

# THE EQUILIBRIUM BETWEEN IODINE AND BARIUM IODIDE IN AQUEOUS SOLUTIONS

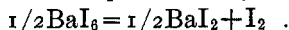
J. N. PEARCE AND W. G. EVERSOLE

Since the discovery of the fact that iodine dissolves more readily in aqueous solutions of metallic iodides than in pure water the nature of the equilibria existing in these systems has been the subject of numerous investigations. That a compound is formed between the iodine and the iodide is generally accepted. Although the literature covering these investigations is extensive in scope, reference will be made only to those articles which bear directly upon the present work.

Jakowkin<sup>1</sup> was the first to make a systematic study of the equilibria involved. He assumed the reaction:  $MI + I_2 = MI \cdot I_2$ , and he has calculated the corresponding equilibrium constants by means of the relation,

$$K = \frac{C_{MI} \cdot C_{I_2}}{C_{MI_2}}$$

In the case of barium iodide Jakowkin assumed that both iodine atoms of the salt are equally active in combining with the dissolved iodine and he has based his calculations upon the reaction represented by the equilibrium,



The corresponding equilibrium constant is given by the relation:

$$K = \frac{[2a - (b - x)]x}{b - x},$$

where  $a$  is the original concentration of the barium iodide,  $b$  is the total concentration of the iodine as determined by titration and  $x$  is the concentration of the free uncombined iodine, all in moles per liter in the water layer. For equivalent concentrations of the iodides studied Jakowkin has found that at 25° the equilibrium constants thus calculated are approximately equal to 0.0014.

Herz and Kurzer<sup>2</sup> also have carried out a short series of determinations, using different concentrations of iodine with only one concentration of the salt. They assumed that only one of the two iodine atoms of barium iodide combines with iodine and they have based their calculations upon the equilibrium:  $BaI_2 = BaI_2 + I_2$ . The expression representing this equilibrium is,

$$K = \frac{[a - (b - x)]x}{b - x}$$

The values of  $K$  thus calculated show a fair degree of constancy over the range of iodine concentration studied.

<sup>1</sup> Jakowkin: *Z. physik. Chem.*, **13**, 539 (1894); **20**, 19 (1896).

<sup>2</sup> Herz and Kurzer: *Z. Elektrochem.*, **16**, 869 (1910).

The most recent work on the study of iodine-polyiodide equilibria is that of Van Name and Brown<sup>1</sup>. They have investigated the iodides of zinc, strontium, nickel, cadmium, mercury and lanthanum, and they have recalculated the data of Herz and Kurzer for barium iodide, using the method of Jakowkin. They conclude that the constant calculated by Jakowkin, rather than that of Herz and Kurzer, holds in general not only for the iodides of the bivalent metals, but also for the iodide of the trivalent metal lanthanum.

In a series of papers Van Name and his co-workers<sup>2</sup> report the results of a study of the rate of reaction of metals with halogens dissolved in aqueous solutions of metallic halides. They found that the rate of reaction of metals with a given solution of a halogen, e.g., iodine dissolved in a solution of potassium iodide, is independent of the nature of the metal and depends only on the rate of diffusion of the iodine to the metal. This is in harmony with the diffusion theory of heterogeneous reactions. Moreover, the rate of reaction was found to be markedly increased by increasing the concentration of the potassium iodide.

In a study of the rate of diffusion of iodine in solutions of potassium iodide Edgar and Diggs<sup>3</sup> have found that the rate of diffusion increases with the concentration of potassium iodide and, furthermore, that the increase is distinctly of the same order of magnitude as the increase in the velocity constants for the reaction between the metals and dissolved iodine. Believing that an increase in the potassium iodide concentration may increase the rate of diffusion of iodine indirectly, i.e., by influencing the fluidity, they determined the rate of diffusion of iodine in and the fluidity of solutions over a wide range of potassium iodide concentration. They found that the increase in the rate of diffusion is much too great to be accounted for by the increase in fluidity alone. They assume that  $KI_3$  molecules are present and that these molecules diffuse more slowly than the  $I_3^-$  ion. Since an increase in the potassium iodide concentration must repress the ionization of the  $KI_3$ , the rate of diffusion of the iodine for this reason decrease as the concentration of the potassium iodide is increased. No satisfactory explanation for the influence of the salt on the diffusion of iodine was found.

