XVI.—*On Manganese Trioxide.*

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THE chemical changes attending the action of sulphuric acid upon dry potassium permanganate have been variously described by different observers. It would seem, in the first place, that the nature of the reaction is very considerably modified by the purity of the salt and the strength of the acid. Wöhler (*Annalen*, **86**, 373) observed that when concentrated oil of vitriol was poured over the crystallised salt, the permanganate was decomposed with explosive violence and with the evolution of much heat and even flame, and the formation of a

cloud of finely divided oxide of manganese. Large quantities of oxygen were simultaneously disengaged. Hence Wöhler concluded that free permanganic acid is a gas which at the moment of its liberation is decomposed by the heat of the reaction into oxygen and manganese dioxide. It is not improbable that the phenomena thus described by Wöhler were to some extent caused by the presence of chlorate or perchlorate of potassium in the permanganate. Pure dry potassium permanganate readily and quietly dissolves in the concentrated acid without any very extraordinary rise of temperature. If concentrated sulphuric acid be used, a clear sage-green solution will be obtained. If the monohydrated acid, $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, is employed, the colour of the solution is dark-brown, and it is seen to contain a number of oily drops which gradually sink, forming a dark reddish-brown liquid which remains fluid at -20° . This substance is extremely unstable: on exposure to the air, it slowly evolves oxygen, and the gaseous bubbles as they burst at the surface of the liquid form a violet-coloured cloud. It is highly hygroscopic, and gradually decomposes under the action of the attracted moisture. On dropping it into water, it dissolves with a purple colour, and with the evolution of so much heat that it suffers partial decomposition. Its solution, even when dilute, is gradually but completely resolved on heating into manganese dioxide and oxygen. It dissolves in concentrated sulphuric acid without decomposition, forming the olive-green or sage-green solution before mentioned. It is apparently non-volatile: it may be heated under reduced pressure to about 60° or 65° without the slightest evolution of vapour. At higher temperatures, it is decomposed with a sudden and violent explosion into oxygen and manganese dioxide. The rapidity of the decomposition is probably due to the action of the separated manganese oxide, since Thenard has shown that a minute quantity of this substance when added to the liquid instantly resolves it, even in the cold, into oxygen and manganese dioxide. Silver oxide acts in the same way. It sets fire to paper, and explodes with sulphuretted hydrogen and the vapours of alcohol and ether.

The composition of this body was first correctly ascertained by Aschoff (*Pogg. Ann.*, 3, 217). On analysis, it gave numbers in exact accordance with the formula of manganese heptoxide, Mn_2O_7 .

If potassium permanganate is dropped in small quantities at a time into pyrosulphuric acid, or oil of vitriol to which sulphuric anhydride has been added, as each successive portion of the salt reaches the acid, flames are emitted, together with a cloud of sulphur trioxide, darkened in colour by particles of manganese dioxide. The solution obtained is of a lavender-blue colour, and on standing deposits a pink-coloured salt; this on treatment with cold water

forms a deep brown solution which ultimately deposits brown oxide of manganese.

According to Franke (*J. pr. Chem.*, **14**, 1887), the dark-green solution obtained by the action of concentrated sulphuric acid upon potassium permanganate contains an oxysulphate of manganese of the composition $(\text{MnO}_3)_2\text{SO}_4$, but no direct evidence for the existence of this compound is adduced by him. The possibility of its existence seems to be mainly based upon the fact that the analogously constituted oxychloride, MnO_3Cl (Aschoff), and oxyfluoride, MnO_3F (Wöhler), are known. The difference between the colours of the solutions obtained by using the concentrated and the monohydrated acids may also be held to indicate differences in the chemical nature of the solutions.*

On cautiously adding a small quantity of water to the well-cooled green solution, manganese heptoxide is obtained. Its formation, according to Franke, may be thus expressed:—

Hence we may thus explain the production of permanganic anhydride by the use of monohydrated sulphuric acid, and its non-formation when the concentrated acid is employed.

On very cautiously heating the dark-green solution of the permanganate in sulphuric acid in a current of moist air, it gives off small quantities of a violet-coloured body—*apparently* gaseous, which can be condensed in a well-cooled receiver, when it forms a dark-red somewhat viscid mass. This substance was regarded by Terreil as permanganic acid, HMnO_4 (*Bull. Soc. Chim.*, 1862, 40), but as it can also be obtained, according to Aschoff, by the gradual decomposition of the heptoxide, it is probably free from hydrogen.

