0.2 cal./deg. mole, a value recommended by Owen and Brinkley[4] to be the most probable value at 25°.

Summary

The solubility and activity coefficient of silver iodate in potassium nitrate solutions have been determined at 10, 20, 25, 30 and 35°. The activity product of silver iodate and the standard potential of the silver–silver iodate electrode have been calculated at these temperatures. Values of ΔS^0, ΔH^0 and ΔC^0_p have been calculated for the electrode reaction and for the reaction $AgIO_3 = Ag^+ + IO_3^-$ at various temperatures. The ionic entropy and heat capacity of the iodate ion also are given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YENCHING UNIVERSITY]

Solubility Studies. III. The Ionization Constant of Iodic Acid at 25, 30 and 35°

BY NORMAN C. C. LI[1] AND YING-TU LO

In this study we have determined the solubility of silver iodate in solutions of nitric acid at 25, 30 and 35°. By using these results, together with the results we reported in our previous paper[2] on the solubility of silver iodate in potassium nitrate solutions, we have calculated the ionization constant of iodic acid.

Experimental

The nitric acid solutions were made by a series of dilutions from a stock solution standardized against pure sodium carbonate, using methyl orange as indicator. The solubility determination, method of analysis and per cent. accuracy were the same as reported in our previous paper.[2]

The results obtained are given in Table I. The first column gives the molarity *m* of nitric acid and the second column the solubility, *S*, in moles per liter at the different temperatures.

TABLE I

SOLUBILITY OF SILVER IODATE IN NITRIC ACID SOLUTIONS

	$S \times 10^4$		
m	25°	30°	35°
0	1.785	2.152	2.587
0.001301	1.829		
.006503	1.949	2.373	2.844
.01410	2.070	2.520	3.045
.07050	2.660	3.256	3.922
.1213	3.040	3.750	4.537
.2528	3.820	4.738	5.688
.5050	5.027	6.350	7.718
.8738	6.522		

Log *S* is plotted against $\sqrt{\mu}$ in Fig. 1. For comparison data in potassium nitrate solutions given in Table I of our previous paper[2] are also graphed. The increased solubility of silver iodate in solutions of nitric acid, as compared to its solubility in the corresponding solutions of potassium nitrate, is due to the incomplete dissociation of iodic acid formed by double decomposition between silver iodate and nitric acid.

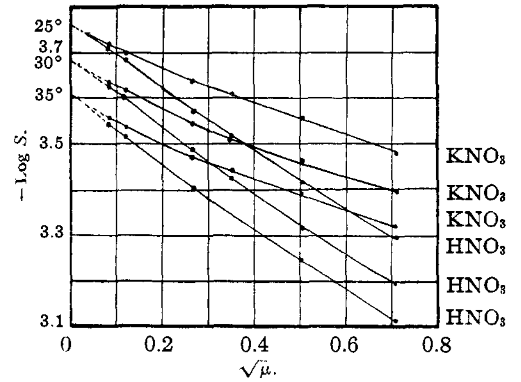

Fig. 1.—Solubility of silver iodate in electrolyte solutions.

Discussion

If we assume with Naidich and Ricci[3] that the mean activity coefficient of a slightly soluble salt is the same in solutions of the same total ionic strength, regardless of whether the electrolyte is the acid or the potassium salt of a given anion, we may set the solubility product of silver iodate in solutions of nitric acid to be equal to its solubility product in the potassium nitrate solution of the same ionic strength.

The various ionic concentrations in the acid solutions are calculated by means of the following equations

$$m_{IO_3^-} = K_{sp}/S_a = S_s^2/S_a \qquad (1)$$

$$m_{HIO_3} = S_a - m_{IO_3^-} \qquad (2)$$

$$m_{H^+} = m_{HNO_3} - m_{HIO_3} \qquad (3)$$

$$\begin{aligned} \mu &= S_a + m_{HNO_3} - m_{HIO_3} \\ &= m_{HNO_3} + m_{IO_3^-} \end{aligned} \qquad (4)$$

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[2] Li and Lo, THIS JOURNAL, **63**, 394 (1941).

[3] Naidich and Ricci, *ibid.*, **61**, 3270 (1939).

