

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

THE SOLUBILITY OF STANNOUS IODIDE IN WATER AND
IN SOLUTIONS OF HYDRIDIC ACID.

By S. W. YOUNG.

Received July 31, 1897.

THE following experiments have been made in order to determine the solubility of stannous iodide in water and in different strengths of hydriodic acid at different temperatures.

The stannous iodide used was prepared by the action of hydriodic acid on tin. The hot saturated solutions thus obtained were cooled and the separated crystals of stannous iodide were filtered off by suction, dried on bibulous paper for a few minutes, and then transferred to a large test-tube and shaken repeatedly with carbon bisulphide in order to dissolve out the stannic iodide which is always present. The product was kept under carbon bisulphide in tightly stoppered tubes until wanted.

The hydriodic acid used was prepared by the action of hydrogen sulphide on iodine and water. It was found convenient in preparing an acid of given strength to weigh out the requisite amounts of water and iodine and allow the hydrogen sulphide to act on them. It is possible in this way to prepare acids of any strength with very considerable accuracy. For instance, in one case it was desired to make an acid of thirty per cent. After the acid was prepared analyses gave 29.93 per cent. and 29.97 per cent.

The method used in determining the solubility was as follows :

The requisite solvent and stannous iodide were placed in a large 100 cc. test-tube, which was closed by a stopper with three holes, one for a thermometer reading to tenths, one for a stirrer, and one for the introduction of a pipette for removing the samples. A layer of coal oil about one inch deep was placed upon the solution to prevent oxidation. The whole was heated nearly to boiling for a few moments and stirred constantly to insure saturation. The whole was then supported in a large beaker of boiling water. When the thermometer had remained constant for some time a weighing pipette was introduced and a sample withdrawn, weighed, and the amount of stannous salt determined by titration with standard iodine solution, according to the method described in a previous paper.¹

In withdrawing the sample in the pipette it was necessary that the solution should be filtered to avoid drawing out more or less solid stannous iodide. This was accomplished by affixing to the tip of the pipette a short piece of rubber tubing, in which was placed a wad of absorbent cotton. The solution, after passing through this filter, was perfectly clear.

Following are the results of two series of determinations of the solubility of stannous iodide in pure water :

Series 1.		Series 2.	
T.	P.	T.	P.
98.5	3.43	97.3	3.70
84.9	3.05	87.4	3.24
73.9	2.56	77.6	2.75
60.1	2.09	67.5	2.34
51.5	1.79	59.7	2.03
41.0	1.50	49.5	1.72
30.5	1.21	39.4	1.38
20.8	1.03	29.6	1.11
		19.8	0.96

T = Temperature.

P = Parts stannous iodide in 100 of solution.

The two series show very good agreement with the exception of the first numbers, the second series having a value of 3.70 parts soluble at 97.3°. while the first series shows only 3.43 parts at 98.5°. This is undoubtedly due to incomplete saturation in the first series. This is indicated by the fact that the curves plotted from the data are more nearly normal with the higher value. The same thing was noticed in some other series.

¹ This Journal, 19, 809.

In Table I, following, are the results of eight series of determinations of the solubility of stannous iodide, in solutions of hydriodic acid, varying in strength from five to thirty-seven per cent. Some of the numbers are averages of duplicates, while some are single determinations. A few experiments showed the method of determination to be very reliable and it seemed probable that the error introduced by oxidation on standing sufficiently long for two parallel determinations to be made, would be greater than any error introduced by the method.

Two peculiarities are immediately noticeable from a study of these data. The first one is that the presence of hydriodic acid up to above fifteen per cent. renders the stannous iodide less soluble than in pure water. In order to show more clearly the nature of this effect the following series of experiments was made :

Solutions of hydriodic acid varying from three to fifteen per cent. were prepared by taking strong acid of known strength and diluting with the calculated amounts of water. These were saturated with stannous iodide by warming and allowed to cool to 23.5° C., at which temperature they were allowed to stand for some time with frequent stirring, in order to insure equilibrium. Portions were taken out from each in a weighing pipette and titrated. Following are the results. They cannot lay claim to extreme accuracy, owing to the rather large probable error introduced by the method of making up the dilute acids used :

Strength of acid. Per cent.	P. ¹	Strength of acid. Per cent.	P.
0	1.00	9	0.21
3	0.26	10	0.26
4	0.22	11	0.30
5	0.19	12	0.45
6	0.16	13	0.58
7	0.16	14	0.62
8	0.17	15	0.81

P = Parts of stannous iodide in one hundred of solution.

