of SiO_2 (or other oxides) in Bi_2O_3. However, the lattice constant of γ-Bi_2O_3 (10.245 Å.) was found to be larger than that of the impure phase (10.090 Å.) formed by fusing mixtures of Bi_2O_3 and SiO_2. Hence, the latter phase would have to represent a substitutional type of solid solution—if it were a solid solution at all—inasmuch as in an interstitial type of solid solution "solute atoms are crammed in between the solvent atoms and as a result always cause an enlargement of the unit cell regardless of the size of solute atoms."[13] Moreover, the possibility of this phase representing a substitutional solid solution is rendered unlikely by the very unfavorable size factor for the replacement of Bi by Si atoms and by the lack of variation in lattice constant with composition exhibited by the Bi_2O_3–SiO_2 fusion products. The possibility that this phase represents a compound between Bi_2O_3 and SiO_2 (or other oxides) seems more favorable and a likely composition of such a compound, $Me^{III}{}_2Bi_{24}O_{39}$ or $Me^{IV}{}_2Bi_{24}O_{40}$, has been advanced by Sillén,[9] based mainly upon structural considerations. The most direct attack upon the problem would be a determination of the equilibrium temperature-composition diagram for the Bi_2O_3-SiO_2 system, but this awaits the availability of a crucible material which will not be attacked by molten Bi_2O_3 at temperatures above 800°.

The "simple cubic form" is probably an intermediate phase in the multi-component system formed by bismuth oxide and porcelain.

Summary

1. Pure Bi_2O_3 has been found to crystallize in at least three forms.

2. The tetragonal, β, form has been found to represent a high temperature modification with respect to the monoclinic, α, variety, and the transition temperature has been determined as 710°.

3. A new form of Bi_2O_3 (γ-Bi_2O_3) has been discovered and found to be body-centered cubic; a_0 = 10.245 Å. No region of stability between 25° and the melting point has been found for this phase.

4. A new method of preparing β-Bi_2O_3 and a method of preparing γ-Bi_2O_3 have been described.

5. Evidence has been cited to indicate that it is hardly to be expected that the cooling curve technique applied to molten Bi_2O_3 could furnish any indication of a transition occurring in the solid state. A more likely interpretation of Guertler's cooling curve evidence for the existence of two polymorphic forms of Bi_2O_3 with a transition temperature at 704° has been proposed, namely, that contamination of the molten oxide by the containing vessel led to a two-component system.

6. The impure "body-centered cubic" and "simple cubic" phases previously reported have been indicated to be of substantially different composition from that represented by the formula Bi_2O_3.

7. The solubility of Bi_2O_3 in NaOH has been found to be proportional to the NaOH concentration up to 2.46 *N*, from which the molecular species present in the solution has been shown to be $NaBiO_2$.

Cambridge, Massachusetts

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[13] I. M. Kolthoff and D. R. Moltzau, *Chem. Reviews*, **17**, 316 (1935).

[Contribution from the Department of Chemistry of Duke University]

Complex Ions. IV. Monammine-silver Ion

By W. C. Vosburgh and Ruth Stockdale McClure

In the determination of the instability constant of the diammine silver ion Randall and Halford[1] and Derr, Stockdale and Vosburgh[2] assumed that the diammine ion is the only complex ion formed when silver chloride and silver iodate, respectively, are dissolved in ammonia solutions. The constants found in the two investigations agreed well and were consistent with the assumption. Bjerrum[3] has found evidence that a monammine exists.

Bjerrum's method involved a fairly large uncertainty in the determination of the stability constants of the silver-ammonia ions. It was thought desirable, therefore, to check his results for the monammine ion by a different method, and some solubility determinations have been made

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[1] Randall and Halford, This Journal, **52**, 178 (1930).

[2] Derr, Stockdale and Vosburgh, *ibid.*, **63**, 2670 (1941).

[3] Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 130.

with the use of silver salts of larger solubility than the chloride or iodate. With these solutes, the formation of the monammine ion is favored, and fairly satisfactory data were obtained. The results agree with those of Bjerrum and make necessary a recalculation of the data of Derr, Stockdale and Vosburgh.

Materials.—Silver sulfate was prepared by slow precipitation from silver nitrate and sulfuric acid solutions. It was allowed to digest, washed well, and after drying was heated to 300° to remove sulfuric acid. The entire preparation was carried out in the absence of strong light.

Silver iodate was prepared similarly from silver nitrate and potassium iodate solutions. It was dried at room temperature.

Ammonium nitrate and potassium sulfate were recrystallized and dried at temperatures of 100 to 110°.

Standard solutions of hydrochloric acid, potassium thiocyanate, silver nitrate, sodium thiosulfate and sodium hydroxide were prepared by standard methods.

