

phoryl fluoride present themselves, a satisfactory one cannot be advanced until more data have been acquired.

The sulfur-fluorine distance in sulfuryl fluoride, 1.56 Å., is 0.12 Å. less than the single bond distance predicted by the covalent radius table.<sup>13</sup> This shortening is not as great as is observed in the fluorine derivatives of phosphorus. A similar situation obtains for the corresponding chlorine compounds of sulfur and phosphorus.

It is of interest to note that, although there is much more shortening in the sulfur-halogen bond in sulfuryl fluoride than in sulfuryl chloride, the sulfur-oxygen distance in sulfuryl fluoride, 1.43 Å., is just that found for this distance in sulfur dioxide,<sup>15</sup> sulfur trioxide,<sup>3</sup> and sulfuryl chloride.<sup>3</sup>

In conclusion it should be remarked that the

(15) V. Schomaker and D. P. Stevenson, to be published.

large uncertainty in the fluorine-sulfur-fluorine angle,  $\pm 8^\circ$ , introduces an uncertainty of less than 0.1 E. U. into the calculation of the rotational entropy from the structure of the molecule.

### Summary

The structures of sulfuryl fluoride and thiophosphoryl fluoride have been investigated by the electron diffraction technique. The interatomic distances and bond angles are: for sulfuryl fluoride,  $S-F = 1.56 \pm 0.02$  Å.,  $S-O = 1.43 \pm 0.02$  Å.,  $\angle F-S-O = 105 \pm 2^\circ$ , and  $\angle F-S-F = 100 \pm 10^\circ$ ; and for thiophosphoryl fluoride,  $P-F = 1.51 \pm 0.02$  Å.,  $P-S = 1.85 \pm 0.02$  Å.,  $\angle F-P-F = 99.5 \pm 2^\circ$ , and  $\angle F-P-S = 118 \pm 2^\circ$ . The relationship between the structures found and the resonating valence bond structures is briefly discussed.

PASADENA, CALIF.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

## Solubility of Barium Iodate Monohydrate in Solutions of Uni-Univalent Electrolytes at 25°, and the Calculation of the Dissociation Constant of Iodic Acid from Solubility Data<sup>1</sup>

BY SOLOMON NAIDICH AND JOHN E. RICCI<sup>2</sup>

Barium iodate was one of the first salts to be used in the testing of theories of solutions of electrolytes through the effect of added electrolytes on the solubility of difficultly soluble salts. Such measurements for barium iodate were made by Harkins and Winninghoff,<sup>3</sup> in barium nitrate, potassium nitrate and potassium iodate solutions; by Polessitskii<sup>4</sup> in potassium nitrate and calcium nitrate solutions up to very high concentrations; and by Macdougall and Davies,<sup>5</sup> in dilute solutions of potassium chloride, nitrate, chlorate and perchlorate, and of calcium chloride.

In the present work, at the expense of repeating some of the measurements already found in the literature, it was decided to attempt to calculate the dissociation constant of iodic acid through the relative effects on the solubility of barium iodate

of the simple electrolyte potassium chloride and of the corresponding acid, hydrochloric, and, similarly, through the relative effects of the pair potassium nitrate and nitric acid on the same solubility. Measurements are therefore presented giving the effect of these four uni-univalent electrolytes on the solubility of  $Ba(IO_3)_2 \cdot H_2O$  at 25°, calculation of the various Debye-Hückel parameters for the mean activity coefficient of  $Ba(IO_3)_2 \cdot H_2O$  in these solutions, and, finally, calculation of the dissociation constant of iodic acid, based on the observed solubility data and certain assumptions to be stated.

### Experimental

$Ba(IO_3)_2 \cdot H_2O$ , c. p. grade, was washed eight to ten times with distilled water, the smaller particles being removed by a regulated process of sedimentation and decantation. Analysis of the product (dried at about 100°) before use, gave 96.5%  $Ba(IO_3)_2$  as compared with the theoretical figure of 96.43% for the monohydrate. The analytical method here and in the solubility determinations themselves was the iodometric titration of the iodate by means of 0.05 *N* sodium thiosulfate solution, previously standardized against pure potassium iodate. The procedure, involving the use of weight burets, was standard; blanks were taken to correct for any iodate in the potassium iodide

(1) Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Boston, September, 1939.

