LXIX.—*The Solubility of Iodine in Water.*

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THE solubility of iodine in water has been determined by a number of observers, and their results lead to very different values. For instance, at 25·5°, Meyerhoffer (*Zeitsch. physikal. Chem.*, 1888, **2**, 594) found 0·426 gram per litre, Noyes and Seidensticker (*Zeitsch. physikal. Chem.*, 1898, **27**, 388) at 25° found 0·3404 gram per litre, and McLauchlan (*Zeitsch. physikal. Chem.*, 1903, **44**, 687) at 25° found 0·279 gram per litre. Determinations at other temperatures have been made by Dossios and Weith (*Jahresber.*, 1869, 52, and 220), Wittstein (*Jahresber.*, 1857, i, 123), and Dietze (*Chem. Centr.*, 1898, i, 1094), and they do not show much better agreement.

Some of these discrepancies in the older values are probably due to

the presence of impurities in the water or in the iodine, or to the use of soft glass vessels from which the water dissolved alkalis, as the solubility is greatly increased by any substance which gives rise to the formation of polyiodide in the solution.

In the experiments now described, care was taken to purify both iodine and water as far as possible, and the determinations were carried out in borosilicate glass apparatus, in which the conductivity of the water showed practically no change even after long standing.

Our result at 25° is in excellent agreement with Noyes and Seidensticker's experimental value, and we agree with the same authors in finding that the solubility of iodine in water does not increase progressively with time, as found by Dossios and Weith.

Materials.—The iodine was purified by Ladenburg's method (*Ber.*, 1902, 35, 1256). Silver iodide was shaken with concentrated ammonia for twenty-four hours to dissolve any traces of silver chloride or bromide, then filtered and washed, and reduced with zinc and dilute sulphuric acid. The solution was treated with a mixture of oxides of nitrogen from nitric acid and starch, the precipitated iodide filtered, twice distilled in steam, then mixed with barium oxide and sublimed, and kept in a desiccator over calcium iodide. All the materials used were carefully tested to see that they were free from chlorine and bromine.

The water was distilled from alkaline and acid permanganate, and its specific conductivity varied from 1 to 1.5 gemmhos at the room temperature.

EXPERIMENTAL.

For the first series of experiments, iodine and water were stirred rapidly in a Jena glass flask, placed in a thermostat, but it was found that true saturation was never attained in an open flask, owing to the rapidity with which the iodine volatilised from the surface layer, so a closed apparatus was used of the form shown in the figure. It held about a litre of water, and to this was added excess of iodine, the glass caps, *A* and *B*, were then fixed firmly on with rubber tube and wire, and the vessel was rocked in a thermostat in the way shown in the figure, the connecting rod, *R*, having an eccentric attachment to a small flywheel driven by a motor. In order to withdraw a sample of solution for analysis, the vessel was detached from the rocker, both caps were removed, and the flask, *D*, was attached to *B* by means of the ground-joint, *C*, and immersed in the thermostat. The solution was then sucked over into *D*, any solid iodine being stopped by the glass-wool in *E*.

The flask, *D*, which had a ground-stopper, was weighed before and after the solution was drawn over, some solid potassium iodide being

placed in it to diminish the volatility of the iodine and thus prevent loss. Excess of $N/100$ sodium arsenite solution was then added to the iodine solution, the amount being determined by weighing, and the small excess was titrated back with $N/100$ -iodine solution, using starch as indicator. In working with $N/100$ sodium arsenite, it was found necessary to add about 12 grams of sodium bicarbonate per litre in

order to secure a quick indication of the end point. The starch solution was sterilised in the way described by Treadwell. For each determination, a quantity of iodine solution, varying from 90 to 160 grams, was withdrawn in this manner.

In the following table, column I gives the time in hours, and column II gives the weight of iodine in grams per 1000 grams of solution :

Temp. 18°.		Temp. 25°.		Temp. 35°.		Temp. 45°.		Temp. 55°.	
I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
32½	0·2783*	42	0·3318	46½	0·4631†	35	0·6452	42	0·9259*
57	0·2841	66½	0·3393*	70½	0·4659*	47½	0·6473*	53	0·9157*
97	0·2915	26	0·3371	94½	0·4659*	60	0·6435±	107	0·9233*
66	0·2998	47½	0·3393*	—	—	71	0·6467*	147½	0·9163§
90	0·3006	71½	0·3395*	—	—	—	—	—	—
98½	0·3130	—	—	—	—	—	—	—	—
39	0·2743*	—	—	—	—	—	—	—	—
69	0·2785*	—	—	—	—	—	—	—	—
113	0·2746*	—	—	—	—	—	—	—	—

* Value used in calculating mean.

† Stirring stopped during night.

± Slight uncertainty in titration.

§ Temperature not constant.

The mean values for the five temperatures are :

18°	0·2765	gram of iodine per 1000 grams of water			
25	0·3395	"	"	"	"
35	0·4661	"	"	"	"
45	0·6474	"	"	"	"
55	0·9222	"	"	"	"

It will be seen that the solutions took from one to two days to reach the point of saturation even in a closed vessel. The results show fair agreement considering the possible experimental errors and the large temperature-coefficient of the solubility. The deviations at 18° must have been due to some impurity introduced during the first withdrawal of solution, as in the third series, when fresh material was introduced, the solubility fell to its original value.

The molecular heat of solution of iodine in water has been calculated by means of the formula

$$\log_e \frac{C_1}{C_2} = \frac{Q}{2} \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

where C_1 and C_2 are the concentrations at temperatures T_1 and T_2 , and Q is the molecular heat of solution, which is assumed to be constant between T_1 and T_2 , a condition which is not strictly fulfilled.

Baxter, Hickey, and Holmes (*J. Amer. Chem. Soc.*, 1907, **29**, 127), from their determination of the vapour pressures of iodine between 0° and 55°, calculated its molecular heat of vaporisation to be approximately constant and equal to 15·1 Cals.; the molecular heat of vaporisation from solution must be equal to the difference between heats of vaporisation and of solution.

The values are given in the following table :

Temp.	Mol. heat of solution in Cals.	Mol. heat of vaporisation from solution in Cals.
21·5°	5·09	10·01
30·0	5·82	9·28
40·0	6·44	8·66
50·0	7·38	7·72

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