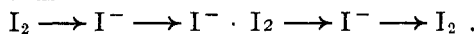
It seems very probable that these authors have overlooked one possible and plausible explanation of the mechanism of the process whereby the rate of diffusion of iodine may be increased by increasing the concentration of the potassium iodide. If we consider a potassium iodide solution containing dissolved iodine in contact with an equivalent solution of the potassium iodide alone, diffusion of iodine may take place in two ways. (1) Owing to the difference in concentration of the  $KI_3$  molecules and their ions ( $K^+$  and  $I_3^-$ ) in the contiguous phases these species will diffuse from higher to lower concentration. Obviously, at the same time  $KI$  molecules and their ions will diffuse in the opposite direction. (2) At the same time iodine may be transferred by a

<sup>1</sup> Van Name and Brown: *Am. J. Sci.*, **44**, 105 (1917).

<sup>2</sup> Van Name and co-workers: *Ibid.*, **29**, 237; **32**, 207.

<sup>3</sup> Edgar and Diggs: *J. Am. Chem. Soc.*, **38**, 253 (1916).

second process. Suppose a molecule of iodine,  $I_2$ , temporarily free, diffuses from left to right, thus



When it comes in contact with an  $I^-$  ion, or with a KI molecule, it will combine with this to form the tri-iodide ion, or molecule. This in turn may again dissociate and liberate free  $I_2$  to be taken up by succeeding  $I^-$  ions or KI molecules. As a homely illustration of the process meant we need but recall the old-fashioned bucket brigade in action at a fire. The iodine molecules may be likened to the buckets which are passed on from man to man. Thus, the distance passed over in the diffusion process in a given time has been increased by the diameter of the  $I^-$  ion or KI molecules. Incidentally the actual rate of transfer of KI molecules and  $I^-$  ions in the opposite direction has been increased by this transfer of iodine. The polyiodides are relatively unstable. Hence there is always some free iodine in the solution and the interchange of iodine molecules between molecules of KI or  $I^-$  ions within the solution will become easier and more frequent as the concentration of the potassium iodide is increased. Excepting for possible differences in fluidity, the rate of diffusion of iodine of a given concentration should be the same in any given concentration of any alkali iodide. The general direction and velocity of the diffusion process will be governed by the concentration gradient of the polyiodide.

In a study of the system, potassium iodide-iodine-alcohol-water, Parsons and Corliss<sup>1</sup> conclude, from phase rule considerations, that no solid polyiodides are formed and that probably no polyiodides exist in solution. While experience teaches that the solubility of iodine in alcohol is decreased by the addition of water and that the solubility of potassium iodide in water is decreased by the addition of alcohol they find that the solubility of iodine and potassium iodide together is nearly the same in 40% or 60% alcoholic solutions as in pure alcohol or pure water. They believe that the increase in solubility is due to the mutual solvent effect of the iodine and potassium iodide on each other. They state that "the mutual solubility of the potassium iodide and iodine increases in proportion to the amount of the other present". As proof of the nonexistence of polyiodides these authors offer the results of a few diffusion experiments in which an agar cup separates a solution of potassium iodide from a second solution of this salt saturated with iodine. They assume that the ions diffuse through the agar at the same rate as through the solvent. While this may be true for very dilute agar sols it is not necessarily true for solid emulsoids, and the specific effect on the diffusion speeds will be different for different ions. Furthermore, their agar cup walls were about 11 mm. thick and were made by dissolving agar in an 0.1 N solution of potassium iodide. Obviously, the actual concentration of the salt in the free water of the solid agar is greater than 0.1 N because of the water taken up by the agar on swelling. Hence, because of unequal osmotic pressures, when this agar membrane is placed in an 0.1 N KI solution water will either pass into the agar or potassium iodide will pass into the solution. For the purposes of this discussion it will be neces-

