[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Solubility of Arsenious Oxide in Dilute Solutions of Hydrochloric Acid and Sodium Hydroxide. The Character of the Ions of Trivalent Arsenic. Evidence for Polymerization of Arsenious Acid

BY A. B. GARRETT, OSCAR HOLMES AND ARTHUR LAUBE

The purpose of this paper is to present data on the solubility of arsenious oxide in dilute hydrochloric acid and sodium hydroxide solutions. Such data should make possible the determination of the character and free energy of formation of the ions of trivalent arsenic.

Earlier work on solubility measurements[1,2] and the work leading to the determination of the ionization constant of arsenious acid have been very helpful in the solution of this problem. Wood's values of $K_a = 26.5 \times 10^{-10}$ and 6.3×10^{-10} determined by electrical conductivity and by velocity of saponification of methyl acetate; Hughes'[3] value and Britton and Jackson's[4] values of 6.0×10^{-10} and 5.7×10^{-10} (at 18°), respectively, determined by the pK_a method with a glass electrode; and Goldfinger and Graf von Schweinitz's[5] value of 4.0×10^{-10} by the pK_a method with the aid of the standard colorimetric method all point to the fact that the value of the ionization constant of arsenious acid (assumed to be in the monomeric form as $HAsO_2$) is of the order of 10^{-10} (see ref. 6).

Additional aid on this problem is the work of Auerbach (see ref. 6) who has shown by means of distribution experiments that boric acid and arsenious acid are similar with respect to their tendency to form polymers in alkaline solutions. This information together with the magnitude of the value of K_a obtained above makes possible a more complete treatment of the data of this research.

Preparation of Chemicals.—All the preparations and solubilities were determined in conductivity water, under an atmosphere of nitrogen and at 25 ± 0.02° as described in earlier publications.[7,8] The purification of the sodium hydroxide is also described in earlier publications.[7,8] The hydrochloric acid was Grasselli C. P. acid.

The arsenious oxide was Baker and Adamson reagent. It was recrystallized from hydrochloric acid as described by other investigators.[1,9,10] The recrystallization was then followed by washing the oxide fifteen times with conductivity water and three times with the solvent that was to be used for the solubility determination. Several samples of the arsenious oxide were prepared by the Randall-Doody method[11] preceded by recrystallization from hydrochloric acid solutions.

The Analyses.—The concentration of the acid or alkali, in which the oxide was equilibrated, was determined by preparing the samples from standard acid or alkali. The pH values of the equilibrated solutions were determined by means of glass electrode measurements and by a standard colorimetric method. The glass electrode was calibrated against a phthalate buffer at pH 4.1 and a standard boric oxide–sodium hydroxide–potassium chloride buffer system over the entire range of these measurements. The same buffer system was used for the indicator-color-comparators. The arsenic content of each sample was determined after equilibration and sedimentation by the potassium iodate method described by Scott.[12] The standard solution of potassium iodate was re-standardized against standard solutions of arsenious oxide.

Miscellaneous Items in Procedure.—The methods used for the preparation of the samples, the equilibration, the sedimentation, and the filtration, were similar to those described earlier.[7,8]

The Data.—The data are given in Tables I, II, III and IV and in Figs. 1, 2, 3, and 4. All values are expressed in moles per 1000 g. of water. Since the equilibrated samples were made from standard solutions, the sodium hydroxide

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(1) Wood, *J. Chem. Soc.*, **93**, 411 (1908), gives data on the solubility of arsenious oxide in hydrochloric acid solutions but the data are apparently in error by approximately 17% and the data are recorded in normalities.

(2) Schreinemakers and de Baat, *Chem. Weekblad.*, **14**, 262–267, 288–290 (1917), give the phase diagram for the As_2O_3–Na_2O system but their lowest solubility measurement is in 0.96 molal alkali.

(3) Hughes, *J. Chem. Soc.*, 491 (1928).

(4) Britton and Jackson, *ibid.*, 1048 (1934).