(2) The experimental part of this paper is taken from a thesis submitted by Mr. S. Naidich to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, June, 1939.

(3) Harkins and Winninghoff, *THIS JOURNAL*, **33**, 1827 (1911).

(4) Polessitskii, *Compt. rend. l'acad. sci., U. R. S. S.*, **14**, 193 (1935).

(5) Macdougall and Davies, *J. Chem. Soc.*, 1416 (1935).

used, and for any air oxidation of the excess iodide during the fixed time allowed for the titration.

The electrolyte solutions used as solvents were prepared, in the case of potassium chloride and nitrate, by weight, directly from c. p. recrystallized salts, followed by proper dilution, and by proper aliquoting and dilutions, for the very low concentrations. The hydrochloric acid solvents were made by a series of dilutions from a stock solution standardized gravimetrically; the nitric acid solutions, similarly, from a stock solution standardized volumetrically against pure sodium carbonate, using methyl orange as indicator.

The solubility determinations were carried out in Pyrex glass-stoppered bottles (250 ml. capacity), rotated for several days in a water-bath kept at  $25 \pm 0.01^\circ$ . To ensure equilibrium and accuracy, the determinations, for each strength of solvent, were made both from under- and from super-saturation, the analyses moreover being repeated after a day or two in almost every case. Hence in most cases four determinations were made for each point of the reported solubility curves. The saturated solutions were analyzed by withdrawing by means of suction (after allowing some time for settling) a 50 or 100 ml. sample into a calibrated pipet, fitted with quantitative filter paper at the tip, delivering the sample into an Erlenmeyer, and titrating the iodate as described above.

### Results

Table I lists the observed solubilities in the presence of various concentrations of potassium chloride, hydrochloric acid, potassium nitrate and nitric acid. The first column gives the molarity,  $m$ , of the solvent electrolyte; the second, the solubility,  $S$ , in moles per liter, averaged, in each case, from very closely agreeing results obtained from both under- and super-saturation; the third column lists the square root of the stoichiometric ionic strength, calculated on the assumption of complete dissociation for all electrolytes added.

$\log S$  is plotted against  $\sqrt{\mu}$  in Fig. 1. It will be observed that although the chloride curves are distinctly different from the nitrate curves, the relation of the acid to the salt effect is evidently very nearly the same for both cases. The increased solubility of the barium iodate in the presence of acid, as compared to its solubility in the corresponding concentration of potassium salt, evidently is due to the incomplete dissociation of iodic acid formed by double decomposition.

Assuming the Debye-Hückel equation in the form

$$\log f_{\pm} = -\frac{B\sqrt{\mu}}{1+A\sqrt{\mu}} \quad (1)$$

$m$	Average $S \times 10^4$	$\sqrt{\mu}$	$m$	Average $S \times 10^4$	$\sqrt{\mu}$
0	8.177	0.0495	0	8.177	0.0495
KCl added			KNO <sub>3</sub> added		
0.001	8.357	0.0593	0.001	8.387	0.0593
.005	8.977	.0877	.005	8.937	.0876
.01	9.297	.1131	.01	9.427	.1133
.05012	11.28	.2313	.05012	11.78	.2316
.1002	12.75	.3226	.1002	13.66	.3230
.2454	15.66	.5000	.2454	17.60	.5006
.4908	18.95	.7040	.4908	22.90	.7054
.9817	23.78	.9944	.9817	32.37	.9957
HCl added			HNO <sub>3</sub> added		
0.0001	8.249	0.0507	0.001101	8.455	0.0603
.0005	8.328	.0548	.005505	9.178	.0909
.001	8.400	.0593	.01101	9.806	.1181
.0025	8.649	.0714	.05505	13.75	.2433
.005	8.986	.0877	.1101	17.53	.3397
.01	9.554	.1135	.2474	25.83	.5050
.05012	12.74	.2323	.4948	39.39	.7117
.1002	15.57	.3239	.9895	68.78	1.005
.2454	22.28	.5021			
.4908	32.39	.7075			
.9817	52.43	.9987			

to hold for the data involving the potassium salts as solvent electrolytes, the results can be used first to calculate, for the chloride and for the nitrate series separately, values of the parameter

