

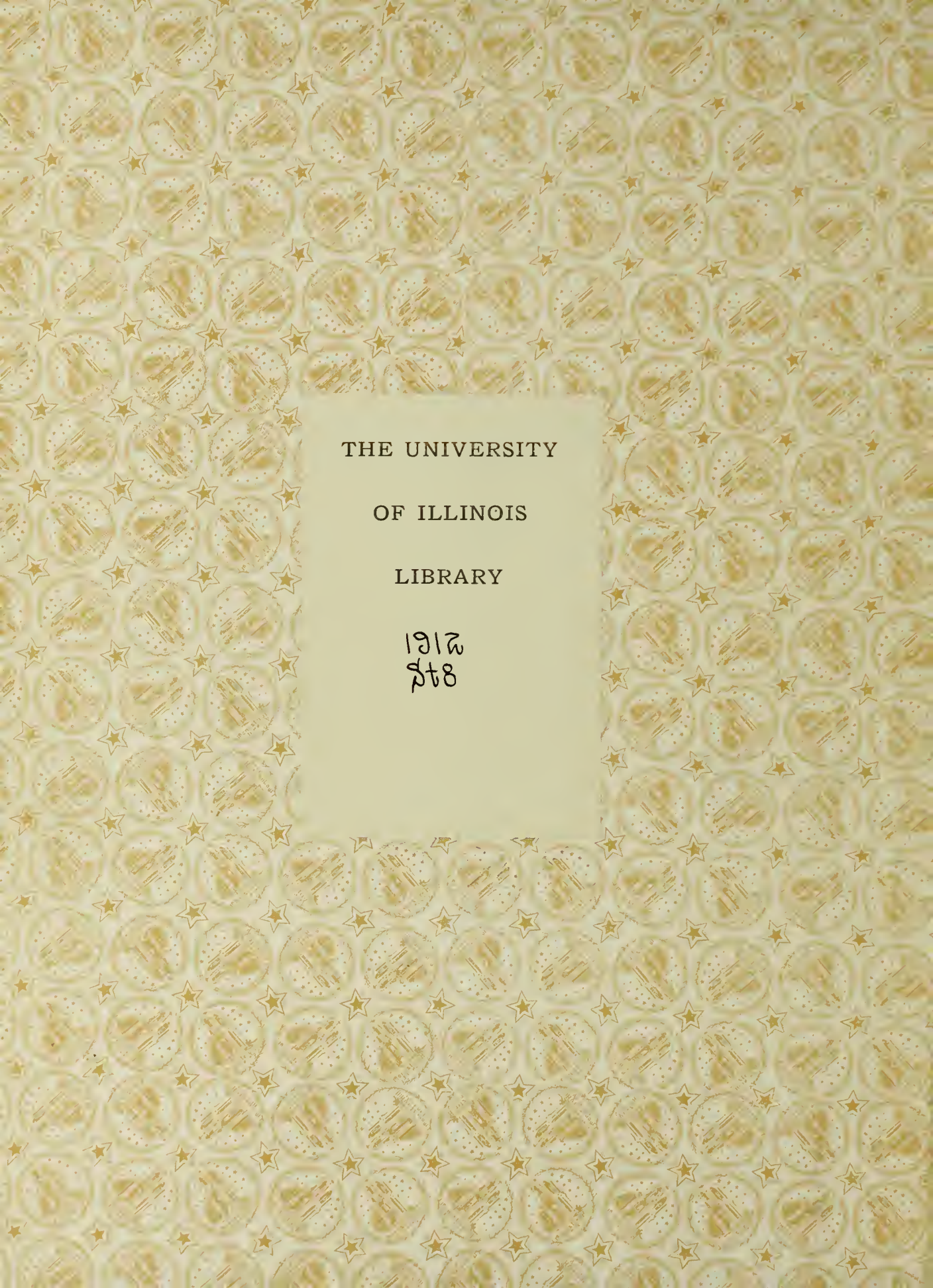
STRACHAN

**The Equilibrium between Arsenious
Acid and Iodine in Aqueous Solution**

Chemistry

Ph. D.

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THE EQUILIBRIUM BETWEEN ARSENIOS ACID
AND IODINE IN AQUEOUS SOLUTION.

BY

EARLE KENNETH STRACHAN

B. S. Worcester Polytechnic Institute, 1908

M. S. University of Illinois, 1910

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

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IN

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UNIVERSITY OF ILLINOIS
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May 14, 1942

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Earle Kenneth Strachan

ENTITLED THE EQUILIBRIUM BETWEEN ARSENIOUS ACID AND IODINE IN
AQUEOUS SOLUTION

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy in Chemistry.

E. H. Washburn

In Charge of Major Work

Earl Parr
acting

Head of Department

Recommendation concurred in:

W. H. Bayley
Edward Barlow
R. S. Cantow
C. W. Balke

Committee

on

Final Examination

THE REACTION BETWEEN ARSENIOS ACID AND IODINE
IN AQUEOUS SOLUTION.

1.- Introduction and Purpose of This Investigation.

In connection with the study of the reaction between arsenious acid and iodine in aqueous solution, Roebuck¹⁾ determined approximately the position of equilibrium between these two substances and their reaction products, arsenic acid and hydriodic acid, at 25°. His work showed that a definite equilibrium was reached, and that the same result was obtained when the equilibrium was approached from either direction. His method consisted in mixing together solutions of sodium arsenite, sulphuric acid (or hydriodic acid), potassium iodide, and iodine dissolved in potassium iodide. These solutions were all of known concentration, and the proportions of each used in making up any given reaction mixture were so calculated that only a very small amount of iodine had to be added to bring about equilibrium, thus the concentrations of the various substances were almost unaffected by the reaction. After equilibrium was established, the concentration of the free iodine and tri-iodide was determined by titrating the mixture with sodium thiosulphate. The chief objections to this method are, first that in the analysis of the equilibrium mixture, the equilibrium itself is disturbed, and secondly, that as carried out by Roebuck, several other substances, namely sodium and potassium salts, and in some cases sulphuric acid, were also present in the solution, thus making the calculation of the ion concentrations very uncertain. The values given by Roebuck for the constant, $\frac{(H_3AsO_4)(H_2SO_4)^2(KI)^3}{(HAsO_2)(I_2)} = K$ varied between 1.76×10^5 and 0.5×10^5 (or expressed in volume concentrations

1) Roebuck, J. Physic. Chem. 6, 365; 9, 727.

1.91×10^{-3} and 1.32×10^{-2}), and in calculating this, no attempt was made to estimate the degree of dissociation of the different electrolytes. More recently Roebuck's data have been recalculated by Luther ¹⁾ and by Washburn ²⁾ taking into account as well as possible, the actual ion concentrations. Luther based his calculations on those experiments in which sulphuric acid was used, and Washburn on those in which hydriodic acid was employed. Both observers give the same value, namely 7×10^{-2} , for the constant at 25° , a value which may be easily in error by as much as 100 percent, owing to the uncertainty in the data themselves, and to the difficulty of estimating correctly the ion concentrations in mixtures containing so many different substances, and at such high concentrations as those employed by Roebuck. In many cases the concentrations of some of the substances were as high as 0.3 molal.

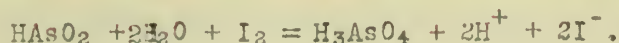
Since this equilibrium lies at the basis of an important analytical method ²⁾, it seemed desirable to determine it under conditions permitting the attainment of a greater degree of accuracy. Such is the purpose of this investigation.

2- Outline of Method.