(5) Goldfinger and Graf von Schweinitz, *Z. physik. Chem.*, **B19**, 219 (1932).

(6) The K_a values determined by the pK_a method may be in error if the system contains an appreciable concentration of $HAs_2O_4^-$ or a higher polymer. This criticism is partially met by the fact that Auerbach, [*Z. anorg. Chem.*, **37**, 353 (1903)] has shown the presence of $HAs_2O_4^-$ in relatively concentrated solutions but of only low concentration in dilute solutions such as were used by Goldfinger,[5] Hughes,[3] and Jackson and Britton.[4]

The criticism is still further answered by the fact that freezing point data of Roth and Schwartz (*Ber.*, **56**, 338 (1923)) indicate that, in aqueous solutions, arsenious acid is almost entirely in the monomeric form, $HAsO_2$ (or H_3AsO_3).

Lastly, it may be concluded from the work of Goldfinger[5] that if an appreciable amount of the dimer ($H_2As_2O_4$) is present at these concentrations it must have about the same K_a value as the monomer ($HAsO_2$) otherwise a second inflection would appear in the titration curve. However, the titration curve is symmetrical with but one inflection point. Furthermore, the titration seems to give a stoichiometric end-point in accordance with the calculated value for the equivalents of sodium hydroxide and monomeric arsenious acid.

(7) Garrett and Hirschler, THIS JOURNAL, **60**, 299 (1938).

(8) Garrett and Howell, *ibid.*, **61**, 1730 (1939).

(9) Kolthoff, "Die Massanalyse," J. Springer, Berlin, Germany, 1931, p. 378.

(10) Anderson and Storey, THIS JOURNAL, **45**, 1102–1105 (1923).

(11) Randall and Doody, *J. Phys. Chem.*, **43**, 613 (1939).

(12) Scott, "Standard Methods of Chemical Analysis," 4th edition, Vol. I, D. Van Nostrand Company, New York, N. Y., p. 44.

or hydrochloric acid content was known to ±0.2 of 1%; also the arsenic content could be determined with an accuracy within ±0.2 of 1%. The m_{OH^-} values could be determined with an accuracy of ±0.1 of a pH unit to $m_{OH^-} = 5 \times 10^{-5}$, above this value the variation was not more than ±0.2 of a pH unit.

The water solubility value is determined from direct measurements and by extrapolation of the $m_{As_2O_3}/m_{NaOH}$ graph and the $m_{As_2O_3}/m_{HCl}$ graph. The direct measurements indicate the water solubility to be 0.104 mole of As_2O_3 per 1000 g. of water. This value is verified by the extrapolation methods described above and is also in agreement with the values determined by Schreinemakers and De Baat,[2] 0.1037, and by Anderson and Storey[10] of 0.01035 mole per 1000 g. of water.

TABLE I

THE SOLUBILITY OF ARSENIC TRIOXIDE IN WATER

Moles/1000 g. H_2O	
0.1042	Recrystallized and washed fifteen times with conductivity water
.1034s	
.1031u	
.1033s	
.1025s	
.1038u	
.1018u	
.1056s	
0.1035 Average	
.1026	Recrystallized then sublimed by method of Randall and Doody
.1040	
.1040	

TABLE II

THE SOLUBILITY OF ARSENIC TRIOXIDE IN SODIUM HYDROXIDE SOLUTIONS

Moles NaOH/1000 g. of H_2O	Moles of As_2O_3/1000 g. of H_2O
0.000	0.1035
.0300	.1237
.0700	.1542
.1003	.1752
.200	.258
.300	.3261
.300	.349u
.503	.484u
.604	.573
.700	.651u
.902	.805u
1.003	.896u
1.000	.912s
1.501	1.21
2.010	1.63u
3.00	2.10
4.00	3.07
6.00	4.24