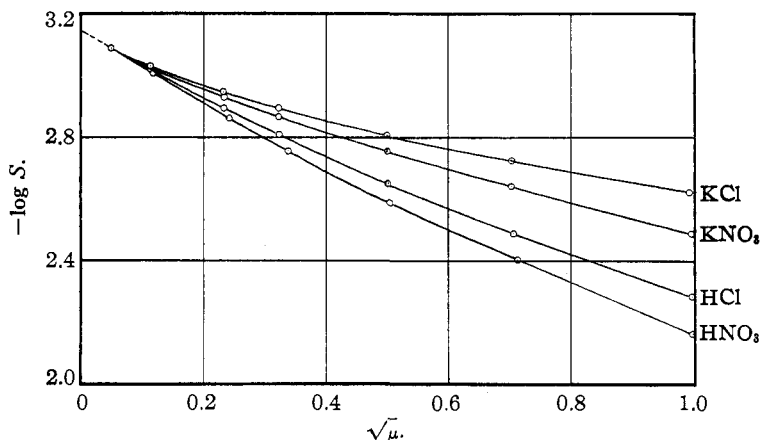


Fig. 1.—Solubility of  $\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$  in electrolyte solutions.

$A$ , of  $S_0$  (solubility in zero ionic strength) and of  $f_{\pm}$ , the mean activity coefficient, for the salt in its pure saturated solution. The coefficient  $f_{\pm\mu} = S_0/S_{\mu}$ ; hence by solving successive sets of simultaneous equations of the form

$$\begin{aligned} \log S_0 - \log S_{\mu_1} &= \frac{-1.01\sqrt{\mu_1}}{1+A\sqrt{\mu_1}} \\ \log S_0 - \log S_{\mu_2} &= \frac{-1.01\sqrt{\mu_2}}{1+A\sqrt{\mu_2}} \end{aligned} \quad (2)$$

in which  $S_{\mu_1}$  and  $S_{\mu_2}$  are the observed solubilities in the ionic strengths  $\mu_1$  and  $\mu_2$ , respectively, values of both  $S_0$  and  $A$  are obtained. By omitting the determinations in very low concentration of added electrolyte, and combining the solubility in pure water, successively, with the determinations in the strengths shown in column 1 of Table II, the corresponding values of  $A$  are calculated.

TABLE II  
VALUES OF  $A$ , CALCULATED

$m$	In KCl	In KNO <sub>3</sub>
0.05	1.08	0.57
.10	1.10	.64
.25	1.06	.65
.50	1.03	.62
1.0	0.97	.56
Av.	1.05	.61

From these values the mean effective ionic diameter  $a$  may be calculated, through the relation  $A = 0.328 a$ , yielding  $a = 3.20 \text{ \AA}$ . for the potassium chloride solutions, and  $a = 1.86 \text{ \AA}$ . for the potassium nitrate solutions.  $S_0$  can also be calculated, through the solubility in pure water, by the relation

$$\log S_0 = 0.9126 - 4 - \frac{1.01(0.0495)}{1 + A(0.0495)}$$

Using  $A = 1.05$  (KCl series),  $S_0 = 7.33 \times 10^{-4} M$ ; with  $A = 0.61$  (potassium nitrate series),  $S_0 = 7.31 \times 10^{-4}$ . These values, averaging  $7.32 \times 10^{-4}$ , agree fairly well with the value obtained by the graphical extrapolation of the curves of Fig. 1 to zero  $\mu$ ; these curves, it is to be noted, give a limiting slope (observed  $-1.0_1$  in each case) in agreement with the theoretical value of  $-1.01$ , and a value of  $S_0$  of  $7.31$  (KCl curve) and  $7.36 \times 10^{-4} M$  (KNO<sub>3</sub> curve). The mean activity coefficient of barium iodate monohydrate in its pure saturated solution at  $25^\circ$  is then calculated to be

$$f_{\pm} = \frac{S_0}{S_w} = \frac{0.000732}{0.000818} = 0.895$$

where  $S_w$  is solubility in water; Brönsted and La Mer<sup>6</sup> calculated 0.894 from the data of Harkins and Winnihoff.<sup>3</sup>

