

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.

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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.

Several unsuccessful attempts to dry samples of the product for analysis were made. In the first instance the product was filtered off by suction and transferred to a vacuum desiccator. It almost immediately began to turn red. A sample was next placed in a current of dry hydrogen, but this suffered the same discoloration as the first. It was next attempted to dry a sample in a current of dry hydrogen, the vessel containing the sample, as also the hydrogen, being kept at 0°C . by ice-water. Again the substance became red, but more slowly than in the previous experiments.

The most natural inference from these preliminary experiments was that the compound was iodostannous acid, H_2SnI_4 , or $\text{SnI}_2 \cdot 2\text{HI}$, analogous to chlorostannous acid, H_2SnCl_4 . It was thought that if this were the case it might be possible to dry the compound at low temperatures in an atmosphere of gaseous hydriodic acid. Accordingly a sample was placed in a weighing bottle, which in turn was placed in a wide-mouthed glass-stoppered bottle, which also contained pieces of glacial phosphoric acid. A current of dry hydriodic acid gas was then conducted into the bottle to displace the air, the bottle immediately stoppered tightly and immersed in ice-water. After a few hours, however this sample too had begun to redden and the attempt to obtain the composition of the body by direct analysis was abandoned.

In the meantime experiments were carried on to study more closely the solubility of the bodies at lower temperatures.

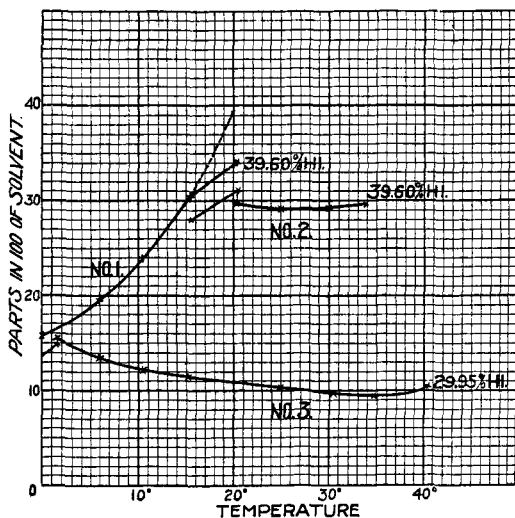
The method was to take hydriodic acid of known strength, add to it stannous iodide more than sufficient to saturate the solution, cool in ice-water and determine the amount of stannous iodide in the solution by titration with standard iodine solution by the process described in the previous paper. Following are the data obtained, all results being given in terms of stannous iodide :

Temperature.	SOLUBILITY OF STANNOUS IODIDE AT LOW TEMPERATURES IN 39.6 PER CENT. HYDRIODIC ACID.		Parts in 100 of solvent.
	Parts in 100 of solution.		
	I.	II.	
0°	13.52	13.56	15.66
5.7°	16.44	16.37	19.71
10.5°	19.47	19.60	24.27
15.7°	23.56	23.68	30.92
20.3°	25.50	25.60	34.30

The solution gave out at this point and another one was prepared in the same way with the same acid. Readings in this case were begun at 15.5° .

Temperature.	Parts in 100 of solution.		Parts in 100 of solvent.
	I.	II.	
15.5	22.00	22.11	28.20
20.2	23.49	23.59	30.77
20.1	22.93	23.02	29.86
25.3	21.98	...	28.20
30.0	21.97	...	28.18
34.7	22.49	...	29.10

After making the reading at 20.2° the solution was allowed to stand for some hours, at the end of which time the solid in the solution which at the time of the first reading had been of the light-yellow sort, had changed completely into red stannous iodide. The yellow compound was thus stable under the conditions of the experiment up to about 20° . By reference to the accompanying curves it will be seen that in the preceding set of



Curves showing the solubility of iodostannous acid and of stannous iodide at low temperatures. All parts soluble in terms of stannous iodide.

experiments also, the solubility diverges from the normal between 15° and 20° . It will also be noticed that in the present series of determinations the solubility falls from 20° to 30° , and

thereafter rises. This may perhaps be taken to indicate that the system represented by the yellow compound is more or less stable in solution after it has ceased to be stable in the solid form in contact with solution.

One other series of solubility determinations was made, using acid of 29.95 per cent. Following are the results of this series :

Temperature.	Parts in 100 of solution.	Parts in 100 of solvent.
1.5°	12.96	14.89
1.5°	13.15	15.14
6.0°	12.35	14.09
10.5°	11.01	12.36
15.2°	10.48	11.70
24.8°	9.36	10.33
30.7°	8.78	9.62
34.8°	8.70	9.50
40.3°	9.51	10.50

Between the two readings at 1.5° the same transition of the yellow solid into the red that was spoken of above as occurring at 20° had taken place. As is noticed it was not accompanied by any marked change in solubility as was the case above. It is also to be noticed that what change there is is toward increase, while in the previous case it was toward decrease. The probable explanation of this will be made later.