According to Franke this compound is manganese trioxide, MnO_3 . Its formation from the green-coloured solution may be expressed as follows:—

and from the heptoxide thus:—

All observers agree that its formation is invariably accompanied by the evolution of oxygen, which, according to Schönbein and Böttcher, is strongly ozonised. Subsequent observations have shown that the

* Franke explains the formation of the oxysulphate by the equations—

oxygen is quite free from ozone, the ozone reactions being caused by the evolved manganese compounds, or probably in certain cases by chlorine or its oxides.

On treating the condensed manganese trioxide with water, it is at once decomposed into manganese dioxide and permanganic acid—

Franke, in his first paper (*loc. cit.*) states that the heptoxide is decomposed into manganese dioxide and trioxide, and a blue gas giving certain of the reactions of ozone, but differing from that substance in being decomposed at 150° and in being soluble in concentrated sulphuric acid. In a subsequent paper (*loc. cit.*, p. 166), he regards this blue gas, which he also obtained by the action of moist air upon the sulphuric acid solution of potassium permanganate, as *manganese tetroxide*, and represents its formation thus :—

According to Franke, the blue gas is best made by passing a stream of carbonic acid gas saturated with moisture on to the surface of the olive-green liquid, and leading the escaping gases through two U-tubes, one of which is empty, and the other filled with calcium chloride. The manganese trioxide condenses in the first tube, whilst the second retains the tetroxide. No analyses of this compound are given. It is said to be more volatile than the trioxide, to be more blue in colour, and to be less readily attacked by water.

A manganiferous gas of a blue colour seemed to be a sufficiently remarkable substance to merit further investigation. We have been led therefore to repeat Franke's experiments, but although we have carefully followed the directions given for its preparation, we have not been so fortunate as to observe the slightest indication of a blue gas, or to obtain any evidence of the existence of manganese tetroxide.

We have, however, succeeded in obtaining manganese trioxide. As our conclusions, however, differ in certain particulars from those of Franke, it may be desirable to describe our experiments in detail.

The first method described by Franke of leading moist carbonic acid gas on to the surface of the solution of potassium permanganate, and collecting the product in empty U-tubes, gave such an extremely small yield of the new oxide, that it seemed hopeless to expect that quantities sufficient even for analysis could be so made. Better results were obtained by the second method. This consists in dropping the acid solution of the permanganate, contained in a tap funnel, on to dry sodium carbonate. As each drop of the solution comes in contact with the carbonate, a slight burst of pink-coloured fume is observed,

which is mechanically carried forward in the current of carbonic acid. After a time the evolution of the coloured fume ceases, but on attaching a fresh flask containing sodium carbonate it can be renewed—

In order to collect the oxide, the evolved products were passed through a small U-tube filled with fragments of broken glass and immersed in a mixture of ice and salt. If the broken glass be omitted, the greater portion of the pink fume passes through the apparatus along with the carbonic acid. The freezing mixture is necessary to retard the decomposition of the condensed product, since at ordinary temperatures it gradually loses oxygen, and is converted into manganese dioxide. The curious behaviour of the pink fume has led us to conclude that it is really an extremely finely-divided solid. It floats in the air like a cloud of sal-ammoniac or sulphur trioxide, and like these substances may, if suspended in a sufficiently large volume of air or carbonic acid, be passed through water practically unabsorbed.

The U-tube containing the broken glass was connected with a second U-tube containing dilute sulphuric acid, and immersed in ice-cold water. The flask containing the sodium carbonate was also surrounded by cold water in order to moderate the intensity of the action, and prevent as far as possible rise of temperature. This form of apparatus was adopted after a number of trials with other arrangements, as it was found to be best adapted to the plan of analysis which we employed in order to ascertain the composition of the condensed product.

The amount of the oxide obtained even from a well-conducted operation is so very small that the ordinary gravimetric methods for the estimation of manganese are difficult of application. If large quantities of the strongly acid solution be allowed to come in contact with the carbonate at a time, the local heating is so great that the product is liable to be contaminated with manganese dioxide; on the other hand, if the operation be unduly prolonged, the same oxide is apt to be formed by the gradual decomposition of the trioxide. Fortunately we have in Chatard's process a volumetric method of estimating even minute quantities of manganese with a high degree of accuracy. This method consists in boiling the solution containing the manganese compound, which should be free from chlorine, with nitric acid and lead dioxide, and determining the amount of permanganate formed by means of a decinormal solution of ammonium oxalate. A preliminary examination of this method enabled us to determine the conditions under which it was applicable to the present case (see p. 182).

The details of one of the experiments in which the trioxide was prepared and analysed will serve to show the mode in which the operations were carried out.

