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EQUILIBRIUM IN THE SYSTEM: POTASSIUM IODIDE, IODINE AND AQUEOUS ALCOHOL.

BY CHARLES L. PARSONS AND H. P. CORLISS.

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The question of the existence or non-existence of polyiodides of potassium and the various physical and chemical constants of a solution of iodine in potassium iodide has been for years an interesting problem and is still a subject of investigation. Two previous researches upon the subject have been conducted in this laboratory which accomplished little more than to develop the intricacies of the problem and the various precautions necessary to eliminate errors of manipulation and analysis. The question was first attacked in water solution and second in pure alcohol. In both of these the concentration of the solutions became so great near the invariant point (1 liquid and 2 solid phases at the constant temperature 25°) that, at the time, duplication of results could not be depended upon. In pure alcohol, at least, equilibrium in the strongest solutions was reached with extreme slowness and it has since been discovered that filtration through glass wool which was used at the time was inadequate to separate the solid from the liquid phase. As the liquid in these solutions reaches a specific gravity above 3, is absolutely opaque and somewhat viscous, only the most careful filtration can insure the removal of the small solid particles held in suspension which no optical examination will expose.

Since the addition of water to alcohol greatly diminishes the solubility of iodine in the solvent and the addition of alcohol to water likewise affects the solubility of potassium iodide, it was reasoned that by using aqueous alcohol as the solvent, solution of much lower concentrations would be produced at the saturation point and many difficulties thereby eliminated. That this reasoning was incorrect is readily seen from the results that follow, for the degree of saturation when both iodine and potassium iodide are present in the solid phase differs little whether the solvent be water, alcohol or a mixture of the two. Accuracy of analysis was at last attained, however, as results will show, and there is no good reason why the curve can not be traced as well and with equal accuracy in aqueous or alcoholic solution. The problem divides itself into two distinct parts: (*a*) Do polyiodides of potassium exist as solid phases? and (*b*) Do polyiodides exist in solution? The phase rule enables us to give a positive answer to the first part of the problem but unfortunately it has its limitations, and the second query must still remain open to dispute.

Composition of Solid Phases.

As usually happens the literature contains claims for the existence of solid polyiodides of potassium and also evidence of the non-existence at least of the tri-iodide. Johnson[1] states that he succeeded in obtaining lustrous dark blue crystals by evaporating concentrated solutions of iodine in both aqueous and alcoholic potassium iodide, which analysis showed him to be the tri-iodide. As all the mixed crystals obtained from these strong solutions have much the same appearance and can not be separated from the mother liquor, his conclusions are not to be relied upon, especially as analysis is no criterion whatever of the formula of a substance unless its identity as a single compound is proven by other means. The more recent work of Abegg and Hamburger[2] upon solutions of iodine in aqueous potassium iodide is extensive, and they conclude that no polyiodide of potassium exists of less complexity than KI_7. A difference of opinion may be held as to whether the solid phase they analyzed as near to KI_7 was in reality homogeneous. Foote and Chalker[3] give results which, if correct, prove the existence of KI_3 and KI_7. They are in direct opposition to our own and both can not be right. We must leave the judgment to others. We can only suggest that possibly equilibrium was not attained, that the analyses of the solutions supposed to be constant are not in sufficient agreement to prove constancy of composition and that in these concentrated solutions the potassium iodide content of the solid phase, after pressing between filter paper, is alone no real criterion of its true composition. Furthermore, we are unable to plot their results on any semblance to a solubility curve.

In order to study this question a mixture of pure alcohol and pure water containing 60.04 per cent. of alcohol was prepared and saturated with both iodine and potassium iodide in the presence of varying amounts

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[1] *Jour. Chem. Soc.*, **31**, 249 (1877).

[2] *Z. anorg. Chem.*, **50**, 403 (1906).

[3] *Am. Chem. J.*, **39**, 561 (1908).

of the other. In order to make doubly certain any results obtained a solution containing 40.03 per cent. of alcohol was treated likewise. The alcohol was carefully freed from aldehydes and ketones. The potassium iodide was J. T. Baker's "special" and was found to be free from iodate and otherwise pure as claimed. The iodine, with the exception of a few of the last experiments, was distilled from water containing potassium iodide, drained, resublimed in dry air and kept for weeks over sulphuric acid before use. In the exceptions noted, our stock being exhausted, a pure resublimed iodine was used and it was proven to have no impurity affecting results by addition to bottles which had already arrived at equilibrium. The potassium iodide was powdered and dried at 180°.

