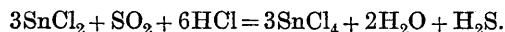


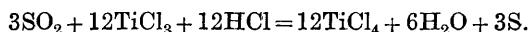
CXXIV.—*The Oxidising Properties of Sulphur Dioxide.* *Part I. Iron Chlorides.*

By WILLIAM WARDLAW and FRANCIS HERBERT CLEWS.

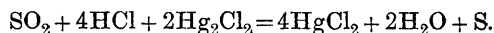
As this paper has to deal with the reactions of sulphur dioxide and metallic chlorides, it may be well to summarise our present knowledge relative to this subject. The oxidation of stannous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid has been shown (Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1914, **5**, 187) to proceed quantitatively to completion according to the equation



Sulphurous acid is reduced by titanous chloride to hyposulphurous acid (Knecht, *Ber.*, 1903, **36**, 166), and its further reduction to sulphur was noticed by the same investigator. Smythe and Wardlaw (*loc. cit.*) further proved that when sulphur dioxide is passed into a warm, strongly acid solution of titanous chloride hydrogen sulphide is freely evolved. Sulphur is formed by secondary reaction between the hydrogen sulphide and the sulphur dioxide, and if the escaping hydrogen sulphide is led into an excess of sulphur dioxide in concentrated hydrochloric acid, the reaction which goes to completion may be quantitatively summarised as follows:



The same authors (*loc. cit.*) have shown that sulphur dioxide oxidises mercurous chloride in the presence of concentrated hydrochloric acid according to the equation



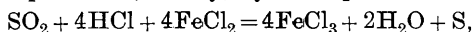
In the same paper it was mentioned that in concentrated hydrochloric acid, ferrous chloride is oxidised by sulphur dioxide to ferric chloride, with the formation of sulphur. No sulphuric acid was detected in the solution. This reaction differed from those already quoted in that oxidation under the most favourable conditions proceeded only to a limited extent, the average yield of ferric iron in all the experiments being 7 per cent. of the total iron present, the extremes being 4 and 11.6 per cent. In these experiments, rigid control was not exercised over the conditions of temperature, concentration, etc., and it seemed desirable, therefore, that a systematic investigation of this reaction should be carried out.

EXPERIMENTAL.

The general method of procedure was as follows. Pure electrolytic iron was dissolved in pure concentrated hydrochloric acid contained in a flask made entirely of glass, and such that the reacting gases could be passed through the solution contained in it. This was connected with wash-bottles containing water and sodium hydroxide solution respectively. These served to absorb the effluent sulphur dioxide and hydrogen chloride and to exclude air, and so prevent atmospheric oxidation. The temperature of the flask was controlled by immersion in an oil-bath. A stream of carbon dioxide was continuously passed through the apparatus during the solution of the metal. When the iron had completely dissolved, the flask was connected with a sulphur-dioxide syphon and the gas passed for a stated period. It was noticed that after the sulphur dioxide had passed for a few minutes the solution changed to olive-green, then to reddish-brown, and became distinctly opalescent, owing to the separation of sulphur. After the reaction had proceeded for the required time, the sulphur dioxide was displaced by carbon dioxide, the solution cooled in a stream of the same gas, and the iron titrated, after suitable dilution with air-free water, with standard potassium dichromate according to Zimmermann and Reinhardt's method. The sulphur was determined by filtration and direct weighing.

Quantitative Aspect of the Reaction.

There are two possible reactions involved, corresponding (a) with direct reduction of the sulphur dioxide to sulphur, and (b) with initial reduction of the sulphur dioxide to hydrogen sulphide, which reacts with excess of sulphur dioxide, forming sulphur. Both reactions are represented, finally, by the equation



so that it is impossible to decide quantitatively between the two. Moreover, owing to the fact that the limit of reaction has been shown to be so soon reached, the accurate estimation of the small quantity of sulphur is very difficult.

The following are examples of the results obtained by Smythe and Wardlaw (*loc. cit.*).

TABLE I.

Experiment.	Concentration of ferrous solution.	Ferric iron produced. Gram.	Sulphur.	
			Found. Gram.	Calc. Gram.
1	5.893 grams Fe per 100 c.c.	0.683	0.062	0.098
2	4.458 " " 200 c.c.	0.392	0.040	0.056
3	5.450 " " 200 c.c.	0.340	0.035	0.048

The conclusion to be drawn is that the equation mentioned above represents the reaction. From general considerations, one is also led to infer that it undoubtedly follows the course (a). Although hydrogen sulphide has never been directly detected in the reaction, from the fact that sulphur is formed in the neck of the flask and in the outlet tubes, it is possible that the reaction follows the course (b) to a very limited extent.

