XXXII.—*The Combination of Sulphur Dioxide and Oxygen.*

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IN the course of a number of analyses involving the separation of sulphur dioxide and oxygen by means of a pellet of manganese dioxide, it was noticed that the amount of gas absorbed was always greater than the amount of sulphur dioxide present, some of the oxygen being taken up and sulphuric acid formed. Part only of the sulphur dioxide was absorbed in accordance with the equation $\text{SO}_2 + \text{MnO}_2 = \text{MnSO}_4$, the rest combined with oxygen in a manner that suggested surface action on the part of the manganese dioxide, thus: $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$. This apparent surface action occurring in the cold, was thought to be of sufficient importance to deserve further investigation, especially as up to the present sulphur dioxide and oxygen are only known to combine directly at high temperatures.

I. ACTION OF SULPHUR DIOXIDE ON OXYGEN IN PRESENCE OF MOIST OXIDES.

The apparatus consisted of a laboratory vessel and eudiometer connected together and filled with mercury. Air was introduced into the

eudiometer and its volume measured; sulphur dioxide, delivered from a syphon of the liquid, was bubbled into the laboratory vessel, transferred to the eudiometer, and its volume measured. By introducing the gases in this order, and never having too great an excess of sulphur dioxide, the deviation of this gas from Boyle's law became very slight.

FIG. 1.

The gases were mixed thoroughly, and a small portion sent over into the laboratory vessel and allowed to stand for a few minutes in contact with a pellet of the substance under investigation; this portion was drawn off and the main portion measured and sent over. This preliminary treatment is necessary in order to avoid the disturbing effects of occlusion of gases by the pellet. Readings of the volume were taken from time to time, and finally the pellet was removed and caustic potash added to complete the absorption of the sulphur dioxide. The volume was again measured. From the data thus obtained, the amount of sulphur dioxide absorbed by the pellet and the amount of sulphur trioxide formed can be calculated.

In order to show that the substance formed is sulphuric acid, the pellets of pyrolusite, after exposure to the mixed gases, were left for $1\frac{1}{2}$ hours in a stream of dry carbon dioxide to remove any sulphur dioxide mechanically held, and then washed with water. Part of the washings was tested for sulphur dioxide with a strip of paper soaked in a potassium iodate and starch solution, and the rest with methyl-orange solution. Sulphur dioxide was found to be absent, and methyl-orange showed that the solution was strongly acid. Since manganese sulphate is neutral to this indicator, the acidity must be due to sulphuric acid.

It was next necessary to find out how much, if any, oxygen was taken up by the sulphur dioxide dissolved in the water present in the pellet, or by the potassium sulphite formed in the final operation. For this purpose, experiments were made as described above, but recourse was had to pellets of moistened silica instead of manganese dioxide, in order to match as far as possible the surface conditions under which the water acted. In no case did the absorption of oxygen exceed 1/15 of that observed in the experiments in which manganese dioxide was used. It is evident, therefore, that this absorption must be due to some action exercised by the manganese dioxide.

A series of experiments was next made with manganese dioxide in different states. We used the native oxide in experiments 1—14, and the precipitated oxide in experiments 15—18.

TABLE I.

No. of expt.	Vol. of air.	Vol. of SO ₂ .	SO ₂ absorbed (=MnSO ₄).	SO ₂ unchanged.	SO ₂ con- verted into SO ₃ .	Time of exposure.	Substance used.
1	93	100	56	39	5	40 mins.	Small pellet of pyrolusite.
2	93	"	60	30	10	40 "	Same sample, pellet double size.
3	107	"	47	47	6	60 "	Fresh sample, small pellet.
4	101	"	68	12	20	60 "	Same sample, pellet double size.
5	77	"	56	19	25	50 "	Pyrolusite, lump not moistened.
6	77	"	57	21	22	50 "	
7	60	"	91	2	7	10 "	Pyrolusite, powdered and made into pellet, moistened.
8	59	"	94	1	5	10 "	
9	94	"	67	26	7	6½ hrs.	The same, after standing 18 hours in air at ordinary temperatures.
10	56	"	44	47	9	18 "	The same, after standing 4 days in air at ordinary temperatures.
11	83	"	70	4	26	48 "	The same, after standing 21 days in air at ordinary temperatures.
12	81	"	58	26	16	18 "	Pyrolusite, moistened and dried for 2 hours at 100°.
13	76	"	28	66	6	18 "	
14	66	"	47	42	11	48 "	Precipitated MnO ₂ dried in air for 1 day.
15	78	"	84	1	15	15 mins.	
16	75	"	83	2	15	15 "	Precipitated MnO ₂ dried in air for 12 days.
17	76	"	87	3	10	15 "	
18	80	"	91	2	7	15 "	

The pellets used were about the size of a large pea, except in experiments 2 and 4, in which they had, as nearly as we could judge, about twice the surface of the others.