A 0.5 *M* ammonium hydroxide solution was prepared by dilution of a fresh portion of concentrated solution and was protected from carbon dioxide and action on glass.

A standard ammonium sulfate solution was prepared by careful neutralization of a standard sulfuric acid solution with ammonia.

Solubility Determinations.—The solubilities of the silver salts in water, salt solutions and ammonia solutions were determined essentially as described previously.[2] In saturated solutions of silver sulfate, total silver was determined by titration with thiocyanate. Total sulfate molality was considered equal to half the total silver molality plus the molality of potassium or ammonium sulfate, if either of these was added in the preparation of the solution. One determination in water (with no ammonia present) and two in potassium sulfate solutions agreed excellently with the results of Harkins.[4] In water the solubility at 25° was found to be 0.02683 *m* as compared with 0.02685 *m* by Harkins. With a different preparation of silver sulfate Mr. Sumter A. Cogswell in this Laboratory found a solubility of 0.02687 *m*. Davis, Ricci and Sauter[5] give 0.02693 *m*. In 0.02015 *m* and 0.04873 *m* potassium sulfate solutions the solubilities were found to be 0.02502 *m* and 0.02404 *m*, respectively. The agreement with Harkins is shown in Fig. 1. The solubility of silver sulfate in potassium sulfate solutions can be expressed by the equation

$$2 \log [\mathrm{Ag}^+] + \log [\mathrm{SO}_4^=] - 3\sqrt{\mu}/(1 + \sqrt{\mu}) = 0.360\mu - 4.8035 \quad (1)$$

in which $[\mathrm{Ag}^+]$ is the silver ion molality in the saturated solution, $[\mathrm{SO}_4^=]$ the total sulfate molality, and μ the ionic strength. In Fig. 1 the left-hand side of Equation 1 with experimental data substituted for μ and the molalities is plotted against μ. The straight line is the graph of Equation 1. The average deviation of the points from the line corresponds to between three and four parts in a thousand of the solubility product, which is found by extrapolation to be $K_{\mathrm{S.P.}} = 1.57_2 \times 10^{-5}$.

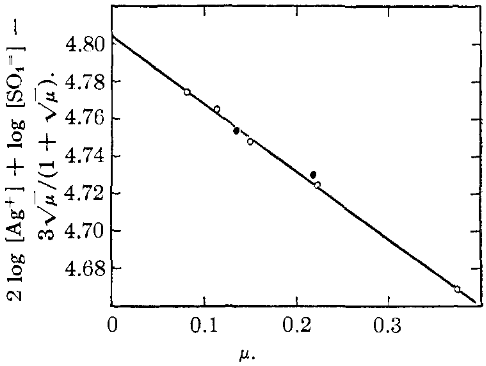

Fig. 1.—Solubility of silver sulfate in water and potassium sulfate solutions: ○, Harkins; ●, this investigation.

The solubility of silver sulfate in ammonia solutions containing ammonium sulfate is shown in Table I. The total ammonia and total silver molalities (the latter in terms of gram-atoms of silver per 1000 g. of water) were determined analytically and the ammonium sulfate molality was calculated from data on the preparation of the solution. The free silver ion molality $[\mathrm{Ag}^+]$ was calculated from Equation 1. The free ammonia molality $[\mathrm{NH}_3]$ was calculated from the simultaneous equations

$$[\mathrm{NH}_3, \text{total}] - [\text{Complex Ag}] = [\mathrm{Ag(NH_3)_2}^+] + [\mathrm{NH}_3] \quad (2)$$

$$[\mathrm{Ag}^+][\mathrm{NH}_3]^2/[\mathrm{Ag(NH_3)_2}^+] = 6.2 \times 10^{-8} \quad (3)$$

in which [complex Ag] is the difference between the total silver and silver ion molalities. It is assumed that "complex Ag" consists of the two ions $\mathrm{Ag(NH_3)^+}$ and $\mathrm{Ag(NH_3)_2^+}$. The constant in Equation 3 was determined by recalculation of the data of Derr, Stockdale and Vosburgh, as described below. An approximation method with the preliminary assumption that $[\mathrm{NH}_3]$ was negligible usually served for the solution of the two equations. Then, with $[\mathrm{NH}_3]$ and $[\mathrm{Ag(NH_3)_2}^+]$ both known, $[\mathrm{AgNH_3}^+]$ could be determined by difference. Finally the instability constant k_1 of the monammine ion was calculated.

$$[\mathrm{Ag}^+][\mathrm{NH}_3]/[\mathrm{AgNH_3}^+] = k_1 \quad (4)$$

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[4] Harkins, THIS JOURNAL, **33**, 1812 (1911).

[5] Davis, Ricci and Sauter, *ibid.*, **61**, 3275 (1939).

