LXXXI.—*The Existence of Solid Polyiodides of Potassium at 25°.*

By NORMAN SINGERS GRACE.

SOLID polyiodides of cæsium, rubidium, and ammonium have been shown definitely to exist at ordinary temperatures by the work of Johnson (J., 1878, **33**, 397), Wells and Penfield (*Z. anorg. Chem.*, 1892, **1**, 86), Wells and Wheeler (*ibid.*, p. 442), and Briggs, Greenawald, and Leonard (*J. Physical Chem.*, 1930, **34**, 1951). On the other hand, no solid polyiodides of sodium or lithium are reported. The intermediate case of the existence of solid polyiodides of potassium has been the subject of several researches which have led to conflicting conclusions.

Johnson (J., 1877, **31**, 249), by slow evaporation of a concentrated aqueous solution of iodine in potassium iodide, obtained prismatic crystals which had the empirical formula KI_3 and melted at about 45°. Wells and Wheeler (*loc. cit.*) repeated this preparation and obtained monoclinic crystals which they considered to be tri-iodide (no analysis was given) and which melted at about 38°.

Foote and Chalker (*Amer. Chem. J.*, 1908, **39**, 561) carried out a phase-rule study of the problem : in a condensed ternary system, the presence of three phases reduces the system to isothermal invariance. In the system iodine–potassium iodide–water at 25°, they reported three invariant solutions which they considered to be in equilibrium with (1) KI and KI_3, (2) KI_3 and KI_7, and (3) KI_7 and I_2, respectively. Parsons and Corliss (*J. Amer. Chem. Soc.*, 1910, **32**, 1367) criticised this work on the grounds that (1) the analytical results do not agree sufficiently well amongst themselves, (2) the wet solid was dried between filter papers and only one component determined, and (3) equilibrium may not have been established. The latter authors then studied the system iodine–potassium iodide–aqueous alcohol, using two different concentrations of alcohol (40% and 60%); in each case only one invariant point was found, from which they conclude that no solid polyiodides of potassium exist under the conditions of their experiments.

Parsons and Whittemore (*ibid.*, 1911, **33**, 1933) studied the system iodine–potassium iodide–water at 25° and found only one invariant point, which they stated was in equilibrium with both solid iodine and potassium iodide. Assuming that water cannot enter into the composition of the solid phase, they conclude that no solid polyiodide of potassium exists at 25°.

The binary system iodine–potassium iodide has been studied by Abegg and Hamburger (*Z. anorg. Chem.*, 1906, **50**, 403), by Kre-

mann and Schoulz (*Monatsh.*, 1912, **33**, 1087), and quite recently by Briggs and Geigle (*J. Physical Chem.*, 1930, **34**, 2250). Although the earlier workers obtained rather conflicting results, the last showed from the temperature–concentration diagram (from 70° to 191°) that iodine and potassium iodide are the only stable solids in contact with the melt, and they obtained no evidence for the existence of solid polyiodides in this binary system. The eutectic between iodine and potassium iodide occurs at about 80°, which is 40° higher than the melting point reported by Johnson and by Wells and Wheeler for the tri-iodide.

Abegg and Hamburger (*loc. cit.*), from a study of the equilibrium of iodine between a benzene solution and solid potassium iodide at 25°, considered the compound KI_7 to be the only stable polyiodide of potassium existing at 25°.

Clark and Duane (*J. Opt. Soc. Amer.*, 1923, **7**, 472) prepared monoclinic crystals by Johnson's method (no analysis is given) and studied the structure of these crystals by a new X-ray method. Their results indicated that the material was a definite compound and not merely a mixture of iodine and potassium iodide.

Ephraim (*Ber.*, 1917, **50**, 1069) prepared the tri-iodide by Johnson's method (no analysis is given) and determined its dissociation pressure over the temperature range 91—169°. He found pressures higher than the vapour pressures of iodine at corresponding temperatures.

Up to the present, four investigators have considered that they have prepared the tri-iodide, although only one reports analyses supporting his results, whilst two have obtained evidence for the existence of the tri-iodide. On the other hand, at least four investigations have failed to show evidence in favour of the tri-iodide or have yielded evidence against its existence. Two investigators have reported the heptaiodide, while four others have obtained no evidence for it.

Possibly the most significant fact emerging from these conflicting results is that when an equimolecular mixture of dry iodine and potassium iodide is heated, the first melt does not appear till a temperature of 80° is reached, whereas potassium tri-iodide prepared from aqueous solution is reported to begin to melt at as low a temperature as 38°. Abegg and Hamburger (*loc. cit.*) have suggested that this difference in melting temperature is due to moisture in the material crystallised from solution, but do not appear to have tested this hypothesis experimentally.

In the present work the cause of the difference in melting points of the dry and the crystallised material was first studied, and led to the idea that potassium tri-iodide crystallises from aqueous solution

as a monohydrate. This suggestion, which explains Ephraim's results, is not in disagreement with the published phase-rule work and is strongly supported by additional data now advanced.