The conclusions we draw from this series of experiments are :

1. The percentage of sulphur trioxide formed depends on the extent of surface of the pellet (experiments 1—4).

2. Ordinary pyrolusite only slowly absorbs sulphur dioxide, but forms a large percentage of sulphur trioxide (experiments 5 and 6).

3. If the pyrolusite is moistened, the rate of absorption of sulphur dioxide very much increases, but the percentage of sulphur trioxide formed diminishes (experiments 7 and 8).

4. As the moisture is removed, either by slow evaporation in the air or by more rapid evaporation at 100°, the rate of absorption of sulphur dioxide diminishes, and the percentage of sulphur trioxide formed increases.

5. The oxide obtained by precipitation produces less sulphur trioxide than the native compound. This is probably accounted for by the difference in surface.

A second series of experiments was made, using lead peroxide. The commercial precipitated oxide was digested with dilute nitric acid, well washed with water, and allowed to stand in the air for the periods specified below :

TABLE II.

No. of expt.	Vol. of air.	Vol. of SO ₂	SO ₂ absorbed (= PbSO ₄).	SO ₂ unchanged.	SO ₂ con- verted into SO ₃ .	Time of exposure.	Substance used.
1	75	100	97	3	nil	15 mins.	Lead peroxide, dried for 2 days in air at the ordinary temperature.
2	85	"	98	2	"	15 "	
3	77	"	98	2	"	15 "	
4	79	"	98	2	"	15 "	
5	86	"	92	3	5	20 "	Same sample, dried for 20 days in air.
6	72	"	91	3	6	20 "	
7	97	"	95	2	3	15 "	Last sample moistened.
8	87	"	95	2	3	15 "	

The conclusions to be drawn are :

1. Lead peroxide, when freshly washed, causes practically no combination of sulphur dioxide and oxygen, hence its suitability for determining sulphur dioxide in gas analysis.

2. After standing for some time in the air, it becomes capable of causing the union of sulphur dioxide and oxygen.

3. Samples which have once acquired this property do not lose it at once on moistening.

We have frequently noticed, during gas analysis, that unless the lead peroxide is freshly washed, there is always a disappearance of oxygen even after moistening. This is in agreement with the results of experiments 7 and 8.

A third series of experiments was now carried out, to find out how far this surface action was a general property of the metallic oxides.

TABLE III.

No. of expt.	Vol. of air.	Vol. of SO ₂ .	SO ₂ absorbed by oxide.	SO ₂ unchanged.	SO ₂ converted into SO ₃ .	Time of exposure.	Substance used.
1	67	100	39	51	10	18 hrs.	Chromium dioxide, CrO ₂ .
2	77	"	88	12	nil	15 mins.	} Barium dioxide, moistened and dried 18 hours in air.
3	92	"	100	nil	"	25 "	
4	81	"	93	7	"	40 "	} *Stannic oxide washed with nitric acid.
5	84	"	78	22	"	2 hrs.	
6	94	"	85	15	"	45 mins.	} Chromium trioxide, CrO ₃ .
7	89	"	98	2	"	20 "	
8	124	"	90	10	"	15 "	} Barium hydroxide.
9	81	"	89	11	"	20 "	
10	66	"	4	96	"	60 "	} Granular copper oxide.
11	57	"	5	95	"	60 "	
12	95	"	96	4	"	2 hrs.	} Aluminium hydroxide dried at 100°.
13	90	"	94	6	"	25 mins.	
14	82	"	55	31	14	30 "	} Chromium hydroxide dried at 100°.
15	92	"	73	14	13	30 "	
16	82	"	74	20	6	40 "	} Ferric hydroxide dried at 100°.
17	61	"	80	16	4	30 "	
18	73	"	81	19	nil	25 "	} Same sample moistened.
19	73	"	70	27	3(?)	20 "	
20	83	"	41	50	9	3 hrs.	} Ferric oxide moistened.
21	77	"	51	36	13	25 mins.	

* On coming into contact with the sulphur dioxide, the stannic oxide became yellow in colour.

These results show :

1. That this surface action is exhibited only by the neutral peroxides MnO₂, PbO₂, and CrO₂, and by ferric and chromic oxides and hydroxides.

2. This surface action is very different from the ordinary oxidation of sulphur dioxide and of sulphites. Water, caustic potash, barium and aluminium hydroxides, and copper and tin oxides have all been exposed to mixtures of sulphur dioxide and oxygen, but under the conditions of these experiments no oxygen was taken up, although quantities of sulphur dioxide were in each case absorbed.