#### Dissociation Constant of Iodic Acid

A.—The numerical results just presented can be used to evaluate the ionization constant of iodic acid, first, on the assumption that the only incompletely dissociated species present is iodic acid. As we shall see later, under B, the final re-

sult is changed to a negligible extent only if we correct further for the possible presence of undissociated  $\text{BaIO}_3^+$  ion.

The assumption underlying the calculations is that the mean activity coefficient of the salt  $\text{Ba}(\text{IO}_3)_2$  remains constant in solutions of the same total ionic strength, regardless of whether the principal electrolyte present is the acid or the potassium salt of a given anion; in other words, that  $f_{\pm}$  for  $\text{Ba}(\text{IO}_3)_2$  is the same in solutions of either potassium chloride or hydrochloric acid, at the same  $\mu$ , and has a different but again a constant value in solutions of either potassium nitrate or nitric acid of the same  $\mu$ . This amounts to assuming that the parameter  $A$ , in the Debye-Hückel expression for  $\log f_{\pm}$ , is the same, in respect to the effect on  $f_{\pm}$  of  $\text{Ba}(\text{IO}_3)_2$ , for both the acid and the potassium salt of the same anion. For the particular reaction under consideration, of course,  $A$  for the two acids cannot be determined directly without, in fact, assuming a value for the dissociation constant of iodic acid. The equality of  $A$  for potassium chloride and for hydrochloric acid solutions therefore remains an assumption here. This assumption seems to be justified to some extent on the basis that the Debye-Hückel parameter  $A$ , for potassium chloride, in respect to other reactions, while differing rather regularly from that for potassium nitrate, is apparently the same for the corresponding acid, hydrochloric. Butler,<sup>7</sup> quoting the work of Harned and Åkerlöf<sup>8</sup> (electromotive force measurements), lists  $a$  for both potassium chloride and hydrochloric acid as  $3.38 \text{ \AA}$ .

If  $f_{\pm}$  is the same in hydrochloric acid and in potassium chloride solutions of the same ionic strength, then it follows that the mean ionic concentration  $m_{\pm}$  ( $= \sqrt[3]{4S}$ ) is also the same in the two solutions, since  $f_{\pm}m_{\pm}$  = the mean ionic activity, which is constant. Consequently it follows that we can treat the solubility product likewise as constant in the two corresponding solutions. This last was the assumption made by Pedersen<sup>9</sup> in Bjerrum's laboratory, for the solubility product of calcium oxalate in solutions of either sodium chloride or magnesium chloride, in his recent similar calculation of the dissociation constant of magnesium oxalate; it can be seen of course that the assumption of the constant mean

(7) Butler, "Chemical Thermodynamics," The Macmillan Co., New York, 1934, Vol. II, p. 132.

(8) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

(9) Pedersen, *Trans. Faraday Soc.*, **35**, 277 (1939).

(6) Brönsted and La Mer, *THIS JOURNAL*, **46**, 555 (1924).

