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THE SOLUBILITY OF IODINE IN DILUTE POTASSIUM IODIDE SOLUTIONS.[1]

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FROM the investigation of Jakowkin[2] on the distribution of iodine between carbon disulphide and tolerably dilute potassium iodide solutions, it would seem almost beyond doubt that the iodine in these solutions is present chiefly in the form of the compound KI_3. This assumption, however, is apparently in contradiction with the well-known fact, which has been quantitatively confirmed by the experiments of Dossios and Weith,[3] that from a strong solution of potassium iodide which has been saturated with iodine, the iodine is, for the most part, precipitated by dilution with water, for the following equation of equilibrium must evidently hold true :

$$KI_3 = k\ (KI) \times (I_2)$$
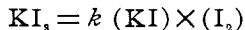
where the symbols represent the concentrations of the substances, and k is a constant. If now the solutions are kept saturated

[1] Read at the Boston meeting of the American Chemical Society, August 25, 1898.

[2] Ztschr. phys. Chem., 13, 539; 20, 19.

[3] Ztschr. Chem., 1869, 379.

with iodine, then its concentration is constant, and the above equation becomes

$$(KI_3) = k \ (KI).$$

That is, the concentration of the periodide is directly proportional to that of the iodide, and dilution should bring about no separation of iodine. It seemed now not improbable that this apparent contradiction between the results of Jakowkin and those of Dossios and Weith could be explained by the fact that the former results have reference to fairly dilute, and the latter to concentrated solutions.   The purpose of this investigation was to test this explanation, and at the same time to establish the application of the law of mass action in such a case ; namely, a case where a salt solution is saturated with a substance which forms with the salt a simple chemical compound.   To this end, we have determined the solubility of iodine in potassium iodide solution between the concentrations of 0.1 and 0.0008 normal, as well as in pure water.

The requisite potassium iodide was obtained by twice recrystallizing a commercial preparation, and the iodine was prepared by sublimation from a mixture of it with potassium iodide.   Two solutions of known strength, about 0.1 and 0.0067 normal, were prepared by weighing out the salt, and from these six others were obtained by dilution.   To four portions of these solutions of each concentration, there was added an excess of finely divided iodine ; and the mixtures were then rotated in bottles with glass stoppers in a thermostat at 25°, by means of the earlier described apparatus.[1]   Duplicate determinations were always made in such a way that the state of saturation was approached both from a higher and from a lower temperature. Furthermore, each pair of determinations was checked by a second, in which fresh solutions prepared by weighing out the iodide anew were used.   After the bottles had been rotated from four to five hours, the solutions were allowed to stand over night to settle ; twenty-five or fifty cc. were then pipetted out, and the dissolved iodine was titrated by means of sodium thiosulphate with starch as an indicator.   In determining the solubility in water, particular regard was paid to the purity of the water, which was distilled from alkaline permanganate, and proved pure by measur-

[1] *Ztschr. phys. Chem.*, **9**, 606.

ing its conductivity. In order to detect any slight influence due to the formation of hydriodic acid, the bottles were rotated in the thermostat during different lengths of time; but no difference in the results could be detected.

The following table contains the results in millimols, or thousandths of a molecular weight, per liter. Under the heading "undersaturated", the values are given which were obtained by warming from a lower temperature up to $25°$, while under "supersaturated", those appear which were obtained in the opposite way.

SOLUBILITY OF IODINE.

Millimols of KI per liter.	Millimols of dissolved iodine (I_2) per liter.				Mean.
	Undersaturated.		Supersaturated.		
	I.	II.	III.	IV.	
106.3	55.20	55.39	55.14	55.38	55.28 ±0.05
53.15	28.03	27.97	28.16	27.96	28.03 ±0.03
26.57	14.70	14.65	14.72	....	14.68 ±0.02
13.29	8.018	7.992	7.998	8.003	8.003±0.004
6.643	4.678	4.712	4.589	4.688	4.667±0.019
3.322	3.138	3.061	2.906	3.102	3.052±0.036
1.661	2.223	2.214	2.241	2.262	2.235±0.008
0.8304	1.830	1.838	1.779	1.809	1.814±0.010
0	1.363	1.347	1.465[1]	1.283[1]	
0	1.302	1.337	1.341	1.357	1.342±0.004[2]
0	1.333	....	1.329	1.351	
0	1.343	....	1.360	....	

An inspection of the table shows that no regular difference exists between the "undersaturated" and the "supersaturated" values, which proves that the solutions had reached the state of equilibrium. The degree of concordance of the single results is best shown by the values of the deviations from the mean in the last column. From the results with pure water, it is obvious that the amount dissolved was independent of the time during which the bottles were rotated. The solubility found (1.342 millimols) agrees also well with that obtained by Jakowkin (0.3387 gram or 1.335 millimols per liter).

In order now to test the application of the law of mass action, we must first of all subtract from the total amount of dissolved

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[1] Omitted in the calculation of the mean.

[2] In determining the amount of iodine necessary to saturate pure water, the bottles were rotated during different lengths of time; namely, as follows: first series, two hours; second series, four hours; third series, one day; fourth series, seven days.

iodine, the amount of iodine soluble in pure water. In this way, the amount of iodine is found which is present in the form of the complex salt ; and, if the ratio of this quantity to the total amount of potassium iodide is calculated, it can be seen at once to what extent the simple proportionality exists which the law of mass action requires in case only the compound KI_3 is formed. The results (expressed in millimols) of this calculation are arranged in the following table :

$KI+KI_3$.	$KI+I_2$.	KI_3.	Ratio. $KI_3 : (KI+KI_3)$.
106.3	55.28	53.94	0.5074
53.15	28.03	26.69	0.5021
26.57	14.68	13.34	0.5021
13.29	8.003	6.661	0.5012
6.643	4.667	3.325	0.5005
3.322	3.052	1.710	0.5148
1.661	2.235	0.893	0.5376
0.8304	1.814	0.472	0.5684

It is evident from the last column of this table that between the concentrations 0.1 and 0.006 normal the iodine present in the form of a complex salt is closely proportional to the total quantity of potassium iodide. In the case of the more dilute solutions, however, the relation of these two quantities seems to increase ; but this is probably to be attributed to experimental error, for the quantity of iodine present as complex salt is less in these cases even than the solubility in pure water. Aside from these very dilute solutions, the assumption that the iodine exists exclusively as free iodine and as a constituent of the salt KI_3 (or of its anion) is therefore in complete accord with the law of mass action. The conclusion of Jakowkin in regard to the constitution of the complex salt is thus confirmed by the solubility relations.

THE NATURE OF VALENCE.

[SECOND PAPER.]

BY F. P. VENABLE.

AS the preceding paper upon this subject was in the form of an address before one of the local sections of the society, the hypothesis as to the cause of valence there suggested was given in outline only and could not be enlarged upon as far as