All the oxides so far investigated have absorbed sulphur dioxide, but this absorption has not invariably been accompanied by the surface action.

The next point was to find out whether this surface action could take place in the cold, unaccompanied by any absorption of sulphur dioxide by the reagent used.

Hæmatite, platinised pumice, platinised asbestos, and finely-divided platinum (obtained by slow reduction by means of sodium formate acting in the cold) were all tried with negative results. In the last case, some absorption of sulphur dioxide occurred, due, no doubt, to moisture adhering to the platinum, but oxygen was not absorbed.

We must, then, conclude that when this surface action takes place, it is dependent on a simultaneous combination of the oxide used with sulphur dioxide, and, in fact, seems to proceed simultaneously with this combination.

Discussion of the Results.

In the case of chromic and ferric hydroxides, the action might of course be due to the formation of a sulphite with subsequent oxidation to sulphate, but it then becomes difficult to understand why the percentage of sulphur trioxide should be less in experiments 18 and 19 than in experiments 16 and 17 in Table III; one would rather expect it to be the converse.

We have sought for some reason why there should be more combination over manganese peroxide than over lead peroxide, and more over lead peroxide than over barium peroxide. These three were selected because there can be no doubt that the reactions are simply the two already given, namely :

Surface conditions may account for the different amounts of sulphur trioxide formed, but we would suggest that the heat evolved by the combination of the sulphur dioxide with the peroxide may exert a considerable influence. The thermal data are :

The second only is the result of direct experiment (Tscheltzow, *Compt. rend.*, 1885, 100, 1459), the others are calculated from the figures given in Berthelot's "Thermochemie" (1897).

It has long been suspected, and recently proved, that the condition most favourable for the formation of sulphur trioxide from sulphur dioxide and oxygen in presence of spongy platinum is that the heat of reaction shall be conducted away as rapidly as possible. In the cases before us, it will be noticed that barium and lead peroxides rapidly absorb sulphur dioxide (15 to 30 minutes only being required) and disengage large quantities of heat. This sudden development of a large quantity of heat is not favourable to the formation of sulphur trioxide. Manganese peroxide, on the other hand, if fairly dry, only

slowly absorbs sulphur dioxide, and there is a smaller heat evolution ; this slow dissipation of a smaller quantity of heat favours the production of sulphur trioxide. If, however, the peroxide is moistened, its combination with the sulphur dioxide becomes more rapid and the heat is more quickly liberated so that the conditions are rendered unfavourable, and the percentage of sulphur trioxide diminishes.

A mixture of sulphur dioxide and oxygen affords an instance of "false equilibrium." There is no appreciable amount of combination, but if combination occurred, energy would be dissipated. The necessary factors for this seem to be certain conditions of surface and the constant addition of a limited supply of energy. Our experiments are interesting as showing that the latter can be supplied in the form of chemical energy from a simultaneous reaction, and need not be supplied in the form of heat.

II. EXPERIMENTS WITH DRIED SUBSTANCES.

Having found that the combination of manganese peroxide with sulphur dioxide ceases when moisture is absent, we proceeded to further test our conclusion that the formation of sulphur trioxide is dependent on a simultaneous combination of the peroxide with sulphur dioxide, by repeating some of the experiments given in Table I with carefully dried substances, and found that the surface action also ceased, there being no absorption whatever.

The manganese dioxide was prepared by two methods :

(a) Ignition of carefully recrystallised manganese nitrate, the temperature being raised by slow stages during 7 days to 120° , and finally kept for 6 hours at 155° .

(b) Precipitation by Volhard's method, manganese sulphate, nitric acid, and potassium permanganate being allowed to react under the conditions given in Wright and Menke's paper (Trans., 1880, 37, 22). The precipitated oxide was digested with nitric acid, washed by decantation, collected by the aid of the pump, and dried at 100° . In order to exclude dust during filtration, the funnel containing the substance was closed by a glass plate through which a hole had been drilled. A tube, fitting tightly through this, delivered air purified by passing through a long column of sulphuric acid.

The oxides thus obtained were placed in porcelain boats and kept sealed up in exhausted tubes with phosphorus pentoxide. After standing in a warm place for two or three weeks, they were introduced into the experimental tubes.

The sulphur dioxide was prepared by heating a concentrated solution of potassium hydrogen sulphite. A very steady stream of the gas is thus obtained and is easily kept under control.