<sup>1</sup> Parsons and Corliss: J. Am. Chem. Soc., 32, 1637 (1910).

sary to review briefly the experiments performed by Parsons and Corliss. In the first experiment a 0.16 N solution of potassium iodide saturated with iodine was placed in the cup and the whole then immersed in an 0.1 N solution of the salt. According to the authors, "if the tri-iodide is formed, as shown by Jakowkin and others, the initial condition of the two solutions will be

Outer solution			Inner solution	
(A)	0.1 N KI	agar KI	0.08 N KI	
			0.08 N KI <sub>3</sub>	
			0.0013 N I <sub>2</sub>	

and the KI will diffuse from left to right. If, however, no compound is formed, the initial condition will be

Outer solution			Inner Solution	
(B)	0.1 N KI	agar KI	0.16 N KI	
			0.0813 N I <sub>2</sub>	

and KI will diffuse from right to left."

They did find that an appreciable amount of KI did diffuse into the 0.1 N solution ahead of any iodine, and hence concluded from this that no polyiodide is formed. Another experiment apparently confirming this was arranged in which an 0.1 N solution of potassium iodide surrounded the cup containing a similar solution saturated with iodine, thus

Outer solution			Inner solution	
(C)	0.1 N KI	agar KI	0.05 N KI	
			0.05 N KI <sub>3</sub>	
			0.0013 N I <sub>2</sub>	

"If a compound is formed KI should pass from left to right. But if no compound is formed then we should have as the initial conditions,"

Outer solution			Inner solution	
(D)	0.1 N KI	agar KI	0.1 N KI	
			0.0513 N I <sub>2</sub>	

and the concentrations of the potassium iodide being equal at the start they should remain so during the diffusion of the iodine. This they actually found to be the case. Hence they reasoned that the iodine is free and uncombined. It is obvious at a glance that they are basing their conclusions solely upon the relative concentrations of the potassium iodide as indicated in the initially chosen conditions.

It will be interesting to observe that the results obtained are exactly what one might predict on the assumption of the existence of polyiodides. Let us consider the cases (A) and (C) only. In respect to the I<sup>-</sup> ion the outer solution is in each case hypertonic to the inner solution, and for this reason the salt should diffuse from left to right as Parsons and Corliss have assumed. Let us now take case (A). Both KI and KI<sub>3</sub> are strong electrolytes and hence at the dilutions used they are highly dissociated. As a rough approximation we may consider them as completely dissociated without vitiating the argument. The difference in concentration of the K<sup>+</sup> ion is roughly 0.06 N, that of the

$I^-$  ion is about 0.02 N and that of the  $I_3^-$  ion 0.08 N. These differences in concentration of the respective ions represent the diffusion pressure gradients of the ions, the dominating pressure gradient being that of the potassium ion. Under these conditions the  $K^+$  and  $I_3^-$  ions must diffuse into the outer solution. The dissociated ions from a molecule electrostatically attract each other; the speed of the slower moving ion is accelerated by that of the faster, and vice versa. The velocities of the  $K^+$  and  $I^-$  ions are approximately equal, that of the  $I_3^-$  is less. Therefore, in diffusing the  $K^+$  ions will drag with them both  $I^-$  and  $I_3^-$  ions, and possibly more of the faster moving  $I^-$  ion than of the  $I_3^-$  ion. The concentration of the  $I^-$  ion thus increased in the outer solution later adjusts itself to an isotonic condition by diffusing into the cup, accompanied simultaneously by the outward diffusion of  $I_3^-$  ions and the outward transference of iodine by the process described above. In case (C) the inner and outer solutions are initially isotonic with respect to the  $K^+$  ions; the concentration gradients of the  $I^-$  and  $I_3^-$  ions are equal and opposite. The  $I_3^-$  ions and the  $I_2$ , by secondary diffusion, diffuse outward; the  $I^-$  ions diffuse to the inner solution and the extent of this latter diffusion is less than it would be normally by the number of  $I^-$  ions set free in the secondary diffusion of iodine. It is obvious therefore that the conclusions of Parsons and Corliss regarding the nonexistence of polyiodides in solution are entirely untenable.