Influence of Concentration of Total Iron.

A range of concentrations of iron was investigated by dissolving varying quantities of iron (1—10 grams) in 250 c.c. of concentrated hydrochloric acid. Sulphur dioxide was passed through the solution for four hours at 115°, and the amount of ferric salt subsequently determined by titration.

TABLE II.

Experiment.	4.	5.	6.	7.	8.
Grams of iron dissolved in 250 c.c. of acid	1	3	5	7	10
Ferric iron per cent.	5.3	4.2	3.4	3.3	3.6

These results tend to show that the limit of oxidation is not influenced by the initial concentration of the iron. The concentration of the hydrochloric acid is not exactly constant in these experiments, owing to the varying losses of hydrogen chloride during the solution of the different quantities of metal, and this undoubtedly influences the degree of oxidation.

TABLE III.

Influence of Temperature.

Concentration.—Two grams of iron in 100 c.c. of concentrated hydrochloric acid.

Duration of Experiments.—Two and a-half hours.

Experiment	9.	10.	11.	12.	13.	14.	15.
Temperature	61°	70	79	93	115	125	gently boiling.
Ferric iron per cent....	1.6	3.0	3.5	5.2	3.8	3.0	2.8

The existence of an optimum temperature (approximately 95°) is the result of two or more opposing factors. The reaction-velocity will be favoured by an increase in temperature, whilst the higher temperature will lead to a more rapid loss of hydrochloric acid,

especially in the early stages of the reaction. It is also highly probable that the solubility of the sulphur dioxide decreases with rise in temperature.

Influence of the Concentration of Hydrochloric Acid.

The three following experiments are modifications of those described in table III with a view to change the concentration of hydrochloric acid. Values from table III are added for comparison.

TABLE IV.

Concentration.—Two grams of iron dissolved in 100 c.c. of concentrated hydrochloric acid.

Duration of Experiment.—Two and a-half hours.

Ex- peri- ment.	Description.	Tem- pera- ture.	Ferric iron Total iron $\times 100$.	From Table III. Ferric iron. Per cent.
16	Sulphur dioxide passed through concentrated hydrochloric acid at 95° before being led into the ferrous chloride solution	95° *	7.8	5.2
17	Mixture of hydrogen chloride and sulphur dioxide (60 per cent. of HCl by weight)* passed into ferrous chloride solution	115	4.7	3.8
18	Carbon dioxide passed through ferrous chloride solution at 115° for 30 minutes and then sulphur dioxide for 2½ hours	115	1.3	3.8

* In all cases the composition of gaseous mixtures of sulphur dioxide and hydrogen chloride will be expressed by the percentage of each constituent by weight.

The increased yields in experiments 16 and 17, and diminished yield in experiment 18, in which excess of hydrochloric acid is removed from the solution, show that the oxidising effect of sulphur dioxide is only appreciable at concentrations exceeding that of the mixture of constant boiling point.

Accordingly, in the next experiments (table V) iron was dissolved in hydrochloric acid diluted to the concentration of the mixture of constant boiling point, and a mixture of hydrogen chloride and sulphur dioxide in different proportions passed into the ferrous chloride solution.

The ratio of sulphur dioxide to hydrogen chloride was observed by diverting a small proportion of the gases, by means of a T-piece, while the experiment was in progress. The acid gases were absorbed in 50 c.c. of *N*-sodium hydroxide, the chloride being sub-

sequently titrated with standard silver nitrate and ammonium thiocyanate, and the sulphite with standard iodine and sodium thiosulphate.

TABLE V.

Concentration.—Two grams of iron dissolved in 100 c.c. of hydrochloric acid (22 per cent. HCl).

Duration of Experiment.—Four hours.

Temperature.—115°.

Experiment.	Percentage composition of mixed gases.		$\frac{\text{Ferric iron}}{\text{Total iron}} \times 100.$
	SO ₂ .	HCl.	
19	81.7	18.3	2.3
20	56.7	43.3	2.2
21	22.5	77.5	4.2
22	15.8	84.2	8.6
23	10.1	89.9	3.9

The results show that for the conditions described in the above experiments there is a comparatively narrow range of composition between 10 and 20 per cent. of sulphur dioxide which is most favourable for the oxidation of ferrous chloride, a maximum being reached in the neighbourhood of 16 per cent. of sulphur dioxide.

Limiting Concentration of Hydrochloric Acid for Oxidation of Ferrous Chloride by Sulphur Dioxide.