TABLE I

SOLUBILITY OF SILVER SULFATE IN AMMONIA SOLUTIONS AND THE INSTABILITY CONSTANT OF THE MONAMMINE SILVER ION

NH_3, total $m \times 10^2$	Ag, total $m \times 10^2$	$(NH_4)_2SO_4$ $m \times 10^2$	$[Ag^+]$ $m \times 10^2$	$[NH_3]$ $m \times 10^5$	$[AgNH_3^+]$ $m \times 10^2$	$[Ag(NH_3)_2^+]$ $m \times 10^2$	$k_1 \times 10^4$
0.940	5.670	2.520	4.92	4.8	0.56	0.19	4.2
1.825	6.228	3.017	4.87	7.7	.90	.46	4.2
1.967	6.338	2.517	4.90	8.1	.92	.52	4.3
2.070	6.434	2.514	4.89	8.1	1.02	.52	3.9
2.653	6.766	2.513	4.89	9.9	1.11	.77	4.4
3.467	7.234	2.514	4.87	11.8	1.27	1.09	4.5

TABLE II

SOLUBILITY OF SILVER IODATE IN DILUTE AMMONIA SOLUTIONS

NH_3, total $m \times 10^4$	IO_3^- $m \times 10^4$	NH_4NO_3 $m \times 10^2$	$[Ag^+]$ $m \times 10^4$	$[NH_3]$ $m \times 10^4$	$[AgNH_3^+]$ $m \times 10^4$	$[Ag(NH_3)_2^+]$ $m \times 10^4$	$k_1 \times 10^4$
1.26	2.25	1.018	1.71	0.615	0.44	0.105	2.4
1.94	2.39	1.018	1.61	0.93	.55	0.23	2.7
8.42	3.43	...	0.940	3.45	.69	1.80	4.7
41.0	13.02	0.501	.282	16.2	.8	11.9	5.7
82.3	25.9	1.020	.152	31.8	.9	24.8	5.4

It was assumed that the activity coefficients would cancel in Equation 4. The average value of k_1 was found to be 4.3×10^{-4}.

It was thought desirable to repeat the measurements with a different silver salt since it was possible that the sulfate ion might have taken some part in the equilibrium. Silver bromate was tried since its solubility is favorable, but the results were less satisfactory than those for the sulfate. The values of k_1 varied erratically from 3.7 to 6.4×10^{-4}, with an average of 5×10^{-4}. Two preparations of silver bromate gave appreciably different solubilities in water, which seems to be in accord with the experience of others.[6]

Some additional measurements were made of the solubility of silver iodate in very dilute ammonia solutions with the results shown in Table II. Analytical difficulties in the most dilute solutions and the small proportion of the monammine in the more concentrated, exaggerating the experimental error, account for the variation in k_1. The average for k_1, 4×10^{-5}, is again in approximate agreement with the value from the sulfate series, 4.3×10^{-5}, which is the most reliable value. This agreement together with the agreement with Bjerrum's constant makes it seem probable that the anions had little or no effect on the complex ion equilibrium.

Discussion

The value 4.3×10^{-4} for k_1 agrees as well as can be expected with Bjerrum's value of 4.8×10^{-4} for the reciprocal of his k_1. The amount of monammine is large enough so that its neglect made an appreciable error in some of the results of Derr, Stockdale and Vosburgh. These results have therefore been recalculated. By an approximation method the amount of monammine present has been calculated, using Equation 4 with the value 4.3×10^{-4} for k_1. Correction of the concentrations of diammine and free ammonia followed, and the value of

$$K_2 = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} \qquad (6)$$

was calculated. The results are given in Table III.

TABLE III

INSTABILITY CONSTANT OF THE DIAMMINE SILVER ION. RECALCULATION OF THE RESULTS OF DERR, STOCKDALE AND VOSBURGH

IO_3^- $m \times 10^3$	$AgNH_3^+$ $m \times 10^3$	$Ag(NH_3)_2^+$ $m \times 10^3$	NH_3 $m \times 10^3$	$K_2 \times 10^8$
3.665	0.107	3.548	4.90	6.54*
3.752	.107	3.636	4.98	6.45*
5.488	.110	5.371	7.22	6.45*
7.430	.111	7.31	9.62	6.38*
9.358	.111	9.24	11.75	6.11
19.01	.118	18.89	23.17	6.22
11.45	.120	11.33	13.99	6.34
11.25	.119	11.13	13.61	6.22
4.002	.122	3.869	4.91	6.66*
32.23	.122	32.11	37.5	6.13
39.32	.126	39.20	45.3	6.23
11.48	.128	11.35	12.78	6.18
4.515	.129	4.372	5.15	6.69*
59.37	.129	59.24	64.8	6.09
11.87	.135	11.73	12.55	6.18
81.25	.133	81.1	84.7	5.99
4.049	.141	3.894	4.17	6.47*
4.544	.149	4.381	4.56	6.63*
12.20	.146	12.05	12.01	6.24
12.12	.145	11.97	11.57	6.14

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(6) (a) Hill, THIS JOURNAL, **39**, 220 (1917); (b) Reedy, *ibid.*, **43**, 1443 (1921); (c) Dalton, Weymouth and Pomeroy, *ibid.*, **46**, 61 (1924).