In the previous work upon this subject the concentrations for the most part have been expressed in gram-mols, or gram-equivalents, per liter of solution. It is evident that if very large concentration ranges are used there will be a considerable variation in the amount of solvent present. When the results for the different concentrations are compared on this basis the explanation of any variations in the equilibria observed must take into consideration not only the concentration of the iodide and the iodine, but also of the solvent present. The present work was undertaken with the purpose of eliminating effects due to variation in the amount of solvent by expressing all concentrations in gram-mols per 1000 g. of solvent.

### Purification of Materials

*Barium Iodide.* The pure salt which had been twice recrystallized from a solution containing hydriodic acid was mixed with a small quantity of freshly prepared solid ammonium iodide and fused in a stream of dry nitrogen. The resulting product is a white crystalline solid which can be kept indefinitely over phosphorus pentoxide. The purity of the salt was tested by repeated accurate determinations of both the iodine and the barium content.

*Iodine.* Baker's resublimed iodine was sublimed once from an intimate mixture with pure solid potassium iodide and once alone. All iodine determinations were made with an approximately 0.04 N solution of pure sodium thiosulphate which was frequently standardized against a freshly prepared iodine solution. This in turn was previously checked against a solution of sodium arsenite made from resublimed arsenic trioxide.

*Carbon Tetrachloride.* A large sample of this solvent was washed with water containing a small amount of sodium hydroxide. It was then repeatedly washed with pure water and allowed to stand over solid anhydrous calcium chloride. Before use the solvent was decanted and redistilled.

### Solubility of Iodine in Water

The solubility of iodine in water at 25° was determined by shaking an excess of pure iodine with conductivity water in tightly stoppered bottles of Jena glass. These were rotated in a large thermostat until equilibrium was established. Samples were withdrawn by means of accurately calibrated pipettes and run into tared glass stoppered erlenmeyer flasks containing a solution of potassium iodide, and quickly weighed. The exact weight of the iodine solution was determined by difference and the iodine titrated with the thiosulphate solution. The solubility was calculated in mols of iodine dissolved in 1000 g. of water. Six successive determinations gave the following values: 0.0013291, 0.0013295, 0.0013287, 0.0013294, 0.0013292, 0.0013296. The mean value, viz., 0.001329, agrees well with the value of 0.00132 obtained by Bray and MacKay<sup>1</sup> for mols of iodine in 1000 c.c. of a saturated water solution.

### The Distribution of Iodine between Carbon Tetrachloride and Water

In making these determinations carbon tetrachloride, conductivity water and solid iodine were placed in glass-stoppered bottles, carefully sealed and then rotated in the thermostat at 25° until the iodine was completely dissolved and the distribution equilibrium was attained. 25 c.c. portions of the water layer and 10 c.c. portions of the carbon tetrachloride layer were quickly transferred without loss of iodine or solvent to tared glass-stoppered flasks containing an excess of a strong solution of potassium iodide and then quickly weighed. The iodine was determined by titration and the weights of the solvents by difference. From the data obtained the distribution ratio was calculated on the basis of 1000 g. of each solvent. This constant is not to be confused with the constant as determined by Linhart<sup>2</sup> on the basis of 1000 g. of saturated solution. He found for K the value 56.75.

The results of these determinations are given in Table I. The constancy of the ratios is all that can be expected when one considers the extremely low concentrations of the iodine in the water layer and also the fact that slight errors are considerably multiplied in reducing concentrations to mols per 1000 g. of solvent.

---

<sup>1</sup> Bray and MacKay: J. Am. Chem. Soc., **32**, 914 (1910).

<sup>2</sup> Linhart: J. Am. Chem. Soc., **40**, 158 (1918).

TABLE I

The Distribution of Iodine between Water and Carbon Tetrachloride.