These results show that the solubility of stannous iodide decreases with the increase in concentration of the hydriodic acid up to between six and seven per cent., and thereafter increases. The decrease in solubility reminds one of the conduct of common salt and hydrochloric acid. The later increas-

TABLE I.

SHOWING SOLUBILITY OF STANNOUS IODIDE IN SOLUTIONS OF HYDRIODIC ACID OF DIFFERENT CONCENTRATIONS.

Strength of hydro- dic acid used = 5.83 per cent.		9.50 per cent.		10.60 per cent.		15.20 per cent.		20.44 per cent.		24.80 per cent.		30.40 per cent.		36.82 per cent.	
T. ¹	P. ²	T.	P.	T.	P.	T.	P.	T.	P.	T.	P.	T.	P.	T.	P.
98.2	2.06	89.5	1.39	98.1	2.11	95.0	2.68	98.7	5.44	99.4	8.15	89.7	13.35	97.6	24.80
80.6	1.23	79.8	1.12	84.3	1.38	83.3	1.96	81.0	3.65	89.5	7.23	79.6	11.65	85.0	22.12
70.6	0.90	69.7	0.83	69.0	0.87	70.9	1.44	69.0	2.88	79.4	5.96	69.9	10.70	73.3	20.66
57.9	0.63	59.5	0.57	59.4	0.64	60.4	1.03	59.5	2.46	68.4	5.07	59.3	9.87	59.2	19.74
49.8	0.39	50.0	0.40	49.8	0.45	50.0	0.84	49.5	2.15	59.8	4.54	49.3	9.44	49.5	19.32
41.1	0.37	40.0	0.29	40.2	0.33	40.3	0.77	40.1	1.87	50.0	4.16	39.1	9.05	40.0	18.80
30.3	0.23	29.8	0.23	30.0	0.23	30.0	0.67	30.9	1.80	39.7	3.96	31.0	9.52	30.0	18.88
23.3	0.16	18.3	0.21	20.3	0.20	17.6	0.56	17.7	1.75	30.0	3.86	18.7	9.87	21.0	20.10
..	20.0	4.06
..	14.5	4.20
..	4.5	4.94

¹ T = Temperature.

² P = Parts stannous iodide in one hundred of solution.

ing solubility would seem to indicate the introduction of a new system in about seven per cent. concentration of hydriodic acid. The nature of this new system will be discussed later.

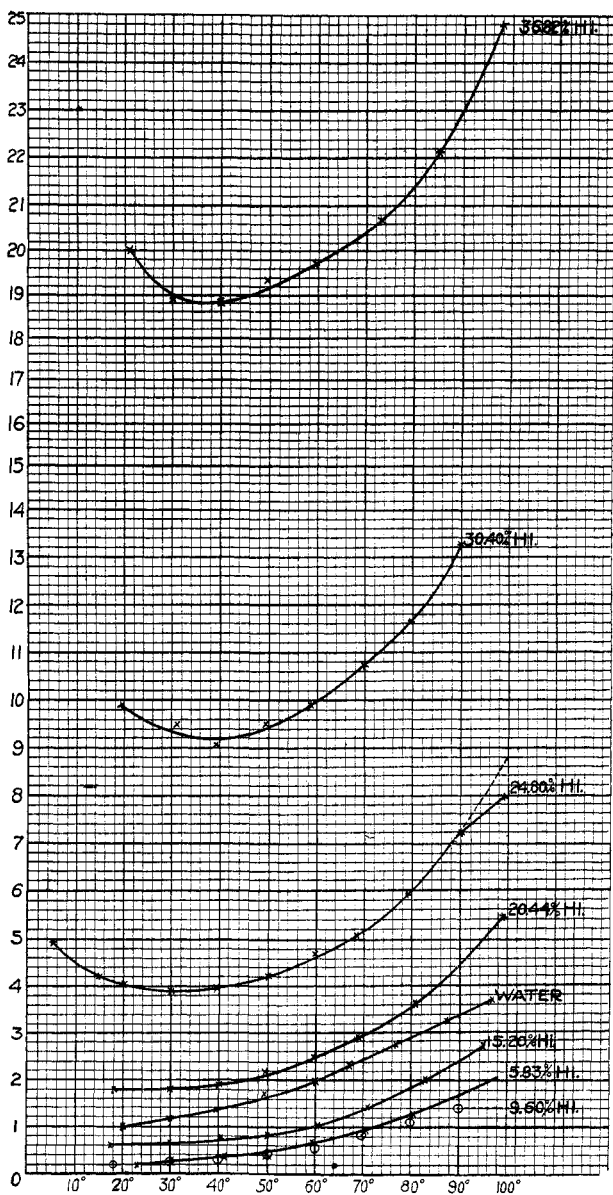
The second notable peculiarity in the result is that in concentrations of hydriodic acid, from twenty-five per cent. up, there is a very notable *increase* in the solubility with *decreasing* temperature from somewhere between 30° and 40° . This is most strikingly shown by the accompanying curves.