Since in dilute hydrochloric acid solution sulphur dioxide completely reduces ferric chloride to ferrous chloride, there will be

TABLE VI.

Temperature.—95°.

Duration of Experiment.—Four hours.

Solution.—Five grams of iron dissolved in acid specified in columns 2 and 3.

Experi- ment.	Concentrated hydrochloric acid. c.c.		Water. c.c.	Free HCl in 1000 c.c. of solution. Gram.	Remarks.
40	160	+	90	210.5	Little oxidation; about 0.5 per cent.
41	140	+	110	179.3	Very little oxidation; not measured.
42	130	+	120	165.8	Minute oxidation as shown by sulphur deposit.
43	125	+	125	165.1	No oxidation as shown by sulphur deposit.

some concentration of acid below which it is impossible to observe the oxidation of ferrous chloride by sulphur dioxide.

Iron was dissolved in acids of different concentrations, and the action of sulphur dioxide for four hours at 95° was observed.

For the analysis, a portion of the solution was withdrawn, weighed, and, after removal of the sulphur dioxide, diluted to a convenient volume. The iron and total chloride were determined, and from the difference the "free" hydrochloric acid was calculated. The specific gravity of the remainder of the solution was determined in order to state the concentration in grams per litre (see table VI).

It is concluded that oxidation by sulphur dioxide does not occur in ferrous chloride solutions containing less than 165 grams per litre of "free" hydrogen chloride.

Limit of Oxidation of Ferrous Chloride by Sulphur Dioxide in Hydrochloric Acid Solution.

(a) *Experiments at Atmospheric Pressure.*—With the purpose of determining the limit of oxidation, use was made of a rather larger flask fitted with a water-cooled exit tube, and containing an amount of solution sufficient to provide two samples for analysis.

Five grams of iron dissolved in 250 c.c. of concentrated hydrochloric acid (33 per cent.) were treated with hydrogen chloride and sulphur dioxide at 115°, as described in the following experiments

TABLE VII.

Experi- ment.	Description.	Time of taking sample from commence- ment of experiment.	Ferrie iron Total iron $\times 100$.
24	Hydrogen chloride and sulphur dioxide (80 and 20 per cent.) passed continuously into ferrous chloride solution.	4 hours	2.2
		8 "	3.0
25	Hydrogen chloride and sulphur dioxide (50 per cent.) passed into ferrous chloride solution.	4 "	4.3
		6½ "	4.1
26	Sulphur dioxide alone passed for half an hour, then hydrogen chloride and sulphur dioxide (50 per cent.) continuously.	4 "	4.8
		8 "	4.7
27	Sulphur dioxide alone passed for half an hour, then hydrogen chloride and sulphur dioxide (80 and 20 per cent.)	3 "	3.5
		6½ "	7.1

TABLE VII (*continued*).

Experi- ment.	Description.	Time of taking sample from commence- ment of experiment.	Ferric iron Total iron $\times 100$.
28	*The ferrous chloride solution was alternately cooled to 30° (1 hour) and then quickly raised to 115° (heated for 2 hours), hydrogen chloride and sulphur dioxide (50 per cent. of each) passed continuously).	3 hours	6.5
		6 „	7.0
29	Experiment 28 repeated but cooled for 1 hour and heated to 115° for 1 hour.	6 „	8.8

* This procedure enabled the solution to absorb a large amount of the gases at the lower temperatures. On rapidly raising the temperature to 115° the solubility values would not be attained immediately, and during this interval the temporarily increased concentration of hydrochloric acid and sulphur dioxide would be available for reaction with the ferrous salt.

An oxidation of 8.8 per cent. (in experiment 29) is the highest obtained by the action of sulphur dioxide on ferrous chloride operating under a pressure slightly in excess of the atmospheric.

† (b) *Experiments with Sealed Tubes*.—A rather higher degree of oxidation was obtained by the use of a sealed tube.

Expt. 30.—Half a gram of iron was dissolved in 10 c.c. of concentrated hydrochloric acid in a Carius tube in a current of carbon dioxide. The tube was immersed in ice, the solution saturated with sulphur dioxide, and the tube sealed. It was then heated at 100° for six hours and allowed to cool overnight. Titration showed that oxidation had occurred to the extent of 9.5 per cent., a value only slightly in excess of those obtained under normal pressures.

Limit of Reduction of Ferric Chloride by Sulphur Dioxide in Concentrated Hydrochloric Acid Solution.