The apparatus, shown in figure 2, was constructed from glass tubing which had been carefully washed with fuming nitric acid to remove dust and grease; after completion, it was again washed and then dried by heating in a large flame and passing a current of dry air. The bulb, A, contained sulphur dioxide standing over distilled phosphorus pentoxide, whilst B was filled with nitrogen and contained the manganese dioxide and more phosphorus pentoxide. The tap and stoppers were lubricated with deliquesced phosphorus pentoxide, and coated on the outside with a mixture of beeswax and vaseline to keep moisture

FIG. 2.

away from the lubricant and prevent sticking. The apparatus, with the tap closed, was allowed to stand for 15 days, and during this period the fluctuations of the gauge C, which of course were due to atmospheric changes only, were found to be small. The tap was then opened and the sulphur dioxide allowed to diffuse into B, the temperature and pressure being noted. The apparatus was left for a further period of about 15 days so as to give the sulphur dioxide ample time to react with the manganese peroxide, but without result, as the gauge showed practically no change in volume.

(1).—May 19, apparatus filled.

June 1, tap opened. Bar. 766.2 mm., temp. 19.4°, gauge 13 mm.

„ 13, „ „ 764.6 „ „ 19.6° „ 9 „

Eliminating the effect due to the change in atmospheric conditions, we find that, as a matter of fact, there is a slight increase in volume.

(2).—May 19, apparatus filled.

June 1, tap opened. Bar. 766.2 mm., temp. 19.4°, gauge 16.5 mm.

„ 13, „ „ 764.6 „ „ 19.6° „ 12.0 „

Here again the increase is slightly greater than it should have been.

(3).—June 3, apparatus filled.

June 16, tap opened. Bar. 762.2 mm., temp. 20.2°, gauge 1.0 mm.

„ 26, „ „ 765.6 „ „ 17.9° „ 0.0 „

In experiments 1 and 2, the oxide used was prepared by ignition; in experiment 3 by precipitation. In no case was any diminution in volume noticed. The apparatus would readily indicate any diminution, as a preliminary experiment had shown that when the materials were not dried the mercury in the gauge rapidly rose, on one occasion to the extent of 450 mm. in one hour.

Having shown that dry manganese peroxide is without action on dry sulphur dioxide, we proceeded to examine the effect of exposing dried mixtures of sulphur dioxide and oxygen to the dried peroxide and found that in no case did any diminution in volume occur, consequently no interaction took place. The same apparatus was used, but the bulb A was filled with a mixture of sulphur dioxide and oxygen whilst B contained oxygen instead of nitrogen.

(4).—June 13, apparatus filled.

June 26, tap opened. Bar. 765.7 mm., temp. 18.2°, gauge 11 mm.

July 4, „ „ 763.2 „ „ 18.0° „ 12 „

(5).—June 13, apparatus filled.

June 26, tap opened. Bar. 765.7 mm., temp. 18.2°, gauge 10 mm.

July 4, „ „ 763.2 „ „ 18.0° „ 9.5 „

(6).—July 4, apparatus filled.

July 15, tap opened. Bar. 763.4 mm., temp. 19.6°, gauge 21 mm.

„ 21, „ „ 761.8 „ „ 20.4° „ 19 „

The conclusion cannot be drawn that the formation of sulphur trioxide has ceased because the combination of manganese peroxide and sulphur dioxide has also ceased, for it may happen that when the materials are pure, "contact action," even with the addition of energy, is no longer effective in producing combination of sulphur dioxide and oxygen. This point was tested in the next series of experiments.

III. COMBINATION OF SULPHUR DIOXIDE AND OXYGEN IN PRESENCE OF HEATED PLATINUM.

This reaction affords a very good instance of the point we wished to investigate. In ordinary circumstances, the contact action of the platinum, aided by the energy continuously supplied from the source of heat, brings about combination. Our object was to discover whether this would still be the case when care was taken to dry and purify all the materials. The apparatus used is shown in Fig. 3.

The glass tube, A, contains platinised pumice, and is heated by means of a Ramsay burner to 400—450°. It is sheathed with a copper jacket and provided with asbestos screens to protect the rest of the apparatus from the heat. One end is fused on to the glass vessel B, which contains oxygen standing over mercury. B also contains a quantity of phosphorus pentoxide scattered about so as to coat the surface of the glass and mercury. The other end of A is fused on the vessel C, also of glass, filled with mercury and connected by flexible tubing with the reservoir D. C also contains phosphorus pentoxide covering the walls and the ground-in tube running from I to the bottom of C. In case any air should leak in between the glass and the india-rubber tubing at I, a T-piece was inserted at E and connected with a pump. Any leakage could be at once detected and the air pumped out. The phosphorus pentoxide used was distilled in oxygen, and the mercury sent several times through a Meyer's purifying apparatus.