EXPERIMENTAL.

Relation between Melting Point and Moisture Content.—Potassium tri-iodide was prepared according to Johnson's method from resublimed iodine and B.P. potassium iodide once recrystallised and free from iodate. After being dried for 3 weeks over phosphoric oxide in an attempt to remove all mechanically held moisture, the crystals were analysed (Found, mean of two analyses : KI, 37·74; free I, 61·07. Calc. for KI_3 : KI, 39·55; free I, 60·45%). The free (polyiodide) iodine was determined by titration with $N/10$-sodium thiosulphate, and potassium iodide was determined on a separate portion by gentle ignition at about 250°.

This material did not melt at all sharply, liquid first appearing at 40°; it was opaque, making it difficult to follow the progress of melting or crystallisation. For this reason, phase changes were followed by means of cooling curves, which were taken in a sealed glass apparatus because of the very hygroscopic nature of the material. Temperatures were measured by a sensitive thermo-couple protected by a thin-walled glass sheath and embedded in the midst of the sample. The curves for this specimen showed only one temperature arrest, *viz.*, at about 35°. A dry mixture of iodine and potassium iodide in equimolecular proportion showed an arrest at 78° and none at a lower temperature (compare Briggs and Geigle, *loc. cit.*).

Two samples of this tri-iodide were sealed up so that the vapour was in contact with phosphoric oxide. The first sample, after drying thus for one week at 95°, gave a cooling curve in which the temperature arrest occurred at 78° instead of 35°. After 2 more weeks' drying at 95°, the arrest was at 79° : further drying produced no change. The second sample, after drying for 4 months at room temperature, was sealed off from the phosphoric oxide, and cooling curves were obtained which showed no temperature arrest below 72°. Thus, by removal of moisture, the m. p. of the tri-iodide is changed from about 35° to 79°, which is the temperature at which dry iodine and potassium iodide first begin to melt.

These results also indicate how difficult it is to remove all the moisture from the tri-iodide, since even after 4 months' drying over phosphoric oxide the cooling curve gives a slightly lower temperature arrest than in the case of the dry mixture.

When the tri-iodide is dried over phosphoric oxide at atmospheric pressure, the crystals lose their shiny blue-black appearance and

seem to decompose; and when drying is effected in a high vacuum in a sealed glass apparatus at room temperature, crystals of iodine sublime on to the walls of the vessel. After 6 weeks in the latter conditions, the decomposition of the crystals appeared complete, all the iodine having sublimed away from the original sample, leaving a white residue of potassium iodide. After a further 3 months, the appearance of the potassium iodide was unchanged, indicating that no recombination was occurring. Moreover, when the tube was opened, the sample was found to contain only 0·5% of free iodine. A duplicate experiment gave similar results. These experiments suggest, not only that the tri-iodide prepared from aqueous solution contains moisture, but that the moisture is combined, and essential for the existence of solid potassium tri-iodide. It is significant that tri-iodide remains bright and crystalline for months either at atmospheric pressure or in high vacuum when sealed up without a drying agent being present.

The Estimation of Water in Potassium Tri-iodide.—In previous work on this subject, no direct estimation of the water present in the material has been made. Johnson is the only worker reporting analyses of the tri-iodide. In his first series of analyses he assumed that his material was free from moisture, and determined either iodine or potassium iodide, finding the other by difference. If his results are recalculated without this assumption, we obtain : KI, 37·70; free I, 59·02; total, 96·73%; KI : I_2 = 1 : 1·023; his second series, in which he determined total iodine as silver iodide and potassium as sulphate (on separate samples), gave K, 9·25; I, 90·21; total, 99·46%.

The totals of iodine and potassium iodide found by analysis for two different preparations of potassium tri-iodide in the present work are 98·81 and 98·69%. Each of these samples had been dried in a desiccator over phosphoric oxide for 3 weeks. The fact that all these analyses, carried out by different methods and on different samples, give totals which fall considerably below 100% is further evidence that the tri-iodide prepared from aqueous solution contains moisture, and made it necessary to determine this moisture by a direct method.

A method was devised which possessed the advantage of enabling the three constituents to be determined simultaneously on one sample. The apparatus employed is illustrated in Fig. 1; A is a glass tube, equipped at one end with a ground-glass stopper, and fitted at the other by a ground joint to the tube D, which is packed with fine strips of silver foil and heated to about 325° by an electric furnace E. D is connected to two tubes of phosphoric oxide, F and G, by short pieces of pressure tubing. In carrying out an analysis, a sample is weighed into a boat contained in a well-

stoppered weighing bottle. The boat is then rapidly transferred to A, and a stream of nitrogen, dried by passage over phosphoric oxide, is passed *via* H through the apparatus. The boat is gently heated to drive off the volatile constituents, leaving the potassium iodide, which is weighed as such. The iodine is weighed as silver iodide in D and the moisture in F. The method gave quantitative results on known mixtures. The potassium iodide, even after being strongly heated, always retained a little iodine : this was determined by titration with thiosulphate, and a correction (generally less than 0·05%) applied for it.