Grams I <sub>2</sub> 1000 g. H <sub>2</sub> O	Grams I <sub>2</sub> 1000 g. CCl <sub>4</sub>	I <sub>2</sub> (1000 g. CCl <sub>4</sub> ) I <sub>2</sub> (1000 g. H <sub>2</sub> O)	I <sub>2</sub> (1000 c.c. CCl <sub>4</sub> ) I <sub>2</sub> (1000 c.c. H <sub>2</sub> O)
0.0745	3.8990	52.35	82.60
0.1020	5.3584	52.53	82.62
0.1078	5.6775	52.64	82.86
0.1432	7.5145	52.49	82.69
0.2432	12.6950	52.21	82.37
	Mean	52.5	82.6

The distribution ratio of iodine between water and carbon tetrachloride has also been determined by Jakowkin.<sup>1</sup> He calculated his results on the basis of 1000 c.c. of solution and found that the ratio increases from 80.5 in dilute solutions to a value of 89 as the concentration of the iodine is increased. We have found that the value of the ratio for the range of concentrations used is independent of the concentration of the iodine when calculated on either basis. The mean value of the distribution ratio ( $K=52.5$ ) is used throughout the work which follows:

#### Solubility of Iodine in Barium Iodide Solutions

For this purpose solutions of an approximate definite normality were first prepared from the purified salt and air-free conductivity water. Accurately weighed samples of these solutions were taken and the barium precipitated as barium sulphate. The concentrations were then calculated on the basis of mols of barium iodide in 1000 g. water. To make the different dilutions used accurately measured volumes of these solutions were transferred to previously weighed 100 c.c. volumetric flasks and weighed. The solution was then diluted to 100 c.c. at 25° with air-free water and again weighed. From these data it is possible to calculate the concentration at all dilutions on both the weight and volume basis. The solutions were then transferred to dry glass stoppered bottles and an excess of solid iodine was added. The bottles were sealed and rotated in the thermostat for 24 hours, and then allowed to stand in the bath until the finely divided solid iodine had completely settled. Definite samples of the saturated solution were then transferred to accurately tared flasks containing solutions of potassium iodide, weighed and the iodine determined by titration. From the weight of iodine found, the weight of the sample taken and the concentration of the barium iodide solution we calculated the total concentration of the dissolved iodine.

The results of these determinations are shown in Table II. The molal concentration of the combined iodine was obtained by subtracting the molal solubility of iodine in water from the total amount of the dissolved iodine.

<sup>1</sup> Jakowkin: Z. physik, Chem., 13, 539 (1894).

TABLE II

The Solubility of Iodine in Barium Iodide Solutions at 25°

Mols BaI <sub>2</sub> 1000 g. H <sub>2</sub> O	Mols I <sub>2</sub> 1000 g. H <sub>2</sub> O	Mols I <sub>2</sub> (combined)	Mols I <sub>2</sub> Mols BaI <sub>2</sub>
0.000000	0.001329	0.000000	
0.000686	0.002044	0.000715	1.042
0.003120	0.004482	0.003153	1.010
0.006287	0.007574	0.006245	0.993
0.031674	0.032199	0.003087	0.975
0.047716	0.048413	0.04702	0.985
0.080477	(0.079370)	0.07804	(0.969)
0.16497	0.16872	0.16739	1.015
0.34880	0.39500	0.39367	1.129
0.39633	0.45460	0.45327	1.144
0.57189	0.81690	0.81557	1.426
0.87640	1.4674	1.4661	1.673
1.1922	2.2880	2.2867	1.918

Particularly interesting and significant are the data of the last column. It will be observed that the ratio of the mols of combined iodine to the mols of barium iodide decreases to a minimum with increasing concentration of barium iodide and then increases rapidly again as the concentration of the salt is further increased. Furthermore, the value of the ratio approaches 2 at the highest concentration.