DETERMINATION OF THE COMPOSITION OF THE YELLOW COMPOUND.

It was shown above that the determination of the composition of the yellow compound by direct analysis appeared to be impossible. The composition of the body has, however, been determined by the following method :

If a solution of hydriodic acid of known strength be saturated, or nearly so, with stannous iodide at ordinary temperatures, and the amount of stannous iodide contained in the solution be then determined, it is evident that we may very easily calculate the amounts of stannous iodide and hydriodic acid contained in one hundred parts of water.

If now this same solution be cooled to, say zero, and the yellow compound be allowed to crystallize out, it is evidently possible by analyses of the mother-liquor to determine the percentages of hydriodic acid and stannous iodide remaining, and from

this to calculate the parts of stannous iodide and of hydriodic acid remaining in one hundred parts of water. Then, if the yellow body be a compound of stannous iodide with hydriodic acid, both the parts per hundred of water of stannous iodide and of hydriodic acid will be decreased, and the ratio of the decrease will be the same as the ratio in which the two constituents are combined in the yellow solid. Following are the data essential for the calculation.

1. Determination of the strength of the hydriodic acid, used by titration with standard alkali, gave :

I.	II.
35.91	35.96

2. After saturating the requisite amount of the above acid and filtering the solution through cotton-wool under oil, the percentage of stannous iodide was determined and found to be :

I.	II.
16.94	16.92

3. From these data it follows by simple calculation that the original solution was constituted as follows :

Water	100	parts.
Stannous iodide.....	31.94	"
Hydriodic acid.....	56.14	"

4. The solution was now cooled to 0°C . and allowed to stand for some time to insure equilibrium. Very considerable quantities of the yellow body separated out.

5. The percentage of stannous iodide was determined by the usual method and found to be :

I.	II.	Average.
12.66	12.84	12.70

6. Since titrations with alkali cannot be made in presence of tin salts, the determination of the free hydriodic acid in the solution was found by taking weighed samples, diluting to 100 cc., and taking aliquot parts, and therein determining the total iodine by distilling off the iodine with ferric chloride in the Bunsen apparatus. Knowing the amount of stannous iodide in the solution already, the corresponding amount of iodine can be calculated. Subtracting this from the total iodine found, the remainder is the amount of iodine present as hydriodic acid. The follow-

ing determinations of total iodine in separately weighed samples were obtained :

I.	II.
38.73	38.55

Since the percentage of stannous iodide in this solution was found to be 12.70, it follows that the percentage of iodine in combination with tin is 8.71. Subtracting this from 38.60 (total iodine) gives 29.9 per cent. of iodine as hydriodic acid. This is equivalent to 30.14 per cent. hydriodic acid. Calculated to the basis of one hundred of water we get for the composition of the solution after crystallization :

Water	100	parts.
Stannous iodide	22.22	"
Hydriodic acid	52.72	"

These results show one hundred parts of water to have lost by crystallization 9.72 parts of stannous iodide and 3.42 parts of hydriodic acid, and these must be in combination in the yellow compound. A simple calculation shows this result to accord very closely with the formula $\text{SnI}_2 \cdot \text{HI}$, for

$$\begin{aligned} \text{Mol. wt. SnI}_2 &: \text{Mol. wt. HI} : : \text{Amt. SnI}_2 : x \\ 370.43 &: 127.54 : : 9.72 : x \\ &x = 3.35. \end{aligned}$$

Theoretically then, in the compound HSnI_3 or $\text{SnI}_2 \cdot \text{HI}$, the amount of hydriodic acid in combination with 9.72 parts of stannous iodide would be 3.35. The value found was 3.42, which, considering the complexity of the process, should be considered very fair agreement.

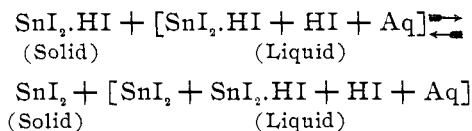
The fact that the compound contains only one molecule of hydriodic acid instead of two, as was at first thought possible, is not particularly surprising, since it appears to be generally true that those double halides of stannous chloride which contain only one molecule of the alkali chloride are the most stable.

EXPLANATION OF SOME OF THE PECULIARITIES NOTICED IN THE
SOLUBILITY CURVES OF STANNOUS IODIDE
AT LOW TEMPERATURES.

Certain peculiarities in the solubility curves accompanying are noticeable, and some of them have been pointed out. The sudden breaks in the curves are particularly noticeable. The fact that this

break is not seen in curve No. 1, is undoubtedly due to the fact that the observations were not carried far enough, the solution having given out at 20°. Breaks are noticed in curve No. 2, at 20.2°, and in curve No. 3, at 1.5°. Since these breaks indicate the points at which rapid decomposition of the iodostannous acid takes place according to the equation, $\text{SnI}_2 \cdot \text{HI} \rightleftharpoons \text{SnI}_2 + \text{HI}$, it follows that the iodostannous acid is stable at higher temperatures in contact with stronger acid. This is, of course, to be expected, since the stronger acid would exert greater pressure than would the weaker acid, against the entrance into the solution of new molecules of acid.