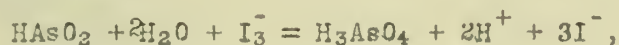
In order to determine accurately the equilibrium constant of the reaction, $\text{HAsO}_2 + 2\text{I}_2 + \text{I}_3^- = \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 3\text{I}^-$, the method should if possible be so designed that the equilibrium is not itself disturbed in the process of measuring the concentrations of the different substances concerned in it. Moreover, the measurement should also be carried out in solutions which contain only the substances (molecules or ions) directly concerned in the equilibrium, and no one of the substances should be present at higher concentrations than 0.1 or 0.2 normal. These conditions are fulfilled if an excess of solid iodine is allowed to react with a solution of arsenious acid. The latter is then

1) Luther, Z. Electrochem. 13, 292. 2) Washburn, J. Am. Chem. Soc. 30, 31.

oxidized to arsenic acid in accordance with the following equation:



Immediately, however, the iodide ions react with some of the iodine forming I_3^- and HI_3 , and when equilibrium is attained, the reaction may be expressed by the following equation:



and then the solution contains, as will be shown later, only the substances HAsO_2 , AsO^+ , H_3AsO_4 , H_2AsO_4^- , H^+ , I_2 , HI , HI_3 , I^- , and I_3^- at appreciable concentrations. Now if the total arsenic content, the total iodine, and the concentration of I_2 in the solution are determined, the concentrations of each of the substances in the reaction mixture can be calculated as follows.

Let the total arsenic in the solution be ΣAs , and the total iodine be ΣI gram atoms. Then

$$\Sigma\text{As} = (\text{HAsO}_2) + (\text{AsO}^+) + (\text{H}_3\text{AsO}_4) + (\text{H}_2\text{AsO}_4^-) \quad (1)$$

and
$$\Sigma\text{I} = 2(\text{I}_2) + (\text{HI}) + (\text{I}^-) + (\text{HI}_3) + (\text{I}_3^-) \quad (2)$$

Moreover,
$$\frac{(\text{I}_2)(\text{I}^-)}{(\text{I}_3^-)} = k_1 \quad (3)$$

As will appear later, hydriodic acid and hydrotri-iodic acid are dissociated to the same extent, γ . Hence by combining (2) and (3),

$$\Sigma\text{I} - 2(\text{I}_2) = \frac{1}{\gamma}(\text{I}^-) + \frac{3(\text{I}_2)(\text{I}^-)}{\gamma k_1} \quad (4)$$

Since (I_2) is known from the solubility of iodine in water, this expression gives at once (I^-) . (HI) , (HI_3) , and (I_3^-) can be obtained from the equations

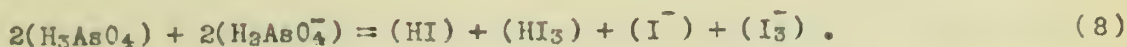
$$(\text{HI}) = \frac{1-\gamma}{\gamma} (\text{I}^-) \quad (5)$$

$$(\text{I}_3^-) = \frac{(\text{I}_2)(\text{I}^-)}{k_1} \quad (6)$$

$$(\text{HI}_3) = \frac{1-\gamma}{\gamma} (\text{I}_3^-) \quad (7)$$

Now as all the iodide, both ionized and un-ionized, results from the oxidation of arsenious acid, whereby for every molecule of arsenic acid formed, two molecules of hydriodic acid are obtained, and as all the tri-iodide results

from the reaction $I^- + I_3 = I_3^-$, then the sum of all the molecules of hydriodic acid and hydrotri-iodic acid is twice the total number of molecules of arsenic acid, or



In order to obtain (H_3AsO_4) , use is made of the ionization constant of arsenic acid,

$$\frac{(H_2AsO_4^-)(H^+)}{(H_3AsO_4)} = k_2 \quad (9)$$

the hydrogen ion concentration being obtained by the method of successive approximation. The value of $(HAsO_2)$ can be obtained from equation (1) and the equilibrium relation

$$\frac{(AsO^+)(OH^-)}{(HAsO_2)} = k_3 \quad (10)$$

The concentration of iodine existing as I_3 in the mixture may be obtained in either of two ways. The first of these is the establishing of the equilibrium in the presence of solid iodine as mentioned above. In this case however, the reaction would run so far to the right that if the arsenious acid were maintained at a measurable concentration, the hydrogen ion concentration would rise to about two tenths normal. Since the degree of ionization of the various substances in the reaction mixture can not be determined with certainty at concentrations much above tenth normal, this method of determining the iodine concentration was employed only in one experiment. The second method consists in establishing the equilibrium in the presence of another liquid phase in which only the iodine is soluble. Then by analysis of the second liquid phase, and with knowledge of the partition constant, the iodine concentration in the water layer can be calculated. This method has also the added advantage that the iodine concentration in the water layer can be varied at will. This is the method employed in this investigation, carbon tetrachloride being the second solvent employed, as preliminary experiments showed that none of the other substances present were appreciably soluble in it.

3. Purification of Materials and Preparation of Stock Solutions.

ARSENIOUS ACID.- Kahlbaum's Ph G IV arsenic trioxide was crystallized once from hydrochloric acid and twice from conductivity water. After the first crystallization from water the substance went into solution completely, leaving no residue (sulphides of arsenic and antimony). To avoid oxidation of the arsenious acid by the air, the following method was used in making up the solution for equilibrium determinations. The desired amount of conductivity water was collected from the still boiling hot, and at once sufficient arsenic trioxide to make a 0.05 molal solution was added to it. The water was then boiled until the arsenic trioxide had completely dissolved. While still hot the solution was transferred to a bottle of resistance glass. This bottle was fitted with a rubber stopper through which two glass tubes passed, one of them reaching just through the stopper, and the other to the bottom of the bottle. As soon as the solution had been introduced into the bottle, the longer tube was stopped and the shorter one connected to a supply of nitrogen gas. In this way the solution was kept out of contact with the air. By attaching the short tube to the gasometer containing the nitrogen, and opening the long tube, and increasing the pressure on the nitrogen, the arsenious acid could be forced out of the bottle in any amount desired. The exact strength of the solution was determined by titrating it against pure iodine.

ARSENIC ACID.- This was prepared from the arsenic trioxide purified as above by evaporating it to dryness with a large excess of aqua regia. The residue was taken up in pure water and evaporated to dryness several times, and was finally dissolved in enough conductivity water to make a twice molal solution. The exact strength of the solution was determined by precipitation as magnesium ammonium arsenate.

IODINE.- Kahlbaum's resublimed iodine was ground with potassium iodide and sublimed. The resulting product was then resublimed without the

addition of potassium iodide.

HYDRIODIC ACID.- This was prepared by reduction of iodine with hydrogen sulphide, and subsequent distillation. After several distillations, the distillate was very pale yellow, and free from sulphur. This acid was shaken with benzene (Kahlbaum's thiophen free) until colorless, whenever an acid free from iodine was required.

CARBON TETRACHLORIDE.- Kahlbaum's carbon tetrachloride was saturated with iodine and allowed to stand over night. The iodine was then removed by shaking with a solution of sodium thiosulphate, and the carbon tetrachloride washed several times with conductivity water. It was finally distilled in a current of nitrogen, and the distillate preserved under nitrogen.

NITROGEN.- This was prepared by passing dry air over hot granulated copper.

WATER.- The water used in this investigation was prepared from the ordinary laboratory supply of distilled water by redistilling it from alkaline permanganate in the special still described by Dr. D.A. MacInnes¹⁾. This still gives water having a specific conductance of 1×10^{-6} at 25° .

4.- Apparatus.

The thermostat used in this research was the Frees type made by V. Weber and Co., Chicago. It was heated electrically by incandescent lamps. The mercury regulator was about a meter long and two centimeters in diameter, except at the place of contact with the platinum point, where it was drawn down to about 2mm. Regulation to 0.01° was easily obtained. The temperature was measured by a thermometer calibrated by the National Bureau of Standards. It was graduated to 0.05° , and could be easily read to 0.01° . All experiments were made at $25.00^{\circ} \pm 0.01^{\circ}$.

Liter and half liter bottles of resistance glass served as equilib-

1) Washburn and MacInnes, J. Am. Chem. Soc. 33, 1688.

rium vessels. They were well steamed out before use.

Conductivity measurements were made in the pipette form of cell by the Kohlrausch method, as described by Dr. MacInnes ¹⁾.

5.- Auxilliary Determinations.

