due to the association of particles. The increase of association degree is initially gradual, and then a rapid

(6) G. S. Hartley and C. Robinson, *Proc. Roy. Soc. (London)*, **A 134**, 20 (1932).

(7) C. Robinson, *Proc. Roy. Soc. (London)*, **A148**, 681 (1935); *Trans. Faraday Soc.*, **31**, 245 (1935).

(8) E. Valkó, *Trans. Faraday Soc.*, **30**, 231 (1935).

(9) S. Lenher and J. E. Smith, *J. Phys. Chem.*, **40**, 1005 (1936).

(10) R. O. Herzog and A. Polotzky, *Z. physik. Chem.*, **A 87**, 449 (1914).

(11) R. Fürth and E. Ullmann, *Kolloid-Z.*, **41**, 304 (1927).

increase begins when the concentration of sodium chloride exceeds about 3 *N*, and at last precipitation by coagulation is observed. No tendency to minimize the particle size by a small addition of electrolyte was recognized. Such a peptization effect has been reported by W. Schramek and E. Götte,⁽¹²⁾ and contradicted by many authors.

In order to discuss the particle size from diffusion data, some other factors should also be considered; for example, the shape of particle, the distribution of particle size, and so on. As an approximate treatment, however, the discussion described above will be sufficient.

Summary

The apparent diffusion coefficient of congo red

in water, obtained by Auerbach-Ostwald's method, changes with concentration. Solving the Fick's equation with the assumption that the diffusion coefficient is a function of concentration, the apparent diffusion coefficient can be recalculated to differential diffusion coefficient. From the value extrapolated to infinite dilution, the particle radius of congo red was calculated using Einstein-Sutherland's equation. On the assumption that the particle is spherical and not hydrated, the particle weight and association degree were obtained. The diffusion coefficient, obtained by this method for congo red solution containing various concentration of NaCl, agrees well with the data reported by others. With the increase of salt concentration, the particle size increases gradually. No decrease was observed in the particle size with a small addition of electrolyte.

(12) W. Schramek and E. Götte, *Kolloid-Beih.*, **34**, 218 (1932).

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On the Anomalous Thermal Diffusion Observed in Mixed Electrolyte Solution

By KOZO HIROTA

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The appearance of a kind of diffusion potential caused by thermal separation or thermal diffusion potential in solid systems⁽¹⁾ was pointed out by Wagner. The similar phenomenon in aqueous systems, though expected theoretically, seems not to have been observed.

The present writer made a series of experiments on a number of electrolytes in aqueous solutions with a thermal diffusion apparatus of Clusius and Dickel type, and observed, independently of Gillespie and Breck,⁽²⁾ an anomalous phenomenon, i.e., so-called "negative effect" or enrichment of some ions at the hotter region of the apparatus in the mixed electrolyte solutions.⁽³⁾ By his investigation continued thereafter,⁽⁴⁾ it seemed probable that the effect was brought about by a kind of potential produced by the difference of thermal diffusion velocity of each ion. An experimental basis of this proposition was the absence of the

mutual effect when a non-electrolyte, such as urea, was added to sodium chloride or when sulfuric acid, having the same degree of thermal diffusion velocity, was added to the solution of hydrogen chloride. Finally, though qualitatively, the mechanism was theoretically supported after the method of Abegg and Mose⁽⁵⁾ who, introducing the idea of diffusion potential, could derive the change of diffusion velocity of an electrolyte by the uniform addition of another electrolyte, but the negative effect could not be derived.

Recently, Guthrie, Wilson and Schomaker⁽⁶⁾ made a theoretical formulation of the separation of solution in general with the same idea of thermal diffusion potential even in the case when the Clusius-Dickel's separation column was used. Thus the treatment of G. W. and S. is much valuable to the discussion about the anomalous effect mentioned above.

According to Guthrie and others, separation ratio of AX-BX type, R_a , which is defined by the ratio of the concentration of A ion at the bottom of the separation apparatus to that at

(1) C. Wagner, *Ann. der Phys.*, (5) **3**, (1929); **6**, 370 (1930).

(2) L. J. Gillespie and S. Breck, *J. Chem. Phys.*, **9**, 370 (1941).

(3) K. Hirota, this Bulletin, **16**, 232 (1941); *J. Chem. Soc. Japan* **63**, 105 (1942).

(4) K. Hirota, *J. Chem. Soc. Japan*, **64**, 112 (1943); cf. *Chem. Abst.*, **41**, 3346 (1947).

(5) Abegg and Mose, *Z. physik. Chem.*, **30**, 545 (1899); W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(6) G. Guthrie, J. N. Wilson and V. Schomaker, *J. Chem. Phys.*, **17**, 310 (1949).

the top, is given by

$$R_a = \left\{ (u_a + u_x) R_{ax} c_a + [(u_a + u_x)(u_b + u_x) R_{ax} - u_a(u_b + u_x) R_{ax}] \frac{c_b}{u_x} \right\} \times \frac{1}{(u_a + u_x) c_a + (u_b + u_x) c_b} \quad (1)$$

where R_{ax} and R_{bx} are the separation ratios of AX and BX, respectively, while u_i is ionic mobility of i -ion and c_a and c_b , concentrations of AX and BX, respectively.

Applying the formula to HCl-NaCl and HCl-NH₄Cl systems, G. W. and S. could derive the negative effect with much success. However, as these systems are only a special part of writer's data, it will be interesting to extend the check of the formula over the other systems when the concerned electrolytes are different

- b) The separation ratios of both components increase: NaOH-NaCl.
- c) The separation ratios of both components decrease: H₂SO₄-Na₂SO₄.
- d) The separation ratio of one component ion increases and that of the other and of the same electric sign decreases: NaOH-Na₂CO₃; HCl-NaCl; HCl-NH₄Cl; NaCl-NH₄Cl.

Among these systems, it is unnecessary to discuss on a), while the system having, at least, one bivalent ion is not suited for the check of Eq. (1), due to the marked change of activity by the existence of other ions. Therefore, the following systems, HCl-NaCl, HCl-NH₄Cl, NaCl-NH₄Cl and NaOH-NaCl will be discussed. The calculated result, as shown in Table 1, is obtained from the following constants.

The ionic mobility at 50° used in the cal-

Table 1
Summarised Results for the Check of Eq. (1)

Expt. No.	Concentration		Separation ratio**)				Remark
	c_a	c_b	A(obs.)	A(calc.)	B(obs.)	B(calc.)	
I. HCl (A)-NaCl (B)							
1	0.50	0.50	1.34	1.39	0.97	0.96	—
2	0.050	0.530	1.47 ₇	$\left\{ \begin{array}{l} 1.78 \\ (1.51) \end{array} \right.$	1.02 ₉	$\left\{ \begin{array}{l} 1.02 \\ (1.03) \end{array} \right.$	$\left\{ \begin{array}{l} R_{ax} \text{ 1.16} \\ R_{bx} \text{ 1.046} \end{array} \right.$
3	0.35	2.54	1.47 ₆	$\left\{ \begin{array}{l} 1.07 \\ (1.78) \end{array} \right.$	1.03 ₃	$\left\{ \begin{array}{l} 1.01 \\ (1.02) \end{array} \right.$	$\left\{ \begin{array}{l} R_{ax} \text{ 1.25} \\ R_{bx} \text{ 1.06} \end{array} \right.$
4	0.130	2.79	1.54	$\left\{ \begin{array}{l} 1.81 \\ (1.68) \end{array} \right.$	1.05 ₄	$\left\{ \begin{array}{l} 1.03 \\ (1.05) \end{array} \right.$	$\left\{ \begin{array}{l} R_{ax} \text{ 1.20} \\ R_{bx} \text{ 1.06} \end{array} \right.$
5	0.0186	2.51	1.65	$\left\{ \begin{array}{l} 1.88 \\ (1.59) \end{array} \right.$	1.05 ₅	$\left\{ \begin{array}{l} 1.04 \\ (1.06) \end{array} \right.$	$\left\{ \begin{array}{l} R_{ax} \text{ 1.17} \\ R_{bx} \text{ 1.06} \end{array} \right.$
II. NH ₄ Cl (A)-NaCl (B)							
6	0.01	0.10	1.00 ₄	$\left\{ \begin{array}{l} 0.99 \\ (1.02) \end{array} \right.$	1.04 ₄	$\left\{ \begin{array}{l} 1.06 \\ (1.05) \end{array} \right.$	$\left\{ \begin{array}{l} R_{ax} \text{ 1.026} \\ R_{bx} \text{ 1.044} \end{array} \right.$
7	1.00	0.96	0.99*)	0.99	1.05 ₂	1.06	—
III. HCl (A)-NH ₄ Cl (B)							
8	0.50	0.50	1.42	1.46	0.89	0.86	—
IV. NaOH (A)-NaCl (B)							
9	0.044	0.089	1.42	1.75	1.13	0.88	—

Calculated values not in parentheses are determined by use of R_i 's of one normal, i.e., 1.22 for HCl, 1.047 for NaCl, 1.010 for NH₄Cl and 1.30 for NaOH, while those in parentheses by use of R_i 's in the last column of the table.

*) R_i at the third hour is used.

**) Slight difference of the calculated values from the values of Guthrie and others (Nos. 1 and 8) will be due to the difference of ionic mobilities used in the calculation.

or when the concentrations of both electrolytes are not equal, as will be done in the present note.

It is found by the writer that mixed solutions, having one ion in common, can generally be classified into following four categories, according to the change of separation ratio of each component as a result of mixing.

- a) The separation of the components is independent of each other: HCl-H₂SO₄; Urea-NaCl.

culation is: H⁺ 450, Cl⁻ 116, NH₄⁺ 115, Na⁺ 82 and OH⁻ 280.⁽⁷⁾ The separation ratios adopted in the table are those at the second hour, except the case of Expt. No. 7, though the values extrapolated to the infinite hour are more desirable from the theoretical reason. This is partly due to the convenience of comparing the results with those of G. W. and S.

(7) Interpolated values taken from Landolt-Börnstein's Table.

Separation ratio of each component electrolyte of one normal is identified with R_i of mixed electrolyte solution: i. e., HCl 1.22, NaCl 1.047, NH_4Cl 1.010 and NaOH 1.30. It may be a matter of discussion that such a constant value of R_i is adopted throughout all the systems inspite of their conspicuous dependency on concentration.

In order to restrict the argument concerning the ambiguity in question, the concentration dependency upon R_i of hydrogen chloride, sodium chloride and ammonium chloride is determined with the same apparatus, the result being shown in Table 2.

Table 2

Separation Ratio at the Second Hour of Hydrogen Chloride, Sodium Chloride and Ammonium Chloride

Concn. HCl (Normal)	R_{HCl}	Concn. NaCl (Normal)	R_{NaCl}	Concn. NH_4Cl (Normal)	$R_{\text{NH}_4\text{Cl}}$
0.010	1.19	0.010	1.041		
0.029	1.16	0.025	1.042	0.020	1.018
0.037	1.15				
0.100	1.20	0.100	1.044	0.100	1.025
0.300	1.24				
0.500	1.26				
1.000	1.22	1.000	1.047	1.00	1.010
		2.91	1.065	3.06	1.007

It is noteworthy that in these concentration range there is no possibility of the negative effect regarding NaCl and NH_4Cl . Thus the argument against the proposition of thermal diffusion potential by ascribing the effect to the concentration dependency of the electrolyte concerned may be disappeared.

It can be said that the agreement is good when the concentration of both component is equal (Nos. 1, 6, 7 and 8 in Table 1), and that, besides the systems of HCl-NaCl and HCl- NH_4Cl , the negative effect is confirmed in NaCl- NH_4Cl system (No. 7) which is devoid of HCl. The situation is theoretically not wonderful, because with respect to thermal diffusion velocity which is nearly proportional to (Sep. ratio -1) owing to the narrow annular space of the apparatus used, sodium chloride is much larger than ammonium chloride, contrary to ordinary diffusion velocity.

On the other hand, the agreement becomes fairly worse when their concentrations are not equal (Nos. 2, 3, 4 and 5). Such deviation

can be ascribed to the assumption of fixing R_i independently of concentration. Really it is found that by adopting such proper R_i 's described in the last column of Table 1, the degree of coincidence is improved very much in every system except No. 3.

The unexpected positive effect of Cl^- -ion, perfectly opposite to the theory, in NaOH-NaCl system cannot be explained by the above formula. It seems possible that this phenomenon is due to the concentration effect which, however, cannot be checked owing to the absence of data regarding sodium hydroxide. Nevertheless, it can generally be concluded that the system belonging to categories b) and c) cannot be derived from the theory, i. e., the theory can derive only the system belonging to the categories a) and d). Because, transforming Eq. (1), we obtain

$$R_a = R_{ax} + \frac{c_b(u_b + u_x)(R_{ax} - R_{bx})}{c_a(u_a + u_x) + c_b(u_b + u_x)} \cdot \frac{u_a}{u_x}, \quad (2)$$

it is clear that the ion of larger R_i increases and that of the smaller and of the same electric sign decreases by mixing two electrolytes which have the same ion in common. Thus the result might be ascribed to an effect of non-electrical interaction of ions, but it seems now that further experimental study is required before the attempt of detailed discussion on the systems of category b).⁽⁹⁾

However, it may be said that the occurrence of the thermal diffusion potential is reasonable by the description hitherto made and also that the negative effect is a particular case of such electric interaction between ions.

Summary

The application of the theoretical formula of Guthrie and others on the "negative effect" of thermal diffusion which was found by the writer is extended to the new data. The agreement of the theory with experiment is good in the systems of HCl-NaCl, HCl- NH_4Cl and NaCl- NH_4Cl , even when both components are of unequal concentration. However, in the system of NaCl-NaOH, the theory is perfectly failed, the reason being unknown.

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(8) The specification of the apparatus used: equidistance annular space, 1.5 mm.; its length, 94 cm.; volume of reservoirs, 23 cc.; higher temperature 76°; lower temperature 25°. (cf. *this Bulletin*, 16, 475 (1941).

(9) There is another possible point of discussion concerning the "forgotten effect" in the Clusius' apparatus, as shown by de Groot, Hoogenstraaten and Gorter [*Physica*, 9, 923 (1942).] This effect seems not to be able to explain the anomaly of this system, as a result of simplified calculation attempted by the author.

Fundamental Studies on the Current-Voltage Curve in Polarography.

III. The Equation for the Current-Voltage Curve of the Complex Ion—Especially for the Irreversible Wave⁽¹⁾By Reita TAMAMUSHI⁽²⁾ and Nobuyuki TANAKA⁽²⁾

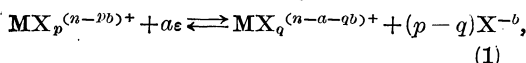
(Received February 20, 1950)

The polarographic literature contains numerous papers dealing with the behavior of complex metal ions, but all the discussion rests on the fact that the oxidation and reduction at the dropping mercury electrode is reversible, or the electrode process is controlled by the diffusion process.⁽³⁾ In the present paper the polarographic wave, especially of the irreversible type, which is obtained by the oxidation and reduction of the complex metal ion at the dropping mercury electrode, is discussed from the viewpoint of the chemical kinetics.

Derivation of the General Formula

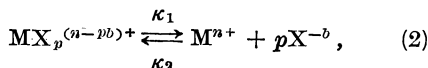
There are various possible types of the electrode reactions which involve complex metal ions, but in this treatment only the reaction, which consists of the oxidation and reduction from one ionic oxidation state to the other, is taken up as an example.

The oxidation-reduction of a complex metal ion may be represented by

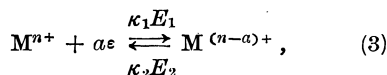


where X^{-b} is the complex-forming substance. In this reaction there may be various cases of the intermediate processes, but in the present paper the consideration will be restricted to the case when the reaction occurs through the following three steps.

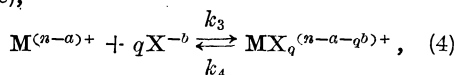
(i) Decomposition of the complex ion,



(ii) Oxidation-reduction reaction,



(iii) Formation of the complex ion (reduced type),



where M^{n+} and $\text{M}^{(n-a)+}$ symbolize the simple or hydrated metal ions and the terms k_1 , k_2 ,

k_3 and k_4 represent the rate constants for each process, respectively. $\kappa_1 E_1$ and $\kappa_2 E_2$ are the rate constants of the reduction (forward) and oxidation (reverse) processes and are represented by the equations:

$$\begin{aligned} \kappa_1 E_1 &= s \cdot \frac{kT}{h} e^{-\Delta F_1/RT} e^{-a\alpha VF/RT} \\ \kappa_2 E_2 &= s \cdot \frac{kT}{h} e^{-\Delta F_2/RT} e^{a(1-\alpha)VF/RT}, \end{aligned}$$

where ΔF_1 and ΔF_2 are the free energies of activation for the forward and reverse reactions, V is the potential difference between the dropping mercury electrode and the interior of the solution, a is the number of the electrons which participate in the reaction, and s is the proportionality constant concerning the nature of the electrode. The value of α is the portion of the total electrode potential which promotes the forward reaction. In the polarography, there exist the diffusion processes at the surface of the dropping mercury electrode besides the reactions mentioned above.

According to the same method as mentioned in the previous paper⁽⁴⁾ the current flowing can be written as follows:

$$\begin{aligned} I &= a\varepsilon K_{C.O.} ([C_{C.O.}]^{\circ} - [C_{C.O.}]) \\ &= a\varepsilon \frac{K_{C.O.}}{f_{C.O.}} ([A_{C.O.}]^{\circ} - [A_{C.O.}]) \\ &= a\varepsilon K'_{C.O.} ([A_{C.O.}]^{\circ} - [A_{C.O.}]) \end{aligned} \quad (5)$$

$$\begin{aligned} I &= a\varepsilon \sigma (k_1 [A_{C.O.}] - k_2 [A_O] [A_X]^p) \\ &= a\varepsilon (k_1' [A_{C.O.}] - k_2' [A_O]), \end{aligned}$$

$$\begin{aligned} k_1' &\equiv \sigma k_1, \quad k_2' \equiv \sigma k_2 [A_X]^p \\ I &= a\varepsilon (\kappa_1 E_1 [A_O] - \kappa_2 E_2 [A_R]) \end{aligned} \quad (6)$$

$$\begin{aligned} I &= a\varepsilon \sigma (k_3 [A_R] [A_X]^q - k_4 [A_{C.R.}]) \\ &= a\varepsilon (k_3' [A_R] - k_4' [A_{C.R.}]), \end{aligned}$$

$$\begin{aligned} k_3' &\equiv \sigma k_3 [A_X]^q, \quad k_4' \equiv \sigma k_4 \\ I &= a\varepsilon K_{C.R.} ([C_{C.R.}] - [C_{C.R.}]^{\circ}) \\ &= a\varepsilon \frac{K_{C.R.}}{f_{C.R.}} ([A_{C.R.}] - [A_{C.R.}]^{\circ}) \end{aligned} \quad (7)$$

(4) N. Tanaka and R. Tamamushi, *Reports of the Radiation Chemistry Research Institute*, **3**, 20 (1948); this Bulletin, **22**, 187 (1949).

R. Tamamushi and N. Tanaka, *Reports of the Radiation Chemistry Research Institute*, **4**, 20 (1949); this Bulletin, **22**, 227 (1949).

(1) Presented at the 3rd annual meeting of the Chemical Society of Japan, in April 1950.

(2) Present address: Institute of Science and Technology, the University of Tokyo, Tokyo.

(3) J.J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

$$= a_{\varepsilon} K'_{C.R} ([A_{C.R}] - [A_{C.R}]^{\circ}) \quad (9)$$

$$\begin{aligned} I &= a_{\varepsilon} \frac{K_X}{p-q} ([C_X] - [C_X]^{\circ}) \\ &= a_{\varepsilon} \frac{K_X}{f_X(p-q)} ([A_X] - [A_X]^{\circ}) \\ &= a_{\varepsilon} \frac{K_X'}{p-q} ([A_X] - [A_X]^{\circ}) \end{aligned} \quad (10)$$

In these equations,

$[C_{C.O.}]$, $[C_{C.O.}]^{\circ}$: the concentrations of the oxidized complex ion at the electrode surface and in the interior of the solution.

$[C_{C.R.}]$, $[C_{C.R.}]^{\circ}$: the concentrations of the reduced complex ion at the electrode surface and in the interior of the solution.

$[C_X]$, $[C_X]^{\circ}$: the concentrations of the complex-forming substance at the electrode surface and in the interior of the solution.

$[A_{C.O.}]$, $[A_{C.O.}]^{\circ}$, $[A_{C.R.}]$, $[A_{C.R.}]^{\circ}$, $[A_X]$, $[A_X]^{\circ}$: the activities for each of the corresponding terms.

$[A_O]$: the activity of the ion M^{n+} at the electrode surface.

$[A_R]$: the activity of the ion $M^{(n-a)+}$ at the electrode surface.

$f_{C.O.}$, $f_{C.R.}$, f_X : the activity-coefficients of the oxidized and reduced complex ions and of the complex-forming substance at the electrode surface.

σ : the constant concerning the nature of the electrode and others.

Let us consider the case when the rate of the reaction by which the reduced complex ion is formed from $M^{(n-a)+}$ is very rapid in comparison with the diffusion process of the ion.

From these relations, the general formula for the current I and the electrode potential V is obtained as below:

$$I/a_{\varepsilon} = \frac{K'_{C.C} K'_{C.R} (k_1' k_3' \kappa_1 E_1 [A_{C.O.}]^{\circ} - k_2' k_4' \kappa_2 E_2 [A_{C.R.}]^{\circ})}{k_2' k_3' K'_{C.O} K'_{C.R} + \kappa_1 E_1 k_3' K'_{C.R} (k_1' + K'_{C.O}) + \kappa_2 E_2 k_2' K'_{C.O} (k_4' + K'_{C.R})} \quad (11)$$

Dividing the numerator and denominator of the right-hand side of Eq. (11) by $K'_{C.O} K'_{C.R} \times k_1' k_3' \kappa_1 E_1$, the relation

$$I/a_{\varepsilon} = \frac{[A_{C.O.}]^{\circ} - \frac{k_2' k_4' \kappa_2 E_2}{k_1' k_3' \kappa_1 E_1} [A_{C.R.}]^{\circ}}{\frac{k_2'}{k_1' \kappa_1 E_1} + \left(\frac{1}{K'_{C.O}} + \frac{1}{k_1'} \right) + \frac{k_2' k_4' \kappa_2 E_2}{k_1' k_3' \kappa_1 E_1} \left(\frac{1}{K'_{C.R}} + \frac{1}{k_4'} \right)} \quad (12)$$

is obtained. For convenience' sake, the abbreviations,

$$\begin{aligned} k_1' \kappa_1 E_1 / k_2' &\equiv [\kappa_1 E_1], \\ k_4' \kappa_2 E_2 / k_3' &\equiv [\kappa_2 E_2], \end{aligned} \quad (13)$$

$$[\kappa_2 E_2] / [\kappa_1 E_1] \equiv [E],$$

and

$$[\kappa_1 E_1] / [\kappa_2 E_2] \equiv [E]',$$

are introduced into Eq. (12), resulting with the

equations,

$$I/a_{\varepsilon} = \frac{[A_{C.O.}]^{\circ} - [E] [A_{C.R.}]^{\circ}}{\frac{1}{[\kappa_1 E_1]} + \left(\frac{1}{K'_{C.O.}} + \frac{1}{k_1'} \right) + [E] \left(\frac{1}{K'_{C.R.}} + \frac{1}{k_4'} \right)} \quad (14)$$

$$= \frac{[E]' [A_{C.O.}]^{\circ} - [A_{C.R.}]^{\circ}}{\frac{1}{[\kappa_2 E_2]} + \left(\frac{1}{K'_{C.R.}} + \frac{1}{k_4'} \right) + [E]' \left(\frac{1}{K'_{C.O.}} + \frac{1}{k_1'} \right)} \quad (14')$$

where $[\kappa_1 E_1]$ and $[\kappa_2 E_2]$ can be regarded as to represent the over-all rate constants of the reduction and oxidation processes at the electrode surface. That is, the over-all rate of the reduction process expressed by (1) is promoted by the terms k_1' and $\kappa_1 E_1$ but retarded by the term k_2' , and, therefore, it can be expressed by $k_1' \kappa_1 E_1 / k_2'$. Eqs. (14) and (14') are the general formulae for the polarographic wave of the oxidation-reduction of the complex metal ion. It is mentioned here that if the solution is bufferized with regard to the complex-forming substance, then the quantity $[A_X]$ is equal to $[A_X]^{\circ}$ in these equations.

In the following section the analysis is set forth in two or three special cases, according to the equations described above.

When the Decomposition Rate of Complex Ion is Very Rapid

In the first place, if the rate of the decomposition of the complex ion at the electrode surface is very rapid in comparison with the rate of the diffusion of the ion, then the following conditions,

$$K'_{C.C} \ll k_1' \quad \text{and} \quad K'_{C.R} \ll k_4'$$

are settled. By considering these conditions, Eqs. (14) and (14') are reduced to

$$I/a_{\varepsilon} = \frac{[A_{C.O.}]^{\circ} - [E] [A_{C.R.}]^{\circ}}{\frac{1}{[\kappa_1 E_1]} + \frac{1}{K'_{C.O.}} + [E] \frac{1}{K'_{C.R.}}} \quad (15)$$

$$= \frac{[E]' [A_{C.O.}]^{\circ} - [A_{C.R.}]^{\circ}}{\frac{1}{[\kappa_2 E_2]} + \frac{1}{K'_{C.R.}} + [E]' \frac{1}{K'_{C.O.}}} \quad (15')$$

Now, two further cases, (A) the case when the diffusion process is rate-determining, and (B) the case when the process which contains the transfer of the electron between the electrode and the ion (activation process) is rate-determining, will be discussed.

(A) Diffusion-controlled Case

The diffusion-controlled case will be defined

as a case when the conditions, $[\kappa_1 E_1] \gg K'_{C.O}$ and $[\kappa_1 E_1] \gg K'_{C.R}$, are satisfied in the potential region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$. Under these conditions the relation between the current and the electrode potential takes the forms:

$$I/a\varepsilon = \frac{[A_{C.O}]^\circ - [E][A_{C.R}]^\circ}{\frac{1}{K'_{C.O}} + [E] \frac{1}{K'_{C.R}}} \quad (16)$$

$$[E] = \frac{\frac{[A_{C.O}]^\circ - I}{a\varepsilon K'_{C.O}}}{\frac{I}{a\varepsilon K'_{C.R}} + [A_{C.R}]^\circ} \quad (17)$$

in the region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$.

Furthermore, as $[\kappa_1 E_1]$ becomes much larger than $[\kappa_2 E_2]$, the current is represented by

$$I = a\varepsilon K'_{C.O} [A_{C.O}]^\circ = a\varepsilon K_{C.O} [C_{C.O}]^\circ \equiv (I_a)_{C.O}, \quad (18)$$

on the other hand, when $[\kappa_1 E_1]$ is smaller than $[\kappa_2 E_2]$,

$$I = -a\varepsilon K'_{C.R} [A_{C.R}]^\circ = -a\varepsilon K_{C.R} [C_{C.R}]^\circ \equiv (I_a)_{C.R}. \quad (19)$$

These relations correspond to the limiting currents controlled by the diffusion process.

From Eqs. (17), (18) and (19) the following equation is derived:

$$[E] = \frac{K'_{C.R} (I_a)_{C.O} - I}{K'_{C.O} I - (I_a)_{C.R}}, \quad (20)$$

which is quite the same as obtained from the Nernst's formula for the reversible wave.

The detailed discussion on the half-wave potential and the other properties of the wave has been set down by J. J. Lingane.⁽⁴⁾

(B) Activation-controlled Case

The activation-controlled case will be defined as a case when the conditions, $[\kappa_1 E_1] \ll K'_{C.O}$ and $[\kappa_1 E_1] \ll K'_{C.R}$, are satisfied in the potential region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$. However, on the current-voltage curve, there may be a region in which the relation, $[\kappa_1 E_1] \gg [\kappa_2 E_2]$ or $[\kappa_1 E_1] \ll [\kappa_2 E_2]$, is satisfied, where the condition, $[\kappa_1 E_1] \ll K'_{C.O}$ or $[\kappa_1 E_1] \ll K'_{C.R}$ is not necessarily fulfilled. To analyse, therefore, the current-voltage curve, it must be divided into the following three parts according to the value of the electrode potential.

(I) $[\kappa_1 E_1] \cong [\kappa_2 E_2]$.—In this case when, according to the above definition, $[\kappa_1 E_1] \ll K'_{C.O}$, Eq. (15) is reduced to the form,

$$I/a\varepsilon = [\kappa_1 E_1] [A_{C.O}]^\circ - [\kappa_2 E_2] [A_{C.R}]^\circ. \quad (21)$$

From this equation, the condition for the point where the current is zero, is obtained as follows:

$$[E]_{I=0} = \frac{[A_{C.O}]^\circ}{[A_{C.R}]^\circ} \quad (22)$$

Eq. (21) means that the current in this part is fully defined by the rates of the activated reaction.

(II) $[\kappa_1 E_1] \gg [\kappa_2 E_2]$.—In this part, the term $[E]$ becomes vanishingly small (and can be regarded as nearly equal to zero). As for convenience, this part is sub-divided into two cases.

(a) $[\kappa_1 E_1] \cong K'_{C.O}$.—Here, the equation which represents the current-voltage curve is

$$I/a\varepsilon = \frac{[A_{C.O}]^\circ}{\frac{1}{[\kappa_1 E_1]} + \frac{1}{K'_{C.O}}}, \quad (23)$$

or

$$[\kappa_1 E_1] = \frac{K'_{C.O} I}{a\varepsilon K'_{C.O} [A_{C.O}]^\circ - I} \quad (24)$$

From these equations it is obvious that the properties of the wave of this part are independent of the reverse reaction.

(b) $[\kappa_1 E_1] \gg K_{C.O}$.—In this case the condition for the limiting current is obtained, i.e.,

$$I = a\varepsilon K_{C.O} [C_{C.O}]^\circ \equiv (I_a)_{C.O}. \quad (18)$$

These equations, which are formally the same with those obtained for the oxidation-reduction of the simple metal ion⁽⁵⁾, show the fact that the part (II) corresponds to the reduction wave with the characteristics of the "irreversible" one.

Introducing the condition for the limiting current into Eq. (24), the next formula is obtained,

$$[\kappa_1 E_1] = K'_{C.O} \frac{I}{(I_a)_{C.O} - I}, \quad (25)$$

or by solving this equation regarding the electrode potential, V , we obtain

$$V = \frac{RT}{a\alpha F} \left(\ln s \cdot \frac{kT}{h} + \ln \Gamma - \ln K'_{C.O} \right) - p \frac{RT}{a\alpha F} \ln [A_X] - \frac{RT}{a\alpha F} \ln \frac{I}{(I_a)_{C.O} - I} - \frac{\Delta F_1}{a\alpha F}, \quad (26)$$

where Γ represents the dissociation constant of the oxidized complex ion and is equal to k_1/k_2 .

For the half-wave potential, the relations

$$[\kappa_1 E_1]_{(I_a)_{C.O}} = K'_{C.O} \quad (27)$$

and

$$[V]_{(I_a)_{C.O}} = \frac{RT}{a\alpha F} \left(\ln s \cdot \frac{kT}{h} + \ln \Gamma - \ln K'_{C.O} \right) - p \frac{RT}{a\alpha F} \ln [A_X] - \frac{\Delta F_1}{a\alpha F} \quad (28)$$

are obtained. Therefore, if α and the ionic strength of the solution are constant, the half-wave potential is the characteristic constant for each complex ion and is independent of the activity of the ion.

From Eq. (28) it can be said that the relation between $[V]_{\alpha, C_{c.o.}}$ and the activity of the complex-forming substance $[A_X]$ is a straight line, the tangent of which is $p \times 0.059/a\alpha$ volt at 25° . Hence, by determining the tangent of this relation and the values of a and α , the coordination number of this complex ion, p , will be calculated.

It must be noted, that if the net electrode process is diffusion-controlled the tangent of the above relation is $(p-q) \times 0.059/a$ volt, while the tangent of the activation-controlled one is $p \times 0.059/a\alpha$ volt and is independent of q .

Moreover, it is concluded from Eq. (25) that the relation between V and $\log I/(I_d - I)$ is a straight line whose tangent is $0.059/a\alpha$ volt (25°), if ΔF_1 , p , α and $[A_X]$ remain constant. This means that the current-voltage curve is symmetrical about the half-wave potential. The value of α can be obtained from the measurement of the tangent of the above relation, if the value of a is known.

Quite the same discussion as described above can be applied to the case, $[\kappa_1 E_1] \ll [\kappa_2 E_2]$, and it can be shown that this part corresponds to the oxidation wave. In the following, only the results are cited.

$$(III) \quad [\kappa_1 E_1] \ll [\kappa_2 E_2].$$

$$(a) \quad [\kappa_2 E_2] \cong K'_{C.R.}$$

$$I/a\epsilon = \frac{-[A_{C.R.}]^0}{\frac{1}{K'_{C.R.}} + \frac{1}{[\kappa_2 E_2]}} \quad (29)$$

and

$$[\kappa_2 E_2] = \frac{-K'_{C.R.} I}{a\epsilon K'_{C.R.} [A_{C.R.}]^0 - I} \quad (30)$$

$$(b) \quad [\kappa_2 E_2] \gg K'_{C.R.}$$

$$I = -a\epsilon K_{C.R.} [C_{C.R.}]^0 \equiv (I_d)_{C.R.} \quad (19)$$

From the above equations it is obvious that the oxidation wave is quite independent of the forward reaction.

All the consideration mentioned above about the activation-controlled case has been made, being based on the definitions, (1) $K'_{C.O.} \ll k_1'$ and $K'_{C.R.} \ll k_4'$ and (2) $[\kappa_1 E_1] \ll K'_{C.O.}$ and $[\kappa_1 E_1] \ll K'_{C.R.}$ when $[\kappa_1 E_1] \cong [\kappa_2 E_2]$, for which some discussions will be carried out. In the first place, the relation (1), shows that the decomposition rate of the complex ion is much larger than the rate of the diffusion of the ion. In this case, the limiting current will be the same as the diffusion current, and will be represented by the Ilković equation. In the

second place, the relation (2) means that the rate of the activation process is much smaller than the rate of the diffusion of the ion at the electrode potential where the rate constants of the forward and reverse processes are nearly the same. According to Eq. (13), $[\kappa_1 E_1]$ is represented by $k_1' \kappa_1 E_1 / k_2'$. This means that the over-all rate constant of the reduction process is accelerated by k_1' and $\kappa_1 E_1$ but retarded by the term k_2' . $\kappa_1 E_1$ is the rate constant of the reaction corresponding to the transfer of the electron between the ion and the electrode, and generally, it is regarded as to be very rapid. Moreover, by the condition (1) k_1' is much larger than $K'_{C.O.}$, then k_2' must be much larger than k_1' and $\kappa_1 E_1$ in order to fulfill the relation (2). This behavior will be satisfied when the relating complex ion is very stable in the solution, and it can be said that the more stable the complex ion, the larger the irreversibility is (and that it is reduced more difficultly) as far as the electrode process is carried out according to the mechanism mentioned above.

When the Decomposition Rate is Slower than that of the Diffusion

In this case when $K'_{C.O.} \gg k_1'$ and $K'_{C.R.} \gg k_4'$, the general equations, Eqs. (14) and (14') assume the forms respectively,

$$I/a\epsilon = \frac{[A_{C.O.}]^0 - [E][A_{C.R.}]^0}{\frac{1}{[\kappa_1 E_1]} + \frac{1}{k_1'} + [E] \frac{1}{k_4'}} \quad (31)$$

$$= \frac{[E]'[A_{C.O.}]^0 - [A_{C.R.}]^0}{\frac{1}{[\kappa_2 E_2]} + \frac{1}{k_4'} + [E]' \frac{1}{k_1'}} \quad (31')$$

If we compare these equations with Eqs. (15) and (15'), it is easily seen that the only difference between them is the fact that $K'_{C.O.}$ and $K'_{C.R.}$ in (15) and (15') are replaced by k_1' and k_4' , respectively. Therefore, for the present case, the completely analogous consideration can be made as discussed above, if both k_1' and k_4' are the constants independent of the electrode potential. So that only the results obtained in the next section.

(A) Decomposition-controlled Case

This case obviously corresponds to the diffusion-controlled case in the previous section. Hence, the equation for the current-voltage curve in the region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$ is represented by

$$I/a\epsilon = \frac{[A_{C.O.}]^0 - [E][A_{C.R.}]^0}{\frac{1}{k_1'} + [E] \frac{1}{k_4'}}, \quad (32)$$

and the limiting currents are

$$I = \alpha \varepsilon k_1' [A_{C.O}]^{\circ} \equiv (I_k)_{C.O.} \quad (33)$$

$$I = -\alpha \varepsilon k_4' [A_{C.R.}]^{\circ} \equiv (I_k)_{C.R.} \quad (34)$$

for the reduction and oxidation waves, respectively.

(B) Activation-controlled Case

From Eqs. (19)~(30) the following relations can be obtained directly by introducing k_1' and k_4' in place of $K'_{C.O.}$ and $K'_{C.R.}$.

$$(I) \quad [\kappa_1 E_1] \cong [\kappa_2 E_2]$$

$$I / \alpha \varepsilon = [\kappa_1 E_1] [A_{C.O.}]^{\circ} - [\kappa_2 E_2] [A_{C.R.}]^{\circ} \quad (35)$$

$$(II) \quad [\kappa_1 E_1] \gg [\kappa_2 E_2]$$

$$(a) \quad [\kappa_1 E_1] \cong k_1'$$

$$I / \alpha \varepsilon = \frac{[A_{C.O.}]^{\circ}}{\frac{1}{k_1'} + \frac{1}{[\kappa_1 E_1]}} \quad (36)$$

$$(b) \quad [\kappa_1 E_1] \gg k_1'$$

$$I = \alpha \varepsilon k_1' [A_{C.O.}]^{\circ} \equiv (I_k)_{C.O.} \quad (33)$$

$$(III) \quad [\kappa_1 E_1] \ll [\kappa_2 E_2]$$

$$(a) \quad [\kappa_2 E_2] \cong k_4'$$

$$I / \alpha \varepsilon = \frac{-[A_{C.R.}]^{\circ}}{\frac{1}{k_4'} + \frac{1}{[\kappa_2 E_2]}} \quad (37)$$

$$(b) \quad [\kappa_2 E_2] \gg k_4'$$

$$I = -\alpha \varepsilon k_4' [A_{C.R.}]^{\circ} \equiv (I_k)_{C.R.} \quad (34)$$

According to the consequences obtained above it is said that, when the decomposition-rate of the complex ion is slower than the rate of the diffusion, the limiting current is defined by the rate of the decomposition of the ion at the electrode surface and it is necessarily smaller than the limiting current which is defined by the diffusion process. This limiting current caused by the kinetic term probably corresponds to the "kinetic current" mentioned by Brdicka and others.⁽⁵⁾

The kinetic current can be distinguished from

(5) R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 212 (1947); J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947).

the diffusion current by its dependence on the temperature change and the geometrical characteristics of the dropping mercury electrode and so on.

Summary

The fundamental equations for the current-voltage curve of the complex ion, especially for the irreversible type, have been derived under the assumption that the over-all oxidation-reduction process at the electrode surface follows the mechanism represented by (1)~(4). Moreover, the two cases, of which one is based on the assumption that the decomposition-rate is much larger than the rate of the diffusion, and the other corresponds to the case when the relation between the two rates is reverse, have been discussed and it has been pointed that the limiting current of the former is the same as the diffusion current, but the limiting current of the latter corresponds to the kinetic current. It has been concluded that, if the electrode process is activation-controlled, the wave which has many properties of the irreversible one appears. The meaning of the half-wave potential of such a wave has been analyzed, and from the results it has been found that the value of the half-wave potential would be the parameter for the degree of difficulty of the oxidation-reduction process of the complex ion, even if the corresponding wave is irreversible. It should be noted here, that all the discussion cited above rests on the fact that the complex-forming substance exists in a sufficient quantity.

It is likely that the treatment for the oxidation-reduction reaction of the complex ion is essentially the same as for the discussion about the organic compounds.

The authors are grateful to express their thanks to Dr. Horiuti for his kind advice given to this study and, also, to the Ministry of Education for its financial support.

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Preparation, Properties and Application of the Lead Peroxide Electrode Manufactured by a New Method

By Kiichiro SUGINO

(Received December 19, 1949)

This contribution is the abstract of our papers on "Preparation, Properties and Application of the Electrodeposited Lead Peroxide Anode, Part 2-13" already published in Japanese in the *Journal of the Electrochemical Society of Japan*, (Part 2, 3, 7, 10, 11, 12), the *Journal of the Chemical Society of Japan* (Part 6, 7, 8) and the *Journal of the Society of Chemical Industry, Japan* (Part 4, 5, 13).

Our lead peroxide electrode newly prepared consists entirely of pure lead peroxide PbO_2 and has the shape of a rectangular piece or of a hollow cylinder with a bottom. It can be used as an insoluble anode for the electrolysis of aqueous solutions containing such anions as Cl^- , Br^- , I^- , F^- , ClO^- , ClO_3^- , ClO_4^- , SO_4^{--} , NO_3^- , CO_3^{--} , $\text{C}_2\text{H}_3\text{O}_2^-$, etc. It has a high oxygen overvoltage comparable to that of platinum. So it can also be used as an anode for electrolytic oxidation in place of platinum.

layer could be deposited electrolytically from neutral lead nitrate solution upon the inner surface of iron or nickel cylinder which acts as anode. An example of the electrolysis was as follows: electrolyte—24.1% lead nitrate solution; anode—iron cylinder with surface polished inside, length 1,000 mm., inside diameter 252 mm., thickness 9 mm., weight 60 kg., available surface area 78.85 dm^2 ; cathode—copper rod (diameter 45 mm.); mean current—549 amp.; anodic current density (D_A)—6.96 amp./ dm^2 ; voltage—10.7 v.; temp.—79.7°; flow velocity of electrolyte—12 l./min.; duration of electrolysis—47 hrs.

During the electrolysis, $p\text{H}$ of the electrolyte and the concentration of Pb^{++} must be maintained as constant as possible by running the electrolyte at constant velocity and neutralizing the increasing acidity by $\text{Pb}(\text{OH})_2$. The apparatus is shown in Fig. 1.

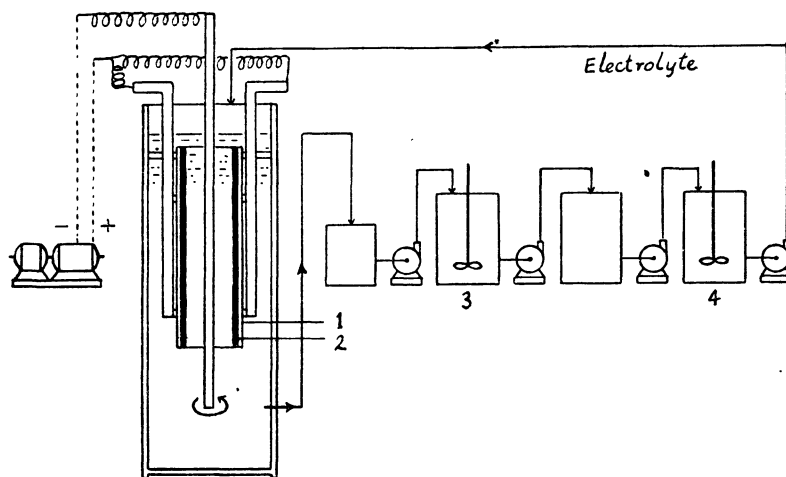


Fig. 1.—1, Iron cylinder; 2, lead peroxide layer deposited; 3, neutralization tank; 4, heating tank.

Preparation of the Lead Peroxide Electrode

Two different methods were established by the authors.

(a) **Method 1.**⁽¹⁾—Compact lead peroxide

In an example, the lead peroxide deposited was 8-10 mm. thick. At first, two cylinders of 300 mm. in length were cut from the mother cylinder, then by cutting the iron part of the cylinder lengthwise, a lead peroxide cylinder of suitable strength and compactness as well as of a smooth outer surface was obtained (dia.,

(1) K. Sugino, K. Kawamichi, T. Osga and S. Kitahara, Part 9 of this series (unpublished). A

part of this research was reported in Part 2 of this series.

250 mm.; length, 300 mm.). The lead peroxide cylinder was then separated into sixteen parts by cutting it again lengthwise. One part of the lead peroxide thus obtained has the shape of a rectangular piece shown in Fig. 2. Its di-

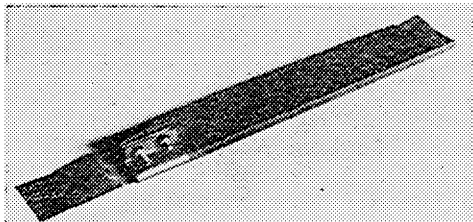


Fig. 2.

mensions are as follows: length—300 mm. $\times$ 45 mm.; thickness—8~10 mm.

(b) **Method 2.**⁽²⁾—If the outer surface of the metal cylinder was used as anode in the above method, the deposition of lead peroxide was very brittle and easily breakable due to the difference of expansion coefficient between the metal and the oxide. It proved later, however, that a compact and strong layer could be obtained by a similar method to (1) even on the outer surface of cylindrical anode if a soft and non-metallic conductor was used as anode surface of electro-deposition under suitable conditions.

For example, compact lead peroxide layer was deposited from the neutral lead nitrate solution to a considerable thickness on the outer surface of a rotating rod whose surface was consisted of paraffine-graphite mixture. The electrolytic apparatus is shown in Fig. 3.

By taking out the rod by a suitable method,

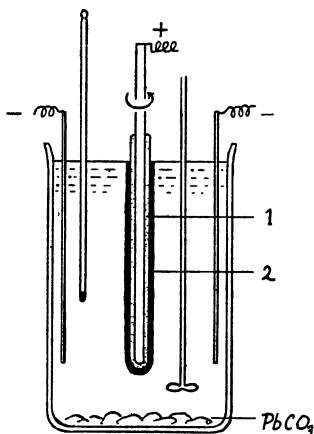


Fig. 3.—1, Paraffine-graphite mixture; 2, lead peroxide deposited.

a hollow cylinder of lead peroxide with sufficient strength and compactness was obtained. It has the same shape as the magnetite anode commonly used as is shown in Fig. 4.

It can be therefore readily used for the electrolytic bath for chlorate. An example of the electrodeposition was as follows. Conditions of electrodeposition: electrolyte— $\text{Pb}(\text{NO}_3)_2$ 330~380 g./l., $\text{Cu}(\text{NO}_3)_2$ 10~30 g./l., NaClO_4 60~80 g./l.; D_A —7 amp./dm²; voltage—5~6 v.; temp.—27~31°, acidity—0.01~0.03 N.; neutralization reagent— PbCO_3 (electrolyte is not flowed); duration of electrolysis—23 hrs.; lead peroxide electrode obtained: length—550 mm.; thickness—6.5 mm.; diameter (outer)—54 mm.; diameter (inner)—41 mm.; weight—4.8 kg.

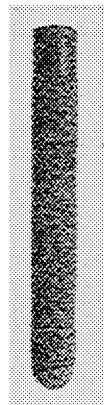


Fig. 4.

Application of the Lead Peroxide Electrode

A. As an Insoluble Anode

Electrolytic Production of Potassium Chlorate.⁽³⁾—From the standpoints of conductivity and durability, our lead peroxide electrode appears to be superior to graphite or magnetite as anode material for chlorate production. This electrode is a good conductor carrying the current of above 20 amperes per square decimeter of the surface. In addition, it is almost perfectly insoluble, practically no decrease of weight being perceptible during the course of electrolysis of sodium chloride solution. Our experiments showed that this electrode was a most suitable material as anode for chlorate production. An example of the preparation of potassium chlorate was as follows. Conditions of electrolysis: cathode—Fe; electrolyte—KCl 32 g./100 cc. solution, 0.2 g. $\text{Na}_2\text{Cr}_2\text{O}_7$ added, slightly acidified with HCl during the electrolysis; D_A —20 amp./dm²; voltage—3.3~4.0 v.; temp.—60~80°. After 33.0 amp. hr. was passed, 20.35 g. of KClO_3 (crystal obtained at 15°, 19.02 g.) was formed. Current efficiency, 81%. KClO_4 was not produced at all.

B. As Anodes for the Electrolytic Oxidation

(a) Electrolytic Production of Sodium

(2) K. Sugino and Y. Shibasaki, *J. Electrochem. Soc. Japan*, **16**, 9, 10 (1948), (Part 10, 11).

(3) K. Sugino and M. Yamashita, *J. Electrochem. Soc. Japan*, **16**, 123 (1948), (Part 12).

Perchlorate.⁽⁴⁾—Since the oxygen overvoltage of lead peroxide is thought to be comparable to that of platinum, it is easily conceivable that it can be used for the electrolytic oxidation of sodium chlorate. So far, however, the lead peroxide anode formerly used has been a thin film electrolytically formed on the surface of a lead plate and proved to be useless for perchlorate production as the lead dissolves readily. But our lead peroxide electrode was found to be perfectly insoluble when it was used for the same purpose. So the authors have carried out fundamental and semicommercial experiments for the electrolytic preparation of sodium perchlorate with this anode. Main results obtained are shown in Table 1.

direct process for the electrolytic production of sodium perchlorate. By the use of our lead peroxide anode, it is easily conceivable that the electrolytic preparation of sodium perchlorate is performed by a single electrolysis of sodium chloride solution. The results showed that with a current efficiency of about 60%, almost pure sodium perchlorate (purity being above 99.4–99.9%) was easily obtained directly from sodium chloride. The conditions of electrolysis were as follows: electrolyte—saturated sodium chloride solution; anodic current density (D_A)—15~20 amp./dm².; temp.—Cl→ClO₃ 60~65° (initial stage of electrolysis), ClO₃→ClO₄ 30~35° (final stage of electrolysis). Main results obtained are shown in Table 2.

Table 1

Expt. No.	Cathode	Cathodic current density, amp./dm ² .	NaF, g./l.	Current concn., amp./l.	Mean voltage, v.	Temp., °C.	Reaction percentage NaClO ₃ →NaClO ₄ , %	Current efficiency, %
1	18-8 stainless steel	20	0	80	4.4	29~30	99.91	40.9
2	"	"	2	"	4.5	"	99.60	82.9
3	"	"	2.5	"	4.6	35	98.40	81.8
4	"	26	2	55	5.1	50~52	99.53	72.2

Electrolyte: Saturated sodium chlorate solution (20°). Anodic current density (D_A): 20 amp./dm².

Table 2

Cathode	Quantity of NaCl used, g.	Voltage, v.	Current, quantity consumed, amp. hr.	After electrolysis			Reaction percentage, ClO ₃ →ClO ₄ , %	Current efficiency, %
				NaCl, g.	NaClO ₃ , g.	NaClO ₄ , g.		
18-8 stainless steel	40	3.9~5.5	250.5	0	0.0216	83.77	99.97	58.5
"	"	3.9~5.4	237	0	0.0352	83.75	99.95	61.9
"	"	3.9~5.3	222.5	0	0.3600	83.38	99.51	65.9
Cr plating iron	"	4.0~5.5	231	0	0.4610	83.26	99.37	63.4

As is clear from the table, an addition of 2 g./l. of sodium fluoride was found to have a very marked effect in increasing the current efficiency. Thus, in Expts. 2 and 3, the result is about the same as the case of platinum anode. Expt. 4 was a semi-commercial experiment, using 600 ampere cell. With a current efficiency of 72%, the reaction proceeded to 99.5%.

(b) Direct Electrolytic Production of Sodium Perchlorate from Sodium Chloride.⁽⁶⁾

—The authors established a new simple and

As the two different electrolytic processes (Cl→ClO₃, ClO₃→ClO₄) seemed to take place successively, a small amount of hydrochloric acid was added from time to time during the primary stage in order to maintain the electrolyte slightly acidic, and when the chlorate formation was almost completed, a small amount (2 g./l.) of sodium fluoride was added at a time for increasing the current efficiency of electrolytic oxidation.

(c) Electrolytic Preparation of Ammonium Persulfate⁽⁶⁾ (Hydrogen Peroxide).—

(4) K. Sugino and M. Yamashita, *J. Electrochem. Soc. Japan*, **15**, 61 (1947), (Part 3). S. Kitahara and T. Osuga, *J. Electrochem. Soc. Japan*, **10**, 409 (1942), (Part 2). A part of this research was reported in the earliest paper of this series: Y. Kato, K. Sugino, K. Koizumi and S. Kitahara, *Electrotechnical Journal, Japan*, **5**, 45 (1941), (in English).

(5) Reference (4), (Part 3).

(6) K. Sugino, J. Mizuguchi, M. Yamashita and K. Odo, *J. Soc. Chem. Ind. Japan*, **50**, 34, 36 (1948), (Part 4, 5). K. Sugino, J. Mizuguchi and M. Yamashita, *J. Chem. Soc. Japan*, **67**, 108 (1946), (Part 6). K. Sugino and M. Yamashita, *J. Chem. Soc. Japan*, **67**, 110 (1946); *J. Electrochem. Soc. Japan*, **16**, 120 (1948), (Part 7). K. Odo, *J. Chem. Soc. Japan*, **67**, 129 (1946), (Part 8).

Electrolytic preparation of ammonium persulfate has also only been successfully accomplished by the use of platinum anode. Trials of electrolytic formation of persulfate by the anodes other than platinum (PbO_2 , MnO_2 , Fe_3O_4 , graphite etc.) were already undertaken in vain by a few authors.⁽⁷⁾ The authors have therefore tried the application of our new lead peroxide electrode for this purpose.

Preliminary experiments have been conducted in the same conditions as in the case of platinum anode. The conditions of electrolysis were as follows: cathode—Pb; anolyte and catholyte—a mixture of 28% $(\text{NH}_4)_2\text{SO}_4$ and 30% H_2SO_4 ; D_A —50 amp./dm²; porcelain diaphragm was used; addition agent—none.

Though the formation of ammonium persulfate was definitely observed in each experiment, its maximum concentration in anolyte never exceed 2–3%, which was followed by a gradual decrease by the prolonged electrolysis, the total current efficiency being also only a few percent as already reported by another author.⁽⁸⁾ Upon examining the electrolytic conditions specially suited for lead peroxide anode, the following ones were found as such:

- (1) Lowering of the anodic current density to about 10 amp./dm².
- (2) Selection of a suitable composition of electrolyte: 10~20% sulfuric acid solution saturated with ammonium sulfate.
- (3) Addition of hydrofluoric acid to anolyte: 10~60 g./l.
- (4) Increase of current concentration, if desired.

The addition of 50~60 g./l. of hydrofluoric

the industrial preparation of ammonium persulfate.

Furthermore, the plan of the flow diagram of the new process of the preparation of concentrated hydrogen peroxide by this electrolytic method was established and a semi-commercial experiment has been conducted and completed successfully by Assist. Prof. J. Mizuguchi. But the results are omitted in this paper.

Oxygen Overvoltage of Lead Peroxide Anode in Sulfuric Acid and its Variation in the Presence of HF⁽⁹⁾

Oxygen overvoltage of lead peroxide anode in sulfuric acid solution (1*N* and 30%) was measured at various current densities by the direct method and the values obtained were compared with that of the smooth platinum anode.^{(10),(11)} The oxygen overvoltage of lead peroxide was found to be somewhat lower than that of platinum at a definite current density (for example, 0.16 v. lower at 1 amp./dm²). The overvoltage (π) is shown in Fig. 5 against the logarithm of the anodic current density (D_A).

The variation of overvoltage with current density could also be expressed by the usual equation,

$$\pi = a + b \log I$$

(from 10 milliamp./dm² to 1 amp./dm²),

and the value of b of lead peroxide and platinum was found to be 0.13 and 0.18 respectively at ordinary temperatures. The inferiority

Table 3

Expt. No.	Quantity of anolyte, cc.	Mean current, amp.	Current concentration, amp./l.	Anodic current density, amp./dm ² .	Mean voltage, v.	Temp., °C.	Current quantity consumed, amp. hr.	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ formed, g.	Concn. of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in anolyte, g./100cc.	Current efficiency, %	Variation of acidity of anolyte, <i>N</i>
1	100	4	40	10	5.0–5.4	30	6	15.92	16.58	62.3	4.76 → 4.53
2	150	3	20	11	4.6–4.8	28–29	9	23.76	17.60	62.0	4.81 → 4.60
3	300	3	10	11	4.7–4.9	30–32	18	48.62	17.06	63.5	4.61 → 4.72

Cathode—Pb; anolyte—98% H_2SO_4 10 g./100 cc., $(\text{NH}_4)_2\text{SO}_4$ 58 g./100 cc., HF 5~6 g./100 cc.; catholyte—saturated ammonium sulfate solution. Porcelain diaphragm was used.

acid to anolyte was of a specially marked effect: about 20% ammonium persulfate solution could be obtained with a current efficiency of about 60% as is seen from Table 3. This result offers a possibility of the use of this anode for

(7) Skirrow and Stein, *Trans. Am. Electrochem. Soc.*, **38**, 209 (1920).

(8) R. Matsuda, *This Bulletin*, **12**, 331 (1937).

(9) K. Sugino, T. Tomonari and M. Takahashi, *J. Soc. Chem. Ind. Japan*, **52**, 75 (1949), (Part 13).

(10) Oxygen overvoltage at platinum anode has been found to be higher than that at lead peroxide anode by several investigators, (for example, E. Müller, *Z. Elektrochem.*, **10**, 61 (1904)).

(11) A few authors recorded a higher value of overvoltage of lead peroxide than that of platinum (E. Müller, *Z. Elektrochem.*, **11**, 865 (1905); Tsutusi, *Bull. Electrotech. Lab. Japan*, **6**, 91 (1942)).

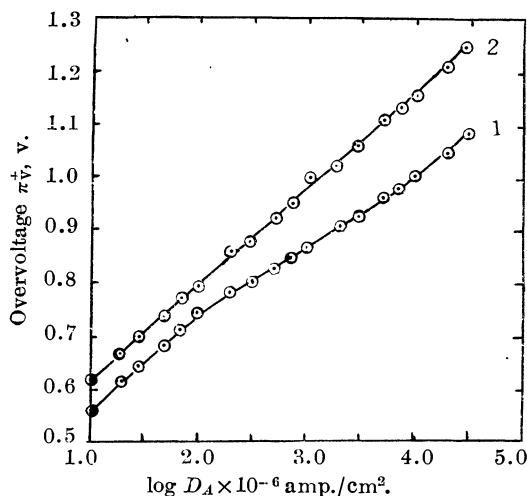


Fig. 5.—Overvoltage of lead peroxide and platinum in H_2SO_4 (1 N) at 30°C .: Curve 1, PbO_2 , Curve 2, Pt.: at $D_A=1$ milliamp./ cm^2 . PbO_2 0.86 v., Pt 0.99 v.; at $D_A=10$ milliamp./ cm^2 . PbO_2 1.00 v., pt 1.16 v.

of the current efficiency of electrolytic oxidation process at lead peroxide anode may be due mostly to the above difference of overvoltage at definite current density.

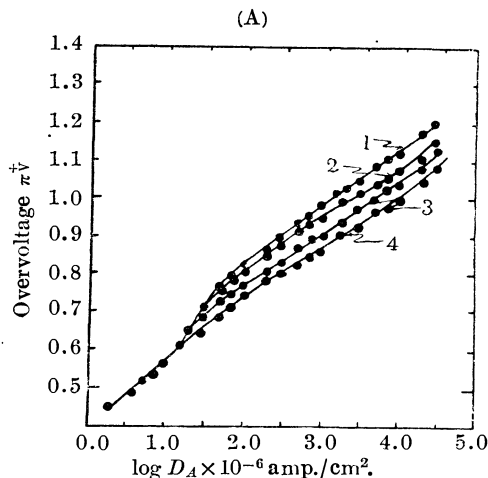
The variation of overvoltage of lead peroxide due to the addition of various amount of hydrofluoric acid was also measured.⁽¹²⁾ The result obtained is shown in Fig. 6.

It was found that the overvoltage increased in a linear manner with the logarithm of the concentration of hydrofluoric acid added. This relation may be expressed by the following equation.

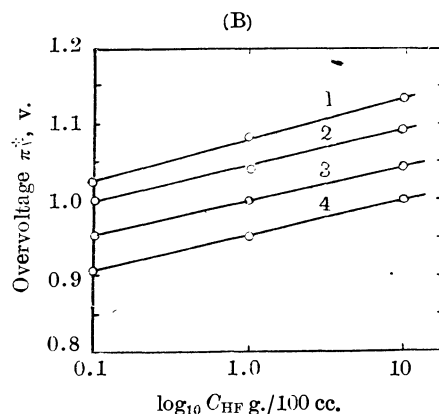
$$\pi = 1.10 + 0.04 \log C_{\text{HF}} (\text{mol./l.}) \text{ at } 1 \text{ amp./dm}^2. (C_{\text{HF}}=0.05\sim 5 \text{ mol./l.})$$

The study of the rate at which the potential of the anode falls after the polarising current being switched off has been also made by the authors using a modified Beath circuit, and it was found that the plot of the potential against the logarithm of the time was a straight line and the discontinuity could not be found in that curve on the contrary of Isgarischew's observation.⁽¹²⁾

In conclusion, the author wishes to express his sincere thanks to Dr. Y. Kato, a professor emeritus of Tokyo Institute of Technology, for his kind advice and encouragement in the initial stage of this research. The author also extends his thanks to the Nippon Carbide Industries Company Inc. and Mr. Okumura, President of the said company, for the conveniences and funds furnished to this research, and to Mr. K. Kawamichi, Director of the



Curve 1, 10 g. HF; Curve 2, 1 g. HF. Curve 3, 0.1 g. HF; Curve 4, without HF.



Curve 1, 10×10^{-3} amp./ cm^2 ; Curve 2, 5×10^{-3} amp./ cm^2 ; Curve 3, 2×10^{-3} amp./ cm^2 ; Curve 4, 1×10^{-3} amp./ cm^2 .

Fig. 6.—The variation of overvoltage of lead oxide anode in H_2SO_4 (1 N) due to the addition of various amount of HF.

same company, for his kindness and collaboration for the industrial production of this electrode. Thanks are also due to his collaborators, specially to Mr. T. Osuga of the same company, Assist. Prof. J. Mizuguchi and Mr. M. Yamashita of Tokyo Institute of Technology, Prof. Dr. T. Tomonari and Assist. Prof. Y. Shibasaki of the Yokohama Institute of Technology who gave earnest and valuable assistance and collaboration in the investigations. A part of the cost of this study was defrayed from the Scientific Research

(12) It has already been noted that the presence of fluoride ion in the electrolyte increases anodic overvoltage (E. Müller, *Z. anorg. Chem.*, **48**, 112 (1906); *Z. Elektrochem.*, **13**, 257 (1907); N. Isgarischew, *Z. Elektrochem.*, **30**, 138 (1924)).

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Über den Reaktionsmechanismus der Dianthracenbildung aus Anthracen. III

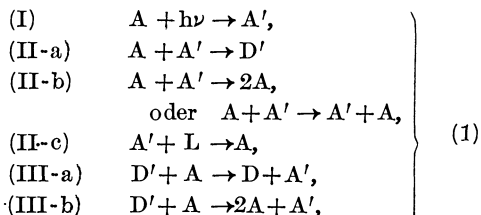
von Momotaro SUZUKI

(Eingegangen am 27. Dezember, 1949)

Kürzlich habe ich berichtet⁽¹⁾ über die Versuchsergebnisse der photochemischen Umsetzung des Anthracens ins Dianthracen. Hier spielte sich die Stosszahl zwischen verschiedenen normalen bzw. aktivierten Molekülarten gelegentlich eine wichtige Rolle, und ergab sich unter anderem ein selektiver Einfluss der Konzentration des Substrats d.h. die Elementarprozesse, die unter dieser photochemischen Umsetzung nebeneinander vor sich gehen können, je nach dem drei Konzentrationsgebiete des Anthracens, verschiedene Reaktionsgeschwindigkeitswerte annehmen, und zwar können einige bestimmten Elementarprozesse im bestimmten Konzentrationsgebiete bevorzugen.

In der vorliegenden Arbeit habe ich um den Reaktionsmechanismus dieser Umsetzung über ganze Konzentrationsgebiete des Anthracens ausführlich bearbeitet sowie auch nach dem vorgeschlagenen Reaktionsschema berechneten Werte mit den gemessenen vergleicht. Es befand sich dass, durch dieses vorgeschlagene Postulat den ganzen Reaktionsmechanismus dieser Umsetzung die gute Übereinstimmung zwischen Mess- bzw. Rechnungsergebnisse klar veranschaulicht wurde.

In dem Verlauf der ganzen Reaktion, d.h. von der Absorption des Lichtes durch Anthracenmoleküle bis zur Bildung des Endprodukt Dianthracens, sind alle möglichen Elementarprozesse, die man überhaupt annehmen kann, etwa folgendermassen zu formulieren.



L: Lösungsmittelmolekül

Die erste Stufe ist der Lichtabsorptionsvorgang, dessen Produkte die angeregten Moleküle sein sollen, da hier die freien Atome oder Radikale keine Rolle spielen⁽²⁾. Die Zeit, die diese Prozesse in Anspruch nehmen werden, ist vermutlich höchstens 10^{-10} Sek.⁽¹⁾; das schliesst jeglichen Einfluss dieser Prozesse auf die Reaktionsgeschwindigkeit aus. Auch kann man wohl annehmen, dass die Quantenausbeute dieser Elementarprozesse 100 % ig ist. Wir wollen uns über das Verhalten solcher angeregten Gebilde in unserem photochemischen Vorgang etwas eingehender orientieren, soweit man darüber nicht aus vorliegenden unterrichtet ist. Die Prozesse (II-a), (II-b) oder (II-c) sind solche, worin die angeregten Anthracenmoleküle (A') auf dreierlei Weise verschwinden. Erstens bildet ein A' -Molekül durch den Stoss mit einem normalen Anthracenmolekül A ein Dianthracenmolekül. Dabei muss man berücksichtigen, dass die Wärmetönung dieser Umsetzung sehr klein, ja sogar fast Null ist⁽³⁾ und daher die aufgenommene Lichtenergie beim Stoss mit einem A -Molekül wieder an das neugebildete Dianthracenmolekül als überschüssige oder Aktivierungsenergie dessen übertragen werden sollte, wenn nicht der angeregte Zustand durch äussere Störungen, wie etwa dreier Stösse, zu einer Rückkehr in den normalen Zustand gezwungen wird. Es handelt sich also bei einem so gebildeten Dianthracenmolekül um kein normales sondern um ein angeregtes (D'). Zweitens wird ein A' -Molekül durch den Stoss mit einem A -Molekül deaktiviert und dabei könnte der Stosspartner A -Molekül wieder aktiviert werden. Der Nutzeffekt der Deaktivierung bei

(2) J. Franck und T. Rabinowitsch, *Trans. Faraday Soc.*, **36**, 128 (1934); M. Volmer, *Ann. d. Phys.*, (4) **40**, 775 (1913).

(3) Luther und Weigert, *Z. physik. Chem.*, **53**, 385 (1905).

(1) M. Suzuki, I Mitteilung, *Dies Bulletin*, **18**, 146 (1943); II Mitteilung, *ibid.*, **22**, 172 (1949).

diesem Stoss sollte viel grösser sein als der beim Stoss mit Lösungsmittelmolekül. Wie wir bereits früher darauf hingewiesen haben,⁽¹⁾ soll die Wahrscheinlichkeit der Desaktivierung eines A-Molekül durch Stoss mit einem L-Molekül (II-c) beträchtlich geringer sein als die mit einem A-Molekül. Aus diesem Grunde können wir jetzt diese dritte Möglichkeit ohne weiteres ausschliessen und nur (II-a) und (II-b) zuwenden.

Die dritte Stufe, wo ein D'-Molekül verschwindet, ginge dann ganz analog wie oben vom A'-Molekül gesprochen wurde, und dabei spielen wieder das A- und L-Molekül eine Rolle als Stosspartner. Beim D'A-Stoss in (III-a) und (III-b) unterscheidet sich nur das D'-Molekül vom A'-Molekül in (II-a, b, c), und die darauf folgende Entstehung ist ein normales D-Molekül und ein A'-Molekül (III-a). Hierbei spielt die Zerlegung eines D'-Moleküls wieder eine Rolle, wo es zusammen mit dem Stosspartner A-Molekül in zwei A- und ein A'-Molekül zerlegt wird. Der A'L-Stoss (II-c) kommt hier auch in Frage, aber bei diesem Fall ist auch solche Wahrscheinlichkeit so viel geringer, dass man sie durchaus unberücksichtigt lassen darf, soweit es sich um den Fall handelt, wo die Wirkungsstosszeit von AA'-Stoss kleiner als die vom A'L-Stoss ist. Hier muss wieder in Rücksicht gezogen werden, dass die erst durch Anthracenmolekül aufgenommene Lichtenergie ohne wesentliche Veränderung auf das angeregte Dianthracenmolekül übertragen und wieder auf das angeregte Anthracenmolekül zurückübertragen wird.⁽³⁾

Auf das Auftreten einer Übergangsmolekülart zwischen einem aktivierten Anthracenmolekül und einem Dianthracenmolekül hat Weigert⁽⁴⁾ schon hingewiesen als ein Anthracenmolekül mit dreiwertigem C-Atom (9- oder 10-Stellung). Ob ein solches Molekül überhaupt vorhanden ist, kann noch nicht genau bewiesen werden, immerhin ist man berechtigt, es als ein aktiviertes Dianthracenmolekül zu bezeichnen. Eine röntgenographische Untersuchung zeigt,⁽⁵⁾ dass ein Dianthracenmolekül aus zwei Anthracenmolekülen besteht, die mit beiden parallelen Ringebenen genau übereinander liegen und mit zwei an 9- und 10-Stellung gegeneinander ausübten Bindungen. Diese Behauptung ist aber noch nicht als ganz berechtigt anerkannt. Wenn man sich vorläufig das Molekül so vorstellt, so ist die Vermutung kaum wahrscheinlich, dass beim AA'-Stoss die Verbindung bei der beiden 9- und 10-Stellung auf einmal

stattfinden könnte; sondern man muss vielmehr annehmen, dass beim ersten Stoss die Verbindung beider Moleküle nur an die 9- oder 10-Stellung veranlasst wird und die andere Stellung unverbunden oder sogar unter ganz lockerer Verbindung bestehen bleibt. Nun mit darauf folgendem AD'-oder D'L-Stoss wird dieses Dianthracenmolekül in zwei Anthracenmoleküle zerlegt oder in ein normales Dianthracenmolekül stabilisiert. Ob darüber hinaus irgend eine Energieumsetzung erfolgt oder nicht, bleibe einstweilen dahingestellt.

Durch die eben erwähnten Überlegungen kann man sich ein Gebilde von einem angeregten Dianthracenmolekül vorstellen, und wir wollen nun versuchen, möglichst genau den Verlauf der ganzen Reaktion in allen Konzentrationsgebieten des Anthracens zu veranschaulichen.

Im Gebiet A, wo die Konzentration des Anthracens sehr klein ist, würde die Desaktivierung durch ein Lösungsmittelmolekül ziemlich stark beeinflusst, da die Wirkungsstosszahl der AA'-Stösse beträchtlich geringer ist als die A'L-Stösse. Demgemäss würde die Reaktionsgeschwindigkeit der Dianthracenbildung mit der Molekülzahl des Anthracens und zwar des normalen, die zur Vereinigung mit Aktivierten ins Dianthracenmolekül sowie zur Desaktivierung dessen vor sich gehen zunehmen. Dieser Vorgang zeigt sich in dem linken Teil der Kurven in Fig. 1 und 2 in der II Mitteilung. Die Fluoreszenzerscheinung, kommt bei der Anthracenkonzentration oberhalb 10^{-4} Mol/l. schon nicht mehr in Betracht, daher spielt sie hier in diesem Gebiet keine Rolle.⁽⁶⁾

Ist nun im mittleren Konzentrationsgebiet B des Anthracens, also oberhalb bei einer bestimmten Konzentration d. h. ungefähr 10^{-3} Mol/l. der Reagierenden die Wirkungsstosszahl der AA'-Stösse grösser als die der A'L-Stösse, so wird die Reaktionsgeschwindigkeit beherrscht von der Stufe, worin die AA'-Stösse die Hauptrolle spielen. Darüber ist bereits in der ersten Mitteilung noch etwas ausführlicher diskutiert worden.⁽¹⁾

Mit kleiner Lichtintensität der Bestrahlung verlängern sich die Kurventeile des Gebietes B, wie man aus der Fig. 1 in der II Mitteilung ersieht, d. h. der Bereich der Anfangskonzentration des Anthracens, worin die Reaktion der Dianthracenbildung nach nullter Ordnung

(4) Weigert, *Naturwiss.*, **15**, 124 (1927); A. Schöneberg, *Trans. Faraday Soc.*, **32**, 514 (1936).

(5) J. Hengstenberg u. J. Polceios, *Ann. d. Soc. Espan. d. Fis. y. Quim.*, **30**, 5 (1932).

(6) P. K. Seshan, *Proc. Acad. Sc. A.*, **3**, 148 (1936); *Trans. Faraday Soc.*, **32**, 689 (1936); D. Radulescu u. C. Dragulescu, *Bull. Soc. Chem. Rumania*, **17**, 9 (1936); A. A. Shiahlovskij, *Comp. Rend. Acad. Sc. URSS*, **15**, 29 (1937); P. Pringsheim, *Trans. Faraday Soc.*, **35**, 15 (1939); G. B. Banerjea u. B. Mischra, *Z. Phys.*, **106**, 669 (1937); S. Sambursky u. G. Wolfson, *Trans. Faraday Soc.*, **36**, 427 (1940).

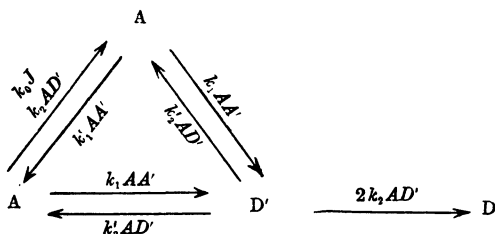
verläuft, vergrößert sich noch weiter.

Mit wachsender Anfangskonzentration des Anthracens würde dann die stationäre Konzentration des A'-Moleküls immer grösser und der Vorgang (II-a) ginge so schnell, dass das Stadium nicht mehr als reaktionsgeschwindigkeitsbestimmend gilt, oder würde die Bildungsgeschwindigkeit der D'-Moleküle durch die AA'-Stöße grösser, so spielt dann der Prozess (III-a) eine wesentliche Rolle d. h. der Reaktionsverlauf nimmt die Art des Gebietes C an.

Im obigen Sinne können wir die Bildungs- bzw. Zersetzungsgeschwindigkeit der einzelnen Molekülarten im Gebiet C folgenderweise zum Ausdruck bringen.

$$\left. \begin{aligned} (2-a) \quad \frac{dA}{dt} &= -k_0J - (k_1 - k_1')AA' \\ &\quad - (k_2 - k_2')AD' \\ (2-b) \quad \frac{dA'}{dt} &= k_0J - (k_1 + k_1')AA' \\ &\quad + (k_2 + k_2')AD' \\ (2-c) \quad \frac{dD'}{dt} &= 2k_1AA' \\ &\quad - 2(k_2 + k_2')AD' \\ (2-d) \quad \frac{dD}{dt} &= 2k_2AD' \end{aligned} \right\} \quad (2)$$

Oder schematisch ausgedrückt,



Dabei sind A, A', D und D' die Anzahl der Moleküle der jeweiligen Molekülarten und k_0 die Konstante für den Lichtabsorptionsvorgang, k_1 , k_1' , k_2 und k_2' die Geschwindigkeitskonstanten und zwar k_1 bzw. k_2 für die Bildung der A' bzw. D'-Moleküle und k_1' bzw. k_2' für das Verschwinden der A'- bzw. D'-Moleküle. Für die Bildung und das Verschwinden der D'- und D-Moleküle haben wir oben zwei A-Moleküle in Umrechnung gezogen.

Unter Eliminieren von AA' und AD' findet man nun aus den Gleichungen (2-a), (2-b) und (2-c) folgende Beziehung

$$\lambda \frac{dA}{dt} + \mu \frac{dA'}{dt} + \nu \frac{dD'}{dt} = \text{Konst.} \quad (3)$$

wo λ , μ sowie ν gewisse bestimmte Konstanten sind. Daraus kann man diejenige Lösung mit

der Randbedingung, wobei für $t = 0$, $A = A_0$, $A' = 0$ und $D' = 0$ annimmt, in der Form:

$$\lambda(A_0 - A) + \mu A' + \nu D' = \alpha t \quad (4)$$

ausgedrückt werden, wobei α eine neue Konstante ist. Man sieht also, dass die Reaktionsvariable immer auf eine Ebene im vierdimensionalen Raum von A, A', D' und t beschränkt sind.

Wir wollen nun wieder annehmen, wie wir es bereits in der I Mitteilung für das Gebiet B getan haben, auch hier für das Gebiet C, dass der Konzentration der A'-Moleküle einen bestimmten stationären Wert zuzuschreiben ist, da es sich hier wieder um einen analogen Reaktionsmechanismus genau wie in Gebiet B handelt.

Setzen wir also (2-b) gleich Null, so bekommen wir

$$\begin{aligned} \frac{dA'}{dt} &= k_0J - (k_1 + k_1')AA' \\ &\quad + (k_2 + k_2')AD' = 0 \end{aligned} \quad (5)$$

oder

$$\begin{aligned} AD' &= \frac{1}{k_2 + k_2'} \{ (k_1 + k_1')AA' - k_0J \} \\ &= \frac{1}{K_2} (K_1AA' - k_0J), \end{aligned} \quad (6)$$

wobei $K_1 = k_1 + k_1'$ bzw. $K_2 = k_2 + k_2'$ ist. Setzen wir (6) in (2-a) ein, so erhalten wir, dass

$$\begin{aligned} \frac{dA}{dt} &= -k_0J \left(1 - \frac{K_2'}{K_2} \right) - \left(K_1' - \frac{K_2' K_1}{K_2} \right) AA' \\ &= -a - bA \end{aligned} \quad (7)$$

wobei $K_1' = k_1 - k_1'$ bzw. $K_2' = k_2 - k_2'$ und $a = k_0J \left(\frac{K_2'}{K_2} \right)$ bzw. $b = \left(K_1' - \frac{K_1 K_2'}{K_2} \right) A'$ sind.

Daraus folgt dann durch die Integration von (7)

$$t = \frac{1}{b} \ln \frac{a + bA_0}{a + bA} \quad (8)$$

mit der Randbedingung von $A = A_0$ bei $t = 0$. Unter Umformen von (8) erhalten wir weiter

$$A_0 - A = (1 - e^{-bt}) \left(\frac{a}{b} + A_0 \right) \quad (9)$$

Wir kommen jetzt zur Schätzung der Grössenordnung von A'. Aus der Gleichung (4') in der II Mitteilung, haben wir bereits $\frac{dD}{dt} = k'JV \exp\left(-\frac{E}{RT}\right)$, weiter $\varphi = \frac{dD}{dt} / J \sim 10^{-1}$, $v \sim 10^1$ und $\exp\left(-\frac{E}{RT}\right) \sim 10^{-3}$, so ist $k' \sim 10^2$.

Nun aber unter Benutzung von gaskinetischer Berechnung bekommen wir

$$Z_{A=1, A'=1} = 4\sigma^2 \sqrt{\frac{\pi RT}{M}} \quad (10)$$

wo σ der Radius des Anthracenmoleküls und M das Molekulargewicht des Anthracens sind. Setzt man die Zahlenwerte in diesen Ausdruck ein, indem man berücksichtigt, dass $T = 273$, $M = 178$ und $\sigma = 1.33 \times 10^{-8} \left(\frac{M}{d}\right)^{\frac{1}{3}} = 6.96 \times 10^{-8}$, wobei Dichte des festen Anthracens $d = 1.24$ ist, so erhält man für den Zahlenwert von $Z_{A=1, A'=1}$ 4.0×10^{-10} . Aus (2) und (3) in der II Mitteilung

$$n_{A'} = \frac{J}{n_A V Z_{A=1, A'=1}} \sim 1.7 \times 10^5, \quad (11)$$

indem man die Zahlenwerte, unter Versuchsbedingungen $J = 2.6 \times 10^{15}$ für die gesamte Strahlung aus der Lichtquelle, $V = 5$ cm., und n_A für die Konzentration von $1.0 \cdot 10^{-2}$ Mol/l. einsetzt. Da der Wert von A' gegen A sehr klein ist, darf man $e^{-bt} = 1 - bt$ setzen. Und weiter erhält man aus (9)

$$A_0 - A = bt \left(\frac{a}{b} + A_0 \right). \quad (12)$$

Andererseits aus der Gleichung (5), erhält man

$$A = \frac{k_0 J}{K_1 A' - K_2 D'} \quad (13)$$

Daraus folgt aus (2-c)

$$\frac{dD'}{dt} = (2k_1 A' - 2K_2 D') \frac{k_0 J}{K_1 A' - K_2 D'}. \quad (14)$$

Durch Integration dessen bekommt man

$$D' + \frac{k_1 A'}{K_2} \ln \frac{K_1 A' - K_2 D'}{K_1 A'} = 2k_0 J t \quad (15)$$

mit der Randbedingung von $D' = 0$ bei $t = 0$. Berücksichtigt man hier aber, dass (III-a) in (1) die geschwindigkeitsbestimmende Stufe ist, so ist man berechtigt $D' \ll A'$ zu setzen. Dann folgt $\ln \frac{K_1 A' - K_2 D'}{K_1 A'} \sim -\frac{K_2 D'}{K_1 A'}$, oder mit wesentlich konstantem A' ist D' eine lineare Funktion von t , und unabhängig von A_0 . Nun ist offenbar

$$(A_0 - A) - A' - D' = D. \quad (16)$$

Nun ist aber, aus der Gleichung (12), $A_0 - A$ linear von t und A' konstant und schliesslich D' wieder linear von t . In der Messung der Dianthracenbildung in der bestimmten Belichtungszeitdauer d. h. mit konstantem t ist D also linear von A_0 . Dass diese Schlussfolgerung mit den Versuchsergebnissen in Gebiet C gut übereinstimmt ist in den Tabellen 1 und 2 sowie in den Fig. 1 und 2 in der II Mitteilung klar dargestellt.