TABLE III

THE SOLUBILITY OF ARSENIC TRIOXIDE IN HYDROCHLORIC ACID SOLUTIONS

Moles HCl/1000 g. of H_2O	Moles of As_2O_3/1000 g. of H_2O
0.000	0.1035
.0402	.1004
.0820	.1005
.1030	.1010
.3040	.0992
.703	.0950
1.000	.0916
1.035	.0919
1.525	.0845
2.080	.0820
2.600	.0816u
2.900	.0805
3.17	.0742s
3.45	.0771s
3.75	.0790
4.35	.0921
4.90	.0980
8.10	.495u

The Character of the Arsenite Ions.—It may be assumed that the reaction represented by Equation (1)

$$As_2O_3 + H_2O \rightleftarrows 2HAsO_2 \text{ (or } 2H_3AsO_3) \qquad (1)$$

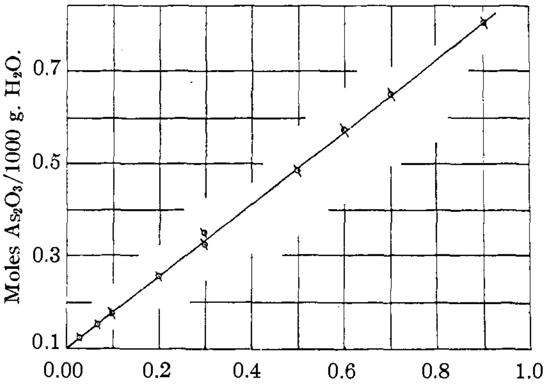

Fig. 1.

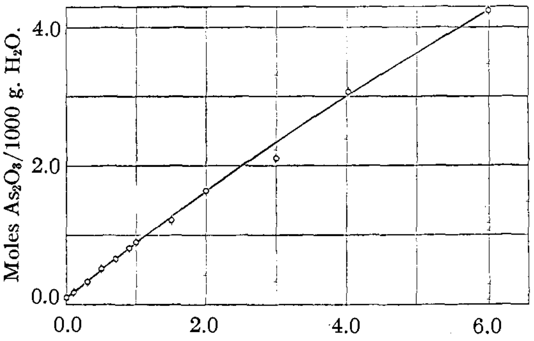

Fig. 2.

accounts for the solubility of arsenious oxide in water and in dilute acids since Roth and Schwartz[6] have shown that arsenious acid is not appreciably polymerized in water. The solubility in dilute alkali can be accounted for on the basis of the reactions represented by Equations (2), (3) and (4)

$$As_2O_3 + 2OH^- \rightleftarrows 2AsO_2^- \qquad (2)$$

or

$$As_2O_3 + OH^- \rightleftarrows HAs_2O_4^- \qquad (3)$$

or

$$3As_2O_3 + 2OH^- + H_2O \rightleftarrows 2H_2As_3O_6^- \qquad (4)$$

since Schreinemakers and De Baat[2] have shown that the solid phase remains as As_2O_3 until approximately 10 M alkali, and Fig. 3 shows a linear relationship between m_{OH^-} and $m_{\text{(ionized arsenic equivalent)}}$ which indicates the monobasic character of the anions formed.

Evidence for the formation of a polymer, as indicated by Equations (3) and (4), is shown by Fig. 4, which indicates that the slopes of the acid and the base solubility curves are discontinuous at or near water solubility. This suggests that a reaction in addition to the H^+ or OH^- ion effect is taking place on one side or the other; that an