In order to determine the solubility curves and corresponding solid phases for the system various mixtures were prepared and placed in 100 cc. hard glass bottles, the glass stoppers of which had been carefully ground. The bottles were then rotated in a large thermostat carefully regulated at 25°. The rotating was started December 1, 1909, and the bottles were removed from time to time for analysis and for the addition of more potassium iodide or of iodine as the case might require should examination show that the solid phase had all disappeared.

Equilibrium was reached most quickly in the more concentrated solutions, which was directly contrary to previous experience in pure alcohol. Many of the bottles had not reached equilibrium on March 1st after three months rotation. Practically all were at equilibrium by April 1st, but No. 12 and No. 35 where pure iodine alone was present in solution still showed slight gains on June 1st over analyses made some two weeks previously. They were, however, very near to saturation.

For removing portions of the liquid for analysis a special filter was made, consisting of a glass tube enlarged at the end to hold a platinum disk. This tube was fitted by a ground glass joint to a small pipette and a fine asbestos felt was prepared on the disc, which was washed with alcohol and dried. By drawing through this felt the liquid was absolutely separated from any solid present and the slight diminution in pressure necessary to fill the pipette caused no loss of iodine that could be detected. Many analyses made in duplicate showed that this method could be depended upon to give results varying less than 0.1 per cent. among themselves even in the most concentrated solutions. The liquid so withdrawn was weighed in a glass-stoppered weighing bottle, diluted to 100 cc. with alcohol and aliquot parts taken for analysis. The iodine was determined by titration with an approximately tenth normal thiosulphate solution, carefully standardized against arsenious oxide and pure iodine. The potassium iodide was estimated by careful evaporation in platinum and direct weighing, care being taken to drive off the last traces of iodine by redissolving the residue in water and again evaporating to complete dryness. When equilibrium was reached, as shown by duplicate analyses made many days apart, a portion of the solid phase was removed in a small platinum cup, quickly placed in a weighing bottle and analyzed in like manner. No special attempt to free the solid from mother liquor was made otherwise than to decant off the liquid from the cup before removal from the bottle. Having analyzed the liquid and solid the specific gravity of the liquid was determined in a small Sprengel pycnometer.

The following data are given from which the curves are plotted:

TABLE I.—THE MUTUAL SOLUBILITY OF IODINE AND POTASSIUM IODIDE IN 60 PER CENT. ALCOHOL.

		Analysis of liquid phase.		Analysis of solid phase, together with adhering mother liquor.	
Serial No.	Sp. gr.	Per cent. KI.	Per cent. I.	Per cent. KI.	Per cent. I.
		(*a*) In equilibrium with excess KI.			
1	1.148	30.93	0.0	KI	0.0
2	1.191	29.87	4.51	89.13	0.71
3	1.285	28.39	12.48	86.60	2.27
4	1.368	28.00	18.60	87.30	3.21
5	1.427	27.60	21.80	85.75	4.25
6	1.533	27.00	28.00	84:39	6.05
7	1.776	25.90	40.52	81.05	10.30
8	2.250	24.90	52.42	76.21	16.73
9	2.507	24.40	58.93	73.20	21.04
10	2.845	22.49	65.75	71.66	24.15
11	...	21.50	68.95	70.04	26.42
		(*b*) In equilibrium with excess I.			
12	1.134	0.0	23.04[1]	0.0	I
13	1.530	7.36	43.05	1.40	88.76
14	1.721	10.60	49.38	2.50	88.21
15	1.90	12.44	55.33	3.72	87.10
16	2.11	13.74	59.26	4.41	86.60
17	2.22	15.20	62.66	5.80	85.20
18	2.80	17.72	69.10	7.15	85.49
19	2.99	19.30	71.90	7.45	88.96
		(*c*) Invariant point. Excess KI and I.			
20	3.162	20.11[2]	72.51	...	...
20	Apr. 18	20.03	72.46	21.84	74.64 KI & I
20	Apr. 28	20.05	72.54	...	...
20	May 6	19.98	72.44	7.40	89.81 I
20	May 13	20.08	72.51	20.61	74.09 KI & I
20	May 20	20.06	72.44	...	...
20	May 23	20.05	72.48	33.46	63.19 KI

Comments on the above table and its graphical representation in Fig. 1 are almost unnecessary. The analyses given are the final ones after equilibrium had been proven. Their accuracy may be judged from the seven analyses given of the most concentrated liquid at the invariant

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[1] Final analysis June 1, saturation point may not have been quite reached.