Six grams of potassium permanganate, free from perchlorate, were dissolved in 100 c.c. of concentrated sulphuric acid, and the solution allowed to drop from a tap-funnel on to dry sodium carbonate contained in a distilling flask. The carbonic acid carrying with it the oxide of manganese was first passed through a U-tube filled with fragments of glass and immersed in a mixture of ice and salt; the oxide of manganese which escaped condensation then passed through 20 c.c. dilute sulphuric acid contained in a bulbed U-tube. The product in the first U-tube was then treated with water, the solution filtered through glass wool and titrated with ammonium oxalate (1 c.c. = 0.0088 O or 0.001558 MnO). The solution required 11.5 c.c. of the oxalate solution for decolorisation. On reoxidation with nitric acid and lead oxide, it needed 11.4 c.c.

Available oxygen	0.01012
MnO	0.01776
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MnO _x	0.02788

$$0.01776 \text{ MnO} = 0.01375 \text{ Mn.}$$

$$\text{Per cent. Mn} = \frac{0.01375 \times 100}{0.02788} = 49.3.$$

$$\text{Per cent. O} = \frac{0.01413 \times 100}{0.02788} = 50.7.$$

The acid solution decanted from the bulbed U-tube was titrated with the standard ammonium oxalate, of which it required 4.8 c.c. for decolorisation. After reoxidation by lead dioxide and nitric acid, 6.15 c.c. were required—

$$\begin{aligned} \text{Available oxygen} &= 0.00088 \times 4.8 = 0.00422 \\ \text{MnO} &= 0.001558 \times 6.15 = 0.00958 \end{aligned}$$

$$0.00958 \text{ MnO} = 0.00742 \text{ Mn.}$$

$$\text{Per cent. Mn} = \frac{0.00742 \times 100}{0.0138} = 53.8.$$

$$\text{Per cent. O} = \frac{0.00638 \times 100}{0.0138} = 46.2.$$

The results of the various analyses made in this way are seen in the following table:—

	In aqueous solution.		In acid solution.	
	P. c. Mn.	P. c. O.	P. c. Mn.	P. c. O.
Experiment I	49·3	50·7	not determined	
" II	49·1	50·9	53·9	46·1
" III	48·8	51·2	not determined	
" IV	49·3	50·7	53·8	46·2
" V	49·6	50·4	53·1	46·9
" VI	49·0	51·0	52·8	47·2
" VII	49·3	50·7	52·5	47·5
" VIII	49·3	50·7	52·7	47·3
" IX	49·4	50·6	52·9	47·1
" X	not determined		52·5	47·5*

Means—

Aqueous Solution.

	Found.	Mn ₂ O ₇ calculated.
Mn	49·25	49·46
O	50·74	50·54
	99·99	100·00

Acid Solution.

	Found.	MnO ₃ calculated.
Mn	53·03	53·31
O	46·97	46·69
	100·00	100·00

From these results, it appears that when a solution of potassium permanganate in concentrated sulphuric acid is dropped on to dry sodium carbonate, manganese trioxide is formed in very small quantities as a reddish-pink cloud. The finely-divided powder is deposited upon the smaller glass tubes of the apparatus as a reddish, amorphous, deliquescent mass. The substance appears to be fairly stable when kept in a freezing mixture, but at ordinary temperatures it slowly decomposes. As obtained in a U-tube kept in a freezing mixture, it has upon the sides of the tubes a reddish-pink colour by transmitted light, but at the bottom of the tube where the greater part collects, the colour by reflected light is almost black. Treated with water, it is decomposed in accordance with the equation—

* Vapour passed directly into the acid, *i.e.*, without intermediate U-tube.

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The validity of this equation was experimentally verified. The manganese dioxide obtained on treating the product formed in Experiment VIII with water was determined: the ratio of its amount to that in solution as permanganic acid was exactly as 1 to 2.

When the substance is absorbed by dilute sulphuric acid, a clear pink or reddish-pink solution is obtained, in which the manganese and oxygen are in the ratio of 1 to 3. There is no evidence to show that this solution contains free manganic acid. If the substance were decomposed as in the aqueous solution, the ratio of O to Mn would be as 1 to 3, provided that all the manganese were retained in solution.

When manganese trioxide is dissolved in concentrated sulphuric acid, it forms a solution of the same colour as that obtained on dissolving potassium permanganate in oil of vitriol. This may be regarded as additional evidence for the existence of $(\text{MnO}_3)_2\text{SO}_4$. The substance is soluble in caustic potash, and gives a green solution similar to that of potassium manganate.

Manganese trioxide gives the reactions for ozone: it affects mercury and liberates iodine from potassium iodide. It blackens silver, but the stain can be shown to be due to manganese dioxide.

There is no proof that ozone is liberated by the action of oil of vitriol upon pure potassium permanganate.