TABLE IV

ROUNDED VALUES OF SOLUBILITY OF As_2O_3 IN NaOH

m_{NaOH}/1000 g. H_2O	m_{OH^-} calcd. from formula $m_{OH^-} = a_{OH^-}/\gamma_{OH^-}$	$m_{As_2O_3}$/1000 g. H_2O	m(ionized arsenic equiv.)/1000 g. H_2O = 2(Total $m_{As_2O_3}$ − water soly. of As_2O_3).	$m_{AsO_2^-}$/1000 g. H_2O	$m_{HAs_2O_4^-}$/1000 g. H_2O	$m_{H_2As_3O_6^-}$/1000 g. H_2O	$\sqrt{K_2} = m_{AsO_2^-}/m_{OH^-}$	K_5	$\sqrt{K_4}$	$K_3 = a_{H^+}a_{AsO_2^-}/a_{HAsO_2}$
0.00		0.104								
.1	1.0×10^{-5}	.178	0.148	0.064	0.024	0.012	$6.4 \times 10^{+3}$	2.4×10^3	1.2×10^3	3.0×10^{-10}
.2	2.1	.260	.312	.107	.074	.019	5.1	3.5	0.91	2.4
.3	3.2	.335	.462	.169	.100	.031	5.3	3.1	.97	2.5
.4	4.4	.413	.618	.222	.138	.040	5.1	3.1	.91	2.4
.5	5.6	.490	.772	.278	.172	.050	5.0	3.1	.90	2.4
.6	6.6	.570	.932	.327	.214	.059	4.9	3.2	.90	2.3
.7	7.8	.645	1.081	.390	.239	.071	5.0	3.1	.91	2.4
					Best values		5.1×10^3	3.1×10^3	9.1×10^4	2.4×10^{-10}

additional reaction is taking place on the alkaline side is indicated by the data in Table IV, Column 4 which show about 50% more arsenite equivalents in solution than can be accounted for on the basis of a 1:1 ratio of m_{NaOH} to $m_{AsO_2^-}$. Other evidence in favor of this interpretation is given by Auerbach[6] from data on distribution experiments. He concludes ". . .arsenite ions form monobasic diarsenite ions and probably higher polymers. . . ."

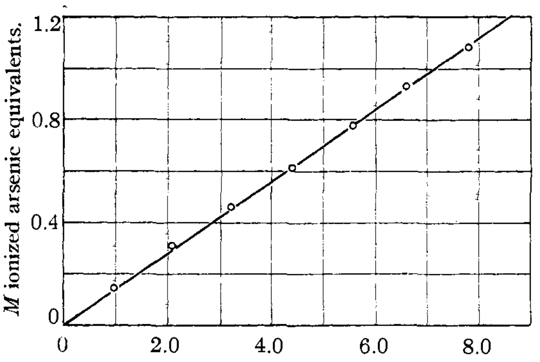

Fig. 3.

The relative amounts of these ions may be determined from the following relationships

$$m_{AsO_2^-} + 2m_{HAs_2O_4^-} + 3m_{H_2As_3O_6^-} = m_{\text{ionized arsenic equivalents}} \quad (5)$$

and

$$m_{AsO_2^-} + m_{HAs_2O_4^-} + m_{H_2As_3O_6^-} = m_{NaOH} - m_{OH^-} \quad (6)$$

or essentially

$$m_{AsO_2^-} + m_{HAs_2O_4^-} + m_{H_2As_3O_6^-} = m_{NaOH} \quad (7)$$

since the value of m_{OH^-} is very small as compared with the value of m_{NaOH}. Equation (7) indicates that a relatively large amount of the arsenic must be in solution in the form AsO_2^-, otherwise a much higher value of m_{OH^-} would be observed. One would predict smaller amounts of $HAs_2O_4^-$ and a still smaller amount of $H_2As_3O_6^-$. An estimate of the relative amounts of these ions may be obtained by averaging the ratios of the concentrations of these ions from the higher values (the more concentrated solutions) of Auerbach's[6] data; this indicates that the ratio $m_{H_2As_3O_6^-}/m_{AsO_2^-}$ is approximately 0.18.. This information together with the relationships given in Equations (6) and (7) and the values of m_{NaOH} and $m_{\text{ionized arsenic equivalents}}$ given in Table IV makes possible the determination of the values of $m_{AsO_2^-}$, $m_{HAs_2O_4^-}$ and $m_{H_2As_3O_6^-}$. The values so determined are given in Table IV Columns 5, 6 and 7.