[2] Analysis April 12th.

point No. 20. At this point the liquid was shown to be in equilibrium with iodine, with potassium iodide and with two mixtures of iodine and potassium iodide. It was first found to be in equilibrium with two solid phases, which could from the nature of the curve be only iodine and potassium iodide. For the sake of further demonstration the liquid was separated from the solid, pure iodine added and further rotated in th thermostat without change in composition. Potassium iodide was now added and it was later found to be still in equilibrium with this new mixture. It was again separated from the solid and rotated in contact with pure potassium iodide but no change in composition took place. As only two solid phases can co-exist at the invariant point, no polyiodide can be present. It might also be well to call attention to the highest concentration and the interesting fact that a mixture of twenty grams

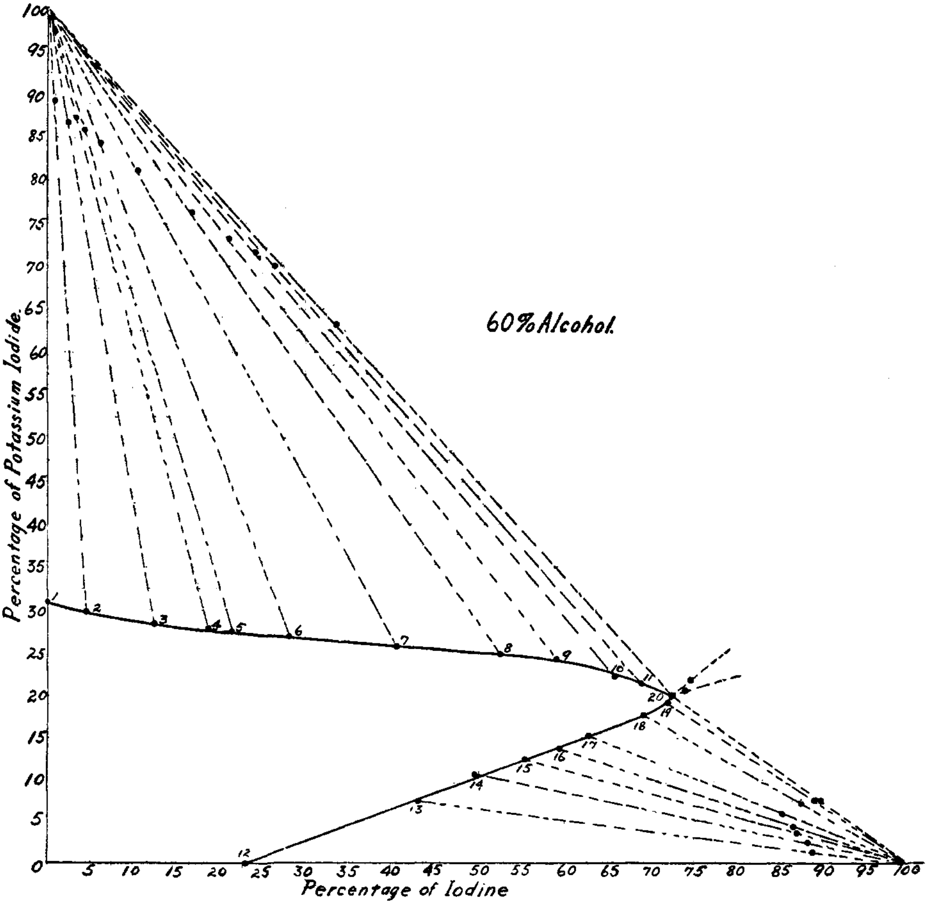

Fig: 1.

of potassium iodide and 72.5 grams of iodine can be kept in solution by 7.5 grams of 60 per cent. alcohol at 25°. Also the mutual solubility of potassium iodide and iodine increases in proportion to the amount of the other present, although the *percentage* composition of the potassium iodide decreases. At the invariant point the liquid phase contains nearly two and one-half mols of iodine for each mol of iodide.

