

CLXXXIX.—*The Ternary System Barium Iodide-Iodine-Water and the Formation of Polyiodides.*

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VARIOUS attempts have been made to define the equilibrium relations existing between polyiodides and their constituents and to assign formulæ to the former. That a tri-iodide, such as that of potassium or barium, may exist in solution is very generally assumed.

Clark and Duane (*Physical Rev.*, 1922, **20**, 85), in fact, claim to have made a detailed examination by X-ray methods of the crystal structure of potassium tri-iodide, but they do not state how the salt was prepared. Many others have failed to obtain it: neither from aqueous solution (Parsons and Whittemore, *J. Amer. Chem. Soc.*, 1911, **33**, 1933) nor from 60 or 40% alcoholic solutions (Parsons and Corliss, *ibid.*, 1910, **32**, 1367) can any solid polyiodide of potassium be isolated. From thermal examination of the binary system potassium iodide-iodine, Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1081) concluded that KI_4 , highly dissociated, existed in the fusion, but they could find no evidence for the presence of a polyiodide poorer in iodine. According to Abegg and Hamburger (*Z. anorg. Chem.*, 1906, **50**, 403), no polyiodide of potassium of less complexity than KI_7 exists.

Pearce and Eversole (*J. Physical Chem.*, 1924, **28**, 245) obtained results in dilute solutions of barium iodide, unsaturated with iodine, which were fairly consistent with a supposition of the presence of tri-iodide; but in *M*-solutions and upwards, saturated with iodine, they considered that penta-iodide was formed. From measurements of conductivities, viscosities, migration numbers, distribution coefficients, and other properties, usually over very limited ranges of concentration, other authors have obtained indications of polyiodides to which, on more or less satisfactory grounds, they have been able to assign formulæ.

In order to obtain quantitative information over a much wider range of temperature and concentration of components than has yet been recorded, the system barium iodide-iodine-water has been investigated between -15.8° and 90° . Barium iodide (B.D.H.), recrystallised from water as the hydrate $2BaI_2 \cdot 15H_2O$, and lower hydrates obtained by heating, were used with resublimed iodine (A. R.) and water in the preparation of suitable complexes. These were rotated in sealed tubes in a thermostat at the required temperature from 0° to 90° until equilibrium was attained. Shorter times, with only intermittent stirring and shaking, were given at -15.8° , the temperature being maintained by means of ammonium chloride and ice. Solutions were drawn off into pipettes through cotton-wool plugs, any iodine removed by reaction with the cotton being negligible. Iodine was estimated by direct titration of one sample with thiosulphate, whilst in another sample, from which the iodine had been completely removed by evaporation, the iodide was estimated volumetrically against silver nitrate with thiocyanate as indicator. At 0° and 25° the usual "rest" method was employed to give information as to the composition of the solid phase. At lower and higher temperatures the wet solid was not readily separ-

ated without alteration of composition. The initial complex was therefore carefully synthesised and its composition used instead. Provided that the complex is not very near in composition to the saturated solution, this method is fairly accurate.

Table I contains the results at 0° and 25°, and Table II those at -15.8°, 50°, 75.2°, and 89.9°. Compositions are given in % by weight, those of water (not given) being obtainable by difference. In the last column hydrates are specified by figures in parentheses, giving first the number of barium iodide molecules, and secondly the number of water molecules.

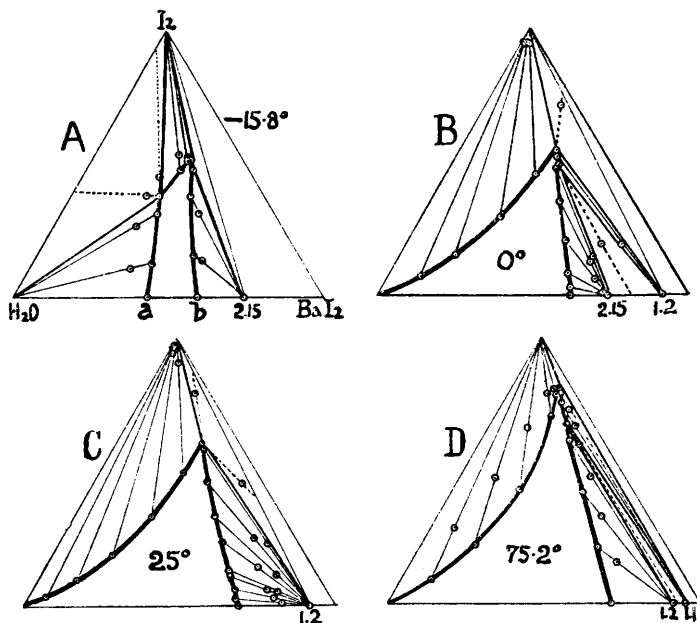
TABLE I.
Composition, % by weight.