2)

1.-THE DISTRIBUTION CONSTANT.- Jakowkin has determined the partition constant of iodine between carbon tetrachloride and water, and has found that it decreases with decreasing iodine concentration. For the purposes of this investigation, the partition constant should be known with a fair degree of accuracy, since an error in it of one percent causes an error of four percent in the equilibrium constant. Jakowkin's values, when plotted graphically seem to indicate a decided increase in the partition constant at the lowest concentration measured by him. This is not what would be expected from theory. Moreover as his investigations were carried out at considerably higher concentrations than those used in this work, it was thought desirable to make determinations of the partition constant at the concentrations actually used. To do this, an accurately known weight of iodine was placed in a resistance glass bottle together with accurately known volumes of water (10 liters), and of carbon tetrachloride (1 liter). An amount of sulphuric acid (5cc. of 1.84 sp. gr. acid) sufficient to prevent hydrolysis of the iodine as calculated from the relation ³⁾
$$\frac{(HI)(I^-)(H^+)}{(I_2)} = 0.6 \times 10^{-13}$$
 was added to the water. The mixture was then shaken at 25 until equilibrium was established, after which the carbon tetrachloride layer was pipetted off and analysed. The total iodine minus the iodine in the carbon tetrachloride layer was the iodine in the water. From this the partition constant could be calculated. Two determinations gave the ratio of the concentration of the iodine in the carbon tetrachloride to that in the water as 85.6 and 84.7 respectively, when the iodine in the water layer was 5×10^{-5} moles per liter. The mean of these two agrees very well with Jakowkin's results, if the value obtained at the lowest

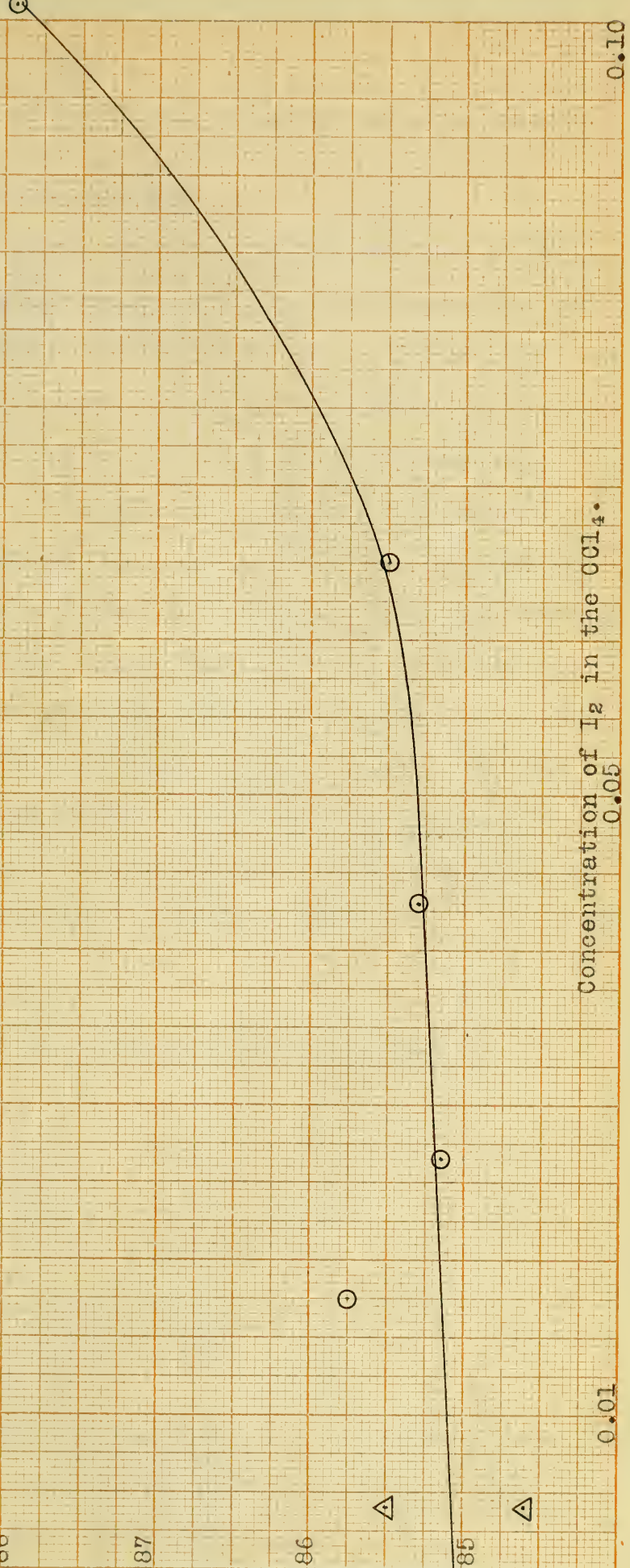
1) Washburn and MacInnes, *ibid.* 2) Jakowkin, *Z. physik. Chem.* 18, 586.

3) Bray, *J. Am. Chem. Soc.* 32, 932.

FIGURE 1
THE PARTITION CONSTANT.

K
88
87
86
85

○ Jakowkin
△ W and S.



Concentration of I_2 in the OCl_4 .
0.05
0.10

concentration he used is omitted, as will be seen by an examination of figure 1.

2.- THE DEGREE OF DISSOCIATION OF HYDRIODIC ACID.

1)

Ostwald has determined the conductance of hydriodic acid at 25°

2)

but as recent measurements have shown his determination of the conductance of hydrochloric acid to be in error by about 3 percent, it was thought best to measure the conductance of hydriodic acid at those concentrations at which it occurs in the equilibrium mixtures. The solutions used for this purpose were obtained from the stock solution of hydriodic acid by shaking with benzene until a colorless solution was obtained. These were then analysed, and remained colorless until the conductance measurements were completed. The results obtained are recorded in table 1. Columns I and II give respectively the concentrations shown by analysis, and the measured equivalent conductances. Columns III and IV give values of the concentration and conductance read off a smooth curve drawn through the experimentally determined points. Column V gives the degree of dissociation calculated on the assumption that the ionized portion of the hydriodic acid had an equivalent conductance of 437.3 as explained below.

Table 1.

Conductance and Ionization of HI at 25° (1912 At. Wts.)

I	II	III	IV	V
c	\wedge	c	\wedge	γ
0.1710	386.8	0.1500	389.5	0.890
0.1028	395.0	0.1000	395.6	0.903
0.09020	397.7	0.0800	398.5	0.911
0.05140	403.7	0.0500	404.3	0.924

Ostwald obtained values considerably lower than these, e.g. 386 in 0.1 n solution.

1) Ostwald, J.pr. Chem. 32, 302. 2) Bray and Hunt, J. Am. Chem. Soc. 33, 786.