In Fig. 1 are shown the two solubility curves meeting at the invariant point 20. The numbered points represent the composition of the liquid phases and the unnumbered points the solid phases together with adhering mother liquor in equilibrium with them. The extension of the lines joining these points shows the actual composition of the solid phases present.

As before stated, the solubility curves for solution in 40 per cent. alcohol were also determined and their perfect analogy to the 60 per cent. curve are interesting and confirmatory.

The data follow. Again point 35, pure iodine in aqueous alcohol,

TABLE II.—THE MUTUAL SOLUBILITY OF IODINE AND POTASSIUM IODINE IN 40 PER CENT. ALCOHOL.

		Analysis of liquid phase.		Analysis of liquid phase, together with adhering mother liquor.	
Serial No.	Sp. gr.	Per cent. KI.	Per cent. I.	Per cent. KI.	Per cent. I.
		(*a*) In equilibrium with excess KI.			
21	1.339	42.10	0.0	KI	0.0
22	1.377	40.83	3.76	89.21	0.70
23	1.455	38.94	10.09	88.80	1.90
24	1.532	37.41	15.71	88.19	3.02
25	1.605	36.25	20.52	87.04	4.21
26	1.655	35.38	24.44	86.08	5.11
27	1.847	33.26	33.62	83.61	8.41
28	2.024	31.71	39.99	82.06	10.76
29	2.169	30.59	44.76	80.80	12.35
30	2.558	28.56	55.30	75.90	18.63
31	2.784	26.95	60.27	74.77	20.86
32	...	24.52	65.93	72.98	23.61
33	...	23.04	69.93	72.45	25.04
		(*b*) In equilibrium with excess I.			
35	0.962	0.0	2.97[1]	0.0	I
36	1.292	8.45	28.70	1.85	84.51
37	1.581	12.56	40.63	3.41	84.02
38	...	15.20	49.95	4.98	83.81
39	2.000	16.02	52.95	5.60	82.96
40	2.173	17.18	57.37	6.61	83.60
41	2.749	19.20	66.89	8.45	85.16
42	2.902	20.12	69.10	7.08	88.81
		(*c*) Invariant point. Excess KI and I.			
34	3.246	22.50	70.79	19.48	76.24
34[2]	...	22.43	70.88	69.37	26.14

[1] Final analysis June 1st. Saturation point may not have been quite reached.

[2] After addition of KI and further rotation.

reached equilibrium with extreme slowness and may not be quite saturated after six months' rotation. Point 34 was also shown to be in equilibrium with two different mixtures of two solid phases, but no attempt was made to put it in contact with pure iodine or pure iodide, as the proof was already complete.

The data in Table II are graphically represented on the two solubility curves in Fig. 2, which is drawn on the same principle as Fig. 1.