Temp.	D_4^{20}	Solution.				Wet solid.		Solid phases.
		BaI ₂ .	I ₂ .	BaI ₂ .	I ₂ .			
0° ± 0.05°	1.169	10.5	7.4	0.6	94.9		Iodine.	
	1.365	17.9	15.2	1.1	94.6		"	
	1.780	25.5	29.5	1.8	94.7		"	
	2.415	29.0	45.4	3.0	94.1		"	
	—	31.4	54.0	24.3	71.0		Iodine and (1, 2).	
	—	32.7	51.8	69.8	19.0		(1, 2).	
	—	34.6	49.4	63.0	19.2		(1, 2) and (2, 15).	
	—	35.1	47.7	62.8	14.2		(2, 15).	
	2.561	41.7	35.1	62.7	12.5		"	
	2.322	50.4	20.3	66.9	6.2		"	
	2.167	57.7	8.2	72.3	1.0		"	
	2.108	60.7	3.0	72.2	0.5		"	
	2.071	62.5	0.0	—	—		"	
	25° ± 0.02°	1.081	5.8	3.7	0.1	96.7		Iodine.
1.214		12.4	10.0	0.4	97.3		"	
1.436		19.3	19.5	1.2	94.6		"	
1.827		24.8	33.2	1.5	96.3		"	
—		26.6	50.0	4.9	90.8		"	
—		27.2	61.1	16.3	79.7		Iodine and (1, 2).	
—		27.6	60.9	47.3	45.9		" "	
—		28.8	58.6	66.8	23.4		(1, 2).	
—		36.4	46.8	61.4	25.3		"	
—		44.8	33.8	75.6	11.5		"	
—		52.0	24.0	68.0	14.2		"	
2.405		59.7	13.3	78.9	5.2		"	
—		60.6	11.7	75.0	6.2		"	
2.339		64.3	6.5	78.5	3.1		"	
2.31	66.7	2.7	82.8	0.9		"		
2.277	68.8	0.0	—	—		"		

From these tables and the triangular diagrams, the succession of changes may readily be followed. At -15.8° (Fig. 1A) there are three curves, the solids being ice, iodine, and the hydrate (2, 15). At -33.5°, the eutectic temperature of the binary system barium iodide-water (Packer and Rivett, J., 1926, 1061), the points *a* and *b* coincide, and below it all liquid phases are ternary in composition. A little below 0° the hydrate (1, 2) appears, and there are then four solubility curves. At 0° (Fig. 1B) the ice curve vanishes and the

system is one showing three solids, iodine, (1, 2), and (2, 15). The latter hydrate cannot exist above 25.7° , and for a considerable temperature range beyond this the system is a simple one of two curves, as in Fig. 1C, the solids being iodine and (1, 2). Actually at 25° , for which this figure holds, there must be still a very small curve of (2, 15), but this has been omitted. The relations between compositions of solutions and "rests" at 25° give proof that the highest hydrate is (2, 15), and not either (1, 7) or (1, 6), as has been commonly assumed (compare Packer and Rivett, *loc. cit.*, p. 1062).

FIG. 1.



The temperature at which the hydrate (1, 1) first occurs in the ternary system could not be determined accurately by the thermometric method, but at 75.2° its solubility curve is as shown in Fig. 1D: that of (1, 2) vanishes at 98.9° .

Apart from the fact that no solid polyiodide is obtained, the interest of the system lies in the solubilities attained by iodine. In Table III are set out figures for the iodine saturation curves, compositions of solutions being given in equivalents per 1000 g. of water. In the last column is given the ratio of iodine atoms to iodide ions in solution. The amount of combined iodine is presumably the total found by titration with thiosulphate less that merely dissolved in the water. The amount of the latter cannot be

TABLE II.
Composition, % by weight.