FIG. 1.
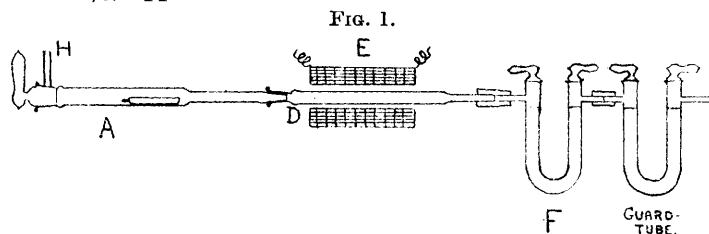
Potassium Tri-iodide.—Since, as already shown, drying with phosphoric oxide decomposes the tri-iodide, it is very difficult to free the crystals entirely from mother-liquor, and therefore they were dried by the method devised by Baker and Adlam (J., 1911, **99**, 507), in which excess moisture is absorbed by some of the same material previously partially dehydrated. In this way it was possible to prepare material of reproducible moisture content which corresponded closely with the composition KI_3,H_2O (see Table I).

A part of sample No. 7, dried as above, melted fairly sharply at 31°. These crystals contained slightly more than $1H_2O$, and as this system is very sensitive to small changes in moisture content, this melting point is probably low. The differences in melting temperatures recorded by Johnson and others for potassium tri-iodide are therefore probably due to variations in the water content of the material used.

TABLE I.

Analyses of potassium tri-iodide prepared by Johnson's method.

Sample No.	Treat-ment.	Percentages.			Molar ratios (KI = 1).	
		KI.	I_2.	H_2O.	I_2.	H_2O.
7	Not dried	37·01	57·95	5·05	1·02	1·26
8	,,	36·77	58·48	4·90	1·04	1·23
7	*	37·48	58·24	4·41	1·02	1·09
7	*	37·10	58·37	4·50	1·03	1·12
8	*	37·02	58·53	4·50	1·03	1·12
				Mean of last three	1·03	1·11

* These samples were dried till constant in weight over partially dehydrated KI_3,H_2O (period of drying, about one month).

Potassium Heptaiodide.—During certain crystallisations, a solid was obtained in which the ratio $KI : I_2$ was nearly $1 : 3$, whilst that in the solution was only $1 : 1.54$. This seemed to indicate that the solid separating was a compound and not a mixture. By saturating a solution with both potassium iodide and iodine at room temperature (16°), care being taken to have a large excess of iodine in the solid phase, decanting the solution, and then evaporating it slowly over phosphoric oxide, crystals were obtained which gave analyses close to the composition KI_7,H_2O, as shown in Table II.

TABLE II.

Analyses of potassium heptaiodide.

Sample No.	Treatment.	Percentages.			Molar ratios ($KI = 1$).	
		KI.	I_2.	H_2O.	I_2.	H_2O.
1	Not dried	17.75	79.59	2.80	2.93	1.45
2	,,	17.38	79.70	2.98	3.00	1.58
3	,,	17.29	80.06	2.76	3.03	1.47
1	*	17.75	79.93	2.36	2.94	1.23
2	*	17.51	80.20	2.30	2.99	1.21
				Mean of last two	2.97	1.22

* Crystals dried to constant weight over partially dehydrated KI_7,H_2O.

It is of interest that potassium heptaiodide, as well as the tri-iodide, appears to exist in a hydrated form. Since one molecule of water of crystallisation constitutes only 1.90% of the molecular weight, and since the material is very hygroscopic, the molar ratio $H_2O : KI_7 = 1.22 : 1$ is as close to unity as could be expected. Similar difficulties occurred in determining the degree of hydration of the tri-iodide. Samples of the hepta-iodide, dried as above, began to melt at about 38°, but melting extended over a large temperature range.

On being dried over phosphoric oxide in a high vacuum in a sealed glass vessel, the heptaiodide, like the tri-iodide, decomposes completely, iodine subliming on to the glass walls and leaving a white residue of potassium iodide. After 5 months' drying in a vacuum, a sample contained only 0.7% of iodine (initial iodine content 79.0%). These results indicate that the heptaiodide exists only in the hydrated form.