In der Tabelle 1 hat man die aus der experimentellen Resultate gewonnenen Zahlenwerte von den in der Formel (12) aufgetretenen beiden Koeffizienten a sowie b zusammengestellt. Die beiden sind, wie man schon erwartete, unabhängig von der Belichtungszeitdauer bei jeglicher Temperatur. Übrigens ist $a = k_0 J \times \left(1 - \frac{K_2'}{K_2}\right)$ fast unabhängig von der Tempe-

Tabelle 1

Die Werte von a und b in der Gleichung (12) bei Verschiedener Temperatur und Verschiedener Belichtungszeitdauer

Belichtungszeitdauer, Stunden	10.0		7.0		5.0	
	a	b	a	b	a	b
-10°C.			0.58	0.56	0.60	0.58
0°C.	0.60	0.91	0.58	0.93	0.60	0.90
30°C.			0.58	1.00	0.60	1.00

ratur. Und dieser Befund verträgt sich mit der Annahme, dass das Verhältnis $\frac{K_2'}{K_2}$ nicht wesentlich von der Temperatur beeinflusst wird.

Aus der Tatsache, dass der Wert von b stark mit der Temperatur zunimmt, braucht man nur zu postulieren, dass die stationäre Konzentration des A' Moleküls stark mit der Temperatur zunimmt.

Es bleibt noch übrig, dass das Verhalten der Kurve im Gebiet C nicht weiter unendlich anhalten könne, da sonst die Konzentration der angeregten Gebilde weiter unendlich zunehmen würde. Dazu wurden unsere Messungen mit zu weniger Belichtungszeitdauer und zu kleinem Konzentrationsbereich durchgeführt. Man muss hier postulieren, dass unter einer sehr langen Messungszeitdauer die Konzentration des Anthracens allmählich kleiner wird und infolgedessen die Bildungsgeschwindigkeit des Dianthracens sich wieder verlangsamt.

Zusammensetzung

1. Wir haben die Elementarprozesse dieser Umsetzung ausführlich überlegt und ohne weiteres den Reaktionsmechanismus massgebend erörtert.

2. Die aus der obigen Überlegung gewonnenen Rechnungsergebnisse stimmten mit dem experimentellen Befund sehr gut überein.

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A Study on the Solubility of Sparingly Soluble Salt. VIII. Solubility of Lead Sulfate in Various Mixed Solvents with Isodielectric Constant

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To investigate the relation between the solubility of sparingly soluble salt and the dielectric constant of the solvent, the solubility of lead sulfate was measured by the present author in the following various isodielectric solvents composed of the mixture of water with dioxane,⁽¹⁾ acetone,⁽²⁾ glycerine,⁽³⁾ ethanol⁽⁴⁾ and methanol,⁽⁵⁾ in the small range of change in dielectric constants of the solvents.

The observed solubility in the mixed solvent with isodielectric constant are listed in Table 1.

Table 1
Solubility of Lead Sulfate in the
Isodielectric Solvents

Temp. °C.	Dielect. const.	Solubility (mol./l. × 10 ⁶)				
		Di- oxane	Ace- tone	Glyce- rine	Etha- nol	Me- thanol
20	80.37	142.1	142.1	142.1	142.1	142.1
	78.10	117.4	85.0	100.8	95.0	91.6
	75.90	103.8	45.0	61.0	57.0	61.0
25	78.54	148.1	148.1	148.1	148.1	148.1
	76.35	121.0	92.0	109.5	100.2	96.0
	74.10	109.2	50.8	69.2	60.2	61.8
30	76.73	154.4	154.4	154.4	154.4	154.4
	74.50	129.8	95.2	115.3	102.8	96.8
	72.35	116.2	54.4	77.4	61.7	63.8

The above data were considered by means of various theoretical relations between the solubility and the dielectric constant of the solvent. They are the Born's,⁽⁶⁾ Davis's,⁽⁷⁾ Flatt's⁽⁸⁾ and (1)⁽³⁾ equations.

$$\ln \frac{C_0}{C_1} = \frac{Z^2 \epsilon^2}{2RT\gamma_s} N \left(\frac{1}{D_1} - \frac{1}{D_0} \right) - \frac{Z^2 \epsilon^2}{2kT} \sqrt{\frac{8\pi N Z^2 \epsilon^2}{10^3 kT}} \left(\frac{C_1^{1/2}}{D_1^{3/2}} - \frac{C_0^{1/2}}{D_0^{3/2}} \right) \dots (1)$$

(1) *J. Chem. Soc. Japan*, **68**, 81 (1947).

where R , N , k and ϵ are the gas constant, Roschmidt number, Boltzman number and electric elementary quantum, respectively; and C_0 and C_1 are the solubilities of the solutes in two media of different dielectric constants D_0 and D_1 .

In conclusion, we may say that ;

(1) The assumption of the constancy of solvation radius, which is assumed in the induction of the equation (1), may be admitted in the range of this research except in the case of dioxane solution, but it calls for further investigation.

(2) Even if the dielectric constant of the mixed solvent is equal, the solubility is not so. In other words, the solubility is not determined solely by the dielectric constant of the solvent.

The dioxane, which shows an extraordinarily great difference in the above two conclusions (1) and (2), is a peculiar substance that has a symmetrical structure in the molecular construction, and the dipole moment of which is almost equal to zero, its dielectric constant being very small when compared with the other solvents. As the concentration of the organic solvent in the solution is sufficiently low in each mixed solvents, the molecular association of each organic solvent itself may not exist, but the intermolecular reaction of each solvent and the water molecule must be noted. Such non-polar solvent as dioxane cannot easily approach to the solute as it is intercepted by the water molecule ; consequently, the solute (lead sulfate) may be partly dissolved indirectly in the dioxane solution

(2) *ibid.*, **70**, 271 (1949).

(3) *ibid.*, **70**, 407 (1949).

(4) *ibid.*, **69**, 40 (1948).

(5) *ibid.*, **68**, 29 (1947).

(6) M. Born. *Z. Physik.*, **1**, 45 (1920).

(7) Ricci and Davis, *J. Am. Chem. Soc.*, **62**, 407 (1940).

(8) Flatt and Jordan, *Helv. Chim. Acta.*, **16**, 37 (1933).

under the condition of the solvated ions. So the solubility of lead sulfate in the dioxane solution may be greater than that in the other solvents. Such effect of the dipole moment on the solubility, along with that of the change in the value of a , should become more remarkable as the concentration of the organic solvent in the mixed solvent increases, it is, therefore, desirable to extend this experiment still further. In short, the solubility of the slightly soluble salt does not solely depend upon the dielectric constant of the solvent,

but it may also depend on the difference in the chemical constitution of the solvent.

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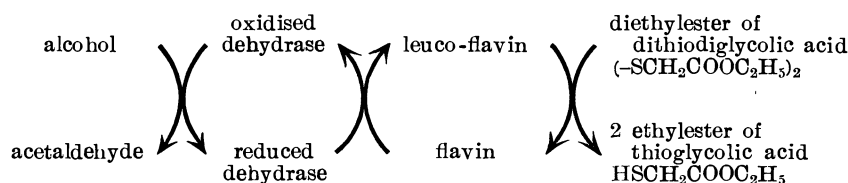
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The Sunflavor of Beer. III. Mechanism of Sunflavor Development

By Tei YAMANISHI and Yataro OBATA

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In the previous paper the authors reported that the development of the sunflavor in beer, exposed to the sunlight, was due to the reduction of diethylester of dithiodiglycolic acid (oxidised-type) to ethylester of thio-glycolic acid (reduced-type). This is produced by the following reaction system.



By further investigation in the direction of the absorption-spectra, it was found that the flavin was activated by the sunlight, particularly by the rays ranging from 441 to 452 $m\mu$, and then the reaction of this system was accelerated.

A few works has appeared in the literature relating to the light-effect on dehydrase system, and it was reported by all workers that the light activates the dehydrase system.⁽¹⁾⁽²⁾⁽³⁾

According to the results of the authors' experiments on the absorption-spectra of the visible rays with the flavin and the dehydrase, the maximum absorption of the flavin takes place at the rays ranging from 441 to 452 $m\mu$. in the wave

(1) Hans von Euler, *Z. physiol. Chem.*, **232**, 16 (1935).

(2) H. v. Euler and E. Klusmann, *Naturwiss.* **22**, 777 (1934).

(3) Krestownikoff, *Skand. Arch. für Phys.* **52**, 199 (1927).

length, as far as the rays which can pass the glass plate are concerned, while the dehydrase shows no special absorption band.

On the other hand, there are two kinds of beer bottles; one is made of brown colored glass and the other green colored glass. That the sunflavor developed more slowly in the

brown bottle than in the green bottle was actually observed in a model experiment as well as in the bottled raw-beer on the market. By studying the absorption-spectra

of these two kinds of bottles, it was found that the brown bottle absorbed the rays with the wave length smaller than 452.5 $m\mu$, while the green bottle absorbed the rays with the wave length ranging from 523 to 561 $m\mu$, as well as those with the wave length smaller than 406 $m\mu$. Then it is concluded that the rays which are concerned with the development of sunflavor have the wave length ranging from 406 to 452 $m\mu$. This range of the wave length coincides in general with the range in which the maximum absorption of the flavin takes place. To prove the effect of the rays in this range of the wave length the authors have carried out a model experiment by exposing the beer to the light filtered through a yellow glass plate which does not pass the rays in question and a violet glass plate which passes them exclusively. The result has proved just as the authors had expected that the

development of the sunflavor of beer was more rapid when the violet filter was employed.

From these results it has become clear that the sunlight activates the flavin and in consequence of this the sunflavor of beer develops.

Experimental Part

The components of the reaction system, used in the model experiment to prove the mechanism of the sunflavor development in beer, are as follows:

Dehydrase solution*	5 cc.
Flavin**	0.3 mg.
Diethylester of dithiodiglycolic acid	0.1 g.
Ethyl alcohol	0.3 cc.
Phosphate buffer (pH 7.2)	5 cc.

* Prepared according to the method described in the second part of this report.

** Preparation of B₂ for injection, manufactured by the Sankyo Co.

Model Experiment with the Green and Brown Bottles.—A test tube filled with the solutions of the above mentioned reaction system and tightly closed with a rubber-stopper is hanged with a string in each of the bottles with close stoppers. These bottles are exposed to the direct summer sunlight. The air temperature in the closed bottles rises to 44-45°. The result of the experiment is shown in Table 1.

Table 1

The Result of Model Experiment with Green and Brown Bottles

Color of bottle	Exposure		
	3 hrs.	5 hrs.	9 hrs.
brown	almost no change (-)	flavin is slightly discolored (-)	flavin is considerably discolored (±)
green	almost no change (-)	flavin becomes colorless (±)	flavin becomes considerably colorless (+)

Note: (+) and (-) denote respectively the high and low extent of the sunflavor development.

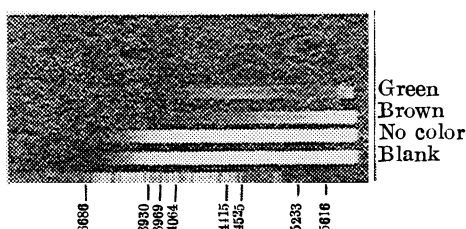


Fig. 1.—The absorption-spectra of the beer-bottles.

As we can learn from Fig 1, the green bottle absorbs the rays with the wave length ranging from 523-561 mμ as well as those with the wave length smaller than 406 mμ, and the brown bottle absorbs the rays with the wave length smaller than 452 mμ.

The Absorption-Spectra of the Flavin and the Dehydrase.—The absorption-spectra of the flavin and the dehydrase solutions are shown in Figs. 2 and 3 respectively.

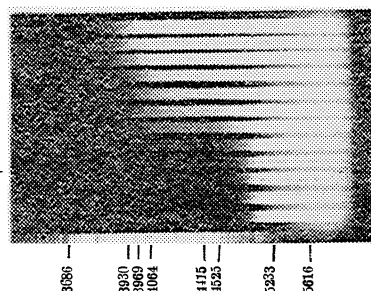


Fig. 2.—The absorption-spectra of the flavin.

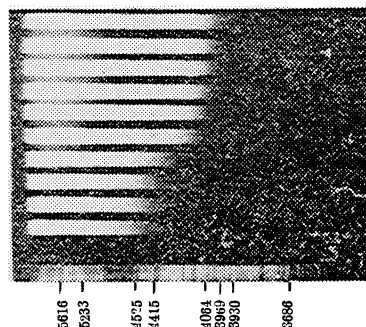


Fig. 3.—The absorption-spectra of the dehydrase.

As it is clearly shown in these figures, the absorption bands of the flavin are situated at the position of the rays with the wave length ranging from 441 to 452 mμ (Maximum absorp-

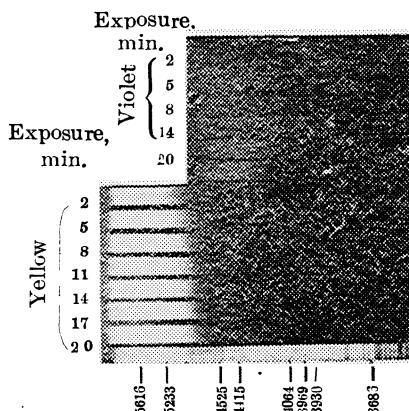


Fig. 4.—The absorption-spectra of the filters

tion band at $440\text{ m}\mu$) and of the rays with the wave length smaller than $388\text{ m}\mu$. The dehydrase has no special absorption band.

The Effect of the Sunlight Filtered through the Yellow and Violet Glass Plates.—The absorption spectra of the colored glass plates used as the filter are shown in Fig. 4.

The violet glass filter passes exclusively the rays with the wave length ranging from $453\text{ m}\mu$ to $406\text{ m}\mu$ or the rays in which the maximum absorption bands of the flavin are situated. The yellow glass filter absorbs entirely the rays with the wave length smaller than $453\text{ m}\mu$.

The reaction system was exposed for five hours to the sunlight filtered through each of these colored glass plates, and then the development of sunflavor was examined. Under the violet filter the color of the solution faded away into slight as the flavin changed to leucoflavin and a slight development of sunflavor was recognised. Under the yellow filter, on the other hand, the solution maintained the yellow color of flavin and the sunflavor could not be detected.

The result of the above experiment is shown in Table 2.

From the results of these experiments it has become clear that the rays which have concern with the development of sunflavor in beer are those in which the flavin has its maximum absorption and range from 453 to $406\text{ m}\mu$ in the wave length.

The development of sunflavor in beer exposed

Table 2
The Effect of the Filtered Sunlight

filter color	Exposure		
	3 hrs.	5 hrs.	9 hrs.
violet	almost no change	flavin becomes leucoflavin ($\pm$)	flavin becomes leucoflavin ($+$)
yellow	"	almost no change ($-$)	flavin is slightly discolored ($\pm$)

to the sunlight is thus due to the activation of the flavin by the light.

In these experiments it took a very long time to get the development of sunflavor. This is considered to be owing to the free flavin employed. If the flavin enzyme is used instead, the results will probably be obtained more rapidly and distinctly.

The authors are now under research to solve the problem concerned.

The expenses of the present study was partly defrayed from the Scientific Research Encouragement Fund granted by the Ministry of Education for which the authors thanks are due.

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Studies on Foams. VI. Theory of Foam Formation

By Masayuki NAKAGAKI

(Received March 27, 1950)

It is supposed, in the first instance, that the surface tension may play an important rôle in the foam formation, as it is a surface chemical phenomenon. Plateau's rule⁽¹⁾ states that the liquid of smaller surface tension foams better. This rule is, however, inconsistent with experiences. For instance, pure liquids do not foam at all, both liquid of small surface tension as ethyl ether and liquid of large surface tension as water. This was ascertained by Foulk and Miller⁽²⁾ and Nakagawa and Sameshima⁽³⁾. Solutions of surface active substances, such as alcohol or soap, as well as solutions of surface in-

active substances as inorganic electrolytes produce foams. As to the aqueous solutions of surface active substances, the surface tension decreases monotonously with the increase of concentration, while the foam formation shows a maximum and again decreases with the further increase of concentration. Considering these facts in all respects, the surface tension seems to have no simple relation to the foam formation. This was already stated by Wo. Ostwald.⁽⁴⁾ It is not yet clear what the predominant factor is, though some qualitative ideas have been proposed.

Bartsch⁽⁵⁾ proposed "heterogeneity" theory. Talmud and Suchowolskaja⁽⁶⁾ suggested a

(1) Cf., S. Berkmann and G. Egloff: "Emulsions and Foams," New York, (1941), pp. 121.

(2) C. W. Foulk, *Ind. Eng. Chem.*, **21**, 815 (1926); **33**, 1086 (1941); C. W. Foulk and J. N. Miller, *ibid.*, **23**, 1283 (1931).

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

(4) Wo. Ostwald and A. Steiner, *Kolloid-Z.*, **36**, 342 (1925).

(5) O. Bartsch, *Kolloid-Z.*, **38**, 177 (1926).

(6) D. Talmud, S. Suchowolskaja and N. Lubman, *Z. physik. Chem.*, **A151**, 401 (1930); D. Talmud and S. Suchowolskaja, *ibid.*, **A154**, 277 (1931).

relation between foam duration and surface rigidity. Hazlehurst and Neville⁽⁷⁾ stated cybotaxis theory. Sasaki⁽⁸⁾ emphasized that the concentration gradient of surface tension is large when the foam formation is large. Foulk⁽²⁾ proposed balanced-layer theory. These theories are all qualitative. In this report, some semi-quantitative consideration will be given.

When the viscosity of the solution is not too large, the foaminess and foam duration are parallel to each other, while the foaminess is small and foam duration is large, when the solution, such as sulfuric acid or glycerol solutions, is of high viscosity. This has been reported, in the foregoing paper.⁽⁹⁾ Viscous solutions take a long time to flow down the wall of foam, and this is the cause of large duration of foam. Ross⁽¹⁰⁾ and Miles, Leo Shedlovsky and Ross⁽¹¹⁾ carried out some calculations from this point of view. In ordinary solutions, however, the viscosity is not large compared to water, so the effect of it is not large. The effect of viscosity is, therefore, neglected in the following discussion.

The existence of adsorption layer, whether positive or negative, seems to be necessary for the foam formation, since pure liquids do not foam while solutions foam considerably well. This is suggested also by the fact that the dye solution of larger surface activity foams better.⁽¹²⁾ It may be supposed that the collapse of foam occurs when an area, S , of adsorption layer is first removed by some accidental reason, and a crack is formed in this area. If the area of bare surface was smaller than S , the surface might be easily covered again by the thermal motion of adsorbed molecules and foam would not collapse. Let the energy, required to remove the unit area of adsorption layer, be U_r . Then, SU_r will play just like the activation energy. If the area S does not largely vary by the properties of solution, the foam duration will be parallel to U_r .

Let the energy required to remove one mole of solute from adsorption layer to bulk solution be U_1 , and the concentration of solute in the solution and the layer be C and C_r (mole/cc.), respectively. Then, according to Boltzmann's distribution law:

$$\left. \begin{aligned} C_r &= C \exp.(U_1/RT) \\ \text{or } U_1 &= RT \ln (C_r/C). \end{aligned} \right\} \quad (1)$$

For the positive adsorption, $C_r > C$ and $U_1 > 0$, and for negative adsorption, $C_r < C$ and $U_1 < 0$. Let the activity of solute in the solution be a_2 , and the molar volume of the solution be V (cc./mole). Then, it is better to replace C by

$$a_2/V. \quad (2)$$

So equation (1) is written as :

$$U_1 = RT \ln (C_r V/a_2). \quad (3)$$

The adsorption layer of the solution of surface active substance may be assumed to be a monomolecular of layer solute molecules lying upon the surface of solution, and the surface film of solute contains no solvent. So the amount of solute contained in the unit area of adsorption layer equals to the surface excess of solute for the unit area of surface, $\Gamma_2^{(1)}$ (mole/cm.²) given by Gibbs' equation :

$$\Gamma_2^{(1)} = - \frac{1}{RT} \frac{\partial \sigma}{\partial \ln (f_2 N_2)}, \quad (4)$$

where σ is the surface tension, f_2 the activity coefficient of solute referred to the infinite dilution as unity, and N_2 the mole fraction of solute. The activity of solute is,

$$a_2 = f_2 N_2. \quad (5)$$

According to the surface chemical studies of higher alcohols, the sectional area of alcohol molecules is said to be about 20 Å². The amount of alcohol molecules closely packed on 1 cm.² of surface, N_a , is, therefore,

$$N_a = 8.33 \times 10^{-10} \text{ (mole/cm.}^2\text{)}. \quad (6)$$

If the mole volume of pure alcohol is V_2 (cc./mole), the volume of adsorption layer per unit area is $N_a V_2$. Therefore :

$$C_r = \Gamma_2^{(1)}/N_a V_2. \quad (7)$$

$$\text{So : } U_1 = RT \ln (\Gamma_2^{(1)} V/f_2 N_2 N_a V_2). \quad (8)$$

For electrolytes, the surface excess of solute given by Gibbs' equation $\Gamma_2^{(1)}$ is

$$\Gamma_2^{(1)} = - \frac{1}{\nu RT} \frac{\partial \sigma}{\partial \ln (m \gamma)}, \quad (9)$$

where m is molality, that is moles of salt per 1000 g. of water, and γ is the mean activity coefficient of salt. The activity of salt a_2 is

(7) T. H. Hazlehurst and H. A. Neville, *J. Phys. Chem.*, **44**, 592 (1940); *Ind. Eng. Chem.*, **33**, 1084 (1941).

(8) T. Sasaki, *Bull. Chem. Soc. Japan*, **13**, 517 (1938).

(9) M. Nakagaki, *Bull. Chem. Soc. Japan*, **21**, 30 (1948).

(10) S. Ross, *J. Phys. Chem.*, **47**, 266 (1943).

(11) G. D. Miles, Leo Shedlovsky and J. Ross, *J. Phys. Chem.*, **49**, 93 (1945).

(12) M. Nakagaki, *This Bulletin*, **22**, 200 (1949).

$$a_2 = a_{\pm}^{\nu} = (\gamma m)^{\nu} (\nu_+^{\nu_+} \nu_-^{\nu_-}) \quad (10)$$

$$\text{where } \nu = \nu_+ + \nu_- \quad (11)$$

ν is the number of ions formed by the dissociation of one molecule of electrolyte, and ν_+ and ν_- are the numbers of positive and negative ions formed from one molecule respectively. The surface excess given by Gibbs' equation (9) is defined as the amount by which the quantity of solute in the system A, having unit area of surface, exceeds that in the system B, having no surface, when these systems A and B contain the same amount of solvent. This is discussed in detail by Guggenheim and Adam.⁽¹³⁾ In this case, the adsorption layer is considered, on the contrary to the case of surface active substances, to contain both solute and solvent. Let the molality of solute in the adsorption layer be m_F , and the thickness of adsorption layer be d (Å). The amount of water contained in 1 cm.² of adsorption layer, that is $d \times 10^{-8}$ cc. is assumed to be $d \times 10^{-8}$ g. Accordingly, by the definition of adsorption amount,

$$\Gamma_2^{(1)} = (m_F - m) d \times 10^{-8} / 1000$$

or

$$m_F = m + \frac{10}{d} \times \Gamma_2^{(1)} \times 10^{10}. \quad (12)$$

Let the mole volume of adsorption layer be V_F , the activity of solute in adsorption layer a_F , and activity coefficient in adsorption layer γ_F . Then,

$$a_F = (\gamma_F m_F)^{\nu} (\nu_+^{\nu_+} \nu_-^{\nu_-})$$

and it is better to replace C_F by the following terms:

$$a_F / V_F = (\gamma_F m_F)^{\nu} (\nu_+^{\nu_+} \nu_-^{\nu_-}) / \nu_F. \quad (13)$$

From equations (10) and (3), we get

$$U_1 = \nu RT \ln \frac{\gamma_F m_F V}{\gamma m V_F}.$$

Now, if we assume,

$$V \cong V_F \quad \text{and} \quad \gamma_F \cong 1. \quad (14)$$

$$\text{then, } U_1 = \nu RT \ln \frac{m_F}{m \gamma}. \quad (15)$$

As to the structure of adsorption layer on the aqueous solution of electrolyte, the idea was proposed that the adsorption layer is constructed from pure water by the positive ad-

sorption. The thickness of adsorption layer is calculated under this premise by Reh binder,⁽¹⁴⁾ Goard,⁽¹²⁾ Harkins and McLaughlin,⁽¹⁶⁾ Harkins and Gilbert⁽¹⁷⁾ and some others. The unreasonableness of this idea has already been pointed out by Adam⁽¹⁸⁾. In the present paper the concentration of the adsorption layer is assumed to be m_F .

The energy U_1 , calculated from equations (8) or (15), is the increase of energy accompanied with the transference of one mole of solute from the adsorption layer to the bulk solution. The energy required to remove the unit area of adsorption layer U_F is,

$$U_F = \Gamma_2^{(1)} U_1, \quad (16)$$

where $\Gamma_2^{(1)}$ is given by equations (4) or (9). U_F is thought to relate to the foam formation of the solution. The change of the free energy of the system, that is the difference of dynamic and static surface tension, is not equal to U_F , because the change of free energy accompanying to the change of concentration, from the concentration in the adsorption layer to that in bulk solution, has not been taken into consideration. This change of available energy was not taken out of the system in irreversible process. So the work required to remove the unit area of adsorption layer equals to U_F . In the case of electrolytes, both $\Gamma_2^{(1)}$ and U_1 are negative. This means that the concentration is smaller and the energy of solute molecule is higher in the adsorption layer than in the bulk solution, and U_F given by equation (16) equals to the energy required to bring solute from interior to surface as far as the concentration of adsorption layer equals to that of the bulk solution.

One of the best investigated system is the aqueous solution of ethyl alcohol. The amount of adsorption in this system has been calculated by Butler and Wightman⁽¹⁹⁾ and Guggenheim and Adam.⁽¹³⁾ The adsorption amount is calculated also by the present author using the data of surface tension cited in the "International Critical Tables" and that of activity in the "Landolt-Börnstein's Physikalisch-Chemische Tabellen," using equa-

(14) P. Reh binder, *Z. physik. Chem.*, **111**, 447 (1924); **121**, 103 (1926).

(15) A. K. Goard, *J. Chem. Soc.*, **127**, 2451 (1925).

(16) W. D. Harkins and H. M. McLaughlin, *J. Am. Chem. Soc.*, **47**, 2083 (1925).

(17) W. D. Harkins and E. C. Gilbert, *J. Am. Chem. Soc.*, **48**, 604 (1926).

(18) N. K. Adam, "The Physics and Chemistry of Surfaces," 2nd ed., (1938), Oxford, pp. 125.

(19) J. A. V. Bulter and A. Wightman, *J. Chem. Soc.*, **1932**, 2089.

(13) E. A. Guggenheim and N. K. Adam, *Proc. Roy. Soc. London*, **A 139**, 218 (1933).

tion (4). The results agree well with those obtained by the above authors. U_r calculated from equations (4), (8) and (16) is depicted in Fig. 1. Mole volume used in this calculation is obtained from the data of density cited in the "International Critical Tables." The same calculation has been done for methyl alcohol and the results are shown in Fig. 1.

The method of the observation on foam formation is the same as that described in the preceding paper.⁽²⁰⁾ Twenty cc. of solution is shaken in a test tube of 40 cc. in capacity. The maximum height of foam zone after shaking A_m (cm.) and the time required to col-

lapse the foam zone t_0 (sec.) are recorded and plotted in Fig. 1. Experiments were done at room temperature of about 25°. As already reported in the foregoing reports^{(9),(21)}, two maxima of foam formation are observed at the concentration of about 3% and 30% for ethyl alcohol, and about 5% and 50% for methyl alcohol. The general tendency of curves agrees well with that of U_r . Relation between curves for methyl and ethyl alcohol is also similar to that of U_r .

Though electrolytes are surface inactive, their solutions foam considerably well as studied by Talmud and Suchowolskaja⁽²²⁾ and others. The foaminess A_m and foam duration t_0 measured by the method described above

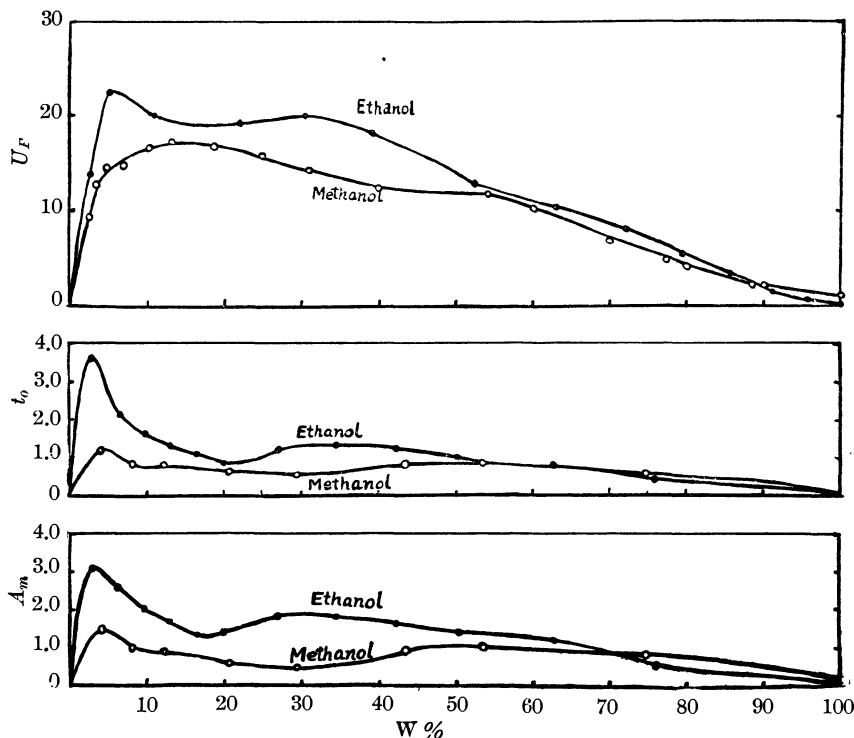


Fig. 1.—Alcohol solutions.

lapse the foam zone t_0 (sec.) are recorded and plotted in Fig. 1. Experiments were done at room temperature of about 25°. As already reported in the foregoing reports^{(9),(21)}, two maxima of foam formation are observed at the concentration of about 3% and 30% for ethyl alcohol, and about 5% and 50% for methyl alcohol. The general tendency of curves agrees well with that of U_r . Relation between curves for methyl and ethyl alcohol is also similar to that of U_r .

As U_1 is the energy required to transfer one mole of solute from absorption layer to the bulk solution, U_1 is supposed to be a

function of concentration of solution. In dilute solution, the energy required to bring the hydrophobic alkyl group of alcohol molecule into the solution, shoving water molecules aside, will be large. In concentrated solution, however, the value of U_1 will be small, since alcohol dissolves many organic substances well. In fact, U_1 calculated by equation (8) becomes smaller as the concentration increases.

(22) D. Talmud and S. Suchowolskaja, *Z. physik. Chem.*, **A154**, 277 (1931).

(23) R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

(20) M. Nakagaki, *This Bulletin*, **23**, 102 (1950).

(21) M. Nakagaki, *This Bulletin*, **22**, 21 (1949).

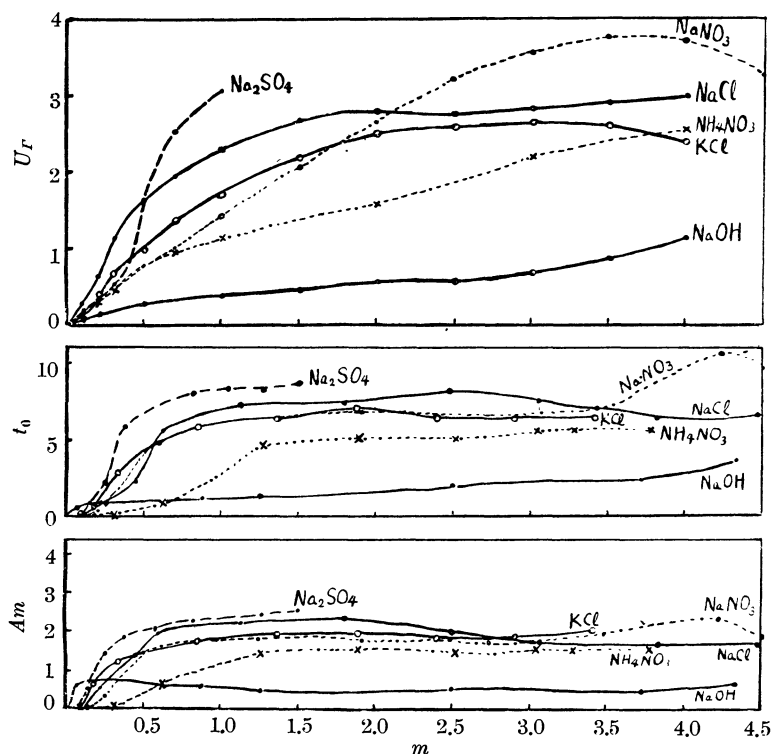


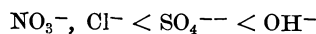
Fig. 2.—Electrolyte solutions.

Table 1

Value of d , Å.

NaCl	4.0	NaNO ₃	3.6	Na ₂ SO ₄	6.8
KCl	3.8	NH ₄ NO ₃	4.4	NaOH	9.0

Å. for hydroxide. Factors determining the thickness of adsorption layer is not yet clear, but following qualitative consideration may be acceptable. Since ions are hydrated in aqueous solution, the distance from the surface to ions lying nearest to the surface is greater than the radius of hydrated ion, if ion is surrounded by the same thickness of the layer of bound water as in the interior of solution, even when the ion is entered in the adsorption layer. This may be one of the reasons of the negative adsorption of ions. It is usual, moreover, that the negative ion approaches to the surface closer than the positive one. This has been assured by many experiments on the surface potential. The thickness of the adsorption layer will, therefore, relate to the degree of the hydration of anion. This idea is supposed by the fact that the sequence of the thickness of adsorption layer,



agrees with the lyotropic series. In addition, the thickness of adsorption layer agrees with the radius of hydrated anions in its order of magnitude.

Summary

Foam formation of aqueous solutions of both alcohols and electrolytes are accounted under the assumption of parallelism between the foam formation and the energy required to remove the unit area of adsorption layer from the surface. The maximum observed at the concentration of about 45 % for alcohol solutions are also accounted. The relative relation between some electrolyte solutions is accounted under the assumption that the thickness of adsorption layer increases in the sequence of lyotropic series of anions: $\text{Cl}^-, \text{NO}_3^- < \text{SO}_4^{--} < \text{OH}^-$.

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On the Structure of Humic Acids. An X-ray Diffraction Study

By Katsuya INOUE

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Introduction

Coal is considered as substance built by independent molecules possessing the same crystallographic meaning and a more or less highly developed aromatic character, but continuously changing van der Waals forces. J. Biscoe and B. E. Warren⁽¹⁾ coined the word "turbostratic" systems to express such crystallographic character for carbon blacks. H.E. Blayden, J. Gibson and H. L. Riley⁽²⁾ have proved that the coal structure is also described by the word. And they suggested that the peripheral nature of crystallites might be essential for coal properties. By the concept of turbostratic system, however, the carbon cannot be distinguished from the caking coal which shows entirely different rheological characters. The author has shown from the experiments on Young's modulus of coal⁽³⁾ that the weak van der Waals forces between coal molecules and strong solvation of molecules with inorganic ash are the necessary conditions for essential (caking) properties of coal. The most considerable reason of such differences of the intermolecular forces appears to be in the peripheral conditions of coal molecules. The present study is concerned from this view with humic acids.

The humic acid is defined in this paper as the chocolate-color substance which is produced by the extraction with 1% sodium hydroxide solution up to 90°, and is precipitated by adding the excess of mineral acids. This substance is interesting not only from the peripheral problem of coal molecules but for discussing the coalification mechanism from vegetable debris.

On the structure of humic acid, we have theories rather in confusion. Stadnikoff⁽⁴⁾ gave a chain-like molecule for this substance, but

W. Fuchs⁽⁵⁾ showed from organo-chemical studies some aromatic structure. H. L. Riley⁽⁶⁾ suggested recently that there should be a third possible arrangement of carbon structure having tilted benzene rings, but regretfully with insufficient experimental evidence.

The present X-ray diffraction study falls into two sections. The first deals with the humic acids from various "rank" of coal. The second section describes similar diffraction experiments on some derivatives from humic acids of same origin.

As to the X-ray diffraction study we have a study by J. Sedletzky and B. Brunowsky⁽⁷⁾ on three samples of humic acids from German brown coal. Most recently the author was informed from the Chem. Abst. that H. Brusset⁽⁸⁾ has published an X-ray study on humic acids from lignite and of the products obtained by treating it with dil. HNO₃ and solvents.

Experimental Method and Description of Samples

The generally used Debye-Scherrer diffraction method was used. Copper K α radiation filtered by nickel foil was employed. Exposures of 4.5 hours were necessary at a potential of 30 kv., and a tube current of 6 milliamp. After development, the photographic film was micro-photometered and the lattice parameters were obtained from the maxima on the photometer curve and the values of crystallite dimensions were calculated from the breadth of bands, drawing at both cases the back-ground blackening due to the incoherent scattering.

The descriptions of the samples are in the following. The samples from No. 1 to 5 were made from lignites, i.e. Komatsu, Takayama, Kitomo and Nagasakayama lignite respectively. Extraction by 1% alkaline solution and precipitation by hydrochloric acid were repeated twice, washed by distilled water repeatedly and then dialysed for a week. No. 6 is the humic acid prepared by "Merck." No. 7 is the humic acid extrated from the soil of a pond in Tokyo by the Oden's method.⁽⁹⁾ The samples from No. 8

(1) J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

(2) H. E. Blayden, J. Gibson and H. L. Riley, *Proc. Conf. Ultrafine Structure of Coals and Cokes*, London, 1944, 176; *J. Inst. Fuel*, 1945, *Wartime Bulletin*, 117.

(3) Katsuya Inoue, Presented at the 3rd annual meeting of the Chem. Soc. Japan, Apr. 1950. The manuscript has just been sent to the *J. Colloid Sci.*, May, 1950.

(4) "Die Chemie der Kohle," W. Fuchs, S. 455, 1931.

(5) W. Fuchs, *Angew. Chem.*, **44**, 111 (1931).

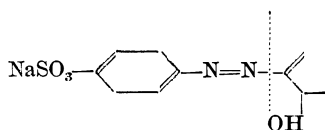
(6) H. L. Riley, *J. Soil Sci.*, **1**, 104 (1947).

(7) J. Sedletzky and B. Brunowsky, *Kolloid-Z.*, **73**, 90 (1935).

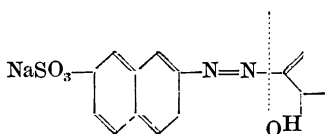
(8) H. Brusset, *Chem. Abst.*, **43**, 6395 (1949). (*Bull. soc. chim. France*, 1949, 319).

(9) S. Oden, *Kolloid-Beihfte*, **11**, 75 (1919).

to 11 are the so-called "regenerated" humic acids⁽¹⁰⁾ obtained by ca. 150 hours' air oxidation at 150° from the bituminous coals, i.e. Yubetsu producer gas coal, Takashima caking coal and Shishimachi strongly caking coal respectively. Purification was carried out as at the lignite humus. Nos. 12 and 13 are the acid azo dyes from humic acids Nos. 1 and 2 respectively, coupled with diazo-sulfonic acid in alkaline solution under cooling. These brown dyes are remarkable to be able to make aqueous solutions easily. No. 14 is another acid dye from humic acid No. 2 coupled with diazo-J-acid. It is noteworthy that this dye has a beautiful violet color entirely different from the original humus. These dyes were purified twice by salting-out method with sodium acetate and alcohol. No. 15 is the methoxy-derivative of the humic acid No. 2 obtained by the reaction with dimethyl sulfate.⁽¹¹⁾ The methoxy humic



Acid dyes Nos. 12 and 13.



Acid dye No. 14.

acid is less hydrophilic brown powder. (See the figure.)

Results and Discussions

The obtained bands are highly diffused and generally give only two reflections with sufficient intensity to permit of their use in particle size determinations. The calculated lattice parameters for these bands and crystallite dimensions are tabulated in Table 1.

It is noteworthy that all these parameters, with the only exception of No. 7, suggest these samples to possess the so-called "amorphous carbon" lattices. So naturally the author has to recognize, at least from the X-

Table 1

No.	Sample	Lattice parameter		Crystallite dimension	
		$\overbrace{a}^{c/2}$	$\overbrace{c}^a$	$\overbrace{a}^c$	$\overbrace{c}^a$
1	Lignite Humus (Komatsu)	2.11Å	3.66Å	8.9Å	9.4Å
2	Lignite Humus (Takayama)	2.19	3.70	8.5	9.1
3	Lignite Humus (Tomowo)	2.16	3.60	7.2	9.7
4	Lignite Humus (Kitomo)	2.17	3.65	11.2	8.8
5	Lignite Humus (Nagasakayama)	2.19	3.58	8.3	10.9
6	Humic acid "Merck"	2.19	3.67	8.9	9.6
7	Soil Humus	1.63	3.43	—	—
8	Regenerated Humus (Yubetsu)	2.32	3.54	12.4	12.3
9	Regenerated Humus (Takamatsu)	2.27	3.57	9.6	17.5
10	Regenerated Humus (Takashima)	2.32	3.54	14.3	21.0
11	Regenerated Humus (Shishimachi)	2.12	3.44	7.8	17.9
12	Sulfanilic dye (1)	2.15	3.85	10.3	10.8
13	Sulfanilic dye (2)	2.29	3.63	8.7	10.8
14	J-acid dye (2)	2.40	3.73	—	—
15	Methoxy Humus (2)	2.24	3.70	7.0	13.2

ray stand-point, the humic acid is essentially of the "turbostratic" carbon structure. The soil humus, however, shows different a-parameter and there remains little doubt that this does not yet form the highly aromatic lattice for its low maturity.

One of the results from these data is the fact that the "humic" substances, namely of the same chemical character, show various crystallite dimensions according to the maturity of their original coals. Even in the series of lignite humus, the samples from relatively high rank lignites, for example, of Kitomo or Nagasakayama lignite, have larger dimensions. Furthermore, the "regenerated" humus shows remarkably large dimensions, because of the crystallographic development of the crystallites. In other words, the coal molecules grow up in spite of the same chemical "humic" nature when they are added some peripheral groups.

In the other way from the data of derivatives of humic acids, we can understand the changing of chemical nature only by adding peculiar radicals to the peripheries of the molecules. By adding some diazo radicals, "humic" molecules change soluble in water and furthermore if we choose the adequate kind of added groups, the color can change from brown to violet.

(10) G. T. Morgan and J. I. Jones, *J. Soc. Chem. Ind.*, 1938, Sept., 239.

(11) The author is indebted to Mr. Kozo Higuchi for preparing these derivatives (No. 12—15). He is going to publish the preparation and characteristics of these substances. According to his analysis, diazo components are coupled at the *o*- or *p*- positions for phenolic radicals up to almost saturation, and methoxy radicals are produced by substituting the phenolic hydroxyl groups.

In the chemical common-sense, these dyes are of never "humic" nature, but they have the same crystallographic dimensions as of the original samples. (Compare Nos. 13 and 14 with No. 2, and also No. 12 with No. 1). The same consideration is available for the data of methoxy derivative which has lost hydrophilic character of humus. These facts appear to be another evidence of the importance of periphery of molecule to the nature of coal.

The long oxidation of coal means the addition of some oxygen containing radicals to periphery, and in consequence of the strengthening of intermolecular forces, as generally known, the caking properties of coal diminish and in alkaline solution the coal molecules can dissolve to produce the "regenerated" humic acid, followed by, perhaps, base-exchange reactions. It seems therefore interesting to note that the base-exchange capacities of lignite humus and regenerated humus are

Table 2

Sample	No. in Table 1	Base-exchange capacity
Lignite Humus	2	3.6×10^{-2} meq./g
Lignite Humus	4	5.5
Regenerated Humus	10	4.8
Regenerated Humus	11	3.9

almost same as shown in Table 2. These data were measured by treating the sample with 200

times of 0.1 *N* sodium chloride solution during seventy hours.

Conclusion

Some organic chemists discuss the structure of the humic acid and often reach the conclusions in confusion. It seems not to be of essential meaning to discuss the chemical structure as if there exists a definite substance named humic acid. From the above described data and considerations, "humic" is naturally the name for a nature, not for a definite substance. The coal molecule "grows up" with same "humic" nature and on the other hand the chemical character can be changed at our option by adding adequate peripheral radicals, and the peripheral conditions appear often to be of the fundamental meaning to the essential properties of coal.

The diffraction apparatus used in this study was lent to use by the Chemical Institute, the University of Tokyo, and the author takes great pleasure in acknowledging his indebtedness to Dr. Hideo Akamatsu, without whose kind permission the author doubts whether he could have done the work, and also to Mr. Hiroshi Takahashi for his help in taking photometer curves.

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The Synthesis of 3-Hydroxykynurenine (+Chromogen)*

By Yoshimasa HIRATA and Koji NAKANISHI

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+Chromogen (W-substance) (1) of *Bmbyx mori*, corresponding to the cn^+ -substance of *Drosophila* and A-substance of *Ephesia*, is widely distributed among insects and animals belonging to *Arthropods*. It is considered to be an important intermediate in the conver-

sion of tryptophan to various pigments⁽¹⁾ and nicotinic acid,⁽²⁾ and prior to its isolation in a pure crystalline state, a structure corresponding to 3-hydroxy-kynurenine (2-amino-3-hydroxybenzoylalanine) (VIII) was postulated⁽³⁾ in 1948. H. Kikkawa⁽⁴⁾ and we have recently

*) These results were presented before the Third Annual Meeting of the Chemical Society of Japan at Kyoto, April, 1950. At the same Meeting, S. Seno and T. Sakan (Osaka University) also reported the synthesis of +chromogen by applying the Kotake-Sakan method for the synthesis of kynurenine.

(1) H. Kikkawa, *Sanshi-shikenjo Hokoku (Re-*

ports of Sericultural Exp. Stat.), **11**, 311 (1943). *Kagaku no Ryoiki*, **3**, 2 (1949).

(2) F. A. Haskins and H. K. Mitchell, *Proc. Nat. Acad. Sci.*, **35**, 500 (1949).

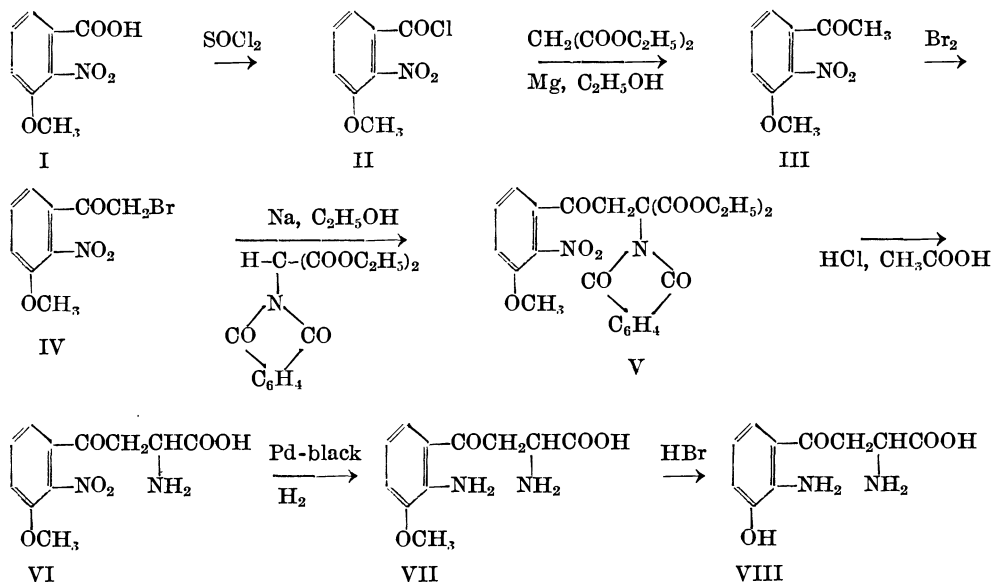
(3) H. K. Mitchell and J. F. Nyc, *ibid.*, **34**, 1 (1948).

(4) Y. Hirata, K. Nakanishi and H. Kikkawa, *J. of Genetics (Japan)* (in press). *Science* (U. S. A.) (in press).

succeeded, for the first time, in isolating 50 to 60 mg. of light-yellow crystals from 400 g. of new-laid eggs of *Bombyx mori*,⁽⁵⁾ positive to the qualitative and biological tests of +chromogen. In the following paper the synthesis of 3-hydroxykynurenine is reported. The synthesized sample was identical with the natural specimen (excepting optical behavior⁽⁶⁾), thus establishing the structure of +chromogen to be 3-hydroxykynurenine.

modified procedure of Butenandt *et al.*⁽⁹⁾ for the synthesis of kynurenine (2-amino-benzoyl-alanine) was applied, resulting in 2-amino-3-methoxybenzoylalanine (VII). This was finally converted into 2-amino-3-hydroxy-benzoylalanine (VIII) hydrobromide by hydrolysing with hydrobromic acid. The treatment of the hydrobromide with sulfuric acid and then with barium hydroxide gave free DL-2-amino-3-hydroxy-benzoylalanine. Excepting the con-

Fig. 1



The starting substance for the synthesis of 2-amino-3-hydroxy-benzoylalanine was 2-nitro-3-methoxybenzoic acid (I), which was prepared by the method of Nyc and Mitchell⁽⁷⁾ from 3-methoxy-benzoic acid. 2-Nitro-3-methoxy-benzoic acid was converted into its chloride (II) and then to 2-nitro-3-methoxyacetophenone (III). The latter step was carried out by submitting the chloride to the method employed in the synthesis of p-nitroacetophenone,⁽⁸⁾ an intermediate in the synthesis of chloromycetin. After bromination of 2-nitro-3-methoxyacetophenone, which yielded 2-nitro-3-methoxyphenacyl bromide (IV), the suitably

version of IV to V, in which several by-products were obtained, every step in this synthesis proceeded quite smoothly with a high yield.

The synthetic sample possessed the following natures, thus proving the identity with the natural substance, +chromogen. The ninhydrin, xanthoprotein and diazo (Ehrlich's) reactions were positive. The alkaline solution, with a deep yellow color, gave a jasmine-like odor when heated, and a dilute solution of potassium permanganate also changed its color into deep yellow (urochromogen test of Weiss). Furthermore, employing the ninhydrin or Ehrlich's reagents or the light blue fluorescence as means for location, paper chromatography with various solvents could be used for the identification of 3-hydroxykynurenine. The solvents used were butanol, lutidine, phenol and the butanol-acetic acid mixture, each giving satisfactory results.

(5) It is reported in the forementioned reference (2) that W. Weidel has isolated the substance from *Calliphora erythrocephala*, but the details seem to be yet unreported.

(6) Natural specimen: $[\alpha]_{589}^{17} = -30^\circ$ (approximately).

(7) J. F. Nyc and H. K. Michell, *J. Am. Chem. Soc.* **70**, 1847 (1948).

(8) Walter and Hauser, *ibid.*, **68**, 1386 (1946); L. M. Long and H. O. Troutman, *ibid.*, **71**, 2474 (1949).

(9) A. Butenandt, W. Weidel, R. Weichert and W. von Derjungen, *Z. physiol. Chem.*, **279**, 27 (1943).

Experimental

2-Nitro-3-Methoxy-benzoyl-chloride (II).—

2-Nitro-3-methoxy-benzoic acid (I) (m.p. 255°) was prepared by the method of Nyc and Mitchell⁽⁷⁾ from 3-methoxy-benzoic acid. After converting 2-nitro-3-methoxy-benzoic acid into its chloride with thionyl chloride, the excess reagent was completely removed by evaporation *in vacuo*. The chloride could be recrystallized from carbon tetrachloride (m.p. 76°), but the crude sample was directly submitted to the following procedure.

2-Nitro-3-methoxy-acetophenone (III).—

This compound was prepared by a slight modification of the method of Long and Troutman⁽⁸⁾ for the synthesis of *p*-nitro-acetophenone. 3.15 g. (0.13 mole) of freshly ground magnesium turnings and a solution of 0.5 cc. of dry carbon tetrachloride in 3cc. of absolute ethanol were placed in a 500cc. flask and as the reaction began to occur, 35cc. of dry chlorobenzene was added. A solution of 21g. of diethyl malonate (0.13 mole), 20cc. of dry chlorobenzene and 15cc. of absolute ethanol was added while shaking and cooling at such a rate as to keep the temperature at about 65°. When the removal of the cooling bath did not result in a rise in temperature, the mixture was heated to 85° on a water-bath until the reaction ended (two hours). The solution was cooled and a solution of 24g. (0.11 mole) of II in 35cc. of dry chlorobenzene was added by stirring and cooling so as to keep the temperature below 35° (usually, cooling was unnecessary). The mixture gradually changed into a brown gelatinous mass and the stirring was continued for 30 minutes. The flask was cooled in an ice-bath and a solution of 10cc. of concentrated sulfuric acid in 70cc. of water was added. The lower layer, saturated with sodium sulfate, was discarded and the chlorobenzene layer was slightly warmed, whereby precipitates of magnesium sulfate appeared. This was filtered and the chlorobenzene layer of the filtrate was concentrated *in vacuo* until the solvent was almost completely removed. The residue was hydrolysed with a mixture of 40cc. of acetic acid, 5cc. of hydrochloric acid and 30cc. of water for 5 hours and then ice-cooled. A crystalline mass was obtained, which was filtered and boiled with a solution of 15g. of sodium bicarbonate in 150cc. of water to remove the acidic by-products. The residue was crystallized from acetic acid. Yield, 20.5g. (93 %), m.p. 129°.

2-Nitro-3-methoxy-phenacyl Bromide (IV).—To a solution of 20.5g. (0.15 mole) of III in 150cc. of acetic acid, some aluminium chloride and equimolecular bromine (1.7g.) dissolved in 50cc. of acetic acid were added. By slightly warming the mixture for 30 minutes the reaction ended. A crude crystalline mass was obtained by pouring the mixture into cold water. This was filtered and water was gradually added to its acetic acid solution. 22.5g. (78 %) of IV was obtained as white crystals by adding water until a brown syrupy mass gradually began to precipitate, m.p. 84–86°.

2-Nitro-3-methoxyphenacyl-phthalimidomalonate Ester (V).—The sodium salt of phthalimidomalonate ester was prepared by the method of Sørensen⁽¹⁰⁾. 21g. (6.9 millimoles) of phthalimidomalonate ester was added to a solution of 167mg. (7.3 millimoles) of sodium in 10cc. of absolute ethanol and dissolved by slight warming. The ethanol was completely evaporated *in vacuo* and 10cc. of dry acetone was added twice, each time being removed *in vacuo*. The residue was completely dried *in vacuo* at 145° for one hour and a half and finally dissolved in 140cc. of dry acetone, giving a yellow-orange solution. 20g. (7.3 millimoles) of IV in 10cc. of dry acetone was added and after refluxing the mixture for 15 hours, it was ice-cooled for 5 hours to complete the precipitation of sodium bromide. This was discarded and the acetone evaporated *in vacuo*. The residual brown syrup containing V was directly submitted to the following procedure.

2-Nitro-3-methoxy-benzoylalanine (VI).—The syrup was refluxed on the water-bath with a mixture of 15cc. of hydrochloric acid and 15cc. of acetic acid for two hours and after further addition of 10cc. of hydrochloric acid, refluxed for two additional hours, by which the evolution of carbon dioxide ceased. The cooled mixture was filtered and the filtrate evaporated to dryness *in vacuo*. Dry acetone was added, whereby a considerable amount of crystalline glycine hydrochloride (identified by means of paper chromatography and analysis of nitrogen) remained undissolved. The acetone solution was concentrated and 15cc. of water was added. Acetone was further removed from the mixture, and the residue, a turbid aqueous solution, submitted to centrifugal separation. The clear solution was concentrated somewhat *in vacuo*, whereby white crystals (m.p. 197°) appeared. They were discarded and the residue was evaporated and dried *in vacuo*, resulting in 45 mg. of 2-nitro-3-methoxy-benzoylalanine hydrochloride (2.2 %, calculated on the basis of IV).

2-Amino-3-methoxy-benzoylalanine hydrochloride (VII).—The aqueous solution of 45 mg. of VI-hydrochloride was reduced, using palladium black as catalyst, and the solution, possessing a blue-green fluorescence, was evaporated *in vacuo* after the addition of a few drops of concentrated hydrochloric acid. 37mg. (80%). m.p. (decomp.) 153°.

3-Hydroxykynurenine (+chromogen) (VIII).—A solution of 37mg. of VII-hydrochloride in 20cc. hydrobromic acid and 10cc. acetic acid was refluxed for three hours. The removal of the solvent *in vacuo* yielded white needles, m.p. (decomp.) 230°, with a positive diazo reaction (Ehrlich's). The hydrobromide was dissolved in dilute sulfuric acid and somewhat concentrated under carbon dioxide. The solution was neutralized with barium hydroxide and the barium sulfate discarded. By concentrating the filtrate

(10) S. P. L. Sørensen, *Z. physiol. Chem.*, **44**, 454 (1905).

in vacuo and cooling, 22mg. (77 %) of+chromogen was obtained as yellow needles. m.p. (decomp.) 217°. *Anal.* Calc. for $C_{10}H_{12}O_4N_2$: C, 53.57; H, 5.36. Found (dried for 3 hours at 140°): C, 53.16; H, 5.84. The sample thus obtained gave all the qualitative natures expected for+chromogen and was positive to biological tests using the Malpighian tubes of *Drosophila*. Details regarding biological tests are to be published elsewhere.

The authors are greatly indebted to Prof. F. Egami for his encouragements given in the course of this study and Dr. H. Kikkawa (Sericultural Expt. Stat., Taketoyo Branch) for carrying out the biological tests.

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On the Structures of Fibrous Proteins. I. A New Polypeptide Structure of α -Keratin

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(Received October 31, 1949)

I. Introduction.—A question of the first importance for the structural-chemical study of proteins is to determine by the results obtained from physical and chemical experiments how the polypeptide chains are constructed from their constituent molecules or molecular residues, and how they are assembled. For fibrous proteins several model structures have been proposed by different authors, but all of them appear to be still unsatisfactory. Astbury's model for α -keratin,⁽¹⁾ for example, involves some unreasonable points.⁽²⁾ Simanouti and Mizushima⁽³⁾ offered a bent form model for α -keratin and an extended form for β -keratin, concluding that these models could reasonably explain many problems concerning the structures of proteins to an appreciable extent. However, the tetrahedral configuration they assumed to represent the C atom of the carbonyl radical does not accord with experimental facts. It is known from the results of electron diffraction experiments on formaldehyde⁽⁴⁾ and acetaldehyde⁽⁵⁾ that the three bonds of the C atom in a carbonyl radical lie in one plane, making angles of about 120° mutually. Mizushima and Simanouti⁽⁶⁾ reported also that the identity distance of α -keratin chain calculated from their bent form model, using Pauling's covalent radii, agrees very well with the ob-

served $5.15 \text{ \AA}$.⁽¹⁾ If we calculate this distance, taking $109^\circ 28'$ for the bond angles on each of the α -carbon and the N atoms, and 120° for those on the C atom in the carbonyl radical, it becomes $5.12 \text{ \AA}$. However, the N...O distance of the N-H...O hydrogen bond comes out to be $1.98 \text{ \AA}$. This is much shorter than the ordinarily accepted value for this bond of about $2.85 \text{ \AA}$. Assuming the tetrahedral angles also for the C atom in the carbonyl radical, as indicated in Simanouti and Mizushima's figure, the identity distance becomes $4.91 \text{ \AA}$, and then the overall N-H...O distance shortens to a much smaller value $1.82 \text{ \AA}$. This would mean the existence of a steric hindrance between the N and the O atoms.

Recently Mizushima, Simanouti *et al.*⁽⁷⁾ studied the structure of N-methyl acetamide, which they regarded as a constructive unit of polypeptide chains, by ultraviolet absorption, Raman effect, infrared absorption and dipole moment measurements. They found that this molecule has no *enol*-form, and it involves a resonance between two structures, and the two methyl radicals were concluded to be in *trans* position in a coplanar configuration. These findings all seem to favor their bent and extended models for keratins, but whether the relative orientations of atoms found in the simple N-methyl acetamide molecule would directly represent the circumstances obtaining in a highly polymerized substance like keratin chains is a question we must be very cautious about. Their conclusions appear to need more experimental verifications in this very point, although their results about the N-methyl acetamide molecule itself appears very good. We would rather consider that the -C-N-C-C-chain structure in the N-methyl acetamide

(1) W. T. Astbury and A. Street, *Phil. Trans. Roy. Soc.*, **A230**, 75 (1931). W. T. Astbury and H. T. Wood, *Phil. Trans. Roy. Soc.*, **A232**, 333 (1933).

(2) K. H. Meyer and H. Mark, "Hochpolymere Chemie, II" (1940).

(3) T. Simanouti and S. Mizushima, *This Bulletin*, **21**, 1 (1948).

(4) D. P. Stevenson, J. E. Lu Valle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2508 (1939).

(5) D. P. Stevenson, H. D. Burnham and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2922 (1939).

(6) S. Mizushima and T. Simanouti, "Structures of Proteins." (in Japanese), p. 77. Gakuzyutu Tosho Syuppansha, Tokyo (1949).

(7) S. Mizushima and T. Simanouti, *Kagaku* (in Japanese), **19**, 252 (1949).

molecule does not necessarily be kept exactly in fibrous proteins, where long polypeptide chains are tangled and sidely connected at various positions in a very complicated way.

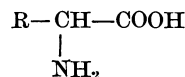
We now turn to examine Huggins' model,⁽⁸⁾ proposed and discussed in detail early in 1943, for the polypeptide structures of silk-fibroin, α - and β -keratins and collagen. In his structures Huggins assumed bond distances and angles based on Corey's data⁽⁹⁾ of X-ray analyses for diketopiperazine,⁽¹⁰⁾ glycine⁽¹¹⁾ and alanine.⁽¹²⁾ However, in his model for α -keratin [Fig. 11 on p. 210, Fig. 14 (a), (b) and (c) on p. 212 of his paper], the calculated N...O distance of the N-H...O bond is 2.17 Å. (for the case of the identity distance 5.15 Å), disagreeing with 2.85 Å. given in his Table 1 for this distance. If we stretch the chain to obtain a model for β -keratin until all bonds in the main chain come in one plane, the calculated identity distance becomes 7.48 Å, which is very much larger than the observed value 6.64 Å. In glycine and alanine molecules there are positive and negative charges and the N—C α and C α —C bond distances are apt to be influenced by these charges. In the diketopiperazine molecule several resonating structures are proposed. However, there is no charge in the polypeptide main chain, and the occurrence of resonance phenomena has not been confirmed. Therefore we cannot agree with Huggins in assuming the same bond distances and angles for fibrous proteins as occurring in simple molecules of glycine, alanine and diketopiperazine. Moreover, if we look into the stereochemical significance of C α atom in his models [Fig. 11 and 12 on p. 210, Fig. 13 on p. 211, Fig. 14 (a), (b) and (c) on p. 212], we may easily verify that these models are constructed solely from D-acids. As a matter of fact, most of his models can as well be constructed from L- as from D-constituents. In this respect it may be mentioned that Simanouti and Mizushima's bent form model is also derivable even if we interchange the positions of R and H.

No explanation seems to have ever been offered as to why D-type amino acids do not exist in natural proteins. So long as we assume protein structures in which the positions of R and H attached to C α are interchange-

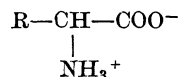
able, we should expect both D- and L-amino acid products in the hydrolyses of natural proteins. That this is not the case is shown by every evidence, and we are forced to consider that the true structures for proteins are those in which only one single type (L) of amino acids are contained as constituents.

From the above arguments it is clear that both Huggins' and Simanouti and Mizushima's models for keratins are not entirely satisfactory. We are going to propose, in this and in the succeeding paper, new models for α -, β -, and feather-keratins and silk-fibroins which appear more reasonable than those of the above authors, and in this paper we shall limit ourselves to the treatment of the structure of α -keratin.

II. Amino Acids.—We shall describe here briefly about amino acids constituting polypeptide chains of proteins from the structural-chemical standpoint. Amino acids obtained by hydrolysis of natural proteins are all α -amino acids and their general formula is given by

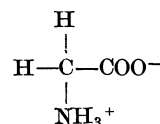


but in accordance with the X-ray diffraction results of crystals of glycine⁽¹¹⁾ and alanine,⁽¹²⁾ we had better write the formula as

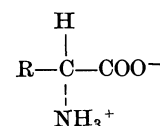


Amino acids are classified into three kinds.

(1) When R=H, this is optically inactive glycine. Two H atoms are attached to the C α atom and three to the N atom.



(2) When R=CH₃, C₂H₅, etc. (about 27 radicals), the acids are all optically active. Here we naturally expect the existence of D- and L-type antipodes, whereas α -amino acids obtained by hydrolysis



of natural proteins are all of the L-type. By the studies of Freudenberg,⁽¹³⁾ Kuhn,⁽¹⁴⁾ etc. the absolute configuration of L-alanine is concluded, by analogy to the configuration of L-lactic acid, to be the one shown in the next figure. Thick horizontal bonds point to the front of the paper and thin vertical bonds

(8) M. L. Huggins, *Chem. Rev.*, **32**, 195 (1943).

(9) R. B. Corey, *Chem. Rev.*, **26**, 227 (1940).

(10) R. B. Corey, *J. Am. Chem. Soc.*, **60**, 1598 (1938).

(11) G. Albrecht and R. B. Corey, *J. Am. Chem. Soc.*, **61**, 1087 (1939).

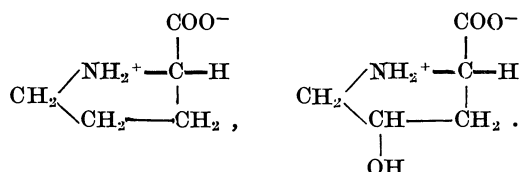
(12) H. A. Levy and R. B. Corey, *J. Am. Chem. Soc.*, **63**, 2095 (1941).

(13) K. Freudenberg, "Stereochemie," 662 (1932).

(14) W. Kuhn, *Naturwiss.*, **26**, 289, 305 (1938).

point to the back of it. For amino acids other than L-alanine proper radicals are to be substituted in place of CH_3 . In this configuration one H atom is connected to the C_α atom and three to the N atom.

(3) When R becomes longer and is connected to the N atom to form a ring, we



obtain proline and hydroxyproline. Here one H atom is attached to the C_α and two to the N atom.

III. Polypeptide Chain.—In fibrous proteins it is considered that α -amino acids con-

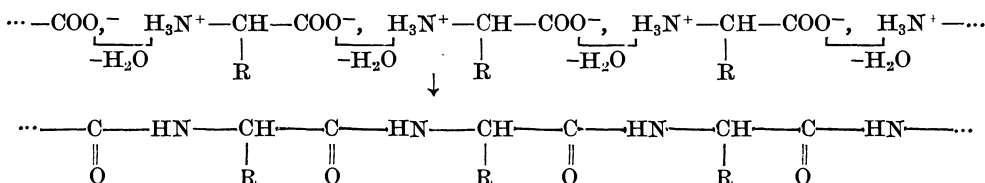
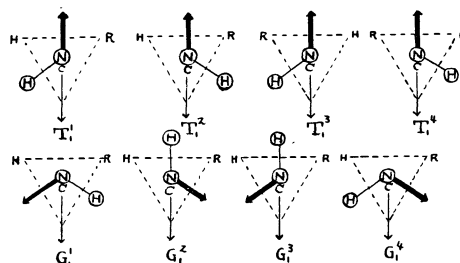


Table I

Bond Lengths and Bond angles*	
Bond Lengths*	Bond Angles
N— C_α 1.47 Å.	Tetrahedral configuration.
C_α —C 1.54 "	
C—N 1.47 "	Each angle $109^\circ 28'$
N—H 1.00 "	
C_α —H 1.09 "	: Plane triangular configuration.
C_α —R 1.54 "	
C—O 1.22 "	Each Angle 120°
C_α : Carbon atom in the α -position. C : Carbon atom in the carbonyl radical	
	: Pyramidal configuration. Each Angle 109°

* L. Pauling: "The Nature of the Chemical Bond," p. 164 (1940).

Fig. 1.—Bond direction types in N— C_α

stitute the polypeptide chain, after dehydration in the interaction of the COO^- radical of an amino acid molecule and the NH_3^+ radical of another.

In the polypeptide chain thus formed we shall assume for the various bond lengths and angles the values given in Table 1. The intramolecular rotation about the C—C single bond in dihalogenoethane, $\text{CH}_2\text{X}-\text{CH}_2\text{X}$, has been studied by Mizushima, Morino, *et al.*⁽¹³⁾ In

analogy to their papers, we can consider a great many possibilities of bond orientations in our polypeptide chain. In our case, however, the reduced symmetry makes a rigorous treatment extremely difficult, so we may, at least qualitatively, assume the bond directions shown in Figs. 1, 2 and 3 as the most probable. The N or C atom enclosed by a circle is the atom nearer to the reader in a N— C_α or a C_α —C bond seen in its direction, and its other bond which will be used in the chain formation is shown by a thick arrow. In a T-type configuration the main bonds (chain bonds) are in the *trans* form. A G-type is obtained from a T-type by rotating the upper or the lower atom with its arrow-indicated bond through a proper angles ($< 180^\circ$) about the central bond as an axis in either direction. In our figures we show the cases of the upper atom turned. For the N— C_α bond (Fig. 1) we obtain as the T-Type T_1^1 and T_1^2 , but we must exclude T_1^3 and T_1^4 as they correspond to the cases of D-amino acids. Hereafter D-type bond directions shall all be omitted. For the G-type G_1^1 and G_1^2 are derived from T_1^1 , and G_1^3 and G_1^4 from T_1^2 . Fig. 2 shows bond directions of C_α and C atoms in a C_α —C bond. T-type: only T_2 . G-types: turning the upper atom

through 120° we get G_2^1 and G_2^2 , by 90° rotation G_2^3 and G_2^4 , by 60° rotation G_2^5 and G_2^6 . In Fig. 3 bond directions of C and N atoms in C—N are shown. T-types: T_3^1 , T_3^2 . G-types: turning the upper atom of T_3^1 type through 120° we get G_3^1 and G_3^2 , by 90° rotation G_3^3 and G_3^4 , by 60° rotation G_3^5 and G_3^6 . Similarly we get G_3^7 , G_3^8 , G_3^9 , G_3^{10} , G_3^{11} and G_3^{12} from the T_3^2 type.

IV. Polypeptide Structure of α -Keratin.—Protein of mammalian hair or wool is keratin. Important amino acids constituting it are leucine (11.5 g.), glutamic acid (12.9 g.), cystine (13.1 g.), arginine (10.2 g.) and so on (in 100 g. wool). In addition there is a little content of glycine (0.6 g.). Proline is also present in a relatively small amount (4.4 g.).⁽¹⁵⁾ Therefore amino acids of the kind described in I (2) takes a greater part. An X-ray diffraction study of keratin was carried out by Astbury and Street.⁽¹⁾ Keratin in an ordinary

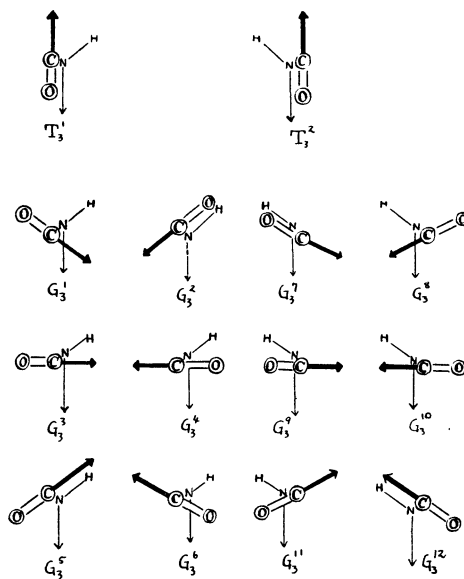


Fig. 3.—Bond direction types in C—N

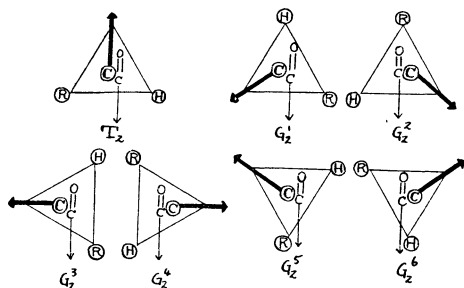


Fig. 2.—Bond direction types in C_α —C

The structure of the polypeptide chain of α -keratin must suffice all the conditions described in II (2) and III. Also it must explain the identity distance 5.15 Å., and at the same time must be arranged on the principle of no steric hindrance. Among many different combinations of bond directions shown in Figs. 1, 2 and 3 the only structure satisfying all of the above conditions is the one given in Fig. 4, in which the chain structure is shown projected on three planes. The main chain is not contained in one plane. Carbonyl radicals are

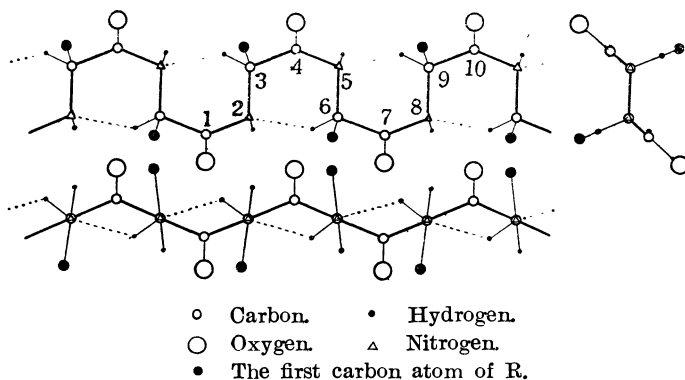


Fig. 4.—Polypeptide structure of α -keratin

state is α -keratin, and it has a rectangular cell ($a=27$ Å., $b=10.3$ Å., $c=9.8$ Å.). The half of b , i.e., 5.15 Å. is called the identity distance, and $c=9.8$ Å. is termed the side chain spacing.

Table 2		
← C (1) — N (2) →	G_3^1	
← N (2) — C_α (3) →	T_3^1	
← C_α (3) — C (4) →	G_2^1	
← C (4) — N (5) →	G_3^1	
← N (5) — C_α (6) →	T_3^1	
← C_α (6) — C (7) →	G_2^1	
← C (7) — N (8) →	G_3^1	
← N (8) — C_α (9) →	T_3^1	
← C (9) — C (10) →	G_2^1	

attached alternately up and down. The C=O radical attached to the 1 or 7 C atom points down forwards, and that attached to the 4 or 10 C atom up backwards. As amino acids are all of the L-type, C_α —R points down backwards from C_α (6), and from C_α (3 or 9) it points up forwards. When C_α —H makes a

(15) C. Rimington, *Biochem. J.*, **23**, 41 (1929).

tetrahedral angle with $C_\alpha-R$, an N atom approaches it and a $C-H\cdots N$ hydrogen bond is formed. In many literatures (for examples (3), (8), (16)), $N-H\cdots O$ hydrogen bonds are assumed as the intramolecular hydrogen bonds in α -keratin, but if that kind of hydrogen bonds were included in our prerequisites, we would obtain no stable main chain and the identity distance would become much smaller than 5.15 Å. Evidences that the C-H vibration frequency 2960 cm^{-1} is observed in the infrared absorption of proteins⁽⁸⁾ seems unfavorable for our $C-H\cdots N$ bond. However, for this frequency we would rather assume that a C-H vibration in side chains is responsible, such as in the CH_3 radical of alanine residue. That $N-H\cdots O$ bonds actually are present in quantity in proteins has been confirmed by infrared studies,⁽⁸⁾ but there seems to be no evidence that they must be contained in the main chain. Therefore we want to assume $C-H\cdots N$ hydrogen bonds in the polypeptide structure of α -keratin. The circumstance that a single H atom is attached to C_α in the α -amino acid molecule seems very favorable for the formation of $C-H\cdots N$ bonds.

Now let us look at the mutual orientation of various bonds in our main chain (Fig. 4). If we pick up two consecutive atoms arbitrarily in the chain and place the atom labeled with a smaller number in the position of the upper atom in one of the figures in Figs. 1, 2 and 3, we obtain Table 2. We see here only the series $T_1^1-G_2^1-G_3^1$ repeats. If we took G_1^1 for T_1^1 , and some other types in places of G_2^1 and G_3^1 , steric hindrances would come in, and even if no steric hindrance occurs the identity distance deviates from 5.15 Å. greatly. The calculated value of the identity distance of the structure shown in Fig. 4 is 5.20 Å, the $C\cdots N$ distance in $C-H\cdots N$ hydrogen bond 2.60 Å. and the $N\cdots H$ distance 1.93 Å.

Out of the bond direction types shown in Figs. 1, 2 and 3 those leading to steric hin-

drances, such as T_1^2 and G_3^7 , must be excluded. All other types derived from these two, i.e., G_1^3 , G_1^4 , T_3^2 , G_3^8 , G_3^9 , G_3^{10} , G_3^{11} and G_3^{12} , are excluded. Next, if we interchanged R and H in every amino acid constituent in our structure, we would obtain a chain from T_1^3 etc., which is made up solely of D-types. But obviously this structure cannot arise because of steric hindrances necessarily introduced. It can be concluded that the polypeptide chain of α -keratin derivable solely from L-amino acids must have the structure shown in our Fig. 4.

Naturally we might imagine a chain structure which is exactly a mirror image of the one shown in Fig. 4. It would be composed solely of D-amino acid constituents and yet has no steric hindrance. However, this structure is unnatural on the experimental ground repeatedly stated above, inasmuch as we exclude the chance that all the D-amino acids in proteins infallibly convert themselves into their antipodes in the process of hydrolytic decomposition.

Resumo.

(1) Aminoacidoj estas klasigitaj en tri klasojn.

(2) Pri polipeptida ĉeno valoroj de atomvalentaj longecoj kaj anguloj, kaj atomvalentaj direktoj montritaj en Tabelo 1, Fig. 1, 2 kaj 3 estas supozitaj.

(3) Nova polipeptida strukturo de α -keratino derivebla eksklusive el L-aminoacidoj estas proponita, en kiu nur la uniĝtipa serio $T_1^1-G_2^1-G_3^1$ ripetas, kaj samtempe tre probabla apero de $C-H\cdots N$ hidrogena uniĝo en la polipeptida ĉeno de α -keratino estas emfazita.

In conclusion, the author wishes to express his hearty thanks to Prof. S. Imanishi for the kind guidance and valuable discussions, and also to the Ministry of Education for grants in aid out of the Scientific Research Expenditure.

(16) W. T. Astbury, *Trans. Faraday Soc.*, **36**, 871 (1940); A. E. Alexander and E. K. Rideal, *Nature*, **147**, 541 (1941).

On the Structures of Fibrous Proteins. II.

New Polypeptide Structures of β - and Feather-Keratins, and Three Silk-Fibroins of *Bombyx mori*, *Saturnia pyri* and *Antheraea mylitta*

By Yoshiya KANDA

(Received October 31, 1949)

I. Introduction.—In Part I of this series⁽¹⁾ the author presented a new structure for α -keratin by assuming reasonable values for bond lengths, bond angles and bond directions. In this paper we shall proceed to present new structures for the polypeptide chains in β -keratin, feather-keratin and three silk-fibroins of *Bombyx mori*, *Saturnia pyri* and *Antheraea mylitta*.