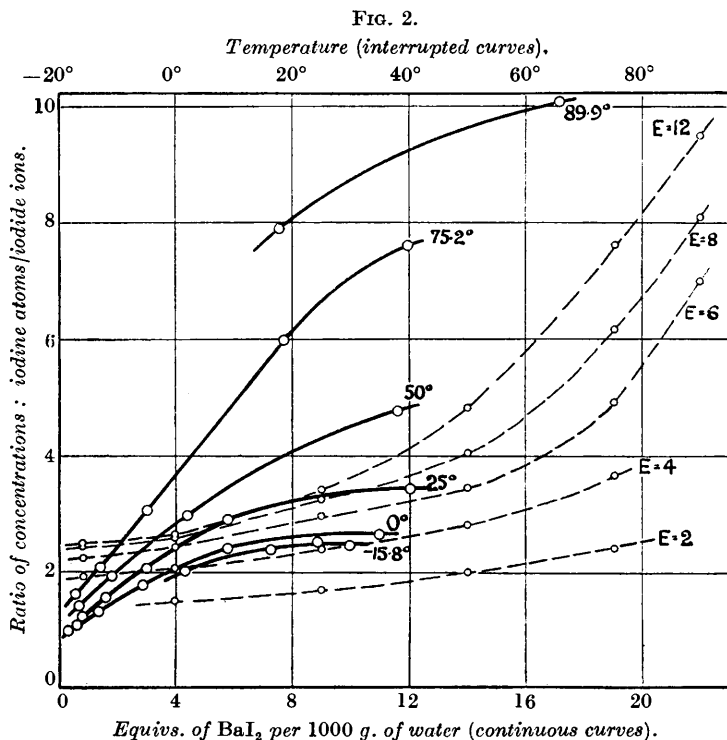
Temp.	Solution.		Initial complex.		Solid phases.
	BaI ₂ .	I ₂ .	BaI ₂ .	I ₂ .	
-15.8° ± 0.1°	43.5	—	—	—	Ice.
	38.7	12.7	32.5	10.6	„
	31.4	31.3	26.7	26.8	„
	28.5	37.6	24.3	38.2	Ice and iodine.
	28.7	37.6	24.9	45.4	„
	30.8	47.5	27.1	53.3	Iodine.
	31.2	50.8	30.2	52.5	„
	32.2	51.4	34.6	47.8	Iodine and (2, 15).
	38.7	37.6	44.4	31.4	(2, 15).
	50.4	15.9	54.1	13.5	„
	50° ± 0.02°	11.0	10.1	8.1	24.6
19.9		24.9	14.3	42.2	„
24.5		47.2	18.6	57.2	„
22.1		68.3	21.5	69.4	„
75.2° ± 0.05°	9.4	9.8	7.4	28.5	Iodine.
	17.0	23.0	11.6	47.0	„
	21.4	42.5	12.7	65.6	„
	18.0	70.0	12.8	78.5	„
	15.7	77.6	14.1	79.8	„
	14.3	82.0	—	—	Iodine and (1,1) (extrap.).
	16.8	78.3	22.6	72.4	(1, 1).
	18.9	74.9	27.2	66.3	„
	24.2	67.2	32.2	59.3	(1, 1) and (1, 2).
	28.6	60.7	42.1	47.4	(1, 2).
	41.8	41.6	52.3	32.7	„
56.6	21.0	65.3	15.7	„	
89.9°	12.8	83.4	8.9	88.0	Iodine.
	14.7	75.3	9.7	83.2	„

TABLE III.
(Solutions saturated with iodine.)