Phase-rule Studies.—It is necessary to reconcile the two polyiodides KI_3,H_2O and KI_7,H_2O with the results of Parsons and his associates, whose work (*locc. cit.*) has been interpreted to disprove the existence of solid polyiodides of potassium at 25°. Parsons and Whittemore base their conclusion largely upon three sets of observations, serial Nos. 8, 9, and 18 (see their Table I); the data for No. 18 show that, although an invariant point was established,

the potassium iodide content of the wet solid was varied only between 11·3 and 16·1%, and therefore the whole range was not covered. These scanty data of No. 18 do not justify those authors in stating that this was the only invariant point which occurred in the system, for Foote and Chalker, from seven sets of analyses, found three invariant points. Nos. 8 and 9 are stated to be in equilibrium with excess potassium iodide, and yet the wet solid in each case contained over 56% of iodine, whilst the solutions contained 63 and 66% of iodine respectively. This would imply for No. 8 that the wet solid contained 89% of mother-liquor. If, however, Schreinemakers's method is employed for No. 8, the composition of the solid phase is very definitely not potassium iodide alone, but a mixture of iodide and either iodine or a polyiodide. If this were a mixture of potassium iodide and iodine, then the solution in equilibrium in No. 8 should be the invariant solution of No. 18; since, however, this is not the case, No. 8 must have been in equilibrium with potassium iodide and a polyiodide, *i.e.*, two solid phases, and this makes No. 8 another invariant point. Schreinemakers's construction for point No. 9, while indicating the solid phase as potassium iodide, intersects the line for No. 8 at such an angle that the experimental data for these points appear incompatible.

These results of Parsons and Whittemore, being incomplete and rather contradictory, certainly do not disprove the existence of solid polyiodides, and made it necessary to work out the phase-rule system in greater detail.

Only the more concentrated solutions in the system iodine–potassium iodide–water were therefore now studied. Reagents of the same purity as those described earlier were employed. Mixtures of the desired compositions were made up in glass bottles, the stoppers of which were carefully ground to ensure absence of leakage. After the bottles had been filled, the stoppers were pushed well home and waxed over, and the bottles rotated in a thermostat at 25°. Samples of solution for analysis were removed by suction through an asbestos filter supported on a glass sieve, and wet solid was taken out on a glass spoon. During sampling, each bottle was placed in a beaker of water at 25°, and the sampling apparatus was previously warmed to this temperature. The attainment of equilibrium was followed by titration of the iodine in weighed portions of solution with $N/10$-thiosulphate. By initially heating the mixtures to about 50°, it was found that equilibrium was generally reached within one month, a time considerably shorter than that given by Parsons and Whittemore. At least one week was allowed to elapse after equilibrium had been attained, and then both solution and wet solid were analysed by the complete method described on

p. 597. The two methods employed for determination of the iodine present in the solution gave concordant values. The results obtained are given in Table III and appear graphically in Figs. 2 and 3. In Fig. 2 only that portion of the field which was

FIG. 2.
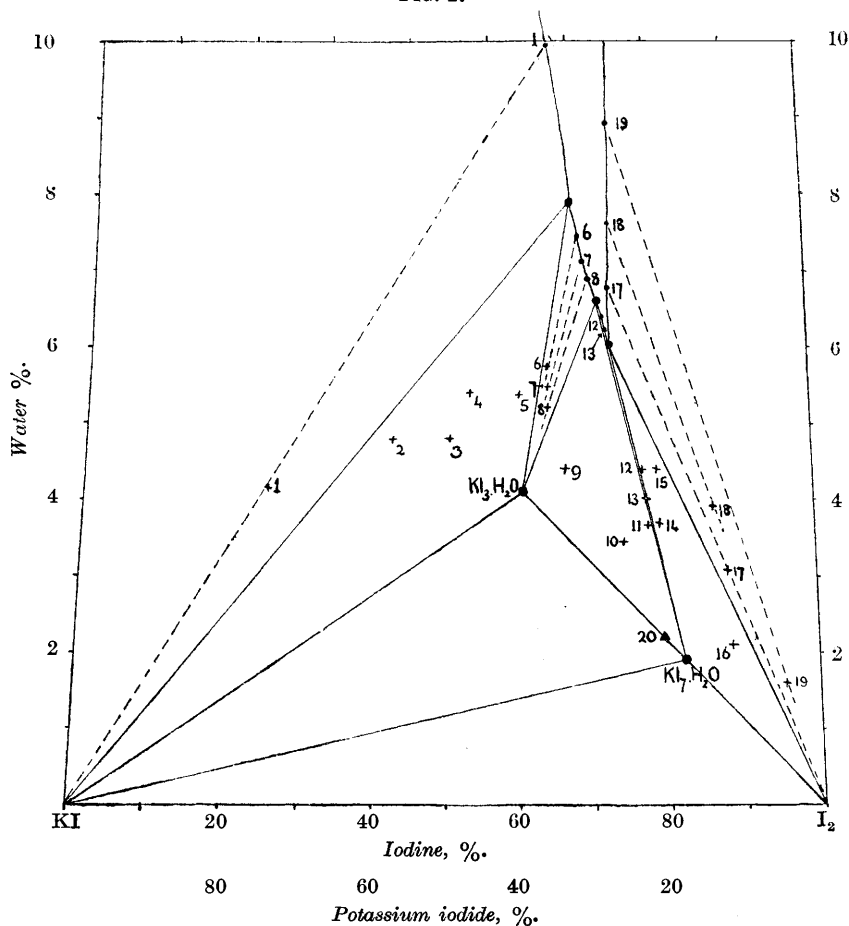
(*The points are numbered as in Table III.*)

investigated is shown. The results are plotted on the ordinary trilinear system, with the modification that the scale of water concentrations is magnified ten-fold on account of the small water content of the most concentrated solutions. Fig. 3 represents the complete system, plotted in mols. % and constructed from the present and earlier phase-rule data.