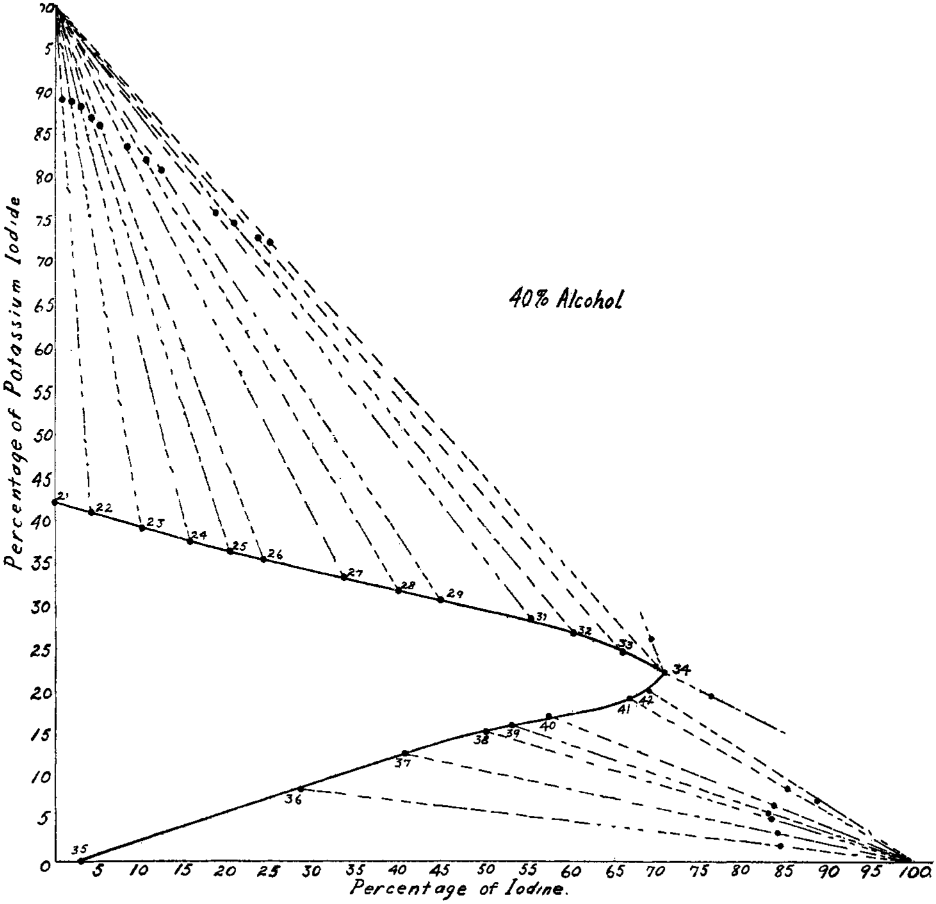

Fig. 2.

Composition of Liquid Phase.

While the non-existence of solid polyiodides of potassium is no proof that they may not exist in solution, it is at least strange that they can not be separated therefrom. Especially is this true when all the evidence in favor of their existence shows that in all solutions of potassium iodide saturated with iodine about one-half of the iodine present must be so combined and that in concentrated solutions the amount of iodine present and unaccounted for as KI_3 is much greater than this proportion. It is not the purpose of this paper to enter into an extended discussion of the problem. From the viewpoint of the dissociation theory, applied to *dilute* solutions, the ground is already well covered in literature, but as the solutions pass above 0.1 normal all formulas obtained begin to lose their force and at higher concentrations do not agree at all with observed facts. While the assumptions made apply well to dilute solutions, they do not show that other assumptions may not explain the conditions equally well, and they all have to discard the mass law as inapplicable as the concentrations increase.

Dossius and Weith[1] early pointed out that strong solutions of iodine in aqueous potassium iodide precipitate iodine on dilution; which is contrary to the mass law if the iodine is present as tri-iodide. LeBlanc and Noyes[2] explain the rise of the freezing point and the decrease in the conductivity when iodine is dissolved in aqueous potassium iodide by assuming the formation of polyiodides. Jakowkin[3] by experiments on the distribution of iodine between aqueous potassium iodide and carbon disulphide developed a mass law constant for dilute solutions indicating that potassium tri-iodide was present and was the only polyiodide present in any amount. His conclusions were based on the relative solubility of iodine in pure water and in carbon disulphide, assuming the potassium iodide present to have no simple solvent effect on the iodine. Dawson,[4] Burgess and Chapman[5] and Laurie[6] have also studied the matter from a similar standpoint and from considerations of transference and electromotive force. In dilute solutions they are in fair agreement. One of us[7] has already pointed out that the conclusions of Jakowkin, upon which most of the subsequent work is either grounded or to which the results obtained are compared, are untenable if dissolved potassium iodide itself has a simple solvent action for iodine such as added alcohol or acetic acid would possess. Furthermore, it was shown that these solutions of iodine in aqueous potassium iodide were perfectly analogous in their osmotic and conductance properties to such ternary mixtures as camphor in aqueous acetic acid and, osmotically at least, to all ternary mixtures where one of the dissolved substances was rendered less soluble by dilution of the mixture with that component which separated out first

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[1] *Z. Chem.*, 1869, 379.

[2] *Z. physik. Chem.*, 6, 401 (1890).

[3] *Ibid.*, 20, 36 (1896).

[4] *J. Chem. Soc.*, 79, 239 (1901); 81, 524; 93, 1308, 2063.

[5] *Ibid.*, 85, 1305.

[6] *Z. physik. Chem.*, 64, 615; 67, 627.

