Summary.

It has been shown:

(1) That the solutions obtained by dissolving ammonia in (anhydrous), formic acid are excellent conductors.

(2) That the substance formed in these solutions (ammonium formate), although a very highly ionized electrolyte, obeys the law of mass action (in the more concentrated solutions).

(3) That, in accordance with the conception that the salts of the halogens are in formic acid solution really the salts of strong bases (the formates) and of weak acids, potassium chloride, bromide and iodide and sodium and ammonium chlorides are decomposed by "formic acid hydrolysis."

Further work along the lines suggested is in progress, using formic acid as well as other acidic and basic solvents.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

EQUILIBRIUM IN THE SYSTEM, POTASSIUM IODIDE, IODINE AND WATER.

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The question of the existence of polyiodides of potassium has been for years one of deep interest to physical chemists, involving as it does so many theoretical questions. In July, 1910,[1] one of us in collaboration with H. P. Corliss, presented a paper at the San Francisco meeting of the American Chemical Society, attacking the problem through phase rule considerations in aqueous alcohol solutions. Experimental difficulties had previously made accurate work in aqueous solutions impossible in our hands, owing to the high specific gravity and great concentration. Aqueous alcohol was chosen in the expectation that more dilute solutions would result. Such, however, did not prove to be the case, but the experimental difficulties were overcome and the experience then gained seemed to make it desirable to study the mutual solubility of potassium iodide and iodine in pure water with special reference to that portion of the curve representing complete saturation, which had never before been plotted.

In describing the results it is unnecessary to refer again to the literature of the subject, which will be found in the article above mentioned, or indeed to describe methods of procedure or of analysis, for they were precisely the same as those previously used. The portion of the curve covered by dilute solutions was also not studied, as it has been carefully covered by Noyes and Seidensticker[2] and others.

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[1] THIS JOURNAL, 32, 1367.

[2] *Z. physik. Chem.*, 27, 357 (1898).

The bottles carrying solutions of varying concentration were placed in the thermostat in the late fall of 1910 and were rotated under water kept at 25° until equilibrium was shown to have been reached. During the early stages the bottles were examined every few days and more iodide or iodine added as the case might require, if the solid phase had all disappeared.

The results follow:

TABLE I.—THE MUTUAL SOLUBILITY OF IODINE AND POTASSIUM IODIDE IN WATER.

Serial No.	Sp. gr.	Analysis of liquid phase. Per cent. KI.	Analysis of liquid phase. Per cent. I.	Analysis of solid phase with adhering mother liquor. Per cent. KI	Analysis of solid phase with adhering mother liquor. Per cent. I.	Date of anal. 1911.
		(*a*) In equilibrium with excess of KI.				
1........	1.733	60.39	0.0	KI	0.0	Apr. 4
		60.39	0.0	KI	0.0	Apr. 11
2........	1.888	54.34	11.66			Mar. 24
		54.49	11.60	84.92	4.05	Apr. 1
3........	2.066	49.04	23.06			May 20
		49.05	23.11	85.94	6.32	May 27
4........	2.216	44.90	31.01			Mar. 27
		44.74		80.46	10.84	Apr. 29
5........	2.539	38.04	44.54			Mar. 27
		38.09	44.58	78.56	15.23	Apr. 30
6........	2.560	37.71	45.54			Feb. 27
		37.60	45.56	77.32	16.73	Mar. 30
7........	2.665	35.77	49.65			May 18
		35.84	49.57			June 1
8........	3.232	29.65				Apr. 5
		29.77	62.81	39.99	56.10	Apr. 11
9........	3.246	27.98	66.42			May 21
		27.86	66.48	38.78	56.27	June 1
		(*b*) In equilibrium with excess of I.				
11........	1.349	15.99	18.51			June 1
		16.06	18.47	3.04	85.43	May 8
12........	1.516	19.77	26.11			May 24
		19.64	26.21	4.48	83.87	May 30
13........	1.769	22.84	36.04			May 18
		22.92	36.08	3.70	89.33	June 2
14........	1.910	23.64	40.52			Mar. 8
		23.46	40.51	6.49	83.62	Apr. 3
15........	2.403	24.73	53.62			Mar. 6
		24.83	53.59	8.62	83.81	May 11
16........	2.904	24.90	63.11			Mar. 9
		25.09	63.14	4.82	92.41	Apr. 28
17........	3.082	25.28	66.10			Mar. 14
		25.08	65.98	4.00	94.39	Apr. 25
		(*c*) Invariant point. Excess of KI and I.				
18........	3.316	26.05	68.06			May 12
		25.96	68.01	16.14	83.77	May 17
		26.04	68.16			May 22
		25.92	68.13	11.32	86.56	May 30