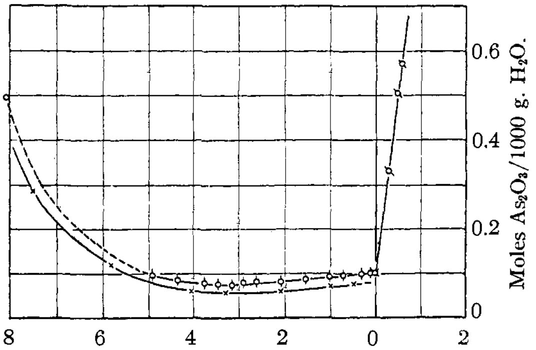

Fig. 4.—×, Wood; ⌽, Garrett–Holmes–Laube.

The values of K_2 are calculated from the values of $m_{AsO_2^-}$ and the values of m_{OH^-}, taken from a smooth curve. The m_{OH^-} values were obtained from the *p*H values and transformed to $m_{\mathrm{OH^-}}$ values by dividing the $a_{\mathrm{OH^-}}$ by the value of $\gamma_{\mathrm{OH^-}}$ for each ionic strength, since the glass electrode measurement is really the $a_{\mathrm{OH^-}}$. The value of $m_{\mathrm{OH^-}}$ rather than $a_{\mathrm{OH^-}}$ is necessary since the formula

$$\sqrt{K_2} = \frac{m_{\mathrm{AsO_2^-}}\ \gamma_{\mathrm{AsO_2^-}}}{m_{\mathrm{OH^-}}\ \gamma_{\mathrm{OH^-}}}$$

reduces to

$$\sqrt{K_2} = m_{\mathrm{AsO_2^-}}/m_{\mathrm{OH^-}}$$

for $\gamma_{\mathrm{AsO_2^-}}/\gamma_{\mathrm{OH^-}}$ may be set equal to unity.[7] The constancy of the values of K_2 (see Table IV, Col. 8) indicates that essentially the correct value of the ratio $\mathrm{H_2As_3O_6^-}/\mathrm{AsO_2^-}$ has been chosen.

Our results on the determination of the *p*H values of these solutions were reasonably consistent and reproducible for alkali concentrations up to approximately 0.6 *M* but were difficult to reproduce at higher concentrations. This is no doubt due to the failure of classical methods of making *p*H measurements in this *p*H range especially in the presence of relatively large amounts of salts. Consequently, we feel it is necessary to limit the use of the measured *p*H values to that *p*H range in which it was possible to obtain consistent results.[13]

The value of K_8 for the reaction

$$\mathrm{HAsO_2} \rightleftarrows \mathrm{H^+} + \mathrm{AsO_2^-} \qquad (8)$$

may be calculated from the values of $\sqrt{K_2}$, the ion product of water, and the value of $m_{\mathrm{HAsO_2}}$ which may be taken essentially as water solubility ($m_{\mathrm{As_2O_3}} = 0.104$ or $m_{\mathrm{HAsO_2}} = 0.208$). This gives $K_8 = 2.4 \times 10^{-10}$ and the corresponding value of $\Delta F^\circ_{298} = 13{,}100$ cal. which is in good agreement with other values[3,4,5] and is probably the most reliable one.

The $\mathrm{As_2O_3}$–HCl Equilibria.—Unfortunately the minimum solubility occurs at $m_{\mathrm{HCl}} = 3$–4, hence an exact treatment of the data of the $\mathrm{As_2O_3}$–HCl equilibria is not possible; furthermore, due to the near non-polar type of As–Cl bond, the reaction of both $\mathrm{H^+}$ and $\mathrm{Cl^-}$ must be considered, hence the determination of the basic dissociation constant from these data is not possible. A satisfactory interpretation of the acid solubility data is also complicated by the difficult, if not impossible, problem of the direct determination of the exact identity of the solid phase.[14] One may reason indirectly, however, that a change in the solid phase would be indicated by a break in the solubility curve; no such break is observed in our data to $m_{\mathrm{HCl}} = 8$ or in the data of Wood[1] to still higher concentrations. Furthermore, the constant for one of the reactions that one would predict should occur (see Equation 11) seems to fit the data satisfactorily. These observations would indicate that the solid phase, through this range of concentration, is $\mathrm{As_2O_3}$. If that is true then one can interpret the solubility of the oxide qualitatively in hydrochloric acid in terms of the reaction represented by Equations (9), (10), and (11)