TABLE III  
CALCULATION OF  $K_m$  FOR IODIC ACID WITHOUT CORRECTION FOR THE PRESENCE OF UNDISSOCIATED  $BaIO_3^+$

No.	$m_{acid}$	$S_A \times 10^4$	$S_S \times 10^4$	$m_{IO_3^-} \times 10^4$	$m_{HIO_3} \times 10^4$	$m_{H^+}$	$\sqrt{\mu}$	$\log \frac{K_m}{+1}$
In HCl								
1	0.001	8.400	8.357	16.17	0.09	0.000991	0.0593	0.2235
2	.005	8.986	8.974	17.94	.03	.004997	.0877	1.6515
3	.01	9.554	9.297	18.34	.77	.009923	.1131	0.3747
4	.05012	12.78	11.28	21.23	4.25	.04970	.2313	.3949
5	.1002	15.57	12.75	23.08	8.06	.09942	.3226	.4544
6	.2454	22.28	15.66	26.26	18.30	.2436	.5003	.5435
7	.4908	32.39	18.97	29.03	35.75	.4872	.7050	.5973
8	.9817	52.43	23.75	31.97	72.89	.9744	.9951	.6308
In HNO <sub>3</sub>								
1	0.001101	8.455	8.404	16.76	0.15	0.001086	0.0602	0.0840
2	.005505	9.178	8.995	17.81	.55	.005450	.0906	.2467
3	.011101	9.806	9.503	18.72	.89	.01092	.1177	.3611
4	.05505	13.75	12.01	22.45	5.05	.05454	.2422	.3847
5	.1101	17.53	13.97	24.94	10.12	.1091	.3382	.4295
6	.2474	25.83	17.68	29.26	22.40	.2452	.5029	.5055
7	.4947	39.39	23.01	35.18	43.60	.4903	.7087	.5973
8	.9894	68.78	32.34	44.36	93.20	.9801	1.0004	.6688

activity coefficient is implicit in that of the constancy of the solubility product, and that any uncertainty in the values of the various  $A$  parameters involved affects the applicability of the solubility product principle which must be used in the calculations.

Setting then the solubility product of barium iodate in solutions of hydrochloric acid equal to its solubility product in the corresponding potassium chloride solution of the same total ionic strength, the various ionic concentrations in the acid solutions can be calculated as follows. If  $S_S$  = the observed solubility in salt solution, and  $S_A$  that in acid (of the same  $\mu$ )

$$m_{IO_3^-} = \sqrt{\frac{K_{SP}}{S_A}} = \sqrt{\frac{4S_S^3}{S_A}} \quad (3)$$

$$m_{HIO_3} = 2S_A - m_{IO_3^-} \quad (4)$$

$$m_{H^+} = m_{HCl} - m_{HIO_3} \quad (5)$$

$$\mu = S_A + m_{HCl} + m_{IO_3^-} \quad (6)$$

The value of  $m_{IO_3^-}$  thus calculated is a first approximation, based on a value of  $S_S$  interpolated on the potassium salt curves to correspond to the uncorrected value of  $\sqrt{\mu}$  for the acid solution yielding the observed  $S_A$ . On correcting the ionic strength for the undissociated iodic acid,  $\mu$  now being equal to  $m_{HCl} + S_A + m_{IO_3^-}$  (Equation 6), a second approximation was made in the calculation of  $IO_3^-$  by re-evaluating  $S_S$  to correspond to the corrected value of  $\sqrt{\mu}$ . The final concentrations thus obtained are given in Table III; the last two columns of this table give the corrected ionic strength (to the half power) and

the logarithm of the ionization constant,  $K_m$ , of iodic acid in terms of concentrations.

It will be seen that the first two values (lowest concentrations) must be discarded in both the hydrochloric acid and the nitric acid series. This was probably to be expected, since the calculation is based essentially on the difference  $S_A - S_S$ , which becomes very small in this range and subject to too large a relative error. The thermodynamic constant,  $K_a$ , is now calculated from the remaining values of the mass constant,  $K_m$ , by an algebraic process similar to the calculation of  $S_0$  from the values of  $S_\mu$  in the foregoing part. Since, for iodic acid

$$K_a = K_m - \frac{f_{H^+}f_{IO_3^-}}{f_{HIO_3}} \quad (7)$$

we can, by assuming  $f_{HIO_3} = 1$ , set

$$\log K_a = \log K_m - \frac{1.01 \sqrt{\mu}}{1 + A \sqrt{\mu}} \quad (8)$$

$K_a$  can then be calculated by finding a proper value of the parameter  $A$  for the data to yield a constant value of  $K_a$  through the algebraic solution of successive sets of simultaneous equations of the form

$$\begin{aligned} \log K_a &= \log K_{m_1} - \frac{1.01 \sqrt{\mu_1}}{1 + A \sqrt{\mu_1}} \\ \log K_a &= \log K_{m_2} - \frac{1.01 \sqrt{\mu_2}}{1 + A \sqrt{\mu_2}} \end{aligned} \quad (9)$$