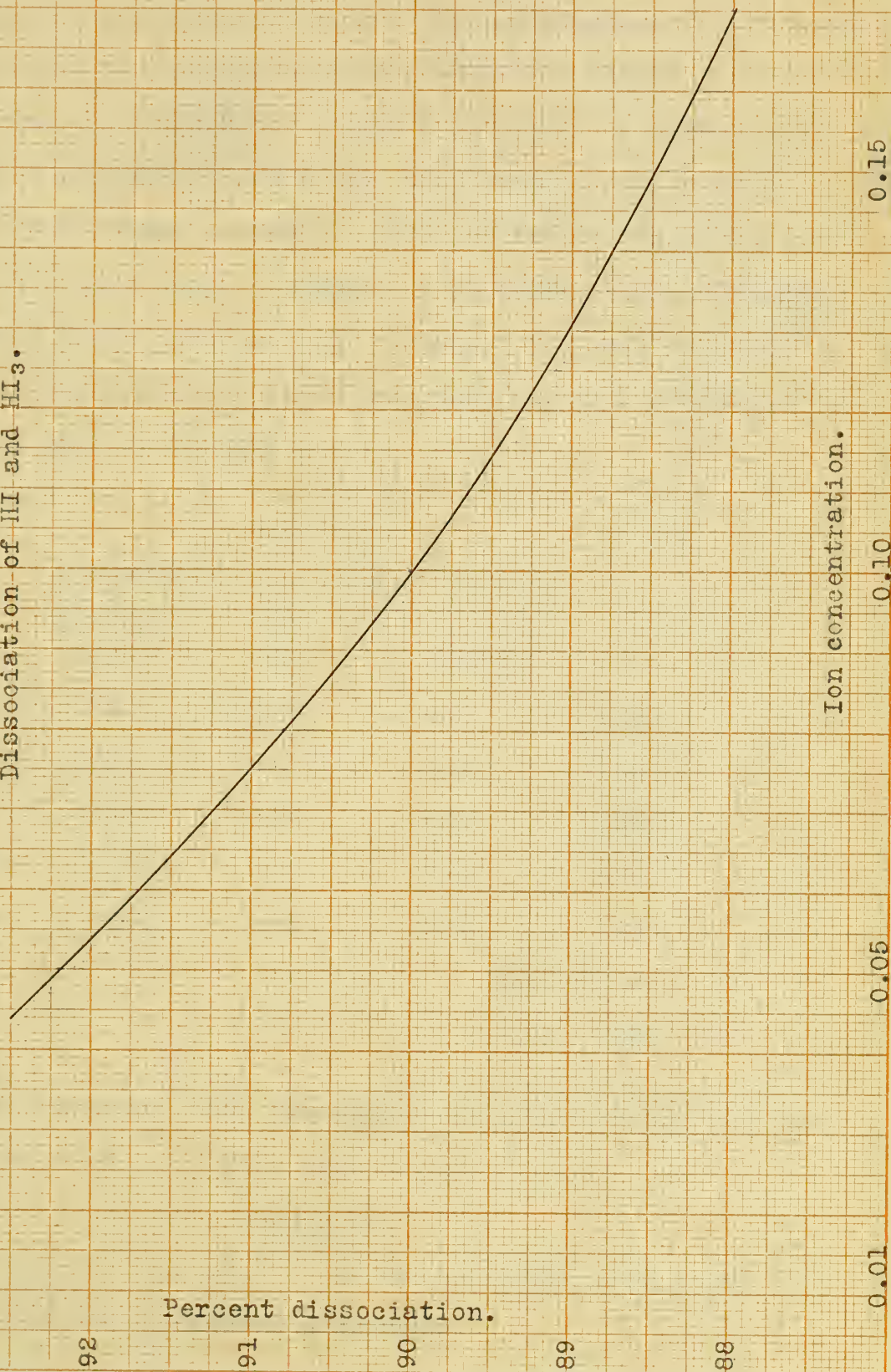
B. and H. give 390.4 for 0.1 n HCl while Ostwald gives 381.0.

The conductance of a 0.1 n solution of hydriodic acid if it were completely dissociated can be calculated in the following way. Washburn ¹⁾ has shown that $\Lambda_c = \Lambda_0 \left(\frac{\eta_0}{\eta}\right)^m$ when Λ_c is the equivalent conductance of an ion in a solution of concentration C, whose relative viscosity is $\frac{\eta}{\eta_0}$, Λ_0 is the equivalent conductance of the ion at zero concentration, and m an empirical constant not very different from unity. The value of m for the chloride ion is 0.88 ²⁾. The relative viscosity of 0.1 n hydrochloric acid is 1.007 at 25 ³⁾, and the equivalent conductance of the chloride ion at the same temperature and zero concentration is 75.5. Therefore, $\Lambda_{Cl^-} = 75.5 \left(\frac{1}{1.007}\right)^{0.88} = 75.0$. Now, the mobility of the chloride ion divided by the transference number gives the conductance of the hydrochloric acid if it were all dissociated; that is, $\Lambda_H^+ + \Lambda_{Cl^-} = \frac{\Lambda_{Cl^-}}{t}$. The transference number of the anion of 0.1 n hydrochloric acid solution estimated from the data compiled by Noyes and Falk ⁴⁾ is 0.175 at 25 ⁵⁾. Hence, $\Lambda_H^+ + \Lambda_{Cl^-} = \frac{75.0}{0.172} = 436.3$, or $\Lambda_H^+ = 361.3$, a value which agrees very well with that obtained by Noyes and Sammet ⁶⁾ (365) from transference measurements made in 0.02 n solution. The Λ_0 value of the iodide ion at 25 ⁶⁾ is 76.5, and assuming that the relative viscosity of 0.1 n hydriodic acid is the same as that of 0.1 n hydrochloric acid, and that $m = 0.9$, then $\Lambda_{I^-} = 76.5 \left(\frac{1}{1.007}\right)^{0.9} = 76.0$ in 0.1 n solution. Hence, $\Lambda_H^+ + \Lambda_I^-$ or the molecular conductance of 0.1 n hydriodic acid if it were completely dissociated would be 437.3. Hence the degree of ionization of 0.1 n hydriodic acid is $\gamma = \frac{395.6}{437.3} = 0.903$. In a similar way the values of γ shown in table 1 were calculated.

For use in calculating the equilibrium constant, the value of γ was plotted against $C\gamma$, thus making it possible to read the value of γ for any ion concentration directly from the curve (figure 2).

- | | |
|--|---|
| 1) Washburn, J. Am. Chem. Soc. <u>33</u> , 1469. | 4) Noyes and Falk, J. Am. Chem. Soc. <u>33</u> , 1454. |
| 2) Washburn, <i>ibid</i> , p 1468. | 5) Noyes and Sammet, J. Am. Chem. Soc. <u>24</u> , 965, |
| 3) Green, J. Chem. Soc. <u>93</u> , 2023. | 6) Bray and MacKay, J. Am. Chem. Soc. <u>32</u> , 921. |

FIGURE 2.
Dissociation of HI and HI₃.



3.- THE TRI-IODIDE EQUILIBRIUM.

The equilibrium constant $\frac{(I_2)(I^-)}{(I_3^-)} = k$ can be calculated from the solubility of iodine in potassium iodide as determined by Noyes and Seidensticker¹⁾. In table 2, column I contains the concentration of the original potassium iodide solution, and column II, the solubility of iodine in it as determined by Noyes and Seidensticker. Column III contains the concentration²⁾ of KI_3 obtained by subtracting 0.00132, the solubility of iodine in water, from the corresponding values in column II. Column IV contains the concentration of KI in the mixture as obtained by subtracting the values in column III from those in column I. Column V contains $k \cdot 10^3$ calculated from the expression $\frac{(KI)(I_2)}{(KI_3)}$ ³⁾, which, since potassium iodide and tri-iodide are dissociated to the same extent, is equal to $\frac{(I^-)(I_2)}{(I_3^-)}$.

Table 2 .

I Original KI	Concentrations in millimoles per liter.				
	II Solubility of I_2	III (KI_3)	IV (KI)	V $k \cdot 10^3$	
106.3	55.28	53.96	52.3	1.28	
53.15	28.03	26.91	26.24	1.16	⁴⁾
26.57	14.68	13.36	13.01	1.28	
13.29	8.003	6.68	6.61	1.32	
6.643	4.667	3.35	3.29	1.30	
			Mean	1.30	
			A.D.	0.015	

5)

Bray and MacKay also, have measured this constant, and find that

1) Noyes and Seidensticker, Z. physik. Chem. 27, 357.

3) Bray and MacKay, J. Am. Chem. Soc. 32, 923.

2) Bray, J. Am. Chem. Soc. 32, 936.

5) Bray and MacKay, *ibid.* p 924.