[7] Parsons, *J. Physic. Chem.*, 11, 669 (1907).

on freezing. Indeed it was definitely pointed out that Miller[1] had thermodynamically shown that in all such binary solvents the freezing point must of necessity rise on addition of the third component. Accordingly, the assumption of complexes was not necessary to qualitatively explain the facts. Many published instances were cited of such ternary mixtures where the same reasoning as is applied to the demonstration of the polyiodides would lead to incomprehensible complexes. Bray and McKay,[2] on the assumption that the decrease in conductivity on dissolving iodine in dilute aqueous potassium iodide is due solely to the formation of KI_3, arrive at results in excellent agreement with those of Burgess and Chapman which they believe prove the existence of this polyiodide. They have also attempted to account for the abnormalities in concentrated solutions and find that the deviations from the mass law are not very serious below 0.1 normal potassium iodide but still are not negligible even below this concentration. While admitting the character and force of their arguments, especially when viewed from their standpoint, it should not be forgotten that similar reasoning would probably lead to poly-camphor compounds of acetic acid and other equally improbable complexes wherever the conductivity is diminished by adding a solute to a binary solvent. Furthermore, these results, and the results of the other authorities mentioned are applicable, without other assumption, only to that very limited portion of the solubility curve, which is less than tenth-normal. This is the only portion of the curve where the actual iodine solubility is equivalent in mols to one-half the iodide present and quantitatively meets the theory of Jakowkin. It appears to the authors of this paper that the phenomena accompanying mixtures of potassium iodide, iodine and water (or alcohol) are much more analogous to those known to apply to some ternary alloy mixtures than they are to the properties of known complexes such as some of the double cyanides.

In the paper by one of us[3] already cited it was shown that while known complexes such as potassium silver cyanide, potassium ferrocyanide, etc., pass through a membrane as such without decomposition, such was not the case with hypothetical potassium tri-iodide, which was shown to behave similarly to certain double salts like the alums that are supposed to exist as simple molecules in solution. Exception having been taken to these experiments on the basis that the solutions used were too concentrated, containing more iodine than any conception previously advanced could account for, and also that a membrane was an unknown quantity in dialysis, it was decided to attack the matter again, using sufficiently dilute solutions to carry conviction to all and agar-agar jelly

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[1] *J. Physic Chem.*, 3, 160.

[2] *J. Am. Chem. Soc.*, 32, 914.

[3] *J. Physic. Chem.*, 11, 659 (1907).

in place of a membrane. Agar-agar was chosen because it has been shown to offer little, if any, resistance to electrolytes while allowing true diffusion phenomena to take place unaffected by convection currents. The experimental work was conducted, under the supervision of one of us, by Mr. George A. Perley, to whom our acknowledgments are due.

Cylinders closed at one end were made of 3 per cent. agar jelly, using 0.1 normal potassium iodide as solvent. They resembled tall beakers, having walls approximately eleven millimeters thick. They were kept immersed in 0.1 normal potassium iodide until needed. When in use these cylinders were placed in 400 cc. Jena beakers containing 200 cc. 0.1 normal potassium iodide and were then filled nearly full with the iodine-saturated potassium iodide solution employed in the particular experiment and the whole placed in a thermostat at 25°. All the solutions had previously been brought to this temperature, the level of the liquids within and without the cylinder was kept the same and both liquids were mechanically stirred by plungers throughout the experiment.

According to Jakowkin's researches and the theory of those who believe in the presence of polyiodides, a solution of potassium iodide saturated with iodine must have one-half of the potassium iodide converted into tri-iodide and contain also a small, almost neglible amount of iodine dissolved as such in the water present.

In the first experiment tried the outer solution was 0.1 normal potassium iodide and the inner solution was 0.16 molar potassium iodide saturated with iodine.

According to Jakowkin the following conditions should exist and the potassium iodide should, of course, diffuse from higher to lower concentration or from left to right.

Outer solution.	Inner solution.
0.1 molar KI	0.08 molar KI 0.08 molar KI_3 0.0013 molar I_2

If there is no complex present, the following conditions should exist and potassium iodide should diffuse from right to left.