TABLE III.

The three-component system iodine–potassium iodide–water at 25°.

	Composition of liquid phase.				Composition of moist solid phase.		
No.	KI, %.	I_2, %.	H_2O, %.		KI, %.	I_2, %.	H_2O, %
1	32·18	57·83	9·96		71·27	24·59	4·16
2	30·25	61·93	7·87		54·70	40·49	4·82
3	30·20	61·91	7·82	Invariant A.	47·32	47·96	4·83
4	30·30	61·99	7·77		44·37	50·21	5·42
5	30·26	61·98	7·80		38·02	56·58	5·36
6	29·09	63·40	7·45		34·20	60·01	5·76
7	28·92	63·88	7·16		34·54	59·92	5·49
8	28·35	64·85	6·87		34·28	60·55	5·20
9	27·28	66·15	6·57		32·12	63·60	4·39
10	27·30	66·13	6·59	Invariant B.	24·01	72·63	3·45
11	27·23	66·05	6·69		21·78	74·60	3·70
12	27·04	66·65	6·38		22·06	73·58	4·41
13	26·52	67·34	6·20		21·65	74·42	4·02
14	26·01	68·02	6·02		19·70	76·54	3·71
15	26·09	67·90	5·98	Invariant C.	20·30	75·31	4·41
*16	25·92	68·13	—		11·32	86·56	—
17	25·82	67·30	6·79		11·11	85·90	3·05
18	25·47	67·01	7·62		13·02	83·00	3·92
*19	25·08	65·98	—		4·00	94·39	—

* These values were determined by Parsons and Whittemore, *loc. cit.*

(The points in Fig. 2 are numbered as in the above table, and the lettering of the invariants corresponds with Fig. 3.)

Three invariant solutions were obtained in this system at 25°, involving four solid phases : iodine, potassium iodide, and two polyiodides. The phase rule furnishes evidence that KI_3,H_2O represents the composition of one polyiodide, and does not disagree with the empirical formula of the other. The heptaiodide, however, exists in equilibrium with such a limited range of solutions that Schreinemakers's method hardly furnishes a critical test of the composition of this solid.

Further information regarding the composition of the hepta-iodide was obtained from the following experiment. Samples of potassium iodide, tri-iodide, and heptaiodide, the last two being somewhat moist with mother-liquor, were placed in three communicating limbs of a glass apparatus which was evacuated and sealed. After 3 months, the apparatus was opened and the samples were analysed. The heptaiodide gave a composition lying on the line joining KI_3,H_2O to I_2 (Fig. 2, Point 20) very close to the point which corresponds with the composition KI_7,H_2O, but slightly nearer the tri-iodide ; the tie lines joining solutions with wet solids on the heptaiodide range intersect with this line almost exactly at the point KI_7,H_2O, which establishes with some certainty that the heptaiodide is a monohydrate.

Phase-rule Studies with Aqueous Alcohol.—When Parsons and

Corliss used 60% alcohol as the solvent, they showed one invariant solution of the system to be in equilibrium with iodine, potassium iodide, and mixtures of the two; with 40% alcohol, they also found only one invariant point. This invariant solution was shown to be in equilibrium with two different mixtures of iodine and potassium iodide, but it was not shown to be in equilibrium with pure iodine.

FIG. 3.