4) This value was omitted in calculating the mean.

in 0.1 n potassium iodide saturated with iodine, it is 1.31×10^{-3} . Moreover, they find that as the concentration of KI decreases, k also decreases until it becomes 1.50×10^{-3} in 0.001 n KI solution, and they calculate ^{from the} data obtained by Maitland ¹⁾ that as the iodine concentration decreases, k increases, until it reaches the value 1.39×10^{-3} in a solution containing 0.00004 moles of iodine per liter. For the purpose of this investigation we need to know the value of k quite accurately. It therefore seemed desirable to determine this constant at those concentrations of iodine and hydriodic acid actually used in determining the arsenious acid and iodine equilibrium. Moreover by doing this an opportunity would be afforded of testing the assumption that hydriodic acid and hydrotri-iodic acid are dissociated to the same extent, by measuring the conductance of the mixture. Accordingly the following experiments were made. Solutions of iodine in hydriodic acid of various concentrations were rotated in the thermostat at 25° in the presence of carbon tetrachloride until equilibrium was established. The two layers were then drawn off and analysed. The iodine in the carbon tetrachloride was determined by titration with thiosulphate, and the iodine in the water layer calculated by use of the partition constant. The water layer was analysed as follows ²⁾. A portion of the solution was shaken with successive portions of carbon tetrachloride until colorless. The carbon tetrachloride was then titrated with thiosulphate, two equivalents of the latter being required for every mole of I_2 , and two, for every mole of HI_3 . A fresh portion of the water layer was then taken and the total iodine determined by titrating it cautiously with permanganate until all the hydriodic acid was oxidized to iodine, excess of permanganate being avoided. The iodine was removed as fast as formed by shaking the solution with carbon tetrachloride, the latter then being titrated with thiosulphate. The results are given in table 3. Columns I, II, and III contain the concentrations of HI , HI_3 , and I_2 respectively. Column IV contains

1) Maitland, Z. Electrochem. 12, 264. 2) Method of Bray, J. Am. Chem. Soc. 32, 1193.

the constant $k = \frac{(HI)(I_2)}{(HI_3)}$. Column V contains the observed specific conductance L, and column VI, the degree of dissociation of HI and HI₃ calculated from the formula $\gamma = \frac{10^3 L}{(HI)\Lambda_{oHI} + (HI_3)\Lambda_{oHI_3}}$ (11). Column VII contains the total ion concentration calculated by means of the value of γ in column VI, and column VIII, the degree of dissociation of hydriodic acid at the total ion concentration given in column VII.

Table 3.

THE IODIDE - TRI-IODIDE EQUILIBRIUM.

Data and results. Concentrations in millimoles per liter.

I (HI)	II (HI ₃)	III (I ₂)	IV k.10 ³	V s 10 L	VI γ by equation (11)	VII (ΣC_i)	VIII γ_{HI} at (ΣC_i) in column VII
80.1	82.1	1.32	1.29	6195	(0.910)	0.1475	0.886
55.4	56.7	1.32	1.29	4250	0.905	0.1001	0.900
67.62	37.08	0.720	1.31	3973	0.893	0.0935	0.902
64.96	33.36	0.684	1.33	3761	0.898	0.0883	0.904
87.62	46.36	0.0694	1.31	3652	0.908	0.0887	0.904
72.95	13.49	0.0241	1.30	2982	0.918	0.0682	0.913
57.15	9.04	0.0202	1.28	2342	0.923	0.0535	0.920
		Mean	1.30				
		A.D.	± 0.01				

The average deviation of the observed degree of dissociation from the calculated is 0.005, if the value in parenthesis is rejected.

From these experiments it may be concluded that at ion concentrations between 0.15 n and 0.05 n, when the solution is dilute with respect to iodine, k is constant, and is equal to 1.30×10^{-3} . This differs from the results obtained

1) For Λ_{oHI} the value 437 was employed, and for Λ_{oHI_3} the value $\Lambda_{oHI} - \Lambda_{oI} + \Lambda_{oI_2} = 437 - 76 + 41 = 402$. The value $\Lambda_{oI_2} = 41$ is that determined by Bray and MacKay.

by Bray and MacKay, but agrees well with those obtained by Noyes and Seidensticker in solutions saturated with iodine.

Since the average deviation of γ in the mixture from that of pure hydriodic acid at the same total ion concentration is only 0.5 percent, it may be assumed that hydriodic acid and hydrotri-iodic acid are dissociated to the same extent at the same ion concentration .

4.- THE DISSOCIATION CONSTANT OF ARSENIC ACID.

Walden has measured the conductance of arsenic acid and of mono-sodium and mono-potassium arsenates at 25°. By plotting his values of $(\sigma\Lambda)^{n-1}$ against $\frac{1}{\Lambda}$, using $n = 1.45$ for the sodium salt, and $n = 1.50$ for the potassium salt, the value of Λ_0 was found to be 86.5 for the sodium salt, and 112 for the potassium salt. By subtracting from these two values the equivalent conductance of the sodium ion (51.2) and that of the potassium ion (74.8) respectively, the equivalent conductance of the H_2AsO_4^- ion appears to be 35.2 and 37 respectively. The value $\Lambda_{\text{H}_2\text{AsO}_4^-} = 36$ was adopted, and may be in error by one or two units owing to hydrolysis of the salts, especially at the lower concentrations, but it is sufficiently accurate for the present purpose. Then if the equivalent conductance of the hydrogen ion is 361, Λ_0 for arsenic acid is 397. The dissociation constant of arsenic acid calculated from Walden's conductance data by use of the formula $k = \frac{\Lambda^2 C}{\Lambda_0 (\Lambda_0 - \Lambda)}$ is 4.45×10^{-3} in the most dilute solutions (0.002 n, $C_1 = 0.0015$) and it increases with increasing ion concentration. In order to determine the ionization constant at the ion concentrations used in the equilibrium measurements, the conductances of several hydrochloric acid solutions were measured, and then to the same solutions a known amount of arsenic acid was added, and the

1) The only alternative hypothesis, i.e. that one acid has an abnormally large degree of dissociation in the mixture and that the other an abnormally small one, is improbable.

2) Walden' Z. physik. Chem. 2, 49.

conductance again determined. The concentrations of the various constituents of the mixture were then calculated by use of the formulas $(H_2AsO_4^-) = \frac{10^3(L'-L)}{\Lambda_{H^+} + \Lambda_{H_2AsO_4^-}}$, $(H^+) = \frac{10^3L}{\Lambda_{H^+} + \Lambda_{Cl^-}} + (H_2AsO_4^-)$, and $(H_3AsO_4) = (\sum As) - (H_2AsO_4^-)$, L being the specific of the pure hydrochloric acid, and L' that of the mixture. The results are given in table 4.

Table 4.

Concentrations in millimoles per liter.

I	II	III	IV	V	VI	VII
($\sum As$)	L	L'	($H_2AsO_4^-$)	(H^+)	(H_3AsO_4)	$k \cdot 10^3$
52.96	0.04903	0.05004	2.52	114.8	50.4	5.75
53.04	0.03952	0.04071	2.99	93.6	50.0	5.60
52.83	0.02022	0.02219	4.99	51.4	47.8	5.30

1)

In a recent article by Noyes and Falk appears the empirical formula $k = k' + D(\gamma C)^m$ suggested by Kraus, in which k' , D , and m are constants for any given salt, and are independent of the concentration. When applied to the dissociation constant of arsenic acid, the above expression becomes $k = (4.32 + 4(\gamma C)^{0.5}) \times 10^{-3}$, the values of k' , D , and m having been calculated from those of k in column VII of table 4. This expression holds over quite a wide range of concentrations, and was used in calculating ($H_2AsO_4^-$) in the equilibrium mixture.

5.- THE DISSOCIATION CONSTANT OF ARSENIOS ACID.

Arsenious acid is a very weak acid, having an ionization constant of 2×10^{-8} ²⁾, and hence in the presence of a strong acid its ionization as an acid is quite negligible. Owing to its amphoteric nature it can, however, function as a base in strongly acid solution. This is shown by the decrease in conductance

1) Noyes and Falk, J. Am. Chem. Soc. 34, 484.

2) Zawidzki, Ber. 36, 1434.