After averaging the results ( $\sqrt{\mu}$  and  $\log K_m$ ) for both the hydrochloric acid and the nitric acid data into one series, combinations of values sufficiently far apart in respect to  $\sqrt{\mu}$  were used as simultaneous equations, the calculated  $A$  param-

ter having the values listed in Table IV, which shows also the degree of variability in this "constant."

Table V lists, in the last column, the values of  $K_a$  calculated (with  $A = 1.25$ ) from the averaged values of  $\sqrt{\mu}$  and of  $\log K_m$  taken from Table III.

The average value of  $K_a$  thus calculated, without the consideration of the possible presence of undissociated  $\text{BaIO}_3^+$ , is then 0.163.

TABLE IV  
VALUES OF  $A$  CALCULATED TO FIT EQUATIONS (9)

Combinations used	$A$
0.01-0.5 $N$	1.67
.01-1 $N$	1.66
.05-0.25 $N$	1.13
.05-.5 $N$	1.09
.05-.1 $N$	1.28
.1-.5 $N$	1.12
.1-1 $N$	1.28
.25-1 $N$	1.37
Average used	1.25

TABLE V  
CALCULATION OF  $K_a$  FROM  $K_m$ , WITH  $A = 1.25$

No.	$m_{\text{Acid}}$	$\sqrt{\mu}$	$K_m$	$K_a$
3	0.01	0.1154	0.233	0.185
4	.05	.2368	.245	.161
5	.1	.3304	.277	.161
6	.25	.5016	.335	.162
7	.5	.7069	.396	.166
8	1.0	.9978	.447	.157
	Average			.165
	Average, omitting no. 3			.161

**B.**—Macdougall and Davies<sup>5</sup> showed that barium iodate cannot be considered to be completely dissociated even in very low concentrations; they calculated the equilibrium constant for the dissociation of the barium mono-iodate ion to be

$$\frac{m_{\text{Ba}^{2+}} + m_{\text{IO}_3^-}}{m_{\text{BaIO}_3^+}} = 0.08 \quad (10)$$

As this circumstance would be expected to affect the final result for the dissociation constant of iodic acid to some extent, the calculations were repeated, taking into account therefore the formation of the ion  $\text{BaIO}_3^+$ . The concentration of this ion in the potassium salt solution, ( $x_s$ ), can be calculated in the potassium chloride and nitrate solutions through the equation

$$\frac{(S_s - x_s)(2S_s - x_s)}{x_s} = K_{\text{BaIO}_3^+} \quad (11)$$

which approximates to

$$x_s = \frac{2S_s^2}{K_{\text{BaIO}_3^+} + 3S_s} \quad (12)$$

since  $x_s$  is small compared to  $S_s$ .

The value of  $K_{\text{BaIO}_3^+}$  in terms of concentrations will vary markedly with the ionic strength, according to the expression

$$\log K_{\text{BaIO}_3^+} = \log (0.08) + \frac{2.02 \sqrt{\mu}}{1 + A \sqrt{\mu}} \quad (13)$$

(where 2.02 is the Debye-Hückel coefficient for a bivalent ion), and was evaluated accordingly for the various solutions by assuming  $A = 1$ ; the magnitude of the effect here involved, on the final result, is so small that a value of 1 for  $A$ , which is reasonable, was taken merely for convenience.