H_2O

Invariant soln. at 25°.	Mol. %.		
	KI.	I_2.	H_2O.
A	21·2	28·4	50·4
B	20·7	32·9	46·4
C	20·7	35·3	44·0
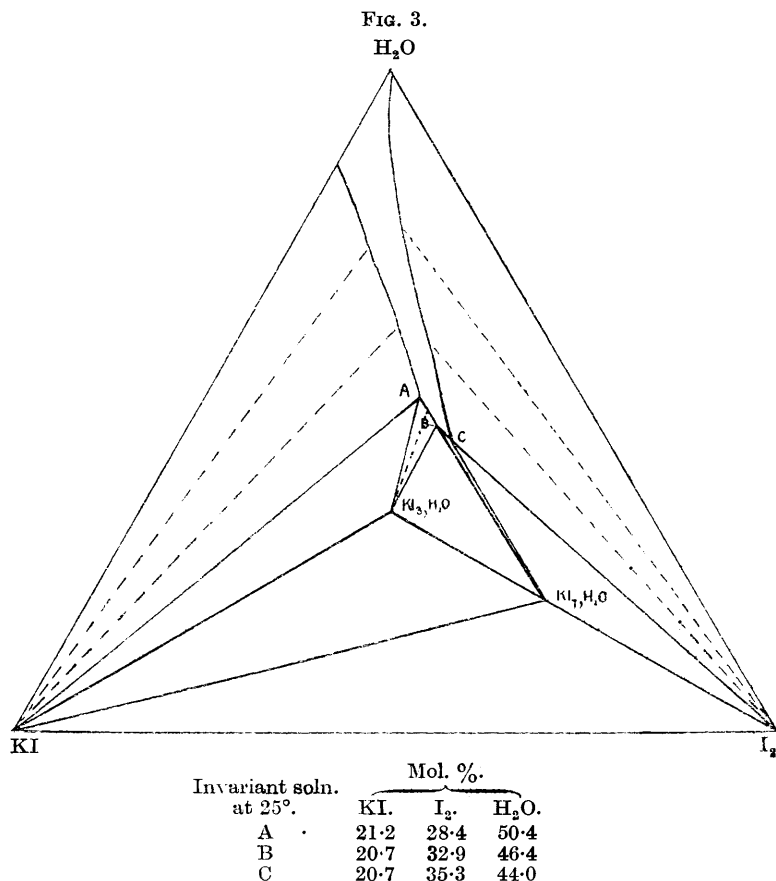
The result is therefore inconclusive. The invariant solutions in these cases contained 7·5 and 6·7% of solvent respectively, or 3 and 4% of water. It is quite probable that the pressure of water vapour over these solutions is so low that hydrated polyiodides could not exist in equilibrium with them; but if anhydrous polyiodides exist, the first of these studies should have detected them. Phase-rule studies in which a mixed solvent is employed are unsatis-

factory if one or both of the components of the solvent can enter the solid phase, as the complexity of the system is thereby increased.

Equilibria involving Non-aqueous Solvents.—The evidence presented in the preceding pages is not consistent with the existence of anhydrous potassium polyiodides at 25°, yet Abegg and Hamburger (*loc. cit.*) reported what they considered to be anhydrous heptaiodide. In their study, solid dry potassium iodide was shaken with a solution of iodine in benzene in sealed bulbs in a bath at 25°, and the potassium iodide, though not entering the liquid phase, removed iodine from it and formed a polyiodide in the solid phase. Convincing evidence is presented, almost entirely from synthesis, that the ratio iodide : iodine in this compound is 1 : 3.

Since these results do not appear to be in harmony with the deductions from the work on equilibria with aqueous solvents, the method was further investigated. Instead of benzene, tetrachloroethane (westron) was used as solvent; it was dried with calcium chloride, then with quicklime, filtered, and distilled, the fraction of b. p. 145—146° being retained. A solution of iodine in this solvent did not change in concentration when kept for a month at 25°. A saturated solution of iodine therein at 25° was found to be $0.328N$, and the solubility of potassium iodide in such a solution did not exceed 0.007%.

Iodine dissolved in tetrachloroethane, together with dry finely powdered potassium iodide, was shaken in a thermostat at 25° in bottles similar to those described earlier. The results obtained (Table IV) by using 100 c.c. of solvent and titrating 10 c.c. portions show that potassium iodide does not remove iodine from dry tetrachloroethane solution. In the table, the column headed " titre " refers to the number of c.c. of $N/10$-sodium thiosulphate required per c.c. of solution.

TABLE IV.

The influence of solid potassium iodide on the concentration of iodine in tetrachloroethane at 25°.

Time, days.	KI, g.	Titre.	Time, days.	KI, g.	Titre.	Time, days.	KI, g.	Titre.
0	—	3·27	0	5·64	3·10	0	8·00	2·58
0	0·72	3·27	7	—	3·10	7	—	2·57
7	—	3·28	11	—	3·09	7	0·03 c.c. of	
20	—	3·28	18	—	3·10		H₂O added	—
			25	—	3·09	8	—	2·46
						12	—	2·47
						18	—	2·46

(Experiment 1 covers the first group, 2 the second, and 3 the third.)

The fact that the titre fell only when a drop of water was added (Expt. 3) is very strong evidence that unsolvated polyiodides of potassium do not exist.

The negative result obtained with tetrachloroethane made it desirable to do similar experiments with benzene as the solvent. A.R. Benzene, which gave a negative test for thiophen by the isatin reaction, was dried with pure calcium chloride, filtered, and distilled (b. p. $80·2°$). A nearly saturated solution of iodine in this liquid did not change in concentration during one week at $25°$. A saturated solution of iodine in benzene, according to Abegg and Hamburger and here confirmed, is $1·09N$. The solubility of potassium iodide in this solution was less than $0·005\%$. Experiments were carried out similar to those employing tetrachloroethane, with the exception that titrations were made with $N/10$-thiosulphate on 1 c.c. portions of the benzene solution. The results are in Table V. (In Expt. No. 1, if all the iodine had been dissolved the titre would have been $12·0$ c.c.)