1)

of hydrochloric and hydriodic acids in the presence of arsenious acid. In order to determine the ionization constant of arsenious acid when it ionizes as a base, the following experiment was resorted to. The conductance of a 0.1 n solution of hydrochloric acid was measured, and then that of the same solution with 0.0494 moles per liter of arsenious acid added to it. The specific conductance of the pure acid was 0.03952, and that of the mixture, 0.03886 mhos. The concentration of the arsenyl ion in the mixture was calculated by means of the expression $(AsO^+) = \frac{10^3(L - L')}{(\Lambda_H - \Lambda_{AsO^+})}$, L being the conductance of the pure hydrochloric acid, and L', that of the mixture. Then $(OH) = \frac{(\Lambda_H + \Lambda_{Cl^-}) 10^{-14}}{10^3 L}$, and the ionization constant, $k = \frac{10^3(L - L')(\Lambda_H + \Lambda_{Cl^-}) 10^{-14}}{(\Lambda_H - \Lambda_{AsO^+}) 10^3 L C}$, C being the concentration of the arsenious acid. The mobility of the AsO^+ ion was assumed to be 40 from analogy to the AsO_2^- ion, which is sufficiently accurate for the purpose. The dissociation constant of arsenious acid as a base was found in this way to be 0.13×10^{-14} , which agrees with the value, 0.18×10^{-14} , which I have calculated from similar measurements made by Zawidzki, using hydriodic acid.

2)

6.- Application of the Mass Action Law.

The mass action law expressed as follows,

$$\frac{p_A^a \cdot p_B^b \dots}{p_M^m \cdot p_N^n \dots} = K_p$$

has been shown to be a thermodynamic necessity for all substances whose vapors obey Boyle's law. Without doubt, at the concentrations employed in this investigation the partial vapor pressure of every substance entering the reaction is so small that Boyle's law is obeyed by it. We therefore may expect the mass action law written as above to hold true. Now, assuming that the solution obeys the ideal solution law, that is, that $p = kN$, the above expression becomes

3)
4)

1) Zawidzki, Ber. 36, 1434. 2) loc. cit.

3) Washburn, J. Am. Chem. Soc. 32, 478.

4) Washburn, ibid. 663.

$$\frac{N_A^a \cdot N_B^b \dots\dots}{N_M^m \cdot N_N^n \dots\dots} = K_N \cdot$$

The equilibrium constant, however, is usually expressed in volume concentrations; i.e. gram molecules per liter, thus:

$$\frac{(A)^a (B)^b \dots\dots}{(M)^m (N)^n \dots\dots} = K_C ,$$

and this latter ratio, K_C , is not necessarily a constant, even if the solution obeys the ideal solution law and the vapor obeys Boyle's law. But the relation between K_C and K_N can be derived, however, and in any particular case, by substituting numerical values, it can be shown whether the deviation of K_C from constancy is negligible. In any case in which K_C deviates from constancy by an amount greater than the experimental error, the equilibrium constant had best be expressed in mole fractions.

The relation between K_C and K_N will now be developed, and the numerical values of the various quantities substituted in the equation. In this way it will be shown that for the equilibrium between arsenious acid and iodine we may expect K_C to be constant over the range of concentrations investigated.

The mole fraction, N_a , of any substance, A, is equal to the number of moles, n_a , of A divided by the total number of moles present $\sum n$, that is,

$$N_a = \frac{n_a}{\sum n} ,$$

and the concentration of A, $C_A = \frac{n_a}{V}$, when V is the volume of the solution.

But, $V = \frac{\sum nM}{D}$, D being the density of the solution, and $\sum nM$ the summation of the number of moles of every substance, each being multiplied by its respective molecular weight. Then $C_a = \frac{Dn_a}{\sum n M}$ and $N_a = C_a \frac{\sum n M}{D \sum n}$. In like manner, a similar relation can be developed for every substance present. Now substituting these values in the equation

$$\frac{N_{H_3AsO_4} N_{H^+}^2 N_{I^-}^3}{N_{HASO_2} N_{I_3^-}} = N_{H_2O} K_N$$

and writing $\frac{n_{H_2O}}{\sum n}$ for N_{H_2O} , the following equation results:

$$\frac{\left(\frac{\sum n M}{D \sum n}\right)^6 C_{H_3AsO_4} C_{H^+}^2 C_{I^-}^3}{\left(\frac{\sum n M}{D \sum n}\right)^3 C_{HASO_2} C_{I_3^-}} = \frac{n_{H_2O}}{\sum n} K_N$$

or

$$\frac{C_{H_3AsO_4} C_{H^+}^2 C_{I^-}^3}{C_{HASO_2} C_{I_3^-}} = n_{H_2O} K_N \frac{D^4 (\sum n)^3}{(\sum n M)^4}$$

Now if we assume a liter of solution, n is the number of moles in a liter, i.e. the concentration of the substance, and both D and $(\sum n M)$ are the weight of a liter. Consequently, $K_C = K_N n_{H_2O} (\sum n)^3$. The numerical values of n_{H_2O} and $\sum n$ can now be substituted in the above, and the difference in K_C when on the one hand the values of n_{H_2O} and $\sum n$ in the most concentrated solution are employed, and on the other hand when those in an infinitely dilute solution are employed, gives the change in K_C which may be expected over the range of concentrations employed.

It is obvious that the number of molecules in a liter of water depends on the degree of association of the water. For that reason the calculation below is made first assuming the water is all single molecules, and secondly, assuming that it is all double molecules, $(H_2O)_2$. For equilibrium number one (see table 5), $\sum n = 0.4026 + n_{H_2O}$. The weight of the water in a liter of solution is $D - (n_{H_3AsO_4} M_{H_3AsO_4} + n_{HASO_2} M_{HASO_2} + n_{HI} M_{HI} + n_{HI_3} M_{HI_3}) = 985$ grams. If all the water molecules are single, $n_{H_2O} = \frac{985}{18} = 54.2$, then for equilibrium number one, $K_C = 54.2 \times (54.6)^3 K_N = 88.2 \times 10^5 K_N$, and for zero concentration, $K_C = 54.2 \times (54.2)^3 K_N = 86.3 \times 10^5 K_N$; that is there will be an increase in K_C of 2 percent as the concentration increases from zero concentration

to that of equilibrium number one. Similarly, if all the water molecules are double, $n_{H_2O} = \frac{985}{36} = 27.4$. Then for equilibrium number one $K_C = 27.4 \times (27.8)^3 K_N$
 $= 58.88 \times 10^4 K_N$, and for an infinitely dilute solution, $K_C = 27.5 \times (27.4)^3 K_N$
 $= 56.39 \times 10^4 K_N$. Hence there will be an increase in K_C of 4 percent as the concentration increases from zero to that of equilibrium number one. The actual change of K_C with the concentration lies somewhere between these limits, and so is within the experimental error. Consequently, for this equilibrium at the concentrations used here, the equilibrium constant if expressed in volume concentrations is independent of the concentration within the limits of experimental error.

7.- The Equilibrium Measurement.

Arsenious acid is slowly oxidized by the oxygen of the air. Should this occur in the equilibrium vessel, the concentrations of the arsenious and arsenic acids could not be calculated by the method of section 2. Therefore the vessel was filled in the following way. The air was first displaced by a current of nitrogen, then the desired amounts of solid iodine, carbon tetrachloride, and arsenious acid were introduced, the first by allowing it to fall in a fine powder through the nitrogen, and the two liquids by means of nitrogen pressure. The bottle was stoppered and sealed with Khotinsky cement. If the equilibrium was to be approached from a higher temperature, the mixture was allowed to stand at room temperature (about 30°) for two days before being placed in the thermostat, but if from a lower temperature, it stood in the ice chest for two days. When the bottle had been rotated in the thermostat for a day at 25°, it was opened, and the contents analysed, preliminary experiments having shown that equilibrium was reached within twenty-four hours, which agrees with the observations of

1) Roebuck. The water layer was removed by means of a pipette, and transferred to a weight burette, from which portions were weighed out for analysis. In order to obtain samples of the carbon tetrachloride layer, use was made of a pipette

1) Roebuck, J. Physic. Chem. 6, 392.

having its lower end sealed together and blown out into a thin bulb. This was lowered into the carbon tetrachloride, and the bulb broken by crushing it against the bottom of the equilibrium vessel. By this device no water was allowed to enter the pipette. The sample was transferred to a weighed flask and weighed. The density of both the water layer and the carbon tetrachloride layer was measured in order that the concentration by volume might be calculated. The iodine in the carbon tetrachloride was determined by titration with tenth normal thiosulphate. In some experiments the free iodine in the water layer was reduced to hydriodic acid by sodium sulphite. The solution was then diluted to about hundredth normal, made acid with nitric acid, and the hydriodic acid precipitated by very dilute silver nitrate. From the weight of the silver iodide obtained, the total iodine in the water layer was calculated. In other experiments, the water layer was titrated with tenth normal arsenious acid, after the addition of sufficient disodium phosphate to make it just neutral when the end point was reached ¹⁾.