$$\mathrm{As_2O_3(s)} + 2\mathrm{H^+} + 2\mathrm{Cl^-} \rightleftarrows 2\mathrm{AsOCl(aq)} + \mathrm{H_2O} \qquad (9)$$

$$\mathrm{As_2O_3(s)} + 4\mathrm{H^+} + 4\mathrm{Cl^-} \rightleftarrows 2\mathrm{As(OH)Cl_2(aq)} + \mathrm{H_2O} \qquad (10)$$

$$\mathrm{As_2O_3(s)} + 6\mathrm{H^+} + 6\mathrm{Cl^-} \rightleftarrows 2\mathrm{AsCl_3(aq)} + 3\mathrm{H_2O} \qquad (11)$$

It is well known that the molecule $\mathrm{AsCl_3}$ is formed for it can be separated quantitatively from strong hydrochloric acid solutions by distillation. Evidence for the existence of AsOCl and $\mathrm{As(OH)Cl_2}$ is meager. However, Hurtzig and Geuther,[15] Wallace and Penny[16] and Partington[17] indicate the existence of AsOCl or $\mathrm{As(OH)_2Cl}$, while Ephraim[18] and Mellor[19] claim no oxy-salt is formed. Evidence for the presence of these molecules could be obtained if one could identify the reaction or reactions to which the increase in the solubility may be attributed; this might be done by the calculation of the equilibrium constants K_9, K_{10} and K_{11}. However, the lack of direct evidence for the character of the solid phase, together with the high ionic strength of the solutions involved, make an exact calculation of the constants K_9, K_{10}, and K_{11} quite uncertain. But it is of interest to indicate the magnitude of the value of the constant K_{11} (assuming that these Equations 9, 10, and 11 are the correct ones).

Using Linhart's[20] values for $a_{\pm}$ of aqueous

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(13) The *p*H values were measured by two independent methods—*i. e.*, the indicator method and the glass electrode method. These two methods agreed well to about *p*H 9.6 but varied considerably in the high range which is what is to be expected of solutions in this *p*H range and containing such a high concentration of salts. One series of *p*H values was taken with the glass electrode calibrated against phthalate buffer at *p*H 4.1; another set of readings was taken with the electrode calibrated for each boric acid–sodium hydroxide–potassium chloride buffer nearest the *p*H value that was being determined. This same procedure and the indicator method were repeated for two different series of saturated arsenite solutions ranging from 0.1 to 1 *M* of added alkali. Such a procedure of determining the *p*H values serves to establish one's confidence in the validity of these *p*H values up to 0.6 *M* of added alkali.

(14) We appreciate the help of Professor Don M. Yost who has kindly shared with us his experiences in this part of the problem.

(15) Hurtzig and Geuther, *Lieb. Ann.*, **111**, 172 (1859).

(16) Wallace and Penny, *Phil. Mag.*, [4] **4**, 361 (1852).

(17) Partington "Textbook of Inorganic Chemistry," Macmillan and Company, St. Martin's Street, London, p. 641.

(18) Ephraim, "Inorganic Chemistry," Gurney and Jackson, 98 Great Russell Street, London, p. 744.

(19) Mellor, "Modern Inorganic Chemistry," Longmans, Green and Company, New York, N. Y., p. 745.

(20) Linhart, This Journal, **39**, 2601 (1917).

hydrochloric acid at 25°, the value of K_{11} is in the order of 10^{-21} at $m_{HCl} = 8$ and the corresponding $\Delta F°_{298} = 27$ kcal.