II. Polypeptide Structure of β -Keratin.

—It was found by Astbury⁽²⁾ that X-ray diffraction patterns of ordinary keratin is different from that of fully stretched one (elongated to about 29%). The stretched keratin is called β -keratin. It has a rectangular cell, the unit cell dimensions being: $a=9.3$ Å, $b=6.64$ Å, $c=9.8$ Å. Astbury called 6.64 Å. the identity distance, 9.8 Å. the side chain spacing, and 4.65 Å. (one half of 9.3 Å.) the backbone spacing.

cording to the X-ray diffraction results of glycine crystal by Albrecht and Corey,⁽⁴⁾ the form of glycine molecule in the crystal is almost planar. From this fact we suggest a structure shown in Fig. 1 for the polyglycine chain formed of only glycine residues. Bond direction types used in this structure are given in Table 1, in which only the series $T_1^1-T_2-T_3^1$ repeats. All of these are *trans*. The calculated identity distance is 7.47 Å, somewhat larger than 6.64 Å. observed for β -keratin. On the other hand the X-ray diffraction experiment of DL-alanine crystal by Levy and Corey⁽⁵⁾ shows that the alanine molecule is not planar. Leucine, one of the major constituents of keratin, has a radical CH_3 $\text{CH}-\text{CH}_2-$

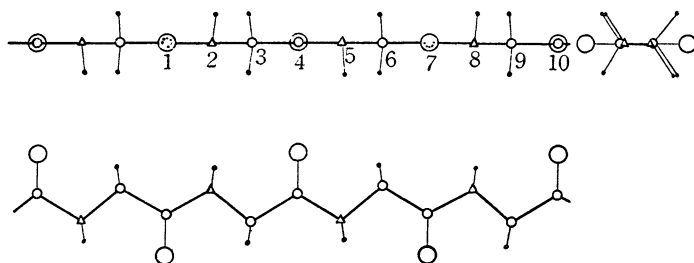
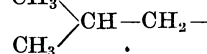


Fig. 1. —Polypeptide structure of polyglycine.

Table 1

← C (1) — N (2) →	T_3^1
← N (2) — C $_{\alpha}$ (3) →	T_1^1
← C $_{\alpha}$ (3) — C (4) →	T_2
← C (4) — N (5) →	T_3^1
← N (5) — C $_{\alpha}$ (6) →	T_1^1
← C $_{\alpha}$ (6) — C (7) →	T_2
← C (7) — N (8) →	T_3^1
← N (8) — C $_{\alpha}$ (9) →	T_1^1
← C $_{\alpha}$ (9) — C (10) →	T_2

It is generally considered that in the polypeptide structure of β -keratin every bond in the chain lies in the *trans*-direction with respect to the next but one bond on either side.⁽³⁾ It appears that this view has been accepted generally without any question, whilst the structure of α -keratin has very much been discussed about by many investigators. Ac-

57 times heavier than a hydrogen atom. If we imagine the interactions among neighboring chains in β -keratin fibres, it seems very unlikely that all bonds in a chain strictly keep the *trans* orientations as stated above.

Now the polypeptide structure of β -keratin should be obtained from that of α -keratin. If we stretched our α -keratin chain (Fig. 4 of Part I) we would have the structure shown in Fig. 2. Bond types appearing in this structure are given in Table 2, in which the series

(1) Y. Kanda: *Bull. Chem. Soc. Japan*, **23**, 137 (1950).

(2) W. T. Astbury and A. Street, *Phil. Trans. Roy. Soc., A* **230**, 75 (1931); W. T. Astbury and H. T. Wood, *ibid.*, **A 232**, 333 (1933).

(3) K. H. Meyer and H. Mark, "Hochpolymere Chemie, II," 1940.

(4) G. Albrecht and R. B. Corey, *J. Am. Chem. Soc.*, **61**, 1087 (1939).

(5) H. A. Levy and R. B. Corey, *ibid.*, **63**, 2095 (1941).

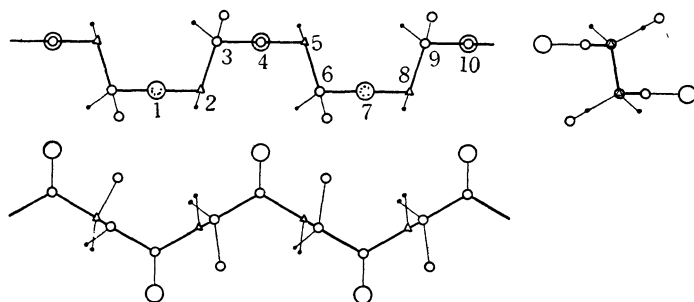


Fig. 2.—Polypeptide structure of feather-keratin.

Table 2		
← C(1) — N (2) →	G ₃ ³	
← N(2) — C _α (3) →	T ₁ ¹	
← C _α (3) — C (4) →	G ₂ ³	
← C(4) — N (5) →	G ₃ ³	
← N(5) — C _α (6) →	T ₁ ¹	
← C _α (6) — C (7) →	G ₂ ³	
← C(7) — N (8) →	G ₃ ³	
← N(8) — C _α (9) →	T ₁ ¹	
← C _α (9) — C (10) →	G ₂ ³	

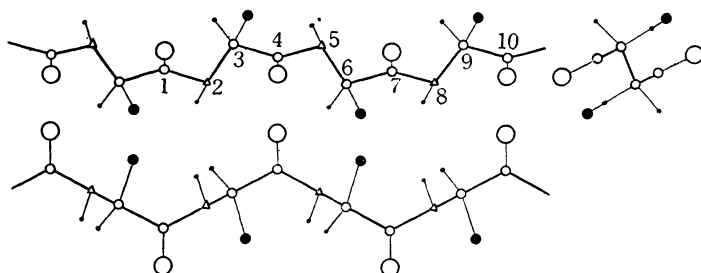
Fig. 3.—Polypeptide structure of β -keratin.

Table 3		
← C (1) — N (2) →	G ₃ ⁵	
← N (2) — C _α (3) →	T ₁ ¹	
← C _α (3) — C (4) →	G ₂ ⁵	
← C (4) — N (5) →	G ₃ ⁵	
← N (5) — C _α (6) →	T ₁ ¹	
← C _α (6) — C (7) →	G ₂ ⁵	
← C (7) — N (8) →	G ₃ ⁵	
← N (8) — C _α (9) →	T ₁ ¹	
← C _α (9) — C (10) →	G ₂ ⁵	

T₁¹—G₂³—G₃³ repeats. The calculated identity distance is 6.06 Å., a little smaller than Astbury's 6.64 Å. for β -keratin. By stretching the chain still more we have the structure shown in Fig. 3 (bond direction types, Table 3), in which T₁¹—G₂⁵—G₃⁵ repeats. In this case the calculated identity distance becomes 6.67 Å., agreeing quite well with the observed value. We would therefore offer the structure of Fig. 3 as that of β -keratin.

III. Polypeptide Structure of Feather-Keratin.—Feather-keratin must have a similar structure to that of mammalian hair or wool keratin, but in the case of quill keratin the length of an amino acid residue was found to be 3.08 Å., different from 3.33 Å. for β -keratin.⁽⁶⁾ The residue length of amino acid in feather-keratin (forol) appears to correspond to 3.07 Å. found by Corey and Wyckoff,⁽⁷⁾ and twice this distance 6.14 Å. could be taken as the identity distance in this substance to which the structure of Fig. 2 corresponds quite well. The fact that feather-keratin can also be stretched into β -keratin as α -keratin can be understood if we consider the transition from Fig. 2 to Fig. 3.

IV. Polypeptide Structure of Silk-

Fibroin of *Bombyx mori*.—Silk-fibroins, as well as α -amino acids constituting them, have extensively been investigated. Important constituents of silk-fibroins are glycine and alanine. Beside these there are tyrosine, arginine, serine, etc. A so-called periodic theory was offered to explain the structures of these substance by Bergmann and Niemann.⁽⁸⁾ Meyer and Mark,⁽⁹⁾ however, found that there are crystalline and non-crystalline parts in silk-fibroin and that the unit cell of the crystal is too small to contain a tyrosine residue, disagreeing with the theory of Bergmann and Niemann. Arginine and other amino acids are contained more often in the non-crystalline than in the crystalline parts. Meyer and Mark considered the chain structure of silk-fibroins in general as consisting of glycine and alanine (or serine etc.) residues alternating. The identity distance of silk-fibroin of *Bombyx mori* was found to be 6.95 ± 0.25 Å. by Kratky and Kuriyama.⁽¹⁰⁾ Heertjes' reinvestigation⁽¹¹⁾ confirmed their results, and the unit cell dimensions were determined as $a = 10.45$ Å., $b = 4.95$ Å.,

(8) M. Bergmann and C. Niemann, *J. Biol. Chem.*, **122**, 577 (1938).

(9) K. H. Meyer and H. Mark, *Ber.*, **61**, 1932 (1938).

(10) O. Kratky and S. Kuriyama, *Z. phys. Chem.*, **B 11**, 363 (1931).

(11) P. M. Heertjes, *Rec. Trav. Chim.*, **60**, 329 (1941).

(6) G. L. Clark, "Applied X-rays," p. 651 (1940).

(7) R. B. Corey and R. W. Wyckoff, *J. Biol. Chem.*, **114**, 407 (1936).

$c = 6.95 \text{ \AA}$, $\gamma = 61^\circ 10'$; its density $\rho = 1.341$ from the macroscopic density measurement.

The identity distance $6.95 \text{ \AA}$. may be interpreted to correspond to the distance between two glycine residues. It is considered that in the polypeptide chain composed of only glycine residues (polyglycine chain) all chain-forming bonds stand mutually in *trans* relations as shown in Fig. 1 and Table 1. But in the residue of amino acid other than glycine, bond

residue (1-2-3-4) of Fig. 1 and the amino acid residue (4-5-6-7) of Fig. 2 alternate, having bond series $T_1^1-T_2-G_3^3-T_1^1-G_3^3-T_3^1$ (Table 5). But as this arrangement is seen to be identical with the one given above, we need not treat it separately. The calculated identity distance for this structure is $7.02 \text{ \AA}$, very near to the observed $6.95 \text{ \AA}$.

V. Polypeptide Structure of Silk-Fibroin of *Saturnia pyri*.—Kratky and Kuriyama⁽¹⁰⁾

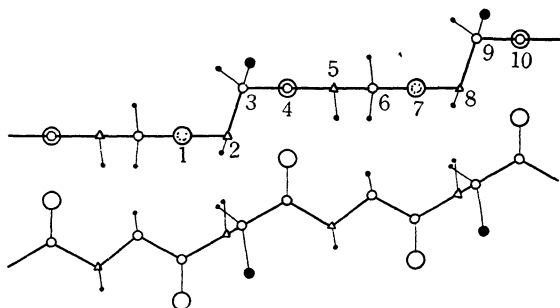


Fig. 4.—Polypeptide structure of silk-fibroin of *Bombyx mori*.

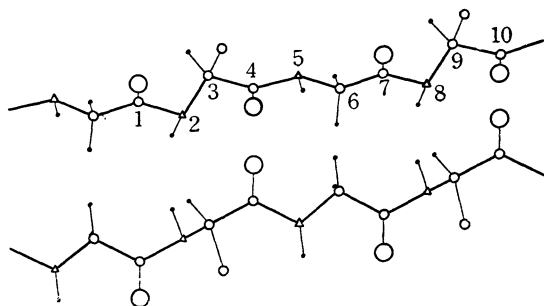


Fig. 5.—Polypeptide structure of silk-fibroin of *Saturnia pyri*.

direction types are not all T but some are G. As the residue lengths of α -amino acids other than glycine are all smaller than that of glycine, it is not correct to take the identity distance for silk-fibroin simply as twice the length $3.5 \text{ \AA}$. as we find in many literatures. The identity distance in β -keratin is smaller than that of silk-fibroin because it does not contain glycine residues. The polypeptide structure of silk-fibroin of *Bombyx mori* is shown in Fig. 4. In this structure we see the amino acid residue (1-2-3-4) which was used in the structure of feather-keratin of Fig. 2 and the glycine residue (4-5-6-7) used in the polyglycine structure of Fig. 1 are joined alternately. Bond direction types used in this structure are given in Table 4, in which the series $T_1^1-G_3^3-T_3^1-T_2-G_3^3$ repeats. For this fibroin we may construct the chain in another way, in which the glycine

Table 4

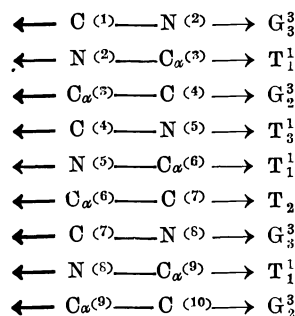
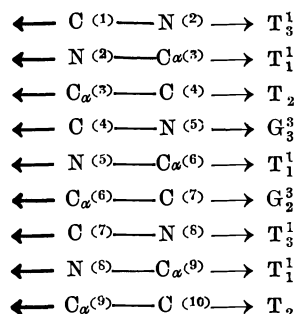


Table 5



determined the unit cell dimensions of the fibroin "Satonia" as $a = 6.46 \text{ \AA}$, $b = 15.43 \text{ \AA}$, $c = 7.2 \text{ \AA}$ and $\gamma = 61^\circ 10'$. According to Simizu⁽¹²⁾ the wild silkworm "Satonia" studied by the above authors might have been *Saturnia pyri*. The structure of this silk-fibroin can be given as shown in Fig. 5, in which we see the amino acid residue (1-2-3-4) used in the β -keratin chain of Fig. 3 and polyglycine chain (4-5-6-7) of Fig. 1 are joined alternately. In this case, however, the plane of the glycine residue is slightly tilted. Bond series $T_1^1-G_2^2-T_3^1-T_1^1-T_2-G_3^3$ repeats in this structure, as given in Table 6. The identity dis-

(12) "The Fibre Structures by X-rays," (in Japanese), p. 99. Kōgaku-Syuppansya, Osaka (1944).

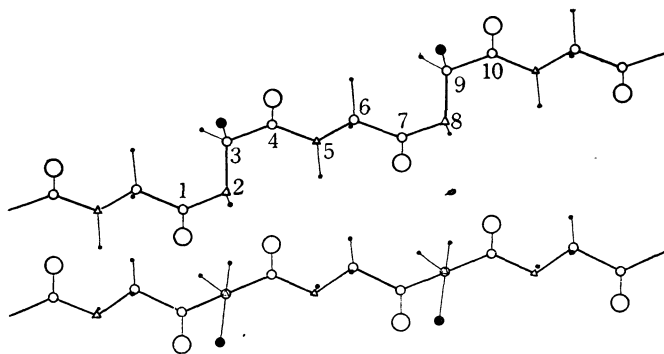


Fig. 6.—Polypeptide structure of silk-fibroin of *Antheraea mylitta*.

Table 7

← C ⁽¹⁾ —N ⁽²⁾ →	G ₃ ¹
← N ⁽²⁾ —C _α ⁽³⁾ →	T ₁ ¹
← C _α ⁽³⁾ —C ⁽⁴⁾ →	G ₂ ¹
← C ⁽⁴⁾ —N ⁽⁵⁾ →	T ₃ ¹
← N ⁽⁵⁾ —C _α ⁽⁶⁾ →	T ₁ ¹
← C _α ⁽⁶⁾ —C ⁽⁷⁾ →	T ₂
← C ⁽⁷⁾ —N ⁽⁸⁾ →	G ₃ ¹
← N ⁽⁸⁾ —C _α ⁽⁹⁾ →	T ₁ ¹
← C _α ⁽⁹⁾ —C ⁽¹⁰⁾ →	G ₂ ¹

tance is calculated to be 7.25 Å., agreeing well with the observed value 7.20 Å. Fig. 5 shows the silk-fibroin chain of *Saturnia pyri*, while the structures (similar to β-keratin) of silk-fibroin discussed by previous workers were limited only to that of *Bombyx mori*.

VI. Polypeptide Structure of Silk-fibroin of *Antheraea mylitta*.—X-ray diffraction studies of silk-fibroin of “Tussahseide” or “*Antheraea mylitta*” were made by Trongs and Hess.⁽¹³⁾ Beside the two characteristic identity distances 6.78 Å. and 6.71 Å., corresponding to the strongest reflections I₁ and I₂ some other values were also obtained. Taking the average of the values for I₁ and I₂ we get 6.75 Å., which is smaller than 6.95 Å. observed for *Bombyx mori* fibroin. The structure of *Antheraea* fibroin can be given as shown in Fig. 6, in which we see the amino acid residue (1-2-3-4) in the α-keratin structure of Fig. 4 of the previous paper (Part I) and that of glycine (4-5-6-7) of Fig. 1 joined alternately (repeating bond series T₁¹—G₂¹—T₃¹—T₁¹—T₂—G₃¹, Table 7). 6.72 Å. calculated for the identity distance agrees quite well with the above mentioned average value.

Table 6

← C ⁽¹⁾ —N ⁽²⁾ →	G ₃ ⁵
← N ⁽²⁾ —C _α ⁽³⁾ →	T ₁ ¹
← C _α ⁽³⁾ —C ⁽⁴⁾ →	G ₂ ⁵
← C ⁽⁴⁾ —N ⁽⁵⁾ →	T ₃ ⁵
← N ⁽⁵⁾ —C _α ⁽⁶⁾ →	T ₁ ¹
← C _α ⁽⁶⁾ —C ⁽⁷⁾ →	T ₂
← C ⁽⁷⁾ —N ⁽⁸⁾ →	G ₃ ⁵
← N ⁽⁸⁾ —C _α ⁽⁹⁾ →	T ₁ ¹
← C _α ⁽⁹⁾ —C ⁽¹⁰⁾ →	G ₂ ⁵

VII. Conclusion—We have determined the polypeptide structures of α-keratin (Part I) feather-keratin, β-keratin and silk-fibroins of *Antheraea mylitta*, of *Bombyx mori* and of *Saturnia pyri*, starting from the conditions stated in Part I together with experimentally obtained identity distances. These six substances seem to have the most typical polypeptide chain structures, but various intermediate type structures may also exist. For example, in the X-ray diffraction studies of collagen, the arc on the meridian at 2.8 Å. has not been clearly explained.⁽¹⁴⁾ Assuming twice this distance 5.6 Å. as the identity distance, we may regard collagen as having a structure intermediate between α- and feather-keratins. Also, sericine⁽¹⁵⁾ (identity distance 6.83 Å.) may be an intermediate type fibroin between those of *Antheraea mylitta* and *Bombyx mori*.

In the six typical structures given above of polypeptide chains, we see only nine bond types T₁¹, T₂, G₂¹, G₃¹, G₃⁵, T₃¹, G₃¹, G₃³ and G₃⁵ occur. For intermediate structures we can assign intermediate bond types, for example, between G₂¹ and G₃³. Heretofore types G₁¹, G₂², G₂⁴, G₂⁶, G₃², G₃⁴ and G₃⁶ among those shown in Figs. 1, 2 and 3 of Part I have not entirely been used. For the explanation of tangled chain structures, however, these types may play important rôles. Resumés for the six typical structures of polypeptide chains are given in Table 8.

Resumo.

(1) La polipeptidaj strukturoj de pluma keratino kaj β-keratino estas akiritaj kiam la α-keratinĉeno estas streĉita kaj uniĝtipa

(14) G. L. Clark and J. A. Schaad, *Radiolog.*, **271**, 339 (1936).

(15) M. Simizu, *Bull. Imperi. Sericult. Experi. Station*, (Tokyo), (in Japanese) **10**, 441 (1941a).

(13) C. Trongs and K. Hess, *Biochem. Z.* **260**, 376 (1933).

Table 8
Typical Structures of Polypeptide Chains

Fibrous Proteins	Identity Distance		Bond Direction Types	Figure (Part 1)
	Obs., Å.	Cal., Å.		
α -Keratin	5.15 "	5.20 "	$T_1^1-G_2^1-G_3^1-T_1^1-G_2^1-G_3^1$	4
Feather-Keratin	6.14 "	6.06 "	$T_1^1-G_2^3-G_3^3-T_1^1-G_2^3-G_3^3$	2
β -Keratin	6.64 "	6.67 "	$T_1^1-G_2^5-G_3^5-T_1^1-G_2^5-G_3^5$	3
Silk-Fibroin of <i>Antheraea mylitta</i>	6.75 "	6.72 "	$T_1^1-G_2^1-T_3^1-T_1^1-T_2^1-G_3^1$	6
Silk-Fibroin of <i>Bombyx mori</i>	6.95 "	7.02 "	$T_1^1-G_2^3-T_3^3-T_1^1-T_2^3-G_3^3$	4
Silk-Fibroin of <i>Saturnia pyri</i>	7.20 "	7.25 "	$T_1^1-G_2^5-T_3^5-T_1^1-T_2^5-G_3^5$	5
Polyglycine*		7.47 "	$T_1^1-T_2^1-T_3^1-T_1^1-T_2^1-T_3^1$	1

* Added for reference, although not a natural fibrous protein.

serio fariĝas $T_1^1-G_2^3-G_3^3$ kaj $T_1^1-G_2^5-G_3^5$ respektive.

(2) La strukturo de silkfibro de *Antheraea mylitta*, *Bombyx mori* aŭ *Saturnia pyri* estas akirita kiam aminoacidaj restaĵo de poliglicino kaj tiu enhavita en α -keratino, pluma keratino aŭ β -keratino estas alterne kunligita.

(3) La strukturoj supre proponitaj povos esti konsideritaj kiel la tipaj strukturoj aldonoj al polipeptidaj ĉenoj en naturaj

fibraj proteinoj, pri kiuj ĉiu ripetdistanco tre proksima al observita valoro estas kalkulita. Rezultatoj estas resumitaj en Tabelo 8.

In conclusion, the author wishes to express his sincere thanks to Prof. S. Imanishi for the kind guidance and valuable discussions, and also to the Ministry of Education for grants in aid out of the Scientific Research Expenditure.

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Wettability of Solid Surface. IV. Wettability of Palmitic Acid Surface towards Aqueous Salt Solutions

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(Received March 30, 1950)

Introduction

The phenomena of wetting of solid surface have been studied by numerous investigators. The present author has also continued the theoretical studies upon these phenomena and reported some results chiefly concerning the wetting of paraffin, palmitic acid, and cetyl alcohol surfaces. According to the preceding report,⁽¹⁾ the surface of palmitic acid proved to be non-wettable at the moment of contact with water, while it showed increase in wettability with time of contact. However, the results of later experiments, made on apparently the same conditions, showed that the surface of palmitic acid remains evidently unwettable even by a long time contact with water. A careful examination of experimental conditions, which lead us to such an apparent

contradiction, revealed the fact that the minute impurities especially ions in distilled water have a great influence upon the wetting phenomena. Such a presumption is also confirmed by the experimental facts reported by Langmuir⁽²⁾ upon the action of polyvalent metallic ion for monolayers on water as well as for built up films. Therefore the present author has studied the wettability of palmitic acid towards some aqueous solutions of electrolytes.

Experimental

a. Material.—Paraffin, palmitic acid and cetyl alcohol were purified similarly as described in the preceding reports.⁽¹⁾⁽³⁾ Potassium, calcium and thorium nitrates, and aluminum sulfate (of extra-pure grading of Takeda Pure Chemical Co.) were used after recrystallization. Water was redistilled,

(2) Langmuir and Schaefer, *J. Am. Chem. Soc.*, **59**, 1406, 1762, 2075, 2400 (1937).

(3) Inaba, *Memoirs of the Faculty of Science, Kyūsyū University*, Ser. C, **1**, 1 (1948).

(1) Inaba, *Memoirs of the Faculty of Science, Kyūsyū University*, Ser. C, **1**, 19 (1948).

using the apparatus made of "Vidrex" glass of Mitsuya Glass Co.

b. Method of Measurement.—Wettability of paraffin, palmitic acid and cetyl alcohol was measured for their solidified surface by means of the modified Du Nöuy tensiometer, the details of which have been described in the preceding paper.⁽³⁾ The apparatus employed was essentially the same as used by Sasaki for the surface pressure measurement.⁽⁴⁾ ζ -potential of palmitic acid in contact with solution was measured for its sol by means of electrophoresis, using the apparatus modified also by Sasaki,⁽⁵⁾ which is illustrated in Fig. 1. This apparatus eliminates the troublesome operations of both obtaining ultrafiltrate and making sharp initial boundary between a sol and ultrafiltrate, because the semi-permeable membrane of the apparatus acts to produce ultrafiltrate and form a sharp boundary automatically as the electrophoresis proceeds. The moving boundary can be seen in position below the membrane as shown in Fig. 1. The two platinum electrodes B serve to measure the potential gradient applied for sol, which is done by means of the compensation method.

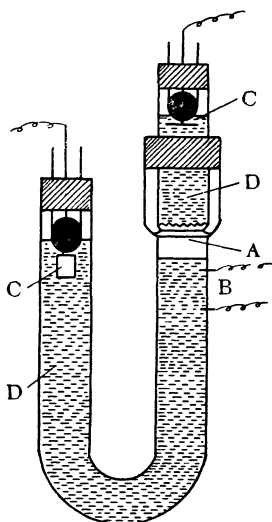


Fig. 1.—Simple apparatus for electrophoresis: A, semi-permeable membrane; B, platinum auxiliary electrodes; C, platinum electrodes; D, colloidal solution.

Experimental Results and Discussion

Wettabilities of the solid surface of paraffin (both crude and purified), palmitic acid and cetyl alcohol towards 0.1 *N* aqueous solutions of potassium, calcium, aluminum and thorium salts were measured, the results of which are shown in Table 1 and are partly illustrated in Figs. 3 and 4, where the wettability is expressed in terms of the work of adhesion, W_a , in the unit of erg/cm². The subscript "a" means that the work of adhesion is calculated using the value of the advancing contact angle.

(4) Sasaki, *J. Chem. Soc. Japan*, **62**, 769 (1941); Sasaki and Takeuchi, *J. Chem. Soc. Japan*, **63**, 372 (1942).

(5) Sasaki and Hidemura, *Kindai Koshitsugaku no Tenbo (The Review of Recent Advance in Colloid Science)*, **1**, 304 (1948).

Table 1

Soln	pH of soln	Time of contact in min.	W_a , erg/cm ² of			
			Purified paraffin	Crude paraffin	Palmitic acid	Cetyl alcohol
Water	6.0	0	46.5	46.3	50.3	108.8
"	"	60	49.5	77.4	49.4	112.2
0.1 <i>N</i> KNO ₃	6.4	0	53.5	46.6	48.6	103.7
"	"	60	54.7	81.0	52.1	96.7
0.1 <i>N</i> Ca(NO ₃) ₂	6.0	0	48.8	55.8	59.2	102.2
"	"	60	47.9	77.0	64.7	96.0
0.1 <i>N</i> Al ₂ (SO ₄) ₃	2.4	0	44.9	58.2	56.1	112.6
"	"	60	48.7	73.8	55.8	109.7
0.1 <i>N</i> Th(NO ₃) ₄	1.5	0	46.7	55.7	120~66	115.7
"	"	60	52.1	70.1	143.4	111.2

(Wettabilities are measured both at the moment and after one hour of contact with solutions.) The table shows that crude paraffin generally exhibits an increase in wettability after one hour's contact both with water and aqueous solutions, while such an effect is absent for pure paraffin. In the case of palmitic acid surface the wettability increases only in the case of thorium nitrate solution, where a remarkable effect is observed. The value of 140 erg/cm² listed in the table corresponds to 0° of contact angle. In the case of cetyl alcohol the wettability changes in a complex manner, showing even a decrease in the case of potassium and calcium salt solutions. Thus we have many problems to make clear, but here we are chiefly interested in the remarkable effect of enhanced wettability due to thorium salt for palmitic acid surface. The aqueous solution of 0.1 *N* thorium nitrate shows as low *pH* value as 1.5 due to its hydrolysis. However, this low *pH* value of the solution proved not to be the cause of the increase in wettability mentioned above, because we cannot observe such an increase in wettability as exhibited by thorium salt in any other solution, though its *pH* value is controlled to 1.5.

Then, the enhanced wettability of palmitic acid surface by thorium salt solution may be ascribed to the change in ζ -potential⁽⁶⁾ of palmitic acid surface in the solution due to the ionic adsorption. To know the effect of ζ -potential upon the wettability, the following experiments were carried out. The palmitic acid hydrosol was prepared by the radiation

(6) Bull, Trans. Faraday Soc., **28**, 597 (1932); *J. Phys. Chem.*, **38**, 401 (1934).

of ultrasonic wave of medium intensity upon the mixture of water and molten palmitic acid, to which various salt solutions were added. The electrophoretic velocity of sol particles in such solutions was measured, from which ζ -potential was calculated. The results are shown in Fig. 2. We can see in this figure that ζ -potential of palmitic acid hydrosol particle in pure water is -0.12 volt and addition of the salt in increasing amount gradually changes it to more positive value. The effect is particularly remarkable for thorium salt even in extreme dilution. In the thorium salt solution of sufficient concentration the surface charge of particle becomes positive. The effect gradu-

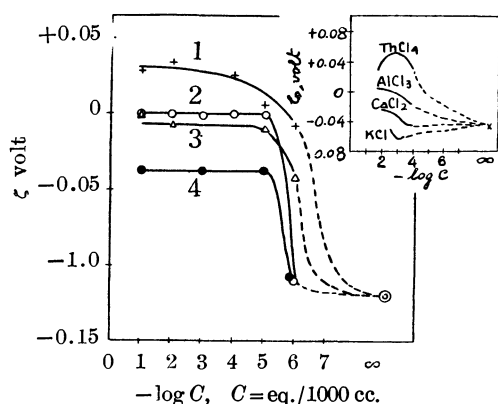


Fig. 2.— ζ -potential of palmitic acid sol particle in various salt solutions: Curve 1, $\text{Th}(\text{NO}_3)_4$; Curve 2, $\text{Al}_2(\text{SO}_4)_3$; Curve 3, $\text{Ca}(\text{NO}_3)_2$; Curve 4, KNO_3 .

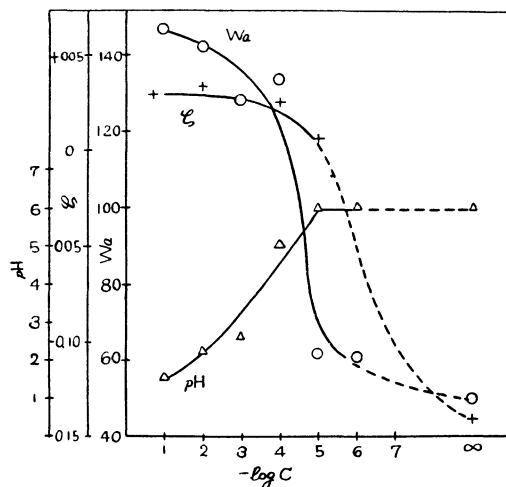


Fig. 3.—Wettability and ζ -potential of palmitic acid surface in $\text{Th}(\text{NO}_3)_4$ solution of various concentrations: $\bigcirc$, W_a (work of adhesion) in erg/cm^2 ; $+$, ζ -potential in volt; $\triangle$, pH of $\text{Th}(\text{NO}_3)_4$ solution; C , concentration of $\text{Th}(\text{NO}_3)_4$ in equiv./1000 cc.

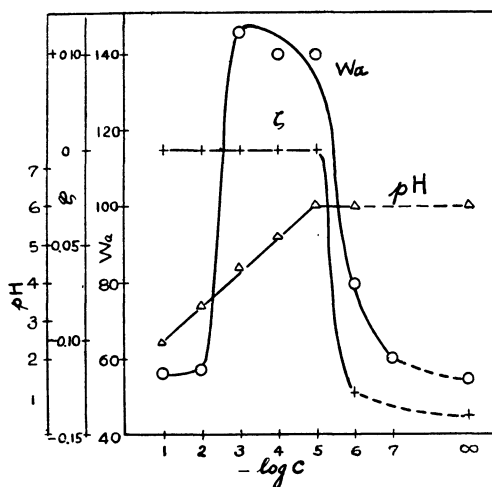


Fig. 4.—Wettability and ζ -potential of palmitic acid surface in $\text{Al}_2(\text{SO}_4)_3$ solution of various concentrations: $\bigcirc$, W_a (work of adhesion) in erg/cm^2 ; $+$, ζ -potential in volt; $\triangle$, pH of $\text{Al}_2(\text{SO}_4)_3$ solution; C , concentration of $\text{Al}_2(\text{SO}_4)_3$ in equiv./1000 cc.

ally decreases in the order of aluminum, calcium and potassium salts. To facilitate a comparison, we may illustrate the degree of wettability and ζ -potential together with the pH of solution for varying concentration of solutions of aluminum and thorium salts in Figs. 3 and 4 respectively.

Under the assumption that ζ -potential of the surface of palmitic acid sol particle is the same as that of the bulk surface, and ignoring a few details, we can see as a whole in these figures that the wettability of palmitic acid surface towards various salt solutions changes parallel with the ζ -potential of the surface. Namely thorium salt solution, showing the most remarkable effect of changing the sign of ζ -potential, exhibits the most pronounced effect on wettability, and aluminum salt solution changing ζ -potential from negative to zero still shows a considerable effect, while the solutions of calcium and potassium salts which merely decrease the value of negative ζ -potential have no influence on wettability. There has been a view concerning the relation between the wettability and the electrical charge of solid surface, that if both the surface of solid and air bubble in solution have the electrical charge of the same sign towards water, solid surface remains in wet condition because the bubble cannot contact with the surface as the results of electrical repulsion between them. On the contrary, when the signs of the charges are opposite to each other, the solid surface is considered to be unwettable for the similar

reason. The wetting property of palmitic acid in contact with the concentrated thorium salt solution may be explained from such a reasoning. It fails however to explain the non-wettability of palmitic acid towards the salt solution of sufficient dilution, where again both the surfaces of solid and bubble have the charges of the same negative sign. Furthermore, it is pointed out that although the ζ -potential curve of paraffin oil measured by Mooney⁽⁷⁾ is similar to that of palmitic acid as shown in the diagram inserted in Fig. 2, thorium salt is not effective for the increase in wettability in the case of paraffin surface. Therefore ζ -potential by itself is not sufficient for the explanation of wettability.

According to Langmuir⁽²⁾ the barium stearate built-up film becomes wettable in the solution of thorium salt because the stearate molecules overturn themselves in the surface layer and polar groups thus exposed contribute to the hydrophilic property of the surface. However, the view can hardly give any explanation of the fact that the ζ -potential of palmitic acid surface which may suffer a remarkable change in magnitude if the overturning occurs, is practically the same as that of paraffin where the possibility of the overturning of molecules cannot be expected.

The explanation has furthermore been offered that the increase in surface potential causes the decrease in the surface free energy and so the change in wettability.⁽⁸⁾ But this theory also does not give sufficient explanation to the experimental results mentioned above.

It is worth while to emphasize here the possibility that the increase in wettability depends on the chemical reaction taking place on the solid surface layer. We can expect that the surface of palmitic acid in contact with salt solution is covered by the corresponding metallic soap.⁽⁹⁾ Then the remarkable wet-

tability due to aluminum and thorium salts is ascribed to the formation of corresponding metallic soaps. In this relation, it may be noteworthy that special features of such metallic soaps, particularly the macromolecular nature of them have attracted much attentions of several investigators.⁽¹⁰⁾ In fact we have confirmed that the polyvalent metallic soap such as aluminum or thorium stearate is the only constituent which causes the enhanced wettability of crude paraffin by the contact with water. The details of experiments and discussions upon these phenomena will be reported in the following papers.

Summary

Wettabilities of purified paraffin, crude paraffin, palmitic acid and cetyl alcohol are measured towards aqueous solutions of potassium, calcium, aluminum and thorium salts. It is pointed out that palmitic acid surface becomes remarkably wettable by the contact with aqueous solution of thorium or aluminum salt even in the extreme dilution. Such an increase in wettability can neither be explained simply by ζ -potential change of the palmitic acid surface in those solutions nor overturning of the molecule in surface layer. Alternative explanations are suggested.

The author wishes to express her thanks to Prof. T. Sasaki for his kind advice. The cost of this research has been defrayed from the Scientific Research Expenditure of the Ministry of Education given to the professor.

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Science, Kyūsyū University,
Fukuoka*

(7) Mooney, *J. Phys. Chem.*, **35**, 331 (1931).

(8) Kabanov, *Kolloid-Z.*, **65**, 101 (1933); Adam, "The Physics and Chemistry of the Surface," Oxford, 350 (1938).

(9) It has also been suggested by Dr. T. Tachibana

(Faculty of Science, the University of Tokyo) in his private communication to the present author that the adsorption of metallic hydroxide towards the palmitic acid surface may be considered to play an important rôle in wetting.

(10) McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949); Gray and Alexander, *J. Phys. Colloid Chem.*, **53**, 26 (1949).

Determination of Zinc and Lead by Means of Sodium Diethyldithiocarbamate

By Yukio MURAKAMI

(Received November 29, 1949)

Introduction

Sodium diethyldithiocarbamate was introduced by Delepine⁽¹⁾ as a reagent for copper. Subsequently Callan and Henderson⁽²⁾ also pointed out the sensitivity of this reagent for copper.⁽³⁾ Then the reagent has been used for the determination of a minute amount of copper.⁽³⁾ The author⁽⁴⁾ also showed in testing this method that it reacts most sensitively with copper among many other metals giving white turbidity or coloration and he improved the method by the extraction with carbon tetrachloride in the presence of hydroxylamine with the result of increasing the accuracy and sensitivity of the determination.

In 1935 Atkins,⁽⁵⁾ while testing copper with this reagent, found that a dense turbidity produced immediately on addition of the reagent to the sample of water taken from a well. He concluded that it was due to the presence of zinc and was quite an unexpected phenomenon. He has given a brief description of the determination of zinc using the Nessler tube and showed that it is as delicate as the ferrocyanide method and superior to the colorimetric method by resorcinol. Then Miller⁽⁶⁾ determined zinc in a sample of water in the same manner with fairly good results. In connection with the study on the colorimetric determination of copper with this reagent, the reaction of zinc and lead were also studied by the author. Thus a possible application for the turbidimetric determination of both of these elements is described in this report.

Experiment

A. Reaction of Zinc

a. Effect of pH on the Turbidity.—The influence of the acid concentration on the turbidity is evident. The influence was tested on various pH values and it was found that maximum turbidity is obtainable at pH 4.8 (Table 1). To make the turbidity maximum, the comparison must be made letting the solution stand for half an hour after the reagent has been added.

The change in turbidity on standing was tested as shown in Table 2.

Table 1

pH	Turbidity (Extinction coefficient)		
	I	II	III
3.8	0.205	—	—
4.8	0.242	0.173	0.456
6.2	0.219	—	0.402
6.8	0.184	0.149	0.395
7.9	0.154	—	0.376
9.8	—	0.105	0.237
11.0	—	0.037	—
11.8	—	0.025	0.029

Table 2

A. The Relation between the Change in Turbidity and Time								
Time, min.	5	10	20	30	60	120	150	
pH 4.8	0.125	0.156	0.170	0.173	0.174	0.176	0.171	
pH 6.2	0.328	0.380	0.380	0.382	0.387	—	—	
pH 8.8	0.091	0.100	0.119	0.118	0.118	0.120	—	

B. The Change in Turbidity after 24 Hours

pH	Turbidity (Extinction coefficient)	
	after 30 min.	after 24 hrs.
2.8	0.103	0.091
4.8	0.186	0.149
6.6	0.159	0.148
8.9	0.121	0.080

The turbidity seems to diminish on standing even at a suitable pH, but in practical use this has no serious effect as the determination will

(1) M. Delepine, *Bull. Soc. Chim.*, (4) **3**, 652 (1908); *Compt. rend.*, **146**, 981 (1908).

(2) T. Callan and J. A. Henderson, *Analyst*, **54**, 650 (1929).

(3) D. L. Drabkin and C. S. Waggoner, *J. Biol. Chem.*, **89**, 51 (1903); C. A. Elvehjem and E. A. Hart, *J. Biol. Chem.*, **91**, 37 (1931); L. A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932); McFarlane, *Biochem. J.*, **26**, 1022 (1932); N. D. Sylvester and L. H. Lampitt, *Analyst*, **60**, 377 (1935); L. W. Conn *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **7**, 15 (1935); F. Nydahl, *Z. anal. Chem.*, **116**, 315 (1939).

(4) Y. Murakami, *Bull. Chem. Soc. Japan*, **22**, 3 (1950).

(5) W. R. G. Atkins, *Analyst*, **60**, 400 (1935).

(6) C. F. Miller, *Chemist-Analyst*, **20**, 8 (1931).

be made before any change occurs, and then any stabilizing agent is not required for it. The higher the pH value of the solution is the less remarkably the turbidity is formed. Therefore no turbidity occurs if the solution is made alkaline with a slight excess of ammonia. The turbidity once formed is easily diminished in the same way and the solution becomes perfectly clear on standing for five minutes.

From these experiments it may be concluded that the solution should be buffered at pH 4.8 with 12.17 ml. of 0.1 N acetic acid and 7.83 ml. of 0.1 N ammonia; the turbidity comparison is preferably performed in half an hour after the reagent is added.

b. Temperature and Turbidity.—A number of experiments were carried out at various temperatures in a thermostat to seek the relation between turbidity and temperature of the solution (Table 3).

Table 3

Temperature and Turbidity (at pH 4.8)					
Temp. °C.,	10	15	20	25	
Turbidity (Extinction coeff.)	I	0.149	0.305	0.360	0.268
	II	0.147	—	0.347	0.238

The results of these experiments indicated that 20° is most favorable for obtaining maximum and stable turbidity.

c. Application of Lambert-Beer's Law.—It has not been known whether the reaction of zinc with the reagent conforms with the Lambert-Beer's law or not, but the author has found it sufficiently conforms with the law if turbidity is produced closely following the conditions recommended above.

Thus the following results were obtained when 10 ml. of 0.1% solution of the reagent is added to the solution to be tested, buffered at pH 4.8 as described above (Table 4).

Table 4

Zinc, γ in 50 ml.	20	40	80	100
Extinction coeff. }	0.181	0.358	0.716	0.910
E_r (calculated)	0.0905	0.0895	0.0895	0.0910

The comparison is made with Pulfrich photometer using S 43 (434 $m\mu$) filter after the solution being made up to 50 ml.

d. Reaction of Other Ions.—The reagent is not specific to copper alone but similarly reactive with many other metals. For details of interference, references may be made to

the reports of Callan *et al.*⁽²⁾ and the author⁽⁴⁾ besides those given below. These interferences, however, were rarely encountered in determining zinc in natural water as well as other water samples. Alkali and alkaline earth metals do not react with it, thus making it superior to the resorcinol method. It is most sensitively reactive with copper. Its sensitivity to some metals can be compared by calculating E_r from the results, which means the extinction coefficient of 1 mm. thickness of the solution containing 1 γ of the element in question in 1 ml. If a considerable amount of iron is present, as is usually the case, a dirty yellow coloration is produced though the sensitivity to iron is much lower than that to the element in question. But it is desirable to prevent the reaction of iron. This is usually performed by removing iron as hydroxide as in the copper determination recommended by Callan and Henderson.⁽²⁾ Haddock *et al.*⁽³⁾ recommended the removal of iron as hydroxide precipitate. However, a considerable amount of zinc is carried down with iron hydroxide though a part of it may also be expected to pass into the filtrate owing to the formation of $Zn(NH_3)_4^{++}$. Therefore it becomes desirable to prevent the reaction of iron with the other method.

Elvehjem *et al.*⁽³⁾ described a method of preventing the precipitation of iron by the addition of citrate and the successive addition of 1% gum arabic solution. McFarlane proposed the use of sodium pyrophosphate for the same purpose. The latter is preferable to the former as the pH of the solution recommended is much nearer to the most suitable pH value than in the former method, though the sensitivity is somewhat decreased. Naturally in this case a standard curve at this pH value should be constructed. Manganese interferes to a considerable extent by imparting a pinkish color to the solution which is an indication of the oxidation of manganese by the air in the solution. However, this coloration is unstable and the solution soon becomes virtually colorless, provided that only a small amount of manganese is present. Pyrophosphate also reduces the coloration.

The interferences of nickel, cobalt and bismuth which are the chief interfering metals in this reaction are rarely encountered because of their rarity in natural waters. The presence of cyanide prevents turbidity but citrate does not interfere even if a considerable amount may be present.

B. Reaction of Lead

The author has determined copper in

biological matters with the reagent after separating lead, zinc and copper from the sample by dithizone and isolating copper from the others by treating it with 0.01 *N* hydrochloric acid.⁽⁴⁾ In this procedure copper remains as dithizonate but zinc and lead are transferred into the hydrochloric acid solution as chlorides. From this point, some attempts were made to the simultaneous determination of the latter two in an aliquot portion of the sample. There exists a more sensitive colorimetric determination after separating both of these elements. However, the turbidimetric determination with the reagent finds some important uses as well.

Tompsett and Anderson⁽⁷⁾ described a method of preliminary separation of lead in excreta and in tissue by this reagent and concluded that it is the most suitable reagent for this purpose as such. A preliminary separation is absolutely required with a sample of a high iron content. Then Tompsett determined lead in potable water in the same way and showed that there are several distinct advantages, e.g., more stable turbidity not affected by oxidant and easy extractability with ether.

A white turbidity is produced by the presence of lead and a perceptible turbidity is observed when the reagent is added to 0.05 mg. of lead in 100 ml. aqueous solution. It was found for the first time by the author that a white turbidity due to lead also conforms with the Lambert-Beer's law as shown in the Table 5.

Table 5

Conformity to the Law

Pb (γ in 50 ml.)	100	200	300
Extinction coefficient { I	0.268	0.532	0.812
II	0.261	0.541	0.841
E_r (calculated)	0.0264	0.0268	0.0275

Table 6

Reproducibility in Determining Lead

Expt.	Extinction coefficient	Pb (γ in 50 ml.)
I	0.122	46
	0.124	47
	0.121	46
II	0.335	128
	0.337	128
	0.340	130
III	0.409	157
	0.411	158
	0.422	161

Evidently the presence of lead interferes the determination of zinc with the reagent. However, a preliminary separation can be successfully made with dithizone in the presence of potassium thiocyanate as recommended by Hibbard or by other appropriate methods.⁽⁸⁾

The author also tested the possibility of the determination of zinc without a preliminary separation from lead. A white turbidity due to lead is not affected by a slight excess of ammonia, while that due to zinc is thoroughly diminished. Some attempts were made to use this remarkable difference. Thereupon the total turbidity first, and the remaining turbidity afterwards, are measured in the same aliquot portion after the turbidity due to zinc is diminished by the addition of 8 ml. of saturated ammonia and 2 ml. of 1 *N* potassium hydroxide.

Table 7

Reproducibility in Determining Zinc

Expt.*	Extinction coefficient	Zn (γ in 50 ml.)
I	0.115	13.0
	0.124	14.0
	0.123	14.0
II	0.177	19.6
	0.168	18.8
	0.168	18.7
III	0.682	76.0
	0.683	76.0
	0.670	75.0

* pH 4.8 to 20°, 30 mm. cell used.

The subtraction of the latter reading from the total will give the experimental value for zinc but it is definitely higher than the true value though the reasons are not yet known. Therefore zinc should be determined from the standard curve thus obtained.

From these results it can be concluded that for a rapid determination of zinc in the presence of lead when speediness is essential and accuracy less questioned, this turbidity subtraction method is found most suitable. Even in this case lead can be directly determined with a good result from the latter reading. Thus it was found that a minute amount of zinc less than 40 γ in 50 ml. is permissible in the determination of lead when it is less than 100 γ .

Method

In the absence of the interfering elements

(7) S. L. Tompsett and A. B. Anderson, *Biochem. J.*, **29**, 1851 (1935); *Analyst*, **60**, 772 (1935); S. L. Tompsett, *Analyst*, **61**, 591 (1936).

(8) E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **9**, 464 (1937); P. L. Hibbard, *ibid.*, **9**, 127 (1937); N. D. Sylvester and E. B. Hughes, *Analyst*, **61** 734 (1936).

described above, zinc may be turbidimetrically determined as follows: the solution to be tested is buffered at pH 4.8 with 7.83 ml. of 0.1 *N* ammonia and 12.17 ml. of 0.1 *N* acetic acid and is kept at 20° after diluted to about 40 ml. Then add 10 ml. of 1% sodium diethyldithiocarbamate solution and make up to a final volume of 50 ml. The turbidity is measured with the Pulfurich photometer using S 43 (434 m μ) filter after 30 minutes. Zinc can be determined with the following accuracy (Table 8).

Table 8

Accuracy in Determining Zinc in Standard Solution

Extinction coefficient	Found Zn, γ in 50 ml.	Present Zn, γ in 50 ml.	Difference, γ
0.177	19.6	20.0	-0.4
0.176	19.5	20.0	-0.5
0.168	18.8	20.0	-1.2
0.187	21.0	20.0	+1.0
0.362	40.8	40.0	+0.8
0.360	40.4	40.0	+0.4
0.347	38.5	40.0	-1.5
0.734	82.0	80.0	+2.0
0.712	79.7	80.0	-0.3
0.704	78.6	80.0	-1.4

In case lead is present in the solution to be tested and speediness is more essential than accuracy, the determination may be performed by the turbidity subtraction method (Table 9). The total turbidity at pH 4.8 is measured in the same way as described above. Next the

Table 9

Turbidity Subtraction Method

Zn, Pb, γ	$\frac{\gamma}{500}$	$\frac{\gamma}{500}$	E (mixed turbidity)	E (due to Pb)	E of Pb (calc.)	Pb (found), γ	Pb (error), γ
25 0	0	0	0.289	0.031	—	—	—
25 50	50	50	0.543	0.167	0.136	52	+ 2
25 100	100	100	0.750	0.339	0.308	118	+18
25 200	200	200	0.894	0.591	0.560	214	+14
40 0	0	0	0.360	0.016	—	—	—
40 50	50	50	0.759	0.161	0.145	53	+ 3
0 100	100	100	0.275	0.265	0.249	95	- 5

remaining turbidity is again measured after the turbidity due to zinc has been eliminated by the addition of 8 ml. of saturated ammonia solution and 2 ml. of 1 *N* potassium hydroxide solution.

Zinc is calculated by subtracting the value from the total value using the empirical standard curve previously constructed. Lead is also determined with the standard curve since it conforms with the law in the case where zinc less than 40 γ in 50 ml. is present with 100 γ lead.

The author's heartfelt and endless gratitude is given to Professor Kenjiro Kimura for his encouragement and suggestion through this investigation.

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An Improved Method of Colorimetric Determination of Vanadium in the Presence of a Relatively Large Amount of Iron

By Yukio MURAKAMI

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Introduction

The following is a description of an improved method for the determination of vanadium in the presence of a comparatively large amount of iron, which is originated by Sandell⁽¹⁾ and considered to be the most accurate and most easily manageable one by which chromium and molybdenum are simultaneously determined in silicate rocks. This method proposed by San-

dell for the element in silicate rocks is a combination of the reaction with oxine reported by Montequi and Gallego⁽²⁾ and the color reaction of phosphotungstic acid with the element reported by Vinogradov.⁽³⁾ It suffices for the determination of as little as 0.001% of vanadium, 0.001% of chromium and 0.0001% of molybdenum in a sample of only one gram.

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

(2) R. Montequi and M. Gallego. *Anales soc. espan. fis. quim.*, **32**, 134 (1934).

(3) A. P. Vinogradov, *Compt. rend. acad. sci. U. R. S. S.*, **1931** A, 249.

The outline of this method is as follows: the melt from the carbonate fusion is leached with water and filtered after adding alcohol to reduce the manganate produced. The filtrate, containing chromate, vanadate and molybdate, is diluted conveniently in a measuring flask up to a definite volume, say to 100 ml. For the determination of vanadium, a stable aliquot portion of the solution is taken (usually 10 ml.), neutralized to methyl orange with sulfuric acid and extracted with chloroform after the addition of 2.5% of oxine in 2 *N* acetic acid.

The residue resulting from evaporation of the chloroform extract is fused with sodium carbonate to convert vanadium into sodium vanadate, and the melt then dissolved with water. The solution obtained is colorimetrically determined by the coloration of intense yellow to orange due to the formation of vanadophosphotungstic acid, after treated with sodium tungstate and phosphoric acid in the acid medium.

When the author tried to use this method for the determination of the element in brown coal ash, he occasionally experienced a serious interference from iron. He conducted a number of experiments and succeeded in devising a new method, by which the interference from iron can be avoided and fairly good results are obtainable.

Experiment

The Presence of Ferrous and Ferric Iron in the Aqueous Extract from the Sodium Carbonate Melt.—In Sandell's original report there were instances in which, it was mentioned, ferric iron diminished the color of vanadophosphotungstic acid and made the results low. The amount of iron going into the filtrate from the sodium carbonate melt of an igneous rocks, however, is too small to cause any appreciable error and hence no quantitative data on its interference have been given.

In the analysis of brown coal ash the interference of iron which passed into the extract seriously affected the color reaction. Contrary to the general belief, the amount of iron is considerably large, as shown in Table 1, even when the determination was performed by the approved method, volumetrically or colorimetrically, using a good quantitative filter paper.

It was found that in 100 ml. of the extract made from the melt of the mixture of sodium carbonate and 1 gram of brown coal ash, n to 0.n mg. of iron was usually present, resulting a serious interference. Yet the use of niter to oxidize iron is undesirable on account of its

Table 1

Iron in the Filtrate			
Exp. No.	Ion	Iron in leached solution (1 g. ash used), γ	Remarks
5	Fe ⁺⁺⁺	275	colorimetrically
	Fe ⁺⁺	469	"
8	Fe ⁺⁺⁺	2125	"
17	Fe ⁺⁺	1252	volumetrically
	Fe ⁺⁺⁺	6904	"
51	Fe ⁺⁺	2091	"
	Fe ⁺⁺⁺	1308	"
50	Total Iron	187	colorimetrically

action on the platinum crucible to develop a yellowish coloration which may be injurious for chromium to be simultaneously determined in the same sample. The presence of iron in the filtrate is presumably due to the peptization of hydrous ferric oxide by silica. In consequence, the greater the content of iron in the sample is, the greater and more serious interference may be expected.

The Action of Iron on the Coloration.—A suitable portion of vanadium standard solution was taken and the following amount of ferric iron added to it. Then vanadium determination was made, the conditions recommended by Sandell being followed. The results are given in Table 2, in which the value was taken soon after the formation of vanadophosphotungstic acid without heating the solution as described below.

Table 2

Interference Due to the Presence of Ferric Iron				
Presented (γ as V_2O_5)	Added (γ as Fe)	Found (γ as V_2O_5)	Error,	
25.3	18.9	24.3	- 1.0 γ	- 3.9%
46.5	18.9	41.2	- 5.3	-11.4
46.5	37.5	40.8	- 5.7	-12.3
46.5	56.8	36.8	- 9.7	-20.9
70.5	2000	34.5	-36.0	-51.4
131.6	2000	72.5	-59.1	-44.9

It was found that the presence of ferric iron apparently leads to lower result.

Ferric iron as well as vanadium easily react with oxine at the pH recommended. Of course the greater part of iron oxiquinolinate, extracted together with vanadium, is removed in the second carbonate fusion, though a small part of it might still pass into the water extract solution. The second carbonate fusion of oxiquinolinate to convert vanadium to vanadate should therefore be cautiously performed.

The interference caused by ferrous iron was found to be different, however, when it was tested in the same way as ferric iron. Ferrous iron does not react with oxine under the condition described, but it easily reduces vanadate to vanadyl ion which does not react with oxine.⁽⁴⁾ Consequently it seriously leads to lower results to such an extent as shown in Table 3.

Table 3

Interference due to the Presence of Ferrous Ion

Presented (r as V_2O_5)	Added ferric ion (r as Fe)	Found (r as V_2O_5)	Error,	
45.0	6.8	21.0	-24.0 r	-53.3%
45.0	13.7	15.0	-30.0	-66.6
45.0	34.0	11.0	-34.0	-77.5
45.0	68.0	9.0	-36.0	-80.0
52.0	0.6	51.0	- 1.0	- 1.9
52.0	1.2	45.0	- 7.0	-13.5
52.0	3.4	48.0	- 4.0	- 7.7
52.0	34.4	19.0	-33.0	-63.5
52.0	68.8	13.0	-39.0	-74.9

It is evident that the interference due to ferrous iron is more serious than that of ferric iron. Next, it was found that the interference, due to ferric iron in the solution with which the color comparison should be made, can be reduced to some extent by heating and keeping it on standing for a while.

The results are the same as given by Wright and Mellon⁽⁵⁾ in which 10 mg. of ferric chloride with 0.0025 mg. vanadium change the hue of color in comparison with the standard solution free from iron, but by heating the solution before the comparison is made, the interference can be, to some extent, diminished.

The Oxidation of Vanadium.—It is evident from the above statement that in the presence of ferrous iron, the oxidation to vanadate from vanadyl ion is necessary for securing good results. This is easily accomplished by the addition of just enough potassium permanganate (0.01 N) to hot solution, though an excess of it is injurious owing to the destruction of oxine and the darkening the coloration. After the addition of permanganate, cool the solution to room temperature, filter and then follow extraction with oxine as described below. It is evident from Table 4 that the oxidation is useful in these cases.

The Separation of Iron from Vanadium.

Table 4

Oxidation of Vanadium with Permanganate

Presented (r as V_2O_5)	Ion	Found, (r as V_2O_5)	Error, r	Remarks
131.6	vanadyl	0	—	not oxidized
		134.9	-3.3	
		128.6	-3.0	
		131.5	-0.1	
70.5	"	0	—	"
		69.5	-1.0	
		72.0	-1.5	
		71.0	-0.5	
		67.9	-2.6	
202.1	vanadate	70.5	—	"
	and	197.5	-4.8	
	vanadyl	199.3	-2.8	
		202.8	-0.7	
		204.7	-2.6	

—Vanadium and iron react with oxine at the intermediate color of methyl orange (3.1 to 4.4) as the reactive pH range of iron with oxine is 2.8 to 11.2 and that of vanadium, from 2.7 to 6.1.⁽⁶⁾ Thus iron extracted together with vanadium results in the serious error as shown already, even though only a small part of it might pass again into the water extracted solution through the melt of the second carbonate fusion. With the increase in the amount of iron, the more is the possibility of the interference. Therefore if a considerably large amount of iron is present, preliminary separation is essential. The following procedure has been devised which is based on the fact that only iron reacts with oxine in an alkaline medium.

The solution is made faintly alkaline to phenolphthalein with sodium hydroxide and iron is extracted with chloroform after adding 2.5% of oxine in 2 N acetic acid solution (Fraction a). Next the solution is buffered at pH 3.8 with 2.5 ml. of sodium citrate⁽⁷⁾ and 10 ml. of 0.15 N acetic acid, and vanadium is extracted in the same way (Fraction b).

The fraction (a) as well as (b) prepared from the model solution containing the two elements in various concentration were thus tested. Then this method of separation was applied to the analysis of two samples of the brown coal ash (No. 5 and No. 7). Vanadium could not be spectroscopically found in fraction (a) of both samples while iron was detected only in fraction (b) of No. 7. It is hereupon confirmed

(4) Lundell, Hoffman and Bright, *Ind. Eng. Chem.* **15**, 1064 (1923).

(5) E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 251 (1937).

(6) H. Goto, *J. Chem. Soc. Japan*, **54**, 314 (1935); K. Shiba, *Repts. Tokyo Imp. Ind. Research Lab.*, **27**, 216 (1932).

(7) Dissolve 4.20 g. of citric acid in 40 ml. of 1 N sodium hydroxide and dilute to 200 ml. with water.

that practically complete separation was accomplished by this method.

Table 5

Spectroscopic Results Obtained with Model Solution Containing the Two Elements

Sample	Iron (III) (γ as Fe)	Vanadium (γ as V_2O_5)	Spectroscopic results (in oxine extract at pH 10.8)
No. 1	33.3	60	} vanadium was not detected
No. 2	25.9	120	
No. 3	18.5	180	

This method of separation is preferably used after oxidation, when a considerable amount of iron is present: e. g., in the determination of vanadium in magnetite sand and other materials abundant in iron.

Procedure.—A preliminary separation of iron from vanadium as mentioned above is recommendable, though this procedure is not always necessary except when the sample is exceedingly rich in iron. The following will be a detailed description of the procedure, though, for practical application, an appropriate abbreviation in the procedure is permissible, depending upon the quality of the sample to be tested.

The water leached solution from the melt of carbonate fusion is made up to a definite volume (say 100 ml.) and an aliquot portion (10 ml.) is taken. Then it is made slightly acid with dilute sulfuric acid and boiled with the addition of potassium permanganate solution just sufficient to oxidize. (Don't add in any excess). After cooling and filtering using a glass filter, it is made slightly alkaline with sodium hydroxide. The compound of iron formed with 2.5% of oxine in 2 *N* acetic acid is extracted by the chloroform.

Next the solution is buffered at pH 3.8 with 2.5 ml. of sodium citrate and 10 ml. of 0.15 *N* acetic acid in the order given. Vanadium is then extracted by shaking with 2 ml. of chloroform and 0.1 ml. of 2.5% of oxine in 2 *N* acetic acid. Repeat the extraction three times in the same way. The last chloroform extract should have a faint yellowish coloration due to the excess of oxine itself. The chloroform extract is drawn off into a platinum crucible, to which 1 ml. of chloroform used to rinse the stem of the funnel is added.

Then to the crucible is again added 0.10 gram of anhydrous sodium carbonate and the solution is gently evaporated on a water bath. A sufficient care must be taken during evaporation because of the tendency of the extract of creeping up the wall of the crucible. Then it is fused thoroughly and warmed after adding a

little water to hasten the dissolution of the melt. After cooling, it is filtered through a filter paper treated with 10% of sodium carbonate solution. The solution should be colorless and free from any marked turbidity at this stage.

The following reagents are added in succession to the filtrate, mixing after each addition: 1 ml. of sulfuric acid, 0.1 ml. of 85% of phosphoric acid and 0.2 ml. of 5% of sodium tungstate solution. The solution is gently

Table 6

Reproducibility

Present, γ (as V_2O_5)	Found, γ (as V_2O_5)	Error, γ (as V_2O_5)	Remarks
70.5	72.4	+1.9	} ammonium metavanadate
	70.0	-0.5	
	72.6	+2.1	
	67.6	+2.9	
	71.1	+0.6	
131.6	133.0	+1.4	} 1 g. of rock powder (Olivin basalt) was used
	132.3	+0.7	
	131.5	-0.1	
	129.5	-2.1	
69.0	67.4	-1.6	
(mean value)	70.9	+1.9	} vanadium standard solution is added to the water leached solution of the above rock.
	68.2	-0.8	
	69.7	+0.7	
139.5	138.1	-1.4	
	139.0	-0.5	
	138.0	-1.5	
	136.1	-3.4	
	139.8	+0.3	

Table 7

Vanadium Determination in Various Samples

Sample	Sample taken, g.	Found, γ (as V_2O_5)	Content %
Brown coal ash No. 1	1.0583	500	0.047
	1.0583	480	0.046
No. 2	1.0484	108	0.010
	1.0567	115	0.010
No. 3	1.0703	125	0.012
	1.0197	110	0.011
No. 4	1.0069	530	0.053
	1.0069	535	0.053
Olivin basalt	1.5006	72.5	0.0048
	1.5006	68.1	0.0045
Hypethene dacite obsidian	1.0004	51.5	0.0051
	1.0002	47.2	0.0047
Nepheline basalt	1.0014	37.7	0.0038
	1.0013	40.6	0.0041
	1.0035	41.2	0.0041
Iron sand	0.9540	728	0.076
	1.0005	734	0.073
Leaves of white birch	0.9942	60.5	0.0063
	0.9942	58.4	0.0059

warmed to hasten the formation of vanadophosphotungstic acid. Thus vanadium is determined by using S 43 (434 m μ) filter with Pulfrich photometer.

Results.—A number of experiments were conducted on the reproducibility of this method as shown in Table 6. Preliminary separation of iron from vanadium was not adopted except in a single case, but oxidizing procedure was applied in these cases. Thus the vanadium contents in magnetite sand, rock, leaves and brown coal ash were determined with satisfactory results as shown in Table 7.

Summary

Contrary to the general belief, the author confirmed the presence of iron in the filtrate from the carbonate fusion melt of brown coal ash or rock. The interference leading to lower results due to ferrous iron is more serious than that due to ferric iron as the vanadate ion is reduced to vanadyl when acidified with sulfuric acid. Consequently the oxidizing procedure with potassium permanganate is required to diminish this undesirable effect. If a considerably large amount of iron is present, it is necessary to make a preliminary separation of

iron from vanadium in a slightly alkaline medium with oxine and chloroform. Hence the vanadium determination can be carried out following the directions recommended.

The separation method proposed by the author was spectroscopically tested and it was shown that a larger amount of iron can be separated without any trace of vanadium being carried down. However this procedure is not always required and can be eliminated as the quality of the sample to be tested varies.

The interference due to the presence of ferric iron can be reduced to some extent, even when a considerably large amount of iron is present in the solution prepared for the color comparison, by warming it and keeping it on standing for several minutes. Some experiments on the determination of the vanadium content of various samples were also conducted, with the results that the modified method can be used as well with a considerable accuracy.

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An Improved Method of the Colorimetric Determination of Chromium with Diphenylcarbazide

By Yukio MURAKAMI

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Introduction

In 1900, Cazeneuve⁽¹⁾ discovered diphenylcarbazide which reacts with sexavalent chromium in acid solution giving an intensely red-violet oxidation product. Since then many successive workers⁽²⁾ had employed this sensitive color reaction in determining a minute

amount of chromium. Sandell⁽³⁾ described a useful and accurate colorimetric method of estimating chromium in silicate rocks with this reagent, stating that a total sample of one gram is sufficient for the determination of as little as 0.001% of chromium.

In Japan, there have been some studies made on the chromium content in hot springs, coal ash, oceanic muds and volcanic rocks by applying this method. A remarkable conclusion through these series of studies is that the chromium content is so exceedingly small that the element is scarcely noticeable in several samples tested. It becomes of importance and interest, therefore, to study whether this

(1) P. Cazeneuve, *Bull. Soc. Chim.*, (3) **23**, 701 (1907); *Compt. Rend.*, **131**, 346 (1900).

(2) A. Moulin, *Chem. News*, **90**, 320 (1904); Mutger and Zon, *Ind. Eng. Chem.*, **4**, 493 (1921); B. S. Evans, *Analyst*, **46**, 285 (1921); N. M. Stover, *J. Am. Chem. Soc.*, **50**, 2363 (1928); B. Jones, *Analyst*, **55**, 318 (1930); F. Feigl, *Ang. Chem.*, **44**, 741 (1931).

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

scarcity is due to a characteristic of the sample tested or a defect in the method of determination used. During the author's geochemical investigation of chromium in Japanese brown coal, he gave a thorough study of this colorimetric method, because Sandell described the tendency of this method to give lower results in the chromium content, without giving any numerical data. The author found, too, that there was a tendency to lower results in this colorimetric method. Hence a number of experiments on this problem were conducted and it was found that this method can be improved to a certain extent by introducing oxidation with sodium peroxide, prior to color comparison.

The oxidation method for this purpose was tested using several oxidizing agents, and sodium peroxide in alkaline medium as well as potassium bromate in an acid medium were finally found most recommendable, though only the former will be described in this report.

In fact, the author was able to obtain remarkable results on the occurrence of chromium in Japanese brown coal and others, which evidently differ from those previously reported. These results will be given in another communication.⁽⁴⁾ In this report, some sources of errors in Sandell's method are pointed out and an improved method will be described.

Experiment

In this color reaction chromium should be in the hexavalent state. But, in successive procedures recommended, there are some possibilities of reduction of the chromate formed in carbonate fusion to chromic ion. The possibilities are (a) the presence of alcohol added to reduce manganate before the melt is leached with water, (b) the presence of iron, especially in ferrous state, contrary to the general belief, in a water-leached solution as reported by the author⁽⁵⁾ in his study of colorimetric determination of vanadium, (c) the inevitable contact of oxine and chloroform necessary to remove vanadium before the color comparison is made and (d) filtration through a filter paper to remove the droplets of chloroform. Naturally the purity of the reagents is taken into a sufficient consideration, but nevertheless it is difficult in actual practice to obtain entirely satisfactory reagents freed from impurities; hence it will cause other possibility of reduction.

The error due to the reason mentioned in

(a) may be avoided by the careful addition of alcohol to reduce any manganate formed in the fusion. But to add alcohol just enough to reduce the manganate is a considerably difficult procedure, because even as little as a drop in excess will reduce the chromate.

Next quinquavalent vanadium interferes by reacting with the reagent in acid solution giving a strongly yellow-colored compound, and it is therefore necessary to remove it previously from the solution by the addition of oxine and the extraction with chloroform of the compound thus formed. But Sandell reported that hexavalent chromium is not reduced in this process. The author's opinion, however, is reverse to this statement.

On this problem, the study set by Hackel⁽⁶⁾ may support the author's opinion that hexavalent chromium is easily reduced in an acid medium during the course of extraction. The author has experienced the reduction of this kind many times in the geochemical study of brown coal ash. Of course, unnecessary standing in contact with oxine after shaking to separate water layer from that of chloroform must be avoided. But it is difficult to separate the chloroform-water interface in a short time, as the trouble is caused by the prevention of coalescence of chloroform droplets after shaking.

Table 1

Reduction Caused by Contact with Oxine

Chromium present, as Cr_2O_3 , γ	Time in contact with oxine, hr.	Chromium found, γ	Error due to reduction, γ
121.7	1	113.3	- 8.4
	2	103.8	-17.9
	5	99.3	-22.4
	18	87.0	-34.7

Errors due to the reasons shown (b) and (d) will be discussed below.

Reduction by a Filter Paper.—Owing to a partial reduction of the chromate when a filter paper is used for the chromate solution, low results⁽⁷⁾ may be obtained. This defect is produced in the case of acid medium and, even in alkaline solutions, it being more marked with a hot rather than a cold solution.

Therefore a sufficient care must be taken to avoid this defect which evidently becomes a

(4) Y. Murakami, this Bulletin, in press.

(5) Y. Murakami, this Bulletin, p. 153.

(6) O. Hackel, *Z. anal. Chem.*, **109**, 91 (1937).

(7) H. Jervis, *Chem. News*, **77**, 133 (1898); A. Allison, *ibid.*, **96**, 1 (1907); R. S. McBride and J. A. Scherrer, *J. Am. Chem. Soc.*, **39**, 928 (1917).

cause for a serious error, especially in a determination of a minute quantity of chromium.

Table 2

Reduction Due to a Filter Paper

With 10% sodium carbonate solution	Acidity of the solution before filtering					
	Expt. I			Expt. II		
	Alka- line	Neu- tral	Acidic	Alka- line	Neu- tral	Acidic
Not digested	80.7 γ	79.6 γ	71.6 γ	19.5 γ	18.2 γ	15.0 γ
Digested	81.6	—	81.6	20.3	—	20.0

It is necessary to remove the reducing matters in the filter paper in advance by digestion with a sodium hydroxide solution.⁽⁹⁾ In order to obtain more accurate results the author recommends the washing of the filter paper previously with a 20% sodium carbonate solution as prescribed by Sandell and also the filtering of the solution containing chromate at room temperature.

Interference with Iron.--The coloration of chromium reacting with diphenylcarbazide is reliable only when it is present as sexavalent ion in acid medium. The author has already

Table 3

Interference Due to Ferric and Ferrous Iron

Present (as Cr_2O_3), γ	Interfering ion, γ		Found (as Cr_2O_3), γ	Difference, γ	Remarks
20.0	444	Fe^{+++}	12.3	- 7.7	FeCl_3
"	888	"	9.4	-10.6	"
20.0	100	Fe^{+++}	17.4	- 2.6	Fe-alum
"	200	"	15.8	- 4.2	"
"	400	"	12.7	- 7.3	"
9.0	76.8	Fe^{++}	4.4	- 4.6	FeSO_4
"	153.6	"	3.5	- 5.5	"
"	230.4	"	3.2	- 5.8	"
18.0	76.8	Fe^{++}	7.0	-11.0	FeSO_4
"	153.6	"	4.7	-13.3	"
"	230.4	"	4.6	-13.4	"
27.0	76.8	Fe^{++}	12.2	-14.8	FeSO_4
"	153.6	"	7.3	-19.7	"
"	230.4	"	6.3	-20.7	"
39.3	0	Fe^{++}	39.3	0	FeSO_4
"	3.8	"	37.4	- 1.9	"
"	7.7	"	34.2	- 5.1	"
"	19.2	"	27.5	-11.8	"
"	38.4	"	22.2	-17.1	"
"	57.8	"	16.9	-22.4	"

(8) W. F. Hillebrand, *U. S. Geol. Survey Bull.*, **422**, 147 (1912); R. S. McBride and J. A. Scherrer, *loc. cit.*; R. W. Curtis and J. Finkelstein, *Ind. Eng. Chem. Anal. Ed.*, **5**, 318 (1933).

described that there are interferences with not only ferrous iron but also with, to a certain extent, ferric iron in the leached filtrate from the carbonate melt in the colorimetric determination of vanadium.⁽⁵⁾ As this interference seems not to have been tested in the colorimetric determination of chromium by any others, a number of experiments have been carried out by the present author.

It has been found that an error occurs with ferrous iron more seriously than with ferric iron as shown in Table 3.

The presence of iron in the leached filtrate, contrary to general belief, results considerably from the peptization of hydrous ferric oxide by silica. It is reasonable to suppose that the reduction of chromate once formed during the carbonate fusion process may also occur owing to the presence of ferrous iron which is leached from the melt, when it is acidified.

Table 4

Rate of Reduction in the Presence of Fe

Time, min.	0	5	10	20	60
Found (as Cr_2O_3), γ	10.6	6.0	5.7	5.7	5.7
Difference, γ	- 7.4	-12.0	-12.3	-12.3	-12.3

Conditions: chromate present, 18.0 γ as Cr_2O_3 , ferrous iron added, 76.8 γ as Fe.

Next a brief experiment on the interference of vanadium which form a strongly yellow-colored compound under the conditions recommended was carried out. It was shown that it is recommendable to remove vanadium by the addition of oxine as described, even if the amount of V_2O_5 does not exceed that of Cr_2O_3 , as it darkens the hue of the solution. Usually it gives an erroneous increase to the results. Besides these ions, other ions such as cited in the following table were tested for the interferences which may be expected in the filtrate, but no serious interference was observed.

Necessity of the Oxidation.--Some sources of errors, especially those responsible for a negative error due to the reduction of chromate to chromic ion in colorimetric determination by diphenylcarbazide have been pointed out and examined, but some of the sources as described above may be easily avoided. However, the errors may be considerable in samples containing a relatively large amount of iron. Among a number of errors, this reduction due to ferrous iron and oxine is especially fatal to the determination, although many other complicated factors also play a part in leading to erroneous results.

The oxidation to chromate is therefore

Table 5
Interference due to Vanadium and Other Ions

Chromate present (as Cr_2O_3), r	Interfering ion, r	Chromate found (as Cr_2O_3), r	Difference, r	Remarks
20.0	10 as V_2O_3	20.5	+ 0.5	Sodium metavanadate
"	20 "	20.3	+ 0.3	
"	30 "	20.8	+ 0.8	
"	40 "	20.3	+ 0.3	
"	100 "	21.1	+ 1.1	
"	300 "	—	—	Darkens the coloration
20.0	{ 10 V_2O_3 0 Fe^{++} }	20.5	+ 0.5	Sodium metavanadate and ferrous sulfate
"	{ 20 V_2O_3 76.8 Fe^{++} }	7.6	-12.4	
20.0	{ 20 V_2O_3 0 Fe^{++} }	20.3	+ 0.3	Sodium metavanadate and ferrous sulfate
"	{ 20 V_2O_3 76.8 Fe^{++} }	8.9	-11.1	
20.0	{ 100 V_2O_3 70 Fe^{++} }	21.1	+ 1.1	Sodium metavanadate and ferrous sulfate
"	{ 100 V_2O_3 76.8 Fe^{++} }	9.4	-10.6	
20.0	1000 Cl^-	19.8	- 0.2	Sodium chloride
"	1009 Al^{+++}	19.3	- 0.7	Aluminium sulfate
"	990 Mg^{++}	19.6	- 0.4	Magnesium sulfate
"	1070 PO_4^{---}	19.6	- 0.4	Sodium phosphate

required for accurate determination. Comparative studies on the oxidation method were performed and it was found that sodium peroxide in an alkaline medium (or potassium bromate in the presence of sulfuric acid) is most appropriate for this purpose.

Oxidation with Sodium Peroxide.—Sodium peroxide has been preferably used for the oxidation of chromium. Some workers have described that the complete decomposition of its excess is possible by boiling the alkaline solution for 10 to 20 minutes. However, others have described that the decomposition is difficult only by boiling if not impossible.

It must be remembered that in an acid solution sodium peroxide or the resultant hydrogen peroxide will cause reduction of chromate, so that it should be expelled out of the alkaline solution before proceeding with sulfuric acid for its complete acidification. As it may be supposed that even a trace of it will cause a serious error in the microdetermination, a number of experiments were carried out for it. To ensure a complete decomposition the addition of glasswool, active charcoal or manganese dioxide previously freed from contaminable

matters, was tried, vigorous and continuous stirring being made during the addition. As a result of these experiments manganese dioxide was found most suitable for this purpose.

The effects of iron as well as vanadate ions were examined on the power to decompose hydrogen peroxide produced from sodium peroxide. However, no significant interference was observed.

The reproducibility and accuracy of this oxidizing procedure are not necessarily sufficient as shown in the following table, but it may serve to remove the difficulties mentioned.

Practically satisfactory results were obtained by the following procedure. Though a complete oxidation can be expected only when a sodium peroxide fusion is used instead of a usual carbonate fusion, the latter was preferably used as iron abundantly appears in the leached filtrate of a sodium peroxide fusion melt.

Procedure.—After vanadium is extracted (as referred to in a separate report)⁽⁵⁾ as oxyquinolate by chloroform, it is made faintly alkaline with sodium hydroxide.

Add 0.05 to 0.01 g. of sodium peroxide to the alkaline solution and boil for approximately 10 minutes, stirring continuously. If necessary, continue the boiling after adding some water. After the bubbling due to the decomposition of sodium peroxide has ceased, add a few lumps of manganese dioxide, previously freed

(10) 1st application will be reported in near future.

from all contaminable matters, which may start the bubbling again.

Then cool the solution under tap water after the bubbling has almost ceased, filter off the manganese dioxide by using a filter paper digested with a 20% sodium carbonate solution, and add 1.5 ml. of 4 *N* sulfuric acid. At this stage the total volume of the solution should not exceed 20 ml. A mixture of 1 ml. of 0.25% solution of diphenylcarbazine in acetone (1:1), 1 ml. of 6 *N* sulfuric acid and 2 to 3 ml. of water is added. Then the solution is thoroughly mixed and made up to 25 ml. The red-violet color develops very rapidly and the comparison is made without unnecessary delay with Pulfrich photometer using S 55 filter (550 m μ .).

To show the improvements made with this procedure, as compared with the old method, the content of chromium in brown coal and rocks was determined. This sufficiently proved the necessity of introducing the oxidizing process in the procedure.

Summary

The colorimetric method of determining chromium in silicate rocks with diphenylcarbazine has the defect resulting in a distinct tendency for producing slightly lower figures as recognized already. After a thorough study of the method the author pointed out the possible sources for the serious errors, especially for those which give negative results. Thus the oxidation method in an alkaline medium was proposed, which was compared with the widely used old method.

The accuracy and reproducibility of this method are not entirely satisfactory but so far

Table 6
Improved Results with Oxidation Method
and its Reproducibility

Sample	Sample taken, g.	Found (as Cr_2O_3), r	Chromium content, %	Remarks
Brown coal ash	No. 1 1.0018	227	0.0227	Oxidation method
		380	0.0373	
	No. 2 1.1972	3.3	0.0003	"
	1.0862	11.5	0.0011	
	No. 3 1.0054	22.5	0.0023	"
	1.0018	38.0	0.0038	
Iron sand	No. 4 0.7036	4.3	0.0006	"
		21.2	0.0030	
	1.0797	270	0.0251	"
Olivin basalt		306	0.0283	
	1.0062	180	0.0175	"
	1.0062	225	0.0221	
		224	0.0223	"
Nepheline bassalt		210	0.0208	
	1.0035	126	0.0126	"
		146	0.0145	
		144	0.0144	"

it will serve as the most accurate method. The content of chromium in brown coal in Japan determined by this oxidation method with sodium peroxide will be reported in a later communication.

The author wishes to express his sincere thanks to Prof. Kenjiro Kimura for his valuable suggestion and the neverfailing encouragement during this investigation.

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Separation of Cations by Thiourea⁽¹⁾

By Yasumitsu UZUMASA and Takeshi OKURA

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The alkaline solution of thiourea, when boiled, decomposes and some sulfide ions are formed. The substance is also known to yield precipitates with some cations,⁽²⁾ from which their sulfides are produced.⁽³⁾ The authors found that such a property of thiourea makes it possible to separate the ions belonging to the copper sub-group from other cations.

Thermal Decomposition of Thiourea in Aqueous Phase.—The neutral solution of thiourea decomposes very gradually only when it is kept in boiling state for some time; but the decomposition takes place even at a comparatively lower temperature i. e., ca. 80° when the solution is made alkaline. For instance, when a solution prepared by adding 1 g. of thiourea to 200 cc. of 0.05 *N* sodium hydroxide was boiled gently for 5 minutes, the decomposition took place. It was found on qualitative test that the product contained, beside traces of carbonate-, sulfate-, sulfite- and nitrate-ions, a considerable amount of sulfide ion. The evolution of sulfur dioxide gas, though very little, was also recognized by its odor.

The Amount of Thiourea Necessary for the Formation of Sulfide Precipitate.—The ions which can be precipitated with the sulfide ion produced by the decomposition of thiourea in an alkaline medium are copper, cadmium, lead, mercury and bismuth, while other cations form no sulfide precipitate under the same condition. The boiling changes almost all sulfur in thiourea into sulfide ion, precipitating the metals of the copper sub-group quantitatively. This may be illustrated by the following example.