The results of the equilibrium measurements are shown in table 5. Column I contains the number of the experiment, the equilibrium having been approached from a higher temperature in the case of those marked *, and from a lower temperature in the case of the others. Column II contains the total arsenious acid in the original solution, column III the total iodine in the equilibrium mixture as given by its analysis, and column IV the total iodine in the carbon tetrachloride layer. The succeeding columns contain the concentrations in the equilibrium mixture of the substances indicated at the tops of the respective columns; these concentrations having been calculated as is shown in the example below.

1) Washburn, J. Am. Chem. Soc. 30, 31.

Table 5.
 Arsenious Acid and Iodine Equilibrium at 25°.

Data and results. Concentrations in millimoles per liter.

$$K = \frac{(\text{H}_3\text{AsO}_4)(\text{H}^+)^2(\text{I}^-)^3}{(\text{HAsO}_2)(\text{I}_3^-)}$$

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
Exp. no.	(ΣHAsO_2) in original solution	(ΣI) in water layer	(I_2) in CCl_4	(ΣHI)	(ΣHI_3)	($\Sigma \text{H}_3\text{AsO}_4$)	(ΣHAsO_2)	χ for ($\text{HI} + \text{HI}_3$)	(H_3AsO_4)	(H^+)	(I^-)	(HAsO_2)	(I_3^-)	$K \cdot 10^3$
1	102.3	92.85	5.261	162.3	7.722	85.00	17.3	0.885	82.80	152.6	143.6	16.84	6.834	4.96
2*	102.3	101.0	8.024	166.0	12.05	89.04	13.26	0.883	86.86	159.4	146.6	12.89	10.64	5.07
3*	50.72	51.41	5.498	93.93	2.951	48.48	2.28	0.904	46.37	98.56	84.82	2.24	2.67	3.71#
4	52.14	52.45	3.027	96.67	2.646	49.66	2.48	0.903	47.54	91.80	87.29	2.44	2.39	4.57
5*	52.14	47.01	0.897	91.85	0.746	49.30	5.84	0.905	44.09	86.00	83.12	5.75	0.675	4.83
6	49.38	53.54	6.120	91.77	4.950	48.36	8.94	0.904	45.59	90.22	82.87	8.93	4.585	5.15

Mean 4.92

A.D. ± 0.17

* Indicates equilibriums approached from a higher temperature.

This value was rejected in calculating the mean.

It is evident from the data that the concentrations of the various substances have been subjected to comparatively large changes. The concentrations of the arsenic acid, hydrogen ion, and iodide ion have been nearly doubled; that of the arsenious acid increased eight fold, and that of the tri-iodide ion over ten fold. The value of K shows no systematic change, however, but deviates irregularly on each side of the mean value, 4.9×10^{-3} , the average deviation being $\pm 0.1 \times 10^{-3}$. Owing to uncertainty in the auxiliary data, errors of ten percent in K are not to be unexpected, hence the close agreement of the values obtained under such widely varying conditions is remarkable. This is the only investigation of the equilibrium of a reaction of this character which has yielded such concordant results. The best previous example of such an equilibrium is the iodate equilibrium investigated by Sammet¹⁾ who obtained an equilibrium constant showing an average deviation from the mean of ten percent.

8.- Calculation of the Equilibrium Constant.

In order to illustrate the use of the equations given in section 2 in obtaining the results given in table 5, calculation of the concentrations of the various substances in equilibrium mixture number one is here given in detail.

The analytical data are, $\Sigma A_s = 0.1023$, $\Sigma I = 0.09285$, and (I_2) in the carbon tetrachloride layer = 0.005261.

(a) Calculation of the iodide and tri-iodide ion concentrations.

Reference to figure one shows that this concentration of iodine the partition constant is 85.1, hence (I_2) in the water layer = $\frac{0.005261}{85.1} = 0.00006183$. preliminary calculation showed the total ion concentration to be 0.153, and from figure two we find the degree of dissociation of HI and HI_3 in this solution to be 0.386. Substituting these values in equation (4) we obtain

$$\frac{1}{0.885} (I^-) + \frac{3}{0.885} \cdot \frac{0.00006183 (I^-)}{1.30 \times 10^{-3}} = 0.1857 - 2 \times 0.00006$$

1) Sammet, Z. physik. Chem. 53, 641.

When solved, this gives $(I_2) = 0.1436$.

Then, on substituting this value in equations (5), (6), and (7) the following results are obtained:

$$(HI) = \frac{1 - 0.885}{0.885} \times 0.1438 = 0.01866,$$

$$(I_3^-) = \frac{0.00006183 \times 0.1438}{1.30 \times 10^{-3}} = 0.006834,$$

$$(HI_3) = \frac{1 - 0.885}{0.885} \times 0.006834 = 0.000888.$$

(b) Calculation of the arsenic acid and hydrogen ion concentrations.

The total arsenic concentration is obtained by use of equation (8) as follows:

$$\begin{aligned} (H_3AsO_4) + (H_2AsO_4^-) &= \frac{1}{2} (0.1438 + 0.0185 + 0.0068 + 0.0008) \\ &= 0.08508 \end{aligned}$$

Assume as a first approximation that

$$\begin{aligned} (H^+) &= (I^-) + (I_3^-) \\ &= (0.1438 + 0.0068) = 0.1506, \end{aligned}$$

Now, k , the dissociation constant of arsenic acid $= (4.32 + 4(0.153)^{0.5}) \times 10^{-3}$.

Then,

$$(H_2AsO_4^-) = \frac{6.04 \times 10^{-3} \times 0.08508}{0.1506} = 0.00341$$

For a second approximation, $(H^+) = (I^-) + (I_3^-) + (H_2AsO_4^-)$

$$= 0.1438 + 0.0068 + 0.0034 = 0.1540$$

and

$$(H_2AsO_4^-) = \frac{6.04 \times 10^{-3} \times 0.08178}{0.1540} = 0.0032.$$

A third approximation gives the same value for the concentration of the arsenate ion. Hence $(H_3AsO_4) = 0.08188$ and $(H^+) = 0.1538$.

(c) Calculation of the arsenious acid concentration.

By substituting the above values of the arsenic acid and the arsenate ion concentrations in equation (1), we find that

$$(HAsO_2) + (AsO^+) = 0.1023 - 0.08508 = 0.01722$$

Then from equation (10) we obtain

$$(\text{AsO}^+) = 0.13 \times 0.01722 \times 0.1538 = 0.00035$$

Hence,

$$(\text{HAsO}_2) = 0.01688$$

Then

$$K = \frac{(0.08188)(0.1538)^2(0.1436)^3}{(0.01688)(0.006834)} = 4.96 \times 10^{-2}$$

9.- The Free Energy of the Reaction, and the Potential of the Normal Arsenic Electrode.

The free energy of the reaction between arsenious acid and iodine may be calculated from the equilibrium constant by means of the relation,

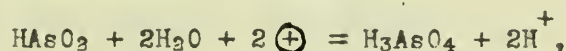
$$W = RT \ln K .$$

Hence, if the value of K is taken as 0.049, the free energy of the reaction

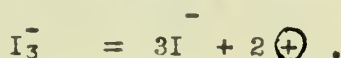


at 25° is 7480 joules.