That decomposition of the solid iodostannous acid begins at temperatures lower than that at which it becomes wholly decomposed is shown by the falling off of curve No. 1 from the normal between 15° and 20°. That no definite temperature of transition exists between the two systems



is very evident, since the transformation of the first system into the second involves a great change in the nature of the solvent by increasing the concentration of the hydriodic acid and of the iodostannous acid, and by introducing a new factor, namely, stannous iodide. The transition is thus a gradual one, occurring over a considerable range of temperature. This is indicated by curve No. 1.

The falling solubility with increasing temperature from the point of complete change of the solid iodostannous acid into solid stannous iodide, must probably be taken to mean that even after the complete change has taken place in the solid forms, there remains in the solution more or less unchanged iodostannous acid. This becomes gradually transformed into stannous iodide and hydriodic acid, and the solution becomes supersaturated as to stannous iodide, which separates, causing the fall in solubility. This continues until all iodostannous acid is decomposed, or more probably, until further decomposition does not supersaturate the solution, and from that point the solubility increases

with the temperature. The curve does not, however, represent the true solubility of stannous iodide until all the iodostannous acid in the solution has been decomposed. This point may or may not agree with that at which the curve begins to rise.

Another peculiarity shown by the curves, which needs explanation, is the lack of coincidence between the portions of curves No. 1 and No. 2, which coincide as to temperatures. The experiments from which the two curves were obtained were made with the same solvent; namely, hydriodic acid of 39.60 per cent. It would seem at first sight that the portions of the two curves lying between 15° and 20° should coincide. The explanation of the lack of coincidence is, however, perfectly apparent. In making the solutions amounts of stannous iodide more than sufficient to saturate the solvent were used. The amounts were taken at random, so that in the two cases there were undoubtedly different excesses of stannous iodide. On cooling the solutions, iodostannous acid not only separates from the solution, but whatever excess of stannous iodide in the solid form may be present, provided it be not too great, is also converted into iodostannous acid. Thus the greater the excess of stannous iodide, the greater the demands made upon the solvent for hydriodic acid, and consequently the greater the weakening of the solvent as to hydriodic acid. Therefore, although both series of experiments were started with the same acid, the nature of the solvent will differ in the two cases after the cooling and the solubilities will naturally vary also.

It will be noticed that the break in the curve No. 2, at about 20° is caused by a sudden fall in solubility, while that in No. 3 at 1.5° is caused by a sudden rise in solubility. The explanation of this is entirely analogous to the foregoing. The direction of the change in solubility depends upon the relative solubilities of the two systems in whatever solvent may exist under the conditions.

As a matter of fact these sudden breaks are probably fictitious, and show in the curves only because sufficient time was not given at lower temperatures and at the temperatures of the breaks to attain perfect equilibrium, and also because the readings were not taken sufficiently close together.

The results of the work so far show mostly only qualitative

relationships. It is hoped soon to carry out a more exhaustive investigation upon the point, and also upon the similar chlorine and bromine compounds.

STANFORD UNIVERSITY,
July 20, 1897.

A COMPARISON OF VARIOUS RAPID METHODS FOR DETERMINING CARBON DIOXIDE AND CARBON MONOXIDE.

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Received September 14, 1897.

THE value of gas analysis as an aid in the control and development of industrial processes is slowly being recognized by American manufacturers. Accompanying the increased use of this branch of analysis there seems to be, however, a tendency to adopt certain faulty methods of work to which it may be well to call attention. In industrial analyses chief stress will naturally be laid upon rapidity, and the accuracy demanded of the chemist will depend upon the nature of the work in hand. For example, in two processes in which carbon dioxide is regularly determined, it is sufficient in one case that the results be correct only within the range of one per cent., while in the other they should vary not more than one-tenth of one per cent. from the truth. In many cases, however, the analyst seems to be inclined to adopt some one form of apparatus and some one rapid method for the determination of each constituent and to adhere to this apparatus and method no matter what may be the conditions. Under such circumstances it is to be expected that the results obtained by different chemists on the same sample may show wide variations and even that the analyses of a single chemist, if his methods are not suited to the particular case in hand, may give rise to false deductions and cause financial loss to his employers. Difficulties similar to these were apparent, some years ago, in the analysis of iron and steel, and led to careful comparisons of the various methods by different chemists and to the development of standard methods of analysis. It was with the idea of making a beginning toward a similar comparison of some of the better known methods of gas analysis and of determining their relative accuracy and of ascertaining within what limits they might be relied upon, that Mr. Edgar undertook the