A series of copper sulfate solutions were prepared and buffered by a mixture of sodium chloride, sodium hydroxide and glycol so that their *pH* was 11.29 at 10°. To each of the solutions containing 0.0144 g. of CuO were added different volumes of the thiourea solution⁽⁴⁾ and they were made up to 40 cc. with

distilled water respectively. The solution was then boiled gently for 2 minutes when a black precipitate was formed. The precipitate, after filtered through Toyo filter paper No. 5 A, was ignited to constant weight.

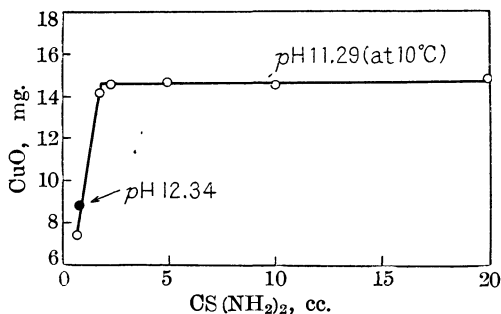


Fig. 1.

The results are summarized in Fig. 1 which shows that the precipitation of copper was complete when as much as 2 cc. of the thiourea solution was added. The theoretical amount of thiourea necessary for the quantitative separation of copper from the said solution is 1.67 cc., provided that all the sulfur in thiourea is available for the purpose. As illustrated in Fig. 1, the addition of 1.7 cc. of thiourea gave 0.0144 g. of CuO, the experimental results being in close agreement with the theoretical values.

The precipitate thus obtained is crystalline and adsorbs little foreign substances. It can be filtered easily with Toyo filter paper No. 5 A or even No. 1 etc., which have larger size of pores. This may be due to the fact that the velocity of precipitation is rather small and also that the precipitate once formed partly as hydroxide changes into sulfide very gradually.

Influence of *pH* on Sulfide Formation by Thiourea.—Thiourea does not produce sulfides in an acid medium. Our investigation has revealed that even when the solution is made alkaline, the precipitation is not complete unless *pH* > 12. This is confirmed by the following experiments.

To 20 cc. of the thiourea solution whose sulfur content was 3.5 mg. per cc. was added the buffer together with a solution containing copper or other ions of the sub-group. The total volume was made up to 55 cc., and the

(1) Read before the Hokkaido meeting of the Chemical Society of Japan, on July 31, 1949.

(2) J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942).

(3) Beilstein, Vol III, 180.

(4) 1 cc. of the solution contains 3.5 mg. of sulfur.

solution was heated until it boiled gently for 2 minutes. The liquid was then cooled and filtered through Toyo filter paper No. 3. The precipitate was washed thoroughly and ignited to constant weight.⁽⁵⁾ The results are shown in Fig. 2. The values are the means of several

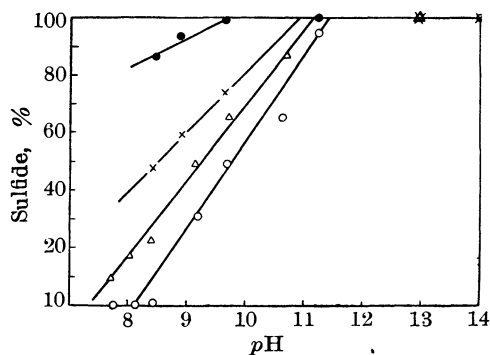


Fig. 2.

•, Cu; Δ, Pb; ×, Hg; ○, Cd

experiments in which about 50 mg. and 100 mg. of the copper sub-group ions were taken. These data show that the velocity of sulfides precipitation depends upon pH of the system and also the concentration of thiourea as well as cations. In consequence, the best result should be expected when pH of the solution is kept 12.

Separation of the Copper Sub-group Ions from Other Cations by Thiourea.—

The results obtained above suggest us a new means of separation of the copper sub-group ions from other cations. In case where Cu^{++} and Fe^{+++} , for example, coexist in a solution, both metals precipitate as hydroxides when the solution is made alkaline. In presence of thiourea, Cu^{++} changes into sulfide while ferric hydroxide remains as such. When a sufficient amount of acetic acid is added, the hydroxide dissolves on boiling⁽⁶⁾ whereas the sulfide remains as precipitate. The experiments were carried out in the following way.

To a solution containing one of the copper group ions, e. g., Cu^{++} as copper sulfate, was added three to five times as much another ion. Thiourea was present in the solution in such a ratio as $\text{Cu} : \text{CS}(\text{NH}_2)_2 = 1 : 5$ (in gram equivalent). Sodium hydroxide was added so that the solution was approximately 0.5 N.

(5) The mercury precipitate was dried at 110° and weighed.

(6) If the solution containing ferric hydroxide is boiled for some time, the hydroxide becomes less soluble.

The mixture was heated and boiled for 2 minutes. After adding 10 cc. of acetic acid, the solution was allowed to stand on the water-bath for about 10 minutes. The precipitate was collected on Toyo filter paper No. 3, washed first with acetic acid and then with water and finally ignited to constant weight. The results are shown in Table 1.

Table 1

Influence of Coexisting Ions on the Precipitation of the Cu Sub-group Ions

Co-existing ions	Cu Sub-group Ions				
	Cu	Cd	Pb	Hg	Bi
Fe	85.3%	93.7%	91.6%	101%	95.3%
Al	92.8	96.4	96	83.2	96
Co	92.8	103.5	93.6	102.4	94.3
Ni	92.8	99.4	109	101.6	101
Mn	76.6	76.4	102.3	101.5	99
Zn	101.1	85.7	106	102.5	96
Cr	86.3	97.6	110	89	86

The values in the table are the separability of the copper sub-group ions from the coexisting ions which are found in the first column. They are the figures found with the solutions containing 0.05 g. and 0.1 g. of copper, cadmium and lead and also with the saturated solutions of mercury and bismuth.

Lead sulfide thus produced adheres to the inner wall of the vessel in which the reaction took place, forming a brilliant mirror. The deposit comes off easily from the wall in its early stage of formation. When the solution is allowed to stand for some time, however, the deposition becomes so firm that the mirror can be removed only on heating with nitric acid.

That the solubility to acetic acid of the sulfides obtained in this manner is very small is illustrated by the following experiments. A sulfide was precipitated in 50 cc. of the solution containing approximately 30 mg. of a copper sub-group ion, and the mixture, together with 30 cc. of acetic acid, was allowed to stand on the water-bath for 1 hour. The precipitate was then filtered and ignited to constant weight. The percentage by which the metal sulfides dissolved in acetic acid is as follows:

Cu 2.1%, Cd 2.8%, Pb 8.6%,⁽⁷⁾ Hg 2.3%, Bi 4%

The separability of all the copper sub-group ions from the mixture of the ions of the third

(7) The error is considered to be large in case of lead because of its nature of adhering to the wall.

group as well as the fourth group was next studied. The experimental procedure is as follows.

To the mixture of copper, cadmium, lead, mercury and bismuth salts, the total amount of which was 0.1114 g. as sulfide, was added approximately five times as much Fe^{+++} , Al^{+++} , Co^{++} , Ni^{++} , Mn^{++} , Zn^{++} and Cr^{+++} . The solution was made up to 100 cc. and treated with sodium hydroxide and thiourea in the same manner as in the previous experiments. It was boiled gently for 5 minutes and, after adding 50 cc. of acetic acid, allowed to stand on the water-bath for 10 minutes. The precipitate was then filtered and weighed. The separations of the copper sub-group from the fourth group, and the third group + the fourth group were also investigated. The results are summarized in Table 2.

Table 2
Separability of the Cu Sub-group
Ions from Other Group Ions

Co-existing ions	Separability
(1) the third group	106.3%
(2) the fourth group	103.4
(3) {the third group and} {the fourth group }	106.4
(4) {tin sub-group, the third} {group and fourth group}	168.3
(5) {the same as (4), but the precipitate} {was washed with conc. NaOH }	94

When the ions of the tin sub-group exist in

the system, they precipitate as hydroxide insoluble in acetic acid, the separation being made difficult. In this case the sulfides are filtered, washed with acetic acid and treated with conc. sodium hydroxide solution. The precipitates of the tin sub-group metals then dissolve and a fairly good separation is performed. This is understood by the figures given at the bottom of the table.

It is thus confirmed that the ions of the copper sub-group can be separated nearly quantitatively from many other cations by thiourea. The present operation suggests us a new scheme of qualitative analysis without hydrogen sulfide which is under investigation in our laboratory. In such a plan, the effect of the excess of thiourea after the separation of copper sub-group ions should by no means be ignored. For instance, because of its reducing nature, thiourea, if present, positively retards the oxidation of Mn^{++} to MnO_2 by means of nitric acid and potassium chlorate. The excess of thiourea must therefore be decomposed by evaporating up the solution with nitric acid to dryness before the solution is subjected to analysis of the fourth group.

A part of the expense of the investigation was defrayed from the research fund granted to one of the authors from the Hattori Hokokai, to which our hearty gratitude is expressed.

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Dosage colorimétrique du chrome d'après la méthode au peroxyde d'argent et à la diphénylcarbazine

par Motoharu TANAKA

(Reçu le 22 Décembre, 1949)

En 1908, M. Moulin⁽¹⁾ a publié une méthode de dosage colorimétrique du chrome à l'aide du réactif organique diphénylcarbazine. Avant M. Moulin, M. Cazeneuve⁽²⁾ avait déjà indiqué l'utilisation possible de ce réactif. La diphénylcarbazine amène la coloration de l'acide

chromique en milieu acide, par conséquent il faut oxyder le chrome trivalent au chrome hexavalent. M. Moulin⁽³⁾ a employé l'ébullition par l'eau oxygénée en présence d'un excès de potasse et Willard et Young⁽⁴⁾ ont utilisé

(1) M. A. Moulin, *Bull. soc. chim., France*, (3), **31**, 295 (1908).

(2) P. Cazeneuve, *ibid.*, (3), **23**, 701 (1900).

(3) M. A. Moulin, *ibid.*, (3), **31**, 295 (1908).

(4) Willard et Young, *Ind. Eng. Chem.*, **20**, 769 (1928); Kolthoff et Sandell, *Ind. Eng. Chem., Anal. Ed.*, **2**, 140 (1930).

le persulfate d'ammonium ou le bromate de potassium, et l'adoption de la fusion avec le carbonate de soude permet d'oxyder le chrome dans l'analyse de la roche.⁽⁵⁾

Nous avons employé le réactif peroxyde d'argent en milieu d'acide sulfurique pour oxyder le chrome trivalent et cette méthode a fourni les résultats satisfaisants comme dans le cas du manganèse.⁽⁶⁾

La condition d'oxydation et de coloration

Nous avons préparé la solution à 1 mg. Cr/cc. en dissolvant le chromate de potasse (Merck, pro analysi), que nous avons réduit ensuite par le gaz d'acide sulfureux, dont l'excès a été complètement chassé par le gaz d'acide carbonique. Cette solution a été utilisée dans l'état de dilution jusqu'à 1 γ Cr/cc.

Pour oxyder le chrome on a employé ce qu'on appelle le peroxyde d'argent,⁽⁷⁾ que l'on peut facilement préparer par le moyen d'un mélange d'une solution de nitrate d'argent et de persulfate d'ammonium qui doit être agité. On a employé 0.10 à 0.15 g. de ce peroxyde d'argent en suspension dans l'eau à chaque dosage.

La concentration de l'acide sulfurique pour l'oxydation.—Les expériences ont été faites pour décider la concentration convenable pour arriver à l'oxydation du chrome par le peroxyde d'argent.

Table 1

Concentration de l'acide sulfurique	moins de 1.5N	1.5N	3N	5N	8N
Cr employé, γ	$\left\{ \begin{array}{l} \text{La destruction de l'excès de peroxyde ne s'effectue que très lentement} \end{array} \right.$				
Cr trouvé, γ					
		5.0 ₀	5.0 ₀	5.0 ₀	5.0 ₀
		4.9 ₆	5.0 ₀	4.9 ₉	3.3 ₃

La table 1 indique que la concentration convenable se trouve entre 1.5 N et 5 N d'acide sulfurique. Nous avons pris la concentration 1.5 N, en tenant compte de ce que la coloration par la diphenylcarbazine est plus stable dans un milieu faiblement acide que dans un milieu fortement acide.

La durée du chauffage.—On ajoute le peroxyde d'argent à une solution froide con-

tenant le chrome trivalent et puis l'excès de ce réactif est éliminé par chauffage au bain-marie. La durée du chauffage produit les effets suivants:

Table 2

La durée du chauffage, minutes	2	5	10	30
Cr employé, γ	5.0 ₀	5.0 ₀	5.0 ₀	5.0 ₀
Cr trouvé, γ	5.0 ₀	5.0 ₂	4.9 ₇	3.7 ₂

Sans doute, on peut conclure que 2 minutes de chauffage suffisent et qu'il ne faut dépasser 10 minutes pour éviter la réduction du chromate déjà oxydé.

La stabilité de la couleur après la coloration.—Le chrome oxydé par le peroxyde d'argent se combine immédiatement avec le réactif diphenylcarbazine, mais ce composé n'est pas tout à fait stable. On dit que sa stabilité varie selon la concentration de l'acide, dont nous avons pris environ 0.3 N. Pour examiner cette stabilité nous avons répété nos observations en variant des intervalles. Voici les résultats:

Table 3

Le temps après la coloration, minutes	3	10	20	30	40
Cr employé, γ	5.0 ₀	5.0 ₀	5.0 ₀	5.0 ₀	5.0 ₀
Cr trouvé, γ	5.0 ₃	4.9 ₂	4.9 ₁	5.0 ₁	6.0 ₃

Plus de 30 minutes après la coloration, une poudre brillante (dont la qualité n'est pas encore étudiée) apparaît parfois dans la solution colorée. Dans ce cas-là, le coefficient d'extinction obtenu devient d'un degré d'intensité supérieur à celui du chrome employé. Mais il n'y a aucune crainte de changement quand la comparaison est terminée dans les 30 minutes qui suivent la coloration.

La quantité du réactif diphenylcarbazine.—10 mg. de ce réactif est dissous dans un mélange de 2 cc. d'acétone et de 2 cc. d'eau. Cette solution est ajoutée dans une solution oxydée par le peroxyde d'argent. Les quantités différentes du réactif employé ne produisent aucun effet sur la coloration, comme la table 4 nous l'indique.

Table 4

La quantité de solution de la diphenylcarbazine, cc.	0.2	0.4	0.8	1.0
Cr employé, γ	5.0 ₀	5.0 ₀	5.0 ₀	5.0 ₀
Cr trouvé, γ	5.0 ₀	4.9 ₉	5.0 ₂	5.0 ₃

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

(6) Y. Murakami, *Bull. Chem. Soc. Japan.*, **22**, 159 (1949).

(7) La contribution à l'étude de ce peroxyde d'argent sera publiée par le même auteur.

Le procédé recommandé

A 5 cc. de la solution à analyser contenant 1 cc. d'acide sulfurique (1:4), ajouter en agitant 0.10 à 0.15 g. de peroxyde d'argent, mettre la solution au bain-marie pendant environ 2 minutes jusqu'à la disparition du peroxyde d'argent pulvérisé et laisser reposer à la température ordinaire, ajouter de 0.2 cc. à 0.4 cc. de la solution de la diphenylcarbazide, diluer la solution à 25 cc. ou à 50 cc. au moyen d'eau distillée et comparer la coloration au bout de 10 minutes et pendant les 10 minutes suivantes, en employant le colorimètre de Duboscq ou le photomètre de Pulrich.

La courbe d'étalon

Quand on examine au spectrophotomètre la coloration de la chrome-diphenylcarbazide, dont le maximum d'absorption se trouve au voisinage de 5500 Å.,⁽⁸⁾ on peut dire qu'il suffit d'employer le filtre S. 55 du photomètre de Pulrich pour ce dosage. Cette coloration obéit à la loi de Lambert-Beer entre les concentrations 0.02 p.p.m. et 1 p.p.m. du chrome. Nous avons obtenu les coefficients d'extinction à diverses concentrations du chrome et nous avons tracé la courbe d'étalon suivante:

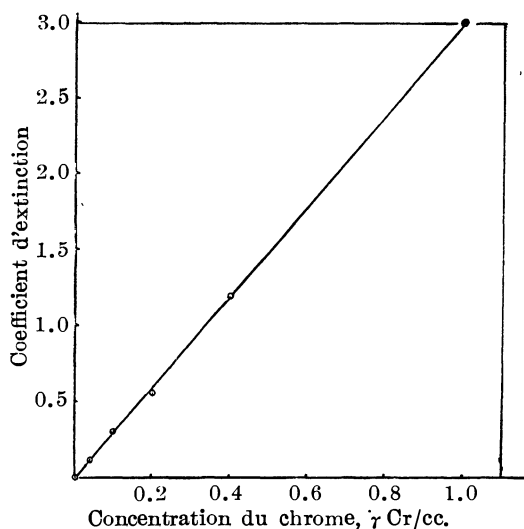


Fig. 1.—La courbe d'étalon. Filtre, S 55; Cuvette 50.00 mm.

La fonction entre les coefficients d'extinction et les concentration du chrome est faite au moyen de la méthode des moindres carrés.

$$C = 1.672 E \text{ (}\gamma \text{ Cr/cc., Cuvette 10 mm.)},$$

où C est la concentration du chrome et E le coefficient d'extinction.

La reproductibilité de cette méthode

A diverses concentrations nous avons répété quelques expériences et étudié la reproductibilité de cette méthode.

Table 5

La concentration du chrome	Cr employé, γ	Cr trouvé, γ	Ecart absolu, γ
0.08 p.p.m.	2.0 ₀	2.0 ₂	+ 0.0 ₂
"	"	2.0 ₅	+ 0.0 ₅
"	"	1.9 ₉	- 0.0 ₁
0.2 p.p.m.	5.0 ₀	4.9 ₆	- 0.0 ₄
"	"	5.0 ₀	0.0 ₀
"	"	5.0 ₂	+ 0.0 ₂
0.4 p.p.m.	10.0 ₀	10.0 ₉	+ 0.0 ₉
"	"	9.9 ₈	- 0.0 ₂
"	"	10.0 ₃	+ 0.0 ₃
1 p.p.m.	25.0 ₀	24.9 ₂	- 0.0 ₈
"	"	24.8 ₁	- 0.1 ₉
"	"	25.0 ₉	+ 0.0 ₉

La table 5 nous montre que nous pouvons déterminer la teneur du chrome avec une précision fort satisfaisante.

Influences des éléments étrangers

Les métaux comme cuivre, nickel, cobalt, mercure, cadmium, magnésium, qui produisent leur complexe coloré avec la diphenylcarbazide en milieu alcalin ou neutre, ne troublent pas ce procédé que l'on effectue dans le milieu acide.

La coloration du chrome par diphenylcarbazide est affaiblie par l'excès d'acide phosphorique ou de fluorure de sodium ajouté pour éliminer la couleur du fer. La coloration due au fer de l'ordre de 1 mg. peut être éliminée par l'addition de 0.2 cc. d'acide phosphorique ou de 30 mg. de fluorure de sodium, lesquels ne troublent pas le dosage.

On dit que la coloration due au molybdène s'affaiblit par l'addition d'acide oxalique.⁽⁸⁾ Néanmoins, l'affaiblissement de la coloration du chrome est causé aussi par l'acide oxalique ajouté. Donc on ne peut éliminer la coloration due aux complexes, vanadium- et molybdène-diphenylcarbazide, qui sont très stables dans le milieu acide. Mais le molybdène de moins de 4 mg. et le vanadium de moins de 8 γ dans 25 cc. ne gênent pas ce dosage.

Les métaux comme fer, vanadium, et manganèse, qui sont en même temps oxydés par le peroxyde d'argent et qui produisent leur

(8) D. Brard, *Ann. chim. anal. chim. appl.*, **17**, 201 (1935).

composé coloré avec le réactif diphénylcarbazine, peuvent être séparés du chrome en utilisant de l'eau oxygénée et de la soude caustique. D'abord, on emploie l'excès de soude qui est neutralisé par l'acide sulfurique étendu jusqu'à pH 7.2. On peut séparer le chrome quantitativement du fer, du vanadium et du manganèse par deux ou trois précipitations. On utilise tout le filtrat pour l'analyse du chrome. La moitié du chrome dans le filtrat se trouve à l'état de hexavalent, mais l'oxydation par le peroxyde d'argent est nécessaire pour obtenir un résultat précis.

Résultats de l'application aux échantillons naturels

L'échantillon ayant été décomposé par un certain acide, le chrome est précipité avec le fer par l'ammoniaque. Cette précipitation est dissoute dans l'acide sulfurique étendu et le chrome est séparé comme nous l'avons vu dans le chapitre précédant. Les résultats obtenus sont donnés ci-dessous:

Table 6

Echantillon	Cr ₂ O ₃ %
1) Jarosite	5.8×10^{-3}
2) 1) + 7.3×10^{-3} % Cr ₂ O ₃	12.9×10^{-3} { calc. 13.1×10^{-3}
3) Pyrolusite (a)	0.5×10^{-3}
4) " (b)	0.0×10^{-3}
5) Basalte olivinique	19.4×10^{-3}
6) Obsidienne dacitique à hyperthène	0.7×10^{-3}
7) Basalte nephélinique	18.5×10^{-3}
8) <i>Opuntia Ficus-indica</i> Mill.	0.0×10^{-3}

Résumé

1. Nous proposons d'employer comme oxydant, qu'on appelle le peroxyde d'argent, pour oxyder le chrome que l'on détermine au moyen de la diphénylcarbazine. L'oxydation dans le milieu acide par le peroxyde d'argent s'effectue avec succès.

2. Nous avons fait des recherches sur l'influence des divers ions susceptibles de réagir avec la diphénylcarbazine et l'influence de ceux qui sont oxydés par le peroxyde d'argent.

3. Les résultats de l'analyse des minéraux, des roches et des plantes ont été donnés.

4. On peut appliquer cette méthode aux échantillons naturels très facilement et très simplement sans recourir à la fusion du carbonate de soude.

5. La destruction complète de l'excès de l'oxydant et l'oxydation complète dans le milieu acide sont les points forts de cette méthode.

Qu'il soit permis à l'auteur, en terminant ce compte-rendu, de rendre un témoignage tout particulier de reconnaissance à ses maîtres M. Prof. Kenjiro Kimura, professeur à l'Université de Tokio et M. Kazuo Kuroda, professeur-adjoint à l'Université de Tokio, qui se sont donné tant de peine pour leur instruction, et à M. Yukio Murakami qui l'a aidé beaucoup par ses conseils très précieux et très utiles.

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Molecular Orbital Treatment of the Ultraviolet Spectra of Cycloöctatetraene⁽¹⁾

By Yuji MORI, Ikuzo TANAKA and Shoji SHIDA

(Received May 15, 1950)

1. Introduction

The energy levels of cycloöctatetraene have been calculated in our laboratory by the HLSP method⁽²⁾ assuming two different structures

D_{2d} ⁽³⁾ and D_{4d} ,⁽⁴⁾ and this calculation has been

(1) Presented at the Annual Meeting of the Chemical Society of Japan, Kyoto, April 2, 1950.

(2) I. Tanaka and S. Shida, *Bull. Chem. Soc. Japan*, **23**, 54 (1950).

(3) H. S. Kaufman, I. Fanckuchen and H. Mark, *J. Chem. Phys.*, **15**, 414-15 (1947); H. S. Kaufman, I. Fanckuchen and H. Mark, *Nature*, **161**, 165 (1948); K. Hedberg and V. Schomaker, *Annual Meeting of Amer. Chem. Soc.*, (1949).

(4) O. Bastiaisen, O. Hassel and A. Langseth, *Nature*, **160**, 128 (1947); O. Bastiaisen and O. Hassel, *Acta chemica scandinavica*, **3**, 209 (1949); E. P. Lippincott, R. C. Lord and R. S. MacDonald, *J. Chem. Phys.*, **16**, 548 (1948).

compared with the experimental results on cyclooctatetraene, namely absorption spectra, magnetic susceptibility and thermochemical data.

The purpose of the present paper is to calculate the energy levels of the molecule from the standpoint of the Goeppert Mayer and Sklar's method,⁽⁵⁾ assuming the symmetry of cyclooctatetraene as D_{2d} , and to show how this calculation is in agreement with the experimental results.

2. The Orbitals

Table 1

	E	C ₂	2iC ₄ =S ₄	2C' ₂	2σ _d
A ₁	1	1	1	1	1
A ₂	1	1	1	-1	-1
B ₁	1	1	-1	1	-1
B ₂	1	1	-1	-1	1
E	2	-2	0	0	0
Γ	8	0	0	0	0

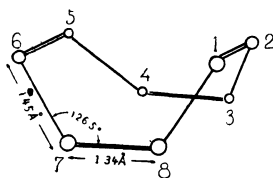


Fig. 1.

First, the wave functions of the π -electrons for cyclooctatetraene assuming the symmetry of D_{2d} ⁽³⁾ are determined by the LCAO approximation. The symmetry of the eight levels of cyclooctatetraene can be found from the group theory. The character of the symmetry group D_{2d} is shown in Table 1. The reducible representation Γ is

$$\Gamma = A_1 + A_2 + B_1 + B_2 + 2E.$$

The energy levels and their wave functions are obtained using the variation method. Since there are two kinds of distances between two neighboring carbon atoms, the two different resonance integrals (and similarly the two overlap integrals) must be distinguished from each other.

$$\left. \begin{aligned} \int \tilde{\psi}_2 \mathbf{V}_2 \psi_1 d\tau &= \beta_d, & \int \tilde{\psi}_2 \psi_1 d\tau &= d_d, \\ \int \tilde{\psi}_3 \mathbf{V}_3 \psi_2 d\tau &= \beta_s, & \int \tilde{\psi}_3 \psi_2 d\tau &= d_s, \end{aligned} \right\} \quad (1)$$

where ψ_f : the $2p\pi$ wave function for the f -th carbon atom,

$\mathbf{V}_f$: the potential from the f -th carbon atom,

and

$$\int \tilde{\psi}_f \left(\sum_{i=1}^8 \mathbf{V}_i - \mathbf{V}_f \right) \psi_f d\tau = \alpha. \quad (2)$$

Putting

$$x = (E_{2p} - E + \alpha) / \{ (E_{2p} - E)d_d + \beta_d \}, \quad (3)$$

$$k = (E_{2p} - E)d_s + \beta_s / \{ (E_{2p} - E)d_d + \beta_d \}, \quad (4)$$

where, E_{2p} is the energy of a $2p$ electron in a carbon atom in the valence state. Then solving the secular determinant for x we obtain

$$x = \pm(1+k), \pm\sqrt{1+k^2}, \pm(1-k). \quad (5)$$

Thus the wave functions are

$$\left. \begin{aligned} \varphi_1 &= \frac{1}{\sqrt{8\sigma_1}} (\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 \\ &\quad + \psi_6 + \psi_7 + \psi_8), \\ \varphi_{+2} &= \frac{1}{\sqrt{8\sigma_2}} (\psi_1 + \psi_2 e^{i\theta_1} + \psi_3 e^{i(\theta_1+\theta_2)} \\ &\quad + \psi_4 e^{i(2\theta_1+\theta_2)} + \psi_5 e^{i(2\theta_1+\theta_2)} \\ &\quad + \psi_6 e^{i(3\theta_1+2\theta_2)} + \psi_7 e^{i(3\theta_1+\theta_2)} \\ &\quad + \psi_8 e^{i(4\theta_1+3\theta_2)}), \\ \varphi_{-2} &= \tilde{\varphi}_{+2}, \\ \varphi_3 &= \frac{1}{\sqrt{8\sigma_3}} (\psi_1 + \psi_2 - \psi_3 - \psi_4 + \psi_5 \\ &\quad + \psi_6 - \psi_7 - \psi_8), \\ \varphi_4 &= \frac{1}{\sqrt{8\sigma_4}} (\psi_1 - \psi_2 - \psi_3 + \psi_4 + \psi_5 \\ &\quad - \psi_6 - \psi_7 + \psi_8), \\ \varphi_{+5} &= \frac{1}{\sqrt{8\sigma_5}} (\psi_1 + \psi_2 e^{i\theta_3} + \psi_3 e^{i(\theta_3+\theta_4)} \\ &\quad + \psi_4 e^{i(2\theta_3+\theta_4)} + \psi_5 e^{i(2\theta_3+\theta_4)} \\ &\quad + \psi_6 e^{i(3\theta_3+2\theta_4)} + \psi_7 e^{i(3\theta_3+\theta_4)} \\ &\quad + \psi_8 e^{i(4\theta_3+3\theta_4)}), \\ \varphi_{-5} &= \tilde{\varphi}_{+5}, \\ \varphi_6 &= \frac{1}{\sqrt{8\sigma_6}} (\psi_1 - \psi_2 + \psi_3 - \psi_4 + \psi_5 \\ &\quad - \psi_6 + \psi_7 - \psi_8), \end{aligned} \right\} \quad (6)$$

where σ_i is a normalizing factor, and

$$\left. \begin{aligned} e^{i\theta_1} &= \frac{1+ik}{\sqrt{1+k^2}}, & e^{i\theta_3} &= \frac{-1+ik}{\sqrt{1+k^2}}, & \theta_1 + \theta_2 &= \frac{\pi}{2}, \\ e^{i\theta_2} &= \frac{k+i}{\sqrt{1+k^2}}, & e^{i\theta_4} &= \frac{-k+i}{\sqrt{1+k^2}}, & \theta_3 + \theta_4 &= \frac{3\pi}{2}. \end{aligned} \right\} \quad (7)$$

These wave functions are

(5) G. Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

$$\begin{aligned}\varphi_1 &\subset A_1, \quad \varphi_{\pm 2} \subset E, \quad \varphi_3 \subset B_2, \\ \varphi_4 &\subset B_1, \quad \varphi_{\pm 5} \subset E, \quad \varphi_6 \subset A_2.\end{aligned}$$

When $k = 1$, the wave functions become

$$\begin{aligned}\varphi_l &= \frac{1}{\sqrt{8}} \sum_{f=1}^8 \psi_f \exp[2\pi i f l / 8], \\ l &= 0, \pm 1, \pm 2, \pm 3, 4,\end{aligned}\quad (8)$$

which are the same as those of Hückel.⁽⁶⁾ These wave functions appear when the symmetry of cyclooctatetraene is assumed as D_{4d} or D_{8h} .

The antisymmetrized molecular orbitals of 8-electron system for the ground state and the lower excited states are

$$\Phi_t = \frac{1}{\sqrt{8!}} \sum_P (-1)^P P \Psi_t \chi_k, \quad (9)$$

where for the ground state

$$\begin{aligned}\Psi_0 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_3(8),\end{aligned}\quad (10)$$

for the excited states

$$\begin{aligned}\Psi_1 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_4(8),\end{aligned}\quad (11)$$

$$\begin{aligned}\Psi_2 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_4(7)\varphi_4(8),\end{aligned}\quad (12)$$

$$\begin{aligned}\Psi_3 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_{+5}(8), \\ \text{or} \quad &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_{-2}(5)\varphi_{-2}(6)\varphi_3(7)\varphi_{-5}(8),\end{aligned}\quad (13)$$

$$\begin{aligned}\Psi_4 &= \varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4) \\ &\quad \times \varphi_3(5)\varphi_3(6)\varphi_{-2}(7)\varphi_4(8), \\ \text{or} \quad &= \varphi_1(1)\varphi_1(2)\varphi_{-2}(3)\varphi_{-2}(4) \\ &\quad \times \varphi_3(5)\varphi_3(6)\varphi_2(7)\varphi_4(8),\end{aligned}\quad (14)$$

and from the group theory

$$\Psi_0 \subset A_1, \quad \Psi_1 \subset A_2, \quad \Psi_2 \subset A_1, \quad \Psi_3 \subset E, \quad \Psi_4 \subset E.$$

χ_k , spin function, is for the singlet states

$$\begin{aligned}\chi_s &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5) \\ &\quad \times \beta(6)\alpha(7)\beta(8), \\ \text{or} \quad &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \\ &\quad \times \frac{1}{\sqrt{2}} \left\{ \alpha(7)\beta(8) - \beta(7)\alpha(8) \right\},\end{aligned}\quad (15)$$

and for the triplet states .

$$\begin{aligned}\chi_t &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5) \\ &\quad \times \beta(6)\alpha(7)\alpha(8), \\ \text{or} \quad &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5) \\ &\quad \times \beta(6)\beta(7)\beta(8), \\ \text{or} \quad &= \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \\ &\quad \times \frac{1}{\sqrt{2}} \left\{ \alpha(7)\beta(8) + \beta(7)\alpha(8) \right\}.\end{aligned}\quad (16)$$

Thus the energy values for these states will be calculated in Section 3 including electronic interaction.

3. Calculations

The average values of Hamiltonian are given by

$$E_t = \int \tilde{\Phi}_t H \Phi_t dV. \quad (17)$$

The Hamiltonian H is

$$H = \sum_{\nu=1}^8 \left(-\frac{\hbar^2}{8\pi^2 m} \Delta_{\nu} + \sum_{f=1}^8 \mathbf{V}_{f\nu} \right) + \sum_{\substack{\nu=1 \\ \nu < \mu}}^8 \frac{e^2}{r_{\nu\mu}}, \quad (18)$$

where ν and μ show the number of a π -electron, f denotes the number of a carbon atom, and $\mathbf{V}_{f\nu}$ is the potential of a neutral carbon atom⁽⁶⁾ minus the potential of a $2p\pi$ electron.

The energies, including electronic interaction, are for the ground state

$$\begin{aligned}({}^1A_1) \quad {}^1E_0 &= 2\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_3 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 4\gamma_{13} + 6\gamma_{22} + 8\gamma_{23} + \gamma_{33} \\ &\quad - 4\delta_{12} - 2\delta_{-22} - 2\delta_{13} - 4\delta_{23},\end{aligned}\quad (19)$$

for the excited singlet states

$$\begin{aligned}({}^1A_2) \quad {}^1E_1 &= 2\varepsilon_1 + 4\varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 2\gamma_{13} + 2\gamma_{14} + 6\gamma_{22} + 4\gamma_{23} \\ &\quad + 4\gamma_{24} + \gamma_{34} - 4\delta_{12} - 2\delta_{-22} \\ &\quad - \delta_{13} - \delta_{14} - 2\delta_{23} - 2\delta_{24} + \delta_{34}, \\ ({}^1A_1) \quad {}^1E_2 &= 2\varepsilon_1 + 4\varepsilon_2 + 2\varepsilon_4 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 4\gamma_{14} + 6\gamma_{22} + 8\gamma_{24} + \gamma_{44} \\ &\quad - 4\delta_{12} - 2\delta_{-22} - 2\delta_{14} - 4\delta_{24}, \\ ({}^1E) \quad {}^1E_3 &= 2\varepsilon_1 + 4\varepsilon_2 + \varepsilon_3 + \varepsilon_5 + \gamma_{11} + 8\gamma_{12} \\ &\quad + 2\gamma_{13} + 2\gamma_{15} + 6\gamma_{22} + 4\gamma_{23} \\ &\quad + 4\gamma_{25} + \gamma_{35} - 4\delta_{12} - \delta_{13} - \delta_{15} \\ &\quad - 2\delta_{-22} - 2\delta_{23} - \delta_{-25} - \delta_{25} + \delta_{35}, \\ ({}^1E) \quad {}^1E_4 &= 2\varepsilon_1 + 3\varepsilon_2 + 2\varepsilon_3 + \varepsilon_4 + \gamma_{11} + 6\gamma_{12} \\ &\quad + 4\gamma_{13} + 2\gamma_{14} + 3\gamma_{22} + 6\gamma_{23} \\ &\quad + 3\gamma_{24} + \gamma_{33} + 2\gamma_{34} - 3\delta_{12} - 2\delta_{13} \\ &\quad - \delta_{14} - \delta_{-22} - 3\delta_{23} - \delta_{34},\end{aligned}\quad (20)$$

(6) E. Hückel, *Zeits. Physik*, **70**, 204 (1931).

and for the triplet states

$$\begin{aligned} {}^3E_1 &= {}^1E_1 - 2\delta_{34}, \quad {}^3E_3 = {}^1E_3 - 2\delta_{35}, \\ {}^3E_4 &= {}^1E_4 - 2\delta_{24}. \end{aligned} \quad (21)$$

The integrals, ε_i , γ_{ij} and δ_{ij} in these expressions are

$$\begin{aligned} \varepsilon_i &= \int \tilde{\varphi}_i(\nu) \left(-\frac{\hbar^2}{8\pi^2 m} \Delta_\nu \right. \\ &\quad \left. + \sum_{j=1}^8 \mathbf{V}_{j\nu} \right) \varphi_i(\nu) d\tau_\nu, \end{aligned} \quad (22)$$

$$\gamma_{ij} = \int \int \frac{e^2}{r_{\nu\mu}} |\varphi_i(\nu)|^2 |\varphi_j(\mu)|^2 d\tau_\nu d\tau_\mu, \quad (23)$$

$$\delta_{ij} = \int \int \frac{e^2}{r_{\nu\mu}} [\overline{\varphi_i(\nu) \varphi_j(\mu)}] \varphi_j(\nu) \varphi_i(\mu) d\tau_\nu d\tau_\mu. \quad (24)$$

Then, ε_i , γ_{ij} and δ_{ij} are expanded in terms of A_i , B_i , B'_i , R_i , C_i , Q , d_i , for instance,⁽⁷⁾

$$\left. \begin{aligned} \varepsilon_2 &= E_{2p} + \frac{1}{\sigma_2} \left[-\mathbf{A}' - \mathbf{Q} - \frac{1}{S} \mathbf{R}_1 - \frac{k}{S} \mathbf{R}_7 \right. \\ &\quad \left. - \frac{1}{S} \left\{ \mathbf{B}_1 + 2(\mathbf{B}_3 + \mathbf{B}_5 + \mathbf{B}_7) \right\} \right. \\ &\quad \left. - \frac{k}{S} \left\{ \mathbf{B}_9 + 2(\mathbf{B}_2 + \mathbf{B}_4 + \mathbf{B}_6) \right\} \right], \\ \gamma_{33} &= \frac{1}{8\sigma_3^2} \left\{ \mathbf{A} + 4(\mathbf{B}_1 + \mathbf{B}_3 + \mathbf{B}_5 + \mathbf{B}_7) \right. \\ &\quad \left. - 4(\mathbf{B}_2 + \mathbf{B}_4 + \mathbf{B}_6 + \mathbf{B}_8) - 8\mathbf{B}'_2 \right. \\ &\quad \left. + 4\mathbf{B}'_3 + 2\mathbf{B}'_5 + 2\mathbf{C}_1 + 2\mathbf{C}_7 \right\}, \\ \delta_{34} &= \frac{1}{8\sigma_3\sigma_4} \left\{ \mathbf{A}_0 - \mathbf{A}_1 - \mathbf{A}_7 + 2\mathbf{A}_2 \right. \\ &\quad \left. - \mathbf{A}_3 - \mathbf{A}_5 + \mathbf{A}_4 \right\}, \\ \sigma_2 &= 1 + \frac{1}{S} d_1 + \frac{k}{S} d_7, \\ \sigma_3 &= 1 + d_1 - d_7 - 2d_2, \end{aligned} \right\} \quad (25)$$

where

$$\left. \begin{aligned} A_i &= \int \int \frac{e^2}{r_{\nu\mu}} \psi_i(\nu)^2 \psi_{i+1}(\mu)^2 d\tau_\nu d\tau_\mu, \\ \sum_{i=0}^7 A_i &= \mathbf{A}, \quad \sum_{i=1}^7 A_i = \mathbf{A}', \\ B_i &= \int \int \frac{e^2}{r_{\nu\mu}} \psi_i(\nu)^2 \\ &\quad \times \psi_i(\mu) \psi_{i+1}(\mu) d\tau_\nu d\tau_\mu, \end{aligned} \right\}$$

(7) In convenience we put $k = \frac{\beta_8}{\beta_d}$ and $S = \sqrt{1+k^2}$.

$$\left. \begin{aligned} B'_i &= \int \int \frac{e^2}{r_{\nu\mu}} \psi_i(\nu) \psi_{i+1}(\nu) \psi_i(\mu) \\ &\quad \times \psi_{i+1}(\mu) d\tau_\nu d\tau_\mu, \\ C_i &= \int \int \frac{e^2}{r_{\nu\mu}} \psi_i(\nu) \psi_{i+1}(\nu) \psi_i(\mu) \\ &\quad \times \psi_{i+1}(\mu) d\tau_\nu d\tau_\mu, \\ R_i &= \int \psi_{i+1}(\nu) \mathbf{H}_{i+1}(\nu) \psi_i(\nu) d\tau_\nu, \\ Q &= \int \psi_i(\nu) (\mathbf{H}_2(\nu) + \mathbf{H}_9(\nu)) \psi_i(\nu) d\tau_\nu, \\ d_i &= \int \psi_i(\nu) \psi_{i+1}(\nu) d\tau_\nu. \end{aligned} \right\} \quad (26)$$

$\mathbf{H}_i(\nu)$ is the potential of a neutral carbon atom.⁽⁸⁾ The $2p\pi$ orbital of a carbon atom is

$$\psi_{2p\pi}(r, \theta, \varphi) = \sqrt{\frac{Z^5}{32\pi}} r \sin \theta \cos \varphi \exp[-Zr/2], \quad (27)$$

where Z is the effective nuclear charge 3.18, calculated by Zener.⁽⁸⁾ The numerical values of A_i , B_i , B'_i , R_i , C_i , Q , d_i ,⁽⁹⁾ are determined from the values of Parr and Crawford's calculation.⁽¹⁰⁾

The results of calculation are shown in Table 2 and 3.

Table 2

$A_0 =$	16.94 e.V.	$B_3 =$	1.39 e.V.	$C_1 =$	1.11 e.V.
$A_1 =$	9.31 "	$B_4 =$	0.56 "	$C_7 =$	0.78 "
$A_2 = A_6 =$	5.61 "	$B_5 =$	1.23 "	$R_1 =$	2.12 "
$A_3 =$	4.63 "	$B_6 =$	0.66 "	$R_7 =$	0.88 "
$A_4 =$	4.33 "	$B_7 =$	1.81 "	$Q =$	1.66 "
$A_5 =$	4.78 "	$B_8 =$	1.84 "	$d_1 =$	0.28
$A_7 =$	8.60 "	$B'_2 =$	0.36 "	$d_7 =$	0.13
$B_1 =$	3.60 "	$B'_3 =$	0.46 "	$d_2 =$	0.02
$B_2 =$	0.92 "	$B'_5 =$	0.36 "	$k =$	0.44

(8) Zener, *Phys. Rev.*, **36**, 51 (1930).

(9) The integral

$\int \int \frac{e^2}{r_{\nu\mu}} \psi_a(\nu) \psi_b(\nu) \psi_c(\mu) \psi_d(\mu) d\tau_\nu d\tau_\mu$ was approximated by

$$d_{ab} \cdot d_{cd} \times \int \int \frac{e^2}{r_{\nu\mu}} \mathbf{K}_{ab}(\nu)^2 \cdot \mathbf{K}_{cd}(\mu)^2 d\tau_\nu d\tau_\mu.$$

Rf. A. London, *J. Chem. Phys.*, **13**, 417 (1945).

(10) R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, **16**, 1049 (1948); cf. C. C. J. Roothaan and R. G. Parr, *J. Chem. Phys.*, **17**, 1001 (1949).

Table 3

$r_{12} = 7.16 \text{ e.V.}$	$r_{35} = 7.63 \text{ e.V.}$	$\delta_{25} = 1.31 \text{ e.V.}$
$r_{13} = 7.38 \text{ "}$	$r_{44} = 8.97 \text{ "}$	$\delta_{34} = 0.72 \text{ "}$
$r_{14} = 7.73 \text{ "}$	$\delta_{12} = 2.37 \text{ e.V.}$	$\delta_{35} = 1.39 \text{ "}$
$r_{15} = 7.35 \text{ "}$	$\delta_{13} = 1.44 \text{ "}$	
$r_{22} = 7.37 \text{ "}$	$\delta_{14} = 1.49 \text{ "}$	$\epsilon_1 = E_{2p} - 45.57 \text{ e.V.}$
$r_{23} = 7.64 \text{ "}$	$\delta_{15} = 1.04 \text{ "}$	$\epsilon_2 = E_{2p} - 46.38 \text{ "}$
$r_{24} = 7.87 \text{ "}$	$\delta_{-22} = 1.50 \text{ "}$	$\epsilon_3 = E_{2p} - 46.85 \text{ "}$
$r_{25} = 7.52 \text{ "}$	$\delta_{23} = 1.94 \text{ "}$	$\epsilon_4 = E_{2p} - 45.73 \text{ "}$
$r_{33} = 8.03 \text{ "}$	$\delta_{24} = 1.58 \text{ "}$	$\epsilon_5 = E_{2p} - 41.00 \text{ "}$
$r_{34} = 7.84 \text{ "}$	$\delta_{-25} = 0.85 \text{ "}$	

4. Considerations

The energy levels of the ground state and the lower excited states of cyclooctatetraene are shown in Fig.

2. The ground state is the singlet state of ${}^1A_1$, and then this is in agreement with the experimental result that the magnetic susceptibility of cyclooctatetraene is diamagnetic. The intensity of the shoulder of the absorption curve⁽¹¹⁾ (max. 2800 Å.) is relatively weak, so this absorption band seems to be due to a forbidden

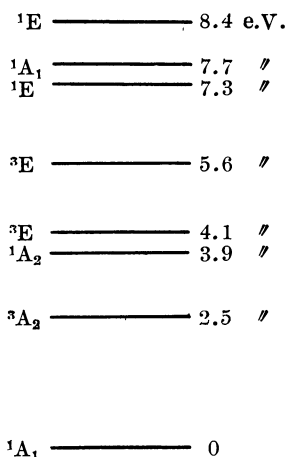


Fig. 2.

transition.

The transitions from the ground state ${}^1A_1$ to the excited states ${}^1E$ are allowed. According to our calculation, the wave lengths for these transitions are 1700 Å. (7.3 e.V.) and 1470 Å. (8.4 e.V.). The ${}^1A_1 \sim {}^1A_2$ forbidden transition is 3.9 e.V. (about 3100 Å.) and the ${}^1A_1 \sim {}^1A_1$ forbidden transition is 7.7 e.V. (about 1600 Å.). The results of the calculation by the HLSP method⁽²⁾ show that the ${}^1A_1 \sim {}^1E$ transition is about 2100 Å. and the ${}^1A_1 \sim {}^1A_1$ forbidden transition is about 2800 Å. band. So the strong band below 2000 Å. may be due to the ${}^1A_1 \sim {}^1E$ transition and the 2800 Å. weak band to the ${}^1A_1 \sim {}^1A_1$ or the ${}^1A_1 \sim {}^1A_2$ transition.

The energy levels of cyclooctatetraene are also calculated by the authors, as having the symmetry of D_4 , in a similar procedure to that in the case of D_{2d} by the GMS method. But the results calculated assuming as D_4 are not in agreement with the observed values of absorption spectra and magnetic properties.

5. Summary

The energy levels of cyclooctatetraene as D_{2d} were calculated by the GMS method. Then it was shown by the authors that the ground state of cyclooctatetraene may be diamagnetic, and that the wave length of the absorption spectra calculated assuming as D_{2d} is approximately in agreement with the experimental results.

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(11) S. Miyagawa and I. Tanaka, unpublished.

Effects of Hydrochloric Acid on the Paper Chromatography of Amino Acids⁽¹⁾

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Paper partition chromatography has been proved to be a useful and convenient tool for

(1) The present paper was read by one of the authors (S. I.) before the 3rd Annual Meeting of the Chemical Society of Japan in Kyoto held on April 1, 1950. A part of the work has been reported in the Report of the Radiation Chemistry

Research Institute, the University of Tokyo, 5, 53 (1950).

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amino acid analysis.^(3,4,5,6) R_f values of amino acids, the specific characters showing the ratios of the distances reached by them to those by the developing solvents, have been determined in their aqueous solutions developed by several solvents, and applied to the identification of each of the amino acids. However, in practice, analysis by this method of the solution containing hydrochloric acid, especially in the hydrolyzed mixture of protein or peptide with hydrochloric acid, is very often carried out in laboratories. Repeated treatments of such solution by evaporating to dryness, with successive addition of water, can never remove hydrochloric acid completely from the solution, a quantity of the acid corresponding to the concentration of *ca.* 1 *N* being retained, although this obviously depends on the concentration of amino acids. Neutralization of the acid with alkali was often tried, but an undesirable effect of the salt produced upon the chromatogram may not then be neglected.⁽⁷⁾ The treatment, moreover, is of very troublesome and fast impracticable in case of treating a minute volume of solution, a case often met with in the paper chromatographic method. It has never been studied whether the presence of hydrochloric acid may affect the R_f values of amino acids or not, though recently H. B. Bull *et al.*⁽⁸⁾ and S. Aronoff⁽⁹⁾ observed the R_f values of amino acids in the solutions of some hydrogen ion concentrations, using phenol as a solvent. The former investigators found no difference between those in neutral and alkaline or acidic solutions, while the latter found a considerable effect of hydrogen ion concentrations on the chromatogram of lysine in alkaline solution, but neither of the investigations has been extended to the range of higher acidity. As a preliminary test proved that the effect of hydrochloric acid on the chromatograms was sometimes so remarkable in cases of some solvents, the present systematic observation was carried out in order to clarify the effect in cases of several amino acids, solvents and concentrations of hydrochloric acid

Experimental Method

Amino acids used in the experiment were

- (3) R. Consden, A. H. Gordon and A. J. P. Martin, *Biochem. J.*, **38**, 224 (1944).
- (4) R. Consden, *Nature*, **162**, 359 (1948).
- (5) A. J. P. Martin, *Ann. N. Y. Acad. Sci.*, **49**, 249 (1948); *Ann. Repts. Progress Chem.*, **45**, 267 (1949).
- (6) D. L. Clegg, *Anal. Chem.*, **22**, 48 (1950).
- (7) A. H. Gordon, *Nature*, **162**, 180 (1948).
- (8) H. B. Bull, J. W. Hahn and V. H. Baptist, *J. Am. Chem. Soc.*, **71**, 550 (1949).
- (9) S. Aronoff, *Science*, **110**, 590 (1949).

L-leucine, DL-valine, DL-alanine, glycine, L-arginine monohydrochloride and L-aspartic acid. Each of them was dissolved individually in 1% concentration, except L-leucine and DL-valine (both in 0.5%), in hydrochloric acid of various concentrations (0–12 *N*). A definite small volume from the solution was applied to a marked spot on each of the paper strips (the Tōyo filter paper, No. 2, 2×40 cm.). After the strip was allowed to stand in the room for about twenty hours, the chromatogram of the one-dimensional type, descending or ascending, was made as usual. As solvents, *n*-butanol, isovalerianic acid, *n*-butanol-acetic acid, phenol and collidine-lutidine were used. These were saturated with water except *n*-butanol-acetic acid and phenol. *n*-Butanol-acetic acid was composed of 4 volumes of *n*-butanol, 1 volume of acetic acid and 1 volume of water. Phenol was used as 80% (W/W) aqueous solution.

After development and drying, the spot of amino acid was revealed by spraying with 0.2% solution of ninhydrin in water-saturated butanol followed by heating. Subsequently, the diffused area of hydrochloric acid on the strip was also revealed by spraying with 0.04% solution of bromophenol blue (B.P.B.) or thymol blue (T.B.) in 95% ethanol. The chromatograms obtained were compared with one another concerning each solvent, the results of which are as follows.

Results and Discussions

***n*-Butanol.**—In case *n*-butanol was used as a solvent, hydrochloric acid was found to

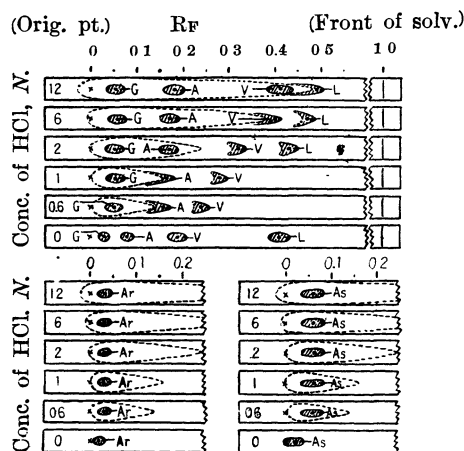


Fig. 1.—Chromatogram of amino acids in hydrochloric acid of various concentrations developed by *n*-butanol: Temperature, 5–10°; development, descending; L, leucine; V, valine; A, alanine; G, glycine; Ar, arginine; As, aspartic acid. Areas surrounded by broken lines mean those of diffused hydrochloric acid. Chromatograms for corresponding concentrations of the acids were shown together in the same figures respectively, although experiments on each amino acid were carried out independently.

increase the R_f value of each amino acid with an increase in the concentration of hydrochloric acid. The results were shown in Fig. 1. In extreme cases, where the concentration of hydrochloric acid was 12 N or 6 N , the position of valine and alanine was moved to the usual one of leucine and valine respectively. Accordingly, the identification of these amino acids may possibly be often mistaken without the knowledge of this fact.

The diffused area of hydrochloric acid revealed by B.P.B. spread more extensively as the concentration of the acid increased, though its size was independent of the kind of amino acids. The area was shown surrounded by broken lines in the figure. Hydrochloric acid seemed to be accompanied thus far with n -butanol as a result of its considerable solubility in the latter. The reason why each amino acid travels abnormally for a longer distance may be understood from the fact that amino acid is more soluble in n -butanol containing hydrochloric acid than in it alone. The relation between the acid areas and the location of amino acids was fairly interesting in this case. The spots of amino acids of higher R_f values went just ahead of the field of hydrochloric acid, forming a distinct saddle shape colored by ninhydrin as strongly as usual. The further the areas of hydrochloric acid extended, the further the spots of amino acids were pushed forward with them. When the formers went too far for the amino acids of lower R_f values to ride on the top of them, the latter were left behind the formers and were included inside of them. The shapes of them were then changed into ovals, while their color became a little paler.

When a chromatogram of a sample containing an unknown concentration of hydrochloric acid is obtained, the paper ought to be sprayed with an alcoholic solution of B. P. B. to show the area of the acid. On comparing this with the figures already obtained, the concentration of the acid and its probable effect upon the chromatogram therefore may also approximately be supposed.

Isovaleric acid.—When isovaleric acid was used as a solvent, contrary to the case of n -butanol, hydrochloric acid was found to decrease remarkably the R_f value and also the strength of coloring of each amino acid, as shown in Fig. 2, with an increase in the concentration of hydrochloric acid. The diffused area of hydrochloric acid revealed by T. B. was now limited to the neighborhood of the original point and did not extend no more. The fact seems to be resulted from the difficult solubility of hydrochloric acid in isovaleric acid, contra-

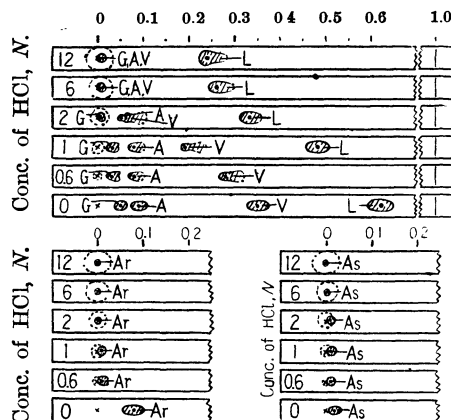


Fig. 2.—Chromatograms of amino acids in hydrochloric acid of various concentrations developed by isovaleric acid: Temperature, 5–10°; development, ascending. Other notes are as Fig. 1.

ry to that in n -butanol. Hydrochloric acid thus retained in the stationary phase near the original point may likely prevent the amino acids from moving.

n -Butanol-acetic acid.—In this case, on spraying of an alcoholic solution of B. P. B. two acidic areas were revealed on a paper of the chromatogram, one was shown extended from one end of the strip to R_f value of about 0.2, the other ahead of the former, as shown in Fig. 3 a (the former was not represented in the figure to avoid confusion). As the size of the former is independent of the concentration of hydrochloric acid, it is inferred that this area does not indicate the presence of hydrochloric acid but that of remaining acetic acid. On the contrary, as the size of the latter area grows larger with an increase in the concentration of hydrochloric acid, obviously this area shows the diffused one of hydrochloric acid. The latter acid was found to increase slightly the R_f values of amino acids which were located near its field, namely alanine, glycine and aspartic acid (see Fig. 3 a). On the other hand the R_f value of arginine was rather decreased, the results of which observed in various concentrations of hydrochloric acid were separately given below, to avoid confusion in the figure. Leucine, located far from the acidic area, was scarcely affected.

(Conc. of HCl): (0 N) (0.6 N) (1 N) (2 N) (6 N) (12 N)
Arginine: 0.19 0.18 0.17 0.16 0.16 0.16

By supplementary experiments, it was also proved that the effect on proline and glutamic acid was similar to that on alanine. Above

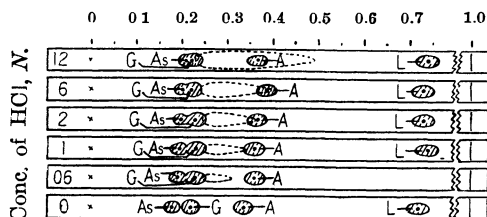


Fig. 3a

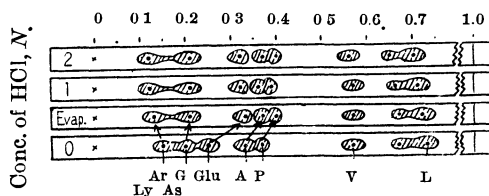


Fig. 3b

Figs. 3a and 3b.—Chromatograms of amino acids in hydrochloric acid of various concentrations developed by *n*-butanol-acetic acid. Temperature, ca. 10°; development, descending; P, proline, Glu, glutamic acid; Ly, lysine. Other notes as Fig. 1.

all, the effect on glutamic acid was the most remarkable. These were shown in Fig. 3b, where 10% solutions of the dried digestion product of casein with trypsin in 2 *N* and 1 *N* hydrochloric acid or merely in distilled water respectively, were used for chromatography as usual. On the one hand, the solution of the above product in 6 *N* hydrochloric acid was also prepared and evaporated to dryness on steam-bath repeatedly four times to remove hydrochloric acid and chromatographed, the result of which was shown in the third strip of the figure. One may notice that a similar effect also appears on it as that of 2 *N* or 1 *N* acid.

Phenol.—When phenol was used as a solvent the effect of hydrochloric acid hardly appeared on the chromatograms of amino acids of higher *R_f* values, namely leucine, valine, alanine and arginine, as shown in Fig. 4.

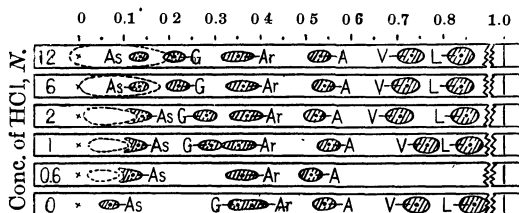


Fig. 4.—Chromatograms of amino acids in hydrochloric acid of various concentrations developed by phenol. Temperature, ca. 20°; development, ascending. Other notes are as Fig. 1.

However, as the diffused area of hydrochloric acid was here revealed near the original point on the strip by B. P. B. (see Fig. 4), the amino acids of comparatively lower *R_f* values and hence located about this area, namely glycine and aspartic acid, were affected by hydrochloric acid obviously as expected; the former decreased, while the latter increased.

Collidine-lutidine.—On developing with collidine-lutidine, a yellow separate band, perhaps connecting with the hydrochloric acid,⁽¹⁰⁾ usually appeared just ahead (at ca. 0.65 in *R_f*) of the location of leucine as shown in Fig. 5, by revealing with B. P. B. The shape of

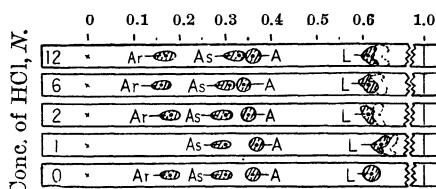


Fig. 5.—Chromatograms of amino acids in hydrochloric acid of various concentrations developed by collidine-lutidine. Temperature, 20°; development, ascending. Other notes as Fig. 1.

leucine was distorted by this band, but its *R_f* value and coloring hardly varied in any concentration of hydrochloric acid. As to the other amino acids, almost none of the effect of hydrochloric acid was found on the *R_f* value, shape and coloring of the chromatogram (see Fig. 5). Among them, glycine was omitted from the figure to avoid confusion, and its *R_f* values observed in various concentrations of hydrochloric acid were given below:

(Conc. of HCl): (0 *N*) (1 *N*) (2 *N*) (6 *N*) (12 *N*)
Glycine: 0.32 0.34 0.33 0.33 0.35

Therefore, it is the most desirable way to use collidine-lutidine as the solvent in case some hydrochloric acid may be contained in the sample to be analyzed by paper chromatography.

Summary

To explain what effect hydrochloric acid, contained in the sample to be analyzed, gives upon the paper chromatograms of amino acids, *R_f* values of some amino acids dissolved in hydrochloric acid of various concentrations were observed with different kinds of solvent.

(10) Probably the hydrochloric acid composes a salt with collidine-lutidine.

In case of *n*-butanol, hydrochloric acid was found to increase the R_F value of each amino acid with an increase in the concentration of hydrochloric acid, while in isovalerianic acid, on the contrary, to decrease that. On the one hand, only the amino acids of lower R_F values were affected by hydrochloric acid in the case of phenol. In butanol-acetic acid, on the other hand, some effect was also found, but in collidine-lutidine it was negligible. In all cases,

the relation between these effects and the diffused areas of hydrochloric acid on the chromatograms was observed with great interest.

The authors wish to express their hearty thanks to the Ministry of Education for the Research Grant given for this work.

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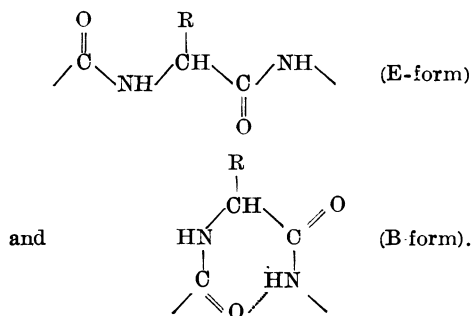
Intramolecular Rotation and the Structure of High Polymers. II. Further Studies on the Structure of Polypeptide Chain

By San-ichiro MIZUSHIMA, Takehiko SHIMANOUCI and Masamichi TSUBOI

(Received June 19, 1950)

I. Proposed Configurations of a Polypeptide Chain

Based on the energy consideration of intramolecular rotation about a single bond as axis, two of us proposed two unit structures of a polypeptide chain,⁽¹⁾



Taking into account that all amino acid residues of the polypeptide chain are in L-forms, we can construct various configurations of a polypeptide chain shown in Fig. 1, of which EEE... corresponds to the extended form presented by Meyer and Mark in 1928,⁽²⁾ BBB... to a possible configuration of α -keratin presented by us in 1947,⁽¹⁾ and independently by Ambrose *et al.* in 1949,⁽³⁾ and BBEBE... to

another possible configuration of α -keratin presented by us in 1948.⁽¹⁾ These figures represent

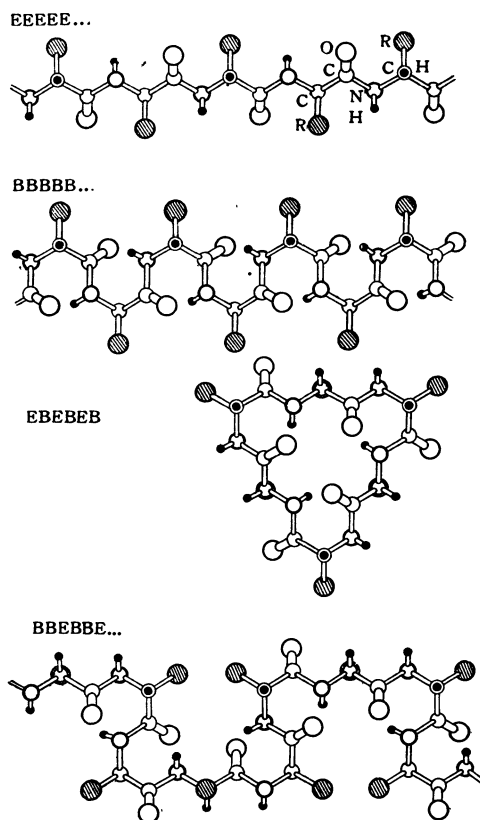


Fig. 1 a.—Various configurations of polypeptide chain.

(1) Shimanouchi and Mizushima, *Kagaku*, **17**, 24 and 52 (1947); *Bull. Chem. Soc. Japan*, **21**, 1 (1948); *Chem. Abst.*, **43**, 8843 (1949).

(2) Meyer and Mark, *Ber.*, **61**, 1932 (1928).

(3) Ambrose, Elliot and Temple, *Nature*, **163**, 859 (1949).

the projections of the molecular configurations on a plane perpendicular to one of the carbon bonds, where for the sake of simplicity all the bond angles of carbon and nitrogen are assumed to be tetrahedral, all the bond lengths of C-C and C-N to be equal and all the intramolecular rotational states about the C-C and C-N bonds as axes to be either the *trans* ($\theta=0^\circ$) or the *gauche* ($\theta=120^\circ$).

and the intramolecular rotational angles to have the following values:

$$\theta(\text{NH}-\text{CO}-\text{C}_\alpha-\text{NH}) = 140^\circ$$

$$\theta(\text{CO}-\text{C}_\alpha-\text{NH}-\text{CO}) = 110^\circ,$$

the period along the chain is calculated as 5.14 Å. in agreement with the observed value 5.15 Å. and the N-H...O distance in the B

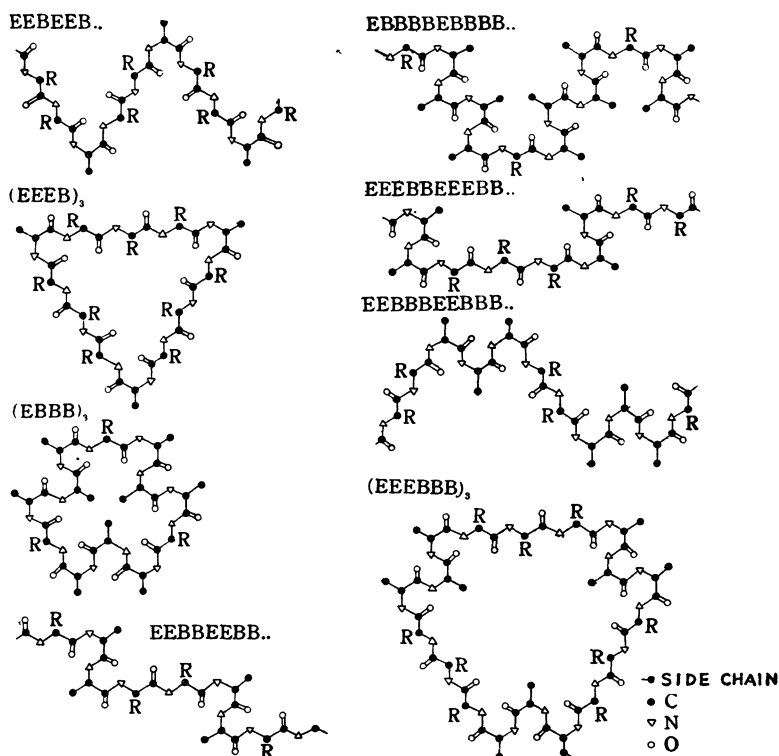


Fig. 1 b.—Various configurations of polypeptide chain.
(Side chains R perpendicular to the plane of the paper are not shown in the figures.)

In an actual case the bond angles and the bond lengths would be in some measure different from these ideal values and, moreover, the intramolecular rotational state would easily be changed to a certain extent under the influence of the neighboring molecules. If, for example, we assume the bond lengths and bond angles of polypeptide chain to have the values equal to those found for glycylglycine:⁽⁴⁾

$$\begin{array}{ll} \text{C}_\alpha-\text{N} = 1.48 \text{ \AA.} & \angle \text{C}-\text{C}_\alpha-\text{N} = 110^\circ \\ \text{N}-\text{C} = 1.29 \text{ \AA.} & \angle \text{C}_\alpha-\text{N}-\text{C} = 122^\circ \\ \text{C}-\text{C}_\alpha = 1.53 \text{ \AA.} & \angle \text{N}-\text{C}-\text{O} = 125^\circ \\ \text{C}-\text{O} = 1.23 \text{ \AA.} & \angle \text{N}-\text{C}-\text{C}_\alpha = 114^\circ \end{array}$$

form as 2.52 Å. which is also reasonable.

As stated in our previous paper and as pointed out by Astbury, the presence of a twofold screw axis seems at first sight to be inconsistent with the fact that the 5.1 Å. meridional reflexion found in α -keratin is strong and well defined.⁽⁵⁾ However, according to the experimental result obtained by Bamford, Hanby and Happey, a kind of synthesized polypeptides gives an α -keratin diagram in which the 5.28 Å. polar arc is weak and diffuse.⁽⁶⁾ In view of this fact it is not unreasonable to propose the BBB... configuration

(5) Astbury, *Nature*, **164**, 439 (1949).

(6) Bamford, Hanby and Happey, *Nature*, **164**, 138 (1949).

(4) Hughes and Moore, *J. Am. Chem. Soc.*, **71**, 2618 (1949).

as one of the possible structure of α -keratin

In the case of BBEBBE..... configuration of α -keratin the reflexion data can be explained more simply. If the mechanism of stretching of keratin fiber is explained in terms of the transformation of BBEBBE..... into EEE....., the amount of elongation is calculated as about 90%, while the side chain spacing remains unchanged. (See Fig.2.)

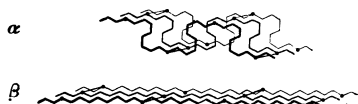
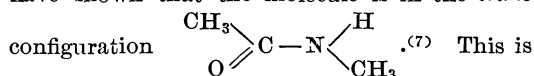


Fig. 2.—Natural α -keratin considered to be in BBEBBE..... configuration and the β -keratin in EEE..... configuration.

II. Experimental Evidence in Support of Our View

Since our previous paper⁽¹⁾ was published, the experimental evidence in support of our view has been accumulated in our laboratory as follows:

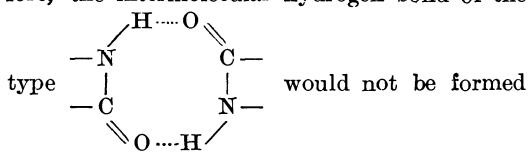
(1) Our experimental results of the Raman effect, infra-red absorption, ultra-violet absorption and dipole moment on N-methyl acetamide have shown that the molecule is in the *trans* configuration



(2) When involved in hydrogen bonding, N-methyl acetamide shows two absorption peaks at 3.0μ and at 3.2μ arising from the N-H vibration.^(7,8) N-ethyl acetamide and N-cyclohexyl acetamide, whose peptide bonds are shown to be in the *trans* configuration, also show two absorption peaks at the same wave lengths.⁽⁹⁾ On the other hand δ -valerolactam, ϵ -caprolactam, diketopiperazine, etc. whose peptide bonds are considered to be nearly in the *cis* configuration, show two absorption peaks at 3.1μ and at 3.2μ .⁽⁸⁾ This difference in wave length of the hydrogen-bonded N-H bands is attributable to the difference in the position of H-atom relative to other atoms and we can tell whether the peptide bond is in the *trans*

configuration or in the *cis* configuration according as the absorption peaks of the hydrogen-bonded N-H bands appear at 3.0μ and 3.2μ or at 3.1μ and 3.2μ .

Since in egg albumin, horse serum albumin, etc. measured in our laboratory⁽⁸⁾ and other proteins measured by Buswell *et al.*⁽¹⁰⁾ only the 3.0μ and 3.2μ absorption peaks are observed except in salmin which shows the 3.1μ peak arising from the side chain, the main chain of polypeptide can be considered to contain peptide bonds always in the *trans* configuration. Therefore, the intermolecular hydrogen bond of the



between two main chains of polypeptide.

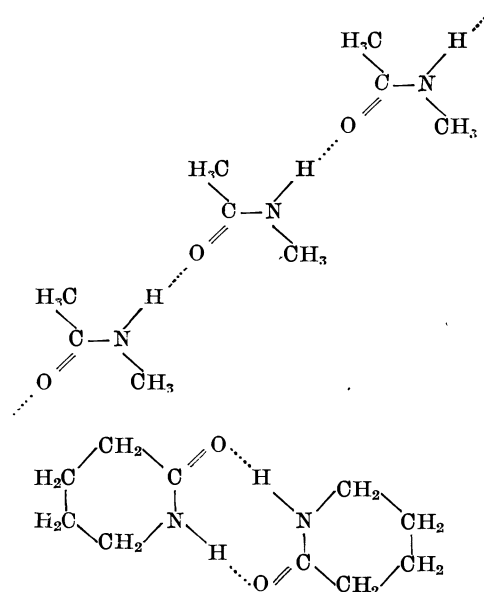


Fig. 3.—Configurations of associated molecules of N-methylacetamide and δ -valerolactam.

(3) It has been shown by our infra-red absorption measurement that all the compounds except the first two shown in Table 1 can take the B form,^(11,12) e.g. acetylglycine N-methylamide can have a configuration:

(7) Mizushima, Shimanouchi, Nagakura, Kuratani, Tsuboi, Baba and Fujioka, *J. Am. Chem. Soc.*, **72**, 3490 (1950).

(8) Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215 and 255 (1949).

(9) Buswell, Rodebush and Roy, *J. Am. Chem. Soc.*, **60**, 2444 (1938).

(10) Buswell, Krebs and Rodebush, *J. Phys. Chem.*, **44**, 1126 (1940).

(11) Mizushima, Shimanouchi, Tsuboi, Sugita and Kato, *Nature*, **164**, 918 (1949).

(12) Mizushima, Shimanouchi, Tsuboi, Sugita, Kato and Kondo, to be published shortly.

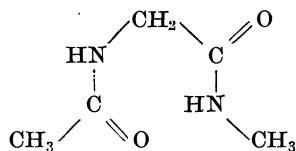
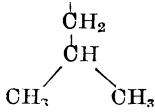
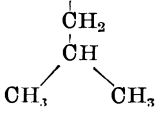


Table 1

Absorption Peaks Arising from N-H Vibrations

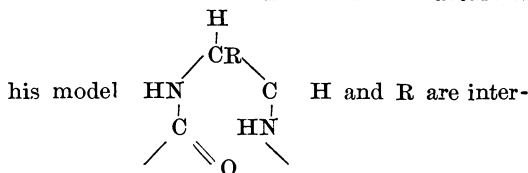
Compound	Absorption peaks arising from the vibration of N-H group	
	in the free state, μ	involved in intramolecular hydrogen bonding, μ
$\text{CH}_3\text{CONHC}_6\text{H}_5$	2.90	2.97 (intermolecular)
$\text{CH}_3\text{CONHCH}_3$	2.88	2.97 (intermolecular)
$\text{CH}_3\text{CONHCH}_2\text{CONHC}_6\text{H}_5$	2.90	3.00
$\text{CH}_3\text{CONHCH}_2\text{CONHCH}_3$	2.90	2.98
$\text{CH}_3\text{CONHCHCONHC}_6\text{H}_5$	2.90	3.00
		
$\text{CH}_3\text{CONHCHCHCONHCH}_3$	2.90	2.98
		

In very dilute solutions these substances show two absorption peaks as shown in Table 1, of which the 2.9μ peak can be assigned to the vibration of N-H group in the free state and the 3.0μ peak to that involved in the *intramolecular* hydrogen bonding. The soundness of the assignment of the 3.0μ peak to the *intramolecular* hydrogen bonding and not to the *intermolecular* hydrogen bonding can be seen from the fact that the intensity ratio of the 3.0μ to the 2.9μ band is independent of the concentration in dilute solutions of acetylglycine N-methyl amide while in solutions of acetanilide and N-methyl acetamide for which only the *intermolecular* hydrogen bonds are formed, the 3.0μ band becomes weaker with increasing dilution until it disappears practically. (See Table 1.) Thus there is no doubt that molecules of the substances shown in Table 1 can take the B form. This would also be an evidence for the existence of the B form for certain amino acid residues contained in the polypeptide chain.

III. Configurations Presented by Other Investigators

Let us next discuss on the molecular con-

figurations presented recently by other investigators. The configuration of α -keratin proposed by Huggins has six membered rings similar to that of our configuration BBB..., but it is different from ours with respect to the position of the side chain.⁽¹³⁾ In the unit structure of



changed when compared with our B form. According to the energy consideration of intramolecular rotation his model containing more *gauche* forms than ours would be less stable than ours. This would be seen, for example, from the molecular configuration of monochlorocyclohexane recently determined by Kojima.⁽¹⁴⁾ Of the two conceivable configurations (equatorial and polar) of this molecule only the former has been observed in the Raman effect. This stable equatorial form corresponds in the present case to our B form and the unobserved polar form containing more *gauche* configurations than the equatorial corresponds to that presented by Huggins. The shape of pyranose rings determined by Reeves would provide us with another evidence in support of this view.⁽¹⁵⁾

Based on the measurement with polarized infra-red radiation Ambrose *et al.* proposed independently a molecular model of α -keratin identical with our model BBB....⁽³⁾ This would be another evidence in support of our view. However, their experimental result can also be explained with our model BBEBBE.... More detailed discussion on the observed dichroic ratio and the real molecular configuration stated in section I would be desirable.

Darmond and Sutherland measured the N-H frequencies of compounds containing peptide bonds, but arrived at a conclusion different from ours.⁽¹⁶⁾ They consider that the $3.0\sim 3.1\mu$ band arises from a configuration different from that to which they assigned the 3.2μ band. According to our measurement, however, both of the 3.0μ (or 3.1μ) and the 3.2μ bands arise from a single configuration in the case of N-methyl acetamide, acetanilide, and diketopiperazine in the solid state and δ -valerolactam and ϵ -caprolactam in solutions.^(7,8) (The proof for the single configuration for these substances is given by the X-ray diffraction, Raman effect,

(13) Huggins, *Chem. Rev.*, **32**, 195 (1943).

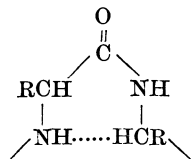
(14) Kojima, Private Communication.

(15) Reeves, *J. Am. Chem. Soc.*, **72**, 1499 (1950).

(16) Darmond and Sutherland, *Nature*, **164**, 440 (1949).

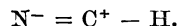
infra-red absorption and dielectric measurement). For the dimer of carboxylic acids it is also known that more than one O—H vibration arise from a single configuration.⁽¹⁷⁾ Therefore, the appearance of more than one N—H stretching frequencies cannot be a proof for the existence of more than one type of hydrogen bond. Thus the objection of Darmond and Sutherland to the structure of α -keratin proposed by us and by Ambrose *et al.* cannot be approved by our infra-red measurement.

Quite recently Kanda has presented another configuration of α -keratin, the unit structure of which has the following form:⁽¹⁸⁾



His discussion is based on the consideration of interatomic distances, but not of the energy relation of the intramolecular rotation. According to the latter point of view, such a configuration is not acceptable and moreover, the hydrogen bond $\text{CH}\cdots\text{N}$ contained in his configuration is supported by no experimental evidence. In the case of $\text{N}\equiv\text{C}-\text{H}$ there is

evidently a hydrogen bond of the type $\text{N}\equiv\text{CH}\cdots\text{N}$ as pointed out by Kanda, but this is due to the abnormal property of the CH group of $\text{N}\equiv\text{C}-\text{H}$ given rise to by the resonance with a structure



On the contrary CH groups contained in the main chain of polypeptide $-\text{CO}-\text{CHR}-\text{NH}-$ have normal property and the nitrogen atoms next to carbon atoms have rather acidic property. Therefore, a resonance structure such as $>\text{C}^+-\text{H}$ cannot be considered and the nitrogen atoms are not qualified to be a proton acceptor. It has never been reported that the hydrogen bond of the type $\text{C}-\text{H}\cdots\text{N}$ is formed between such a CH group and a nitrogen atom.

Kanda's objection to our configuration of α -keratin is based on the consideration of the interatomic distances for the ideal model shown in Fig. 1. However, as stated in Section I, a reasonable change of bond distances, bond angles and intramolecular rotational states from the ideal values reconciles our configuration with the experimental data.

In conclusion we wish to thank Drs. N. Tanaka and K. Kuratani for their discussions. This work was aided by a grant from the Ministry of Education.

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the University of Tokyo, Tokyo*

(17) Buswell, Rodebush and Roy, *J. Am. Chem. Soc.*, **60**, 2239 (1938); Wall and Claussen, *J. Am. Chem. Soc.*, **61**, 2812 (1939).

(18) Kanda, *Report of the Annual Meeting of the Chemical Society of Japan*, (1950).

On the Retardation of Catalysis. The Catalytic Reaction between Acetylene and Hydrogen

By Kenzi TAMARU

(Received June 20, 1950)

Introduction

Generally speaking, when acetylene and hydrogen react on a hydrogenating catalyst, there occur three kinds of reaction simultaneously, that is, hydrogenation of acetylene to ethylene and, further, to ethane, and hydrogenation-polymerization of acetylene.