The reaction between arsenious acid and iodine may be regarded as the resultant of two component reactions, namely,



and



Moreover, the sum of the free energies of the component reactions is equal to the free energy of the resultant reaction. Since the free energies of the component reactions are $W_{\text{As}} = v F \mathcal{E}_{\text{As}}$, and $W_{\text{I}} = v F \mathcal{E}_{\text{I}}$, when v is the number of equivalents of substance reacting, F is the number of coulombs involved when one equivalent reacts, and \mathcal{E}_{As} and \mathcal{E}_{I} are the potential of the normal arsenic and the normal iodine electrode respectively. Hence the free energy of the resultant reaction is

$$W = W_{\text{As}} + W_{\text{I}} = v F \mathcal{E}_{\text{As}} + v F \mathcal{E}_{\text{I}}$$

But as \mathcal{E}_{I} has been found to be - 0.260 referred to the normal calomel electrode, 1)

$$\text{then, } \mathcal{E}_{\text{As}} = \frac{W}{v F} - \mathcal{E}_{\text{I}} = \frac{7480}{2 \times 96540} + 0.260 = 0.299 \text{ volts.}$$

1) Sammet, Z. physik. Chem. 52, 674.

10.- Summary and Conclusions.

1.- The distribution ratio of iodine between carbon tetrachloride and water at 25°, $\frac{\text{concentration in CCl}_4}{\text{concentration in H}_2\text{O}}$, decreases with decreasing iodine concentration, and has the value 85.0 at zero iodine concentration.

2.- The equilibrium constant $\frac{(\text{I}^-)(\text{I}_2)}{(\text{I}_3^-)} = k$, was measured, and found to have the value 1.30×10^{-3} at 25°.

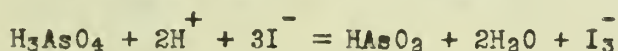
3.- Hydriodic acid and hydrotri-iodic acids are dissociated to the same extent at the same ion concentration.

4.- The dissociation constant of arsenyl hydroxide, $\frac{(\text{AsO}^+)(\text{OH}^-)}{(\text{AsO}^+\text{OH}^-)} = k$, was measured and found to be 0.13×10^{-14} at 25°.

5.- The dissociation constant of the first hydrogen of arsenic acid can be expressed by the relation $\frac{(\text{H}^+)(\text{H}_2\text{AsO}_4^-)}{(\text{H}_3\text{AsO}_4)} = 4.32 \times 10^{-3} + 4(\text{C})^{0.5} \times 10^{-3}$.

6.- The equilibrium constant $\frac{(\text{H}_3\text{AsO}_4)(\text{H}^+)^2(\text{I}^-)^3}{(\text{HAsO}_2)(\text{I}_3^-)}$ was measured, and found to be $(4.9 \pm 0.1) \times 10^{-3}$ at 25°.

7.- The free energy of the reaction

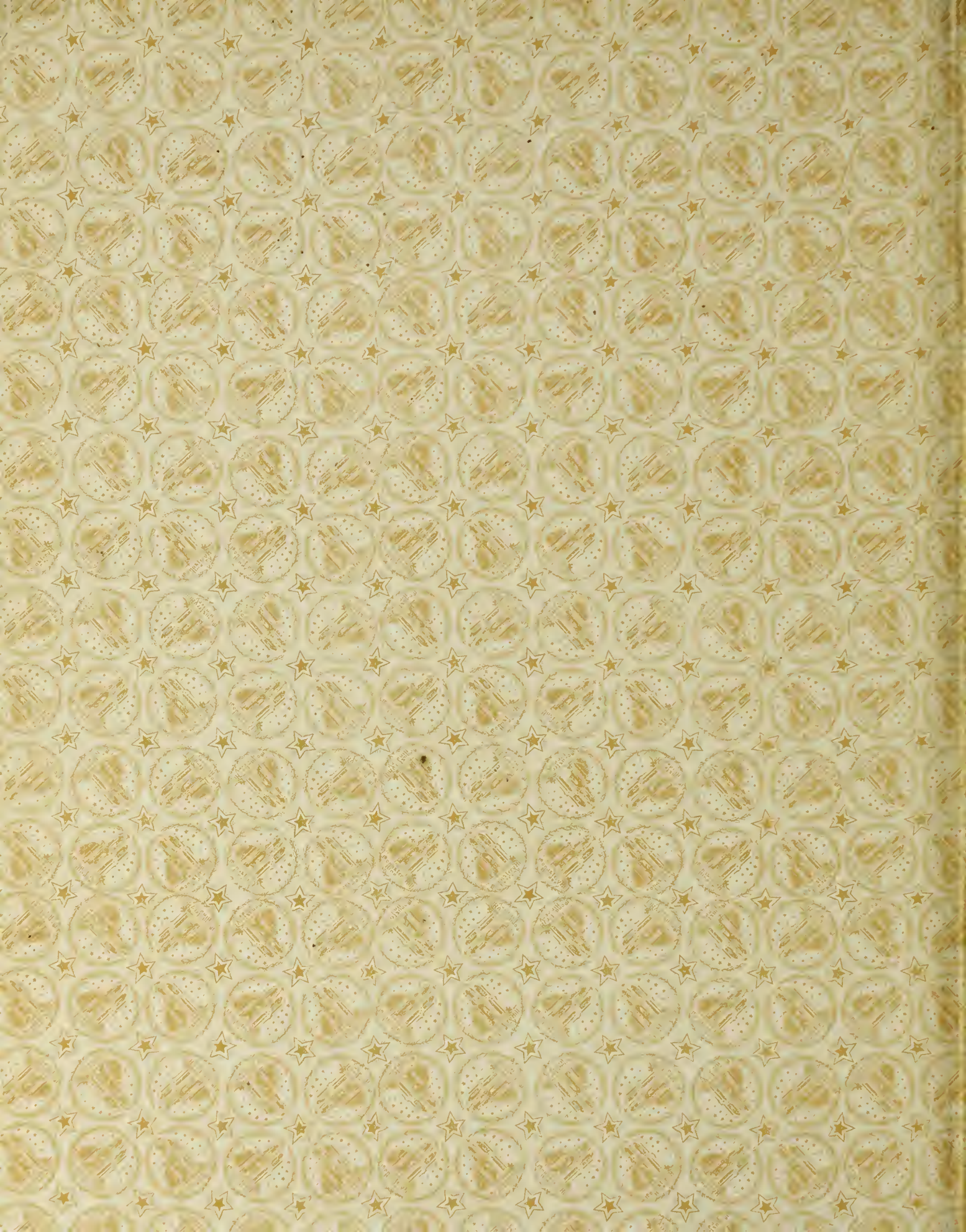


is 7480 joules at 25°, and the potential of the normal arsenic acid electrode is 0.299 volts.

This investigation was carried out under the direction of Professor E. W. Washburn, to whom, for his constant assistance and encouragement, the writer wishes to extend sincere thanks.

Autobiography.

The writer of this thesis received his early education in the public schools of Brockton, Massachusetts, graduating from the high school of that city in 1904. In the fall of the same year he entered the Worcester Polytechnic Institute, Worcester, Massachusetts, and in 1908 he completed the course in chemistry at that institution, and received the degree of Bachelor of Science. He went to the University of Illinois in the fall of the same year for further study, having received appointment there to the position of graduate assistant in chemistry. This position he held for three years, and in 1911 was made a fellow in chemistry, which position he now holds. During his four years at the University of Illinois the writer has studied for the doctorate, specializing both in physical and organic chemistry. In 1910 he received the degree of Master of Science, having prepared a thesis entitled "The Action of the Haloid Acids on Ethyl Oxomalonate". This was later published in conjunction with Dr. R. S. Curtiss, under whose direction the investigation was carried on, in the Journal of the American Chemical Society with the title "Condensations in the Mesoxalic Ester Series". Since that time the writer has been engaged in the research which forms the basis of the accompanying thesis.





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