TABLE II

CALCULATION OF K_m FOR IODIC ACID

m_{HNO_3}	$S_a \times 10^4$	$S_s \times 10^4$	$m_{IO_3^-} \times 10^4$	$m_{HIO_3} \times 10^4$	m_{H^+}	$\sqrt{\mu}$	Log K_m + 1
				25°C.			
0.001301	1.829	1.826	1.823	0.006	0.001300	0.0385	0.5966
.006503	1.949	1.916	1.884	.065	.006497	.0818	.2750
.01410	2.070	2.000	1.932	.138	.01409	.1196	.2949
.07050	2.660	2.303	1.994	.666	.07043	.2659	.3240
.1213	3.040	2.456	1.985	1.055	.1212	.3485	.3580
.2528	3.820	2.790	2.038	1.782	.2526	.5030	.4607
.5050	5.027	3.327	2.201	2.826	.5047	.7108	.5945
.8738	6.522	3.900	2.333	4.189	.8734	.9349	1.6870
				30°C.			
0.006503	2.373	2.327	2.282	0.091	0.006494	0.0820	0.2118
.01410	2.520	2.421	2.326	.194	.01408	.1197	.2274
.07050	3.256	2.843	2.482	.774	.07042	.2660	.3539
.1213	3.750	3.040	2.464	1.286	.1212	.3486	.3659
.2528	4.738	3.426	2.477	2.261	.2527	.5030	.4421
.5050	6.350	4.034	2.563	3.787	.5046	.7108	.5337
				35°C.			
0.006503	2.844	2.788	2.733	0.111	0.006492	0.0823	0.2037
.01410	3.045	2.920	2.800	.245	.01408	.1199	.2066
.07050	3.922	3.382	2.916	1.006	.07040	.2660	.3098
.1213	4.537	3.621	2.890	1.647	.1211	.3487	.3275
.2528	5.688	4.083	2.931	2.757	.2525	.5031	.4289
.5050	7.718	4.812	3.000	4.718	.5045	.7109	.5063

In these equations S_s is the observed solubility in the potassium nitrate salt solutions, S_a that in nitric acid of the same ionic strength. An illustration of the method of calculation should make the method clear: at 25° when $m_{KNO_3} = m_{HNO_3} = 0.5050$, Table I of our previous paper[2] and of the present paper give $S_s = 3.330 \times 10^{-4}$ and $S_a = 5.027 \times 10^{-4}$. By means of eq. (1), $m_{IO_3^-}$ is calculated to be 2.206×10^{-4}. But this value of $m_{IO_3^-}$ is only a first approximation, since we are using the uncorrected value of μ in the acid solution. Taking into account the incomplete dissociation of iodic acid, the first corrected value of μ in the acid solution is then given by eq. (4) and equal to 0.50522. From Table I of the previous paper[2] we interpolate the value of S_s to correspond to the corrected value of $\mu = 0.50522$ and a second approximation of $m_{IO_3^-}$ is obtained. The final concentrations thus obtained are given in Table II; the last column of this table gives the logarithm of the ionization constant, K_m, of iodic acid in terms of concentrations.

It will be seen from Table II that the first value of K_m ($m = 0.001301$) for 25° must be rejected. This is probably to be expected, since the calculation is based essentially on the difference between S_a and S_s, which becomes very small in the lowest concentration and hence subject to a large relative error. The thermodynamic constant, K_a, is related to K_m by the equation

$$\log K_a = \log K_m - B\sqrt{\mu} \qquad (5)$$

where B has the values 0.5045, 0.5101 and 0.5146 for 25, 30 and 35°, respectively. Table III lists the values of K_a calculated by means of eq. (5) for the three temperatures.

TABLE III

CALCULATION OF K_a

m_{acid}	$\sqrt{\mu}$	K_a 25°	30°	35°
0.006503	0.082	0.171	0.148	0.145
.01410	.120	.172	.147	.140
.07050	.266	.155	.165	.149
.1213	.349	.152	.154	.141
.2528	.503	.161	.153	.148
.5050	.711	.172	.149	.138
.8738	.935	.164		
Average K_a		.164	.153	.144

Naidich and Ricci[3] obtained $K_a = 0.163$ at 25° from solubility data of barium iodate monohydrate in electrolytes, with which therefore our present value of 0.164 is in good agreement. They extrapolated a value $K_a = 0.17$ at 25° from the results of Abel, Redlich and Hersch[4] for 0° and 18° derived from conductivity data. Further extrapolation gives $K = 0.157$ and 0.147 for 30 and

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[4] Abel, Redlich and Hersch, *Z. physik. Chem.*, **170A**, 112 (1934).

35°, respectively, with which our values of 0.153 and 0.144, respectively, are to be compared.