(a) *Experiments under Atmospheric Pressure*.—It is well known that excess of hydrochloric acid prevents the complete reduction of ferric chloride by sulphur dioxide (Treadwell and Hall, "Quantitative Analysis," 5th ed., p. 607, footnote). It was not known, however, to what concentration of hydrochloric acid this referred or the extent to which ferric chloride was reduced.

Since the reduction of ferric chloride in concentrated hydrochloric acid was found to proceed slowly, mixtures of ferrous and ferric chlorides were prepared and their compositions determined,

both before and after passing sulphur dioxide and hydrogen chloride (approximately 50 per cent. of each gas) for a definite time. By this means, the value to which the reduction would eventually attain was estimated.

TABLE VIII.

Concentration.—Five grams of iron in 250 c.c. of hydrochloric acid (33 per cent.).

Temperature.—115°.

Gas.— $\text{SO}_2 + \text{HCl}$ (50 per cent. mixture).

Experi- ment.	Duration of experiment. Hours.	$\frac{\text{Ferric iron}}{\text{Total iron}} \times 100.$		Reduction gradient (average reduction per hour).	Remarks.
		Initial value.	Final value.		
31	4.0	100.0	78.2	5.4	Sulphate formed.
32	4.0	72.2	68.3	0.98	"
33	6.3	53.8	48.5	0.84	"
34	4.0	42.1	39.3	0.70	"
35	6.0	20.7	18.3	0.40	"
36	2.5	18.3	18.3	—	—
37	5.6	10.8	10.7	—	No sulphate.

No sulphur was formed in any of the above experiments. Apparently iron solutions containing more than 18.3 per cent. of ferric iron are slowly reduced by sulphur dioxide in the presence of concentrated hydrochloric acid. There seems also to be a range of from 10 to 18.3 per cent. of ferric iron in which there is no evidence of reduction or oxidation by the sulphur dioxide during the time of the experiments. Evidently this represents a zone in which the rate of reaction of the sulphur dioxide is very slow.

The solution in experiment 37 was analysed, and it was shown to contain in 1 litre 239 grams of "free" hydrochloric acid and 0.314 gram of sulphur dioxide.

(b) *Experiments in Sealed Tubes.*—Five grams of ferric chloride were dissolved in 10 c.c. of hydrochloric acid (33 per cent.), and the solution was saturated with sulphur dioxide at 0°. The tube was sealed and heated to 110° for four hours. Analysis showed a reduction of 20.6 per cent., and sulphuric acid was detected in the solution. A similar experiment after twenty-five hours at 110° gave only 22.3 per cent. of reduction. Apparently the high concentration of hydrochloric acid which exists in a closed vessel inhibits the reduction by sulphur dioxide, just as a high concentration of acid appears also to favour the oxidation of ferrous chloride.

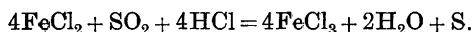
Reduction of Ferric Chloride by Sulphur.

Stokes (*Bull. U.S. Geol. Survey*, No. 186, 1901) has examined the action of pyrites and marcasite on a hot dilute solution of ferric chloride, and observed reduction to a considerable extent (65 per cent. of the sulphur), the sulphur being oxidised to sulphuric acid. The present authors find that the action of sulphur in concentrated hydrochloric acid on ferric chloride is slight.

A solution of 5 grams of ferric chloride in 50 c.c. of concentrated hydrochloric acid was boiled in an atmosphere of carbon dioxide for one and a-half hours. The reduction corresponded with 0.65 per cent., the sulphur being oxidised to sulphuric acid. A solution of 3 grams of ferric chloride in 50 c.c. of concentrated hydrochloric acid to which 50 c.c. of colloidal sulphur solution were added, on boiling for one and a-half hours resulted in 1.7 per cent. of reduction. Sulphuric acid was produced. Experiments on the lines of those shown in table VIII, in which a proportion of finely divided sulphur was added, showed that it exerted very little reducing action in comparison with the sulphur dioxide.

Summary.

(1) The oxidation of ferrous chloride by sulphur dioxide can be represented quantitatively by the equation



(2) The degree of oxidation is independent of the initial concentration of total iron.

(3) The most favourable temperature for the oxidation by sulphur dioxide of a solution of ferrous chloride in 33 per cent. hydrochloric acid is 95°.

(4) Oxidation by sulphur dioxide at 95° does not occur in solutions of ferrous chloride containing less than 165 grams per litre of "free" hydrogen chloride.