In the case of palladium-alumina (1:100)

catalyst, as shown in the preceding paper,⁽¹⁾ the hydrogenation of acetylene proceeds in two distinct steps at room temperature. The first step consists of the reduction and polymerization of acetylene and the second step the reduction of ethylene to ethane. The second

(1) K. Tamaru, *Bull. Chem. Soc., Japan*, **23**, 64 (1950).

reaction starts when all acetylene has been consumed, accompanying a sudden increase in the rate of hydrogenation. This phenomenon shows that acetylene is so strongly adsorbed on the surface of the catalyst that ethylene is not to be reduced till all acetylene has been used up. Consequently, it was found that the final products of the hydrogenation can be wholly made to ethylene or ethane by taking the proper composition of the reactants at the beginning.

As polymers, the polymerization products of acetylene, retard the hydrogenation reaction, the rates of hydrogenation should be corrected for this retardation in the kinetical treatment. In this study, experiments were carried out on the retardation of both steps of the hydrogenation by polymers as well as by some salts. And some considerations were given for the property of the "active region" on the catalyst surface.

Experimental

Hydrogenation of acetylene on the palladium-alumina (1:100) catalyst was investigated by the static method. The preparation of the catalyst and the experimental procedure were the same as those in the preceding paper.⁽¹⁾

The initial hydrogenation velocity of the first step was strictly proportional to the amount of the catalyst, but as the reaction proceeded the polymers that deposited on the surface of the catalyst retarded the reaction with degrees varying according to the amount of the catalyst and thus no proportionality was seen between the amount of the catalyst and the reaction rate. From the same reason the second step of the reaction had also no proportionality between them.

Thus, being able to calculate the amount of the deposited polymers from the gas analysis and the pressure decrease as shown in the previous paper,⁽¹⁾ the relation between the hydrogenation rate of ethylene (k_2) and the amount of the polymers were obtained by varying the amount of the catalyst or the composition of the reactant. This is shown in Fig. 1, where the amount of the

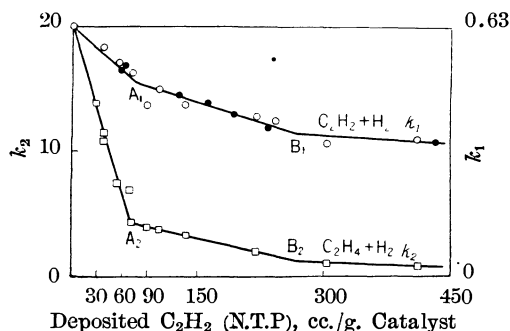


Fig. 1.—Retardation by deposited polymers at 30°C. (Catalyst: Pd-Alumina (1:100)).

deposited polymers were represented by the volume of acetylene in abscissa. The retardation curve of the first step (k_1) was obtained in the following ways. In the first method, k_1 was obtained from the reaction velocity at the last moment of the step, that is just before all acetylene had been used up, and the dependence of k_1 upon the amount of the deposited polymers was found. In the second method, the catalyst was used repeatedly and the progressive retardation caused by the accumulation of the polymers was observed in both steps. The results are shown in Fig. 2, where

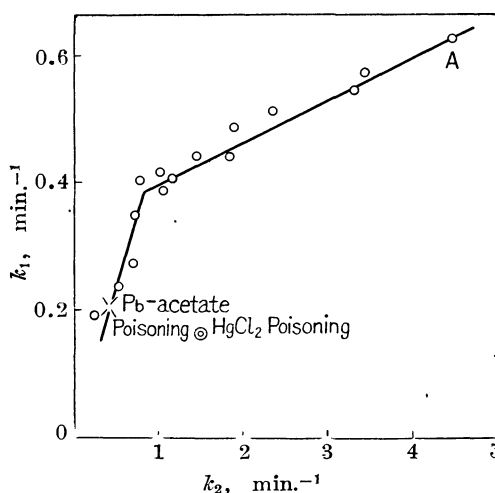


Fig. 2.—Progressive retardation by polymers and poisoning by salts.

k_1 in the ordinate was obtained from the initial velocity of the first step and k_2 in the abscissa was the velocity constant of the following second step calculated without any correction for the retardation of the polymers. Combining this with k_2 curve in Fig. 1, the dependence of k_1 upon the amount of the deposited polymers could also be obtained. Both results coincide with each other as shown in Fig. 1, where the results by the first method is represented by the white circles and the other by the black circles. The value of k_2 at no retardation was obtained from the reaction between ethylene and hydrogen.

It is shown in Fig. 1 that the retardation curves of k_1 and k_2 , as it were, consist of three linear parts up to 450 cc. of acetylene deposited per gram catalyst and the two reflection points are designated by A_1 , B_1 and A_2 , B_2 , respectively.

The hydrogenation rates were affected by washing the catalyst with solutions of some salts. The results of the poisonings by lead acetate and mercuric chloride solutions of which concentrations were 1.0% and 0.003%, respectively, were shown in Fig. 2, where the experimental conditions were the same as those used in the experiments of the progressive retardation mentioned above.

Consideration

Without correcting the retardation of the polymers the hydrogenation rate of acetylene was roughly expressed by the following equation as shown in the preceding paper,

$$-\frac{dP}{dt} = \frac{k_1 P_{H_2}}{1 + b P_{C_2H_2}} \quad (1)$$

where P denotes the pressure of the gas in mm.-Hg, t , time in minute, b and k_1 the constants. This equation was analogous to that given by Cremer and co-workers.⁽²⁾

But when we correct the retardation referring to Fig. 1, it was found that the net hydrogenation velocity of acetylene is to be expressed by the following empirical formula,

$$-\frac{dP}{dt} = \frac{k_1 P_{H_2}}{1 + b\sqrt{P_{C_2H_2}}} \quad (2)$$

instead of Eq. (1). The value of k_1 at 30°, as calculated from Eq. (2), is shown in Table 1, the mean value of which is 0.63, while b is 0.0774. It is seen that the hydrogenation velocity is independent on the pressure of ethylene. k_1 is also obtained to be 0.63 from Fig. 3, in which the hydrogenation velocity of acetylene and the pressure of hydrogen at the moment just before all acetylene has been used up are plotted.

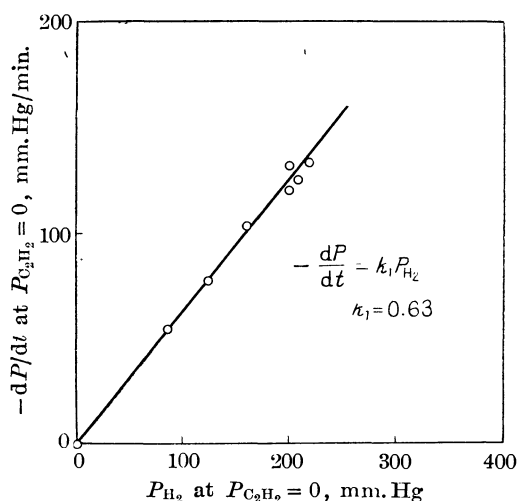


Fig. 3.—A relation between the reaction velocity and hydrogen pressure at the last moment of the acetylene hydrogenation.

(2) E. Cremer, C. A. Knorr and H. Plieniger, *Z. Elektrochem.*, **47**, 737 (1941).

All the deposited polymers are not necessarily to be considered to cover the surface of palladium, as they are also possibly adsorbed by the carrier. Consequently, the reflections of k_1 and k_2 curves in Fig. 1 may be attributed to the sudden change in the deposition of the polymers on the palladium surface, for example, when they saturate the palladium surface. It may also be attributed to another reason, for instance, to the discontinuous change in the fraction of the "active regions" on the catalyst surface by the preferential deposition of the polymers.

Table 1

Velocity Constant of the Hydrogenation of Acetylene at 30°C.

C ₂ H ₂ , mm. Hg	H ₂ , mm. Hg	Acetylene Content, %	k_1 , min. ⁻¹
78	404	16.2	0.60
66	193	25.4	0.67
120	350	25.5	0.63
182	332	35.4	0.64
70	124	36.3	0.68
104	189	35.6	0.61
187	288	39.4	0.59
235	250	48.5	0.65
263	207	55.9	0.69
270	167	61.8	0.68

But when we plot k_1 against the corresponding k_2 of equal retardation calculated from the velocity of the first step at the last moment of the step and the velocity constant of the following step, a reflection is observed at A, while not at B as shown in Fig. 4, where

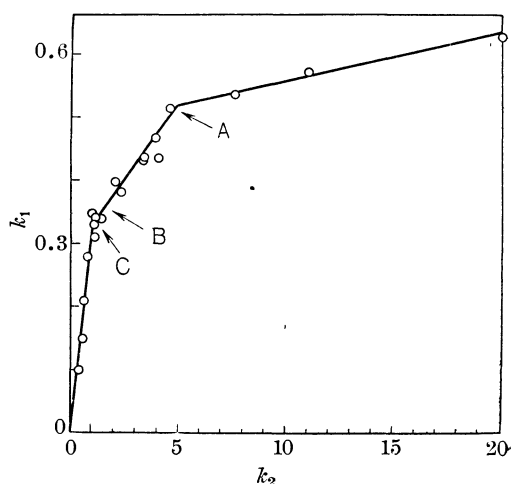


Fig. 4.— k_1 - k_2 relation at equal retardation.

A corresponds to A_1 and A_2 , and B to B_1 and B_2 in Fig. 1. Thus we shall see that the reflection at A_1 or A_2 in Fig. 1 is not caused by the discontinuous change in the deposition of the polymers on the surface of the palladium, but the discontinuous change in the fraction of the "active regions" on the catalyst surface itself. It is not the case, however, at B_1 or B_2 , as it shows no reflection in Fig. 4.

According to the statistical mechanical treatment on the heterogeneous reaction by J. Horiuti,⁽³⁾ the rate of the elementary reaction which proceeds in G equivalent seats of critical complex is given by the following equation,

$$\vec{k} = \kappa \frac{kT}{h} Gq\Theta_0\alpha_1$$

where Θ_0 is the probability that the critical complex is absent and α_1 is the activity of the initial complex of the elementary reaction and q is approximately equal to $e^{-\varepsilon/kT}$, where ε is the activation energy of the reaction.

In the present case κ , kT/h , G , α_1 , in the equation are assumed to be constant in each step, so that

$$\vec{k} = Ce^{-\varepsilon/kT}\Theta_0.$$

Now if we assume that the value of ε is constant and the rate-determining step of the reaction does not change throughout the retardation, the reaction rates are only dependent on Θ_0 and thus k_1 and k_2 are to be parallel.

In Fig. 4 three linear parts are observed and this may be associated with the three kinds of seat of critical complex or of "active region" on the catalyst surface. Accordingly, it seems to be possible to express from Fig. 4 that the ethane formation proceeds on the two kinds of the "active regions", while the hydrogenation of acetylene to ethylene on three kinds of them and that the first "active region" catalyzes the major part of the former, while only one fifth of the latter, and the third one about half of the latter and almost none of the former.

It is to be noted, however, that the preceding consideration is derived by the kinetical treatment of the reaction and, accordingly, is not necessarily associated with any physical meaning such as, for example, plane or edge of the catalyst.

The assumptions which are made for the preceding consideration may not all be available, especially when Θ_0 approaches to zero,

but it is likely to be considered to suggest that the two reactions of ethylene and ethane formation proceed on the various "active regions" with different ratios.

E. F. G. Herington⁽⁴⁾ suggested that acetylene and ethylene are adsorbed on the various planes of nickel or cobalt with different ratios and that acetylene should be held on the long spacing of 3.50 Å., whereas ethylene on the short spacing of 2.47 Å. In the present experiment it is shown that the "active region," on which acetylene is not adsorbed, whereas ethylene hydrogenation can occur, is not present, as the inhibition of the ethane formation by acetylene is pronounced.

When the catalyst was washed by the solution of lead acetate or mercuric chloride, both rates of the hydrogenation were retarded as shown in Fig. 2. It was found that the former solution retards the ethane formation much more than the ethylene formation. T. Yamanaka⁽⁵⁾ recently reported that palladium-kieselguhr catalyst treated by the lead acetate solution was good to apply to ethylene formation from acetylene by the flow method and this fact coincides with the result of the present experiment by the static method. As to the poisoning of mercuric chloride, k_1 and k_2 were approximately equally retarded. The results by the two salts suggest that the inorganic salts do not analogously poison the catalyst.

Summary

1) The retardation of hydrogenation of acetylene on the palladium-alumina (1:100) catalyst by the deposited polymers and some inorganic salts were investigated.

2) By correcting the retardation of the polymers, which deposited on the surface of the catalyst during the reaction, it was found that the net hydrogenation rate of acetylene was expressed by the following equation,

$$-\frac{dP}{dt} = \frac{k_1 P_{H_2}}{1 + b\sqrt{P_{C_2H_2}}}.$$

3) It was suggested that both catalytic hydrogenations of acetylene and ethylene proceeded on a few "active regions" of the catalyst with different ratios, and taking some assumptions, the rôle of the various "active regions" on the two hydrogenations was considered.

(4) E. F. G. Herington, *Trans. Farad. Soc.*, **37**, 361 (1941).

(5) T. Yamanaka, *J. Phys. Chem. Res. Inst., Tokyo*, **25**, 329, 481 (1949).

(3) J. Horiuti, *Bull. Chem. Soc. Japan*, **15**, 210 (1938).

4) It was shown that lead acetate solution poisoned the ethylene hydrogenation much more than the acetylene hydrogenation and this fact coincides with the result of the flow method.

The author expresses his sincere thanks to Prof. J. Sameshima for his kind guidance and encouragement throughout this work and to

Dr. T. Kwan of Hokkaido University for his valuable suggestion.

The expense for the experiments has been defrayed from the Scientific Research Expenditure of the Department of Education.

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Dispersity of Catalyst and Catalytic Activity. Catalytic Hydrogenation of Acetylene on the Pd-Kieselguhr Catalyst

Kenzi TAMARU

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Introduction

In general by the term "carrier" is meant an inert material which acts as a support for the catalyst.⁽¹⁾ A carrier may be used because it provides a larger contact surface and, at the same time, a more equal distribution of the catalyst. By preventing recrystallization, or baking together, it preserves a fine dispersion of the catalyst and hinders aggregation which otherwise would occur. A carrier may influence indirectly the activity of a catalyst by protecting it from poisons. Thus, many functions of a carrier are thought to vary with individual cases. But among these functions the case that a carrier may influence the properties of the catalyst proper is of interest.

Adadurov⁽²⁾ suggested that a carrier is not at all an indifferent support for a catalyst, but that it produces a deforming action upon the atoms or molecules of the catalyst, changing their catalytic properties.

K. Yoshikawa⁽³⁾ found that when acetylene is hydrogenated on a Pd-kieselguhr catalyst by the flow method, the yield of ethylene was much affected by the dispersity of palladium on the carrier, and that the catalyst with 500 ~ 1500 parts of kieselguhr being added to one part of palladium was well employed to get

ethylene from acetylene. This markedly selective action of the catalysts produced by varying the dispersity of the catalytic agent on an inert substance, can not be explained from the standpoint of the problem of the surface area of the catalyst.

To explain this fact, Yoshikawa assumed the co-activation of neighbouring active centers on the catalyst surface by the heat of the reaction. He thought that the heat produced by the reaction on one active center activates the neighbouring hitherto inactive center, and the newly activated center excites in the same manner the next center as well as the original active point by further reaction and thus the proportion of stimulated active points increases and the reaction is correspondingly accelerated. If the dispersity of the catalytic agent is sufficiently large, the distance between the neighbouring active points may be long enough to disable the efficient co-activation, so that the catalytic centers can not display their full activities. There may be cases where the hydrogenation of acetylene to ethylene is possible but the hydrogenation to ethane is impossible.

Recently T. Yamanaka⁽⁴⁾ and T. Takeshima,⁽⁵⁾ having investigated the reaction on the Pd-kieselguhr catalyst by the flow method, discussed the mechanism the reaction on the basis of the modified coactivation theory.

The present author⁽⁶⁾ previously investigated

(1) S. Bergman, J. C. Morrell and G. Egloff, "Catalysis" P. 426, New York (1940).

(2) Adadurov, *Zhur. Fiz. Khim.*, **3**, 489, 496 (1932); **6**, 206 (1935); *Zhur. Khim. Prom.*, **6**, 805 (1928).

(3) K. Yoshikawa, *Bull. Chem. Soc., Japan.*, **7**, 201 (1932).

(4) T. Yamanaka, *Sci. Rep. Sci. Res. Inst., Tokyo*, **25**, 329, 481 (1949).

(5) T. Takeshima, *ibid.*, **24**, 199, 303 (1948).

(6) K. Tamaru, this Bulletin, **23**, 28 (1950).

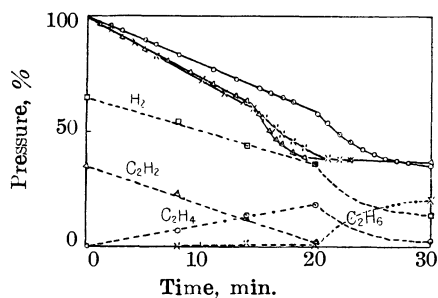
the hydrogenation of acetylene on Pd-alumina catalyst by the static method and found that the hydrogenation of acetylene proceeds in two distinct steps at room temperature. The first step consists of the reduction and polymerization of acetylene and the second step the reduction of ethylene to ethane. The second reaction starts after all acetylene is used up, accompanying a sudden increase in the rate of hydrogenation, and this fact was explained by the strong adsorption of acetylene on the surface of the catalyst proper.

In this study experiments were carried out on the Pd-kieselguhr catalyst of various dispersities and the rôle of the carrier or the problem of the dispersity of the catalyst was considered.

Experimental

As in the previous experiments,^(6,7) Pd-kieselguhr catalyst was prepared from palladium chloride solution, into which kieselguhr⁽⁶⁾ was added, by reduction to metal with formaldehyde. The dispersity of palladium on the kieselguhr was determined by the ratio of palladium to the carrier.

The experiments were carried out by the static method and their procedure was the same as that in the preceding papers.



—×—×—: Pd-Kieselguhr (1 : 750) Catalyst (0.600 g.) C_2H_2 , 153 mm.Hg; H_2 , 295 mm.Hg.
—○—○—: Pd-Kieselguhr (1 : 250) Catalyst (0.192 g.) C_2H_2 , 155 mm.Hg; H_2 , 288 mm.Hg.
—△—△—: Pd-Kieselguhr (1 : 100) Catalyst (0.098 g.) C_2H_2 , 148 mm.Hg; H_2 , 285 mm.Hg.

Fig. 1.—The experiments were carried out at 30° and the composition change of the reactant in the second experiment is shown by the broken lines.

The results of the experiments with the catalysts of various dispersities at 30° are shown in Fig. 1. The second step of the hydrogenation is retarded by the polymers deposited on the catal-

yst surface as discussed in the preceding paper⁽⁷⁾ and, consequently, the velocity of the ethylene hydrogenation was obtained separately from the reaction between ethylene and hydrogen, the results of which are shown in Fig. 2, where the velocity constants are taken to the ordinate and the ratio of palladium to kieselguhr to the abscissa.

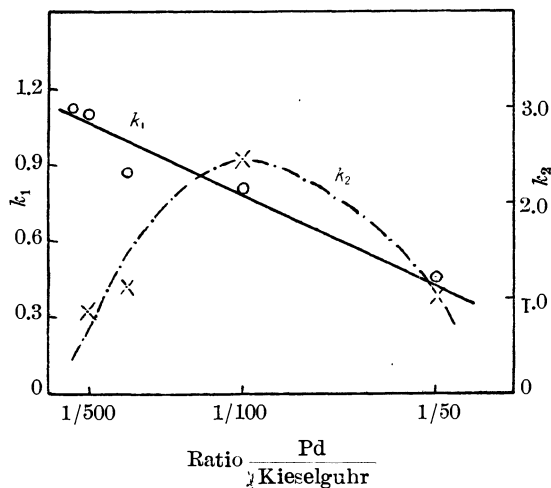


Fig. 2.—The relation between the catalytic activity (velocity constant) and the dispersity¹ of catalyst in the two hydrogenation reactions (k_1 is the velocity constant in acetylene hydrogenation and k_2 in ethylene hydrogenation.)

It is shown in Fig. 2 that the second step of the hydrogenation or ethylene hydrogenation to ethane becomes slower relative to the hydrogenation rate of acetylene when the dispersity gets larger. This tendency is also observed in Fig. 1, in which no correction was made for the retardation of polymers.

As the reaction temperature was raised, the second step became slower as compared to the first step, because the activation energy of the former was smaller than that of the latter, and the catalyst becoming less, the amount of the polymers deposited on the unit area of the catalyst surface was increased, thus retarding the former more extensively than the latter as shown in the preceding paper.⁽⁷⁾

The results of the experiments at various temperatures by Pd-kieselguhr (1 : 750) catalyst are shown in Fig. 3, along with the change of the composition of the reacting gas. It is seen that the second step becomes slower than the first step at the transition of the first and the second steps in the experiment at 74.0°.

The reaction rates of the two steps at various temperatures were expressed by the Arrhenius' equation, respectively, and the activation energy of the reaction was 10 and 8 kcal. in the first and the second steps, respectively.

(7) K. Tamaru, *ibid.* **23**, 180 (1950)

(8) For this sample commercial kieselguhr was purified by boiling with hydrochloric acid.

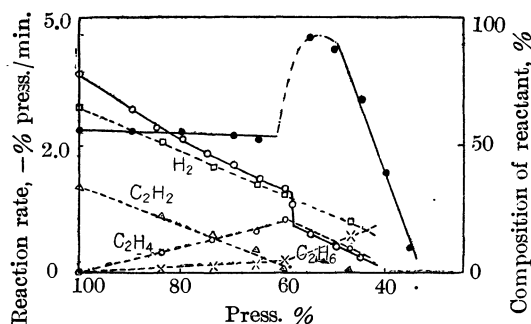


Fig. 3.—Reaction rates in the course of the hydrogenation of acetylene by Pd-Kieselguhr (1:750) catalyst at 30° and 74°. (The former is shown by the curve —●—●—, and the latter by the curve —○—○—, and the composition change of the reactant in the latter case is given by the broken lines.)

Consideration

It had been found,⁽³⁾ as mentioned previously, that acetylene is selectively hydrogenated by Pd-kieselguhr catalyst of larger dispersities by the flow method. This fact was explained by the assumption of co-activation of the neighbouring active centers on the catalyst surface, and it was assumed in this case that the active centers, not displaying their full activities, proceed the hydrogenation of acetylene to ethylene, but not of ethylene to ethane.

But present experiments showed all the catalysts of various dispersities to catalyze the hydrogenation of ethylene as well as acetylene and that in two distinct steps quite similarly with the Pd-alumina catalyst.

We see in Fig. 2 that the hydrogenation rate of the first step increases when the dispersity grows larger and that the ratio of k_1 to k_2 differs according to the dispersity of the catalyst.

If the carrier provides only a larger effective surface of the catalyst proper, the ratio should not differ by the dispersity, though the velocity constants of k_1 and k_2 may increase with the dispersity. This fact suggests that the dispersity contributes to the property, as well as to the area, of the catalyst surface.

In the preceding paper⁽⁷⁾ it was suggested that the hydrogenations of acetylene and ethylene proceed on the various "active regions" with different ratios. Hence, the difference of dispersity is considered to have connection with the appearance of various "active regions" with different ratios, as the ratio of the two hydrogenation rates are differed by the dispersity.

For the practical purpose to obtain ethylene from acetylene by the flow method it was suggested in Fig. 1 and Fig. 2 that the catalysts of larger dispersities are good to apply, as the rate of ethane formation is slow relative to that of ethylene formation. This is supported by the above-mentioned results of Yoshikawa by the flow method.

The reaction rate of the second step became slower than that of the first step at the transition of the two steps as shown in Fig. 3. This inversion temperature was not characteristic to the catalyst proper itself, but was dependent on the dispersity of the catalyst.

The fact that the hydrogenations of acetylene and ethylene proceeded independently, obeying the Arrhenius' equation, and that the two reaction rates at the transition of the two steps inverted each other show that the adsorption of hydrogen on the catalyst surface or the supply of the reacting hydrogen is not rate-determining in the hydrogenation of ethylene, provided that the state of the reacting hydrogen is the same in both hydrogenations.

Summary

1) Hydrogenation of acetylene on the Pd-kieselguhr catalyst of various dispersities was investigated.

2) It was shown that the hydrogenation of acetylene proceeded not only to ethylene, but also to ethane by all the catalysts of various dispersities, and that in two distinct steps quite similarly with the Pd-alumina (1:100) catalyst.

3) The ratio of the hydrogenation rate of acetylene to that of ethylene was affected by the dispersity, suggesting the appearance of the various "active regions" of the catalyst surface to be connected with the dispersity. It was large for the catalyst of larger dispersities and this fact explains the results previously obtained by the flow method.

4) Some considerations were given to the rate-determining step in the hydrogenation of ethylene.

The author expresses his sincere thanks to Prof. J. Sameshima and Dr. H. Akamatsu for their kind guidance and encouragement throughout this work. The expense for the experiments has been defrayed from the Scientific Research Expenditure of the Department of Education.

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Application of Cation Exchange Resin to the Determination of Phosphorus in Foods

By Shohji KUBO and Chuichi TSUTSUMI

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Cation exchange resin was first used by Herlich and Rieman⁽¹⁾ for the determination of phosphorus in phosphate rocks. They converted the hydrochloric acid solution of phosphate into a mixture of hydrochloric acid and phosphoric acid by cation exchange and titrated directly with 0.1 *N* alkali using comparison buffers. Dijkman⁽²⁾ referred briefly to this method, and by the present authors the principle has been applied to the volumetric determination of phosphorus in foods⁽³⁾ and the gravimetric adaptation of the exchange technique has been investigated.⁽⁴⁾ However, it was found later that the volumetric method sometimes results in high values and that this was caused by the interference of carbonate in the concentrated alkali added before the titration. To avoid this difficulty in the present investigation the applicability of sodium regenerated cation exchange resin was examined as a substitute for the previously used hydrogen regenerated type and the following method is now recommended for the determination of phosphorus in foodstuffs.

Reagents

Hydrochloric acid; 20%.

Standard sodium hydroxide solution; 0.05 *N*; carbonate free.

Sodium chloride solution; 5%.

Methyl red indicator; 0.1% alcoholic solution.

Phenolphthalein-thymol blue indicator; to 1 part of 0.1% solution of thymol blue in 50% alcohol add 3 parts of 0.1% alcoholic solution of phenolphthalein.

Acetate buffer, *pH* 4.63; mix 17 ml. of 1.3 moles sodium acetate, 25 ml. of 1.0 mole acetic acid and 360 ml. of water. To 50 ml. of this solution add 3 drops of methyl red.

Borate buffer, *pH* 8.98; mix 130 ml. of 0.1 mole borax, 40 ml. of 0.1 mole hydrochloric acid and 280 ml. of water. To 60 ml. of this solution add

3 drops of methyl red and 6 drops of the phenolphthalein-thymol blue indicator. Each buffer solution should be contained in an Erlenmeyer flask similar in size and color to the one used in the titration.

Preparation of Exchange Column

Cation exchange resin; 100 to 200 mesh phenol-methylenesulfonic resin. Amberlite IR-100 or similar resins may be used. A resin synthesized in our laboratory was used in the present studies. Its total static exchange capacity was 2.28 milliequivalents per gram.

Six grams of the resin were suspended in the water and poured into an ordinary 25 ml. stopcock burette, the bottom of which had been plugged with absorbent cotton. Before each determination the exchanger was regenerated by pouring 100 ml. of sodium chloride solution through the column followed by 60 ml. of water in 3 portions. The rate of flow was adjusted by means of the stopcock to about 1 ml. per minute.

Hitherto, when using the exchange column, it was necessary to maintain the level of the solution several centimeters above that of the resin to prevent the formation of air bubbles between resin particles with the subsequent blocking of the column. However, in the case when the particle size is reduced to less than 100 mesh, the flowage stops automatically with the stopcock open when the solution reaches the bed level. The pressure drop caused by the small particle size did not obstruct the procedure, the maximum rate of flow being 3 ml. per minute under the experimental conditions. It is therefore necessary to regulate the rate of flow only once and thus the analyst is released from the continuous attention. For these reasons, the particle size of resin was reduced to 100-200 mesh. This made possible the simultaneous treatment of an increased number of samples without applying additional skill or the use of special apparatus.

Procedure

Weigh 5 g. of sample (or less in the case of phosphate-rich materials such as rice bran) into a porcelain crucible or a small Pyrex beaker and ash at 550 to 600°. Dissolve the ash in hydrochloric acid and evaporate to dryness on a water bath. Add 0.5 ml. of 20% hydrochloric acid and ca. 5 ml. of water, heat on a water bath, filter,

(1) K. Herlich and W. Rieman, *Anal. Chem.*, **19**, 651 (1947).

(2) J. C. W. Dijkman, *Rec. trav. chim.*, **68**, 57 (1949).

(3) S. Kubo and C. Tsutsumi, *Report of the Food Research Institute (Tokyo)*, **3**, 72 (1950).

(4) *ibid.*, **3**, 83 (1950).

and wash with a small amount of water. Pass the filtrate and washings through the column at the rate of about 1 ml. per minute, collecting the filtrate in a 100 ml. Erlenmeyer flask. Wash with 25 ml. of water in 3 portions at the same rate and collect the washings in the same flask. The total volume will be about 50 ml. Add 3 drops of methyl red solution and adjust to pH 4.63 with 0.05 *N* sodium hydroxide solution using the acetate buffer. Usually less than 5 drops of the alkali will suffice for this purpose. Then add 6 drops of phenolphthalein-thymol blue indicator and titrate to pH 8.98 with 0.05 *N* alkali using the borate buffer. The titration is most preferably done under the light of a fluorescent lamp.

The phosphorus content of the sample is calculated from the volume of standard alkali required for the titration.

Experiments and Discussion

As would be expected from the exchange equilibrium of the resin, any hydrochloric acid solution of phosphates, after passing through an adequate amount of sodium type resin, shows an almost constant pH regardless of the amount of free hydrochloric acid present, providing that it lies within a certain concentration range. In these experiments some salts were added to standard potassium acid phosphate solutions, and to these were added 1, 3, 5 and 10 ml. of *N*-hydrochloric acid respectively. After passage through a 5 g. column of sodium type resin, the solutions were made up to the volume, pH were measured, and the phosphoric acid contents determined by titration. The results are given in Table 1.

Table 1

	pH and Phosphoric Acid in the Effluents							
	<i>N</i> -HCl added, ml.							
	1		3		5		10	
	pH	P ^(a)	pH	P	pH	P	pH	P
KH ₂ PO ₄	4.9	4.13	4.7	—	3.9	—	—	—
" and Soln. A ^(b)	4.0	4.13	4.0	4.10	3.8	4.10	1.3	4.11
" and soln. B ^(c)	3.9	3.92	3.9	4.00	3.1	4.08	1.2	4.18

(a) ml. of 0.05 *N*-NaOH required for the titration. Theoretically expected value is 4.10.

(b) Solution A contains 10 mg. Ca and 6mg. Mg as calcium chloride and magnesium sulfate respectively.

(c) Solution B contains 12 mg. Mg, 9 mg. Fe^{III} and 5 mg. Al as magnesium sulfate, iron alum and potassium alum respectively.

It is seen that when the amount of added hydrochloric acid is limited, the pH of the effluent always approximates to 4.0, and that

the addition of only a few drops of 0.05 *N* alkali is necessary to adjust the pH 4.63. By eliminating the need for neutralization with concentrated alkali, as is required when the H-resin is employed, the method is simplified and carbonate interference is eliminated.

However, it is seen in Table 1 that when solution B is added, and at the same time, smaller amounts of hydrochloric acid are employed, the recovery of phosphorus is low even though cation exchange is complete. It is considered that the exchanged Fe^{III} or Al^{III} ion tends to adsorb some phosphoric acid, especially when the pH of the original solution is relatively high. The effects of the presence of ferric and ferrous iron and aluminum were studied, and from the results shown in Table 2, it is concluded that when smaller amounts of hydrochloric acid are used, only larger amounts of ferric iron will interfere with the accurate determination of phosphorus. Ferrous iron and aluminum showed no such tendency under the experimental conditions. However, in ordinary foodstuffs the contents of iron are not high enough to cause any difficulties. This can be said especially for cereals, beans, meat etc. where the iron levels are about the one hundredth that of phosphorus. Therefore, in practice, the interference of ferric iron can be

Table 2

Effects of Iron and Aluminum

(The figures represent the ml. of 0.05 *N*-NaOH required for titration. P present in each aliquot is 14.28 mg.)

	Fe or Al added, mg.	<i>N</i> -HCl added, ml.			
		0	1	3	5
KH ₂ PO ₄	—	8.21	8.20	8.25	8.23
KH ₂ PO ₄ and Fe ^{II}	1		8.22	8.25	8.23
(Mohr's salt)	3		8.21	8.23	8.25
	5		8.25	8.24	8.29
KH ₂ PO ₄ and Fe ^{III}	1		8.24	8.25	8.26
(iron alum)	3		7.99	8.17	8.22
	5		7.71	8.04	8.19
KH ₂ PO ₄ and Al	1		8.24	8.23	8.22
(potassium alum)	3		8.23	8.21	8.24

Table 3

Control Analysis

(The figures represent the ml. of 0.05 *N* NaOH required for titration.)

Sample	P added	<i>N</i> -HCl added, ml.			
		0	1	3	5
		P found			
Rice bran	8.10	8.07	8.12	8.10	8.14
Soybean	7.82	7.80	7.80	7.80	7.85

considered negligible, and this fact was confirmed by the following control analysis on soybean and rice bran.

A new method was adapted for the control analysis to prepare the sample solution. The sample (rice bran and soybean) was ashed, dissolved in hydrochloric acid, evaporated to dryness, redissolved, heated with dilute hydrochloric acid on a water-bath, and filtered to remove insoluble silica and carbon. The solution was passed through an enough amount of hydrogen regenerated cation exchanger to exchange all the cations in the solution. The resin was washed thoroughly with distilled water and then the adsorbed cations were effluated with 4% hydrochloric acid. The effluent was mixed with a known amount of phosphoric acid (nearly equivalent to the quantity in the original sample), evaporated to dryness, and redissolved in distilled water to a definite volume. By this means we obtained solutions which had the same mineral composition as the ash of the sample, their phosphorus contents being known.

Aliquots were taken and analysed by the above procedure and the values found were compared with the added amounts of phosphorus. As shown in Table 3, very satisfactory results were obtained on both rice bran and soybean.

From the above experiments and considerations, substitution of the sodium type exchanger for the hydrogen type is recommended, since it results in a more simplified and accurate method of determination.

The pH values used for the end points in

the procedure were taken from the potentiometric titration data of Herlich and Rieman.⁽¹⁾ The phenolphthalein used by them was replaced by phenolphthalein-thymol blue indicator because of its greater sensitivity. By this means even the color change resulting from the addition of half a drop of 0.05 *N* alkali can be detected in the ordinary Erlenmeyer flask.

Summary

A new volumetric determination of phosphorus in foods using a sodium type cation exchange resin was devised and critically investigated. The substitution of sodium for the hydrogen type exchanger eliminated errors resulting from the introduction of carbonate present in concentrated alkali. Moreover, the reduction of the resin particle size resulted in simplification of the procedure and reduced the skill necessary for its execution.

This method is accurate and applicable to the determination of phosphorus in ordinary food-stuffs, except when the sample contains unusually large amount of ferric iron. In such cases, the hydrogen type exchanger method⁽³⁾ must be employed.

The authors give their sincere thanks to Taro Nagahara for his kind guidance throughout the course of this study and to Dr. G. J. Mannering for his suggestions about the interferences of iron and aluminum.

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On Some Applications of the Nakamura-Kuroda Theory of the Sedimentation of Colloid in a Vessel having Inclined Walls

By TOMINOSUKE KATSURAI

(Received August 9, 1950)

The increase of sedimentation velocity of a colloid in an inclined test tube was first reported by Boycott.⁽¹⁾ This curious phenomenon drew attention of many workers, and gave rise to the publication of many papers containing tentative theories to explain the pheno-

menon. Among these works the joint work of Nakamura and Kuroda might be considered as representative.⁽²⁾ They made it clear that the inclined wall lying above the colloid (Fig. 1a) gives rise to the increase of

(1) A. E. Boycott, *Nature*, **104**, 532 (1920).

(2) H. Nakamura and K. Kuroda, *Keijo J. Med.*, **8**, 256 (1937). [Keijo = Seoul, Korea].

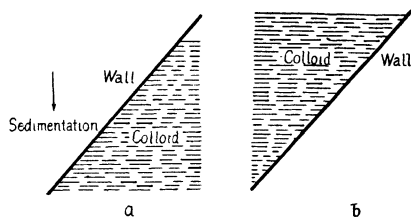


Fig. 1.

sedimentation velocity, while the wall situated below the colloid (Fig. 1 b) does not. From a very simplified assumption taking this fact into consideration, they gave a theory, though phenomenological in nature, which agrees with experiments quite well. Lately Kinoshita examined the applicability of the Nakamura-Kuroda theory (abbreviated as N-K theory hereafter) in the settling of smokes and found that the theory holds as a whole.⁽³⁾ In this paper, some results obtained by extending the fields of application of the N-K theory are given.

Sedimentation of Colloid in a Tube consisting of Two Parts having Different Sectional Area

A simple illustration of the N-K theory can be found in the sedimentation of colloid in a vessel consisting of two cylinders having different radii (Fig. 2). We know that the essential point of the N-K theory is expressed as follows.

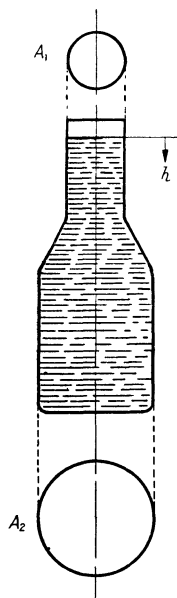


Fig. 2.

$$h \times \text{upper boundary area of suspended phase} \\ = s \times \text{horizontal projection of the upper boundaries of the suspension,} \quad (1)$$

where h = sedimentation velocity of colloid in a vessel having inclined walls,
 s = sedimentation velocity of colloid determined in a vertical cylinder of uniform section.⁽⁴⁾

Applying the relation (1) in this case, we have

$$hA_1 = sA_2 \\ \text{or} \quad h = s \frac{A_2}{A_1}, \quad (2)$$

where A_1 and A_2 are the sectional areas of the upper and lower cylinders. This relation shows that the initial sedimentation velocity of a colloid increases in a vessel having the form of Fig. 2, and that the amount of increase is determined by the ratio of the sectional areas of the lower and upper parts.⁽⁵⁾

Flotation of Emulsion in a Vessel under the Action of Oblique Centrifugal Force. Note on the Design of de Laval Centrifuge

It seems of interest to apply the N-K theory in a problem of centrifugal field. As an example, a problem of the design of de Laval centrifuge, which is usually used as cream separator, has been chosen. As is well known, the diagrammatic sketch of the de Laval centrifuge is given in Fig. 3. Milk is kept in the spaces

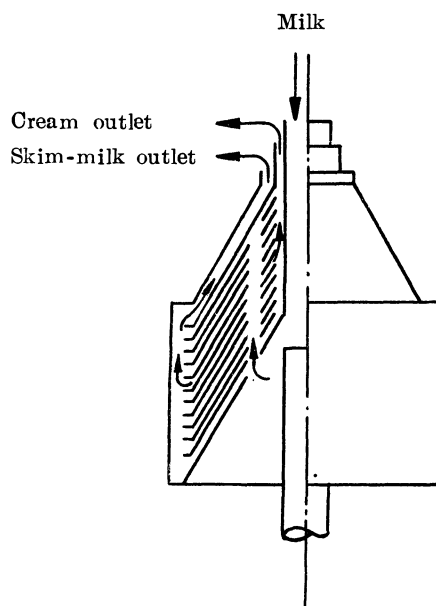


Fig. 3.

confined between two consecutive cones and is subjected to centrifugal force acting obliquely to the walls. In the actual case, the ratio between the slant height of cone and the

(3) K. Kinoshita, *J. Colloid Sci.*, **4**, 525 (1949).

(4) cf. (3) p. 526 below.

(5) A test carried out by Mr. T. Matuhasi, using suspension of blood corpuscle in physiological saline solution, showed that this relation actually holds.

distance between cones is about 120 and the inclination (the angle between the direction of centrifugal force and the slant height) is about 45° . A cursory glance at literature fails to find any study stating how these values were chosen. We shall examine whether the N-K theory is of use in interpreting these values.

In order to apply the N-K theory we neglect the flow of milk and observe only the flotation of fat particles which takes place under the action of centrifugal force. We assume that milk is an emulsion which is characterized by a flotation constant s_0 and confine our attention to the behavior of the milk contained in the space $ABA'D'CD$ between the two cones ABA' and DCD' (Fig. 4). s_0 is a constant

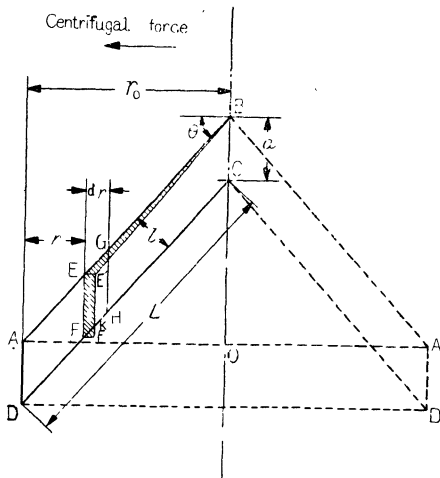


Fig. 4.

such that its product with centrifugal force gives the velocity of flotation. The conception of s_0 herewith is entirely in line with that of the sedimentation constant in ultracentrifuging.

Let us consider the milk in the parallelogram $ABCD$. The point A is taken as the origin of coordinate, and the distance from A toward the axis of rotation is taken as positive r . We denote the inclination by θ , and the angular velocity by ω . At first $ABCD$ is uniformly filled with milk. With the elapse of time, flotation takes place and the boundary between skim-milk and cream moves toward the axis of rotation. We denote the boundary at the time t by EF , the distance of EF from the bottom AD by r , and the position of EF after the time interval dt by $E'F'$. From the definition of s_0 , the distance EE' is given by $s_0 \omega^2 (r_0 - r) dt$. The particles along EB should also move toward the axis of rotation with the elapse of time. From the fact that centrifugal force is proportional to the distance from

the axis of rotation, the particles situated along EB should be found along $E'B$ after the elapse of time dt . Thus the boundary after the time interval dt should be given by the line $F'E'B$. The small triangular area $FF'K$ is neglected in the calculation. However, the actual boundary should remain always parallel to the axis of rotation. Following the principle of leveling action of the N-K theory, the position of the actual boundary GH is determined by the relation

$$\begin{aligned} 2\pi (r_0 - r) a dr &= 2\pi (r_0 - r) a s_0 \omega^2 (r_0 - r) dt \\ &+ \left[\frac{1}{3} \pi (r_0 - r)^2 (r_0 - r) \tan \theta - \frac{1}{3} \pi \left\{ r_0 - r \right. \right. \\ &\left. \left. - s_0 \omega^2 (r_0 - r) dt \right\}^2 (r_0 - r) \tan \theta \right]. \quad (3) \end{aligned}$$

This represents the condition that the volume generated by the revolution of the hatched area $EFF'E'B$ is equal to the volume generated by the revolution of the area $EFHG$ around the axis BO . Neglecting the terms containing the square of dt , and rearranging the remaining terms, we get

$$\frac{dr}{dt} = s_0 \omega^2 (r_0 - r) \left\{ 1 + \mu (r_0 - r) \right\},$$

where $\mu = \frac{\tan \theta}{3a}$.

Integrating and making use of the initial condition, $r = 0$ for $t = 0$, we get

$$r = r_0 - \frac{1}{\left(\mu + \frac{1}{r_0} \right) e^{s_0 \omega^2 t} - \mu}. \quad (4)$$

This is the equation which gives the change of boundary with time. The graph of this equation is given in Fig. 5.

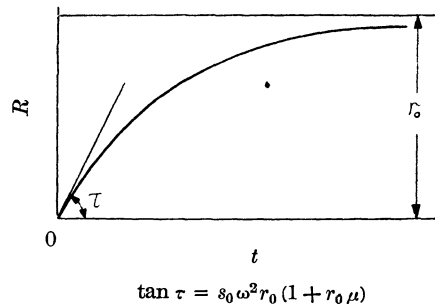


Fig. 5.

As the measure of the efficiency of cream separation, we take the initial velocity of

flotation. We make $\left(\frac{dr}{dt}\right)_{t=0}$ from (4) and study its change with the inclination and the distance between the cones. By means of the relation $r_0 = L \cos \theta$, we get

$$\left(\frac{dr}{dt}\right)_{t=0} = s_0 \omega^2 L \cdot \varphi(\alpha, \theta), \quad (5)$$

where $\varphi(\alpha, \theta) = \cos \theta (1 + \alpha \sin 2\theta)$, (6)

$$\alpha = \frac{L}{6l}.$$

Thus we see that if s_0 , ω and L are given, the initial velocity is determined by the function $\varphi(\alpha, \theta)$. In Fig. 6 the values of $\varphi(\alpha, \theta)$

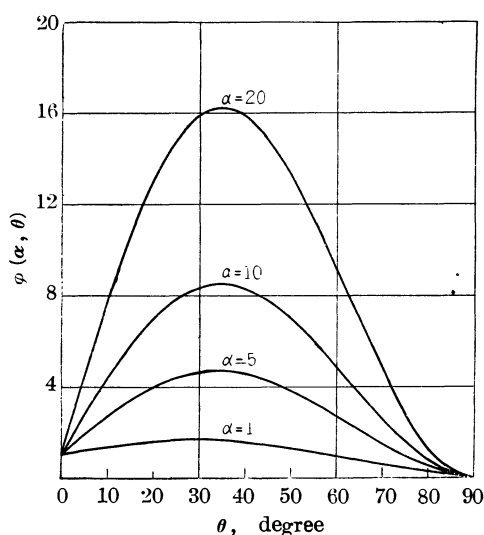


Fig. 6.

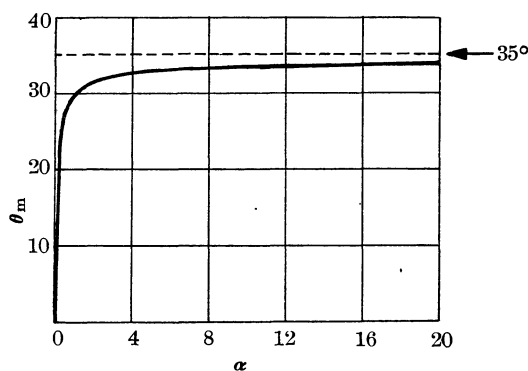


Fig. 7.

are plotted against θ , taking α as parameter. The function $\varphi(\alpha, \theta)$ increases with the increase of α . If we denote by θ_m the value of θ which makes $\varphi(\alpha, \theta)$ maximum, it increases with the increase of α at first suddenly and then approaches the limiting value 35° .⁽⁶⁾ The relation between α and θ_m is given in Fig. 7.

From the result obtained so far, larger value of α is desirable for higher efficiency. However, there is a limit for the value of α from the standpoint of mechanical construction, and we cannot increase it infinitely. The actual construction corresponds to the value 20 of α . The value of θ_m corresponding to α greater than 10 is nearly 35° , while the actual inclination is 45° — 50° . The coincidence is not very good. However, so long as there is no reasonable way of determining the proper inclination, the conclusion obtained hereby might be of some use for the design of the centrifuge.

Summary

As a result of the application of the Nakamura-Kuroda theory of the sedimentation of colloid in an inclined cylinder it has been shown that the initial sedimentation velocity of colloid increases in a vessel consisting of two cylinders having different radii, the radius of the upper cylinder being smaller than that of the lower one. The amount of the increase is determined by the ratio of the sectional areas of the two cylinders.

The N-K theory has been formally extended in the flotation of emulsion in a centrifugal field, and the design of the de Laval centrifuge has been considered in the light of the results obtained. A feasible, though not quite rigorous, explanation of the consistency of the form of centrifuge has been given.

In conclusion, the author would like to express his cordial thanks to Professor S. Oka for his kind interest in this work.

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(6) This is the value of θ which makes $\varphi(\alpha, \theta)$ maximum when α is very great. It is obtained by solving $\frac{d\varphi}{d\theta} = 0$, neglecting the term which does not contain α .

Studies on the Gas Liquid Interface by Surface Potential Measurements. II. On the Solutions of Dicarboxylic Acids

By Toshizo ISEMURA and Hiroshi HOTTA

(Received June 19, 1950)

Molecules of polar-nonpolar substances on the surface of a solution will probably take particular orientation at the gas liquid interface. The orientation of such molecules will be greatly affected with the molecular configuration of the adsorbed substances. Many investigations on the structure of monolayer of insoluble heteropolar compounds or the orientation of the molecules on water have been reported by many investigators.⁽¹⁾ The measurement of the surface potential of monolayer is one of the useful methods for studying the structure or the orientation of the monolayers. The method will also serve as the most useful one for the investigation on the nature of adsorbed surface layer of solutions. Nevertheless, relatively few investigations have already been reported.⁽²⁾ Previously, one of the authors measured surface potential of aqueous solutions of some fatty acids.⁽³⁾ Then, it was found that the surface potential of aqueous solutions of monocarboxylic acids such as *n*-butyric, *n*-valeric and *iso*-caproic acid reverses the sign of the potential in the region of concentration of high dilution. It was concluded that this reversal of the sign of surface potential is probably caused either by the dissociation of adsorbing acid or by the particular orientation of the adsorbed fatty acid molecules. In order to clarify the cause of the sign reversal of potential at high dilution and to obtain some informations of the molecular orientation of the adsorbed layer, we have measured in the present experiments the surface potential of aqueous and acidulated solutions of some dicarboxylic acids such as oxalic, fumaric, maleic, succinic, adipic, suberic, azelaic, sebacic and γ,γ' -sulfonyl dibutyric acids. These acids, investigated in our present experiments, have

polar groups at both ends of linear molecule and may lie probably flat in the adsorbed layer in virtue of two polar groups at the ends. γ,γ' -sulfonyl dibutyric acid has one more polar group at the midst of the molecule. Among the acids investigated, oxalic, maleic, fumaric and succinic acids always gave negative surface potential all over the concentration range. Other acids than these showed reversal of sign of the potential in the region of concentration of high dilution as in the cases of monocarboxylic acids. If the solution were acidulated by addition of small quantity of hydrochloric acid, the potential of the solutions was shifted to more positive values than the values of respective aqueous solutions. These results can readily be interpreted from the viewpoint that negative surface potential is principally caused from adsorbed fatty acid anions. At relatively high concentration, if the chain length of acid is sufficiently long, bending of the hydrocarbon chain of such dicarboxylic acid at the middle of a molecule would be caused by hydrophobic nature of hydrocarbon chain. Consequently, the adsorbed layer will much resemble to the adsorbed layer of monocarboxylic acid as indicated in Fig. 1. It was found that the expected resemblance of the surface layer of dicarboxylic acid solution to that of monocarboxylic acid was in part realized with concentrated solution of sebacic acid. One of the strong evidences which has rendered us to believe that the reversal of sign of potential is not

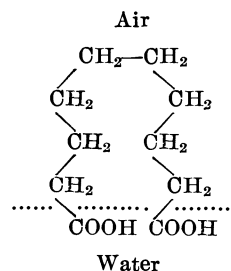


Fig. 1

(1) N. K. Adam, "The Physics and Chemistry of Surfaces," 72-77, Oxford, (1941).

(2) Bichat and Blondlot, *J. phys. Radium*, **2**, 548 (1883); Kenrick, *Z. physik. Chem.*, **19**, 625 (1896); Frumkin, *ibid.*, **109**, 34 (1924); **111**, 190 (1924); Sawai, *Trans. Faraday Soc.*, **31**, 764 (1935).

(3) T. Isemura, "Gendai Koshitsugaku no Tembo (Perspectives in Colloid Science, in Japanese)," Vol. 1, 177, Tokyo (1948).

caused by molecular orientation but mainly by dissociation of acid, is the following fact. The sign reversal of the surface potential was observed even with acidulated solution of γ,γ' -sulfonyl dibutyric acid which has one more polar group at the midst of molecule, so that the molecule can not bend anyway and must always lie flat.

Experimental

The method used for measuring the surface potential is the vibrating plate method, which is the same as used in the previous work of our laboratory. The amplifier, which was constructed for present experiment, was a three stage amplifier of resistance coupling using valves 6C6, 6C6 and 42. The principle of measuring the potential is essentially the same as was originally devised by Zisman.⁽⁴⁾ Surface tension was measured by a simple tensiometer of Du Nouy.

The substances studied are oxalic, maleic, fumaric, succinic, adipic, azelaic, sebacic and $\gamma\gamma'$ -sulfonyl dibutyric acids. The first four acids are the purest commercial samples available. Those acids were repeatedly recrystallized from adequate solvents. Agreement of melting points with literature was satisfactory, excepting maleic acid. Recrystallized maleic acid used in our present experiment melted sharply at 133°. This melting point does not agree with the literature. However, Mr. I. Moritani found that a single crystal of pure sample of maleic acid melts sharply at that temperature.⁽⁵⁾ Suberic and azelaic acids were prepared by usual method of oxidation of castor oil with nitric acid. The obtained azelaic acid was finally recrystallized from benzene (m. p. 106–108°). Suberic acid was fractionally recrystallized using ether repeatedly (m. p. 138–140°). Sebacic acid was prepared also from castor oil by the procedure presented by Sugino and his collaborators,⁽⁶⁾ and was recrystallized from 15% alcohol (m. p. 131°). $\gamma\gamma'$ -sulfonyl dibutyric acid was a pure sample which was given by Prof. S. Murahashi in this Institute.

All measurements were made at room temperature without special regulation of temperature. However, one series of experiments were made within a range of temperature as small as possible, and the variation of temperature never exceeded more than 2°.

Results

The surface potentials observed are shown in Fig. 2 and Fig. 3, and the surface tensions of respective solutions are shown in Fig. 4. In these figures solid lines are the results for aqueous solutions and chain lines are the results for acidulated solution by 1/100 *N* hydrochloric acid. In Fig. 2, the curves for monocarboxylic fatty acids, *i. e.* butyric, valeric and *iso*-caproic acid which were already reported in the previous paper are also shown for comparison. Values of surface potential in relatively low concentration region of respective acids could not be determined as accurately as

in rather concentrated region of the solutions. The parts of curves shown in dotted lines are the parts with somewhat less reliability than that of solid or chain lines. In these parts the potential fluctuated to some extent. Later the cause of the fluctuation of surface potential data in such concentration region will be thoroughly discussed.

Dicarboxylic acids which have relatively short carbon chain such as oxalic, maleic and fumaric acids gave always negative surface potential all over the concentration range examined up to saturation. With oxalic, maleic and fumaric acids, the potential reached to –140, –150 and –129 millivolts respectively at the concentration of nearly saturated solution. Succinic and

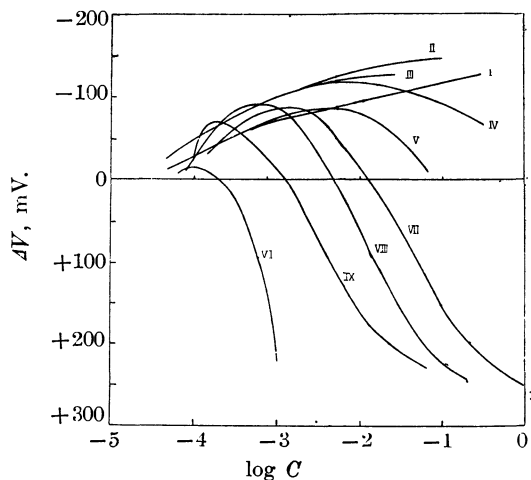


Fig. 2.— I, oxalic acid (11°C.); II, maleic acid (8°C.); III, fumaric acid (8°C.); IV, succinic acid (8°C.); V, adipic acid (10°C.); VI, sebacic acid (10°C.); VII, *n*-butyric acid; VIII, valeric acid; IX, *iso*-caproic acid.

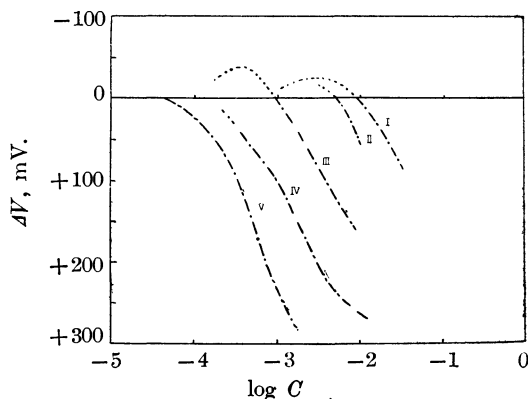


Fig. 3.— I, adipic acid (11°C.); II, $\gamma\gamma'$ sulfonyl dibutyric acid (14°C.); III, suberic acid (13°C.); IV, azelaic acid (14°C.); V, sebacic acid (17°C.).

(4) Zisman, *Rev. Sci. Instrument*, **3**, 7 (1932); Yamins and Zisman, *J. Chem. Phys.*, **1**, 656 (1933).

(5) Private communication.

(6) K. Sugino and collaborators, *J. Soc. Chem. Ind. Japan*, **44**, 706 (1941).

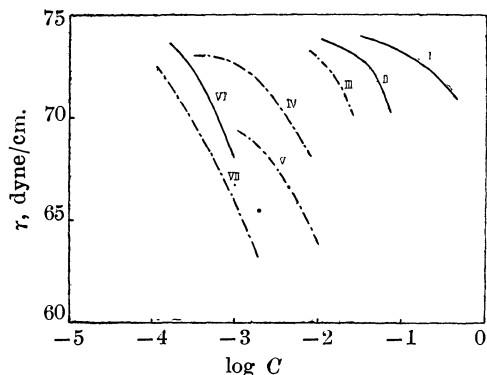


Fig. 4.— I, maleic acid (10°C.); II, adipic acid (9°C.); III, adipic acid + $N/100$ HCl (11°C.); IV, suberic acid + $N/100$ HCl (16°C.); V, azelaic acid + $N/100$ HCl (17°C.); VI, sebacic acid (10°C.); VII, sebacic acid + $N/100$ HCl (17°C.).

$$\Delta V = 4\pi n\mu,$$

with the aid of Gibbs' adsorption formula and our surface tension concentration curves. In the above equation ΔV is surface potential, μ , the vertical contribution of dipole moment of the surface molecule and n , the number of adsorbed molecules per unit area. The vertical contributions of surface moments of suberic, azelaic and sebacic acids and their molecular area on the surface of solution at different surface potentials were tabulated in Table 1. The data of the area occupied and vertical component of dipole moment of adsorbed solute were shown as a function of surface potential and calculated assuming that both the activity coefficient and the dielectric constant were equal to unity.

Table 1

Molecular Area and Vertical Component of Dipole Moment with Respect to Surface Potential of Solutions of Dicarboxylic Acids

(calculated as activity coefficient = 1 and dielectric constant = 1)

Surface potential ΔV (mV.)		280	240	200	160	120	80	40
Molecular area ($\text{\AA}^2$)	Suberic acid				124	140	206	310
	Azelaic acid		92	180	220			
	Sebacic acid	68	92	120	130	170	190	240
Vertical component of dipole moment per each polar group (Debyes)	Suberic acid				0.27	0.23	0.22	0.17
	Azelaic acid		0.30	0.37	0.47			
	Sebacic acid	0.25	0.30	0.33	0.28	0.27	0.20	0.12

adipic acids in aqueous solution also gave always negative potential, however, the potential tends to be less negative if the concentration of the solution approaches to saturation. Sebacic acid gave negative potential in very dilute solution but changed the sign of potential in more concentrated solution. With this acid, surface potential curve plotted as a function of logarithm of concentration (mol/l.) of the acid was similar to the curves of monocarboxylic fatty acids which were mentioned above. The potentials were generally shifted to more positive values when hydrochloric acid was added to the solution and maximum negative potentials were markedly suppressed. Maximum surface potentials of various dicarboxylic acids were not similar as shown in monocarboxylic acid and the more positive potential was observed the longer the carbon chain of the acid. Maximum potential observed in our experiments for adsorbed layer of solutions was 280 mV. for 0.016 mol solution of sebacic acid at 17° acidulated with hydrochloric acid so as to become 0.01 N with respect to hydrochloric acid. The vertical contribution of surface moment of the adsorbed acid was calculated by Helmholtz equation,

Discussion

From the results just mentioned above, it will be noticed that the surface potentials of solutions of dicarboxylic acids near the concentrations of their saturated solutions became more positive value with increase of the length of hydrocarbon chain in the acid molecules. This is a remarkable difference between the results obtained with dicarboxylic acids and those with monocarboxylic acids. With monocarboxylic acids such as butyric, valeric and *iso*-caproic acids, solutions of these acids showed almost the same positive potential, *i.e.* ca, 240 mV. in the concentration ranges near saturation. If the solutions of dicarboxylic acids of moderate carbon chain length were acidulated with hydrochloric acid, the surface potential was generally shifted to more positive value. Then, the curves of surface potential versus logarithm of concentration were almost parallel as shown in Fig. 3, and from the figure it is obvious that about one third concentrated solution is sufficient to attain a certain value of surface potential if the acid has one more CH_2 group in the chain. This fact is analogous

to that found with monocarboxylic acids in the previous investigation. The work of adsorption is increased in the cases of dicarboxylic acids also, by a constant amount for each CH_2 group added to the chain, so that the relation of every CH_2 to the water surface is the same, whatever its position in the chain.

In the previous paper, we inferred that the reversal of sign of surface potential that was observed at high dilution of solution may be the characteristic phenomena for the adsorbed layer of gaseous film type, caused either by molecular orientation, that is lying flat on the surface, or by the dissociation of adsorbed acids. Since the acids investigated in the present work are dicarboxylic and have two polar groups at both ends of the molecule, two water soluble polar groups would naturally make the molecule lie flat, if the surface potential is defined principally by the orientation of the adsorbed molecules, the potentials of solutions of these acids will not reverse the sign at all, and change steadily to a saturation value. With oxalic, maleic and fumaric acids, which have relatively large dissociation constants, this is the case. With dicarboxylic acids of longer chain than adipic acid, however, the reversal of the sign of the potential was observed just as with monocarboxylic fatty acids. Thereupon, these facts cannot be attributed simply to the change of orientation of the adsorbed molecules. Further, if the reversal of potential was caused by the orientation, the calculated vertical contribution of the dipole moment of the molecules of dicarboxylic acids, which lie on the surface of solution, should be independent of the concentration of the solution and of the length of carbon chain of the acids. These inferences were not supported with our experimental results. On the other hand, if we assume the reversal of surface potential are caused by the dissociation of the acid, the experimental results will be explained without any difficulty. In acidulated solutions, the dissociation of dicarboxylic acids will be suppressed and the potential of the surface was shifted to more positive values in comparison with that of non-acidulated solutions. In very dilute range of concentration of the solution, number of molecules of adsorbed acid might be relatively few and a large proportion of the adsorbed acid should be ionized. Hence, surface potential of the solution may be reversed the sign.

These inferences would readily be comprehended by comparing the surface potential curves in Fig. 2 and Fig. 3 with dissociation constants of respective acids tabulated in Table 2. Except oxalic, maleic and fumaric

Table 2
Dissociation Constants at 25°C.

Acids	k_1	k_2
Oxalic acid	3.8×10^{-2}	
Succinic acid	6.5×10^{-5}	2.3×10^{-6}
Fumaric acid	9.3×10^{-4}	1.8×10^{-6}
Maleic acid	1.2×10^{-2}	3.9×10^{-7}
Adipic acid	3.8×10^{-5}	2.4×10^{-6}
Suberic acid	3.0×10^{-5}	2.5×10^{-6}
Azelaic acid	2.6×10^{-5}	2.7×10^{-6}
Sebacic acid	2.8×10^{-5}	2.6×10^{-6}
<i>n</i> -Butyric acid	1.5×10^{-5}	
<i>n</i> -Valeric acid	1.5×10^{-5}	
<i>iso</i> -Caproic acid	1.5×10^{-5}	

(cited from the Beilstein's Handbuch.)

Table 3
Degree of Dissociation Calculated from
Ostwald's Dilution Law

Dissociation constant	Concentration, N				
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
1.5×10^{-5}	0.012	0.038	0.12	0.31	0.68
2.5×10^{-5}	0.016	0.046	0.14	0.39	0.77

acids which have relatively high dissociation constants, all acids investigated have the first dissociation constants of the order of magnitude of 10^{-5} . With the aid of Ostwald's dilution law, the degree of dissociation of dilute solutions of various concentrations can readily be calculated and rough estimate at two different dissociation constants would have values as shown in Table 3. Since hydrochloric acid is practically dissociated completely in 1/100 N solution, the dissociation degree of the acids, having dissociation constant of the order of magnitude of 10^{-5} , will be as much as 3×10^{-3} .

Surface potential changed its value to some extent with time after making surface on the solution according to the kind and concentration of acid. The values plotted in Figs. 2 and 3 were those within one minute after making new surface. The potentials in the range of negative value tend to more negative value with time. It has already been pointed out by some authors that surface tensions of solution of certain substances changed with time,⁽⁷⁾ and at least five minutes were required to attain steady values of surface tension with all aliphatic acids above *n*-butyric acid. Time required to obtain equilibrium surface tensions

(7) H. H. King, *Kansas State Agr. Col., Agr. Exp. Station Techn. Bull.*, No. 9, (1922); Addison, *Nature*, **156**, 600 (1945).

increases very rapidly with chain length of acids. Of course, the cause for the change of surface potential with time might be the same with that for surface tension and attributed probably to slow adsorption of solute. Ions of acids are exceedingly more soluble than undissociated molecules. The latter will immediately be adsorbed. While, ions which have hydrocarbon of moderate length and are considerably soluble in the solution, would be adsorbed very slowly. The rate of adsorption of ions must be slower than that of undissociated molecules and depends on the length of hydrocarbon chain. If such ions of moderate hydrocarbon chain reached to surface, they would be captured by surface layer and partly combined with hydrogen ion and converted into undissociated molecule according to relatively high concentration of such weak acid in the surface phase. Nevertheless, actual concentration of negative ions is gradually increased and surface potential effectively changes to more negative. With acids of sufficiently long chain, solubility of those acids would be decreased markedly and the acids might be often practically insoluble, and the adsorbed layer, which covers the surface of solution completely or surface monolayer closely packed, would be made exclusively of undissociated molecules. Hence the surface potential is positive and has no bearing on time. The surface films of insoluble fatty acids such as stearic and myristic acids, of which dissociation constants are the order of magnitude of 10^{-13} , give generally positive surface potential. Even with such acid of low dissociation constant as myristic acid, however, the change of sign of surface potential was observed recently by Guastella and Michel⁽⁸⁾ at extremely dilute surface concentrations. They found with myristic acid that surface potential changes to negative for molecular area from 1000 to 30000 Å.² They concluded that the results obtained by them at high dilution appeared to indicate that the molecules of myristic acid turn their negative pole upwards. On the other hand, with the concentrated solution of acids which have moderate length of carbon chain and show some solubility, surface layer is completely covered with preferentially occupied undissociated molecules and leaves no space for belated ions. Under these circumstances also, the potential is always positive and does not change with time.

Each molecule of sebacic acid, dicarboxylic acid of ten carbon atoms, occupied an area of

68 Å.² on the surface of its 10^{-3} N solution, whose surface potential of which was 280mV. Calculated from these figures, the vertical component of dipole moment assigned to each polar group was 0.25 D.U. This is nearly identical with the value of vertical contribution of dipole moment of monocarboxylic acid at higher concentration or of monolayer of insoluble saturated fatty acid. In this case the molecule may be anchored by two carboxylic groups at both ends, nevertheless, the hydrophobic hydrocarbon chain is repellent to aqueous phase. So that, the molecule probably bends somewhat at the middle of the molecule as shown in Fig. 1. This conclusion is not strange at all. J. T. Davies measured force area and surface moment area curves for the monolayers of some long chain diesters containing the same number of carbon atoms.⁽⁹⁾ A plot of areas at the same surface pressure against the number of carbon atoms in each end chain was drawn. He found a maximum close to the point where the number of carbon atoms in the end chains is equal to the number in the middle of the molecule. These results together with our own concerning with sebacic acid are both equally understood, if the molecule is considered to bend at its middle. It must be emphasized, however, that the reversal of the sign of surface potential of dicarboxylic acid is not always connected with the bending of molecule. This will be clearly understood by the fact that $\gamma\gamma'$ -sulfonyl dibutyric acid, which has one more polar group of hydrophilic nature in the middle of molecule and for that reason cannot bend the chain molecule, reversed the sign of the surface potential at high dilution. For these reasons, it is believed that the reversal of sign of surface potential would be caused mainly by the dissociation of some weak acid. Some aliphatic non-ionizable substances are to be investigated.

Summary

Surface potentials of solutions of some dicarboxylic acids were measured by vibrating plate method. Dicarboxylic acids of short chain such as oxalic, maleic, fumaric and succinic acids gave always negative potential. However, dicarboxylic acids of moderate chain length gave positive potential at high concentration. While, with these acids, the potential changed to more negative at high dilution as in the cases of monocarboxylic acids. The values of potential were shifted to more positive values when the

(8) J. Guastella and Michel, *Research (London), Suppl., Surface Chemistry*, 127 (1949).

(9) J. T. Davies, *Trans. Faraday Soc.*, **44**, 909 (1948).

solutions were acidulated by hydrochloric acid. Such reversal of sign of surface potential might be attributed mainly to the dissociation of the acid and not to the molecular orientation. Molecule of sebacic acid adsorbed on the surface of nearly saturated solution bends probably its hydrocarbon chain at the middle of the molecule and it behaves as two adsorbed molecules of monocarboxylic acid in regard to molecular area and surface moment.

The authors' thanks are due to Prof. S. Murahashi who kindly gave them the pure sample. The cost of this research has been partly defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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Fluorometric Microdetermination of Uranium. II. Extraction of Uranium

By Masaki NAKANISHI⁽¹⁾

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Various properties of the fluorescent material of sodium fluoride containing a small quantity of uranium were investigated in the previous paper with the same title. To prepare the fluorescent material for the determination, it is required to extract uranium from the sample for analysis in an adequate form of compound.

Precautions must be taken lest any loss of uranium should be made throughout the procedures, and since the fluorescent materials are generally liable to be affected by impurities, they should always be guarded against such effects. But as was mentioned in the previous paper, the fluorescence of sodium fluoride activated by uranium is fortunately less affected by impurities, so far as the analytical application is concerned. For example, heavy metals and insoluble matters are made ineffective in the determination, if their amounts are decreased at least to the amount comparable with that of the uranium present with them. According to the writer's experiences, this is satisfactorily accomplished by the careful operations in the chemical separation procedures.

It is attempted in the present paper to survey each individual process for extracting a minute quantity of uranium from any sample, and to establish a method as satisfactory as possible.

1. Outline of the Extraction from the Sample

In dealing with the solid sample, it must be

first brought into a solution of uranyl salt. For example, a rock sample is ground and fused in a platinum crucible with sodium carbonate, then extracted with hot water.

This treatment must be repeated at least three times, for only one process does not suffice to perfect the extraction. The extraction with hot water instead of any acid makes the following scheme simpler, because many other metals are separated from uranium and the latter is in general completely brought into the solution.

The following represents the outline of extraction method of uranium in usual natural substances, in which are included solutions derived from rock samples, sea-water, hot-spring water, etc. In case when the sample contains unfamiliar constituents, a special scheme of the analysis must be chosen, but this consideration is omitted here for simplicity.

The application of the fluorometric method of analysis is practically limited to the solution, in which the uranium content is so small that the element is not quantitatively precipitated by any direct way. To precipitate uranium from such a dilute solution, iron hydroxide is effectively employed as carrier or co-precipitator, as is often the case with the precipitation of a small amount of substance.

The extract from sodium carbonate fusion is carefully treated with dilute hydrochloric acid and boiled to expel a large amount of carbon dioxide. The resulting solution free from carbonates is evaporated on a water-bath to dryness, and silica is, if necessary, removed as usual from this residue. Since organic matters and carbonates seriously interfere with

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the coprecipitation of uranium with iron, it is better in the case of an aqueous sample, *e. g.*, natural water, to begin with the evaporation to remove silica and then to destroy the organic substances with nitric acid or a mixture of nitric acid and sulfuric acid.

The residue is dissolved into a clear solution. Add ammonium chloride and an adequate amount of ferric chloride solution (corresponding to about 20 mg. of Fe_2O_3), boil for a few minutes, then add ammonia containing no trace of carbonate. Almost all uranium is coprecipitated with iron hydroxide. The precipitate is heated for a while with its mother liquor, which is followed by filtration and washing with a hot ammoniacal ammonium chloride solution containing no trace of carbonate. To complete the precipitation of uranium, this procedure is repeated three times.

Some considerations will be made in the following in connection with these treatments and the coprecipitation phenomenon.

In the next stage of analysis, uranium coprecipitated must be separated from iron and other possible impurities, but this will be detailed in the following papers.

2. Required Amount of Iron for Coprecipitation

The following experiment provides some knowledges how much ferric salt will be needed to precipitate the minute quantity of uranium together with iron hydroxide.

Different quantities of ferric chloride solution were added to 50 ml. of uranyl nitrate solutions, each containing 1.00×10^{-5} g. of uranium. In these mixtures, precipitation with ammonia was performed, and the uranium content of each precipitate was determined by the fluorometric method described later.

Table 1

FeCl ₃ added, mg. as Fe ₂ O ₃	Amount of uranium in each bead, 10^{-7} g.		Observed Expected
	Expected	Observed	
1	8.78	8.27	94
		9.18	104
		9.85	101
3	9.78	8.75	89
		8.85	102
10	8.66	8.27	95
		9.18	106

Table 1 represents the experimental results, which prove that 1 mg. as well as 10 mg. of iron is equally sufficient to precipitate about 10^{-5} g. of uranium. The experiment with the smaller amount of iron than 1 mg. was omitted,

for it is considered unavailable in practical cases.

3. Amount of Uranium not Precipitated

It is generally recommended to repeat the procedure two or three times in precipitating a small amount of substance with carrier. The next experiment reveals the efficiency, with which uranium precipitates with a relatively large amount of iron.

To the hot 100 ml. solution containing 2×10^{-6} g. U and 20 mg. Fe_2O_3 in the forms of uranyl nitrate and ferric chloride respectively, ammonia was added, and the precipitated iron hydroxide was filtered. Then the amount of uranium not precipitated was determined in the filtrate by means of the fluorometric method.

As a result of this experiment it was observed that only a trace of uranium was found in the filtrate and almost all of it was dragged down with the hydroxide precipitate. Approximately from 0.3 to 0.4% of the uranium in the original solution gets rid of the coprecipitation and remains in the filtrate. The values determined were not precise in this experiment, for the uranium content of each bead is in the order of 10^{-9} g., corresponding approximately to the lower limit to produce faint fluorescence.

Since the error in the determination of this fluorometric method amounts to about 10%, a single coprecipitation procedure of uranium with iron will serve in practical cases. But the coprecipitation procedure is preferably repeated three times as a rule, for it is suspected that the efficiency will be lowered if the solution contains various other substances.

4. On Adsorption

The iron hydroxide precipitate adsorbs other impurities, as is well known, on account of its colloidal property. In the experiment mentioned, therefore, special precautions will be needed in the operations, if uranium is precipitated by mere adsorption with iron hydroxide. But it is valid from the following experiments that the adsorption, if any, is neglected, and the suitable condition will be shown thereby.

a. At the room temperature.—The hydrochloric acid solution of uranyl nitrate containing 1.05×10^{-5} g. U was boiled to expel carbon dioxide, left standing to coolness, and ammonia was added, where no noticeable precipitate was produced. On the other hand, the hydrochloric acid solution of ferric chloride containing 2 mg. Fe_2O_3 was kept boiling for a

while, and after cooled to the room temperature iron hydroxide was precipitated with ammonia. The two solutions were mixed together immediately after adding ammonia (volume of the resultant solution being about 100 ml. and the concentration of ammonia 1 *N*), shaken for 5 minutes and filtered through a hard filter paper under suction. The precipitate was dissolved in hot dilute hydrochloric acid and after iron being separated uranium was determined by the fluorometric method. The numerical data are given in Table 2 (a). The amount of uranium apparently included in the precipitate reaches as much as 8.10% of that taken. This fact gives an impression that a part of uranium in the solution is adsorbed on the surface of iron hydroxide precipitate. But in the above treatment, iron precipitate had been completed before mixing with uranium solution, and the filtration followed soon after mixing. Therefore the so-called occlusion or the compound formation may not be the case. Considering that uranium belongs to those elements which are precipitated in an ammoniacal medium, it is suspected that from such a dilute solution uranium may form an unnoticeable precipitate remaining on the filter paper. To make this clear, a similar experiment was made with the solution which contains uranium only, and is not added with iron precipitate. After the filtration, the filter paper was ignited to ash, and the uranium content in the ash was estimated as before. 12.2% of the total amount of uranium taken was found as given in Table 2 (b).

Table 2

Uranium taken, 10 ⁻⁷ g.	FeCl ₃ added, mg. as Fe ₂ O ₃	Temperature, °C.	Uranium found in the precipitate, 10 ⁻⁷ g., and % to the total	
(a) 105.4	2	20	8.53	8.10 %
(b) "	none	"	12.9	12.2 "
(c) 10.54	20	at boiling	1.39	13.2 "
(d) "	"	"	1.33	12.6 "
(e) "	"	"	1.90	18.0 "
(f) "	none	"	1.69	16.0 "

It seems contradictory that in the experimental results the amount of uranium remaining with the iron precipitate ((a) in Table 2) is smaller than that remaining on the filter paper only ((b) in Table 2) where no iron precipitate was present. But the state of uranium precipitate from such a dilute solution might delicately depend upon the conditions in the procedure, and it has therefore almost no meaning to discuss the difference.

In conclusion, the adsorption of uranium to iron precipitate is practically negligible at the room temperature, and its contribution, if any, is not so large as to explain the fact that nearly all of uranium in the solution is precipitated with iron hydroxide as described in the above section (3).

b. At the higher temperature.—Since in practical cases the procedure to precipitate a small amount of uranium with iron is performed at the hot condition, the examination on the adsorption at a higher temperature is more significant than that at a lower temperature. In fact, it is known that the iron hydroxide precipitate changes its structure by aging at a higher temperature,⁽²⁾ and from this fact further examinations are required to see whether uranium is adsorbed to iron hydroxide precipitate at the hot condition or not.

Experiment 1.—A 50 ml. solution containing 1.05×10^{-6} g. U as uranyl nitrate and 1 g. of ammonium chloride was heated to boiling and ammonia was added, where no visible precipitate took place. On the other hand another 50 ml. solution containing 20 mg. Fe₂O₃ in chloride form and 1.5 g. of ammonium chloride was heated to boiling and ammonia was added. The latter solution with iron precipitate in it was immediately transferred to the ammoniacal solution of uranium, the mixture being heated again with stirring for 1 minute, and then filtered under suction without washing. The precipitate remaining on the filter paper was dissolved in hot dilute hydrochloric acid and uranium was determined ((c) in Table 2).

Experiment 2.—After mixing two ammoniacal solutions of uranium and iron treated as before, the combined solution was kept on heating with the precipitate in it for 10 minutes. Other treatments were the same as the above. ((d) in Table 2).

Experiment 3.—Before mixing with an ammoniacal solution of uranium, iron hydroxide precipitate was aged with the mother liquor for 10 minutes at the boiling temperature. Other details were the same as in Experiment 1. ((e) in Table 2).

Experiment 4.—The same treatment as in Experiment 1 was carried out without iron precipitate, to determine the amount of uranium remaining on the filter paper. ((f) in Table 2).

As given in the table, the amounts of uranium

(2) A. Krause, *Z. anorg. allgem. Chem.*, **176**, 398 (1928); **204** (1932); **206**, 328 (1932); **211** (1933); **219**, 213 (1934).

which remain with the precipitate are not constant, but they are in the same order of magnitude as that obtained when uranium solution is treated without iron. Besides, these values are dependent to a large extent upon the conditions of the precipitation procedure. When uranium is precipitated alone, the precipitate of small sizes will perhaps remain adsorbedly on the filter paper.

Conclusions from the experimental results above mentioned are as follows. The precipitation phenomenon of uranium with iron is not attributed to the mere adsorption. Even the adsorption should take place, it may be limited only to a smaller part, and may not play an important role. It is reasonably concluded that a larger part of uranium will be coprecipitated with iron in some structural binding. In consequence, this procedure of precipitation is effectively made at a convenient hot condition, and the washing will not cause any loss of the element.

5. On Aging.

If uranium should combine loosely with iron hydroxide precipitate, it may be possible that the former is let free from the latter and again gets into the solution during digestion at the high temperature. Now that uranium itself is slightly soluble in an ammoniacal medium, there will be almost nothing to apprehend, but an exact proof for it is required, because the amount of uranium taken is negligibly small for the ordinary chemical manipulations. The following experiments will meet the purpose.

A 100 ml. solution containing 1×10^{-6} g. U in nitrate form and 20 mg. Fe_2O_3 in chloride together with 2.5 g. of ammonium chloride was acidified with hydrochloric acid, boiled for 1 minute, and 10 ml. of 6 *N* ammonia was

added. In one experiment the precipitate of iron hydroxide obtained was immediately filtered, while in the others the precipitate was digested at 95° for 3, 10 and 60 minutes respectively before filtration. After filtered in each case uranium remaining in the filtrate was determined by the fluorometric method. The values obtained were very small, which correspond to about 0.5% of the total amount taken in each case. According to our present method of procedures, an amount of uranium close to 10^{-9} g. gives too weak a luminescence to obtain the exact value.