The solubility product in any given salt solution is now given by

$$K_{sp} = (S_s - x_s)(2S_s - x_s)^2 \quad (14)$$

Before calculating the concentrations in the acid solutions, required for the dissociation constant of iodic acid, it is also necessary to calculate the concentrations,  $x_A$ , of the  $\text{BaIO}_3^+$  in the acid solutions, since, with

$$m_{\text{Ba}^{2+}} = S_A - x_A \quad (15)$$

then 
$$m_{\text{IO}_3^-} = \sqrt{\frac{K_{sp}}{S_A - x_A}} \quad (16)$$

To calculate  $x_A$ , we use

$$\frac{m_{\text{Ba}^{2+}} + m_{\text{IO}_3^-}}{m_{\text{BaIO}_3^+}} = K_{\text{BaIO}_3^+} \quad (17)$$

or

$$\frac{(S_A - x_A) \sqrt{\frac{K_{sp}}{S_A - x_A}}}{x_A} = K_{\text{BaIO}_3^+} \quad (18)$$

Since  $x_A$  is small compared to  $S_A$ , this simplifies to

$$x_A = \frac{\sqrt{K_{sp} S_A}}{K_{\text{BaIO}_3^+}} \quad (19)$$

in which  $K_{\text{BaIO}_3^+}$  is the mass constant calculated according to the earlier equation (13). The remaining quantities are calculated by

$$m_{\text{HIO}_3} = 2S_A - m_{\text{BaIO}_3^+} - m_{\text{IO}_3^-} \quad (20)$$

$$m_{\text{H}^+} = m_{\text{HCl}} - m_{\text{HIO}_3} \quad (21)$$

$$\mu = (S_A - x_A) + m_{\text{HCl}} + m_{\text{IO}_3^-} \quad (22)$$

The calculations are summarized in Table VI, to which of course the first three columns of Table III should be added, for completeness.

It is interesting to note that the concentration of  $\text{BaIO}_3^+$  in the salt solutions,  $x_s$ , remains constant, irrespective of the actual concentration of  $\text{Ba}(\text{IO}_3)_2$ , because of the effect of the ionic strength on  $K_{\text{BaIO}_3^+}$ . Although this sort of constancy was actually assumed as a general case, by Pedersen,<sup>9</sup> for undissociated calcium oxalate, in his calculation of the dissociation constant of magnesium oxalate, it is to be noted that at least in the pres-

ent case the same constancy does not hold as well in the acid solutions.

TABLE VI

CALCULATION OF  $K_m$  FOR IODIC ACID, INCLUDING CORRECTION FOR THE PRESENCE OF UNDISSOCIATED  $BaIO_3^+$

No.	$\frac{x_B}{\times 10^4}$ in $m_{BaIO_3^+}$ K <sup>+</sup> soln.	$\frac{x_A}{\times 10^4}$ in $m_{BaIO_3^+}$ acid soln.	In HCl		$m_{H^+}$	$\sqrt{\mu}$	log $K_m$ (+1)
			$\frac{m_{IO_3^-}}{\times 10^4}$	$\frac{m_{HIO_3}}{\times 10^4}$			
1	0.13	0.13 <sub>2</sub>	16.54	0.13	0.000987	0.0590	0.099
2	.13	.13 <sub>6</sub>	17.81	.02	.004998	.0876	1.648
3	.13	.13 <sub>4</sub>	18.20	.79	.00991	.1130	0.3592
4	.13	.14 <sub>0</sub>	21.10	4.24	.04970	.2313	.3932
5	.13	.14 <sub>4</sub>	22.95	8.05	.09942	.3225	.4523
6	.13	.15 <sub>6</sub>	26.14	18.26	.2436	.5001	.5424
7	.13	.17 <sub>3</sub>	28.91	35.70	.4872	.7050	.5960
8	.14	.20 <sub>9</sub>	31.86	72.79	.9744	.9950	.6300
In HNO <sub>3</sub>							
1	0.13	0.13 <sub>3</sub>	16.62	0.16	0.001085	0.0600	0.0520
2	.13	.13 <sub>6</sub>	17.68	.54	.005451	.0904	.2516
3	.13	.13 <sub>8</sub>	18.56	.92	.01092	.1176	.3429
4	.13	.15 <sub>5</sub>	22.34	5.01	.05455	.2422	.3865
5	.13	.16 <sub>9</sub>	24.84	10.05	.1091	.3381	.4307
6	.13	.20 <sub>0</sub>	29.15	22.31	.2452	.5029	.5058
7	.13	.25 <sub>5</sub>	35.08	43.45	.4904	.7087	.5977
8	.14	.37 <sub>9</sub>	44.29	92.89	.9801	1.0003	.6896