(5) A solution of ferrous chloride in hydrochloric acid of constant boiling point (22 per cent.) at 115° gave a maximum oxidation of 8.6 per cent. (ferric iron) when treated with a mixture of sulphur dioxide and hydrogen chloride containing 16 per cent. of sulphur dioxide.

Mixtures containing 10 to 20 per cent. of sulphur dioxide are most favourable for oxidation under the above conditions.

(6) The highest percentage of ferric iron obtained in any of the flask experiments recorded in this paper was 8.8. This result was produced by treatment of a ferrous chloride solution in 33 per cent.

hydrochloric acid at 115° with a 50 per cent. mixture of sulphur dioxide and hydrogen chloride under special conditions.

(7) Sealed-tube experiments gave a maximum oxidation of 9·5 per cent. of ferric iron.

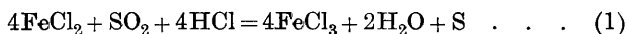
(8) Iron solutions containing 10 to 18·3 per cent. of ferric iron in 33 per cent. hydrochloric acid at 115° showed no evidence of oxidation or reduction when a 50 per cent. mixture of sulphur dioxide and hydrogen chloride was passed into them for varying periods.

(9) Under the same experimental conditions as in (8), iron solutions containing more than 18·3 per cent. of ferric iron were slowly reduced.

(10) Ferric chloride in concentrated hydrochloric acid was reduced to a small extent by sulphur.

Theoretical.

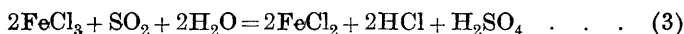
The oxidation of a ferrous chloride solution by sulphur dioxide has been shown to be quantitatively represented by the equation



Moreover, since sulphur is able to reduce ferric chloride to some extent, it seems justifiable to assume that the above equation is reversible.



This fact is generally obscured, however, by the more general equation

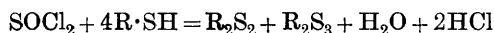


Since no sulphuric acid is detected when a pure ferrous chloride solution is oxidised by sulphur dioxide in the presence of concentrated hydrochloric acid, it can be assumed that under these conditions the reaction that occurs is solely represented by equation (2). Moreover, seeing that sulphuric acid is only detected when sulphur dioxide in the presence of concentrated hydrochloric acid reacts with iron solutions containing more than 18·3 per cent. of ferric iron, it appears that reaction (3) is only operative in such solutions.

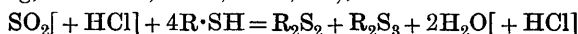
The idea that a reversible reaction takes place when pure ferrous chloride solution is oxidised by sulphur dioxide receives added support from the fact that only a limited yield of ferric salt is possible, and that the reaction is not greatly influenced by the initial concentration of total iron. Applying the law of mass action to equation (2), it appears that for a given concentration of sulphur dioxide and hydrogen chloride the equilibrium position would be

determined solely by the ratio of ferrous to ferric iron, assuming that the active masses of the sulphur and water are constant. The importance of a high concentration of hydrogen chloride to bring about the oxidation also follows logically from the idea of a balanced reaction.

The dependence of sulphur dioxide as an oxidising agent on a high concentration of hydrochloric acid has led to the suggestion that hydrochloric acid and sulphur dioxide interact, forming thionyl chloride to a small extent (Smythe and Wardlaw, *loc. cit.*). This idea receives support from the following reactions with the mercaptans:

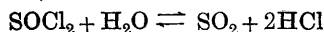


(Holmberg, *Annalen*, 1908, **359**, 81),

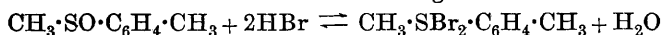


(Smythe and Forster, T., 1910, **97**, 1195).

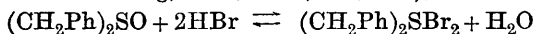
On this assumption, the reaction



must be reversible. Although this has not been proved directly, there is some indirect evidence in that when thionyl chloride reacts with mercaptans at low temperatures (0° to -70°), hydrogen chloride and sulphur dioxide are evolved, and water is found among the residual products (Tasker and Jones, T., 1909, **96**, 1904, 1910). In addition, the reactions of the sulphoxides and the haloid acids are to some extent analogous.



(Zincke and Frohneberg, *Ber.*, 1910, **43**, 837),



(Fromm and Raiziss, *Annalen*, 1910, **374**, 90; Fromm, *ibid.*, 1913, **396**, 75).

From this idea, the question arises as to whether the oxidising properties of sulphur dioxide are only operative in the presence of concentrated hydrochloric acid. Experiments have been in progress to determine this point, and the results will be communicated in a further paper.

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