#### The Distribution of Iodine between Carbon Tetrachloride and Barium Iodide Solutions

These experiments were made by taking a series of concentrations of iodine in an approximately given concentration of barium iodide. A sample of barium iodide, accurately weighed to 1 milligram, was transferred to a dry bottle and dissolved in exactly 75 c.c. of air-free water, 25 c.c. of carbon tetrachloride were then added and finally a quantity of solid iodine insufficient to saturate the two layers. The bottle was tightly sealed and rotated in the thermostat for 24 hours. After allowing the bottles to stand until the separation of the two layers was complete definite portions of each layer were carefully run into weighed freshly prepared solutions of potassium iodide, again weighed and the iodine determined by titration. The titration mixtures from the water layer were then acidulated with hydrochloric acid and the barium iodide content determined by precipitation as sulphate. The weight of the water was determined by difference. The concentration of the free uncombined iodine in the water solution was found by dividing the iodine concentration in the carbon tetrachloride by 52.5. From these data we have calculated the molal concentrations of the barium iodide, the free iodine and the combined iodine, and the equilibrium constants. The results of the determinations are tabulated in Table III.



TABLE III

Equilibrium Constants for Barium Iodide Solutions unsaturated with Iodine.

Mols BaI <sub>2</sub> · a	Mols I <sub>2</sub> · b	Free I <sub>2</sub> · x · 10 <sup>4</sup>	K <sub>1</sub> · 10 <sup>4</sup>	K <sub>2</sub> · 10 <sup>7</sup>	K <sub>3</sub> · 10 <sup>4</sup>	K <sub>4</sub> · 10 <sup>7</sup>
0.02308	0.003953	1.359	6.85	2.05	15.06	4.16
0.02299	0.004806	1.654	6.53	2.48	14.73	5.15
0.02295	0.006980	2.635	6.37	4.27	15.37	8.80
0.02289	0.009544	3.865	5.79	5.97	15.45	13.44
0.02312	0.009813	3.935	5.72	6.05	15.39	13.66
0.02292	0.012686	5.603	4.99	8.73	15.57	20.66
0.04600	0.004598	0.799	7.34	1.23	15.48	2.54
0.04582	0.009902	1.829	6.79	2.82	15.41	5.97
0.04647	0.017210	3.406	5.97	5.23	15.35	11.62
0.04627	0.023049	5.038	5.30	7.87	15.62	18.30
0.06867	0.008051	0.954	7.27	1.46	15.51	3.05
0.06834	0.015505	1.957	6.78	3.03	15.51	6.46
0.06910	0.026387	3.629	6.01	5.68	15.64	12.68
0.06893	0.036852	5.559	5.00	8.65	15.55	20.38
0.13828	0.060679	4.240	5.50	6.46	15.24	14.72
0.13830	0.088340	6.993	4.04	10.54	15.08	25.89

The four simplest assumptions that can be made in regard to the equilibrium conditions are these.

1. We may assume with Herz and Kurzer that only one of the iodide ions of barium iodide is capable of combining with iodine, and it combines with one molecule, thus  $\text{BaI} \cdot \text{I}_3 = \text{BaI}_2 + \text{I}_2$ . The equilibrium constant for this is

$$K_1 = \frac{[a - (b - x)]x}{[b - x]}$$

2. Only one of the iodide ions is capable of combining with iodine and it combines with two mols of iodine. This assumption is represented by the chemical equation:  $\text{BaI} \cdot \text{I}_5 = \text{BaI}_2 + 2\text{I}_2$ . The corresponding constant is

$$K_2 = \frac{[a - \frac{b-x}{2}]x^2}{[\frac{b-x}{2}]}$$

3. Both iodide ions are equally active in combining with iodine and each combines with one molecule only. This is the assumption of Jakowkin and the chemical equation may be written,  $\text{BaI}_3 = \text{BaI} + \text{I}_2$ . For this the constant is

$$K_3 = \frac{[2a - (b - x)]x}{[b - x]}$$

4. Each of the two iodide ions may combine with two molecules of iodine, viz.,  $\text{BaI}_5 = \text{BaI} + 2\text{I}_2$ , where ba corresponds to a half-atom of barium. In this case

$$K_4 = \frac{[2a - \frac{b-x}{2}]}{[\frac{b-x}{2}]}$$

The values for these four constants have been calculated and are tabulated for the different concentrations in Table III.

Using the solubility data of Table I we have calculated the corresponding values for these constants for solutions saturated with respect to iodine. In these calculations we have assumed the molal solubility of the free iodine ( $x$ ) to be 0.001329. The results are given in Table IV.