An inspection of these curves will readily show that there are distinct differences in their characters apart from the merely general increase or decrease in solubility occasioned by the different strengths of acid.

Comparing all curves for solubility in acid with that for solubility in water, it will be seen that the former all differ distinctly from the latter in two particulars. In the first place, above about 40° to 50° the solubility in acids increases more rapidly than does that in water, *i. e.*, the curves above this temperature are steeper for acids than for water. Below this temperature, however, the reverse is true, the curves being less steep for acids than for water, except that with acids of above twenty per cent. the pitch of the curve changes entirely between 30° and 40° and the solubility increases with decreasing temperature.

This abnormality would seem to indicate the introduction of a new system at lower temperatures, which, perhaps, becomes more and more stable with falling temperature, and by its greater solubility produces the peculiar character shown in the curves below 40° . The nature of this new system has been determined and will be made the subject of the following paper.

For convenience of reference the following table has been prepared. It contains the values for the solubilities of stannous iodide in water and hydriodic acid for temperatures from 20° to 100° . The values are taken from the points of intersection of the curves, and are expressed in parts per hundred of solvent instead of parts per hundred of solution as previously.



Curves showing solubility of stannous iodide at different temperatures in hydriodic acids of different strengths.

Ordinates = Parts stannous iodide in 100 of solution. Abscissae = Temperatures.

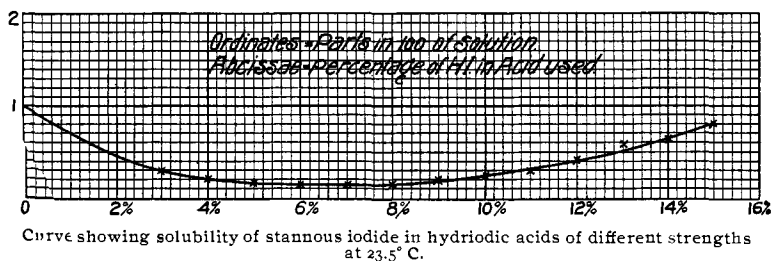


TABLE II.

SHOWING THE VALUES FOR THE SOLUBILITY OF STANNOUS IODIDE IN VARIOUS CONCENTRATIONS OF HYDRIODIC ACID. VALUES TAKEN FROM INTERSECTIONS OF CURVES AND CALCULATED TO PARTS IN 100 OF SOLVENT.

Per cent. strength of HI =	Water.	5.83	9.60	15.20	20.44	24.80	30.40	36.82
Temperature.								
20°	0.98	0.20	0.23	0.60	1.81	4.20	10.86	25.31
30°	1.16	0.23	0.23	0.64	1.81	4.06	10.28	23.46
40°	1.40	0.33	0.28	0.71	1.90	4.12	10.06	23.15
50°	1.69	0.46	0.38	0.82	2.12	4.34	10.35	23.76
60°	2.07	0.66	0.55	1.11	2.51	4.78	11.03	24.64
70°	2.48	0.91	0.81	1.37	2.92	5.43	11.97	25.72
80°	2.95	1.23	1.13	1.83	3.70	6.38	13.30	27.23
90°	3.46	1.65	1.52	2.40	4.58	7.82	15.52	29.84
100°	4.03	2.23	2.04	3.63	5.82	9.60	34.05

STANFORD UNIVERSITY,
July 17, 1897.

ON IODOSTANNOUS ACID.

By S. W. YOUNG.

Received July 31, 1897.

AS has been pointed out in the previous paper, the solubility of stannous iodide in rather strong solutions of hydriodic acid, indicates the formation at low temperatures of a system of different character from that existing at higher temperatures.

In order to become more familiar with the facts of the case, the following experimental work was performed.

In the first place it was noticed that when saturated solutions of stannous iodide in hydriodic acid of about twenty-five per cent. or over, were cooled in ice-water, very light yellow needles crystallized out in greater or less quantity, and it was evident that these were entirely different in character from the red needles of stannous iodide itself.