The values of K_2 do not agree as well as the previous set, but since the data are given in the order of increasing ionic strength, it is obvious that there is no correlation with ionic strength. With the help of Dr. Paul F. Derr it was discovered that the values marked with an asterisk were either obtained before the technique was perfected, or were uncertain because of variation in the analytical results. They were all included in the previous table because of apparent agreement with the more reliable later data, while one or two results which had appeared to be much too low were disregarded. If the values marked with the asterisk are omitted, the average value of K_2 is 6.2×10^{-5}, while the average of all is 6.3×10^{-5}. It is believed that the former figure is the more reliable. An error of 10% in the value of k_1 would make an error of 0.8% in K_2 in the least favorable case, and not more than 0.4% in any of the values used for the average 6.2×10^{-5}. The values for the more concentrated solutions would not be affected appreciably. Bjerrum's value for K_2 is 5.9×10^{-8}.

Summary

Measurements of the solubilities of silver sulfate, silver bromate, and silver iodate in very dilute ammonia solutions confirm the conclusion that a monammine silver ion exists. Its instability constant has been found to be 4.3×10^{-4} in satisfactory agreement with Bjerrum's value 4.8×10^{-4}. Recalculation of previous data gives a value of 6.2×10^{-8} for the equilibrium constant for the dissociation of the diammine silver ion into silver ion and ammonia.

DURHAM, N. C. RECEIVED FEBRUARY 18, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Ternary System: Dioxane–Ethanol–Water

BY CHARLES H. SCHNEIDER AND CECIL C. LYNCH

The system dioxane–ethanol-water is completely miscible, and the three binary systems from these components each shows a minimum azeotrope; a ternary minimum azeotrope should be expected for the system. It is the purpose of this investigation to obtain analysis data for the ternary system and to estimate its minimum azeotropic composition and corresponding boiling point.

The binary system ethanol–water has been examined by several workers.[1,2] Lecat[3] gives for the binary minimum azeotrope the composition 89.43 mole per cent ethanol with boiling point 78.15°. The binary system dioxane–water has been studied by Smith and Wojciechowski[4] by the ebulliometric method. They report the binary minimum azeotrope at 48–49 mole per cent. dioxane with boiling point 87.82°. The binary system dioxane–ethanol has been reported from this Laboratory,[5] with the minimum azeotrope at 5.1 mole per cent. dioxane with boiling point 78.13°.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Co. was purified by the method described by Eigenberger.[6] The product was kept over metallic sodium, from which it was distilled when needed; density d^{25}_4 1.0276, $n^{25}\text{D}$ 1.4201.

Ethanol.—Commercial absolute ethanol was refluxed for twenty-four hours over lime and barium oxide, and distilled from the mixture. The product was treated with metallic sodium to remove remaining water and the redistilled product was used; density at 25° of 0.7852, $n^{25}\text{D}$ 1.3597.

Ordinary distilled water was redistilled for use in all solutions.

The Binary System: Dioxane–Water.—Smith and Wojciechowski,[4] using the ebulliometer, have investigated this binary system. Our method has been to examine vapor–liquid equilibria using the apparatus of Othmer[7]; therefore, the study of this binary system using the Othmer still was made. Mixtures of approximate composition were introduced into the apparatus and runs were made until equilibrium had been established. This required three to four hours for each run. Temperatures were measured with a (0–110°) thermometer with 0.1° division, which was checked frequently for accuracy, the precision ±0.03°. Pressure correction to 1 atmosphere and stem correction were made for all readings. The equilibrium residue and distillate were analyzed through refractive index. Data are given in Table I, and Fig. 1 shows the boiling point–composition diagram for the system. The

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[1] Doroszewski and Polansky, *Z. physik. Chem.*, **73**, 192 (1910).

[2] Noyes and Warfel, THIS JOURNAL, **23**, 463 (1901).

[3] Lecat, "La tension de vapeur des mélanges de liquides l'azéotropisme," Brussels, 1918.

[4] Smith and Wojciechowski, *J. Research Natl. Bur. of Standards*, **18**, 461 (1937), Research Paper 985.

[5] Hopkins, Yerger and Lynch, THIS JOURNAL, **61**, 2460 (1939).

[6] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

[7] Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).