TABLE IV

Equilibrium Constants for Barium Iodide Solutions saturated with Iodine.

Mols BaI <sub>2</sub>	Total Mols I <sub>2</sub>	K <sub>1</sub> · 10 <sup>4</sup>	K <sub>2</sub> · 10 <sup>7</sup>	K <sub>3</sub> · 10 <sup>4</sup>	K <sub>4</sub> 10 <sup>7</sup>
0.000000	0.001329				
0.000686	0.002044	-0.54	16.27	12.21	50.17
0.003120	0.004482	-0.14	17.30	13.01	52.28
0.006287	0.007574	0.09	17.90	13.78	53.47
0.03167	0.03220	0.35	18.58	13.98	54.82
0.04772	0.04841	0.20	18.18	13.65	54.03
0.08048	0.07937	(0.41	18.76	14.12	55.18)
0.16497	0.16872	-0.19	17.15	12.91	53.16
0.34880	0.39500	-1.52	13.64	10.26	44.94
0.39633	0.45460	-1.66	13.23	9.95	44.12
0.57189	0.81690	-3.95	7.11	5.35	31.88
0.87640	1.4674	-5.35	3.46	2.59	24.57
1.1922	2.8800	-6.36	0.76	0.57	19.17

A survey of the data for solutions of barium iodide unsaturated with respect to iodine (Table III) shows that the values of  $K_3$  are fairly constant for concentrations up to 0.14 M. Evidently then we are safe in assuming that each of the iodide ions of the salt is capable of combining with one molecule of iodine to form the compound  $Ba(I_3)_2$ . This confirms the work of Jakowkin and of Van Name and Brown. It is clear also that the values of  $K_1$ , based on the assumption of Herz and Kurzer, do not even approximately represent the equilibrium conditions. The values of  $K_1$  for each single concentration of barium iodide decrease rapidly with increase in the concentration of the iodine. Equally valueless for these concentrations are the relations indicated by  $K_2$  and  $K_4$ .

The data of Table IV show a striking anomaly with regard to the equilibrium conditions. If the equilibria in solutions of barium iodide saturated with iodine are to be explained by the formation of a higher polyiodide, the polyiodide formed is very probably  $Ba(I_5)_2$ , since the two iodide ions are equally active. Under these conditions we should expect a fair degree of constancy for the values of  $K_4$ . The maximum variation in the values of  $K_4$  between the concentration limits 0.003 M and 0.16 M is about 4 percent. On the other hand, the values for  $K_2$  and  $K_3$  for the same range of concentrations are equally good. The values of  $K_1$  (H. and K.) are for the most part negative. It should be observed also that the values for all four equilibrium constants pass through distinct maxima at about 0.03 M BaI<sub>2</sub>, and then decrease rapidly with further

increase in the concentration of the salt. Further, the concentration giving the maximum value for  $K$  is that concentration at which the ratio  $I_2/BaI_2$  is a minimum.

We assume for ternary electrolytes a step-wise dissociation with dilution for moderate concentrations. It is also known that in concentrated solution some ternary electrolytes undergo polymerization and subsequent ionization forming complex ions. Our present ignorance of the nature and extent of the ionization of barium iodide in concentrated solutions renders impossible the calculation of the equilibrium constants for solutions of barium iodide saturated with iodine.

### Summary

1. The solubility of iodine in water and in aqueous solutions of barium iodide at  $25^\circ$  has been determined.
2. The distribution ratios of iodine between carbon tetrachloride and water have been redetermined on the basis of mols in 1000 g. of solvent.
3. We have calculated the equilibrium constants based on four different assumptions of possible equilibria for barium iodide solutions both saturated and unsaturated with respect to iodine. For dilute solutions unsaturated with iodine  $Ba(I_3)_2$  appears to be the only polyiodide present. For concentrated solutions saturated with iodine the data indicate a mixture of the tri- and penta-iodides.

*Physical Chemistry Laboratory,  
The State University of Iowa,  
Iowa City, Ia.*