TABLE V.

The influence of solid potassium iodide on the concentration of iodine in benzene at $25°$.

Days.	Titre.		Days.	Titre.
Expt. No. 1. C_6H_6,50 c.c.;			Expt. No. 3. C_6H_6, 50 c.c.;	
KI, 4·37 g.; I_2, 7·48 g.			KI, 1·67 g.; I_2, 12·61 g.	
0·2	9·70		3	10·8
1	7·00		10	10·6
2	6·66		14	9·34
4	6·70 } 6·68*		17	8·92
6	6·68		22	8·10
			24	7·87
			27	7·83
Expt. No. 2. C_6H_6, 100 c.c.;			31	7·81
KI, 3·41 g.; I_2, 9·89 g.				
0	7·85			
2	6·63 } 6·65*			
4	6·67			

* Equilibrium titre.

Expts. 1 and 2 confirm the results of Abegg and Hamburger, and the concentration of the invariant liquid, *viz.*, $0·666N$, agrees well with their values, which fell between $0·660$ and $0·670N$.

The removal of iodine by solid potassium iodide indicates very strongly the formation of a polyiodide. The method of Expt. 3, in which the proportions were so chosen that the final titre of the solution lay between saturation (10·9) and the invariant (6·66), may be used for preparing this compound. The final titre in Expt. 3, *viz.*, 7·81, is very close to the value calculated on the assumption that heptaiodide is formed, and agrees with the experiments of Abegg and Hamburger in which they show the ratio $KI : I_2$ in the polyiodide is 1 : 3.

Considering the accumulated evidence against the existence of unsolvated polyiodides of potassium, and bearing in mind the

x

negative results obtained with tetrachloroethane, the formation of a polyiodide when benzene is used suggests that benzene might enter into its constitution; this suggestion is supported by the following analyses, which indicate $KI_7,2C_6H_6$ as the empirical formula of this polyiodide.

Material prepared in Expt. 3 was removed from the solution, dried rapidly on a porous plate, and stored in a well-stoppered weighing bottle. This product was a dark green crystalline powder, quite opaque under the microscope, and commencing to melt at about 55°. Analysis of these crystals by the usual method gave (mean of two) : KI, 14·85; polyiodide I, 68·72; C_6H_6 (by diff.), 16·43%; $KI : I_2 : C_6H_6 = 1 : 3·02 : 2·35$. The benzene present was also determined directly by combustion (Found, mean of two : C, 13·85; H, 1·21; whence $C_6H_6 = 15·06\%$; $KI_7 : C_6H_6 = 1 : 2·16$). On account of the high halogen content of the material only small samples were used, and the combustion tube was packed with silver foil for several inches immediately following the sample.

On attempting to remove uncombined solvent by exposing the material over finely divided potassium iodide–iodine mixture and weighing it at intervals, the decrease in weight was quite large and independent of the interval, being due almost entirely to the loss of benzene vapour on opening the vessel. Since this did not afford a solid of reproducible benzene content, the composition of this polyiodide was studied by a vapour-pressure method, using an isoteniscope after the pattern of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1420).

In one experiment, a sample of material wet with equilibrium solution was sealed up in an isoteniscope using concentrated sulphuric acid as the confining liquid. A pressure of 93 mm. of mercury was maintained at 25° as long as visible liquid remained on the sample, and then, with the removal of further benzene vapour the pressure fell rapidly to 49 mm., at which value it remained constant while a considerable quantity of vapour (about 700 bubbles) was withdrawn. Then the removal of a further 18 bubbles reduced the pressure within the isoteniscope to 5 mm. The sample had become reddish-brown and gave on analysis a total potassium and iodine content of 99·73% (and 0·25% of water), showing that all the benzene had been pumped off. The vapour pressures of iodine and benzene at 25° are 0·3 and 95 mm. respectively; the constant pressure of 49 mm. maintained above the heptaiodide is therefore good evidence that benzene is combined with it, since neither iodine nor potassium iodide holds any benzene of crystallisation by itself at this temperature.