Summary

The solubility of silver iodate in nitric acid solutions was measured at 25, 30 and 35°. These results, together with the results obtained previously for the solubility of silver iodate in potassium nitrate solutions, were used to calculate the thermodynamic constant of iodic acid at the three temperatures. Our value for the thermodynamic constant at 25° is in agreement with values given in the literature. Our values for 30 and 35° are in agreement with values extrapolated from the results derived from conductivity data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Bi-univalent Electrolytes. VI. Solutions of Cadmium Iodide from 5 to 40°

BY ROGER G. BATES[1]

Although many workers have found the abnormal behavior of cadmium iodide solutions a subject of interest,[2-6] a thermodynamic study over a range of temperature has never been made. In an earlier paper of this series,[6b] however, activity coefficients calculated from electromotive force measurements of cadmium amalgam–mercurous iodide cells at 25, 30 and 35° were reported. Whereas this range of temperature was not sufficiently large to warrant the calculation of thermodynamic quantities derived from the temperature coefficient, it appeared that the variation of electromotive force with temperature was essentially linear over a wide range of cadmium iodide concentration. The interesting implications of such a relationship made it seem worthwhile to study solutions of cadmium iodide over a wider range of temperature than that previously employed.

Electromotive force measurements of the cell

$$\text{Cd-Hg (2-phase)} \mid \text{CdI}_2\ (m) \mid \text{AgI-Ag} \qquad (1)$$

were made at intervals of 5° over the range, 5 to 40°, and at molalities of cadmium iodide ranging from 0.002 to 2. Activity coefficients, relative partial molal heat contents and relative partial molal specific heats of the solute have been evaluated. Between 0.05 and 2 molal the electromotive force of cell (1) was found to vary linearly with temperature, within the limits of error of the measurements. The relative partial molal specific heat is accordingly constant in this range.

Materials and Experimental Procedure

The mercury–mercurous iodide electrode used in the earlier investigation[6b] of cadmium iodide solutions has been shown[7] to give uncertain results when the iodide ion concentration is greater than *ca.* 0.02 *M*. Although the iodide ion concentration in cadmium iodide solutions is low, the silver–silver iodide electrode was chosen for the work. The solubility of silver iodide is small in iodide solutions containing up to 0.5 mole of iodide per liter.

The cadmium–silver iodide cell was found to be very satisfactory at molalities of cadmium iodide in excess of 0.005. The reproducibility fell off rapidly at molalities below 0.003. In general, the life of cells containing silver iodide electrodes was not as great as that of similar cells utilizing mercurous iodide electrodes,[8] and it was found necessary, for best results, to complete all measurements within thirty-six hours after the cells were made.

The slight acid reaction of cadmium iodide solutions (through hydrolysis) facilitates oxidative decomposition and makes exclusion of air essential. At no time was the presence of oxygen indicated by erratic potentials, by a dull amalgam surface or by a yellowing of the electrolyte

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[2] Transference: Hittorf, *Pogg. Ann.*, **106**, 543 (1859); B. Redlich, *Z. physik. Chem.*, **37**, 673 (1901); Heym, *Ann. phys.*, **12**, 443 (1919).

[3] Conductance: West and Jones, *Am. Chem. J.*, **44**, 508 (1910); Van Rysselberghe, Grinnell and Carlson, THIS JOURNAL, **59**, 336 (1937).

[4] Partial molal volume: Cantelo and Phifer, *ibid.*, **55**, 1333 (1933); Gibson, *ibid.*, **59**, 1521 (1937).

[5] Complex ion equilibria: McBain, Van Rysselberghe and Squance, *J. Phys. Chem.*, **35**, 999 (1931); Riley and Gallafent, *J. Chem. Soc.*, 514 (1932); Bates and Vosburgh, THIS JOURNAL, **60**, 137 (1938).

[6] Activity coefficients: from cells without liquid junctions, (a) Getman, *J. Phys. Chem.*, **32**, 940 (1928); (b) Bates and Vosburgh, THIS JOURNAL, **59**, 1583 (1937); from freezing points of solutions, (c) Getman, *J. Phys. Chem.*, **33**, 1781 (1929); see also (d) Rosenfeld, "Landolt-Börnstein Tabellen," Julius Springer, Berlin, 1931, II, b, 1116; from isopiestic vapor pressure, (e) Robinson and Wilson, *Trans. Faraday Soc.*, **36**, 740 (1940).

[7] Vosburgh, Derr, Cooper and Bates, THIS JOURNAL, **61**, 2592 (1939).

[8] Taylor and Perrott, *ibid.*, **43**, 389 (1921), measured the temperature coefficient of cell (1) with saturated (2.4 *m*) cadmium iodide electrolyte. They encountered difficulty in obtaining good results and suggested the formation of a cadmium–silver complex as the cause. The author has observed the same erratic behavior of the saturated cell but has found no evidence of a similar effect with oxygen-free 2 *m* cadmium iodide.