Temp.	Equivs. per 1000 g. H ₂ O.		Ratio I ₂ : BaI ₂ .	Temp.	Equivs. per 1000 g. H ₂ O.		Ratio I ₂ : BaI ₂ .
	BaI ₂ .	I ₂ .			BaI ₂ .	I ₂ .	
-15.8°	4.35	8.79	2.02	50°	0.70	1.00	1.42
	7.27	17.28	2.38		1.84	3.54	1.93
	8.88	22.28	2.51		4.42	13.13	2.97
	9.99	24.59	2.46		11.65	55.5	5.55
0°	0.65	0.71	1.09	75.2°	0.59	0.95	1.61
	1.37	1.79	1.31		1.45	3.02	2.08
	2.90	5.16	1.78		3.04	9.29	3.06
	5.79	13.97	2.41		7.71	46.2	5.99
	11.0	29.1	2.65		11.98	91.3	7.62
25°	0.33	0.32	0.98	89.9°	7.52	59.3	7.9
	0.82	1.015	1.24		17.2	173.0	10.1
	1.61	2.51	1.56				
	3.02	6.23	2.06				
	5.81	16.84	2.90				
	12.08	41.4	3.43				

accurately estimated without making more or less arbitrary assumptions: in any case it will be small compared with the total iodine concentrations in the cases examined.

Fig. 2 contains two sets of curves which illustrate these results. The continuous lines are isotherms showing the ratio of iodine atoms to iodide ions plotted against equivs. of iodide per 1000 g. of water. At first they are not far from straight lines, but later they flatten, and at the lower temperatures seem to reach maxima. Throughout, the more iodide present, the more iodine is taken up per equiv. of iodide. In very dilute solutions at all temperatures the ratio of atoms to ions approximates to unity (compare Pearce and Eversole,

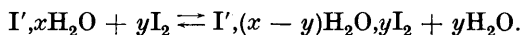


loc. cit., p. 252), and then with increase of salt concentration it rises the more rapidly the higher the temperature. From these curves have been obtained by interpolation the values of the ratio of atom to ion at different temperatures for barium iodide concentrations of 2, 4, 6, 8, and 12 equivs. per 1000 g. of solvent, and in Fig. 2 the interrupted curves show for each of these concentrations the values of the ratios plotted against temperature. The higher the temperature the more iodine is added per equiv. of iodide, and the rate of increase is greater the greater the iodide concentration. Supposing all the iodine to be distributed evenly amongst the iodide

radicals, the composition of the polyiodide radical ranges from I_2' to I_{11} , and at temperatures above the highest investigated, 89.9° , still greater amounts of iodine would certainly be taken up.

Attempts to apply the mass action law in systems like these cannot be expected to succeed; and there seems no reason to suppose that the formation of any one polyiodide represents the sole action at any particular stage. A glance at the continuous curves of Fig. 2 shows how in the less concentrated solutions of barium iodide the ratio of iodine to iodide approximates to 2, corresponding with an ion I_3' . Over selected ranges of iodide concentration one can interpret the results in terms of this or of numerous higher polyiodides.

It is clear that iodination is progressive, increasing in extent per iodide ion with increase of concentration of the latter and with rise of temperature. Whether the temperature effect is due solely to increase of concentration, and hence mass effect, of the iodine in the water present, cannot be stated. One might expect a polyiodide to become more unstable and to dissociate with rise of temperature. It may be that the apparent increase of stability with rise of temperature is due to the fact that the formation of polyiodide is not an addition of iodine molecules to a simple iodide ion, I' , but is a replacement by iodine of the water molecules which the simple ion may attach to itself in numbers sufficient to constitute it a full co-ordination complex. Thus we should have



If hydration and iodination of the ion are both exothermic reactions, but the former more so than the latter, rise of temperature will displace the equilibrium to the side of the latter, other things being equal. In dilute solution the tendency would be for the reaction to go to the left.

Summary.

1. The ternary system barium iodide-iodine-water has been fully examined at -15.8° , 0° , 25° , and 75.2° , and partially at 50° and 89.9° .

2. The hydrate $2BaI_2 \cdot 15H_2O$ has been shown to exist, but neither a hexa- nor a hepta-hydrate has been found. No solid polyiodides have been formed.

3. Assuming the iodine present in solution to be attached to the anion, the mean compositions of the polyiodides present in the solutions examined range up to $BaI_2 \cdot 10I_2$ at 90° ; and at higher temperatures the iodine content will be still greater.

4. For a constant water content of solution, the ratio of iodine to iodide increases with increase of iodide concentration; it also

increases with temperature for a constant iodide concentration. Both facts are explicable if the action be regarded as a replacement of water in a hydrated iodide ion by iodine, the heat of reaction of a simple ion with water being greater than that with iodine, so that the substitution of the latter for the former is endothermic.

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