This is in agreement, in magnitude, with the value calculated by Latimer[21] from thermal data of Yost and Anderson[22] and others for the reaction

$$AsCl_3(l) + H_2O \longrightarrow HAsO_2 + 3H^+ + 3Cl^-; \quad \Delta F = -11.8 \text{ kcal.} \quad (12)$$

which may be converted to reaction (11) by the use of the relationship

$$As_2O_3(s) + H_2O \rightleftarrows 2HAsO_2; \ \Delta F°_{298} = 1900 \text{ cal.} \quad (1)$$

on the assumption that $m_{HAsO_2} = a_{HAsO_2}$, giving

$$2AsCl_3(l) + 3H_2O \rightleftarrows As_2O_3(s) + 6H^+ + 6Cl^-; \quad \Delta F°_{298} = -25.5 \text{ kcal.} \quad (13)$$

The data for ΔF of the reaction

$$AsCl_3(l) \rightleftarrows AsCl_3(aq) \quad (14)$$

are not available, hence the comparison of the values of ΔF for reactions represented by Equations (11) and (13) must be considered as comparison of magnitude only.

The Minimum Solubility.—The minimum in the solubility curve is lower than can be accounted for on the basis of the common ion effect. One explanation may be that it is due to salt effects, but the more probable one seems to be that it is due to a new molecular species possible (AsOCl) in the solution at that point. We have found it impossible to crystallize $AsCl_3$ or AsOCl from a solution of constant boiling hydrochloric acid–water mixture by slow evaporation even at low temperatures; apparently a sufficient amount of arsenic trichloride molecules is present and their vapor pressure is so nearly the same as that of the hydrochloric acid–water mixture that all of the arsenic escapes even at room temperature on slow evaporation.

Summary

The solubility of arsenious oxide has been determined in 0.1–6 *M* sodium hydroxide solutions and in 0.04–8.1 *M* hydrochloric acid solutions.

The arsenious oxide–sodium hydroxide data indicate that monobasic, mono-, di- and triarsenite ions are formed in alkaline solutions. The ionization constant of arsenious acid is 2.4×10^{-10}.

The arsenious oxide–hydrochloric acid data indicate that the minimum solubility occurs from $m_{HCl} = 3$–4 and that AsOCl may be the chief molecule in acid solution from $m_{HCl} = 3$–6.5. The value of the hydrolysis constant of arsenic trichloride is calculated from these data on the assumption that the solid phase is arsenious oxide.

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[21] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 107.

[22] Yost and Anderson, *J. Chem. Phys.*, **2**, 624 (1934).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Magneto-Optic Rotation: Carbon Disulfide and Benzene Solutions

BY CHARLES E. WARING,[1] HERBERT HYMAN AND SAMUEL STEINGISER

The purpose of this investigation was to begin the application and attempt to demonstrate the value of the magneto-optic method as an important tool in physico-chemical research. Eventually we hope to find a correlation between the magneto-optic rotations and structural effects both in pure substances and solutions. We also believe the method offers a possible new experimental approach for the investigation of reaction velocities. Further work in these directions is being continued by the authors.

Experimental

Materials and Apparatus.—The carbon disulfide used was the best available, 98–100% pure, redistilled twice through an efficient fractionating column, collecting the constant boiling middle portion. The final fraction was redistilled from over phosphorus pentoxide and the test using indicator Drierite showed no water. The observed boiling point was 46.3° (cor.), "I. C. T." value being 46.3°. The benzene was C. P. grade, redistilled twice, the second time from over phosphorus pentoxide. The water used was conductance water distilled from alkaline permanganate.

The solutions reported were prepared by direct weighing on a large balance using a counterpoise and correcting to vacuum. The weights were calibrated previously and the accuracy of the weighings was better than 1 mg. Due to the large volumes made up, the small surfaces exposed, and the short time of exposure during filling and emptying, it is believed no appreciable evaporation errors were introduced. The concentrations are given in weight and mole percentages calculated to the nearest hundredth of a per cent. and accurate to about that limit.

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[1] Lalor Foundation Fellow. Address 1939–1940, Trinity College, Oxford Univ., Oxford, England.