These results, shown in Table VI, are averaged for the two series, in Table VII, which further gives the values of  $K_a$  calculated, as above under (A), from the mass constant through the equation

$$\log K_a = \log K_m - \frac{1.01 \sqrt{\mu}}{1 + 1.25 \sqrt{\mu}} \quad (23)$$

in which the same value of  $A$  is used as for the calculations of Table V.

TABLE VII

CALCULATION OF  $K_a$  FROM  $K_m$ , WITH  $A = 1.25$

No.	$m_{Acid}$	$\sqrt{\mu}$	$K_m$	$K_a$
3	0.01	0.1153	0.228	0.178
4	.05	.2368	.245	.160
5	.1	.3303	.276	.160
6	.25	.5015	.334	.163
7	.5	.7069	.395	.165
8	1	.9977	.447	.159
Average				.164
Average (omitting no. 3)				.162

It is to be pointed out that the dissociation constants calculated for the data in very low concentrations (perhaps including the concentration 0.01 *N* in acid) are highly variable and obviously not to be considered for the final value. This low reliability in the results is to be expected for low concentrations because of the nature of the method, which, as already stated, is a differential one, depending primarily on the observed difference between  $S_A$  and  $S_S$  (a measurement subject to very high relative error at the low acid con-

centrations) for the determination of the concentration of undissociated iodic acid, on which of course the ionization constant chiefly depends.

### Discussion

The final value of  $K_a$  therefore, calculated from the solubility data, either with or without the correction for  $BaIO_3^+$ , is about 0.163. Whether or not the agreement is really to be expected, this value nevertheless agrees fairly well with the best values derived from conductivity work. All the values of the ionization constant of iodic acid in the literature are based on conductivity measurements:

Rothmund and Drucker <sup>10</sup> (1903)	$K = 0.18-0.19$ at 25°
Onsager <sup>11</sup> (1927)	$K = .17$ at 25°
Davies <sup>12</sup> (1933)	$K = .18(.20?)$ at 25°
Fuoss and Kraus <sup>13</sup> (1933)	$K = .1686$ at 25°
Abel, Redlich and Hersch <sup>14</sup> (1934)	$K = .26$ at 0°
	.19 at 18°
	.17 at 25°

extrapolating to

The best value is accepted to be that of Fuoss and Kraus, 0.1686 at 25°, with which therefore the present value of 0.163 is to be compared. Pedersen,<sup>9</sup> it should be noted, likewise found agreement between values of the ionization constant of magnesium oxalate calculated from solubility data and from conductivity measurements, obtaining  $3.8 \times 10^{-4}$  and  $3.9 \times 10^{-4}$  in the two cases, respectively.

### Summary

The solubility of  $Ba(IO_3)_2 \cdot H_2O$  was measured at 25° in aqueous solutions of KCl, HCl, KNO<sub>3</sub> and HNO<sub>3</sub>, the results being considered from the point of view of the Debye-Hückel equation.

The results are used to evaluate the ionization constant of iodic acid on the assumption of a constant mean activity coefficient for barium iodate in either the acid or the potassium salt solution of the same anion, at the same total ionic strength. Corrections are made for the possible existence of undissociated  $BaIO_3^+$  in the solution; this effect however is found to be negligible.

The value of the thermodynamic constant  $K_a$  for iodic acid is found to be 0.163, in agreement with the best value (0.1686) derived from conductivity data.

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(12) Also based on the data of Kraus and Parker (ref. 11), "Conductivity of Solutions," London, 1933, p. 107.

(13) Fuoss and Kraus, *This Journal*, **55**, 476 (1933).

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