CXXXVII.—*The Interaction of Sulphuretted Hydrogen and Arsenic Pentoxide in presence of Hydrochloric Acid.*

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THE following investigation was the outcome of some observations on the separation of arsenic from commercial hydrochloric acid by treating it with sulphuretted hydrogen. It was found, as might have been expected, that the arsenic present in the tervalent condition was immediately and completely separated by the action of the gas. The arsenic present in the quinquevalent condition separated slowly, and appeared to be precipitated sometimes as arsenic pentasulphide, sometimes as the trisulphide mixed with sulphur. It appeared interesting to determine under what conditions each of these substances was formed, and, if possible, to investigate the mechanism of the reaction.

Brauner and Tomicek (Trans., 1888, 53, 145), who investigated the interaction of sulphuretted hydrogen with solutions of arsenic acid containing up to 8 per cent. of hydrochloric acid, found that in absence of hydrochloric acid, a solution containing 0.6 per cent. of arsenic pentoxide gave a precipitate which, after removing the free sulphur, consisted of 85 per cent. of the pentasulphide. In presence of 8 per cent. of hydrochloric acid, the precipitate consisted of the pure pentasulphide. They did not, however, carry out any experiments with more concentrated acid.

EXPERIMENTAL.

We have repeated and confirmed Brauner and Tomicek's work in the case of solutions of dilute hydrochloric acid, and have also

extended the investigation to solutions containing up to 32 per cent. of hydrogen chloride, obtaining in the latter case different, and interesting, results, which are given in the following table. The experiments were carried out at about 15°, and in every case the solution contained 0.3664 per cent. of the pentoxide.

HCl per cent.	Composition of precipitate.	HCl per cent.	Composition of precipitate.
1.8	As ₂ S ₅ , 91 per cent.	14.34	As ₂ S ₅ , pure.
7.9	As ₂ S ₅ , pure.	25.10	As ₂ S ₅ , 58 per cent.
10.76	As ₂ S ₅ , pure.	32.27	As ₂ S ₅ , pure.

The solution was contained in a flask, and sulphuretted hydrogen was slowly bubbled through the liquid at the rate of about five bubbles per second. After about twelve hours, the current of gas was stopped, and the precipitate was collected, washed with water and alcohol, and extracted for six hours in a Soxhlet's apparatus with carbon disulphide, the final product being analysed by the usual method.

Study of the Reaction in presence of Small Concentrations of Hydrochloric Acid.—The reaction between arsenic acid and sulphuretted hydrogen, which results in the formation of arsenious sulphide and sulphur, may be supposed to take place in two or more stages. Thus :

The second reaction and possibly an intermediate reaction involving the formation of arsenic trichloride do not concern us, as these reactions are certainly instantaneous.

The reaction which results in the formation of the pentasulphide may be written simply :

although it is probable that one is really dealing with a hydrated form of the pentoxide, and that the equation does not strictly represent the fact.

It was our object to investigate the conditions which favour reactions i and iii respectively, but although it might have been possible to throw some light on the matter by studying the reaction velocity with different concentrations, the experimental difficulties were considerable, and on account of the complex character of the reacting substance, we abandoned this idea.

It appeared probable that the action of the hydrochloric acid was negatively catalytic, either with regard to the oxidising action of the arsenic acid or to the reducing action of the sulphuretted hydrogen. In accordance with this view we first of all studied the reduction and oxidation of these two substances respectively in presence of varying concentrations of hydrochloric acid.

The reduction of a solution containing 0.684 per cent. of arsenic pentoxide by a solution of sulphur dioxide in presence of varying concentrations of hydrochloric acid was first studied. The results are as follows :

As ₂ O ₅ per cent.	SO ₂ per cent.	HCl per cent.	Result.
(a) 0.684	3.272	4.9	Complete reduction in 45'.
(b) 0.684	3.272	20.3	28.3 per cent. reduced in 45'.
(c) 0.684	3.272	32.0	Complete reduction in 45'.

The experiment *c* will be considered later. With regard to *a* and *b*, it is obvious that the rate of reduction of the pentoxide is considerably retarded by the presence of the hydrochloric acid.

We next investigated the rate of oxidation of sulphuretted hydrogen by iodine and by ferric chloride in presence of varying concentrations of hydrochloric acid. The sulphuretted hydrogen was in excess of the second reagent and the concentrations of the hydrochloric acid were 2 and 10 per cent. in the two samples. The time between the commencement of the experiment and the moment at which the last trace of iodine or ferric salt could be detected was observed. The presence of the hydrochloric acid appeared to have no effect on the velocity of the reaction.

It appears then that the effect of the presence of the hydrochloric acid in the reaction between arsenic acid and sulphuretted hydrogen is due to its influence on the arsenic acid. It does not appear possible to give a more detailed explanation, for although arsenic acid is a fairly strong acid, and in dilute solution may be considered as undergoing dissociation, the influence of the increase in concentration of the hydrogen ions, due to the addition of hydrochloric acid, in reducing the concentration of the arsenic-containing ions throws no light on the mechanism of the reaction.

A few experiments were made with solutions containing larger quantities of pentoxide. It is unnecessary to enter into the details of these experiments; it suffices to state that, as might have been expected, the tendency to form the trisulphide increased with the concentration of the pentoxide.

Study of the Reaction in presence of Concentrated Hydrochloric Acid.

It has been observed that the reaction of arsenic acid with either sulphuretted hydrogen or sulphur dioxide in presence of concentrated hydrochloric acid results in its complete and rapid reduction to arsenious compounds.

This reaction probably finds an explanation in the fact that the change may be represented by the equation

which is accompanied by further instantaneous reactions, involving the formation of the trisulphide and sulphur from the sulphuretted hydrogen.

It appears that the condition of equilibrium expressed by the foregoing equation shifts rapidly to the right with increasing concentration of the hydrochloric acid. A small quantity of the dry pentoxide sealed up in a glass tube with pure anhydrous hydrogen chloride in the liquid state was rapidly acted on at the ordinary temperature. After a few hours, the white solid had disappeared, and the tube contained two immiscible layers of liquid.* On cooling the tube in liquid air, breaking off the point, and allowing the tube to regain the ordinary temperature, hydrogen chloride and chlorine, which formed the upper (yellow) layer, were first given off; the gas, however, did not contain arsenic. The contents of the tube were then washed out and were found to contain a solution of an arsenious compound.

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