In another experiment, partly decomposed material, containing

11·58% of benzene (1·6 mols.), was placed in an isteniscope.   The instrument was evacuated with the sample cooled in liquid air, and after warming to 25°, twenty bubbles (representing less than 2% of the total benzene) were withdrawn to sweep out any remaining air. The pressure within the isteniscope due to this material of known composition was 50 mm., or within 1 mm. of the constant pressure in the first experiment.   This indicates that the number of molecules of benzene combined with the heptaiodide is greater than that
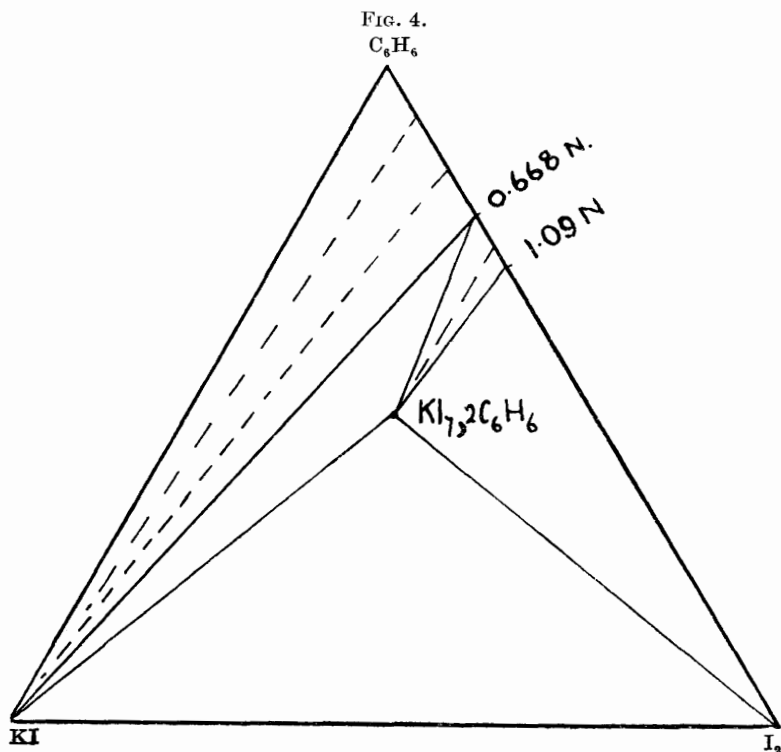
FIG. 4.

present in this sample, *viz.*, 1·6.   Other similar experiments show that this number is below 2·35 : it is therefore probable that the *compound* is represented by the formula $KI_7,2C_6H_6$.   Fig. 4 represents its equilibrium conditions.

That Abegg and Hamburger did not find the heptaiodide to be solvated with benzene is probably due to the fact that they were chiefly concerned with establishing the existence of a compound and determining the ratio of iodine to potassium iodide in it.   They do not report any complete analyses, and give only two determinations on known quantities of material, both of which are

unsatisfactory; in the first case, the iodine content was considerably below the value required for the heptaiodide, and in the second case the iodine was determined as loss on heating, involving the assumption that no other volatile material was present—in any case, the heating was only to 60—80°, which was probably insufficient to ensure complete removal of the iodine. The extreme rapidity with which this compound loses its benzene and reverts to a mixture of potassium iodide and iodine on exposure to the air makes accurate analysis impossible unless special care is taken, and without any clue as to its presence, the benzene might easily be overlooked.

Several instances of inorganic compounds containing benzene of crystallisation afforded precedents for the present case, *e.g.*, $2SbCl_3,C_6H_6$ and $2SbBr_3,C_6H_6$ (Menschutkin, *Isweistja Petersburger Polytech.*, 1910, **13**, 263); $AlBr_3,3C_6H_6$ (Gustavson, *J. Russ. Phys. Chem. Soc.*, 1882, **14**, 354); $AlCl_3,HgCl,C_6H_6$ (Gulewitsch, *Ber.*, 1904, **37**, 1560); and $Ni(CN)_2,NH_3,C_6H_6$ (Hofmann and Höchtlen, *Ber.*, 1903, **36**, 1149).

Abegg and Hamburger also report solid hepta- and ennea-iodides of rubidium and cæsium from benzene equilibria, for which Foote and Chalker and, more recently, Briggs, Greenawald, and Leonard have failed to disclose any evidence from studies of aqueous equilibria. In view of the results outlined above in the case of potassium heptaiodide, it is quite possible that some of the rubidium and cæsium compounds may also contain benzene of crystallisation, which would explain the apparent contradictions of these workers.

Summary.

1. A study of the effect of moisture upon the melting point of iodine–potassium iodide mixtures has been made, and a method evolved for the quantitative determination of water in such material.

2. The more concentrated solutions of the three-component system iodine–potassium iodide–water have been investigated, and the results of other workers critically re-interpreted.

3. Three invariant solutions were found, and two hydrated poly-iodides stable at 25°, *viz.*, KI_3,H_2O and KI_7,H_2O, were isolated.

4. The work of Abegg and Hamburger, which had been interpreted as indicating unsolvated potassium heptaiodide, is shown to be substantially accurate, but their polyiodide was found to contain two molecules of combined benzene ($KI_7,2C_6H_6$).

5. Evidence is produced that no unsolvated polyiodides of potassium exist at 25°.

and to Mr. G. H. Cheesman, B.Sc., for many valuable suggestions. Grateful acknowledgment is also made of a Beit Scientific Research Fellowship, during the tenure of which this work was carried out.