This amount of uranium which gets rid of the coprecipitation with iron, however, agrees satisfactorily with that which remains in the solution after a single coprecipitation procedure as described before (section 3). Therefore it is concluded here that there is no loss even if we keep the precipitate heated with its mother liquor as long as an hour. Furthermore, this procedure of boiling gives a favorable result, for aging for a while at the boiling temperature makes the iron hydroxide precipitate more filterable.

Summary

A minute amount of uranium suitable for the fluorometric method of determination is effectively precipitated from the solution together with hydrous ferric oxide as co-precipitator. The efficiency of co-precipitation seems to be nearly perfect for the purpose, and the adsorption and the digestion effect were observed in particular from the analytical standpoint.

The writer is greatly indebted to Professor Kenjiro Kimura for his kind guidance in the course of this work.

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Fluorometric Microdetermination of Uranium. III. Isolation of Uranium and Preparation of the Fluorescent Material

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This series of reports aims to tell in detail the fluorometric method of determina-

tion of uranium, and the procedure fitted for the estimation of such a small amount of the element as we often encounter in the analysis of some geochemical samples. The most suitable amount to deal with is within the limit from

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10^{-5} g. to 10^{-7} g. of uranium.

The first step in treating the sample is just the same as in the ordinary chemical analysis, the details of which have been mentioned in the preceding paper. To extract uranium from the solution, ferric hydroxide precipitate is effectively used as carrier. A minute quantity of uranium is completely coprecipitated with this carrier, and this phenomenon has been reported in detail from the analytical point. In this report the separation of uranium from iron and other impurities will be taken into account.

1. Separation from Iron

The minute quantity of uranium in the solution from the sample is concentrated in the iron precipitate as was described in the foregoing paper. The coprecipitation procedure must be repeated at least three times for completeness.

If the original solution contains those elements which produce precipitates in the ammoniacal medium, they will naturally contaminate the precipitate of iron. Besides, the colloidal property of the precipitate will also cause adsorption or inclusion of some elements or compounds. As it is, of course, profitable for the following processes to avoid the latter sort of contaminations, the iron precipitate containing uranium is dissolved in hot dilute hydrochloric acid, and reprecipitated along with uranium. In case of the relatively concentrated solution of alkali or alkaline earth metals, e. g., solutions obtained from rocks, minerals, sea water, etc., the re-precipitation is necessary.

In the treatment of ordinary natural substances, except some special ones, impurities by coprecipitation are eliminated in the next stage of procedures, and a smaller part of them remaining with uranium affects, according to our experiences, not so much as to interfere in the fluorometric determination.

The total precipitate of iron hydroxide containing a small amount of uranium obtained from the original solution is dissolved out, as soon as possible after filtration and washing in hot dilute hydrochloric acid. No trace of uranium remains adsorbed to the filter paper. And from this solution the iron hydroxide is again precipitated together with uranium. A little ferric chloride solution corresponding to a few milligrams of Fe_2O_3 is added to the filtrate, and the recovery of uranium is repeated in the same way as in the preceding paper. These precipitates of iron containing uranium too are dissolved in hydrochloric acid.

From this acid solution of iron and uranium,

the most part of the former is separated from the latter, with the aid of ammonia in the presence of ammonium carbonate.⁽²⁾

In this procedure of separating iron, ammonium chloride is added to the acid solution which is *almost neutralized with ammonia*. Keeping the solution at about 60° , ammonium carbonate and ammonia are added, and the solution is kept warm with the iron precipitate in it for several minutes. The decomposition of ammonium carbonate begins here if the temperature rises higher than about 80° . The iron precipitate is now filtered off, which contains almost no uranium if the directions are followed.

But it is not easy to wash the precipitate obtained here, for it has been formed at a rather lower temperature. On this account the washing is omitted in this stage, and the precipitate is re-dissolved in hot dilute hydrochloric acid, and the procedure is repeated as given to complete the dissolution of uranium.

Since the filtrate occasionally contains a trace of iron, it is treated with hydrogen sulphide, and the precipitate formed is filtered off.

2. Separation of Other Impurities

The filtrate separated from iron precipitate contains, besides all of uranium taken, some impurities which behave in the same way as uranium in the coprecipitation with and separation from iron. But these give almost no unfavorable effects on the determination so far as common samples are dealt with. In cases where the samples are rich in beryllium, rare earth metals, zirconium, thorium, etc., special procedures of chemical separation are necessary in addition to the simpler one described in the foregoing sections.

The filtrate is cautiously made acid with hydrochloric acid, and evaporated in a porcelain dish. If any heavy metals are still present, these may be precipitated with the help of organic reagents such as 8-hydroxyquinoline in the presence of ammonium carbonate. Here the repeated operations are necessary to prevent the precipitation of uranium compound.

The filtrate is gently evaporated in a porcelain vessel. The residue mostly consists of ammonium salts, and these must be eliminated. If these are heated directly, a little loss of uranium is likely to occur. So the ammonium

(2) The ammonium carbonate reagent is prepared as follows, 40 g. of the commercial reagent is dissolved in 1 l. of 1 N ammonia, warmed at about 60° for 10 minutes, and filtered if necessary.

salts are preferably removed as follows: Add concentrated nitric acid to the residue, and the vessel covered with a watch glass is warmed on a water-bath. After the violent reaction has ceased it is further evaporated to complete dryness.

That the latter method is superior to the former is evident from the next experiment. The solution containing 1.00×10^{-6} g. U as nitrate and 1 g. of ammonium chloride was evaporated to dryness. The residue obtained was heated into fume, and the fluorometric method was applied to determine the remaining uranium. In comparison with this, the ammonium chloride residue was decomposed with nitric acid, and the remaining uranium determined. Table 1 represents the results obtained.

Table 1

Amount of uranium, 10^{-6} g.			
	Calculated	Observed	
By direct heating	1.00	0.72	mean: 0.83
		0.91	
		0.73	
		0.84	
		0.97	
		0.79	
Decomposition with nitric acid	1.00	0.73	mean: 0.96
		0.89	
		1.03	
		0.94	
		1.02	
		0.97	
		1.10	
		0.90	

It is obvious from the table that the operation to remove the ammonium salts by fuming gives rise to a loss of uranium, and the loss may be due either to the actual loss that a minute quantity of uranium is spattered with the fume of ammonium salts, or to the apparent loss that uranium is transformed by heating into an insoluble compound and is not mixed up into the fluorescent material.

The residue after decomposing the ammonium salts in which the total amount of uranium is contained is very small, if the directions are followed with care, and such a small amount of contamination, does not interfere in the fluorescence test.

Nitric acid is used again, if necessary, to decompose the chlorides completely. Then the content of the vessel is transferred into a small platinum dish, moistened with nitric acid and evaporated again on a water-bath. Mixed with sodium fluoride, the final residue is next

brought into the fluorescent material as given in the section (3).

The impurities in the final residue, if they are much, may interfere with the formation of the normal fluorescent material as a result of contamination. Therefore it is required to pay attention to every stage of the operation, and to perform the separation of impurities if necessary. As for vessels, porcelain of good quality is preferable to glass, especially for the long-during evaporation, since the dissolution of constituents of glass is thus avoided. The platinum vessel is used after chlorides are decomposed with nitric acid.

3. Preparation of the Fluorescent Material

a. Mixing with sodium fluoride.—The total amount of uranium is now brought together in a platinum dish. About 150 mg. of solid sodium fluoride and a little water are added into it. Then the solution is evaporated to complete dryness on a water-bath. The dried mass of sodium fluoride in which uranium is contained is scraped off and preserved in a dessicator. Pour several ml. of water into the dish to dissolve the possible remainder of uranium salt. Then add more 50 mg. of sodium fluoride and evaporate to dryness.

The sodium fluoride masses obtained by the successive operations are gathered together, and heated gently in a platinum dish to remove the moisture completely. The obtained powder mixture is preserved in the desiccator and the fluorescent beads are made from this mixture as will be mentioned in the following section.

Speaking from the writer's experiences, it is not profitable in the last operation of mixing to use hydrofluoric acid instead of water for the following reasons. (i) First, if hydrofluoric acid is used, a molecular compound $\text{NaF} \cdot \text{HF}$ is formed, from which hydrogen fluoride is liberated on heating and the mechanical loss of the fluorescent material takes place at times in the preparation of fluorescent beads. Besides, the beads prepared from such material become much smaller than expected, and do not develop into a disk-shaped bead. (ii) Secondly, there is a fear that impurities of the acid are mingled, while it is rather an undesirable work to purify the acid. (iii) Moreover, the writer experienced no objection in using water instead of hydrofluoric acid.

b. Preparation of fluorescent beads.—Weigh the total of the dried powder mixture of uranium and sodium fluoride, and make it homogeneous in a mortar. The fluorescent bead is prepared from a portion of this mixture

on a platinum loop. But as it is difficult to treat such a powdered sample, this is conveniently pressed into a small tablet of about 20 mg. in weight. Each tablet is weighed exactly.

The preparation of the fluorescent bead runs as follows: A tablet of a known weight is put on the clean platinum loop, and gradually heated by the burner flame to clear fusion in the end. This state of fusion is kept for 5 minutes in the oxidizing flame. Both sides of the disk-shaped bead are to be equally heated, and this condition must be the same for every bead. After 5 minutes' fusion, the bead is quickly cooled down rotating the shaft attached to the loop, by which procedure the surface of the bead becomes flat and suitable for the determining the fluorescence intensity.

To obtain a disk-shaped bead, the proportion of the loop diameter to the amount of the powder mixture is important, and this is decided by trials. The writer uses regularly the loop of 2.5 mm. diameter for about 20 mg. of the mixture.

The time of ignition in the burner flame is fixed to 5 minutes. The intensity of fluorescence depends much upon the time of heating and, during the first few minutes, the longer the time is, the more intense the fluorescence becomes, since it takes some time for heating to form a proper fluorescent material. But the intensity increases very gradually with time when heated for more than several minutes, which means that there is a relative increase of uranium content in the bead due to the evaporation of sodium fluoride under heating. This is the reason why the duration of the heating treatment must be constant for every bead, and the heating for 5 minutes was chosen by trials.

The bead of the fluorescent material prepared

is somewhat hygroscopic. It is not desirable to repeat the ignition since it might cause the change of the intensity. Therefore it is better to prepare the bead immediately before testing the intensity.

c. Preparation of the standard beads.—

The intensity of fluorescence of the bead from an unknown sample is compared, as will be described in the following paper, with those of the standard beads, the uranium contents of which are already known. These standard beads are prepared as follows: to the known amount of purified sodium fluoride in a platinum dish, add an adequate amount of the standard solution of uranyl nitrate, evaporate the mixture up to complete dryness and weigh the total. Make the mixture homogeneous in the mortar. From this prepare tablets of about 20 mg. each and reserve them. The uranium content of each tablet is known from its weight comparing with that of the total mixture. The following procedures of preparation of the standard beads go as in the case of the unknown samples.

Summary

The procedures to isolate uranium, which is coprecipitated with the iron hydroxide, are related. The minute quantity of uranium obtained is mixed with sodium fluoride and the fluorescent beads for the fluorometric determination are made from the mixture.

The writer is indebted to Professor Kenjiro Kimura for his generous advice and criticism in the course of this investigation.

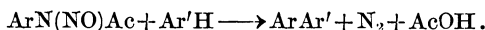
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Influence of Substituent Groups on Nuclear Reactivity in Formations of Substituted Biphenyls through Reactions of Aromatic Diazo and Cognate Compounds with Aromatic Liquids. I. The Nitro Group⁽¹⁾

By Osamu SIMAMURA, Takashi INUKAI and Motonori KANAZASHI

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Diazo hydroxides and *n*-nitrosoacetylarylamines decompose in an aromatic liquid to yield biphenyls according to the following formulae:



The preparative aspects of these reactions have recently been fully reviewed by Bachmann and Hoffman.⁽²⁾ As regards the mechanism of the formation of biaryls there has been amassed a considerable number of evidences to warrant the conclusion that the reaction takes place through a mechanism involving free aryl radicals which, having been produced by decomposition of diazo hydroxides or nitrosoacetylarylamines, react with aromatic compounds giving corresponding biphenyls. In support of the free radical mechanism is, among others, the observation that para and ortho substituted biphenyls are invariably formed in these reactions irrespective of the nature of the substituent groups, a fact which is unaccountable on the basis of the usual polar influences of substituents accepted as operative in the substitution by kationoid or anionoid reagents. Furthermore, it is striking that nitro group was found to exert its influence by activating the benzene nucleus to which it is attached in the substitution reaction by phenyl radical as was shown by the fact that nitrobiphenyls were obtained in a yield greater than methylbiphenyls in a competitive reaction in a mixture of nitrobenzene and toluene.⁽³⁾

With a view to further elucidating the nature of influences of substituent groups in the

substitution by the aryl radical a series of analytical investigations of these reactions has been undertaken in this laboratory, and the results obtained from the investigations on the influence of the nitro group are described in the present report. By determining the ratio in which biphenyl and three isomeric nitrobiphenyls were formed by the reactions of diazobenzene hydroxide and nitrosoacetanilide respectively in a mixture of benzene and nitrobenzene the reactivities of the various nuclear positions of nitrobenzene relative to that of benzene could approximately be estimated.

Results and Discussion

Careful fractionation of a reaction mixture from nitrosoacetanilide and nitrobenzene at 20° yielded a mixture of isomeric nitrobiphenyls in yields varying from 30 to 37% based on the nitrosoacetanilide utilized. From this mixture readily crystallizable *p*-nitrobiphenyl was separated as much as possible and weighed after recrystallization. As the isolation of the other isomerides turned out difficult, recourse was made to the estimation of *m*-nitrobiphenyl by titration with titanous chloride and subsequently with a bromide-bromate mixture according to the method, developed by Francis and Hill,⁽⁴⁾ with a slight modification. Thus, it was found that *m*-nitrobiphenyl constituted as much as 23% of the original mixture, and the *p*-nitrobiphenyl which was isolated as a pure specimen amounted to 17%. The remaining 60% were regarded as composed of the whole of the ortho isomeride formed and of that part of para isomeride which could not be isolated.

When nitrosoacetanilide was decomposed in a mixture of nitrobenzene and benzene (in a molar ratio of 1:30:60), biphenyl and nitrobiphenyls were obtained in yields of 4.6 and 19.7%, respectively, on the basis of the nitrosoacetanilide used. It was found by the same

(1) This paper contains materials presented at the 2nd and the 3rd annual meetings of the Chemical Society of Japan held in Tokyo, April 1949, and in Kyoto, April 1950, respectively.

(2) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 224.

(3) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, **1934**, 1797.

(4) A. W. Francis and A. J. Hill, *J. Am. Chem. Soc.*, **46**, 2498 (1924).

procedure as above that the nitrobiphenyl mixture consisted of 22% of the meta and of at least 19% of the para isomerides, the remaining 59% being made up of the ortho and para isomerides. The isomeric ratio from this competitive reaction agrees well with those obtained in the experiments with nitrobenzene as a sole component of the solvent. Taking the average of these figures and assuming the isomeric ratio to be $o:m:p = 58:23:19$, we estimate the relative reaction rate constants, which may be called reactivities, of the ortho, meta and para positions of the nitrobenzene nucleus to be 15, 5.8 and 9.8, respectively, relative to the rate constant at one position of the unsubstituted benzene nucleus taken as unity. Since the attack on the aromatic compound by the substituting entity, in whatever form it may react, is unimolecular with respect to the aromatic compound, the principle underlying our estimation is similar to that set forth by Ingold and Smith⁽⁵⁾ and therefore it need not be described here. In the above calculation the ortho-para ratio was assumed to be 58:19 on the basis of the amount of the *p*-nitrobiphenyl isolated as a pure specimen, and the actual ortho-para ratio must therefore be smaller. In one experiment, *o*-nitrobiphenyl amounting to 21% of the total yield of nitrobiphenyls was isolated from the mixture of nitrobiphenyls from which para isomeride had already been separated. If this figure, in place of 58%, is taken to express the amount of the ortho isomeride actually formed, and consequently 56, in place of 19%, that of the para isomeride, the reactivities of the ortho and para positions will be altered to 5.4 and 30, respectively. The true reactivity lies, therefore, between 5.4 and 15 for the ortho, and between 9.8 and 30 for the para positions.

From the reaction of diazotized aniline in the presence of aqueous sodium hydroxide with nitrobenzene at 10° there was obtained a mixture of nitrobiphenyls in a yield of 15% based on the aniline used. The percentages of the isomerides formed were estimated to be 46 for the ortho, 18 for the meta and 36% for the para compounds, and the value for the para isomeride being based on the amount isolated as a pure specimen, the figures for the ortho and para nitrobiphenyls are subject to the same uncertainty as in the case described above.

When diazotized aniline was decomposed in a mixture of nitrobenzene and benzene (in a molar ratio of 1:30:60), biphenyl and a mixture

of nitrobiphenyls were obtained in yields, based on the aniline used, of 5.2 and 12.7%, respectively. *m*-Nitrobiphenyl as titrated amounted to 20.3% of the total nitrobiphenyls and the para isomeride actually isolated to 34.4%. Assuming that the isomerides are formed in the ratio $o:m:p = 46:19:35$, the reactivities of the various positions of the nitrobenzene nucleus are estimated to be 6.6, 2.8 and 11 for the ortho, meta and para positions, respectively, relative to one position of the unsubstituted benzene nucleus.

Although ortho-para substitutions were observed in most cases of the formation of biaryls by the reaction under discussion, it was reported by some workers that the reaction between diazobenzene hydroxide and ethyl benzoate gave all of the possible isomeric ethyl biphenylcarboxylates,⁽⁶⁾ and that in the decomposition of 4-nitrosoacetaminobiphenyl in both chloro- and bromo-benzene the substitution by the biphenyl group took place at the meta as well as at the ortho and para positions in the halogenobenzene nucleus.⁽⁷⁾ The present results afford another example of the formation of the meta isomeride in a considerable quantity along with the ortho and para isomerides. In view of these facts together with those that will be later reported from this laboratory it seems that the concomitant formation of all three isomerides in these reactions is the general rule. It is significant too that even the meta position of nitrobenzene was found to be more reactive than the benzene nucleus itself towards the substituting agent formed by the decomposition of nitrosoacetanilide and diazobenzene hydroxide.

Experimental

Materials.—*n*-Nitrosoacetanilide was prepared according to Q. Fischer⁽⁸⁾ by introducing into a solution of acetanilide in glacial acetic acid nitrous fumes generated by reducing concentrated nitric acid with potato starch and by adding the dark green solution thus obtained to a large quantity of water. The precipitated nitrosoacetanilide was separated from the aqueous layer, washed several times with water and dried on a porous plate. Samples prepared in this way melted at 50–51° with decomposition. Benzene and nitrobenzene were purified by repeated fractionations through a Vigreux

(6) D. H. Hey, *J. Chem. Soc.*, **1934**, 1967.

(7) H. France, I. M. Heilbron and D. H. Hey *J. Chem. Soc.*, **1938**, 1364.

(8) O. Fischer, *Ber.*, **9**, 463 (1876).

(5) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, **1938**, 905.

column.

Determination of *m*-Nitrobiphenyl.—

The amount of *m*-nitrobiphenyl in a mixture of isomeric nitrobiphenyls was determined by titration with a standard titanous chloride solution and subsequently with a bromide-bromate mixture. The procedure adopted was essentially that of Francis and Hill.⁽⁴⁾ However, ethyl alcohol proposed by them as a solvent proved inadequate because it consumed bromine. After several experiments, it was found that glacial acetic acid which was refluxed with 2% of chromium trioxide and then twice distilled was a satisfactory solvent for the determination of nitrobiphenyls. The reduction was carried out in an atmosphere of carbon dioxide with boiling for fifteen minutes, and the bromination at 5 to 10°. Separate experiments with pure specimens of nitrobiphenyls showed that the number of bromine atoms taken up could be determined within the accuracy of 2%.

Decomposition of Nitrosoacetanilide.—

When nitrosoacetanilide (0.5 g.) was dissolved in 27 cc. of nitrobenzene at 20°, decomposition took place evolving nitrogen without a perceptible rise in temperature. A set of twenty reaction mixtures similar to the above was prepared and allowed to react simultaneously. After a few days, when the reaction had been completed, the reaction mixtures were combined and the nitrobenzene was removed under reduced pressure through a Vigreux column 30 cm. in length. The residue was subjected to further fractionation under reduced pressure, and 4.18 g. of a reddish-brown viscous oil passed over at 150 to 185° at 15 mm. of mercury. The oil deposited crystals of *p*-nitrobiphenyl, which on recrystallization from petroleum ether melted at 113° (yield 0.560 g.). The mother liquor of recrystallization and the remaining oil were combined and filtered through a column of activated alumina in order to remove a coloring matter. A further crop of *p*-nitrobiphenyl (47 mg.) was obtained by extracting the alumina with alcohol. The remainder was recovered as an oily mixture (3.05 g.), which was analyzed for the nitro group by titration with a standard titanous chloride and was found to contain only nitrobiphenyls. Subsequent titration with a bromide-bromate mixture showed that the mixture contained 28% of *m*-nitrobiphenyl.

In one experiment a fraction, which distilled after a substantial part of nitrobenzene had been removed, was reduced with tin and hydrochloric acid to remove nitrobenzene. Any traces of biphenyl which might have resulted from the dimerization of phenyl radicals were not detected.

The competitive reaction was accomplished by dissolving one gramme of nitrosoacetanilide in a mixture of 18.7 cc. of nitrobenzene and 32.7 cc. of benzene at 20°. Nine of such reaction mixtures were combined and worked up similarly to the experiment described above. That part of biphenyl which passed over with the vapor of nitrobenzene was recovered by converting the latter into aniline by treatment with tin and hydrochloric acid.

Decomposition of Diazobenzene Hydroxide.—

To a stirred mixture of 430 cc. of nitrobenzene and diazotized aniline prepared from 13 g. of aniline, 33 cc. of concentrated hydrochloric acid (d. 1.17), 10.5 g. of sodium nitrite and 26 cc. of water there was added dropwise a solution of 14.4 g. of sodium hydroxide in 75 cc. of water in the course of thirty minutes, the temperature being kept at 8-10°, and stirring was continued for further five hours. The product separated from the aqueous layer was worked up as before. In the competitive reaction a mixture of 215 cc. of nitrobenzene and 373 cc. of benzene was used for the diazotized aniline from 6.5 g. of aniline. Products from two of such reactions were combined and worked up.

Summary

The reactions of both *n*-nitrosoacetanilide and diazobenzene hydroxide with nitrobenzene give all three isomeric nitrobiphenyls, whereas the formation of only the ortho and para isomerides has been reported in the literature.⁽³⁾ All the nuclear positions of nitrobenzene are more reactive than that of benzene towards the substituting phenyl radical.

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Polymerization of Styrene in Heavy Alcohol and Heavy Benzene and the Same Reaction Catalyzed by Heavy Benzoyl Peroxide⁽¹⁾

By Toichi YOSIDA

(Received May 31, 1950)

The author has previously found⁽²⁾ that a certain amount of heavy alcohol was adhered to the polystyrene, which was prepared from styrene by heating its solution in heavy alcohol. In order to obtain some knowledge on the mechanism of this attachment of alcohol molecules to the molecules of polystyrene, the average number of alcohol molecules attached to each molecule of polystyrene has been examined in the present research. It was found to be one, the molecule being presumed to attach at the starting point of the chain molecule of polystyrene. At the same time it has been found that this number of alcohol molecules attached to each molecule of polystyrene decreases when benzoyl peroxide is added to the reaction mixture. These results suggest us that the alcohol molecules are expelled out of their place on the polystyrene molecule by benzoyl peroxide molecules, so that the latter can also attach to the chain molecule of polystyrene at its starting point. The experiment showed that this is actually the case. The polystyrene which was made from styrene in the presence of benzoyl peroxide labelled by heavy hydrogen atoms was found to contain a benzoate group which might be formed by the splitting of a molecule of benzoyl peroxide.

It was found further that the polystyrene contained no heavy hydrogen atoms, when it was prepared from styrene by heating its solution in heavy benzene and the resulted polymer was heated in vacuum at 100° for twenty hours. From this experimental result it can be concluded that no hydrogen atoms are exchanged between styrene and benzene when the former is polymerized in the solution of the latter.

Polymerization of Styrene in Heavy Alcohol

The experiment was at first carried out in the following way. A definite amount (1 cc.)

of styrene, which was purified directly before the experiment by distillation in vacuum, was sealed together with a definite amount (0.2 cc.) of heavy alcohol and various amount of benzoyl peroxide in an evacuated glass tube. The latter substance was added in order to obtain the polymer of various molecular weight. The heavy alcohol used for this experiment was prepared by mixing one volume of C_2D_5OD of 99.6% purity with five volumes of ordinary alcohol and the mixture was purified by the use of silver oxide until no silver mirror reaction was observed. After the sealed tube was heated for twenty hours at $120^\circ \pm 1^\circ$, the heavy alcohol was distilled off in vacuum and the remained polystyrene was dissolved in 5 cc. of purified benzene, in order to wash out the remaining alcohol. Then the benzene was similarly distilled off in vacuum and the remained polymer was heated in vacuum at 100° for 20 hours in order to expel the last trace of mechanically contained heavy alcohol as well as the other volatile substances such as the nonpolymerized styrene.

The larger part (about 0.6 g.) of the so purified polystyrene was then burnt in a stream of purified air and the excess density of the resulted water, which was carefully purified in a specially devised quartz apparatus, was determined by means of a small glass bouyancy balance. The limit of the error for the density determination was ± 1 p.p.m. The remaining part of the purified polystyrene was used for the determination of the molecular weight, which was carried out by the viscometric method. The specific viscosity η_{sp} of the solution in benzene of known concentration c expressed in mole/l. was measured by means of an Ostwald viscometer and the mean molecular weight $\bar{M}$ was calculated according to the Staudinger's relation:

$$\lim_{c \rightarrow 0} \eta_{sp}/c = K_m \bar{M}.$$

The constant K_m used for the calculation was determined by the osmometric method and found 1.2×10^{-4} when no benzoyl peroxide was added and 2.4×10^{-3} when benzoyl peroxide was added without regard to its quantity.

From these data we calculated the average

(1) Preliminarily reported in *J. Chem. Soc. Japan*, **68**, 31, 45 (1947). The delay of the publication of the detailed report was due to the War.

(2) this Bulletin, **16**, 125 (1941).

number of heavy alcohol molecules attached to each molecule of polystyrene, which is denoted by N in Table 1, as well as the average number of heavy alcohol molecules attached to each gram of polystyrene, which is denoted by N' in the last column of the table. When we compare these two figures it will easily be seen that the average number of the alcohol molecules attached to each molecule of polystyrene N remains satisfactorily constant without regard to the molecular weight of the latter, so long as any quantity of benzoyl peroxide is added to the reaction mixture, while the number of alcohol molecules attached to each gram of polystyrene N' remarkably increases as the molecular weight of the latter decreases. This result indicates that the alcohol molecules are not attached uniformly on the polystyrene molecule but at a certain definite point of it.

Table 1

Polymerization of Styrene in Heavy Alcohol
(Resulted polystyrene was heated in vacuum)

Experi- mental No.	Amount of benzoyl peroxide added, g.	Excess density of water, p.p.m.	Mean molecular weight of polystyrene, $\bar{M}$	N	$N' \times 10^{-6}$
1	0	3.0	54100	0.12	2.2
2	0	3.6	45600	0.12	2.6
3	0.005	7.2	12900	0.069	5.3
4	0.010	7.2	11400	0.059	5.1
5	0.020	9.6	8970	0.062	6.9
6	0.040	14.4	6240	0.064	10.2
7	0.040	15.3	5140	0.056	10.8
8	0.040	18.0	4570	0.059	12.9
9	0.100	21.1	3420	0.051	14.9

It will also be seen from Table 1 that the average number N of the alcohol molecules attached to each molecule of polystyrene definitely increases, when no benzoyl peroxide is added (see exp. No. 1 and 2). This result suggests to us that the point occupied by the alcohol molecule on the molecule of polystyrene can also be attached by the benzoyl peroxide molecule and the former is expelled out of the added place by the latter. The same result can also be seen more clearly from the experiments given in Table 2. In these experiments the polystyrene, which was prepared in heavy alcohol solution in the same way as above, was not heated in vacuum after the experiment. After it was dissolved in purified benzene and the latter was distilled off in vacuum at room temperature, however, the same procedure was repeated once more, because the experiments, which will be described later, showed that the polystyrene, which was prepared in heavy

benzene, was found almost completely free from heavy hydrogen, when the polymer was treated in the same way as above, so that the mechanically attached heavy alcohol could also be assumed to be completely removed in this way.

Table 2

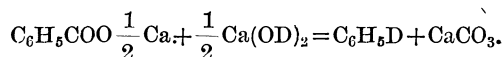
Polymerization of Styrene in Heavy Alcohol
(Resulted polystyrene was not heated in vacuum
but dried in vacuum at room temperature)

Experi- mental No.	Amount of benzoyl peroxide added, g.	Excess density of water, p.p.m.	Mean molecular weight of polystyrene, $\bar{M}$	N
1	0	25	60000	1.1
2	0	20	87400	1.2
3	0.005	13	22300	0.21
4	0.01	14	16000	0.16
5	0.04	33	6750	0.16
6	0.10	64	4250	0.19

When we compare the average number of alcohol molecules N attached to each molecule of polystyrene given in Table 1 and 2, we see that it is in the whole remarkably increased in the latter. This result can be accounted for by the assumption that some of the alcohol molecules which are chemically attached to the molecule of polystyrene are removed when the latter is heated in vacuum as it was the case in the experiments given in Table 1. But the more interesting fact which can be seen from Table 2 is that the number N becomes almost nearly unity, when no benzoyl peroxide is added to the reaction mixture (see exp. No. 1 and 2). From this result it may be concluded that an alcohol molecule is attached presumably at the starting point of the chain molecule of polystyrene, when the styrene is polymerized in alcoholic solution without adding benzoyl peroxide but the most part of such alcohol molecules is expelled out of its added place by the molecules of the benzoyl peroxide, when the latter substance is added to the reaction mixture.

Polymerization of Styrene in Heavy Benzene

The heavy benzene, benzene- d_1 , used in the present experiment was prepared by heating the mixture of calcium benzoate and calcium deuterioxide after the method of Morita⁽³⁾:



(3) N. Morita and T. Titani, this Bulletin, **10**, 557 (1935).

In each experiment one cc. of so prepared heavy benzene was sealed together with one cc. of purified styrene in a glass tube and heated at $120^\circ \pm 1^\circ$ for twenty hours. No benzoyl peroxide was added in some cases, while about 0.02 g. of it was added in other cases. After the heating, the content of the sealed tube was dissolved in five cc. of purified benzene. Then, in the first experiment (No. 1 in Table 3) the benzene was distilled off in vacuum and the remained polymer was heated in vacuum at 100° for five hours. In the second experiment the polymer, which remained after the distillation of benzene, was dissolved once more in benzene and then treated in the same way as in the first experiment. In the third experiment the content of the sealed tube was dissolved in benzene as in the case of the first experiment and the polymer which remained after the distillation of benzene was heated in vacuum at 100° for twenty hours. And in the last forth experiment the polymer was precipitated from its solution in benzene by the addition of purified alcohol and the same process was repeated two times. Then the precipitated polymer was heated in vacuum at 100° for twenty hours as in the case of the third experiment.

In every case the larger part of the purified polymer was burnt to water and its excess density was measured by a glass bouyancy balance. At the same time the remaining part of the polymer was used for the determination of mean molecular weight $\bar{M}$. And from these data the number of heavy benzene molecules, attached to each molecule of polystyrene was calculated. The figure N given in the last column of Table 3 represents this number.

Table 3

Polymerization of Styrene in Heavy Benzene

Experi- mental No.	Amount of benzoyl peroxide added, g.	Temperature and time of drying	Excess density of water, p.p.m.	Mean mole- cular weight of polymer, $\bar{M}$	N
1	0	100°C , 5hrs	7	55900	0.3
2	0	100°C , 5 "	7	50100	0.3
3	0.02	100°C , 20 "	-2	11700	0
4	0.02	100°C , 20 "	-3	12400	0

From the result given in Table 3 it may be concluded that the last trace of the heavy benzene can be expelled out of the polystyrene when the latter is heated in vacuum at 100° for twenty hours. This result is very interesting when it is compared with that of heavy alcohol shown in Table 1, where it was found that a certain amount of heavy alcohol remained in the polystyrene, even if the polymer was heated in vacuum at 100° for twenty hours, when it

was formed in the solution of heavy alcohol. The difference may be accounted for by the polar character of ethyl alcohol and the non-polar character of benzene. From the present result it can also be concluded that no hydrogen atom is exchanged between styrene and benzene when the former is polymerized in the solution of the latter.

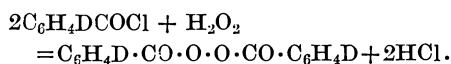
Polymerization of Styrene Catalyzed by Heavy Benzoyl Peroxide

The heavy benzoyl peroxide used in the present experiment was prepared in the following way.

At first benzene- d_1 was prepared in the same way as in the preceding research by heating the mixture of calcium benzoate and calcium deuterioxide. Then, the benzene- d_1 was converted into benzoyl- d_1 -chloride by the use of oxalyl chloride:



Heavy benzoyl peroxide was obtained by the action of hydrogen peroxide on this benzoyl- d_1 -chloride:



Theoretically speaking, the so obtained benzoyl peroxide, therefore, must contain two deuterium atoms in each molecule. But the isotopic analysis showed that this number was little larger than two, namely 2.32. The discrepancy may be accounted for by some side reactions (exchange reaction), which occurred in the first step of the reaction, viz. the preparation of heavy benzene, because its isotopic analysis showed a little larger deuterium content than the theoretical one.

In each case of the experiment, one cc. of styrene, which was purified directly before the experiment, was sealed together with 0.01 to 0.04 g. of heavy benzoyl peroxide in a glass tube and heated at $120^\circ \pm 1^\circ$ for twenty hours. After the heating, the content of the glass tube was dissolved in about five cc. of purified benzene and to this solution purified alcohol was carefully added until no more polystyrene was precipitated. Then the precipitated polystyrene was once more dissolved in benzene. In most cases this procedure was repeated from two to three times, in order to make the polystyrene free from the mechanically adhered benzoyl peroxide as completely as possible.

The larger part of the purified polystyrene was then burnt to water and its excess density

was determined by the use of a glass buoyancy balance. At the same time the remaining part of the polymer was used for the determination of the mean molecular weight $\bar{M}$, in the same way as described in the preceding research. The result of the experiment is shown in Table 4, where the excess density of water given in brackets is the corrected one, which was calculated from the directly observed one under the assumption that exactly two deuterium atoms were contained in each molecule of benzoyl peroxide and the number N given in the last column represents the average number of deuterium atoms contained in each molecule of the polystyrene, being calculated by the use of the above mentioned corrected value of excess density. But as this number is approximately unity, it may be concluded that just half a molecule of benzoyl peroxide is attached to each molecule of polystyrene, when it is taken into account that each molecule of benzoyl peroxide contains two deuterium atoms.

(4) According to the literatures, which have recently fallen into the hands of the author, it became known to him that the same conclusion was achieved by many other authors. But as many of these researches were published during the War, they did not come to the author's knowledge at the time, when the present research was made.

Table 4
Polymerization of Styrene Catalyzed
by Heavy Benzoyl Peroxide

Experi- mental No.	Amount of benzoyl peroxide added, g.	Number of reprecipi- tation with alcohol	Excess density of water, p.p.m.	Mean molecular weight of polystyrene, $\bar{M}$	N
1	0.01	1	112(96)	19000	1.3
2	0.01	2	114(98)	17700	1.2
3	0.01	3	113(97)	19000	1.3
4	0.04	2	326(280)	8200	1.6

It follows therefore that the molecule of benzoyl peroxide is split into two equal parts and the so formed free radical $C_6H_5 \cdot CO \cdot O \cdot$ is attached to the starting point of the chain molecule of polystyrene.⁽⁴⁾

The author wishes to express his sincere thanks to Prof. T. Titani, who suggested this research and helped in the publication. A part of the cost of the present research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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The Effect of Electrostatic Field on the Polymerization of Styrene⁽¹⁾

By Toshizo TITANI and Gisuke MESITUKA

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It has been found previously by Yosida and one of the authors that no exchange reaction of hydrogen atoms occurs during the chain polymerization of styrene in its solution in heavy alcohol or heavy benzene.⁽²⁾ It has been found further that a half of the molecule of benzoyl peroxide is attached at the starting point of the chain molecule of polystyrene, when it is prepared by the thermal polymerization of styrene in the presence of benzoyl peroxide as a polymerizing catalyst.⁽²⁾ The same result has also been reported by many other authors.⁽³⁾

It is also a well known fact that polystyrene can easily be decomposed by heating it at a comparatively low temperature and at this thermal decomposition it gives mainly unaltered monomer molecules of styrene. This fact suggests us that the bond linking the monomer molecules together in the chain is much weaker than the $\text{CH}-\text{CH}_2$ bond in each monomer molecule, because otherwise the chain polymer may give irregular decomposition products at its thermal decomposition just as in the case of the thermal cracking of long chain hydrocarbons.

From these experimental results we came to the conclusion that the chain molecule of

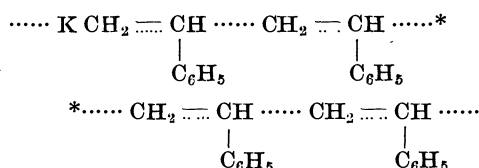
(1) Preliminarily reported in Scientific Papers from the Osaka University, No. 4, 1949.

(2) T. Yosida and T. Titani, this Bulletin **16**, 125 (1941); T. Yosida, *ibid.* **23**, 209 (1950).

(3) B. E. Tate, *J. Am. Chem. Soc.*, **65**, 517 (1943); P. D. Bartlett and J. Cohen, *ibid.*, **65**, 543 (1943); A. T. Blomquist, J. R. Johnson and H. J. Sykes, *ibid.*, **65**, 2446 (1943);

H. F. Pfann, F. J. Salley and H. Mark, *ibid.*, **66**, 984 (1944); C. C. Price, R. W. Kell and E. Krebs, *ibid.*, **68**, 1686 (1946).

polystyrene may have a nature of a sort of free radical. The back bone chain of the molecule is linked together by incomplete single bonds $\cdots$ and incomplete double bonds $\cdots$ alternatively and at the starting point of the chain a fraction K of the molecule of the polymerizing catalyst is attached, so that at the end of the chain a weak free valence bond remains, as may be shown by the formula:



By the incomplete single bond we mean such a bond that is more or less weaker than a normal single bond but is not necessarily a half bond. Similarly the incomplete double bond represents such a bond that is to a certain extent weaker than a normal double bond but is not necessarily a one and a half bond. Moreover, the fraction K of the catalyst molecule may be a free oxygen molecule dissolved in the sample or adsorbed on the wall of the reaction vessel or a fraction of the molecule of some unknown compounds unconsciously contained or formed in the reaction system, when no polymerizing catalysts are intentionally added, as it is the case for the so-called thermal polymerization. The former assumption that the free oxygen molecule plays the role of the polymerizing catalyst is so far plausible as the oxygen molecule having a nature of a free radical and having two non-paired electrons in a molecule. But in any case at the other end of the chain molecule a weak free valence bond always remains, so that the chain polymer must have a nature of a sort of free radical.⁽⁴⁾ However, the free radical nature of the so formed chain molecule is largely minimized through the resonance between the free valence bond remaining at the end of the chain and many benzene nuclei attached to the chain, because the back bone of the chain is linked together through the conjugation of many incomplete double bonds. The situation somewhat resembles to the case of the triphenyl-methyl, whose molecule is stabilized through the resonance between the

free valence bond which remained at the central carbon atom and three benzene nuclei attached to this carbon atom. In other words, the larger part of the cloud of the non-paired electron remaining at the end of the polymer chain is absorbed by many benzene nuclei attached to the chain, through a sort of conjugated double bond system. And as a result of this polarization of the electron cloud, the end of the chain molecule must be positively while the body of the molecule negatively polarized. Accordingly, when the degree of this polarization reaches a certain extent, the positively polarized end of the molecule must be pulled into the negatively polarized clew-formed body of the molecule and in this way the growth of the chain is stopped.

When this is the case, it may be possible to increase the length of the chain by applying an electrostatic field on the growing chain of the polystyrene, so as to pull out the hiding end of the chain out of the clew-formed molecular body and thus subject to further reaction. The present experiments showed that this is actually the case. The molecular weight of polystyrene, which was prepared by heating liquid styrene at 120° for three to four hours under the influence of the electrostatic field of 8,000 to 9,000 volt per cm. was found about 35 to 36% larger than that of the polystyrene formed under the same conditions but without the electric field.

The experiment was carried out in a small glass cell with a glass stopper, through which two platinum electrodes of the same size 0.9×0.9 cm. were introduced. The distance between the electrodes in the cell was 0.8 cm. Two such cells were constructed with due precautions to make their size and form as equal as possible. In each experiment, both cells were charged with same quantities (2 cc.) of purified styrene, and were placed side by side in an electrically heated air thermostat, the temperature of which was kept constant at 120° ± 2° throughout the experiment. To the electrodes of one cell an electrostatic field generated by a vacuum tube rectifier was applied, while the other cell served as a control test. Thus, two equal portions of the same styrene were separately but simultaneously heated at the same temperature, the one being under the influence of the electric field, while the other not. After three or four hours, the experiment was stopped, and the contents of the cells were separately dissolved in 20 cc. of purified benzene. Ten cc. each of the solutions were then subjected to the distillation in vacuum to make the polystyrene completely free from the non-polymerized monomeric

(4) The possibility, that the chain starts without the help of any polymerizing catalyst, can not necessarily be excluded and in this case the resulted chain polymer must have a nature of biradical, having a free valence bond not only at the end but also at the head of the molecule. But as the following discussion is little influenced by this situation, we assume here that the chain polymer has a structure of monoradical.

styrene. The portions of the polystyrene were dissolved once more in a weighted amount of purified benzene and the molecular weight of the polymer was determined by measuring the osmotic pressure of this benzene solution using a denitrificated collodion membrane as a semipermeable septum. The results of the experiments are shown in Table 1, from which it can be seen that not only the degree but also the quantities of polymerization somewhat increase under the influence of the electrostatic field.

Table 1
Polymerization of Styrene under the
Influence of Electrostatic Field

No. of experi- ment	Experimental conditions		Polymerized quantities, %	Molecular weight of polymer
	Voltage applied, per cm.	Dura- tion, hrs.		
3	0	4	29.4	84,000
	9,000	4	33.0	114,000
4	0	3	22.0	85,000
	8,000	3	25.5	115,000

From the present results the same effect may also be expected for the other sorts of vinyl derivatives of the form $R-CH=CH_2$, so long as the side chain radical R has an unsaturated nature, for examples, $-COOH$, $-COOCH_3$, $-OOC\cdot CH_3$, $-Cl$, $-Br$, $-CN$ etc. Such experiments are now going on in our laboratory.

We are deeply indebted to Prof. J. Horiuti of Hokkaido University for his kind and valuable suggestions and to Prof. R. Tsuchida as well as the referee of this Bulletin for their kind discussion for the present research. Our thanks are also due to Mr. Y. Yoshikawa, who helped us in the construction of the vacuum-tube rectifier. A part of the cost of the present research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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The Increase of the Mean Molecular Weight of Polystyrene under the Influence of the Electrostatic Field

By Gisuke MESITUKA

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In the preceding research⁽¹⁾ it has been found that not only the degree but also the quantities of polymerization increases when an electrostatic field is applied during the thermal polymerization of styrene. And this result has been accounted for by the assumption that the positively polarized end of the chain molecule of polystyrene is pulled out of its negatively polarized clew-formed body under the effect of the electrostatic field and in this way the rate of chain growth viz. the rate of addition of the monomer molecule to the growing end of the polymer molecule increases. But if this is the only effect of the electric field, the degree and the quantities of polymerization must increase at the same rate, so long as the rate of formation of the polymerization nuclei may not be greatly influenced by the electric field. As a matter of fact, however, it has been found in the preceding research that the rate of

increase in the degree of polymerization is much larger than that in the quantities of polymerization. This result suggests to us that not only the rate of chain growth viz. the rate of addition of the monomer molecule to the polymer molecule but also the rate of coupling viz. the rate of combination of the polymer molecules with each other must increase under the influence of the electrostatic field. With this presumption we applied in the present research an electrostatic field on the solution of the already polymerized polystyrene and actually found that the mean molecular weight of the latter is remarkably increased by this process.

The apparatus used is generally the same as that was used in the preceding experiment except the form and construction of the electrodes. Instead of the square platinum electrodes, which were introduced vertically into the cell in the preceding experiment, two circular electrodes made of pure nickel were

(1) T. Titani and G. Mesituka, this Bulletin, **23**, 212 (1950).

introduced horizontally into the cell as is shown in Fig. 1. The diameter of the electrodes was

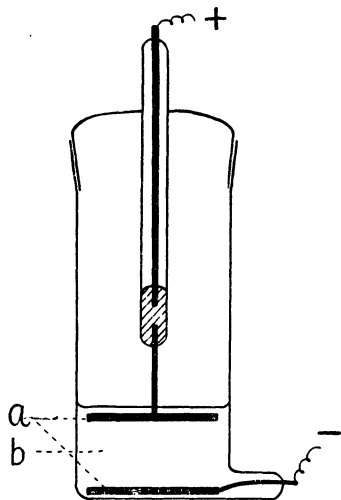


Fig. 1.—Reaction cell.
a, electrode; b, solution.

made a little smaller than that of the inner diameter of the cell (*i.e.* 2 cm.) and the vertical distance of the electrodes in the cell was about 1 cm.

In each experiment the cell was charged with a solution of polystyrene in benzene, which was made by dissolving 0.3 g. of polystyrene in 3 cc. of purified benzene. The meniscus of the solution in the cell was adjusted a little higher than the upper surface of the upper electrode. The charged cell was then placed in an electrically heated air-thermostat and the outer ends of the electrodes were connected with the poles of a vacuum tube rectifier. In this way an electrostatic field of various strength was applied to the solution between the electrodes in the cell at a constant temperature. The temperature of the thermostat was kept constant at $60.0^\circ \pm 0.5^\circ$ throughout the whole series of experiments. After 50 hours the experiment was stopped and the solution in the cell was poured out. A part of the so treated solution was then used for the determination of molecular weight, while the residual part was used for the determination of its viscosity. The determination of the molecular weight was carried out by the osmometric method in the same way as in the preceding research while that of the viscosity by means of an Ostwald's viscosimeter. The results of the experiments are summarized in Table 1, where the quantities with suffix 0 are referred to the original polymer, which was used in the whole series of the experiments.

Table 1

Effect of the Electrostatic Field of Various Strength on the Degree of Polymerization of Polystyrene in Benzene Solution

Expt. No.	Experimental conditions			Mean molecular weight, $\bar{M}$	$\frac{\bar{M}}{\bar{M}_0}$	Viscosity of solution, η	$\frac{\eta}{\eta_0}$
	Voltage applied, volt/cm.	Temperature, $^\circ\text{C}$	Duration, hrs.				
1	0	Room temp.	0	148,000	1.00	0.115	1.00
2	500	60	50	150,000	1.02	0.115	1.00
3	1,000	60	50	160,000	1.08	0.114	0.99
4	2,000	60	50	164,000	1.11	0.114	0.99
5	4,000	60	50	169,000	1.14	0.114	0.99
6	8,000	60	50	240,000	1.62	0.116	1.01

It will be seen from the Table that the mean molecular weight $\bar{M}$ of the polystyrene really increases with the increasing strength of the applied electrostatic field. But quite unexpectedly the viscosity of the solution was found to remain almost constant notwithstanding the increasing molecular weight of the polymer. This interesting result may however be accounted for at least qualitatively in the following way. It has been assumed in the previous communication that a sort of residual valency remains at the end of the chain molecule of the polymer even in its stabilized state. If this is actually the case, the viscosity of the polymer solution will not only be affected by the size of the molecule, as so far being assumed, but also by the strength of the residual valency remaining at the end of each polymer molecule. The viscosity of the solution may increase with the increasing strength of the residual valency just as with the increasing size of the molecule. But as the strength of the residual valency clearly decreases when the size of the molecule increases through the coupling of the molecules under the influence of the electric field, both the effects on the viscosity of the solution may to some extent mutually be cancelled. This may be the reason why the viscosity of the solution does not change so much even when the mean molecular weight of the polymer remarkably increases under the effect of the electrostatic field.

The author wishes to express his sincere thanks to Prof. T. Titani for his interest and encouragement which he showed in the present research. The author is also indebted to Miss K. Oda for her kind help throughout the experiment. A part of the cost of the present research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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Étude des matières en suspension dans l'eau naturelle. I

La construction d'un turbidimètre portatif et la corrélation entre la turbidité et la quantité des matières en suspension dans l'eau

par Takahisa HANYA

(Reçu, le 14 juin 1950)

Introduction

La turbidité de l'eau naturelle est variable selon sa pureté; il est à peu près impossible de l'observer à l'état de pureté absolue excepté dans le laboratoire. L'eau naturelle contient toujours des êtres vivants ou des poussières minérales et organiques. Le rôle de ces matières en suspension est très intéressant au point de vue géochimique ainsi qu'au point de vue de l'industrie de la pêche.

A présent, on emploie généralement, pour préciser la turbidité le moyen du fameux appareil de Secchi. Mais il est évident que par ce moyen nous ne pouvons poursuivre en détail la turbidité et la nature des matières suspendues. En recherchant en détail la turbidité dans la mer ou dans les lacs etc., il faut l'examiner à divers points et à diverses profondeurs. De plus, nous devons l'examiner le plus vite possible, parce que la nature des matières suspendues de l'eau prise dans une bouteille ne se trouve pas longtemps au même état que dans la nature.

Nous avons donc construit un turbidimètre portatif pour suffire à nos besoins. Nous parlerons d'abord brièvement de sa structure et puis de la corrélation entre la quantité des matières suspendues et le degré de la turbidité mesurée par cet appareil.

Construction de turbidimètre et son opération

(1) Le mode principal de la mesure.—

La turbidité se mesure en général dans le laboratoire par l'intensité de la lumière diffusée par des matières suspendues ou qui pénètre à travers l'eau trouble à examiner.^{(1) (2) (3)} Nous avons profité de ce dernier mode.

Une part de la lumière de la source S atteint la cellule photoélectrique (E_A) et l'autre la (E_B)

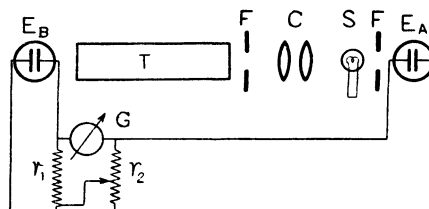


Figure 1.— E_A et E_B , cellules photoélectriques; T, tube d'eau; F, fente; S, source de lumière; C, collimateur; G, galvanomètre; r_1 , résistance fixée 120 ohm; r_2 , résistance variable 120 ohm.

en passant le tube d'eau. La proportion de l'intensité de la lumière E_B/E_A se mesure potentiométriquement par la zéro-méthode.

(2) Le mode opératoire et la calculation:

(a).—On remplit le tube de l'eau pure et on mesure la proportion

$$r_0 = E_B/E_A.$$

(b).—En suite, on le remplit de l'eau naturelle à examiner et on mesure la proportion

$$r = E_B/E_A.$$

(c).—Le degré de la turbidité, $\Delta\lambda$, se calcule par la formule suivante.

$$\Delta\lambda = \frac{2.303}{l} \cdot \log \frac{r_0}{r}$$

(l : longueur du tube d'eau)

(3) La signification de $\Delta\lambda$ (coefficient d'extinction).—Au cas de solution colorée dans laquelle la loi de Lambert-Beer s'applique, la valeur de $\Delta\lambda$ qui se calcule ainsi est indépendante de la structure de l'appareil et s'appelle le coefficient d'extinction de la solution colorée. Au contraire, dans le cas d'eau trouble, $\Delta\lambda$ varie à la même turbidité, selon la structure de l'appareil; $\Delta\lambda$ n'a pas de signification exactement physique. Mais nous prenons pour plus de commodité comme unité de la turbidité ce que nous allons nommer "le coefficient

(1) R. Bowling Barnes et Charles R. Stock, *Anal. Chem.*, **21**, 181-4 (1949).

(2) H. P. Kortschak, *Anal. Chem.*, **19**, 692 (1947).

(3) M. Mukai, *Journal of the Meteorological Society of Japan*, **11**, **19**, 146 (1941).

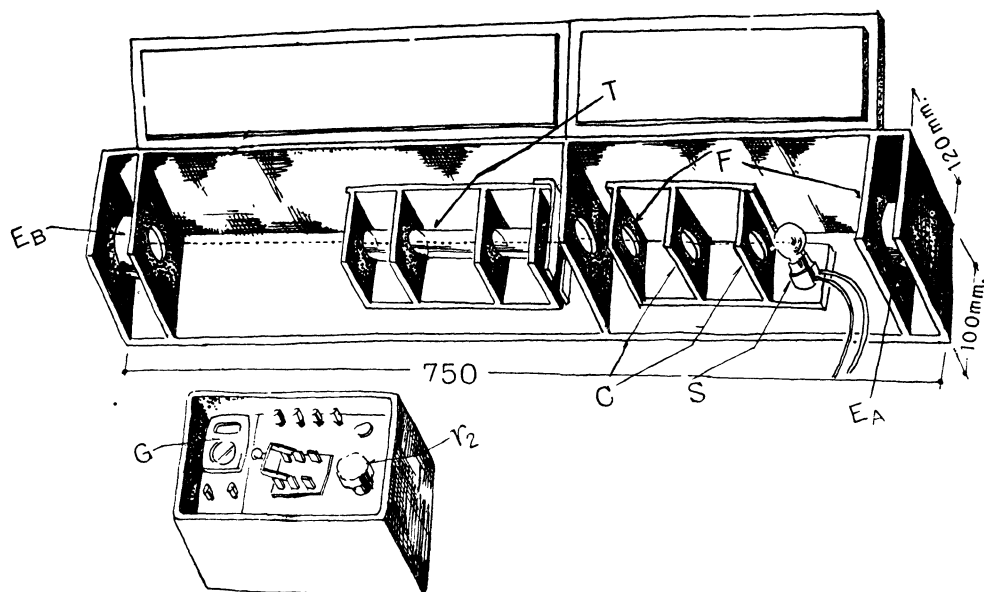


Figure 2 a.—Structure de turbidimètre.

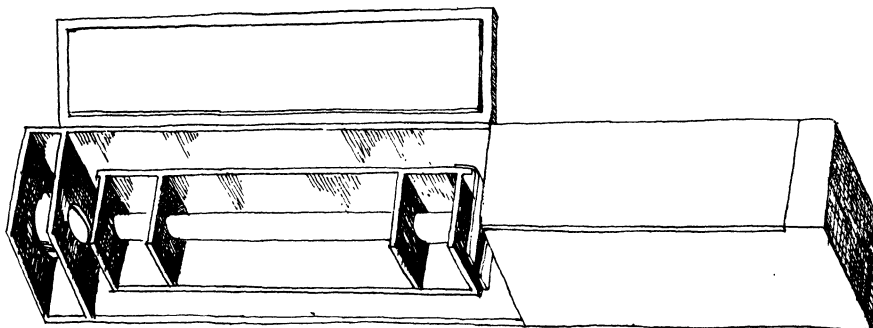


Figure 2 b.

d'extinction" de l'eau trouble. La description à suivre en montrera la commodité.

Correlation entre $\Delta\lambda$ et la quantité des matières suspendues

Un des buts principaux de notre mesure de la turbidité est d'estimer la quantité des matières suspendues dans l'eau naturelle. Naturellement comme le montrent beaucoup d'expériences, il n'y a pas de relation simple entre la turbidité et la quantité.⁽⁴⁾ Mais, il est très important pour avancer notre recherche de connaître cette relation dans le cas où la nature des matières suspendues est claire.

Nous avons donc d'abord poursuivre cette relation dans la suspension des poussières de verre de silice, parce qu'il est à peine soluble dans l'eau et que leur dimension est assez facilement déterminée, par la loi de Stokes, en

mesurant leur vitesse de sédimentation.

Nous pulvérisons aussi finement que possible du verre de silice dans un mortier d'agate, comme on fait dans le cas d'analyse de silicate. Ces poussières se composent de diverses dimensions. Nous en avons donc choisi par le moyen de lavage de cinq sortes dont les distributions de dimension sont montrées à la figure 3.

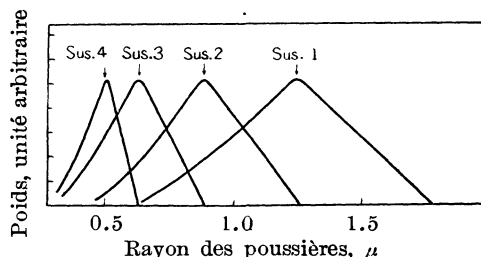


Figure 3.—Distributions des dimensions des poussières de verre de silice. Rayon des poussières à la maximum quantité: Suspension 1, 1.2₆; 2, 0.8₉; 3, 0.6₃; 4, 0.5₁; 5 & 5', 0.5>.

(4) Bechhold und Hebler, *Kolloid Z.*, 31, 70 (1922).

Nous avons déterminé $\Delta\lambda$ de ces cinq sortes de suspensions aux diverses concentrations avec cet appareil de deux manières, en nous servant de deux sortes de tubes. Au premier cas ($\Delta\lambda_{40}$), nous avons employé un tube de 2.8 cm. de diamètre et 40 cm. de long, et l'avons mis à la place montrée à la figure 2 b; Au second cas ($\Delta\lambda_{20}$), un tube de 2.0 cm. de diamètre et 20 cm. de long et à la place montrée à la figure 2 a.

Tableau 1 montre les valeurs de $\Delta\lambda_{40}$ et $\Delta\lambda_{20}$ des suspensions. Nous pourrions exprimer en général la corrélation entre $\Delta\lambda$ et C (quantité de verre de silice milligramme par litre) par la série des formules suivantes.

$$\log nC = m \log \Delta\lambda \quad (1)$$

(unité de $\Delta\lambda = 10^{-3} \text{ cm.}^{-1}$)

où

Suspension		$\Delta\lambda_{40}$		$\Delta\lambda_{20}$	
		m	n	m	n
1	:	1.28	2.63	1.13	8.12
"	2	1.22	3.00	1.11	8.70
"	3	1.20	2.85	1.10	7.08
"	4	1.10	2.48	—	—
"	5	1.08	1.63	—	—
"	5'	—	—	1.05	5.00

Cette équation (1) correspond à

Tableau 1

Suspension	C , mg./l.	$\Delta\lambda_{40}$, 10^{-3} , cm.^{-1}	$\Delta\lambda_{20}$, 10^{-3} , cm.^{-1}	$C_{\Delta\lambda_{40}}$, mg./l.	$C_{\Delta\lambda_{20}}$, mg./l.	$C_{\Delta\lambda_{40}} - C$, mg./l.	$C_{\Delta\lambda_{20}} - C$, mg./l.
1	12.6	15.5	60.8	12.6	12.6	0.0	0.0
	6.3	8.7	33.3	5.9	6.5	-0.4	+0.2
	3.2	5.3	18.1	3.2	3.2	0.0	0.0
	1.6	3.1	9.2	1.6	1.5	0.0	-0.1
2	30.8	39.7	147	29.9	29.5	-0.9	-1.3
	7.7	13.1	48.3	7.8	8.2	+0.1	+0.5
	3.6	7.1	23.9	3.7	3.9	-0.2	0.0
	1.9	4.2	13.5	1.9	2.1	0.0	+0.2
	1.0	2.7	6.6	1.1	0.9	+0.1	-0.1
3	20.5	29.5	93.9	20.4	20.6	-0.1	+0.1
	6.8	12.0	33.0	7.0	6.6	+0.2	-0.2
	3.4	6.7	17.9	3.5	3.3	+0.1	-0.1
	1.7	3.7	9.5	1.7	1.8	0.0	+0.1
4	13.9	25.7	—	14.3	—	+0.4	—
	9.8	18.0	—	9.5	—	-0.3	—
	6.9	13.3	—	6.7	—	-0.2	—
	4.9	9.7	—	5.0	—	+0.1	—
	3.5	7.0	—	3.5	—	0.0	—
	2.4	5.2	—	2.5	—	+0.1	—
5	19.3	24.5	—	19.5	—	+0.2	—
	9.7	12.8	—	9.7	—	0.0	—
	4.8	6.6	—	4.7	—	-0.1	—
5'	20.5	—	85.4	—	20.1	—	-0.4
	10.3	—	43.3	—	10.3	—	0.0
	5.1	—	22.3	—	5.3	—	+0.2
	2.6	—	12.7	—	2.6	—	0.0
	1.3	—	6.0	—	1.3	—	0.0

C : concentration des poussières de verre de silice déterminée par l'analyse gravimétrique.

$C_{\Delta\lambda_{40}}$: concentration donnée par l'équation (1) et par $\Delta\lambda_{40}$.

$C_{\Delta\lambda_{20}}$: concentration donnée par l'équation (1) et par $\Delta\lambda_{20}$.

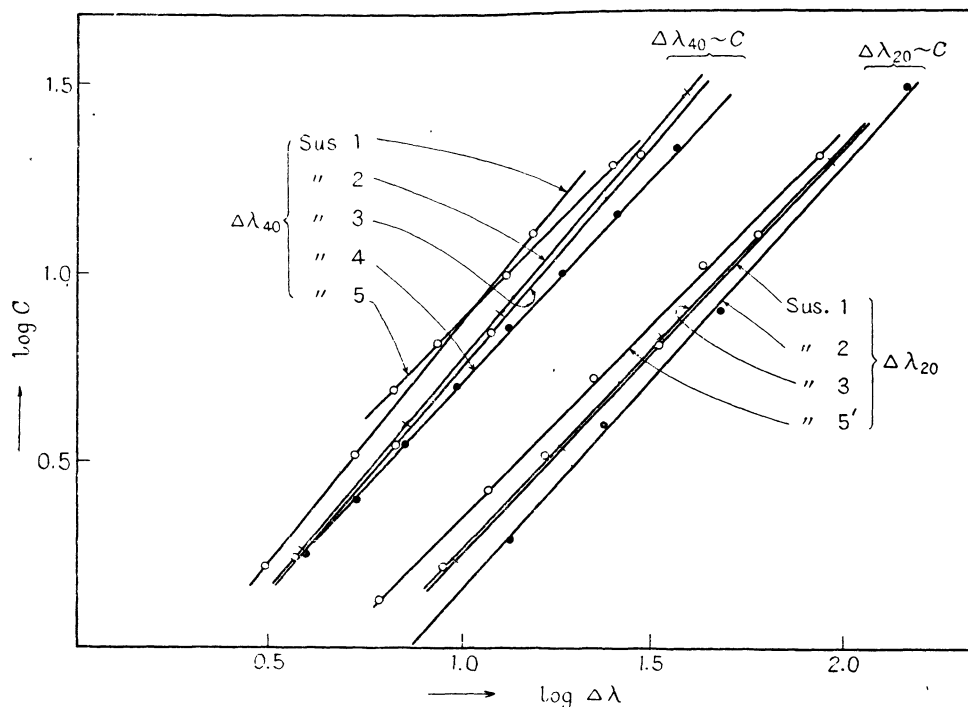


Figure 4.

$$C = p \Delta\lambda$$

dans la solution colorée où s'applique la loi de Lambert-Beer, en prenant respectivement p , C , et $\Delta\lambda$ pour le constant, la concentration et le coefficient d'extinction.

Nous allons montrer pourquoi nous avons déterminé la turbidité par les deux manières en employant les deux sortes de tubes. Il est sans doute désirable pour nous de déterminer la turbidité de l'eau naturelle d'une quantité aussi petite que possible; nous l'avons donc déterminé en employant diverses sortes de longueur de tubes, et trouvé que le tube de 20 cm. de long est la plus convenable pour notre détermination par cet appareil. Nous avons aussi un espoir de connaître jusqu'à un certain point la nature des matières suspendues dans l'eau naturelle en déterminant en même temps la turbidité par les dites deux manières et en comparant les valeurs de $\Delta\lambda_{40}$ et $\Delta\lambda_{20}$. C'est la raison pour laquelle nous avons décrit en détail la corrélation entre la quantité des matières suspendues et la turbidité donnée par ces deux manières. Les descriptions ci-dessus serviront à la compréhension des expériences que nous allons montrer dans une série des mémoires à suivre.

Resumé

Nous avons de nouveau construit un turbidimètre portatif par lequel nous pouvons déterminer sur place plus exactement et plus promptement que par tout autre appareil jusqu'ici construit au Japon la turbidité de beaucoup d'échantillons de l'eau naturelle un peu trouble et en petite quantité.

Nous pouvons exprimer la corrélation entre la quantité des matières suspendues et la turbidité donnée par cet appareil par le type d'équation suivante.

$$\log nC = m \log \Delta\lambda$$

En terminant ce compte-rendu de nos recherches, nous avons l'honneur d'exprimer nos sincères remerciements à M. M. les Professeurs K. Sugawara et R. Ueda et à Docteur A. Azuma pour les aimables et très utiles conseils et surtout nous ne pouvons que rendre nos profondes grâces à M. T. Asai qui a eu la bonté de nous aider en chargeant de la fabrication de cet appareil qui exige des soins à la fois minutieux et accablants

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Researches on the Polarographic Diffusion Current. I. Criticism of the Ilkovič Theory and Theoretical Revision of the Ilkovič Equation

By Tomihito KAMBARA, Makoto SUZUKI and Isamu TACHI

(Received June 23, 1950)

Introduction

The widely known Ilkovič equation representing the diffusion current at the dropping mercury electrode was first derived by D. Ilkovič⁽¹⁾ and later by MacGillavry and Rideal⁽²⁾ and by Stackelberg⁽³⁾; they obtained the same result, although each of them treated this problem in a different manner. Thus derived Ilkovič equation has been examined experimentally in several manners and it is proved that in many features this equation

shows an excellent harmony with the observed facts. Recently, however, it has been pointed out by McKenzie⁽⁴⁾ that the oscillographic investigation of the current-time curves during one drop-life gives a considerable deviation between the theoretical predictions and the experimental observations. Upon examining some fundamental postulates underlying the Ilkovič theory, we have reached to the conclusion that the ignorance of the curvature of mercury drop is not legitimate and that the Ilkovič theory should be revised to some extent.

In this paper the short derivation of Ilkovič equation will be shown in order to criticize

(1) D. Ilkovič, *Collection Czech. Chem. Commun.*, **6**, 498 (1934).

(2) D. MacGillavry and E. K. Rideal, *Rec. trav. chim. Pays-Bas*, **56**, 1013 (1937).

(3) M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

(4) H. A. McKenzie, *J. Am. Chem. Soc.*, **70**, 3147 (1948).

the theory and then our revised theoretical treatment will be described comparing with the old one.

Derivation and Criticism of the Ilkovič Theory

Since in the ordinary polarographic electrolysis an excess amount of indifferent electrolyte is added to the solution to be electrolyzed, the depolarizer is obliged to reach to the dropping electrode surface only by diffusion. Thus the depolarizer is exhausted near the cathode surface and a diffusion layer surrounding the dropping electrode is established. Ilkovič has assumed that the thickness of the diffusion layer should be very small compared with the radius of the mercury drop, and that the movement of depolarizer is expressed by the first and the second laws of Fick; *i. e.*,

$$dn = -D \cdot q \cdot \frac{\partial C}{\partial x} \cdot dt \quad (1)$$

and

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (2)$$

where C is concentration of the depolarizer in mol per cc., x , distance from the dropping electrode surface in cm., t , time in sec., D , diffusion constant of the depolarizer in cm.² per sec. and dn , the amount of the depolarizer which penetrates the cross-section q during the time dt .

Then it is considered that the diffusion of the depolarizer is a unidimensional problem. The boundary conditions are as follows:

$$\left. \begin{array}{l} C = {}^*C \dots \text{when } x > 0, \quad t = 0 \\ C = {}^\circ C \dots \text{when } x = 0, \quad t > 0 \end{array} \right\} \quad (3)$$

where ${}^*C$ and ${}^\circ C$ are the concentration in the bulk of the solution and at the electrode surface, respectively. Hence Eq. (2) can be integrated and the result is

$$C = {}^\circ C + ({}^*C - {}^\circ C) \cdot H\left(\frac{x}{2\sqrt{Dt}}\right), \quad (4)$$

where

$$H(S) = \frac{2}{\sqrt{\pi}} \int_0^S e^{-\alpha^2} \cdot d\alpha.$$

The concentration gradient at the cathode surface ($x=0$) can be expressed as follows:

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{{}^*C - {}^\circ C}{\sqrt{\pi Dt}} = \frac{{}^*C - {}^\circ C}{\delta_1} \quad (5)$$

$$\delta_1 = \sqrt{\pi Dt}, \quad (6)$$

where δ_1 is the differential thickness of the diffusion layer (see Fig. 1).

From Eqs. (1), (5) and (6), the total amount of the depolarizer transferred to the electrode surface by diffusion during the time interval from $t=0$ to $t=t$ is shown to be

$$\begin{aligned} -\int_{t=0}^t \frac{dn}{dt} dt &= \int_0^t D \cdot q \cdot \frac{{}^*C - {}^\circ C}{\delta_1} \cdot dt \\ &= \int_0^t \frac{D \cdot q \cdot ({}^*C - {}^\circ C)}{\sqrt{\pi Dt}} \cdot dt \\ &= \frac{1}{\pi} \left\{ 2q ({}^*C - {}^\circ C) \sqrt{\pi Dt} \right\} \end{aligned}$$

and accordingly

$$\frac{2}{\pi D} \cdot q \cdot \delta_1 = \int_0^t \frac{q}{\delta_1} dt. \quad (7)$$

This equation, which should be called the Stackelberg's integral equation, represents that the differential thickness of the diffusion layer at the time t depends not only on the total amount which has reached the electrode surface in the whole time elapsed after the diffusion has begun, but also on the surface area. Stackelberg considered an integral thickness of the diffusion layer, Δ_1 , which would exist if there were a linear fall of the concentration. The differential and integral thickness of the diffusion layer are related to each other, as shown in Fig. 1, by the equation

$$4\delta_1 = \pi \Delta_1. \quad (8)$$

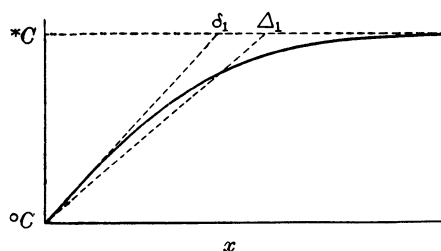


Fig. 1.—Schematic representation of the differential and integral thickness of the diffusion layer at a plane electrode.

Now at the dropping electrode, the volume and also the surface area of mercury drop increase with the time elapsed after the formation of the drop has commenced. Ilkovič has assumed a linear increase in the volume of the drop with time, *i. e.*,

$$\frac{4}{3} \pi \cdot r_1^3 = \frac{m_1}{d} \cdot t, \quad (9)$$

where r_1 is the radius of the drop considered as a sphere at the time t , and m_1 is the rate of flow of mercury from the capillary in g. per sec., and $d=13.6$ is the specific gravity of mercury. Hence the surface area of mercury drop is given by

$$q = 4\pi r_1^2 = 4\pi \left(\frac{3m_1}{4\pi d} \right)^{2/3} \cdot t^{2/3}. \quad (10)$$

If this relation is inserted into Eq. (7), and the equation thus obtained is solved, δ_1 , the thickness of the diffusion layer around the dropping mercury electrode, is shown to be

$$\delta_1 = \sqrt{\frac{3}{7} \pi D t}, \quad (11)$$

which means that at the dropping electrode the diffusion layer is compressed by the expansion of the mercury drop and becomes much thinner compared with that at a stationary electrode. Consequently the concentration gradient at the dropping electrode surface is given by

$$\left(\frac{\partial C}{\partial x} \right)_{x=0} = \frac{*C - {}^\circ C}{\delta_1} = \frac{*C - {}^\circ C}{\sqrt{\frac{3}{7} \pi D t}}. \quad (12)$$

If nF is the electricity equivalent to the electrode reaction of one mol of the depolarizer, it is shown from the Fick's first law that the instantaneous current intensity i is given by

$$i = \left(\frac{112\pi}{3} \right)^{1/2} \cdot \left(\frac{3}{4\pi d} \right)^{2/3} \cdot nF(*C - {}^\circ C) \cdot D^{1/2} \cdot m_1^{2/3} \cdot t^{1/6}. \quad (13)$$

If t_1 is the drop time, the mean current $\bar{i}$ is shown to be

$$\bar{i} = \frac{1}{t_1} \int_0^{t_1} i \cdot dt;$$

accordingly the following equation can be obtained:

$$\begin{aligned} \bar{i} &= \frac{6}{7} \cdot \left(\frac{112\pi}{3} \right)^{1/2} \cdot \left(\frac{3}{4\pi d} \right)^{2/3} \\ &\cdot nF(*C - {}^\circ C) \cdot D^{1/2} \cdot m_1^{2/3} \cdot t_1^{1/6} \\ &= 0.627 nF(*C - {}^\circ C) D^{1/2} \cdot m_1^{2/3} \cdot t_1^{1/6} \quad (14, a) \end{aligned}$$

and also

$$\bar{i} = \frac{6}{7} i_{max}, \quad (15)$$

where i_{max} is the maximum value of in-

stantaneous current which flows at $t = t_1$. Under the condition where the mean value of the limiting diffusion current $\bar{i}_a$ is obtained,

$$\bar{i}_a = 0.627 nF \cdot {}^\circ C \cdot D^{1/2} \cdot m_1^{2/3} \cdot t_1^{1/6}, \quad (14, b)$$

because in this case, ${}^\circ C$, the concentration of the depolarizer at the cathode surface can be regarded to be nearly zero. When $\bar{i}_a$ is measured in microampere (I_a), m_1 in mg. per sec. (m), and $*C$ in millimol per liter (C), then the above equation is transformed to the form

$$I_a = 605 nCD^{1/2} m^{2/3} t_1^{1/6}. \quad (14, c)$$

Note.—Ilkovič⁽⁵⁾ has derived Eq. (12) by the following procedure. The movement of solution near the drop surface owing to the expansion of mercury drop can be represented by

$$q = \text{const.}, \quad (16)$$

and hence the diffusion layer is compressed to a much thinner layer, as already mentioned; Stackelberg⁽⁷⁾ denoted this effect of the convection of solution by the word "Seifenblasenmodell."

Combination of Eqs. (10) and (16) gives v , the velocity of approach of solution to the drop surface; thus

$$v = \frac{dx}{dt} = -\frac{x}{q} \cdot \frac{dq}{dt} = -\frac{2x}{3t}. \quad (17)$$

The concentration of the depolarizer C is completely determined by the two independent variables x and t ; i. e.,

$$C = C(x, t). \quad (18)$$

Hence

$$\frac{\partial C}{\partial t} = \frac{dC}{dt} - \frac{\partial C}{\partial x} \cdot \frac{dx}{dt}. \quad (19)$$

The Fick's second law states:

$$\frac{dC}{dt} = D \cdot \frac{\partial^2 C}{\partial x^2}. \quad (20)$$

Consequently the following differential equation is obtained from Eqs. (17), (19) and (20):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \frac{2x}{3t} \cdot \frac{\partial C}{\partial x} \quad (21)$$

Ilkovič has derived Eq. (21) in such a manner. This equation, however, can be obtained in a different way, i. e., the flux of the depolarizer, f , is given by

$$f = -D \cdot \frac{\partial C}{\partial x} + v \cdot C.$$

Accordingly it follows that

(5) D. Ilkovič, *J. chem. phys.*, **35**, 129 (1938).

$$\operatorname{div} f = -\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} + v \frac{\partial C}{\partial x} + C \operatorname{div} v.$$

Since the medium is approximately incompressible it is seen that

$$\operatorname{div} v = 0.$$

Consequently inserting Eq. (17) into the above equation gives Eq. (21).

Eq. (21) can be integrated, as carried out by Ilkovič, but his procedure is rather difficult. The easiest way is as follows. Let us introduce a new quantity defined by

$$S = x / 2 \sqrt{\frac{3}{7} Dt} \quad (22)$$

then the appropriate solution can be readily seen to be given by

$$C = {}^\circ C + (*C - {}^\circ C) \cdot H\left(\frac{x}{2\sqrt{(3/7)Dt}}\right). \quad (23)$$

From this equation the concentration gradient at the surface of dropping electrode, *i. e.*, Eq. (12) is obtained immediately.

It is quite curious that MacGillavry and Rideal⁽²⁾ obtained the same result although they treated this problem as a tri-dimensional diffusion, *i. e.*, they employed the spherical coordinate system. Upon examining their procedure it becomes evident that their theory is not legitimate because the velocity of approach of solution to the dropping electrode surface is considered to be zero, owing to the erroneous transformation of the coordinate system. This will be discussed again in the following article.

The Theoretical Revision of the Ilkovič Equation

Suppose that a diffusion process is occurring at a stationary spherical electrode. Let r be the distance from the center of the sphere, then in such a spherical coordinate the Fick's laws are written as follows:

$$dn = -D \cdot q \cdot \operatorname{grad} C \cdot dt, \quad (I)$$

$$\frac{1}{D} \cdot \frac{\partial C}{\partial t} \equiv \operatorname{div} \operatorname{grad} C = \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r}. \quad (II)$$

If r is the radius of the spherical electrode, the boundary conditions are given by

$$\left. \begin{aligned} C &= {}^\circ C \cdots \text{when } r = r_1, \quad t > 0. \\ C &= *C \cdots \text{when } r > r_1, \quad t = 0. \\ C &= *C \cdots \text{when } r \rightarrow \infty. \end{aligned} \right\} \quad (III)$$

Thus the appropriate integral of the Eq. (II) is shown to be

$$C = {}^\circ C \frac{r_1}{r} + *C \left(1 - \frac{r_1}{r}\right) + (*C - {}^\circ C) \frac{r_1}{r} \cdot \frac{2}{\sqrt{\pi}} \int_0^{\frac{r-r_1}{2\sqrt{Dt}}} e^{-S^2} \cdot dS. \quad (IV)$$

Accordingly the concentration gradient at the electrode surface is given by

$$\begin{aligned} \left(\frac{\partial C}{\partial r}\right)_{r=r_1} &= (*C - {}^\circ C) \left(\frac{1}{r_1} + \frac{1}{\sqrt{\pi Dt}}\right) \\ &= \frac{*C - {}^\circ C}{\delta_r} \end{aligned} \quad (V)$$

and δ_r , the differential thickness of the diffusion layer at the spherical electrode, is seen to be given by

$$\frac{1}{\delta_r} = \frac{1}{r_1} + \frac{1}{\sqrt{\pi Dt}}. \quad (VI)$$

It can be shown from this formula that in this case the equation corresponding to the Stackelberg's integral equation is given by

$$\begin{aligned} \pi D \int_0^t \frac{r_1^2}{\delta_r} \cdot dt &= r_1^3 \left\{ \left(\frac{\delta_r}{r_1 - \delta_r} \right)^2 \right. \\ &\quad \left. + 2 \left(\frac{\delta_r}{r_1 - \delta_r} \right) \right\}. \end{aligned} \quad (VII)$$

Furthermore, if we assume a linear fall of the concentration at the electrode surface, the integral thickness of the diffusion layer, Δ_r , is obtainable from the following integral

$$\begin{aligned} - \int_{t=0}^{t-t} dn &= \int_{r_1}^{r_1 + \Delta_r} *C \cdot 4\pi r^2 \cdot dr \\ &- \int_{r_1}^{r_1 + \Delta_r} \left\{ {}^\circ C + \frac{*C - {}^\circ C}{\Delta_r} (r - r_1) \right\} 4\pi r^2 \cdot dr, \end{aligned}$$

and it is seen, as illustrated in Fig. 2, that Δ_r is given by the following equation

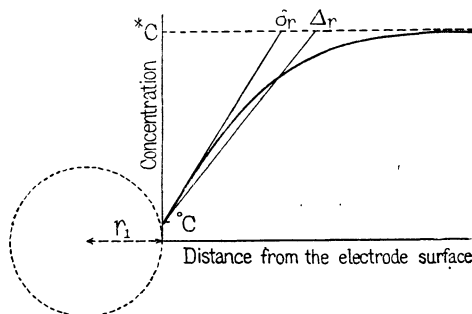


Fig. 2.—Schematic representation of the differential and integral thickness of the diffusion layer at a spherical electrode (dotted circle).

$$\pi \left\{ \frac{1}{12} \left(\frac{\Delta r}{r_1} \right)^3 + \frac{1}{3} \left(\frac{\Delta r}{r_1} \right)^2 + \frac{1}{2} \left(\frac{\Delta r}{r_1} \right) \right\} \\ = \left(\frac{\delta_r}{r_1 - \delta_r} \right)^2 + 2 \left(\frac{\delta_r}{r_1 - \delta_r} \right) \quad (\text{VIII})$$

If we assume a linear increase in the volume of mercury drop, it is evident that (cf. Eq. (9))

$$\left. \begin{aligned} r_1 &= a \cdot t^{1/3}, \\ a &= (3m_1/4\pi d)^{1/3}. \end{aligned} \right\} \quad (\text{i})$$

If this relation is inserted into Eq. (VII), and the integral equation thus obtained is solved, the differential thickness of the diffusion layer around the dropping mercury electrode, denoted by $^a\delta_r$, can be derived as follows;

$$y = \frac{^a\delta_r}{r_1 - ^a\delta_r}$$

and

$$dy/dt = \dot{y},$$

it can be readily seen that

$$\pi D a \int_0^t t^{1/3} \cdot \frac{y+1}{y} \cdot dt = a^3 t (y^2 + 2y).$$

Differentiation of this equation with respect to the time t gives

$$\pi D a t^{1/3} (y+1) = a^3 \{ (y^3 + 2y^2) + 2t(y+1)y\dot{y} \} \\ \doteq a^3 \{ 2(y^3 + y^2) + 2t(y+1)y\dot{y} \},$$

where the condition $0 < y < 1$ is used. Thus it is found that the following relation holds approximately:

$$\pi D t^{4/3} = a^2 (2y^2 t + 2y \dot{y} t^2) = a^2 \frac{d}{dt} (y^2 t^2).$$

Upon integrating this equation, it is seen that

$$t^2 \cdot a^2 \cdot y^2 = \frac{3}{7} \pi D t^{7/3}$$

and

$$\frac{1}{y} = \frac{r_1}{^a\delta_r} - 1 \doteq \left(\frac{r_1^2}{\frac{3}{7} \pi D t} \right)^{1/2},$$

where it can be readily seen that the integral constant is zero.