Outer solution.	Inner solution.
0.1 molar KI	0.16 molar KI 0.0813 molar I_2

At stated periods the outer liquid was removed for analysis and replaced by a fresh portion of 200 cc. each. The first portion was taken off just as the iodine diffused to the outer wall. This took almost exactly two hours and was easily judged by the eye. It will be seen at once that the potassium iodide passed outward and that a notable portion had passed through ahead of any iodine as was to be expected from its smaller molecular weight. The following results were obtained:

Analysis of outer solution after diffusion showing a total gain in outer solution for each 200 cc. and each period:

Period.	Time.	M. mols I_2.	M. mols KI.
1	2	trace	0.876
2	12	2.951	5.26
3	12	2.355	5.75
4	12	1.475	5.46

As a check, the same experiment was performed using simply the 0.1 molar and 0.16 molar potassium iodide solutions without added iodine. Considering the fact that different cylinders of agar-agar were used and that no attempt was made to accurately adjust the height of the liquid to the same diffusing surface as before the results are quite comparative.

GAIN OF KI IN OUTER SOLUTION.

Period.	Time.	M. mols KI.
1	2	1.84
2	12	6.501
3	12	5.64
4	12	5.45

In a second experiment it was decided to use 0.1 molar potassium iodide as the outer solution and a 0.1 molar potassium iodide inner solution saturated with iodine.

According to Jakowkin the following conditions would exist and the solution should therefore pass from left to right:

Outer solution.	Inner solution.
0.1 molar KI	0.05 molar KI 0.05 molar KI_3 0.0013 molar I_2

If no complex exists, then

Outer solution.	Inner solution.
0.1 molar KI	0.10 molar KI 0.0513 molar I_2

Here again the results of experiments are against the conception of any complex being present as the following show:

ANALYSIS OF OUTER SOLUTIONS OF 200 CC. EACH SHOWING TOTAL GAIN.

No.	Time.	M. mols I.	M. mols KI.
1	12	0.889	none
2	13	1.58	none

Analyses of the two portions of outer solution used showed them to be unchanged in their potassium iodide concentration.

In the above analyses the free iodine was titrated with thiosulphate and the total iodine was determined in a separate portion, being set free by ferrous chloride and sulphuric acid and distilled into a solution of potassium iodide, using an apparatus consisting entirely of glass. Many check analyses were run showing the agar to be without effect on the analytical results. Also the experiments were repeated with results entirely in accord with those cited.

We believe the above results strongly indicate that no polyiodide exists to any notable extent in these solutions and that we have here simply a case of "solution in a dissolved solid,"[1] a solid which above 82° has been shown by Abegg and Hamburger[2] to be itself a remarkable solvent for iodine. We have already pointed out that its behavior in regard to rise in freezing point, decrease in conductivity and distribution phenomena, upon which all claims to complexes in solution are based, have interesting analogies to many ternary mixtures where no such combination would be claimed. The idea of simple solution in a binary solvent has the added advantage that it explains the phenomena of the concentrated solutions equally well with those which are more dilute.

Summary.

No polyiodides of potassium exist as solid phases at 25°.

Potassium iodide and iodine, placed together in aqueous solution, apparently diffuse independently of any chemical combination with each other. Judging from this standpoint alone no polyiodide of potassium is present in solution.

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DIFFUSION PHENOMENA OF THE ALUMS.

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In connection with the diffusion experiments on solutions of iodine in potassium iodide described in the preceding paper and those on known complexes reported in a previous paper by one of us,[3] it seemed desirable to make preparatory trials on crystal complexes which were known or supposed to exist as a mixture of simpler molecules when dissolved. For this purpose ordinary alum was chosen and the work proved so inter-

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[1] To explain what is meant by solution in a dissolved solid it may be pointed out that so far as analogy goes the only difference between dissolving potassium iodide in water and water in alcohol is that one is a solid and the other a liquid at the temperature at which most of our ordinary ideas are conceived. Sugar is not soluble in alcohol until water is added, but it is doubtful if any one would claim that the solubility of sugar in aqueous alcohol is due to the formation of sugar hydrates. It is simply because sugar is soluble in water and if one worked at —1° it would be a solid we were adding which, after dissolving, in its turn dissolved the sugar. In like manner working at 15° solid acetic acid dissolving in water acts as a solvent for camphor and the latter gives analogous conditions as to *rise* in freezing point and *decrease* in conductivity to those that exist when iodine, itself practically insoluble in water, is brought easily into solution when dissolved potassium iodide is present.

[2] *Z. anorg. Chem.*, 50, 403 (1906).

[3] Parsons, *J. Physic. Chem.*, 11, 659 (1907).