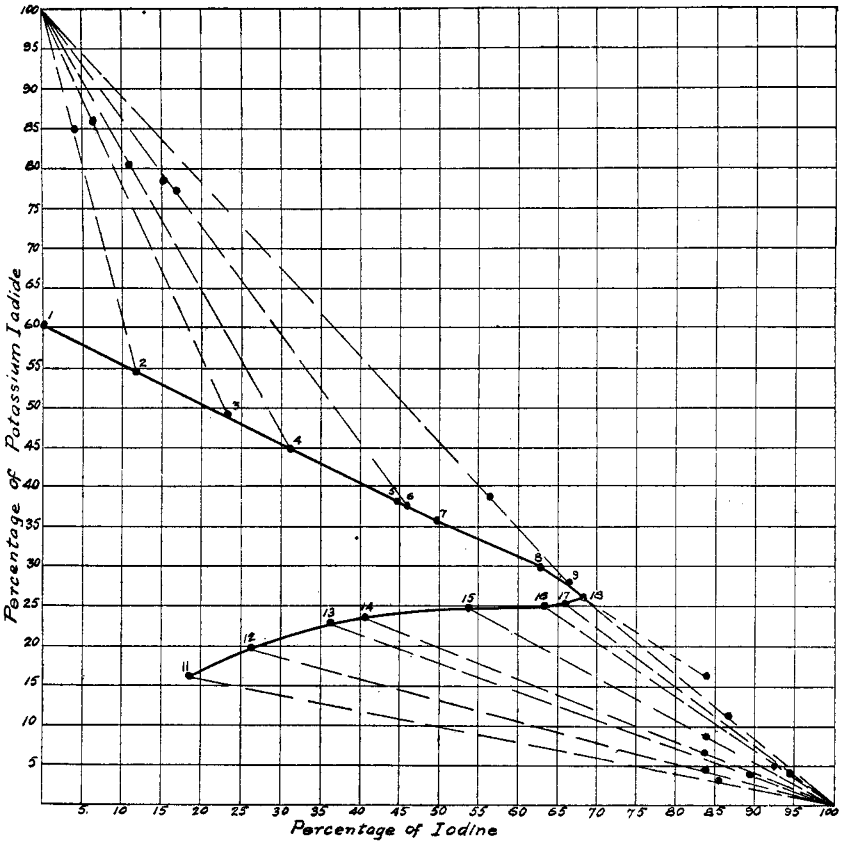
Percentage of Potassium Iodide
Percentage of Iodine
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1
2
3
4
5
6
7
8
9
11
12
13
14
15
16
17
18

Fig. 1

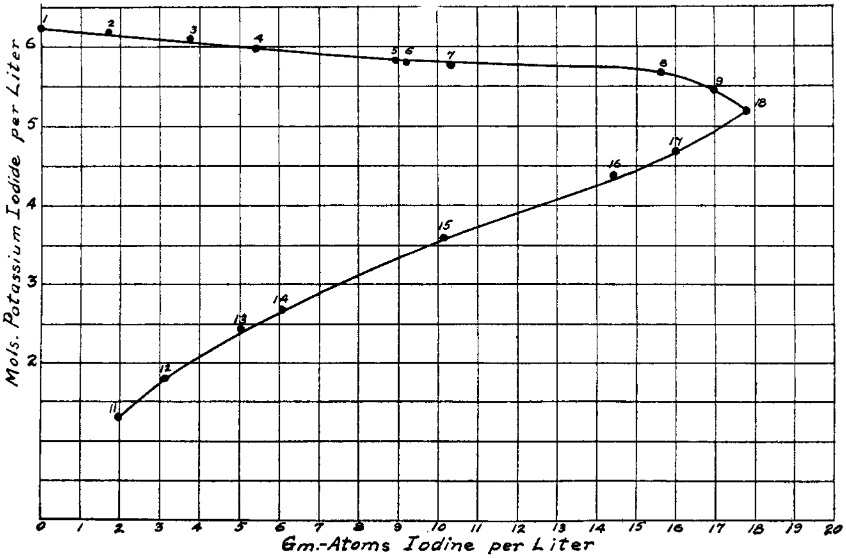
Mols. Potassium Iodide per Liter
Gm.-Atoms Iodine per Liter
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
11
12
13
14
15
16
17
18

Fig. 2.

The preceding data recalculated to moles KI and grams atoms of **I** per liter of solution gave the following results:

Serial No.	KI moles.	I g. atoms.
1	6.23	0.00
2	6.19	1.72
3	6.10	3.77
4	5.97	5.41
5	5.82	8.91
6	5.79	9.18
7	5.73	10.30
8	5.67	15.64
9	5.44	17.00
10	0.00	0.00
11	1.30	1.96
12	1.79	3.13
13	2.44	5.02
14	2.69	6.09
15	3.59	10.15
16	4.38	14.45
17	4.66	16.03
18	5.17	17.80

As water does not enter into the composition of the solid phase but acts simply as a solvent, it is possible to plot the results on an ordinary two-axis diagram, and the prolongation of the lines drawn through the points representing the composition of the liquid phases and those representing the composition of the solid phase with adhering mother liquor in equilibrium therewith will meet at a point representing the composition of the solid phase, if the solid phase is simply one of the components. In the following diagram (Fig. 1), in which the numbered points represent the composition of the liquid phases and the unnumbered points the corresponding solid phases together with adhering mother liquor, it is at once apparent that the only solid phases present throughout the whole series. are potassium iodide on one side of the curve and iodine on the other. The invariant point 18 was shown to be in equilibrium with iodine alone, potassium iodide alone, or any mixture of the two and is therefore the one and only invariant point in the system at 25°.

The compositions of the solutions for the sake of convenience are plotted in another form in Fig. 2.

Conclusion.

While these results must follow if the previous work of Parsons and Corliss[1] is correct, they again prove conclusively that no solid polyiodide of potassium exists at 25°.

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[1] THIS JOURNAL, 32, 1367.