Consequently the thickness of the diffusion layer at a dropping electrode is given by

$$\frac{1}{^a\delta_r} = \frac{1}{r_1} + \frac{1}{\sqrt{\frac{3}{7} \pi D t}} \quad (\text{XI})$$

Therefore the concentration gradient at the surface of the dropping electrode is shown to be

$$\left(\frac{\partial C}{\partial r} \right)_{r=r_1} = (*C - ^\circ C) \left(\frac{1}{\sqrt{\frac{3}{7} \pi D t}} + \frac{1}{r_1} \right) \quad (\text{XII})$$

The above developed theory, taking into account of the curvature of the mercury drop, is reduced to the Ilković-Stackelberg theory which ignores the curvature, when the following three conditions are used:

$$\left. \begin{aligned} q &= 4\pi r_1^2, \\ r - r_1 &= x, \\ r_1 &\rightarrow \infty. \end{aligned} \right\} \quad (\text{ii})$$

There is no doubt that these conditions reduce the Eqs. (I)–(XII) to the Eqs. (1)–(12) respectively; accordingly it is obvious that the Ilković theory of the polarographic diffusion current is only a limiting law of our theory, obtained when the surface of mercury-drop is presumed to be plane. The instantaneous current intensity i can be derived from Eq. (XII); thus

$$\left. \begin{aligned} i &= nF \cdot 4\pi r_1^2 \cdot D (*C - ^\circ C) \left(\frac{1}{\sqrt{\frac{3}{7} \pi D t}} + \frac{1}{r_1} \right), \\ i &= nF (*C - ^\circ C) \cdot D^{1/2} \cdot 4\pi \left\{ \left(\frac{3}{4\pi d} \right)^{2/3} \left(\frac{7}{3\pi} \right)^{1/2} \right. \\ &\quad \times m_1^{2/3} \cdot t^{1/6} + \left(\frac{3}{4\pi d} \right)^{1/3} \cdot D^{1/2} \cdot m_1^{1/3} \cdot t^{1/3} \left. \right\}, \\ i &= 0.732 nF (*C - ^\circ C) D^{1/2} (m_1^{2/3} \cdot t^{1/6} \\ &\quad + 4.46 D^{1/2} \cdot m_1^{1/3} \cdot t^{1/3}). \end{aligned} \right\} \quad (\text{XIII})$$

The mean current $\bar{i}$ is further given by

$$\bar{i} = 0.627 nF (*C - ^\circ C) D^{1/2} (m_1^{2/3} \cdot t_1^{1/6} + 3.91 D^{1/2} \cdot m_1^{1/3} \cdot t_1^{1/3}), \quad (\text{XIV})$$

where t_1 denotes the drop time.

Current-Time Curves

It is required from Eq. (XIII) that the current-time curve at a constant applied voltage is not exactly a parabola of one-sixth order; writing

$$\begin{aligned} i &= k_1 (t^{1/6} + 4.46 D^{1/2} \cdot m_1^{-1/3} \cdot t^{1/3}) \\ k_1 &= 0.732 nF (*C - ^\circ C) D^{1/2} \cdot m_1^{2/3} \end{aligned}$$

and inserting some suitable values for D and m_1 , *e. g.*, for simplicity assuming that

$$D = 16 \times 10^{-6} \text{ cm.}^2 \text{ per sec.,}$$

$$m_1 = 10^{-3} \text{ g. per sec.,}$$

it follows that

$$\begin{aligned} i &= k_1 (t^{1/6} + 0.178 t^{1/3}) \\ &= k_1 \left[\left\{ 1 + \frac{1}{6} (\ln t) + \frac{1}{72} (\ln t)^2 + \dots \right\} \right. \\ &\quad \left. + 0.178 \left\{ 1 + \frac{1}{3} (\ln t) + \frac{1}{18} (\ln t)^2 + \dots \right\} \right] \\ &= 1.178 k_1 \{ 1 + 0.192 \ln t + \dots \} \\ &\doteq 1.178 k_1 \cdot t^{0.192}. \end{aligned}$$

Thus it may be concluded that in the wide range of time, where $|\ln t|$ is not much greater than unity, the current-time curve is approximately parabolic; if we write

$$i \propto t^\alpha, \quad (\text{iii})$$

then α is given by

$$\frac{1}{6} < \alpha < \frac{1}{3}. \quad (\text{iv})$$

Not only the results obtained by McKenzie⁽⁴⁾, but also that by Ilkovič⁽⁶⁾ and by Antweiler⁽⁷⁾ clearly show this relationship.

We also investigated experimentally the change of current intensity during one drop-life; the apparatus employed were the polarographic equipment made by Yanagimoto Co.

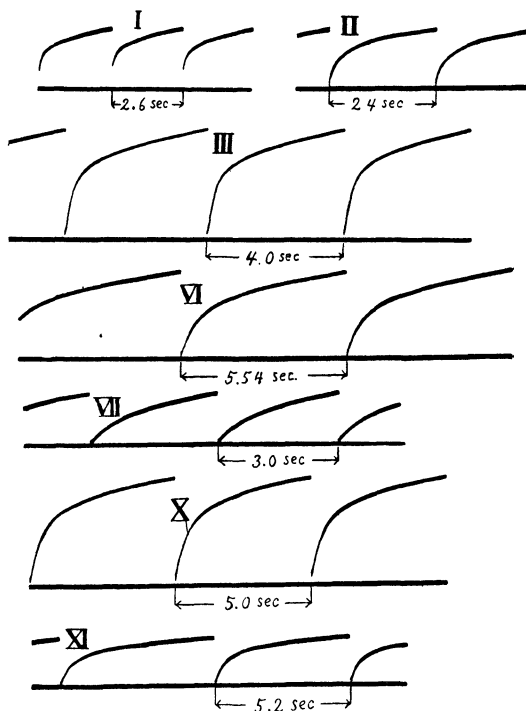


Fig. 3.—Oscillographic recordings of the polarographic current-time curves. Each number corresponds to the solution shown in Table 1.

and the electro-magnetic oscillograph made by Yokogawa Co. Solutions shown in Table 1 were electrolyzed at the room temperature, each

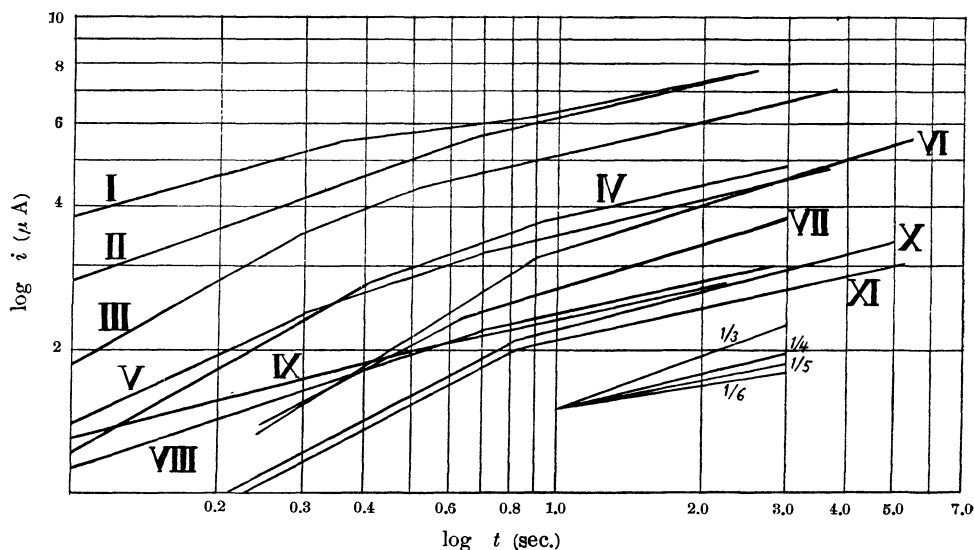


Fig. 4.— $\log i$ vs. $\log t$ curves. Each number corresponds to the solution shown in Table 1.

(6) D. Ilkovič, *Collection Czech. Chem. Commun.*, **8**, 13 (1933).

(7) H. J. Antweiler, *Z. Elektrochem.*, **44**, 888 (1938).

with the suitably applied voltage determined from the current-voltage curve.

Table 1

Number	Depolarizer	Supporting electrolyte	Addition of gelatine
I	$\alpha. 5 \times 10^{-3}$ molar Nitrobenzene	sat. KNO_3 *	+
II	"	"	*
III	$\alpha. 10^{-2}$ molar CoCl_2	0.1 N KCl	+
IV	$\alpha. 10^{-2}$ N CdSO_4	sat. KNO_3	-
V	"	"	+
VI	2×10^{-2} N TiNO_3	0.1 N KNO_3	+
VII	5×10^{-3} N HNO_3	"	-
VIII	$\alpha. 10^{-2}$ N TiNO_3	sat. KNO_3	-
IX	"	"	+
X	2×10^{-2} molar CdSO_4	0.1 N KCl	+
XI	1×10^{-2} molar CdSO_4	0.1 N KNO_3	+

* In buffer solution ($\text{pH} = 7.0$)

Oscillograms obtained are shown in Fig. 3; and Fig. 4 represents the plots of $\log i$ against $\log t$, the slopes of which are obviously not $1/6$ but are nearly $1/4 \sim 1/5$ (the mean value reported by McKenzie is 0.29). It is expected from our theory that the greater the diffusion constant, and the smaller the rate of flow of mercury, then the exponent α in Eq. (iii) will approach much nearer to $1/3$, *i. e.*, α will increase. It is demonstrated in Fig. 3 that with the depolarizers, the diffusion constants of which are comparatively great, *e. g.*, hydrogen ion and thallos ion, the plot of $\log i$

against $\log t$ becomes much steeper in harmony with our theory. It may be concluded from our experiment that the discontinuity in the current-time curve exists at $0.3 \sim 0.9$ sec. (According to McKenzie it lies about at the first 0.3 sec.); and it may be noticed that an addition of gelatine causes a remarkable change in the current-time curve, especially in the very youth of drop-life, as shown in Figs. 2 and 3. Thus it may be said that the results obtained by McKenzie are confirmed by our experiment, although in some points complete coincidences are not found, probably owing to the difference in the experimental conditions; *i. e.*, in our experiment the concentration of depolarizer is appreciably greater than that used in the ordinary polarographic electrolysis and in the McKenzie's investigation.

Summary

The integral equation representing the thickness of the diffusion layer surrounding a spherical electrode is derived; upon solving this equation, the formula for the polarographic diffusion current is obtained. It becomes clear that the Ilkovič theory is not right because of its ignorance of the curvature of drop and that our revised equation can elucidate many oscillographic recordings of the polarographic current-time curves.

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Researches on the Polarographic Diffusion Current. II. Distribution of the Depolarizer in the Vicinity of Dropping Mercury Electrode and Some Experimental Verifications of the Revised Equation

By Tomihito KAMBARA and Isamu TACHI

(Received June 23, 1950)

In Part I⁽¹⁾ of this research, it was reported that the thickness of the diffusion layer around the dropping mercury electrode can be expressed by an integral equation and upon solving this equation the new equation for the polarographic diffusion current is obtained, which is capable of elucidating many oscillographic

recordings of the current-time curves during one drop-life. In this paper this problem will be treated in an orthodox way, *viz.*, it will be shown that the differential equation representing the concentration of depolarizing matter is integrated and also that as for the formula for the diffusion current, the same result is obtained as in Part I, which is shown by numerous data to be more fitted than the old Ilkovič equation.

(1) T. Kambara, M. Suzuki, and I. Tachi, *This Bulletin*, **23**, 219 (1950).

Distribution of Depolarizer and the Revised Equation for the Diffusion Current

It may be assumed that the mercury drop expands concentrically, and let r be the distance from the center of drop considered as a sphere, and t the time elapsed after the growth of the drop has begun. If C is the concentration of the depolarizing substance, it is obvious that C is a function of r and t ; thus

$$C = C(r, t). \quad (1)$$

Hence

$$\frac{dC}{dt} = \frac{\partial C}{\partial t} + \frac{\partial C}{\partial r} \frac{dr}{dt}, \quad (2)$$

where $\partial C/\partial r$ is the variation of concentration with time at a fixed position ($r = \text{const.}$), and so is governed not only by diffusion but also by convection, whereas dC/dr is the variation of concentration due to the diffusion only. The rate of flow of mercury out of the capillary may be regarded to have a constant value m_1 g. per sec., independent of time, as is postulated also in the Ilkovič theory.⁽²⁾ Then the volume of mercury drop being proportional to the time elapsed after the drop has begun to grow, it is evident that

$$r_1^3 = \gamma t = \alpha^3 t, \quad (3)$$

where r_1 denotes the radius of mercury drop, and α is given by

$$\gamma = \alpha^3 = \frac{3m_1}{4\pi d}, \quad (4)$$

where $d = 13.6$ is the density of mercury. A volume element considered in the solution is pushed away from the center by the expansion of drop; hence the movement of solution is governed by the relation

$$r^3 = \alpha^3 t + \text{const.}, \quad (5)$$

because the condition of the incompressibility of the medium holds. Accordingly the velocities with which the drop surface and the solution move are given by

$$v_{r_1} = \frac{\partial r_1}{\partial t} = \frac{\alpha^3}{3r_1^2} \text{ and } v_r = \frac{dr}{dt} = \frac{\alpha^3}{3r^2} \quad (6)$$

respectively. On the other hand, according to the Fick's law in spherical coordinate, it is evident that

$$\frac{dC}{dt} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right), \quad (7)$$

where D is the diffusion constant of the depolarizer. Inserting Eqs. (6) and (7) into Eq. (2) gives

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right) - \frac{\alpha^3}{3r^2} \cdot \frac{\partial C}{\partial r} \quad (8)$$

which is identical with the differential equation derived by MacGillavry and Rideal.⁽³⁾ This equation can not be integrated immediately, but a special solution is readily seen to be

$$C = R(\text{const.}). \quad (9)$$

Next let us introduce a new function φ defined by

$$\varphi \equiv rC = \varphi(r, t). \quad (10)$$

Moreover the origin of coordinate will be transferred from the center of the sphere to the surface of drop, then the position of a volume element considered in the solution can be represented by the new coordinate x given by

$$x = r - r_1. \quad (11)$$

There is no doubt that φ can be expressed perfectly by the two independent variables x and t ; thus

$$\varphi = \varphi(x, t), \quad (12)$$

$$\frac{d\varphi}{dt} = \frac{\partial \varphi}{\partial t} + \frac{\partial \varphi}{\partial x} \cdot \frac{dx}{dt}. \quad (13)$$

The above mentioned Fick's law can be written in the form:

$$\frac{d\varphi}{dt} = D \cdot \frac{\partial^2 \varphi}{\partial x^2}. \quad (14)$$

From Eqs. (6) and (11), the approach of solution to the drop surface is readily seen to be expressed by

$$v_x = \frac{dx}{dt} = \frac{\alpha^3}{3} \left(\frac{1}{r^2} - \frac{1}{r_1^2} \right). \quad (15)$$

Accordingly we obtain the following equation

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} - \frac{\alpha^3}{3} \left(\frac{1}{r^2} - \frac{1}{r_1^2} \right) \frac{\partial \varphi}{\partial x}. \quad (16)$$

Since in the vicinity of the surface of dropping electrode the condition $r_1 \gg x$ holds, it is approximately shown that

(2) D. Ilkovič, *J. chim. phys.*, **35**, 129 (1938).

(3) D. MacGillavry and E. K. Rideal, *Rec. trav. chim. Pays-Bas*, **56**, 1013 (1937).

$$\frac{a^3}{3} \left(\frac{1}{r^2} - \frac{1}{r_1^2} \right) = -\frac{r_1^3}{3t} \cdot \frac{x(x+2r_1)}{r^2 r_1^2} = -\frac{2x}{3t}.$$

Consequently

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} + \frac{2x}{3t} \cdot \frac{\partial \varphi}{\partial x}, \quad (17)$$

which is an equation of the identical form with that derived by Ilkovič.⁽²⁾ In order to integrate this equation, since the procedure given by Ilkovič is very difficult, a new variable S given by

$$S = x \sqrt{2 \sqrt{\frac{3}{t}} Dt} \quad (18)$$

will be introduced. Thus Eq. (17) can be integrated and the result is

$$rC \equiv \varphi = P \cdot \int_0^S e^{-S^2} \cdot dS + Q.$$

Consequently the general solution for the Eq. (8) is approximately given by

$$C = \frac{P}{r} \int_0^{\frac{r-r_1}{2\sqrt{\frac{3}{t}}Dt}} e^{-S^2} \cdot dS + \frac{Q}{r} + R, \quad (19)$$

where P , Q , and R , are constants. The boundary conditions are shown by

$$\left. \begin{aligned} C &= {}^*C \dots \text{when } r \rightarrow \infty, \\ C &= {}^\circ C \dots \text{when } r = r_1, \quad t > 0. \\ C &= {}^*C \dots \text{when } r > r_1, \quad t = 0. \end{aligned} \right\} \quad (20)$$

where ${}^*C$ is the concentration of the depolarizer in the bulk of the solution, and ${}^\circ C$ is that at the surface of the dropping electrode. Thus the appropriate solution is found to be

$$C = {}^\circ C \frac{r_1}{r} + {}^*C \left(1 - \frac{r_1}{r} \right) + ({}^*C - {}^\circ C) \frac{r_1}{r} \cdot \frac{2}{\sqrt{\pi}} \int_0^{\frac{r-r_1}{2\sqrt{\frac{3}{t}}Dt}} e^{-S^2} \cdot dS. \quad (21)$$

The concentration gradient at the electrode surface can be derived from this equation, and it is shown that

$$\left(\frac{\partial C}{\partial r} \right)_{r=r_1} = ({}^*C - {}^\circ C) \left\{ \frac{1}{r_1} + \frac{1}{\sqrt{\frac{3}{t}} \pi Dt} \right\}. \quad (22)$$

If the electricity required by the electrode

reaction of one mol of the depolarizer is nF (F : Faraday), from the Fick's first law the instantaneous current intensity i is shown by

$$i = 0.732 nF ({}^*C - {}^\circ C) \cdot D^{1/2} \times (m_1^{2/3} \cdot t_1^{1/6} + 4.46 D^{1/2} \cdot m_1^{1/3} \cdot t_1^{1/3}). \quad (23)$$

The mean current $\bar{i}$ is given by

$$\bar{i} = \frac{1}{t_1} \int_0^{t_1} i \cdot dt,$$

where t_1 is the drop time; thus it is evident that

$$\bar{i} = 0.627 nF ({}^*C - {}^\circ C) \cdot D^{1/2} \times (m_1^{2/3} \cdot t_1^{1/6} + 3.91 D^{1/2} \cdot m_1^{1/3} \cdot t_1^{1/3}). \quad (24)$$

When the mean value of limiting diffusion current is obtainable, ${}^\circ C$ approaches to zero; then if the following conventional units are employed, *i. e.*,

$$\bar{i}_d \text{ Amp.} = I_d \mu \text{ Amp.},$$

$${}^*C \text{ mol per cc.} = C \text{ millimol per liter},$$

$$m_1 \text{ g. per sec.} = m \text{ mg. per sec.},$$

it can be seen, as described in Part I⁽¹⁾, that

$$I_d = 605 nC \cdot D^{1/2} (m^{2/3} \cdot t_1^{1/6} + 39.1 D^{1/2} \cdot m^{1/3} \cdot t_1^{1/3}) \quad (24,a)$$

Comparison with the Experimental Results

As for the polarographic current-time curves, the old Ilkovič equation can not elucidate the experimentally obtained recordings, and the validity of the above derived equation was described in Part I of this research. In this article, our revised equation will be compared with some other experimental observations.

Empirical Modification by Lingane and Loveridge.—For the polarographic diffusion current of lead ion, Lingane and Loveridge⁽⁴⁾ examined the exponent of m in the Ilkovič equation. With

$$I_d \propto m^\beta, \quad (25)$$

they obtained the result

$$\beta = 0.64 \quad (26)$$

instead of $2/3$ as required by Ilkovič. This result will be considered as follows. Writing

(4) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **68**, 395 (1946).

Eq. (24, a) in the form

$$I_a = k_1(m^{2/3} + 39.1 D^{1/2} \cdot t_1^{1/6} \cdot m^{1/3}),$$

$$k_1 = 605 nC \cdot D^{1/2} \cdot t_1^{1/6},$$

and inserting the values:

$$D(\text{Pb}^{++}) = 9.8 \times 10^{-6} \text{ cm}^2. \text{ per sec. (at } 25^\circ),$$

$$t_1 = 3 \text{ sec.},$$

it is shown that

$$I_a = k_1(m^{2/3} + 0.147 m^{1/3})$$

$$\doteq k_1 \left[\left\{ 1 + \frac{2}{3} (\ln m) + \frac{2}{9} (\ln m)^2 + \dots \right\} \right.$$

$$\left. + 0.147 \left\{ 1 + \frac{1}{3} (\ln m) + \frac{1}{18} (\ln m)^2 + \dots \right\} \right]$$

$$= 1.147 k_1 \{ 1 + 0.624 (\ln m) + \dots \}$$

$$\doteq 1.147 k_1 \cdot m^{0.624}.$$

Thus it is obvious that in general

$$\frac{1}{3} < \beta < \frac{2}{3}. \quad (27)$$

Diffusion Current Constant.—From Eq. (24, a) it is found that

$$K = \frac{I_a}{C \cdot m^{2/3} \cdot t_1^{1/6}} = k_2 + k_3 \cdot t_1^{1/6} \quad (28)$$

where k_2 and k_3 are constants. This equation

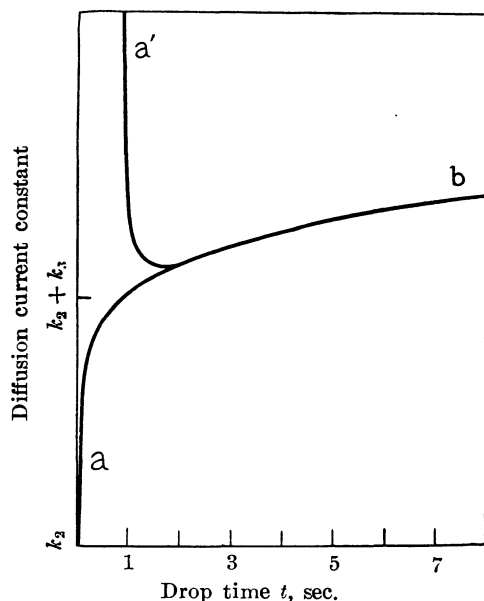


Fig. 1.—Relation between the diffusion current constant and the drop time: Curve ab, theoretical; Curve a'b, experimental.

indicates that the plot of diffusion current constant K against the drop time t_1 is not a horizontally straight line but a gradually increasing curve as illustrated by the curve ab in Fig. 1. The observed curve is reported by Lingane⁽⁵⁾ to be the one, the shape of which is demonstrated by a'b in Fig. 1. The exceedingly rapid increase in the value of K with the increasing shorter drop time, may be caused by the "stirring effect" due to the rapid alternation of drops, as already suggested by Lingane.

Dependence of the Current Intensity on the Height of Mercury Reservoir.—If P is the static pressure of mercury column, since the conditions

$$m \propto P \quad \text{and} \quad P \cdot t_1 = \text{const.} \quad (29)$$

holds,

$$I_a = k_4 \cdot P^{1/2} + k_5 \quad (30)$$

is followed, where k_4 and k_5 are constants. Although the plot of I_a against $P^{1/2}$ is a straight line, the line obtained does not pass the origin. Data by Ilkovič⁽⁶⁾ and O. H. Müller⁽⁷⁾ give the lines demonstrated in Fig. 2; thus it becomes clear that Eq. (30) is better than the equation

$$I_a = k_4 \cdot P^{1/2}, \quad (30, a)$$

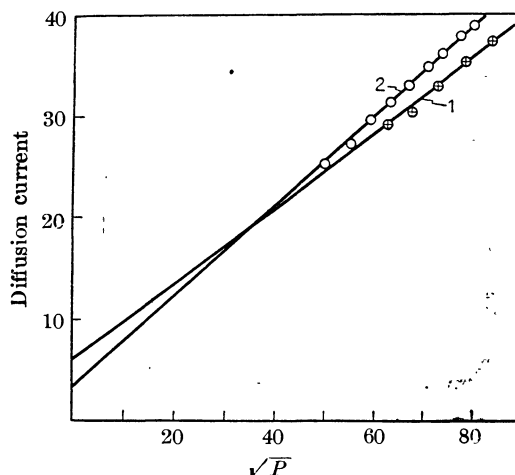


Fig. 2.—Relation between the diffusion current and the square root of the height of the mercury reservoir: Curve 1, data by Ilkovič; Curve 2, data by Müller; P means the height of the mercury reservoir.

(5) J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

(6) D. Ilkovič, *Collect. on Czech. Chem. Commun.*, **6**, 498 (1934).

(7) O. H. Müller, "Polarography" Chapt. XXIII in Weissberger's "Phys. Meth. of Organic Chemistry" Vol. II, 1946.

which results from the Ilkovič equation and Eq. (29). Thus it becomes clear that our equation is more fitted than the original Ilkovič's one.

The Ratio $i_{max}/\bar{i}$.—It can be readily seen that

$$1.166 = \frac{7}{6} < \frac{i_{max}}{\bar{i}} < \frac{4}{3} = 1.33, \quad (31)$$

where i_{max} is the maximum current intensity which flows at the end of drop-life and $\bar{i}$ is the mean current. This equation agrees very well with the results observed by McKenzie.⁽⁸⁾

Discrepancy between the Theory and the Experiment.—That the current increases remarkable slowly in the very infant age of drop-life, as experimented by McKenzie⁽⁸⁾ and also by us⁽¹⁾, is not comprehensible both from the Ilkovič theory and from the present considerations. It may be imagined that some retarding effects are operative in the beginning of each drop-life; if this problem was cleared up, the discontinuity in the current-time curve would be solved and a further progress towards the perfect elucidation would be made.

Note on the Procedure given by MacGillavry and Rideal

In order to integrate Eq. (8), MacGillavry and Rideal⁽³⁾ used the transformation of co-ordinate system given by

$$r^3 - \rho^3 = \gamma t$$

instead of Eq. (11), where ρ denotes the distance from the surface of the drop and is equal to x in our notations. Therefore

$$v_p = \frac{\partial \rho}{\partial t} = 0$$

which means that the solution does not approach to the surface of the drop during the expansion of mercury drop, whereas it is pushed away from the center of the drop; this is clearly erroneous. Thus they obtained the same result as attained by Ilkovič and Stackelberg who ignored the curvature of drop.

Summary

The differential equation representing the distribution of the depolarizer in the vicinity of dropping mercury electrode was integrated and the formula for the polarographic diffusion current was derived, which is identical with the equation obtained, as reported in our previous paper, in another way. Several experimental results were found to be in accordance with this equation; it may be said that our improved theory is not only the denial of the Ilkovič theory but also at the same time inclusive of the old theory.

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(8) H. A. McKenzie, *J. Am. Chem. Soc.*, **70**, 3147 (1948).

Chemical Analysis by Means of Organic Compounds. XVI. Amperometric Titrations. III. Cuprimetric Titrations⁽¹⁾

By Masayoshi ISHIBASHI and Taitiro FUJINAGA

(Received September 4, 1950)

In the previous paper,⁽²⁾ we reported that Mg, Zn, Cu and Fe were directly titrated with oxine (8-hydroxyquinoline) by the amperometric method and that this method was applied to the determination of Mg in aluminium alloys

and sea-water.

We recently devised a simpler method also by using dropping mercury electrode as indicator electrode. The amperometric titration is carried out by connecting the indicator electrode with the saturated mercuric iodide reference electrode³⁾ through microammeter, and no e. m. f.

(1) This work was disserted in the 2nd and 3rd annual meetings of the Chemical Society of Japan held at Tokyo in 1949 and at Kyoto in 1950 respectively.

(2) M. Ishibashi and T. Fujinaga, *Bull. Chem. Soc. Japan*, **23**, 25, 27 (1950).

(3) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

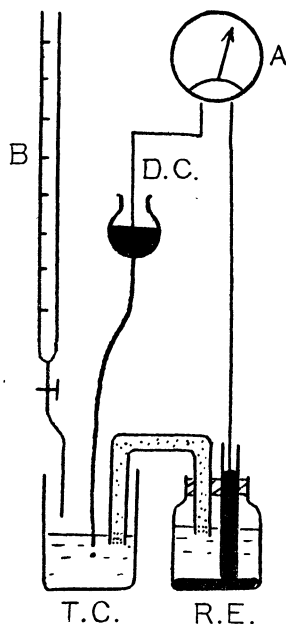


Fig. 1.—Apparatus of titration: A, microammeter; B, burette; T. C., titration cell; D. C., dropping electrode; R. E., reference electrode.

needs to be applied to the cell. So-called "wave compensator"⁽⁴⁾ is used, if necessary, to eliminate the residual current or other disturbing diffusion current, *e. g.*, oxygen current. The reference electrode has an electrode potential of -0.49 volt *vs.* the saturated calomel electrode, so not only single cupric ion but cupriammine ion are reduced at this potential and give the

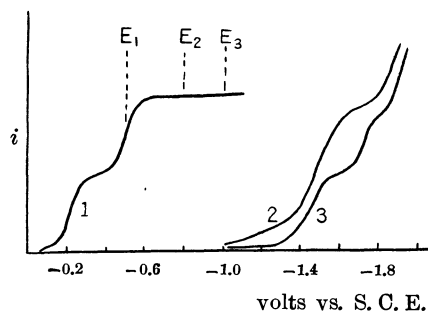


Fig. 2.—Polarograms of cupriammine, α -benzoinoxime and oxine in $1\text{ N-NH}_4\text{OH}$, NH_4Cl : Curve 1, cupriammine; curve 2, benzoinoxime; curve 3, oxine. E_1 , potential of mercuric iodide electrode; E_2 , potential of mercuric sulfide electrode; E_3 , potential of zinc amalgam electrode.

diffusion current proportional to their concentration. Observing this internal electrolytic current due to cupric ion, the end point can be detected amperometrically. So this method of titration should be called the "Amperometric Cuprimetry."

In this paper, the determination of copper, zinc and magnesium with oxine and also copper with α -benzoinoxime by the cuprimetric method were described.

Apparatus and Materials

The apparatus and the circuit are shown in Fig. 1. Electrical connection between reference electrode and the titration cell is made by means of a salt bridge filled with a gel of 3% agar and 30% potassium chloride. The electrolyte solution of the reference half cell is prepared by saturating potassium iodide in saturated potassium chloride solution. A layer of mercury serves as anode.

Standard Solutions Used: Cupric Sulfate.—0.1 mol of pure recrystallized cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was weighed out and 1 ml. of 0.1 mol sulfuric acid was added to it to prevent the hydrolysis of cupric ion and was diluted to one liter as the standard solution.

8-Hydroxyquinoline.—the same as previously reported.⁽²⁾

α -Benzoinoxime.—synthesised from benzaldehyde, sodium cyanide and hydroxylamine in the usual way and recrystallized from ethanol. 1% of this solution (50% ethanol) was prepared for the intermediate standard solution.

Experiments

(1) **Determination of Copper and Zinc with Oxine.**—Copper is determined by the residual titration method. Known volume of excess oxine solution is added to the sample solution buffered by ammonium chloride-ammonia or sodium acetate-acetic acid, and the excess reagent is back titrated with standard cupric sulfate solution. The end point is indicated by the diffusion current of cupric ion added in excess to oxine present in the solution. Copper in the sample is determined by deducing the used volume of cupric sulfate standard solution from its blank value. The titration curves are shown in Fig. 3 and the data are shown in Table 1.

Zinc is titrated by the same method, but zinc oxinate precipitate is filtered off and then the filtrate is titrated in order to avoid the transformation of zinc oxinate to copper oxinate.

(2) **Determination of Magnesium with Oxine.**—Magnesium can be determined by the same method as zinc, but in this case, better results are obtained by dissolving the magnesium oxinate

(4) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **12**, 750 (1940).

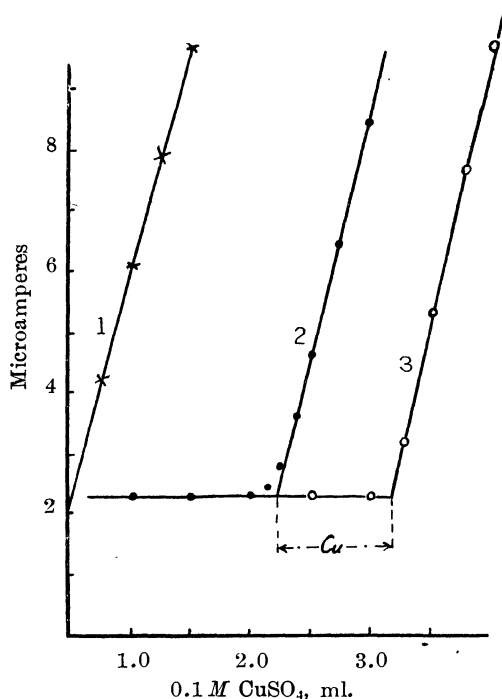


Fig. 3.—Titration of oxine with cupric sulfate: Curve 1, without oxine; curve 2, with Cu and oxine; curve 3, with oxine.

Table 1
Determination of Copper and Zinc
(Using Oxine)

	Sample taken, mg.	0.1 M- CuSO ₄ , ml.	Metal found, mg.	Error, %
Cu	0	0	0	0
	6.357	1.01	6.420	+1.0
	8.357	1.00	6.357	0
Zu	20.395	3.12	20.399	0
	20.395	3.11	20.333	-0.3

These data are mean values of several titrations.

and titrating the freed oxine with cupric sulfate. To sample magnesium solution buffered by ammonia, excess oxine reagent is added and the precipitate is filtered and washed. Then the precipitate is dissolved with hot dilute hydrochloric acid and the dissolved solution is neutralized with sodium hydroxide (turbidity by the formation of magnesium hydroxide or magnesium oxinate shows this neutralisation) and again acidified with acetic acid and titrated with cupric sulfate standard solution. In this case magnesium in sample is equivalent to cupric sulfate used. This method is simple, accurate, sensible and magnesium can be precipitated even at boiling temperature. This method was applied to the determination of magnesium in sea-water and good result was obtained (Table 2).

Table 2
Determination of Magnesium in
Sea-water (Using Oxine)

Sea-water taken, ml.	0.1 M- CuSO ₄ , ml.	Mg. found, mg.	Error, %
5.00	2.61	6.347	+0.7
5.00	2.58	6.275	+0.4
5.00	2.60	6.323	+0.3
3.00	1.57	3.818	+0.9
3.00	1.57	3.818	+0.9
3.00	1.55	3.770	+0.3

(3) **Determination of Copper with Benzoin-oxime.**—Benzoinoxime as a reagent for copper is more specific than oxine and even when a small amount of zinc or nickel is present together with copper, it is not interfered by them, but the copper-benzoinoxime salt is fairly soluble in concentrated ammonium hydroxide (see Table 3).

Table 3
Determination of Copper in Brass
(Using Benzoinoxime)

Brass taken, ml.	Conc. of NH ₄ OH, M/l.	Std. benzoin-oxime added, ml.	0.1 M- CuSO ₄ used, ml.	Cu in brass, %
0	1.0	10.0	—	
0	0.1	10.0	1.32	
0	0.05	10.0	1.48	
0	0.03	10.0	1.52	
0	0.01	10.0	1.53	
0	0.01	10.0	1.54	
0	0.01	10.0	1.53	
5.0	0.01	10.0	0.89	81.21
5.0	0.01	10.0	0.93	77.36
5.0	0.01	10.0	0.90	79.94

In this titration, 501 mg. of brass was dissolved in 500 ml. of dilute nitric acid and the aliquot sample was titrated. By the gravimetric analysis, copper in this sample was determined to be 78.57%.

So, from the result of experiments, it is seen that this titration must be performed below the concentration of 0.03 mol ammonium hydroxide. Benzoinoxime is reduced at $E_{1/2} = -1.53$ volts *vs.* S.C.E. in 1 *N*-ammonium chloride and ammonia (see Fig. 2), so in using the mercuric iodide electrode as anode, it is not reduced at the dropping electrode without an outside e.m.f. The titration curves of benzoinoxime is therefore analogous to that of oxine.

For the application of this titration, copper in brass was decided. The procedure is as follows: A definite weight of brass is dissolved in concentrated nitric acid and evaporated to dryness. A little dilute nitric acid is added to dissolve it and then it is filtered and washed. The filtrate is neutralized with ammonia water to a condition just before the greenish white precipitate of basic copper salt is formed and ammonium chloride-

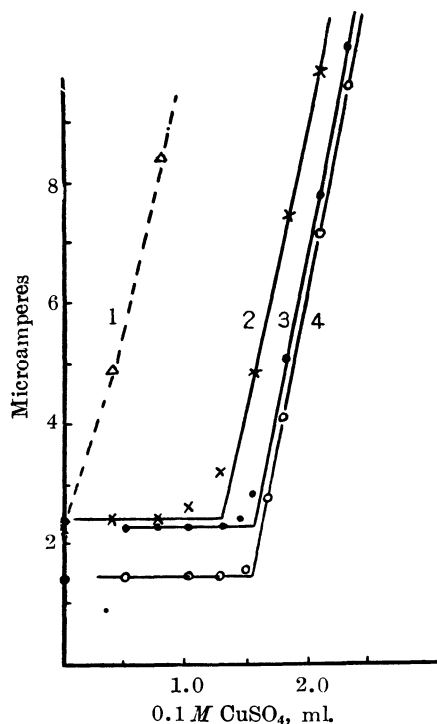


Fig. 4.—Titration of benzoinoxime with cupric sulfate: Curve 1, in 1 *N*-NH₄OH; curve 2, in 0.1 *N*-NH₄OH; curve 3, in 0.01 *N*-NH₄OH; curve 4, same as curve 3, but in H₂ atmosphere.

ammonium hydroxide buffered solution is then added to the solution to about 0.01 mol in ammonium hydroxide. Definite volume of standard benzoinoxime is added in excess and the excess is back titrated with cupric sulfate standard solution as in the case of titration with oxine.

(4) **Determination of Other Substances.**—As

will be seen from the above experiments, many organic substances which react fast and stoichiometric enough with cupric ion such as salicylaldehyde, quinaldic acid, etc. may be determined by the cuprimetric method and the possibilities are now under research.

Discussion

These short-circuited cuprimetric titrations mentioned above are performed by using the mercuric iodide electrode ($E = -0.49$ volt *vs.* S. C. E.). However, we found that mercuric sulfide electrode ($E = -0.81$ volt *vs.* S. C. E.) and zinc amalgam electrode ($E = -1.02$ volts *vs.* S. C. E.) is more conveniently applicable in these titrations and by using them, less noble elements like lead ion can be reduced, so sulfate or chromate etc. can be titrated by this simple amperometric method. These analyses will be discussed in other cases.

Summary

(1) Cuprimetric amperometry using cupric sulfate as a standard solution was introduced in the determination of copper, zinc and magnesium.

(2) Oxine, benzoinoxime or other organic reagents were used as intermediate reagent in this titration, so on the other hand, some organic substances would be determined by this method.

(3) The procedure is simple and sensible to 10^{-4} mol Cu per liter, if suitable measures are taken.

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On the Linear Boundary Energy in Two-Dimensional System

By Hideo AKAMATU and Masayuki NAKAGAKI

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Introduction.—The energy or the tension along the boundary line at which three phases are brought into contact with each other has been frequently conceived and called as the linear tension. When an oil lens is floating on the free surface of water, for example, the thickness of the lens is determined by the equilibrium between the spreading tendencies of oil

and water, F_o^* and F_w^* . Thus, I. Langmuir⁽¹⁾ has assumed that the following equilibrium holds, $F_o^* - F_w^* = \Lambda^*/R$, where R is the radius of the lens and Λ^* is introduced as the linear tension along the periphery of the lens. When a lens has a definite thickness, F_o^* and F_w^* depend

(1) I. Langmuir, *J. Chem. Phys.*, **1**, 756 (1933).

on the phase boundary tensions superimposed with the gravity force.

When, however, the thickness of the lens diminishes infinitely, the gravity force can be neglected and the spreading tendencies depend only upon the surface pressures themselves. This is a case of a two-dimensional system. In this case, we can define the "linear boundary tension" in two-dimensional system corresponding to the surface tension in the three-dimensional system.

As to the surface films of insoluble substances on water, it is known that there are some cases where the heterogeneous phase equilibrium takes place between the gaseous and the liquid films. In such cases, the presence of the islands of coherent liquid film surrounded by the vapor film has been found.⁽²⁾ Accordingly, let the surface pressure of the liquid phase be F_1 and that of the vapour phase F_2 , then for the equilibrium the following relation must be present,

$$F_1 - F_2 = A/R \quad (1)$$

where R is the radius of the island of the liquid film, and A is defined as the linear boundary tension of this surface liquid film.⁽³⁾

It will not be impossible, radically speaking, to measure the linear boundary tension by some experimental device. However, as it will be seen in the following section, its value is supposed to be very small, so that the experimental technique will hardly be found at present.

The Conception of the Linear Boundary Energy in Two-Dimensional System by the Classical Theory.—The surface tension is deduced from the coherent force of the matter. The general idea has been expressed in the classical theory⁽⁴⁾ of Laplace or Gauss. The same theory can be applied to the two-dimensional system, if the "surface mass" could be assumed. Such an assumption may be admitted in the mathematical sense, but physically it seems absurd. However, when we treat a surface film, we can consider it as a two-dimensional system, and the surface mass can be defined as the product of surface density (ρ) and area (S).

Following Gauss's method, we can estimate the potential energy of a condensed film of which area is S_0 and the length of periphery is L_0 . Assuming the potential energy between

two unit "surface mass" being apart at the distance r as $-\varphi(r)$, the energy between any two small parts of a condensed film, ds and ds' , is expressed as $dW = -\rho^2\varphi(r)ds ds'$, where ρ is the surface density of the film. The total potential energy of the system is then,

$$W = -\frac{1}{2}\rho^2 \iint \varphi(r) ds ds' = -\frac{1}{2}\rho^2 \Omega \quad (2)$$

Integration is carried out separately regarding to ds and ds' . Thus ds is fixed at first and ds' is expressed by polar coordinate as $rd\theta_1 dr$ in Fig. 1. Therefore,

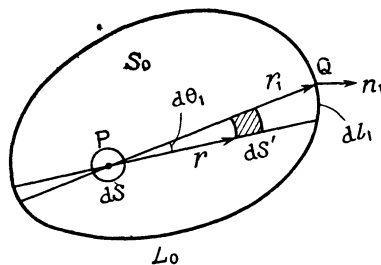


Fig. 1.

$$\Omega = \int ds \int d\theta_1 \int_0^{r_1} r \varphi(r) dr \quad (3)$$

Let us put $\int r\varphi(r)dr = c_1 - \Phi(r)$, where c_1 is a constant, then we will get

$$\begin{aligned} \Omega &= \int ds \int d\theta_1 [\Phi(0) - \Phi(r_1)] \\ &= 2\pi\Phi(0)S_0 - \int ds \int \Phi(r_1) d\theta_1 \end{aligned} \quad (4)$$

Here, let n_1 be a perpendicular to the periphery at Q in Fig. 1, accordingly $r_1 d\theta_1 = dl_1 \cos(n_1 \wedge r_1)$, and

$$\begin{aligned} \Omega &= 2\pi\Phi(0)S_0 \\ &\quad - \iint \frac{\Phi(r_1) \cos(n_1 \wedge r_1)}{r_1} dl_1 ds \end{aligned} \quad (4')$$

As ds is also expressed as $r_1 d\theta dr_1$ in Fig. 2,

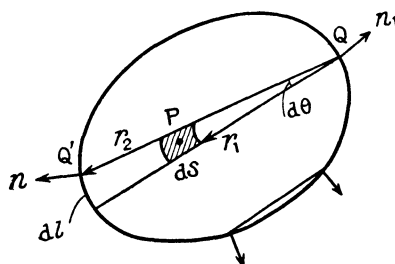


Fig. 2.

(2) N. K. Adam, "The Physics and Chemistry of Surface", Oxford, 1938.

(3) A heterogeneous phase equilibrium between two kinds of condensed films is also possible to consider, however, it has not been investigated hitherto.

(4) G. Bakker, "Handbuch der Experimental Physik." B. 6, 1928, p. 61.

$$\begin{aligned} & \int \frac{\Phi(r_1) \cos(n_1 \wedge r_1) ds}{r_1} \\ &= \int \cos(n_1 \wedge r_1) d\theta \int_0^2 \Phi(r_1) dr_1 \quad (5) \end{aligned}$$

Let us again put $\int \varphi(r) r^2 dr = c_2 - \psi(r)$, where c_2 is a constant, then

$$\int \varphi(r) r^2 dr = \int \Phi(r) dr - r\Phi(r) = c_2 - \psi(r)$$

and Eq. (5) is equal to $\psi(0) \int \cos(n_1 \wedge r_1) d\theta - \int [\psi(r_2) - r_2 \Phi(r_2)] \cos(n_1 \wedge r_1) d\theta$.

Furthermore, let us put $\cos(n_1 \wedge r_1) = \cos \nu$, and since $d\theta = d\nu$, so

$$\begin{aligned} & \int \cos(n_1 \wedge r_1) d\theta = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos \nu d\nu = 2. \\ & \int \frac{\Phi(r_1) \cos(n_1 \wedge r_1) ds}{r_1} = 2\psi(0) \\ & - \int [\psi(r_2) - r_2 \Phi(r_2)] \cos(n_1 \wedge r_1) d\theta. \quad (5') \end{aligned}$$

Now when we put $r_2 d\theta = dl \cos(n \wedge r_2)$ in Fig. 2, the second term in Eq. (5') will be

$$\begin{aligned} & \int [\psi(r_2) - r_2 \Phi(r_2)] \frac{1}{r_2} \cos(n_1 \wedge r_1) \cos(n \wedge r_2) dl. \\ & \Omega = 2\pi \Phi(0) S_0 - 2\psi(0) \int dl_1 \\ & + \int \int \frac{1}{r_2} [\psi(r_2) - r_2 \Phi(r_2)] \\ & \times \cos(n_1 \wedge r_1) \cos(n \wedge r_2) dl_1 dl. \quad (6) \end{aligned}$$

The value of $\psi(r)$ as well as $\Phi(r)$ decreases rapidly with increasing r , hence $\frac{1}{r} [\psi(r) - r\Phi(r)] \div 0$ when r is large. When r is small, on the other hand, $\cos(n_1 \wedge r_1)$ and also $\cos(n \wedge r_2)$ approach to zero (cf. Fig. 2). Thus the third term of Eq. (6) vanishes.

$$W = -\pi \rho^2 \Phi(0) S_0 + \rho^2 \psi(0) L_0 \quad (7)$$

$$\text{or} \quad W = -HS_0 + AL_0 \quad (8)$$

$$\text{where,} \quad H = \pi \rho^2 \int_0^\infty \varphi(r) r dr \quad (9)$$

$$A = \rho^2 \int_0^\infty \varphi(r) r^2 dr \quad (10)$$

Here, we can define A as the total linear boundary energy, corresponding to the total

surface energy in the three-dimensional system, and H is the inner surface pressure.

An Estimation of the Value of the Linear Boundary Energy of the Surface Film.—It will be possible to make a rough estimation about the value of the linear boundary energy, when we assume the proper function for $\varphi(r)$ in Eqs. (9) and (10).

Let us consider a monomolecular film, of which equation of state is written as

$$\left(F + \frac{a}{A^2}\right)(A - b) = kT \quad (11)$$

where F is the surface pressure and A is the area occupied by a molecule. From the statistical consideration of two-dimensional system,⁽⁵⁾ a and b are written as

$$\left. \begin{aligned} a &= -\pi \int_D^\infty \varepsilon(r) r dr \\ b &= 2\pi(D/2)^2 \end{aligned} \right\} \quad (12)$$

where $\varepsilon(r)$ is the potential energy between two molecules in the film, D is the diameter of a molecule, and the potential diagram is assumed as illustrated in Fig. 3. Remembering that

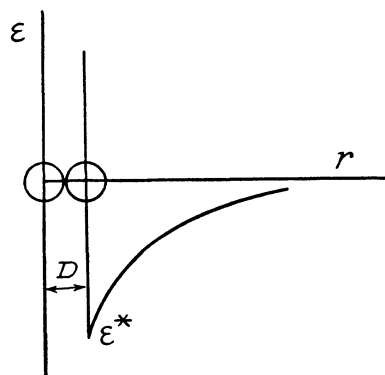


Fig. 3.—The hypothetical potential diagram.
 $\varepsilon = \infty$ when $r < D$, $\varepsilon = \varepsilon(r)$ when $r > D$,
 $\varepsilon = \varepsilon^*$ when $r = D$.

$\varphi(r)$ is the potential energy between two unit surface masses, and $\varepsilon(r)$ is that between two molecules, the relation between them is

(5) The partition function in two-dimensional system is,

$$Z = \left[\frac{2\pi mkT}{h^2} \right]^N \frac{1}{N!} \int \int \dots \int \exp[-\sum \varepsilon(r_{ij})/kT] \\ \times dx_1 \dots dy_N = [] \phi(T)$$

$$\ln \phi(T) = \ln \left(\frac{1}{N!} \right) + N \ln S_0 - \frac{1}{2} N^2 \frac{B}{S_0} + \dots$$

where $B = \int_0^\infty 2\pi r (1 - e^{-\varepsilon(r)/kT}) dr$ is the second virial coefficient for two-dimensional system.

$$\varphi(r) \simeq -\frac{1}{m^2} \varepsilon(r) = -\varepsilon(r) (A\rho)^2$$

where m is the mass of a molecule. Thus,

$$\int_0^\infty \varphi(r)r dr \simeq \frac{-1}{(A\rho)^2} \int_D^\infty \varepsilon(r)r dr$$

$$\int_0^\infty \varphi(r)r^2 dr \simeq \frac{-1}{(A\rho)^2} \int_D^\infty \varepsilon(r)r^2 dr$$

$$H = \frac{-\pi}{A^2} \int_D^\infty \varepsilon(r)r dr = \frac{a}{A^2} \quad (9')$$

$$A = \frac{-1}{A^2} \int_D^\infty \varepsilon(r)r^2 dr \quad (10')$$

We must further assume a proper function for $\varepsilon(r)$, and it is assumed as,

$$\varepsilon(r) = \varepsilon^*(D/r)^6. \quad (13)$$

Now we can integrate Eqs. (9') and (10').

$$H = -\frac{\pi}{A^2} \frac{\varepsilon^* D^2}{4} \quad (9'')$$

$$A = -\frac{1}{A^2} \frac{\varepsilon^* D^3}{3} \quad (10'')$$

Considering that, $H = a/A^2$ and $b = 2\pi(D/2)^2$,

$$A = \frac{4}{3\pi} DH = 0.34 \frac{a\sqrt{b}}{A^2} \quad (14)$$

We take, for an example, the data for myristic acid measured by Adam and Jessop.⁽⁶⁾ From the F - A diagram of myristic acid, the equation of state can be written as,

$$\left(F + \frac{18950}{A^2}\right)(A - 15.5) = 397$$

for liquid condensed film, and

$$\left(F + \frac{35500}{A^2}\right)(A - 24.3) = 397$$

for liquid expanded film. Since the true meaning of the expanded film seems unknown, we take the average value for a and b for those two states.

$$\bar{a} = 27 \times 10^{-29} \text{ dyne} \cdot \text{cm}^3, \quad \bar{b} = 20 \times 10^{-16} \text{ cm}^2.$$

Inserting those values in Eq. (14),

$$A = \frac{41 \times 10^{-37}}{A^2} \text{ dyne.} \quad (15)$$

It has been found from the surface potential measurements⁽²⁾ that the region where coherent and gaseous film coexist together is at all areas between 48 and 800 sq. Å. per molecule for myristic acid. In this region, the islands of coherent film are observed as surrounded by gaseous film. Below 48 and above 800 sq. Å., the surface consists entirely of either coherent or gaseous film. Hence, it is reasonable to consider that in the islands of coherent film, the area occupied by a molecule is the order of 48 sq. Å. or less. If we assume 48 sq. Å. for the value of A in Eq. (15), then A will be 1.8×10^{-7} dyne (or more) for the islands of myristic acid film.

We have nothing to check the value directly at present. However, the latent heat of surface vaporisation of myristic acid film has been measured as 2457 cal. by J. Sameshima.⁽⁷⁾ From this value, the internal latent heat of surface vaporisation per molecule (q) is known as 13×10^{-14} erg. On the other hand, the value of the total linear boundary energy per molecule (λ) is calculated as,

$$\lambda = (1.8 \times 10^{-7}) \div [(1 \times 10^8) \div 2\sqrt{48/\pi}] = 1.4 \times 10^{-14} \text{ erg.}$$

It is supposed as reasonable that the value of λ is a certain fraction, not far from 0.5, of q . Thus the estimated value of A of myristic acid film seems too small to compare it with the observed value of the heat of surface vaporisation, though the order of the value is reasonable.

Summary

A definition of the linear boundary tension of the two-dimensional film was conceived, which corresponds to the surface tension in the three-dimensional system. The physical meaning of this conception was investigated according to the classical Gauss theory. A rough estimation of this value was made for the surface film of myristic acid.

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Fusion and State Equation of Simple Liquids. I. Derivation of the Expressions for State Equation and Free Energy

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1. Introduction

The order-disorder theory of melting proposed by Lennard-Jones and Devonshire⁽¹⁾ promoted not only the theories of the fusion process but also the general theory of liquids based on the hole theory. From this stand point recently Toda⁽²⁾ and Ono⁽³⁾ clarified the critical phenomena. But in these theories the essential difficulty of the estimation of the intermolecular interaction energy is inevitable. A fair development of the theory by Kirkwood and Monroe⁽⁴⁾ lighted a new way to the fusion process in which the liquid-solid transition was attributed to the vanishing of periodic distribution of molecules. Also in the case of Born's theory,⁽⁵⁾ treating the fusion process as an abrupt change of rigidity, the change of a special character of solid and liquid phases was used for the base of fusion theories.

I will present the statistical theory of liquid to treat melting as a phase equilibrium of solid and liquid states and to find the fusion parameters in terms of intermolecular forces. For an estimation of the molecular interaction energies in liquid states an earlier theory of Lennard-Jones and Devonshire⁽⁶⁾ gave a reasonable approximation using the spherical cells around each molecule, but the results obtained did not agree so well with experiments. The source of the disagreements may be considered that the number of the nearest neighbor molecules Z was taken as 12 in each molecule and the formation of cells around the molecules restricts the molecular motion too firm in the expanded state. Therefore the free volume calculated by this method is not satisfactory but when we use the number Z as a parameter it may give a good approximation near the melting point.

In the liquid state the distances between the nearest neighbors are nearly equal to the equilibrium distance between two molecules. Different characters of the intermolecular potential for various substances would give a big influence to the physical properties of the liquids. The use of the inversepower potential might not be satisfactory to express the details of the potential functions, but for simplicity we use the following Lennard-Jones type intermolecular potential,

$$\varepsilon(r) = \varepsilon_0 \left[\frac{6}{n-6} \left(\frac{r_0}{r} \right)^n - \frac{n}{n-6} \left(\frac{r_0}{r} \right)^6 \right] \quad (1)$$

The numerical calculation for the state equation is performed in the case of $n = 12$. As to the fusion process it is possible to discuss what influences will be given on the calculated melting temperature by the variation of the intermolecular potential.

2. Assumptions Regarding the Molecular Arrangements in the Liquids

In the solid state the molecular arrangement is determined by its lattice constants. In the liquid state we can know only about the radial distribution function around one molecule by X-ray experiments. We cannot expect the definite solid like molecular arrangement around each molecule in the liquid, but it may be considered as a little displaced from the regular arrangement. We may consider the nearest neighbors around one molecule as in the case of solids; however the number of the nearest neighbors may differ in each molecule. Among N molecules $NP(Z)$ molecules have Z nearest neighbors and we assume that the number of the nearest neighbors around one molecule is independent of the arrangements of the molecules farther than the nearest neighbors. We can obtain only one function $P(Z)$ for any given molecular arrangement, although there exists a definite number of possible molecular arrangements which give a same function $P(Z)$. Since the density fluctuations in a dense system are small, the actual molecular arrangements may be derived by a small displacement of each

(1) J. E. Lennard-Jones, and A. F. Devonshire, *Proc. Roy. Soc. A*, **169**, 317 (1939); **170**, 464 (1939).

(2) M. Toda, *BUSSEIRON KENKYU* (in Japanese), No. 10, 1 (1948).

(3) S. Ono, *Memoirs of the Faculty of Engineering, Kyushu Univ.*, **10**, 195 (1947); S. Ono, and T. Sato, *J. Phys. Soc. Japan.*, **4**, 103 (1949).

(4) J. G. Kirkwood, E. Monroe, *J. Chem. Phys.*, **9**, 514 (1941).

(5) M. Born, *J. Chem. Phys.*, **7**, 519 (1939).

(6) J. E. Lennard-Jones, and A. F. Devonshire, *Proc. Roy. Soc. A*, **163**, 53 (1937); **165**, 1 (1938).

molecule situated on simple lattice points. When we neglect the differences of molecular arrangements caused by thermal motion of each molecule, we may suppose that almost all of the molecular arrangements are expressed by the assignments of the number Z to these simple lattice points. If we assume the unique determination of the arrangement by an assignment of Z on the N lattice points, we get the number of different molecular arrangements for a given distribution function $P(Z)$ as follows,

$$N! / \Pi_Z (NP(Z)!), \quad (2)$$

which is a number of possible ways of arranging the different values of Z on the localized N points.

When we consider the molecular arrangement neglecting the thermal motion, in the solid state distances between the two nearest neighbors take a definite value r but in the liquid state the molecular arrangement determined by the function $P(Z)$ makes it impossible to take the same definite value for these distances. The distribution of the value r depends on the function $P(Z)$ in a complicated manner, but near the melting point owing to the small variation of $P(Z)$ we may neglect it. Near the critical point the result of numerical calculation shows the smallness of the effects of this distribution on the physical property. Therefore the dependence of $P(Z)$ on the distribution of r may be neglected without a great error and the next simple function for an expression of this distribution is adopted.

$$\left. \begin{aligned} f(R^*) &= \frac{3}{4} R^{-1} \delta^{-3} (\delta^2 - (1 - R^*/R)^2), \\ R^* &= r/r_0, \quad R = [R^*]_{AV}, \end{aligned} \right\} \quad (3)$$

where $f(R^*) dR^*$ gives the probability of finding R^* between R^* and $R^* + dR^*$, and R^* is limited in the range of $R(1 - \delta) \leq R^* \leq R(1 + \delta)$. The average of R^* in this domain is R and the expression (3) takes a maximum in the case when $R^* = R$.

Eisenstein and Gingrich⁽⁷⁾ have shown the radial distribution of the nearest neighbors of liquid argon by the measurements of the X-ray scattering. In order to correspond only formally the expression (3) to the radial distribution thus obtained, we make δ equal to about 1/5. To compare the experimental results with our expression of the radial distribution we have to consider that the actual radial distribution

of the nearest neighbors is obtained by the superposition of thermal motion on the function $f(R^*)$. According to Lindemann⁽⁸⁾ the thermal motion of a molecule in a solid may be considered as a vibration with the amplitude of about $r/10$ at the melting point. In the liquid state this amplitude will become more or less larger. The estimation of this value near the melting point using the Lennard-Jones' cage model shows that the amplitude is smaller than $r/5$. Therefore the agreement between the experimental results of Eisenstein and Gingrich and the radial distribution expected by the superposition of this sort of thermal motion on Eq. (3) may be attained by assuming $\delta = 0.10 \sim 0.15$. This result with respect to the order of magnitude of δ will be confirmed in Part II relating the discussions on the melting points.

3. The Partition Function of Liquid

The method of construction of partition function adopted here is based on the molecular arrangement as mentioned in the preceding section. It may be said that the most probable molecular distribution given by a function $P(Z)$ has a predominant contribution to the partition function. Therefore we may take the partition function for an assembly of the molecular arrangements determined by this function $P(Z)$. We shall use the approximation that the partition function of a whole assembly can be expressed as a product of the partition function of each molecule having Z nearest neighbors and the number of possible molecular arrangements given by expression (2). The thermal motion of each molecule is considered in a cell with the potential field of its immediate neighbors. We then adopt the following form for the partition function of the liquid state:

$$\Omega = (2\pi mkT/h^2)^{3N/2} \frac{N!}{\Pi_Z (NP(Z)!)} \times [\Pi_Z v_f(Z)^{NP(Z)}] \exp(-U/kT) J(T)^N, \quad (4)$$

where $(2\pi mkT/h^2)^{3/2} v_f(Z) J(T)$ is a partition function of a molecule in a cell which consists of Z nearest neighbors situated uniformly on the spherical shell with radius Rr_0 . $J(T)$ denotes the partition function for all the internal degrees of freedom and U is a total potential energy of N molecules when each molecule is at the center of its cell. When we neglect the small variation of R^* from the mean value R , free volume v_f may be written as following as has been obtained by Lennard-Jones and Devonshire.⁽⁶⁾

(7) A. Eisenstein and N. S. Gingrich, *Phys. Rev.*, **58**, 307(1940).

(8) F. A. Lindemann, *Physik. Zeit.*, **11**, 609(1910).

$$\left. \begin{aligned}
 v_f(Z) &= 2\pi(r_0R)^3 \int y^{1/2} \\
 &\quad \times \exp(-\zeta R^{-12}l(y) + 2\zeta R^{-6}m(y)) dy, \\
 l(y) &= (1 + 12y - 25.2y^2 \\
 &\quad + 12y^3 + y^4)(1 - y)^{-10} - 1, \\
 m(y) &= (1 + y)(1 - y)^{-4} - 1,
 \end{aligned} \right\} \quad (5)$$

where the energy of interaction between a pair of molecules is assumed as follows,

$$\varepsilon(r) = \varepsilon_0(R^{-12} - 2R^{-6}).$$

The results of numerical integration of the above expression for various combinations of different values of Z and R agrees with the following expression.

$$v_f = 2\pi(r_0R)^3 \exp\{l_0 + l_1R^{-6}MZ\zeta \\
 + \ln[1 + \exp(\beta_0 + \beta_1R^{-6} + \beta Z\zeta)]\}, \quad (6)$$

where

$$\left. \begin{aligned}
 M &= (h_2R^{-12} + h_1R^{-6} + h_0)^{1/2} \\
 &\quad + m_1R^{-6} + m_0, \quad \zeta = \varepsilon_0/kT, \\
 l_0 &= -2.417, \quad m_0 = -0.03868, \\
 \beta_0 &= -0.6908, \quad \beta = -0.2947, \\
 l_1 &= -5.225, \quad m_1 = -0.1851, \\
 \beta_1 &= 2.993, \quad h_0 = 0.02138, \\
 h_1 &= -0.06566, \quad h_2 = 0.07635.
 \end{aligned} \right\} \quad (6')$$

The differences between two expressions (5) and (6) are smaller than 2% within the range of $12 \geq Z \geq 4$ and $1.0 \geq R^{-6} \geq 0.1$. Even for the more general molecular interaction given by expression (1), v_f may be also expressed well by (5) using different numerical coefficients.

An exact evaluation of the term U is very difficult, but we can estimate it under the assumption of the solid like molecular arrangements in the liquid state. We denote by $\psi(Z)$ the potential energy of one molecule in the ideal arrangement of molecules with the same number of Z nearest neighbors and with the same distance r_0R between the two nearest neighbors. If we neglect the distribution of R^* , U may be written for the given function $P(Z)$ as following,

$$\sum_Z \frac{N}{2} \psi(Z, R) P(Z), \quad (7)$$

where

$$\psi(Z, R) = \frac{\varepsilon_0}{n-6} (6\varphi_r R^{-n} - n\varphi_a R^{-6}), \quad (7')$$

φ_r and φ_a are the functions of Z and they

may be approximately obtained by considering the ideal crystal lattices *i.e.* in the cases of $Z = 12, 8, 6$ and 4 , or may be obtained also from the Bernal's calculations⁽⁹⁾ on the values of Z and R for the molecules farther than the nearest neighbors. In the case of $n = 12$, the rough approximation for φ_a and φ_r may be given by

$$\varphi_a = Z, \quad \varphi_r = Z + 2. \quad (7'')$$

The approximation of these linear expressions becomes bad at the small value of Z . Fortunately the terms with small values of Z give only small effects on free energy and the state equation of liquid state, and we can use expression (7'') for numerical calculations in Part II. The consideration on the distribution of R^* given by expression (3) may be introduced by a simple integral as follows, and we can obtain the approximate formula,

$$\begin{aligned}
 U &= \sum_Z P(Z) \frac{N}{2} \int_{R(1-\delta)}^{R(1+\delta)} f(R^*) \psi(Z, R^*) dR^* \\
 &= \sum_Z P(Z) \frac{N}{2} (\psi(Z, R) + (R^2 \delta^2/10) \\
 &\quad \times d^2\psi/dR^2 + O(\delta^4)).
 \end{aligned} \quad (8)$$

This method of approach to the actual distribution of molecules includes the effects of the molecular distributions farther than the nearest neighbors. Therefore in equation (8) we have taken into considerations on the second and the third nearest neighbors which have respectively the mean distances from the center R_1r_0 and R_2r_0 And they have the radial distributions expressed by Eq. (3) with the alterations of R to R_1 and R_2

4. Free Energy and State Equation

When we substitute Eq. (8) in Eq. (4) and neglecting the last small term of the order δ^4 , we obtain by usual process the free energy

$$\begin{aligned}
 F/N &= -kT \ln \Omega/N = -kT \frac{3}{2} \\
 &\quad \times \ln [(2\pi mkT)/h^2] - kT \ln J \\
 &\quad + kT \sum_Z [(\varepsilon_0/2kT) \Psi(Z, R) \\
 &\quad - \ln v_f + \ln P(Z)] P(Z),
 \end{aligned} \quad (9)$$

$$\begin{aligned}
 \text{where } \Psi(Z, R) &= \psi(Z, R)/\varepsilon_0 \\
 &\quad + (R^2 \delta^2/10 \varepsilon_0) d^2\psi/dR^2 \\
 &= \frac{1}{n-6} [6\varphi_r(1 + \delta^2 n(n+1)/10) R^{-n} \\
 &\quad - n\varphi_a(1 + 4.2\delta^2) R^{-6}].
 \end{aligned} \quad (9')$$

(9) J. D. Bernal, *Trans. Faraday Soc.*, **32**, 27 (1936).

To obtain the pressure from this free energy, we have to know the volume as a function of R and $P(Z)$. Although the dependence of R on volume is easily supposed as proportional to $(r_0 R)^3$ but that of $P(Z)$ is more complicated. A simplified treatment about the face centered cubic lattice with holes derives the dependence of $P(Z)$ as follows. Suppose a molecule and a hole occupy the same volume v_u in liquid and their positions in space form a slightly deformed face centered cubic lattice. Then a molecule with Z nearest neighbors should have $12-Z$ holes around it. When summing up holes around each molecule we count the same hole Z_h times, where Z_h is a mean number of molecules around a hole. Thus the total number of holes N_h is

$$N_h = (12N - \sum_Z ZNP(Z))/Z_h \\ = N(12 - [Z]_{AV})/Z_h.$$

Therefore in the case of $N_h \ll N$

$$Nv = V = (N + N_h)v_u \\ = 12v_u N/[Z]_{AV} = g(r_0 R)^3 N/[Z]_{AV}. \quad (10)$$

In this equation we put Z_h as equal to $[Z]_{AV}$. The constants g is determined as $g=8.49$ using the special case of the face centered lattice, but this value will increase more or less at the expanded state in virtue of the nature of this approximation.

The distribution function $P(Z)$ is determined by the condition that Ω becomes maximum, *i.e.* by the equation $\delta F=0$ with the variation of $P(Z)$ keeping T , P and V constant. From this condition we get

$$0 = \delta F = \sum_Z \delta P(Z) [\ln P(Z) \\ + (\epsilon_0/2kT)\Psi - \ln v_f] \\ + \sum_Z P(Z) \left[(\epsilon_0/kT) \frac{\partial \Psi}{\partial R} - \frac{\partial \ln v_f}{\partial R} \right] \delta R, \quad (11)$$

where δR is a variation resulted from $\delta P(Z)$ and it is obtained by Eq. (10) taking the variation at constant volume, *i.e.*

$$\delta R = (v/3r_0^3 R^2 g) \sum_Z Z \delta P(Z). \quad (12)$$

Lagrange's method of elimination applied to Eqs. (11), (12) and $\sum_Z \delta P(Z) = 0$ results

$$\lambda = \ln P(Z) + \epsilon_0 \Psi / 2kT - \ln v_f \\ + (Zv/3r_0^3 R^2 g) \sum_Z \left[(\epsilon_0/2kT) \frac{\partial \Psi}{\partial R} - \frac{\partial \ln v_f}{\partial R} \right] P(Z), \quad (13)$$

where λ is a constant. By the differentiation of free energy with respect to volume we can obtain the state equation

$$-P/kT = \sum_Z \left[\frac{\partial P(Z)}{\partial v} (\ln P(Z) + \Psi \epsilon_0 / 2kT - \ln v_f) \right] \\ + \sum_Z P(Z) \frac{\partial R}{\partial v} \left[(\epsilon_0/2kT) \frac{\partial \Psi}{\partial R} - \frac{\partial \ln v_f}{\partial R} \right]. \quad (14)$$

The differentiation of Eq. (10) with respect to volume leads the term $\partial R/\partial v$ in the above expression

$$\frac{\partial R}{\partial v} = (v/3r_0^3 R^2 g) \sum_Z Z \frac{\partial F(Z)}{\partial v} + R/3v. \quad (15)$$

Using Eqs. (13) and (15) we can rewrite Eq. (14) in the form,

$$-P/kT = (R/3v) \sum_Z P(Z) \\ \times \left[(\epsilon_0/2kT) \frac{\partial \Psi}{\partial R} - \frac{\partial \ln v_f}{\partial R} \right]. \quad (16)$$

From Eqs. (13) and (16) we can obtain the explicit expression for $P(Z)$ as follows,

$$P(Z) = A \exp \left(\ln v_f - \frac{\xi}{2} \Psi + ZR^{-3} \xi \zeta \right), \quad (17)$$

where

$$\xi = Fv^2/r_0^3 g \epsilon_0.$$

The normalization condition, $\sum_Z P(Z)=1$ defines the constant A and we obtain

$$A^{-1} = \sum_Z \exp \left(\ln v_f - \frac{\xi}{2} \Psi + \xi \zeta ZR^{-3} \right). \quad (18)$$

Using the Eqs. (18) and (17) we can rewrite Eq. (9)

$$F/N = -kT [\ln [(2\pi mkT)^{3/2}/h] \\ + \ln J - \ln A - [Z]_{AV} R^{-3} \xi \zeta]. \quad (19)$$

When we assume the molecular interaction of the expression (1) with $n=12$, we can use v_f given by Eq. (6). The function Ψ becomes

$$\Psi(Z, R) = Z(1 + 15.6\delta^2)R^{-12} \\ - (2Z + 4)(1 + 4.2\delta^2)R^{-6}, \quad (20)$$

using the expressions (7') and (7''). Substitutions of Eqs. (20), (5) and (17) into Eq. (16) yield the state equation in terms of ξ , ζ and R .

$$\zeta = \frac{1 - 2l_1 R^{-6} - 2\beta_1 R^{-6} Y / (Y + X \exp(-\alpha))}{2([Z]_{AV} + 2)(1 + 4.2\delta^2)R^{-6} - 2[Z]_{AV}(1 + 15.6\delta^2)R^{-12} - (R/3)(dM/dR)[Z]_{AV} + R^{-3}[Z]_{AV}\xi}, \quad (21)$$

where

$$\begin{aligned} [Z]_{AV} &= \frac{[X_Z + Y_Z \exp(-\alpha)]}{[X + Y \exp(-\alpha)]}, \\ X &= \sum_Z \exp(\rho Z \zeta), \\ Y &= \sum_Z \exp((\rho + \beta)Z \zeta), \\ X_Z &= \sum_Z Z \exp(\rho Z \zeta), \\ Y_Z &= \sum_Z Z \exp((\rho + \beta)Z \zeta), \\ \rho &= (1 + 4.2\delta^2)R^{-6} \\ &\quad - \frac{1}{2}(1 + 15.6\delta^2)R^{-12} \\ &\quad + \xi R^{-3} + M, \end{aligned} \quad (22)$$

$$\alpha = \beta_0 + \beta_1 R^{-6}.$$

The summations in above expressions are extended to the probable integral values of Z .

Numerical calculations of state equation (21) and comparison with experimental values about critical data are given in Part II.

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Fusion and State Equation of Simple Liquids. II. Critical Data and Fusion Parameters

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1. Numerical Calculations of State Equation and Critical Data

The numerical calculations of state equation (21) were performed using the upper limit $Z=12$ and the lower limit $Z=4$ for the summations in expressions (22). $Z=12$ was selected in accordance with the closest packing arrangement. The selection of the value of lower limit is arbitrary to a certain extent since it gives only a small effect on Eq. (21). The left

side of Eq. (21) contains ζ in the terms of X , X_z , Y and Y_z . Therefore the value of ζ for the given value of R and ξ must be obtained by the successive approximation. The results obtained for the case of $\delta=0.10$ and 0.12 are shown in Table 1. The P - V diagram deduced from these values shows van der Waals' type condensation and the critical constants are determined by a graphical method. The critical constants obtained for three different values of δ are shown in Table 2 in which the com-

Table 1
Values of ζ Calculated from Eq. (21)

R^{-6}	$\delta=0.10$				$\delta=0.12$			
	ξ at				ξ at			
	0	0.05	0.10	0.15	0	0.05	0.10	0.15
0.1	1.419	1.286	1.174	1.080	1.392	1.263	1.156	1.064
0.2	1.178	1.084	1.003	0.933	1.163	1.071	0.992	0.923
0.25	1.144	1.056	0.980	0.913	1.134	1.048	0.973	0.908
0.3	1.128	1.043	0.970	0.905	1.121	1.038	0.964	0.900
0.4	1.098	1.019	0.950	0.889	1.107	1.027	0.957	0.895
0.5	1.086	1.010	0.942	0.882	1.109	1.030	0.960	0.898
0.6	1.127	1.046	0.974	0.909	1.175	1.089	1.012	0.943
0.7	1.265	1.168	1.081	1.004	1.332	1.227	1.130	1.051
0.8	1.541	1.410	1.294	1.192	1.716	1.561	1.427	1.309
0.9	2.196	1.965	1.774	1.612	2.662	2.338	2.075	1.865

parison is done between calculated and empirical values for noble gases and few other gases. Following the variation of δ , the proper values of g are selected to adjust the calculated and experimental values. The agreements are rather good when we take into consideration on the rough approximation of v_f and Ψ for the large value of T and small value of Z .

Table 2

Calculated and Observed Critical Data

	δ	g	$R^{-6}[Z]_{AV}$	$\frac{\epsilon_0}{kT_c}$	$\frac{P_c r_0^3}{\epsilon_0}$	$\frac{v_c}{r_0^3}$	$\frac{RT_c}{PV_c}$
Calc.	0.08	1.1	0.3	9.7	0.99	0.19	1.9
	0.10	1.0	0.3	9.7	1.02	0.17	1.8
	0.12	0.9	0.2	9.6	1.04	0.15	1.8
Obs.	Argon			0.79	0.166	2.22	3.44
	Nitrogen			0.76	0.185	2.06	3.45
	Neon			0.80	0.157	2.36	3.47
	Hydrogen			0.93	0.108	3.04	3.27

Sources: Critical data-Int. Crit. Tab.

ϵ_0 and r_0 from the Table in R.H. Fowler
E.A. Guggenheim, "Statistical Thermodynamics," 285 (1939).

2. Equilibrium between Solid and Liquid States

When we assume that the essential difference between solid and liquid states consists only in the irregularity in the molecular arrangements, then the free energy of solid states of a face centered crystalline state may be given by the equation (9) in which $\delta=0$ and all of the values of $P(Z)$ is zero except in the case of $Z=12$. The free energy expression thus obtained is identical to that given by Lennard-Jones and Devonshire for liquid state lacking the additional term of kT . The Gibbs' free energy for solid state may then be written as follows,

$$\begin{aligned} \mu_s = & -\frac{\epsilon_0}{\zeta} \left[\ln[(2\pi m \epsilon_0 / \zeta)^{3/2} / h^3] \right. \\ & \left. + \ln J - \frac{\zeta}{2\epsilon_0} \Psi(R_s, 12) + \ln v_f(R_s, 12) \right] \\ & + P_s v_s, \end{aligned} \quad (23)$$

$v_s = \gamma R_s^3 r^3$; ($\gamma = 2^{-1/2}$ in the case of a face centered cubic lattice.)

where $\Psi(R_s, 12)$ and $v_f(R_s, 12)$ are respectively given by Eqs. (7) and (5) substituting R_s for R and 12 for Z . R_s which corresponds to R in the solid state is given as a function of ζ and ξ by the state equation for solid state, i. e.

$$\begin{aligned} & 12 R_s^{-3} \xi \zeta \\ = & -\zeta \left(28 R_s^{-6} - 24 R_s^{-7} - 4 R_s \frac{dM}{dR_s} + 4 R_s^{-6} \right) \\ & + 1 - 2 l_1 R_s^{-6} - 2 \beta_1 R_s^{-6} / [1 + \exp(-\alpha \\ & - 12 \beta \zeta)], \end{aligned} \quad (24)$$

which is deduced from Eq. (21) with $[Z]_{AV} = 12$ and $\delta=0$.

To compare the free energy of liquid state with that of solid state we rewrite the term A in Eq. (19) using the Eqs. (18), (5), (20) and (22).

$$\begin{aligned} A^{-1} = & 2\pi(r_0 R)^3 (X + e^\alpha Y) \exp(l_0 + l_1 R^{-6} \\ & + 2(1 + 4.2 \delta^2) \zeta R^{-6}). \end{aligned}$$

Therefore

$$\begin{aligned} -\ln A = & \ln v_f(R, 12) + \ln(X + e^\alpha Y) \\ -\ln(1 + e^{\alpha + 12\beta\zeta}) = & \frac{\zeta}{2} \Psi(R, 12) + 12 \xi \zeta R^{-3} \\ -12 \rho \zeta. \end{aligned}$$

Then the Gibbs' free energy of liquid state obtained by Eq. (19) is as follows,

$$\begin{aligned} \mu_l = & -\frac{\epsilon_0}{\zeta} \left[\ln[(2\pi m \epsilon_0 / \zeta)^{3/2} / h^3] + \ln J \right. \\ & - \frac{\zeta}{2} \Psi(R, 12) + \ln v_f(R, 12) \\ & + \ln(X + e^\alpha Y) - \ln(1 + e^{\alpha + 12\beta\zeta}) \\ & \left. + 12 \xi \zeta R^{-3} - 12 \rho \zeta - [Z]_{AV} R^{-3} \xi \zeta \right] + P v. \end{aligned} \quad (25)$$

The condition for equilibrium between solid and liquid phases with the same temperature and pressure is

$$\begin{aligned} 0 = & (\mu_l - \mu_s) / \epsilon_0 \\ = & \frac{1}{\zeta} \left[\frac{dG}{dR_s} \Delta R + (6 \times 15.6 R^{-12} - 14 \times 4.2 R^{-6}) \delta^2 \right. \\ & \left. - \ln[(X + e^\alpha Y) e^{-12\beta\zeta} / (1 + e^{\alpha + 12\beta\zeta})] \right] \\ & + P(v - v_s) / \epsilon_0 - (12 - [Z]_{AV}) \xi \zeta R^{-3}, \end{aligned} \quad (26)$$

where

$$\begin{aligned} G = & \frac{\zeta}{2\epsilon_0} \Psi(R_s, 12) - \ln v_f(R_s, 12), \\ \Delta R = & R - R_s. \end{aligned}$$

In the solid state pressure is obtained from the expression of free energy given by Eq. (23)

$$P = -\frac{\partial(\mu_s - P v_s)}{\partial v_s} = -\frac{\epsilon_0}{\zeta} \frac{R_s^{-2}}{3\gamma r_0^3} \frac{dG}{dR_s}.$$

Therefore

$$\begin{aligned} \frac{\varepsilon_0}{\zeta} \frac{dG}{dR_s} \Delta R &= -Pr_0^3 \gamma 3R_s^2 \Delta R \\ &= -Pr_0^3 \gamma (R_s^3 - R^3). \end{aligned}$$

Using the above equation, we can simplify the terms regarding the volume change in Eq. (26) as follows,

$$\begin{aligned} &Pr_0^3 \gamma (R_s^3 - R^3) + P(v - v_s) \\ &\quad - (12 - [Z]_{AV}) \varepsilon_0 \xi R^{-3} \\ &= Pv \left(2 - [Z]_{AV} \frac{\gamma}{g} - 12/[Z]_{AV} \right) \\ &= -(\xi R^{-3} \varepsilon_0 / 12) (12 - [Z]_{AV})^2, \end{aligned}$$

where we used the relation $12\gamma = g$ which may hold near the melting point. From this equation we can obtain the condition for melting as following,

$$\begin{aligned} 0 &= (\mu_l - \mu_s) \zeta / \varepsilon_0 \\ &= \ln[(X + e^{\alpha} Y) e^{-12\rho \xi} / (1 + e^{\alpha + 12\beta \xi})] \\ &\quad + (\xi \zeta R^{-3} / 12) (12 - [Z]_{AV})^2 \\ &\quad + (14 \times 4.2 R^{-6} - 6 \times 15.6 R^{-12}) \delta^2. \quad (27) \end{aligned}$$

3. Fusion Parameters

From the above equation we can obtain the melting temperature for the given value of ξ , substituting the value of R determined as a function of ζ and ξ by the state equation (21). The pressure dependence of melting point obtained from this method in the case of $\delta =$

0.1 and 0.12 are shown in Figure 1. Too large theoretical value of ζ_m (see Table 3) was reduced by the use of ζ_c given by Table 2 which are also too large compared with experimental values. Therefore the calculated values in Figure 1 fairly agree with experimental values. The values of melting point derived by this method depend on δ , and ζ_m increases with decreasing values of δ . The variation of n in the expression of the molecular interaction energy gives greater influence on the melting temperature. In the general case of the molecular interaction expressed by Eq. (1), the condition for melting temperature is given by Eq. (27) with the alteration of the last term to the following expression,

$$(29.4 n R^{-6} - 3.6 n(n+1) R^{-n}) \frac{\delta^2}{n-6}. \quad (28)$$

To obtain the melting point for the general cases, we have to calculate R for the given ζ and ξ using the state equation (21) and expression for ρ in (22) with different numerical constants. Also the free volume v_f given by Eq. (5) needs revision which corresponds to the change of n , and this revision may result the changes of numerical values in expression (6'). The change of melting point by this revision may not be of a negligible order, however we may see the inclination of change in the melting point with different values of n by the calculation using the same numerical values in expression (6'). The result obtained is shown in Figure 2 in the case of $\delta = 0.12$. With higher value of δ the curve in Figure 2 shifts downward. It is easily supposed that the melting point has a strong dependence on n since the molecular distances of nearest neighbors at the melting point are so short that the repulsive force plays an important role. To reduce

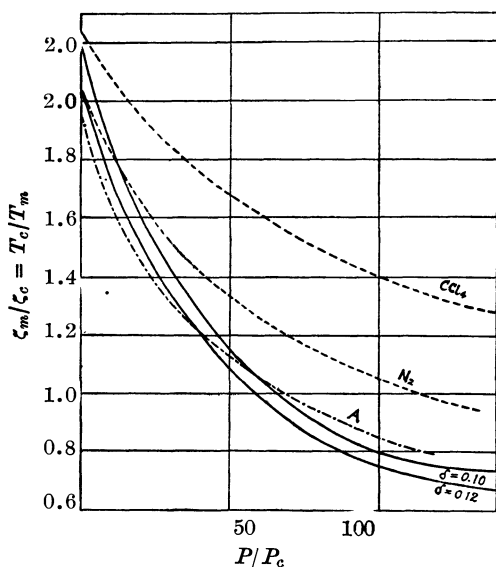


Fig. 1.

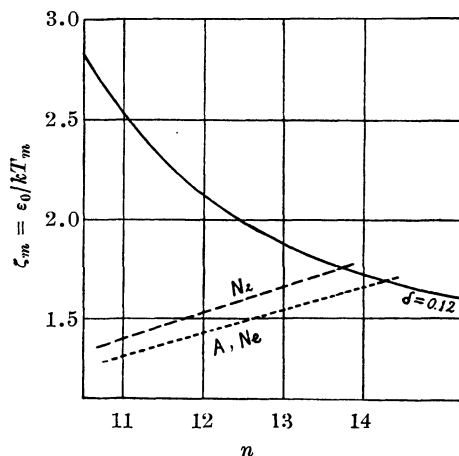


Fig. 2.

the observed melting temperature T_m to $\zeta_m = \epsilon_0/kT_m$ we have determined the values of ϵ_0 . Lennard-Jones and Buckingham have determined the values of ϵ_0 for argon, neon and nitrogen, etc. using the results of exact measurements on isotherms of these gases. These results show a linear dependence of ϵ_0 on n . Estimated values of ζ_m using these values are shown in Figure 2 by the dotted line for argon, neon and nitrogen. The cross points of full line and dotted lines indicate proper values of n with which the calculated melting point agree with the observed values. Therefore we may obtain a rough estimation of the relative values of n for simple molecules by this method. If we assume that the relation $T_c = 4\epsilon_0/3k$ holds for $n=12$ and also ϵ_0 changes with n in a similar way as illustrated for A, Ne and N, we can obtain the relative values of n from the critical and melting temperature. When molecules have an attractive force proportional to r^{-6} we may conclude that the lower value of the ratio T_c/T_m corresponds to a higher value of n . The noble gases have the highest value of n and other molecules having more complex structures show lower values of n .

The volume change Δv by fusion is obtained from the values of R_s , R and $[Z]_{AV}$ at the melting point which are presented in Table 3. R_s is obtained by the solid state equation (24) at the melting temperature and pressure. Using the relation (10) we get

$$\Delta v = v_l - v_s = v_{so} \left[\frac{12}{[Z]_{AV}} \left(\frac{R}{R_{so}} \right)^3 - \left(\frac{R_s}{R_{so}} \right)^3 \right] \quad (29)$$

as a volume change from a liquid state to a

face centered crystalline state, where v_{so} is a volume per molecule and R_{so} is R in a solid at $P=0$, $T=T_m$.

The entropy of fusion per molecule may be written using the following thermodynamic relation,

$$\Delta S = \left(\frac{\partial \Delta \mu}{\partial T} \right)_p = \zeta_m k \left(\frac{\partial \Delta \mu / \epsilon_0}{\partial \zeta} \right)_p \quad (30)$$

From Eq. (27) though we may obtain the derivative of the right side in Eq. (30), it is easier to make numerical or graphical calculation using the following relation,

$$\begin{aligned} \left(\frac{\partial \Delta \mu / \epsilon_0}{\partial \zeta} \right)_p &= \left(\frac{\partial \Delta \mu / \epsilon_0}{\partial \zeta} \right)_\xi + \left(\frac{\partial \Delta \mu / \epsilon_0}{\partial \xi} \right)_\zeta \\ &\quad \times \frac{\xi \left(\frac{\partial (R^6 [Z]_{AV}^{-2})}{\partial \zeta} \right)_\xi}{R^6 [Z]_{AV}^{-2} - \xi \left(\frac{\partial (R^6 [Z]_{AV}^{-2})}{\partial \xi} \right)_\zeta} \end{aligned}$$

The theoretical fusion parameters $\Delta v/v_{so}$ and ΔS thus obtained in the case of $\delta=0.10$ and 0.12 are also given in Table 3. The observed values at high pressure in Table 3 is obtained by the interpolation of Bridgman's measurements, where the values used for P/P_c are the same as those in the case of $\delta=0.10$. At ordinary pressure, calculated fusion parameters agree remarkably well to experimental values in the case of $\delta=0.10$. On the other hand, though the pressure dependence of fusion parameters ΔS and $\Delta v/v_{so}$ agree moderately well with experiments for argon, but the agreement is rather poor when compared with that of the

Table 3

Calculated and Observed Fusion Parameters

	ξ	P/P_c	ζ_m	$[Z]_{AV}$	R^{-6}	R_s^{-6}	$\Delta v/v_{so}$	ΔS , cal./mol
Calc.	0	0	2.124	11.19	0.853	1.005	0.164	3.8
	0.15	13.3	1.715	11.22	0.878	1.009	0.136	3.5
	0.5	48.4	1.175	11.40	0.947	1.055	0.108	3.1
	1.0	109.1	0.769	11.40	1.069	1.173	0.096	2.4
Calc.	0	0	2.208	11.34	0.902	1.010	0.121	3.4
	0.15	12.5	1.776	11.40	0.928	1.022	0.104	3.1
	0.5	45.7	1.239	11.47	1.002	1.080	0.083	2.7
	1.0	103.5	0.817	11.47	1.134	1.209	0.073	2.2
Obs. for argon					Obs. for nitrogen			
P/P_c	T_m	ζ_m	$\Delta v/v_{so}$	ΔS	T_m	ζ_m	$\Delta v/v_{so}$	ΔS
0	83.7	1.433	0.125	3.34	63.1	1.53	0.069	3.45
12.5	97.6	1.229	0.101	2.80	71.8	1.34	0.062	3.38
45.7	131.1	0.915	0.063	2.11	91.8	1.05	0.050	3.17
103.5	180.2	0.668	0.037	1.52	121.0	0.80	0.034	2.72

Sources: ϵ_0 and r_0 are same as in Tab. 2.

Observed values are from Randolt, and Börnstein, "Physik.-Chem. Tab. Eg. IIIc," 2687, 2689.

pressure dependence of melting temperature.

The molecular arrangements at high pressure will become more likely similar to the solid state arrangements. And it may be expected that the higher the pressure becomes, the steeper the distribution of the distances between two nearest neighbors becomes, and also the shorter these distances become. From the general inclination of change of fusion parameter with the change of δ we can expect that a better agreement may be obtained between calculated and observed values of ΔS and $\Delta v/v_0$, when we assume smaller values of δ at higher pressure.

The quantitative agreements between theoretical and experimental values of fusion parameters may be expected when we take into consideration the pressure dependence of the value of δ and a revision regarding a calculation of the free volume which was performed with a model of too restricted molecular motion in this paper. We may therefore conclude that the experimental confirmation of assumption on the molecular arrangements as well as the procedure of the construction of partition function is adequate. To know the behavior of the liquid state and liquid-solid equilibrium at the pressure higher than $P/P_c \sim 100$ we have to check the correctness of the approximate formula for free volume expressed by Eq. (6), since at such pressure R^{-6} and R_s^{-6} becomes larger than 1.2.

4. Summary

The molecular arrangements in liquid state may be characterized by assignment of the number of nearest neighbors on each molecule, and distances between two nearest neighbors. The assumption is made on the distribution of distances r between the two nearest neighbors which does not take a definite value as in the crystalline state but is distributed over the region of $[r(1+\delta), r(1-\delta)]$. The partition function and state equation are deduced under these assumptions using proper values of δ expected by X-ray diffraction on liquid argon. The critical constants for a simple liquid are determined which agree well with experimental values. The condition for the equilibrium between liquid and solid crystalline states is obtained on the basic assumptions that the essential differences of liquid and solid states consist in the difference of values of δ and the number of nearest neighbors around each molecule. The calculated melting temperature, volume and entropy increments by fusion and pressure dependences of these fusion parameters agree well with experimental values.

The author wishes to express his hearty thanks to Dr. Y. Miyake for his constant encouragement on this work.

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Studies on the Purities of Precipitate and Crystal. IV.
The Investigation or Presumption of Solubility
by Co-precipitation Phenomena

By Toshiyuki ÔSAWA

(Received October 25, 1949)

Preparation of pure substance and mechanism of co-precipitation phenomena have long been studied in the fields of analytical and general chemistry.

The colloidal precipitates which are easily soiled by the adsorption of foreign ions become larger particles when formed under suitable conditions, and the adsorption of foreign ions will be decreased. Larger crystals of soluble salts are soiled by the occlusions on inner surfaces, and when they are made small by some method, for example, by the rapid

cooling of hot saturated solution,⁽¹⁾ their occlusions will be decreased.

Therefore, the pure substances which show little adsorption or occlusion will be obtained by a suitable procedure; namely, by making particles of some definite size.

Dr. Takio Katô (Prof. of Faculty of Engineering, Tôhoku University) forecasted as follows⁽²⁾:—"Particles of slightly soluble salts are

(1) T. Ôsawa, *Chem. Anal. & Reag., Japan*, **7**, 256 (1948).
(part I).

(2) T. Katô, *ibid.*, **7**, 248 (1948).

fine, while soluble salts form bigger particles. In conclusion, there will be definite relations between adsorption or occlusion of foreign ions by precipitates and solubilities at their formation. The size of pure precipitate or crystal, in other words, their solubilities will be smaller than potassium chloroplatinate (10^{-1} mol/l. at room temp.), but greater than barium sulfate (10^{-5}). Thus, the substances, having about 10^{-3} mol/l. solubility, or formed under the condition of about 10^{-3} mol/l. solubility will be almost pure."

As to this point, I have obtained almost the same conclusion with chromate of barium, potassium⁽¹⁾ and lead, that is, on the relation between acidity or solubility and coprecipitations of Cl^- , SO_4^{2-} and K^+ . And all pure substances will be obtained by the formation under a definite condition, the solubility being about 2×10^{-4} mol/l. (20°).

If the relations above mentioned were right, the solubilities of substances might be presumed from these relations. And according to the present research on the oxalates, it is concluded by the author that the solubility of zinc oxalate would be greater than that generally used.

Co-precipitation of Ferric Ions by Oxalates

The opinion⁽³⁾ of the present author on the relations between co-precipitations of ferric ions and solubilities of oxalates has been published⁽³⁾ and several opinions have already been reported by some authors. A part of these is shown in Table 1. These are mg. mol of irons in 1.0000 g. of oxalates, precipitated under a definite condition concerning temperature, foreign ions, addition velocity, direction of addition, aging, stirring, washing, drying etc.

Table 1

Oxalates	Solubilities, ⁽⁴⁾ mol/l.	Temp., $^\circ\text{C}$.	Authors	(A)	(B)
Ba	3.8×10^{-4}	18	F. Kohlrausch	0.135	0.193
Sr	$2.5 \times "$	"	F. K. & Rose	0.130	0.183
Cd	$1.7 \times "$	"	F. Kohlrausch	0.121	0.179
Cu	$1.6 \times "$	25	Schöfer		0.174
Ag	$1.1 \times "$	18.5	F. Kohlrausch	0.065	0.107
Ca	4.3×10^{-5}	18	"	0.158	0.459
Zn	$4.1 \times "$	17.2	"	0.104	0.116
Pb	5×10^{-6}	18	"	0.263	0.441

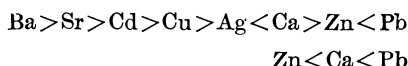
The determination of co-precipitated irons was made as follows:—Oxalate ions were decomposed by permanganate solution, excess

of manganese dioxide by 3% hydrogen peroxide solution, and after being concentrated, iron was determined colorimetrically with potassium thiocyanide solution.

As another method, after the sample had been treated with permanganate, excess of manganese dioxide and iron were reduced in the reductor of liquid zinc amalgam, and titrated with permanganate standard solution.

(A) is mg. mol of irons in 1.0000 g. of oxalates. Oxalates were formed under 0.625 cc./min. add. velocities, washed five times with 50 cc. distilled water and dried at 90° for 5 hours. The same conclusion was obtained with oxalates dried at 105° for 2 hours. Nitrates of each metallic ions were used, when oxalates were found to be purer than those when acetates were used.

(B) is irons in oxalates, separated after the formation by filtration, transferred to another filter paper, pressed on both sides with five sheets of 9 cm. filter paper, and dried at 90° for 5 hours. The determination of purity was made by the same way as before. When oxalates were separated by suction only, the same relation as (B) was obtained. The silver oxalate was precipitated in the dark room.



Presumption for the Solubility of Zinc Oxalate

From Table 1, except zinc oxalate, it is known that the regular relations are held between solubilities of oxalates and co-precipitations of ferric ions by oxalates, which are analogous to those of barium chromate and calcium oxalate.^{(1),(5)} The transition point of adsorption and occlusion of foreign ions is about 2×10^{-4} mol/l. at room temperature. For example, magnesium oxalate (1.3×10^{-3} mol/l.) and uranyl oxalate (2.1×10^{-2}) are not pure on account of occlusion, and cerium oxalate (1.6×10^{-7}) or lead oxalate (5×10^{-6}) is not so pure as copper oxalate (1.6×10^{-4}) or silver oxalate (1.1×10^{-4}) on account of adsorption.

Therefore, the separation of lead or cerium in pure state from foreign ion will be established by increasing the solubility to about 2×10^{-4} mol/l.; for example it will be achieved by using 1.0 ~ 1.5 N nitric acid⁽³⁾ as the solvent. Of course, if acidity of solution increases, then oxalates may become impure again. So it is forecasted that, perhaps, presumption of solubility will be possible by

(3) T. Ôsawa, *J. Chem. Soc. Japan*, **71**, 191 (1950). (part III).

(4) Seidell, "Solubll. inorg. & metal. org. comps." (1940).

(5) T. Ôsawa, *J. Chem. Soc. Japan*, **71**, 68 (1950). (part II).

the use of this phenomenon.⁽⁶⁾

According to F. Kohlrausch⁽⁷⁾ the solubility of zinc oxalate is 4.1×10^{-5} mol/l. at 18° . Therefore, according to the author's surmise, the quantity of co-precipitation of iron by zinc oxalate might be between calcium oxalate (4.3×10^{-5}) and lead oxalate (5×10^{-6}), but is found less than the case of calcium oxalate (Table 1).

From the viewpoint of relations between co-precipitation phenomena and solubilities, the solubility of zinc oxalate would be between silver oxalate (1.1×10^{-4}) and copper oxalate (1.6×10^{-4}), or between silver oxalate and calcium oxalate (4.3×10^{-5}), because the quantities of co-precipitated irons by zinc oxalate are nearer those of copper or silver oxalate rather than those of calcium or lead oxalate.

If the solubility of zinc oxalate is about 4.1×10^{-5} mol/l. (F. Kohlrausch), it seems to act on the acid solvents like lead or calcium oxalate. But the transition point of adsorption and occlusion in zinc oxalate is 0.009 *N* of nitric acid,⁽³⁾ and is more similar to copper oxalate than to oxalate of lead or calcium. It is presumed, therefore, the solubility of zinc oxalate may be $1.1 \sim 1.6 \times 10^{-4}$ mol/l. at room temperature.

Determination of Solubility and Composition of Zinc Oxalate

The oxalate, prepared in a suitable solvent, was stirred with distilled water in a thermostat at $20^\circ \pm 0.05^\circ$, and its solubility was determined by titrating the soluble oxalate ions with the permanganate solution.

As to zinc oxalate, a sample was prepared by the following way:—The equivalents of zinc nitrate and ammonium oxalate were separately dissolved in 0.05 *N* nitric acid, which is a good solvent for zinc oxalate,⁽³⁾ and zinc nitrate solution was stirred at 80° , and then ammonium oxalate was added in the direction of $\text{C}_2\text{O}_4^{--} \rightarrow \text{Zn}^{++}$ to prevent the formation of soluble oxalate complex. The precipitate washed ten times, and after digested in water with stirring to the equilibrium at $20^\circ \pm 0.05^\circ$, it was filtered by using Tôyo roshi No. 5c, No. 4 and platinum filter cone, and the filtrate was titrated with permanganate solution.

The titration was carried out under a definite condition; 5 cc. of 6 *N* sulfuric acid and 2 cc. of *N*/10 sodium oxalate standard solution were added for the end point correction etc. In

Table 2, *x* is titres of *N*/10 KMnO_4 for 2 cc. $\text{Na}_2\text{C}_2\text{O}_4$ solution, 5 cc. of 6 *N* H_2SO_4 and 25 cc. distilled water.

In primary experiments, substances, which have $10^{-4} \sim 10^{-6}$ mol/l. solubility, required about 7 hours to attain equilibrium with distilled water.

And, as expected, with zinc oxalate, greater values than that of F. Kohlrausch were found, but it was presumed that it might be due to the complex formation.

In Table 2, data marked * are for zinc oxalate determined by the following procedure. The composition of zinc oxalate was determined by the estimation of ZnO and C_2O_4 , the former by means of ignition, and the latter by titration with permanganate solution.

Table 2

Stirring hours, hr. min.	<i>N</i> /10 KMnO_4 titres (means),		<i>x</i> factor (means),		Titres Solubility, <i>x</i> , mol/l.	
	cc.		cc.	cc.		
5	1.850	0.929	1.800	0.050	0.9	10^{-4}
2.05	1.860	"	1.790	0.070	1.3	"
7.00	2.820	"	2.745	0.075	1.4	"
7.35	1.876	"	1.800	0.076	1.4	"
16.53*	3.220	1.227	3.170	0.050	1.2	"
70.00*	1.950	1.032	1.890	0.060	1.2	"
72.00*	1.950	"	1.890	0.060	1.2	"
96.02	2.823	0.929	2.740	0.083	1.4	"

The distilled water, used in the experiments, was prepared in this laboratory and its specific conductivity was found to be 3.6×10^{-6} cm.⁻¹ Ω⁻¹.

Table 3

No.	Sample, g.	<i>N</i> /10 KMnO_4 , cc.	ZnO , g.	Zn, %	C_2O_4 , %
1	0.2036	17.50			46.41
2	0.2013	17.31			46.43
3	0.3455		0.1483	34.49	
4	0.2675		0.1149	34.50	
5	0.1980		0.0850	34.49	
6	0.1951	16.81			46.52
7	0.2472	21.29			46.50
8	0.2607	22.41			46.41
9	0.2265	19.49			46.46
means				34.49	46.46

(Chemical factor of *N*/10 KMnO_4 is 1.227.)

The theoretical percentage of Zn and C_2O_4 in various forms of zinc oxalate are as follows:—

Forms of Oxalate	Zn, %	C_2O_4 , %
ZnC_2O_4	42.62	57.38
$\text{ZnC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	38.18	51.35
$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	34.52	46.47
$(\text{NH}_4)_2\text{Zn}(\text{C}_2\text{O}_4)_2$	23.56	63.45

(6) T. Ôsawa, at meeting of Tohoku Branch, Chem. Soc. Jap., July, 1949.

(7) Landolt-Börnstein, "Physik. Chem. Tabellen," 3 auf. 584 (1905).

From above data, it is deduced that the samples used for the determination of solubilities in Table 2 are not oxalate complex, but $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. An investigation was made for other oxalates' solubilities with the same precedures. The results are as follows:—

Table 4

Oxalates	Authors	Temp., °C.	Solubilities reported, mol/l.	Hours equil. hr. min.	Solubility measured, mol/l.
Ba	F. Kohlrausch	18	3.8×10^{-4}	7.0	4.2×10^{-4}
Sr	" & Rose	"	2.5 "	7.45	3.2 "
Cd	"	"	1.7 "	7.0	1.9 "
Cu	Schöfer	25	1.6 "	2.0	1.55 "
Ag	F. Kohlrausch	18	1.1 "	52.0	0.7 "
Ca	Aumerase	20	5.7×10^{-5}	70.0	5.9×10^{-5}
Pb	F. Kohlrausch	18	$5. \times 10^{-6}$	7.0	$7. \times 10^{-6}$

($20^\circ \pm 0.05^\circ\text{C}$)

Silver oxalate was decomposed easily and its solubility differed from F. Kohlrausch's, so the time of stirring seemed short, but the present author always obtained lower values in spite of more than 72 hours stirring. Other oxalates were almost of the same value even more than stirring times of Table 4. And some oxalate were determined by the same procedure and their composition were $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

Summary

The solubility of zinc oxalate has been reported by Kunschert (7×10^{-5} mol/l. at 25°)⁽⁸⁾

or F. Kohlrausch (4.2×10^{-5} at 18°)⁽⁹⁾ but, from the viewpoint of the relations between solubility and co-precipitation phenomena, it would be greater than their values, perhaps about $1.1 \sim 1.6 \times 10^{-4}$ mol/l. at room temperature.

Measurements showed the solubility of zinc oxalate, of which composition was $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, to be 1.2×10^{-4} mol/l. at $20^\circ \pm 0.05^\circ$. This is almost the same with the result obtained by Scholder, Gadene and Niemann (1.36×10^{-4} mol/l. as 18°)⁽⁴⁾ but further details are not clear.

By the relations between solubility and co-precipitation phenomena, a presumption or investigation of solubility may be possible; namely, it may be determined by the use of the transition point of adsorption and occlusion of foreign ions (about 2×10^{-4} mol/l. at 20°). Needless to say, the formation or treatment of precipitate should be done under the same condition. The study on a mechanism for the adsorption or Balarew's occlusion phenomena⁽¹⁰⁾ is in progress.

The author expresses his gratitude to Dr. Matsusuke Kobayashi and Dr. Takio Katô who gave him the valuable guidance, and also to Mr. Seikô Nagasawa for his co-operation.

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(8) Kunscheht, *Z. Anorg. Chem.*, **41**, 337 (1904).

(9) F. Kohlrausch, *Z. Physik. Chem.*, **12**, 234 (1893).

(10) Balarew, *Z. Anal. Chem.*, **101**, 161 (1935); **102**, 241, 408 (1935); **106**, 249 (1936); **107**, 289 (1936); *Z. Physik. Chem.*, **30**, (1935), etc.

Biochemical Studies on Vitamin B₁₂. I~II⁽¹⁾

By Yoshikazu SAHASHI, Masayuki MIKATA and Heiichi SAKAI

(Received September 11, 1950)

Introduction

Since the year 1948 the chemical and biological studies on vitamin B₁₂ have made a very rapid progress due to the effort of E. L. Rickes, E. L. Smith and co-workers who isolated it in crystalline state and established its

biochemical researches. Afterwards, many investigations have appeared on the physiologically active principle of vitamin B₁₂ and the behavior of Animal Protein Factor (A.P.F.) has also been successfully confirmed.

The recent advance of the vitamin B₁₂ chemistry caused the present authors to attempt further studies on a simple preparation of vitamin B₁₂ concentrate (Part I) and biochemical synthesis of vitamin B₁₂ from 5, 6-dimethyl-

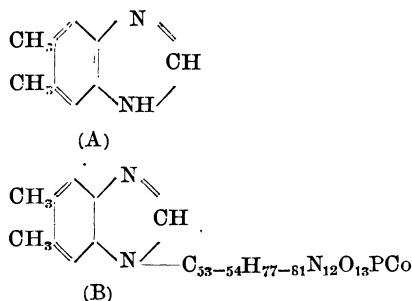
(1) This report was first read, on July 15, 1950, in the 40th meeting of the Vitamin B Research Committee in Japan.

benzimidazole (Part II), because there is little supply of A. P. F in Japan.

In part I, the isolation of vitamin B₁₂ concentrate was carried out with the J. M. Pensack's²⁾ modified method, and physiological tests were thoroughly studied by Dr. S. Ito (bone marrow culture test), Dr. K. Inoue (clinical test) and Dr. K. Sakaguchi (L. L. D. active test).

In part II, the present authors attempted a few studies on the biochemical synthesis of vitamin B₁₂ from 5, 6-dimethyl-benzimidazole.

In 1949, N. G. Brink *et al.*³⁾ isolated a degradation product from crystalline vitamin B₁₂ by acid hydrolysis which has been identified by synthesis as 5, 6-dimethylbenzimidazole (A), and consequently proposed that a provisional formula for vitamin B₁₂ may be represented as follows (B):—



In the same year V. Kocher *et al.*⁴⁾ reported that deoxyribosides of thymine, guanine, cytosine and hypoxanthine can replace vitamin B₁₂ as a nutrient of *Lactobacilli*. In March 1950, T. Tomiyama⁵⁾ also found in the fish liver a new anti-anemia factor containing no cobalt.

Afterwards many investigations have been reported about the further characterization of vitamin B₁₂, but until quite recently (July 15th, 1950) no publication of biochemical studies on the implications of the vitamin B₁₂ and 5, 6-dimethylbenzimidazole has been appeared.

In the physiological investigation of vitamin, it is already well known that the fresh animal tissue contains a substance which activates vitamin B₆ to pseudopyridoxine,⁶⁾ and, on the other hand, microorganisms such as yeast pos-

sess a power of synthesis of vitamin B₁ from pyrimidine portion and thiazole moiety.⁷⁾

Guided by the above literatures, the present authors at first carried out synthetical experiment of (A), and the pure crystal (A) thus obtained was used in the following biosynthetical experiments.

Experimental

A Simple Preparation of Vitamin B₁₂ Concentrate.

Vitamin B₁₂ Concentrate.—A solution of 80 % ethanol was added to the chopped fresh cow liver, and after refluxing for 5 hours, the mixture was filtered. Refluxing process was repeated three times and the extract was consolidated, evaporated and filtered. The filtrate was treated with activated charcoal, and the charcoal adsorbate was eluted with 5 % NH₄OH in 50 % ethanol.

On evaporating the filtrate, vitamin B₁₂ concentrate was obtained in syrupy state. The vitamin B₁₂ concentrate thus obtained was dissolved in saline solution and diluted to 9~10% of pure vitamin B₁₂ per cc. according to our supposition.

Cobalt determination was tested by Dr. I. Tachi with the polarographic method.

Physiological Tests.—Bone marrow culture test was carried out by Dr. S. Ito. 0.1×10^{-3} ~ 0.1×10^{-4} diluted solution of the vitamin B₁₂ concentrate gave the satisfactory responses in red blood cell (R.B.C.), white blood cell (W.B.C.) and reticulocyte. 0.1×10^{-2} diluted solution of the concentrate gave a W.B.C. value similar to that given by 0.1 cc. of normal blood serum and 0.1×10^{-1} diluted solution of concentrate gave a R.B.C. count similar to that given by 0.1 cc. of normal blood serum. Moreover, the bone marrow response given by 0.1 cc. of normal blood serum corresponded to 10% of folic acid.

Antagonistic activity test was negative against aminopterin and so the concentrate was proved to be free from folic acid. Furthermore, comparative studies of the bone marrow culture with standard solution of vitamin B₁₂ (Merck's Cobione) were carried out by Dr. S. Ito. One cc. of the vitamin B₁₂ concentrate was accurately estimated to correspond to 10% of pure vitamin B₁₂.

Clinical test was carried out by the cooperation of Dr. K. Inoue. For macrocytic anemia patients, favorable results were obtained by subcutaneous injection of 1~2 cc. per week. Details were reported in the Proceedings of the Vitamin B Research Committee (Vol. 36~40, 1950).

L.L.D. active test was also carried out with the microbiological assay by Dr. K. Sakaguchi.

Biochemical Synthesis of Vitamin B₁₂ Active substance.

4, 5 - Dimethylphenylenediamine (1, 2) -

(2) J. M. Pensack, R. M. Betheke and D. C. Kennard, *J. Nutrition*, **37**, 363 (1949).

(3) N. G. Brink and K. Folkers, *J. Am. Chem. Soc.*, **71**, 2951 (1949).

(4) V. Kocher and O. Schindler, *Inter. Z. Vitaminforsch.*, **20**, 441 (1949).

(5) T. Tomiyama, Reported in the 38th meeting of Vitamin B Research Committee (1950).

(6) F. Schlenk and E. E. Snell, *J. Bio. Chem.*, **157**, 425 (1945).

(7) J. Ashida, *Bull. Agr. Chem. Soc. Japan*, **18**, 732 (1942); **19**, 719 (1943).

-dihydrochloride (C).—4, 5-Dimethylphenylenediamine was prepared from 3, 4-dimethyl-6-nitroaniline which was previously reserved for the experiments of synthetic flavin⁽⁸⁾ from *p*-nitrotoluene and *s*-dichloromethylether. 3, 4-Dimethyl-6-nitroaniline was dissolved in glacial acetic acid and converted to 4, 5-dimethylphenylenediamine (1, 2) by catalytic reduction with platinum oxide, and to the resulting diamine concentrated HCl was added. On evaporating, the hydrochloride (C) was obtained in colorless needles, melting at above 280° (uncorr.). Found: N, 13.10. Calculated for C₈H₁₄N₂Cl₂: N, 13.39 %.

5, 6-Dimethylbenzimidazole (A).—4, 5-Dimethylphenylenediamine (1, 2)-dihydrochloride (C) was treated with formic acid in a boiling water-bath, and while still hot the mixture was filtered. The filtrate was neutralized with sodium hydroxide to slightly alkaline state, and on standing over night crystalline precipitates separated out. After recrystallizing the precipitates from hot water, (A) was obtained, fine needles melting at 200° (uncorr.). Found: C, 72.69, 72.66; H, 7.62, 7.23; N, 19.44, 19.82; Calculated for C₉H₁₀N₂: C, 73.97; H, 6.84; N, 19.01 %.

Biochemical Synthesis of (B) from (A) with the Fresh Chick Liver Paste.—Ten mg. of (A) was added to 20 g. of the fresh chick liver paste. The mixture was treated with a few drops of toluene, and autolyzed at 37° in a thermostat. After 60 hours, the reaction product was extracted with hot water and the clear filtrate was collected. On evaporating under the diminished pressure, the residual matter was dissolved in 10 cc. of water. The vitamin B₁₂ potency was estimated by the microbiological assay using *Lactobacillus lactis* Dorner. The blank test was also carried out with an ordinary chick liver paste in the same condition. The comparative data are shown in Table 1.

Table 1

Vitamin B₁₂ Contents in the Fresh Chick Liver Paste Treated with 5, 6-Dimethylbenzimidazole Added.

Contents of vitamin B ₁₂	Vitamin B ₁₂ potency in 2 g. of fresh chick liver, γ	Vitamin B ₁₂ potency in 100 g. of chick liver, γ
Fresh liver paste (control)	0.22	11.0
Fresh liver paste treated with 5, 6-dimethylbenzimidazole	0.27	13.5

The above result indicated about 20~25 %

increase of vitamin B₁₂ potency in the chick liver paste by the treatment of (A).

Synthetical Experiments of (B) with Streptomyces from (A).—To the Dulaney broth for *Streptomyces x-28*, (A) was added and after six days' incubation the broth was assayed microbiologically by *Lactobacillus lactis* Dorner. The results obtained are shown in Table 2.

Table 2

Vitamin B₁₂ Potency in the Broth of Streptomyces by Adding 5, 6-Dimethylbenzimidazole.

Broth	Vitamin B ₁₂ potency in the broth, u/cc.*		
	Exp. 1.	Exp. 2.	Control exp.
Dulaney broth	37.5	50.0	0
Dulaney broth } CoCl ₂ 0.06 mg./50cc.	50.0	51.0	0
Dulaney broth } 5, 6-dimethylbenzimidazole 1 mg./50 cc.	90.0	98.0	0

* u = L. L. D. unit (1 γ = 11000 L. L. D. units)

The above experiments demonstrated about 100~150 % increase of vitamin B₁₂ potency in the broth of streptomyces by adding (A), while the addition of CoCl₂ seemed little effective. On the other hand, the effect of pure (A) and inorganic cobalt ions upon the growth of L. L. D. was tested, but no response for the particular increase of vitamin B₁₂ potency was observed.

Summary

In part I, a simple method for isolating vitamin B₁₂ concentrate was studied.

In part II, (A) was decided to be a prosthetic group in natural (B) molecule biochemically, and the biosynthesis of (B) from synthetic (A) could be attained successfully.

The authors wish to express their sincere thanks to Prof. Y. Kuno for his kind guidance. And they are also indebted to Drs. K. Inoue, K. Sakaguchi, I. Tachi and S. Ito for their hearty cooperation. The cost of this research has been defrayed from the Vitamin B Research Committee and the Institute of Pharmaceutical Resources, to which the authors' thanks are due.

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the University of Tokyo, Tokyo

(8) Y. Sahashi, *Proc. Imp. Acad.*, **21**, 14 (1945).

On the Irreversible Reduction Wave of Titanic Ion at the Dropping Mercury Electrode⁽¹⁾

By Reita TAMAMUSHI

(Received October 17, 1950)

It has been shown by Strubl's work⁽²⁾ that the titanitic-titanous system gives a well-defined polarographic oxidation-reduction wave of the irreversible type in the medium of hydrochloric acid. In the previous paper⁽³⁾ the equation for the polarographic oxidation-reduction wave of the irreversible type was derived from the view-point of chemical kinetics. Now, in order to obtain the experimental supports on the results obtained by the theoretical consideration, the polarographic behavior of titanitic ion in the sulfuric acid solution was investigated. In this paper, the results on the cathodic wave due to the electroreduction of titanitic ion will be discussed.

Experiments

Apparatus.—Both the "manually operating polarograph" and the "photo-recording polarograph with the Kalousek's circuits"⁽⁴⁾ were used. Most of the accurate measurements, *e. g.*, the determination of the half-wave potential, were carried out with the former. The Kalousek's method was used to test the reversibility of the polarographic electrode reaction. A normal calomel electrode (N. C. E.), which is connected with the solution of the polarographic cell by 1 *N* KCl solution and 1 *N* KNO₃-agar-bridge, was used as a reference electrode. The atmospheric oxygen was removed from the solution with a stream of pure hydrogen gas obtained by the electrolysis of NaOH solution. The temperature of the polarographic cell was maintained at 25.0 ± 0.1° in a thermostat.

The capillary constant, $m^{2/3} t^{1/6}$, of the dropping mercury electrode in 0.065 *N*-H₂SO₄ free from the oxygen was 1.14 mg.^{2/3} sec.^{-1/2} without applied potential and 1.13 mg.^{2/3} sec.^{-1/2} at -1.0 volt *vs.* N. C. E.

The Preparation of Ti⁴⁺-H₂SO₄ Solution.—A small quantity of purified TiO₂ was dissolved in conc. H₂SO₄ with strong heating, and then this solution was diluted with distilled water. The

concentration of the titanitic ion was determined gravimetrically.

Experimental Results

The Relation of Ti⁴⁺-Concentration and Limiting-Current and that of Ti⁴⁺-Concentration and Half-wave Potential.

—The measurements were carried out with the solutions containing titanitic ion from 0.05 × 10⁻³ to 1.0 × 10⁻³ *M* in concentration. Some of the results are shown in Table 1 and one of the polarographic waves obtained is shown in Fig. 1. The supporting electrolyte contained

Table 1

Ti ⁴⁺ -Concn., mol/l.	<i>I</i> _d , amp.	<i>V</i> _{1/2} , volt <i>vs.</i> N.C.E.	<i>K</i> _d , amp./mol/l.	<i>α</i>
1.0 × 10 ⁻³	2.04 × 10 ⁻⁶	-0.828	2.1 × 10 ⁻⁸	0.58~0.56
" "	2.02 × "	-0.827	" "	0.57~0.56
0.5 × "	9.95 × 10 ⁻⁷	-0.826	2.06 × "	0.62
0.25 × "	5.07 × "	-0.829	2.11 × "	0.61
0.125 × "	2.44 × "	-0.820	2.03 × "	0.67

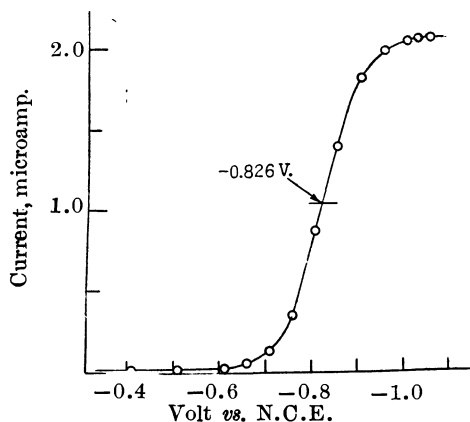


Fig. 1.—Reduction wave of Ti⁴⁺-ion in 0.065 *N* H₂SO₄.

sulfuric acid of the same concentration as contained in the standard solution of titanitic ion, so that the concentration of sulfuric acid in the measured solution was the same with changing the concentration of titanitic ion. The experimental results indicated that the limiting

(1) Presented at the 3rd annual meeting of the Chemical Society of Japan in April, 1950.

(2) R. Strubl, *Collection Czechoslovak Chemical Communications*, **10**, 475 (1938).

(3) R. Tamamushi and N. Tanaka, *This Bulletin*, **22**, 227 (1949).

(4) M. Kalousek, *Collection Czechoslovak Chemical Communications*, **13**, 105 (1948).

current (I_a) is proportional to the concentration of titanic ion, which is in agreement with the results obtained by Strubl.⁽²⁾

As for the half-wave potential of the Ti-wave, Strubl stated that the oxidation wave has the definite half-wave potential of -0.18 volt *vs.* N. C. E. while the half-wave potential of the reduction wave appeared at the potential of about -0.98 volt is not definite.⁽²⁾ However, the present experiment showed that the polarograms obtained in $0.065 N$ sulfuric acid give the definite half-wave potential of -0.825 ± 0.005 volt *vs.* N. C. E. (at 25.0°), which is independent of the concentration of titanic ion as shown in Table 1.

The Effect of the Concentration of the Foreign Electrolyte on the Half-wave Potential. — The half-wave potential was measured with the solutions containing sulfuric acid in concentration from 0.026 to $0.452 M$ for the purpose of finding out the relation between the half-wave potential and the concentration of the electrolyte (Fig. 2). In this measurement, titanic ion was kept at the same concentration. The results showed that the half-wave potential shifts to more negative value with the increase in concentration of sulfuric acid. The same results were obtained

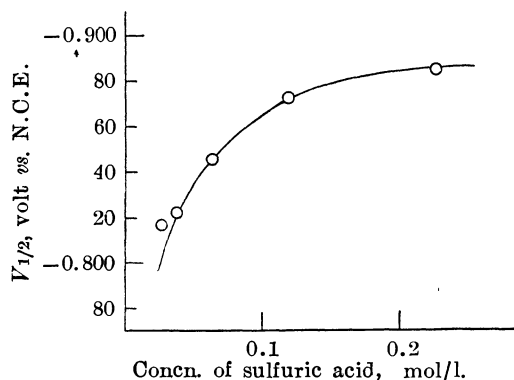


Fig. 2.—The effect of the concentration of sulfuric acid on the half-wave potential of Ti^{4+} -reduction wave.

by changing the concentration either of hydrochloric acid, ammonium sulfate, potassium nitrate, magnesium nitrate or aluminum nitrate (Fig. 3). Furthermore, it is to be mentioned here that Ti^{4+} - H_2SO_4 solution gave the quite different polarographic wave when the concentration of sulfuric acid became to be more than about $1 N$.

Relation of $\log I/(I_a - I)$ and V . — A plot of the potential V against $\log I/(I_a - I)$ gave a straight line as shown in Fig. 4, which

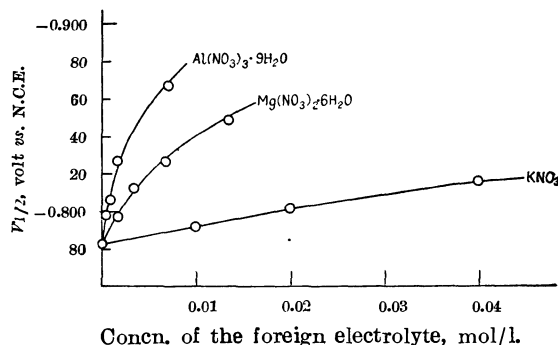


Fig. 3.—The effect of the concentration of the foreign electrolytes on the half-wave potential of Ti^{4+} -reduction wave. The salts mentioned in this figure was added to the Ti^{4+} -solution which contains $0.019 M H_2SO_4$.

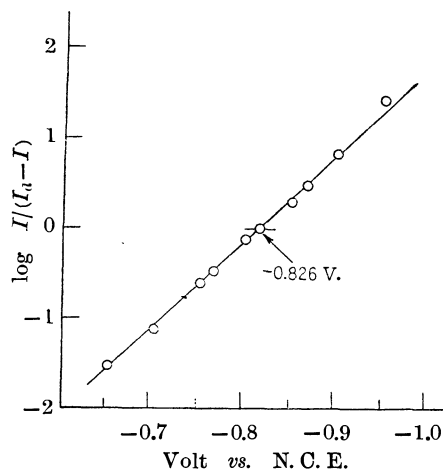


Fig. 4.—Relation between $\log I/(I_a - I)$ and V .

means that the reduction wave of titanic ion in $0.065 N$ sulfuric acid has a center of symmetry at the half-wave potential.

The Test of Reversibility of the Electrode Process with the Kalousek's Method.

— The results obtained with the Kalousek's method are shown in Figs. 5 and 6. The experimental results on the wave of Pb^{2+} ion in KOH solution are also shown in these figures as a typical example of the application of this method to a reversible wave. It can be seen from Fig. 5b that no oxidation current flows when the Kalousek's method I-a is applied to the reduction wave of titanic ion. Moreover, it was found by the Kalousek's method II that the anodic wave of the reduction product of titanic ion is obtained at the more positive potential than that of the cathodic wave of titanic ion. This means that, when the sufficient positive potential is given to the electrode, the reduction product of titanic ion

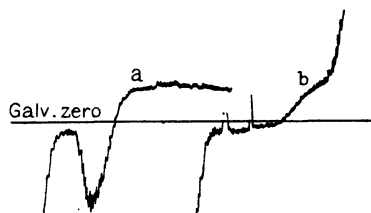


Fig. 5.—Polarograms obtained by Kalousek's method I-a: a, curve due to Pb^{2+} in KOH solution, difference 300 millivolts; b, curve due to Ti^{4+} in ca. 0.07 N H_2SO_4 , difference 100 millivolts.

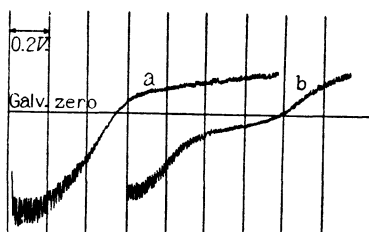
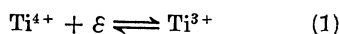


Fig. 6.—Polarograms obtained by Kalousek's method II: a, curve due to Pb^{2+} in KOH solution; b, curve due to Ti^{4+} in ca. 0.07 N H_2SO_4 .

can be oxidized at the dropping mercury electrode. This is in agreement with the fact that titanous ion can be oxidized at the dropping mercury electrode, and it gives the separated anodic wave from the cathodic wave of titanous ion.⁽²⁾

Discussion

Since, according to R. Strubl, the number of electrons concerning the reduction of titanous ion is one,⁽²⁾ it will be assumed that the reduction of titanous ion proceeds as shown in the following;



From the results of the Kalousek's method, it can be said that the polarographic electrode process of titanous ion proceeds irreversibly and that at the potential region of the reduction wave the velocity of the oxidation process is vanishingly small. Then, it is quite certain that the reduction wave of titanous ion is one of the irreversible type, and it may be considered that the activation process involving the transfer of an electron at the electrode surface is the rate-determining step of the over-all process. According to the theoretical treatment described in the previous paper⁽³⁾ the formulae of the current-voltage curve of the reduction wave in the activation-controlled

case can be represented as follows:

$$V = \text{const.} - \frac{RT}{n\alpha F} \ln \frac{I}{I_a - I} + \frac{RT}{n\alpha F} \ln f_o \quad (2)$$

$$I_a = nFK'_o[A_o]^\circ = nFK_o[C_o]^\circ \quad (3)$$

where I_a represents the limiting current of the reduction wave, F , the Faraday constant, n , the number of electrons which participate in the reaction, f_o , the activity coefficient of the oxidized ion, and K_o and K'_o are the constants concerning to the diffusion process, and $[C_o]^\circ$ and $[A_o]^\circ$, the concentration and the activity of the oxidized ion in the body of the solution, respectively. The term α is the portion of the electrode potential which promotes the reduction process, and it takes the value between 0 and 1.

If Eqs. (2) and (3) can be applied to the reduction wave of titanous ion, the half-wave potential will be independent of the activity or concentration of titanous ion, so far as the activity coefficient of the titanous ion remains constant, and the linearity of the relation between $\log I/(I_a - I)$ and V will be satisfied on the polarographic waves obtained experimentally. The experimental results indicated in Table 1 and Fig. 4 show clearly that they are in accord with the theoretical considerations. Consequently, it can be concluded that the reduction wave of titanous ion in the medium of sulfuric acid (less than about 1 N) is one of the activation-controlled type and the formulae of its polarographic wave are represented by Eqs. (2) and (3).

It must be mentioned here that the half-wave potential of the reduction wave of titanous ion varied with the change of the foreign electrolyte in the solution. It was experimentally found that the effect of the concentration of the electrolyte on the half-wave potential became larger when the valency of the cation of the foreign electrolyte increased. A similar result on the deposition potential of the hydrogen ion was reported by Herasymenko and Šlendyk,⁽⁵⁾ and it was explained by them by considering the adsorption of the ion. A. Frumkin⁽⁶⁾ developed his theory on the hydrogen overvoltage, and he interpreted reasonably the effect of the foreign electrolyte by introducing the conception of ζ -potential of Stern.⁽⁷⁾ In the present case, the shift of the half-wave potential of the reduction wave of titanous ion is expected to occur when either one or all of

(5) P. Herasymenko and I. Šlendyk, *Z. physik. Chem.*, **A 149**, 123 (1930).

(6) A. Frumkin, *ibid.*, **A 164**, 121 (1933).

(7) O. Stern, *Z. Elektrochem.*, **30**, 510 (1924).

the following conditions is fulfilled, namely: (1) when the state of titanic ion in the solution changes with the change of electrolytes; (2) when the activity coefficient of the titanic ion changes with the change of the ionic strength of the solution; and (3) when ζ -potential of the surface of the dropping mercury electrode changes with the change of the electrolytes and the value of the half-wave potential is affected by ζ -potential. The experimental results are, though qualitatively, in accord with the change of half-wave potential which is calculated on the assumption that the activity coefficient of titanic ion changes with the change of ionic strength of the solution. It is highly probable that the property of the double layer at the dropping mercury electrode and the value of ζ -potential will play an important role on the value of the half-wave potential. However, from the present study no conclusion can be driven out on the reason of the shift of the half-wave potential due to the change of the concentration of the foreign electrolytes.

Summary

The reduction wave of titanic ion in sulfuric acid medium was investigated in order to give some experimental supports to the theoretical

results on the irreversible wave which were derived from the standpoint of chemical kinetics. The Kalousek's method was used to test the reversibility of the reduction process of titanic ion at the dropping mercury electrode, and it was found that this process proceeds irreversibly. From the constancy of the half-wave potential, which is independent of the concentration of titanic ion, and from the linear relation between $\log I/(I_d - I)$ and V , which were proved by the experiments, it can be said that the theoretical equation (2) explains the feature of the irreversible reduction wave such as that of titanic ion. Furthermore, the effect of the foreign electrolytes on the half-wave potential was measured, on which some discussions were carried out.

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Studies on the Irreversible Polarographic Wave of Nickel-thiocyanate Complex

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The polarographic reduction wave of nickel-thiocyanate complex is one of the problems studied by several researchers from the standpoint of chemical analysis.⁽¹⁾ However, its theoretical treatment has not been carried out and its reduction mechanism has not been clarified, because it is considered to be of irreversible character. For these several years the theoretical treatment for the irreversible wave has been proposed by the author and other researchers, and it has appeared possible theoretically to analyse the irreversible wave of the complex. In this situation the present study

was taken up. One of the purposes was to clarify the reduction mechanism of the complex using the theoretical consequence reported in the previous paper⁽²⁾ and the other was to show that the theoretical consequence is applicable to the analysis of such an irreversible wave.

After some preliminary experiments, however, it was found out that the dissociation of nickel-thiocyanate complex in the solution is not simple and the reduction wave of the complex has most complicated behaviors. In spite of these facts it was possible to explain the result

(1) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **13**, 77 (1941); etc.

(2) R. Tamamushi and N. Tanaka, *this Bulletin*, **23**, 110 (1950).

obtained by the experiment, though partly, with the result derived from the theoretical treatment. In addition of the fact, the reduction wave of this complex is characteristic in several points of view. In the present paper the experimental results of the reduction wave of this complex and the reduction mechanism estimated from them have been presented.

Experiments and Experimental Results

Apparatus. — A manually operating polarograph and a photo-recording polarograph were employed, of which the former was employed for the accurate measurements. A dropping mercury electrode was used for the cathode and a normal calomel electrode, for the anode. Four capillaries were used for the dropping mercury electrode, which have the capillary constants, $m^{2/3} t^{1/6}$, of (a) 1.795, (b) 2.082, (c) 1.203 and (d) 1.336 ($\text{mg}^{2/3} \text{sec}^{-1/2}$), measured in distilled water free from oxygen without the applied potential. Of these capillaries, (c) and (d) were used for measuring the limiting currents at various heights of mercury reservoir. The value of 1.203 for (c) and 1.336 for (d) were the values measured at a 82 cm. of mercury height. All polarographic measurements were made in a thermostat of 25.0° with a normal calomel electrode as a reference electrode.

Standard Solution of Nickel and Supporting Electrolyte. — The nickel standard solution was prepared by dissolving Kahlbaum's nickel chloride (free from cobalt) in distilled water. The concentration of the stock solution was 1.640 milli *M*, which was determined by the gravimetric method.

For the supporting electrolyte the mixtures of potassium thiocyanate and potassium chloride and of potassium thiocyanate and potassium nitrate were used. When the medium of KSCN- KNO_3 was used, gelatine was added by 0.005% in concentration.

Polarograms of Nickel-thiocyanate Complex in the Supporting Electrolyte of Various Concentrations of Potassium Thiocyanate. — (a) **In the Medium of KSCN-KCl.** The current-voltage curves were measured with the solutions containing 0.328 milli *M* of nickel and various concentrations of potassium thiocyanate. Potassium chloride was added to all the solutions by 1 *M* in concentration to eliminate the effect of migration current appearing when the quantity of potassium thiocyanate was insufficient. Some of the polarograms obtained are shown in Fig. 1.

For all the polarograms $\log I/(I_t - I)$ was plotted against V , the plots holding a straight

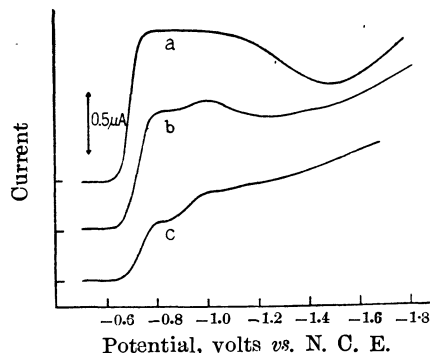


Fig. 1.—Polarograms of nickel-thiocyanate complex: the concentration of nickel, 0.328 milli *M*; supporting electrolyte, 1 *M* KCl +, (a) 0.5 *M* KSCN, (b) 0.02 *M* KSCN, (c) 0.01 *M* KSCN.

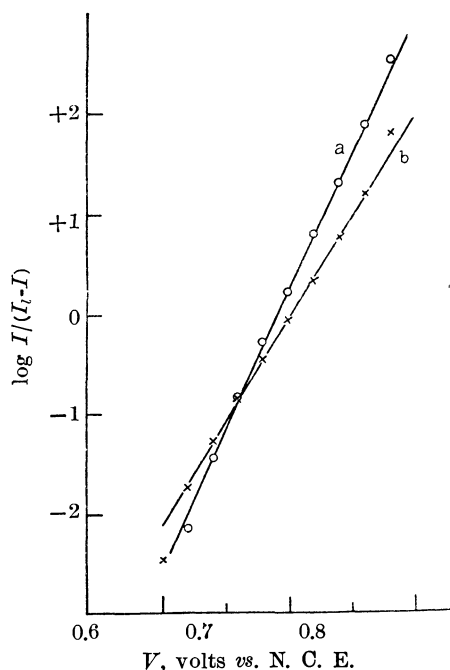


Fig. 2.—Relation of $\log I/(I_t - I)$ and V of polarograms of nickel-thiocyanate complex: supporting electrolyte, 1 *M* KCl +, (a) 0.5 *M* KSCN, (b) 0.04 *M* KSCN.

lines, some of which are shown in Fig. 2. From these log plots their inclinations and the half-wave potentials were obtained, which are shown in Table 1.

Some of the results obtained from these experiments are as follows: (1) The reduction waves of the nickel-thiocyanate complex have the center of symmetry at the half-wave potential, but their inclinations are not in accord with those expected from the reversible reduction wave. (2) Their half-wave potential

Table 1

The Half-wave Potential and the Inclination of Log Plot of the Polarograms Obtained in the Supporting Electrolyte Containing Various Concentrations of Potassium Thiocyanate and 1 *M* of Potassium Chloride

Concentration of KSCN, <i>M</i>	First wave		Second wave	
	Half-wave potential,* V.	Inclination of log plot, mV.	Half-wave potential,* V.	Inclination of log plot, mV.
2.00	-0.720	35		
1.00	-0.704	35		
0.50	-0.691	36		
0.20	-0.687	41		
0.10	-0.689	43		
0.04	-0.704	49		
0.02	-0.716	52	-0.925	48
0.01	-0.725	51	-0.916	79
0.005	-0.725	52	-0.912	82

* The half-wave potential is referred to a normal calomel electrode.

is the most positive when the supporting electrolyte contains about 0.2 *M* of potassium thiocyanate and shifts to negative potential with the increase or the decrease of concentration of potassium thiocyanate in the supporting electrolyte. (3) The second wave appears when the concentration of potassium thiocyanate is less than 0.04 *M*. (4) A minimum of current appears in the part of the limiting current's plateau of the current-voltage curve in the supporting electrolyte containing potassium thiocyanate more than 0.02 *M*, and it disappears when the concentration of potassium thiocyanate decreases down to 0.01 *M*. This is one of the most characteristic features of the polarograms of the complex. Some experiments were carried out on it, but the reason why it appears on the current-voltage curve could not be clarified in the present study.

(b) **In the Medium of KSCN-KNO₃.** The current-voltage curves were measured with the solution containing 0.328 milli *M* of nickel, various concentration of potassium thiocyanate and potassium nitrate and 0.005% of gelatine; the total concentration of potassium thiocyanate and potassium nitrate in the solution being adjusted to be 2 *M* to keep the ionic strength in the solution constant. They were also measured with the solutions containing various concentrations of nickel, 0.2 *M* of potassium thiocyanate, 1.8 *M* of potassium nitrate and 0.005% of gelatine to know whether the half-wave potential varies with the change of the concentration of nickel. The polarograms

obtained showed similar behaviors to those obtained in the medium of potassium thiocyanate and potassium chloride, so far as the appearance, the shift of half-wave potential with the concentration change of potassium thiocyanate and the less reversibility were concerned. The half-wave potentials, the inclination of the log plots and the diffusion current constants obtained in the supporting electrolytes containing various concentrations of potassium thiocyanate are shown in Table 2 and the half-wave potentials and the diffusion current constants obtained with the changing of the concentration of nickel, in Table 3. In this case the log plots were somewhat less linear when the concentration of potassium thiocyanate in the supporting electrolyte is considerably large.

Table 2

The Half-wave Potential, the Inclination of Log Plot and the Diffusion Current Constant of the Polarograms Obtained in the Supporting Electrolytes Containing Various Concentrations of Potassium Thiocyanate and Potassium Nitrate

Concentration of KSCN, <i>M</i>	Concentration of KNO ₃ , <i>M</i>	Half-wave potential vs. N.C.E., V.	Inclination of log plot, mV.	Diffusion current constant, $\mu\text{A}(\text{milli } M)^{-1} (\text{mg.}^2/\text{sec.}^{-1/2})^{-1}$
2.00	0	-0.745	39	3.23
1.50	0.50	-0.732	36	3.15
1.00	1.00	-0.726	43	3.25
0.50	1.50	-0.715	42	3.24
0.20	1.80	-0.708	47	3.03
0.10	1.90	-0.713	48	2.91
0.05	1.95	-0.727	49	2.48
0.03	1.97	-0.737	53	2.27
0.01	1.99	-0.764	63	(1.14)

Table 3

The Half-wave Potential and the Diffusion Current Constant of the Polarograms Obtained with Various Concentrations of Nickel in the Supporting Electrolyte Containing 0.20 *M* of KSCN and 1.80 *M* of KNO₃

Concentration of nickel, $\times 10^{-3} M$	Half-wave potential vs. N.C.E., V.	Diffusion current constant, $\mu\text{A}(\text{milli } M)^{-1} (\text{mg.}^2/\text{sec.}^{-1/2})^{-1}$
0.0656	-0.706	2.92
0.164	-0.704	3.04
0.328	-0.708	3.03
0.656	-0.701	3.22
1.640	-0.700	3.12

Limiting Current Measured at Various Heights of Mercury. — (a) In the Medium of KSCN-KCl. The limiting currents were

measured at various heights of mercury. If the limiting current is determined only by the diffusion process, it should be proportional to the square root of mercury height. The experimental results indicated that when the supporting electrolyte contains less than 0.2 *M* of potassium thiocyanate the ratio of limiting current to the square root of mercury height, $I_l/\sqrt{H}$, increases with the decrease of mercury height, *H*, which means clearly that the limiting current involves the kinetic current besides the diffusion current. Some of the experimental results are shown in Table 4. In the supporting

Table 4
The Limiting Current Obtained at
Various Heights of Mercury

<i>H</i> , cm.	$\sqrt{H}$	$I_{l(1)}$, μA	$I_{l(2)}$, μA	$\frac{I_{l(1)}}{\sqrt{H}}$	$\frac{I_{l(2)}}{\sqrt{H}}$
Supporting electrolyte, 1 <i>M</i> KCl–2 <i>M</i> KSCN					
81	9.00	1.291		0.143	
61	7.81	1.114		0.143	
46	6.78	0.977		0.144	
Supporting electrolyte, 1 <i>M</i> KCl–0.2 <i>M</i> KSCN					
81	9.00	1.341		0.149	
61	7.81	1.174		0.150	
46	6.78	1.033		0.152	
Supporting electrolyte, 1 <i>M</i> KCl–0.005 <i>M</i> KSCN					
82	9.06	0.219	0.308	0.0242	0.0340
62	7.87	0.219	0.292	0.0278	0.0371
47	6.86	0.221	0.270	0.0322	0.0393

electrolyte containing 0.005 *M* of potassium thiocyanate the limiting current of the first wave is completely determined by the rate of the association but not by the diffusion because it is independent of the height of mercury as indicated in Table 4.

(b) **In the Medium of KSCN-KNO₃.** It was found out that in this medium the limiting current is completely determined by the diffusion process even in the case of low concentration of potassium thiocyanate. Since this medium contains 0.005% of gelatine, the disappearance of kinetic current is possibly considered to be due to the existence of gelatine.

Polarograms obtained by the Kalousek's Method.—It has been already reported that the reduction wave of nickel-thiocyanate complex has an irreversible character, and it has been also expected from the ordinary polarographic measurements of the present study: the log plot of the wave does not give the slope expected from the reversible wave, as described above.

The result obtained by P. Delahay⁽³⁾ with a technique of oscillographic polarography shows the reduction of this complex to be irreversible in the supporting electrolyte containing 0.5 *M* of potassium thiocyanate. To these verifications of the irreversibility of the reduction of this complex, the confirmation of the fact has been added by the author using the Kalousek's method.⁽⁴⁾ The polarograms of this complex obtained with the method are shown in Figs. 3 and 4, compared with the polarograms of the reduction wave of lead which is considered to be reversible. When the polarograms are obtained with the circuit I-a of the Kalousek's method, they should give a well-defined minimum of current if the reduction of the substance concerned is reversible, as shown in polarogram (a) of Fig. 3. No minimum of current is clearly seen in the polarograms (b) and (c) of Fig. 3. The polarograms (b) and (c) of Fig. 4 are also quite different from the polarogram (a) in the same figure, although they were all obtained with the same circuit. From these facts it can be concluded that the reduction of this complex is irreversible as already recognized from the other informations.

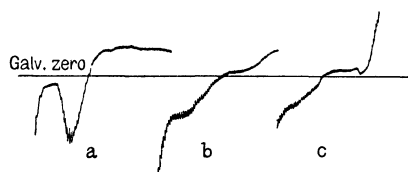


Fig. 3.—Polarograms obtained with the circuit I-a of the Kalousek's method, polarograms of, (a) Pb⁺⁺ in the KOH solution, (b) nickel-thiocyanate complex in the KNO₃-KSCN medium, and (c) nickel-thiocyanate complex in the KCl-KSCN medium. Voltage difference=0.3 volt.

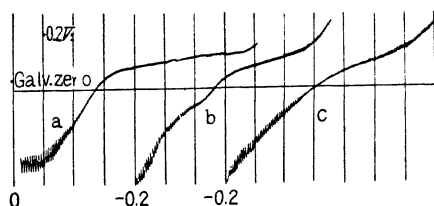


Fig. 4.—Polarograms obtained with the circuit II of the Kalousek's method, polarograms of, (a) Pb⁺⁺ in the KOH solution, (b) nickel-thiocyanate complex in the KNO₃-KSCN medium, and (c) nickel-thiocyanate complex in the KCl-KSCN medium.

(3) P. Delahay, *Jour. Phys. Coll. Chem.*, **54**, 630 (1950).

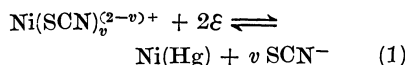
(4) M. Kalousek, *Collection Czechoslov. Chem. Commun.*, **13**, 105 (1948).

Discussion

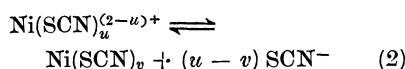
Since the reduction wave of nickel-thiocyanate complex has most complicated behaviors, the reduction mechanism of the complex has been explained incompletely only with the present experiment. However, if the following mechanisms are assumed for the reduction of the complex, the experimental results can be explained at least qualitatively.

(1) In the solution containing an extremely high concentration of potassium thiocyanate, nickel exists mainly in the form of $\text{Ni}(\text{SCN})_u^{(2-u)+}$; in the solution containing a moderate concentration of potassium thiocyanate, mainly in the form of $\text{Ni}(\text{SCN})_v^{(2-v)+}$ ($u > v$); and in the solution containing a low concentration of potassium thiocyanate, mainly in the form of $\text{Ni}(\text{SCN})_w^{(2-w)+}$ ($v > w$).

(2) The polarographic wave appearing at the potential of about -0.7 volt *vs.* N.C.E. is due to the reduction of $\text{Ni}(\text{SCN})_v^{(2-v)+}$ ion without the dissociation, which proceeds according to Eq. (1).

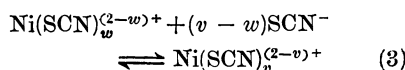


(3) $\text{Ni}(\text{SCN})_u^{(2-u)+}$ is reduced according to Eq. (1), after it dissociates into $\text{Ni}(\text{SCN})_v^{(2-v)+}$ according to Eq. (2).



The rate of the dissociation of $\text{Ni}(\text{SCN})_u^{(2-u)+}$ into $\text{Ni}(\text{SCN})_v^{(2-v)+}$ is considered to be extremely large compared with the diffusion rate of $\text{Ni}(\text{SCN})_u^{(2-u)+}$ or $\text{Ni}(\text{SCN})_v^{(2-v)+}$.

(4) $\text{Ni}(\text{SCN})_w^{(2-w)+}$ is reduced according to Eq. (1), after it associates with SCN^- ion to form $\text{Ni}(\text{SCN})_v^{(2-v)+}$ according to Eq. (3).



The rate of the association of $\text{Ni}(\text{SCN})_w^{(2-w)+}$ with SCN^- ion appears to be comparable in magnitude with the rate of the diffusion in the medium containing potassium thiocyanate and potassium chloride, but it appears to be extremely large in the medium containing potassium thiocyanate and potassium nitrate. This consideration makes it possible to explain the phenomenon that the limiting current of the wave contains the kinetic current in the medium of KSCN-KCl , but it does not in the medium of KSCN-KNO_3 .

(5) The reduction of $\text{Ni}(\text{SCN})_v^{(2-v)+}$ to $\text{Ni}(\text{Hg})$ is of the activation-controlled one.

In the above description any complex-forming substance except thiocyanate ion is not represented. It does not mean necessarily that nickel ion takes only thiocyanate as a complex-forming ion. On the contrary it is considered with a great possibility that nickel ion takes other ions than thiocyanate ion as a complex-forming ion. In the above description they are omitted for simplicity.

If the reduction mechanisms mentioned above are assumed for the reduction of the complex, the polarographic wave of the complex should be explained with the formulas which are obtained by the modification of the formulas described in the previous papers²⁾. The half-wave potential should be independent of the activities of the $\text{Ni}(\text{SCN})_v^{(2-v)+}$ and the relation of $\log I/(I_L - I)$ *vs.* V , a straight line, whether the limiting current is governed by the diffusion process only or not. Moreover, the assumption that the activation-controlled process is rate-determining requires the inclination of the log plot being more than 0.029 volt at 25.0° if the number of electron concerning the reduction equals two.

The experimental results shown in Table 4 indicate clearly that the half-wave potential is independent of the activity of nickel-thiocyanate ion, and these shown in Fig. 2 indicate the relation of $\log I/(I_L - I)$ *vs.* V holding straight lines. From the inclinations of the log plot shown in Tables 1 and 3 and the polarograms obtained by the Kalousek's method the activation-controlled process can be expected for the rate-determining step.

In order to confirm the above assumptions it should be examined whether the shift of the half-wave potential with the change of the concentration of complex-forming substance is in accord with the theoretical consequence. If the complex ion is reduced according to Eqs. (2) and (1) and if the rate of dissociation is extremely rapid compared with the diffusion, the shift of the half-wave potential with the change of the concentration of potassium thiocyanate is represented with the following equation:

$$\Delta V_{1/2} = -(u - v) \frac{0.059}{2\alpha} \Delta \log [\text{SCN}], \text{ (volt)} \quad (4)$$

where $[\text{SCN}]$ represents the activity of thiocyanate ion and α has the meaning described in the previous papers^{(2), (5)}. The half-wave potential should be shifted more to negative

(5) N. Tanaka and R. Tamamushi, this Bulletin, **22**, 187 (1949); R. Tamamushi and N. Tanaka, this Bulletin, **22**, 227 (1949).

with the increase of the concentration of potassium thiocyanate. The experimental results obtained in the supporting electrolyte containing more than about 0.2 *M* of potassium thiocyanate is in accord with the fact. Being treated quantitatively, it was found out that the value of $(u-v)$ approaches to 2 as potassium thiocyanate increases, as shown in Fig. 5.⁽⁶⁾ It means

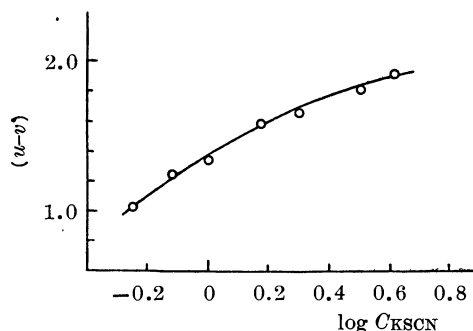


Fig. 5.—Relation of $(u-v)$ calculated with Eq. (4) and the logarithm of the concentration of potassium thiocyanate.

that $(u-v)$ is 2 and that $\text{Ni}(\text{SCN})_w^{(2-w)+}$ still remains in the concentration region of more than 0.2 *M* where the experiments are made.

As for the concentration region where the reduction proceeds according to Eqs. (3) and (1), the following equation is derived if the kinetic current is not concerned.

$$\Delta V_{1/2} = (v-w) \frac{0.059}{2\alpha} \Delta \log[\text{SCN}], \text{ (volt)} \quad (5)$$

The theoretical consequence that the half-wave potential shifts more to positive as the concentration of potassium thiocyanate increases explains the experimental results obtained in the supporting electrolyte containing potassium thiocyanate of less than 0.2 *M*. Taking up the case of medium containing potassium thiocyanate and potassium nitrate because of the absence of kinetic current, $(v-w)$ will be calculated according to Eq. (5) using the value of α and the shift of the half-wave potential both obtained experimentally. Since over the range from 0.05 *M* to 0.01 *M* of potassium thiocyanate the relation of $\log I/(I_t - I)$ holds a straight line, this range was taken for the calculation. The shift of the half-wave potential, $\Delta V_{1/2}$, corresponding to 0.699 of $\Delta \log[\text{SCN}]$ is 0.037

volt and the mean value of α over the range is 0.54.⁽⁶⁾

$$v-w = \frac{0.037}{\frac{0.059}{2 \times 0.54} \times 0.699} = 0.97$$

The result indicates that the value of $(v-w)$ equals approximately 1.

From these discussions it is concluded that the nickel-thiocyanate complex is reduced according to the mechanisms mentioned above. As for the value of u , v and w , 4, 2 and 1 are the most reasonable to be applied to them from the above discussions and the spectroscopic data.⁽⁷⁾

Summary

The polarographic reduction wave of nickel-thiocyanate complex has been studied for the purpose of clarifying the reduction mechanism of the complex. The current-voltage curves of the complex were measured in media of KSCN-KCl and KSCN-KNO₃. In the medium of KSCN-KCl, the reduction wave involved the kinetic current as well as the diffusion current, when the concentration of potassium thiocyanate was less than 0.2 *M*. The relation of $\log I/(I_t - I)$ and V held a straight line, but its slope was not in accord with the value expected from the reversible reduction. From these experimental results and the polarograms obtained with the Kalousek's method, the reduction of the complex was confirmed to proceed irreversibly at the dropping mercury electrode.

The reduction mechanism of the complex and the number of thiocyanate ions coordinated to the centered metal ion in the supporting electrolytes containing various concentrations of potassium thiocyanate were estimated from these experimental results, when the theoretical consequence for the activation-controlled reduction of the complex ion reported in the previous paper was applied.

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(6) In this calculation the concentration was used instead of activity, and ΔF_1 and the ionic strength were assumed to be constant.

(7) Pal Csokan, *Chem. Abstract*, **33**, 1594 (1939).

LETTER

The Relation Between the Structure of γ -Lactones and the Value of their Molecular Rotations—Presumption of Eight Unknown $[M]_D^{20}$

By Shukichi YAMANA

(Received October 16, 1950)

C. S. Hudson reported the quantitative relation between the structure of γ -lactones and the value of their molecular rotations and calculated $[M]_D^{20}$ of six lactones, now unknown. However, since his view had no ground of physical theory, he could not explain the fact that the optical rotatory power of C^5 atom in lactones of Xylonic-Lyxonic type is opposite in sign to that in lactones of Ribonic-Arabonic type.⁽¹⁾ The author tried to apply physical theories of the optical rotation to this idea, and found some empirical rules concerning the quantitative relation from the standpoint of the arrangement of atoms, and by using these rules, he presumed eight unknown $[M]_D^{20}$.

At first, all of γ -lactones are divided into Ribonic-, Arabonic-, Lyxonic-, and Xylonic-types according to the types of their own rings. Next, $[M]_D^{20}$ -change accompanying the change of the side-chain is classified into two parts, one of which corresponds to the change of the end-group or the length of the side-chain in the case when the number of asymmetric atom is constant (G-change), and the other of which corresponds to the change of the number of asymmetric atom in the side-chain in the case when the end-group and the length of the side-chain is constant (O-change). The physical meaning of G-change is the $[M]_D^{20}$ -change accompanying the change of the degree of induced dissymmetry of the CO-group⁽²⁾ in the γ -lactone-ring, under the influence of the chain-length and the chain-end-group. The physical meaning of O-change is the $[M]_D^{20}$ -change accompanying

the appearance of a new asymmetric atom which has its own optical rotatory power. Then the optical rotatory power of the ring itself is not constant in all types, even in R-type, contrary to the Hudson's view. Now the theory of the optical rotatory power of J. G. Kirkwood, based upon the quantum-mechanics,⁽³⁾ was used to explain O-change at C^5 , by using examples of L-talonic-, D-allonic-, L-galactonic-, D-altronic-, L-gulonic-, D-mannonic-, L-idonic-, and D-gluconic- γ -lactones, with success. The outline of his theory is as follows: he calculated the $[M]_D^{20}$ of D-secondary butyl alcohol and concluded that free rotation of the $(CH_3)(H)(OH)-C^*$ -group around the axis of $C^*-C_2H_5$ is possible, and the end-group (CH_3) of the ethyl group can be placed under (CH_3) , (H) or (OH) , each bound to C^* . The $[M]_D^{20}$ of the molecule changes according to the place of the end-group (CH_3) described above. The case when the (C_2H_5) group of D-secondary butyl alcohol is replaced by the γ -lactone-ring is now under discussion.

Possibility of free rotation of the side-chain around the axis of C^5-C^4 , makes O-changes of R- and A-types equal; but, in L- and X-type, it is hindered by O-atom, bound to C^3 , and H, bound to C^5 , is forced to stand upon C^3 . This configuration causes revision of the sign of O-change. Thus, the first rule was deduced: "Each of C atoms in a definite side-chain, whether this chain attaches to R- or A-type-ring, causes O-change of its own constant value." Using this rule, and data of L-epifuconic-, D-allomethylonic-, and L-fuconic- γ lactones, the $[M]_D^{20}$ of D-altromethylonic- γ -lactone was presumed. Using the first rule, other six unknown $[M]_D^{20}$ values—these six have already been calculated by Hudson—were calculated. Two more rules were induced from data. The second rule: "Replacement of (CH_2OH) by (CH_3) at the end of the side-chain causes no large change in O-change". The third rule: "Entfernungssatz der Drehung of L. Tschugaeff⁽⁴⁾ is seen in O- and G-changes, and the magnitude of G-change, caused by replacement of end-group (CH_2OH) by (CH_3) at α -position of the side-chain is 1.9 times of that at β -position". Using

(1) C. S. Hudson, *J. Am. Chem. Soc.*, **61**, 1525 (1939).

(2) T. L. Harris, E. L. Hirst and C. E. Wood, *J. Chem. Phys.*, **2**, 1825 (1934).

(3) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); **7**, 139 (1939).

(4) L. Tschugaeff, *Ber.*, **31**, 360 (1898).

this rule, the $[M]_D^{20}$ of D-ribonic- γ -lactone was calculated. The presumed values of $[M]_D^{20}$ of γ -lactones are as follows; a-D-alloheptonic-, -20.1; L-talloheptonic-, 1.2; D-gala-L-talo-octonic-, 84.7; D-ribomethylonic-, -1.9; D-allo-D-altroheptonic-, 59.9; D-gulo-L-gala-heptonic-, 133.0; L-talo-D-altroheptonic-, 81.2; D-altromethylonic-, 28.4; six of these are different from those, presumed by Hudson by about two degrees in the magnitude of $[\alpha]_D^{20}$.

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New Differential Polarography with One Dropping Electrode.—The Use of Rotating Current Alternator

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(Received December 15, 1950)

In polarography, the derivative $\Delta i/\Delta E$ of the ordinary current-voltage curve is useful and important. For the purpose of obtaining it, a method of employing two mercury dropping electrodes has been proposed.⁽¹⁾ However, it is difficult to get a good result with the method, because of the difficulty of synchronizing the drop rates of both electrodes.

The authors made a new device of simple circuit system for obtaining the differential polarogram with one dropping electrode by the use of rotating switch, connected in series with the usual polarograph. Fig. 1 shows the scheme of the apparatus. In the figure, the voltage of $E + \Delta E$ is applied to the cell and the electrolytic current i flows through the galvanometer, and in the next instant when the alternating switch is half rotated, the voltage of E is applied to the cell, thereby the corresponding current i' flows reversely through the galvanometer. By rotating the switch with adequate speed (ca. 800 r. p. m.), the galvanometer is led to show

the difference between both currents ($\Delta i = i - i'$) and so the polarograph shows the differential polarogram. Fig. 2 shows the differential polarogram compared with the ordinary one.

Some characteristics of this apparatus and the interesting results obtained will be submitted later.

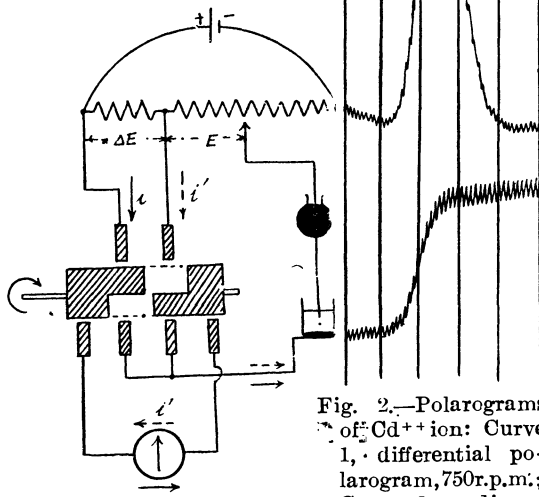


Fig. 1.

Fig. 2.—Polarograms of Cd^{++} ion: Curve 1, differential polarogram, 750 r. p. m.; Curve 2, ordinary polarogram.

The authors wish to express their thanks to Yanagimoto Co. for the kind help in preparing this apparatus.

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(1) J. Heyrovsky, *Chem. Listy*, **40**, 222 (1946); etc.