FIG. 3.

The sulphur dioxide stood over mercury and phosphorus pentoxide in the bulb G provided with a tube dipping under the mercury into reservoir B. It was kept under diminished pressure, the mercury always standing several inches high in the delivery tube. The vessel H contained mercury, and by unscrewing the clamp the sulphur dioxide could be driven out into B.

The platinised pumice was prepared as follows: platinum black was dissolved in aqua regia, and the solution evaporated to dryness on the water-bath, taken up with water, and filtered. Pumice broken into small pieces was boiled for 45 minutes with aqua regia, well washed with water, and dried over the Bunsen burner. It was soaked in the platinum solution, then in ammonium chloride solution, dried at 130°, and ignited over the blow-pipe in a clay crucible for 2 hours. When not in use, it was kept in exhausted tubes with phosphorus pentoxide. A sample of this platinum, tested in the apparatus before drying,

showed a copious production of sulphur trioxide when sulphur dioxide and oxygen were passed over it.

There were three stages in the experiment :

1st Stage. Drying the Platinised Pumice and the Apparatus.—B was clamped firmly in position, A rested on supports, and C stood on smooth blocks, which were well oiled so as to allow a certain amount of movement as A expanded on heating.

After A had been heated for some hours, the reservoir D was lowered, drawing the mercury out of C, and causing some oxygen to pass from B over the pumice to C. Any moisture brought away from A would be absorbed by the phosphorus pentoxide in C. The oxygen was then driven back into B, and this operation was repeated for one hundred times at intervals of one or two hours during the working day. This stage occupied about three weeks.

2nd Stage. Introduction of the Sulphur Dioxide. The Reaction in the Dry State.—While the platinum and oxygen were being dried, the sulphur dioxide was drying in the bulb G. F was now connected with the pump and some of the oxygen withdrawn from B; mercury was run from H into G, and the displaced sulphur dioxide entered B, the total volume being marked. After an hour's diffusion, the mixed gases were passed backwards and forwards over the platinum. In none of the three experiments carried out could any white fumes be seen, but this does not imply that no sulphur trioxide was formed, because there were probably very few particles of dust or aqueous vapour to act as "nuclei of condensation," Aitken having shown that in the absence of these, fumes may sometimes not make an appearance. The proof that sulphur trioxide was not formed lay in the fact that there was no diminution in volume. To find out whether combination had altogether stopped, or had only been retarded, we prolonged this stage in one experiment for 5 hours, but no concentration was observed.

3rd Stage. Introduction of Steam. The Reaction in the Moist State.—The tap F was connected with a vessel containing steam, and opened for an instant while some of the steam was drawn into A. White fumes instantly appeared and a considerable diminution in volume was observed. In one experiment, in which a large quantity of phosphorus pentoxide was present, this diminution fell off after a short time, but on introducing more water vapour a further diminution in volume was observed.

The details of one experiment are given, the results in the case of two others being similar:

Volume of oxygen about	250 c.c.
,, sulphur dioxide	65 ,,
Mixed gases passed backwards and forward over pumice in A.	
After 5 hours. Contraction	Nil.

After introducing steam and again passing over pumice in A.		
1st passage (10 mins.).	Contraction	13 c.c.
2nd „ (½ hour).	„	3 „
After 24 hours.	„	29
More steam introduced and after further standing.	Contraction	27
		} „
Total contraction		56 „

In no case did combination entirely cease. Although no contraction could be observed after the dried gases had stood for 5 hours in contact with the heated platinum, yet an appreciable diminution was noticed when they had been in contact with it during 24 hours. It is, however, very difficult to dry platinised pumice completely, and our experiments, showing, as they do, the great influence of moisture on the velocity of the reaction, point to the conclusion that sulphur dioxide and oxygen will not combine in contact with heated platinum if moisture is carefully excluded.

Conclusions.

(1) When a mixture of sulphur dioxide and oxygen is allowed to stand over certain metallic oxides at the ordinary temperature, combination takes place to a certain extent between the two gases, owing to the “surface action” exerted by the metallic oxide.

(2) With the same oxide, the amount of sulphur trioxide formed depends on the extent of the surface of the oxide.

(3) With the same oxide, this amount depends also on the state of the surface. It appears to be least with freshly precipitated oxides which are not yet dried, and to increase if the oxide has been moderately heated or kept for a long time so as to become dry.

(4) The amount appears to be absolutely dependent on a simultaneous combination of the oxide with sulphur dioxide, and in fact seems to proceed concurrently with this. Several cases have been observed in which sulphur dioxide was absorbed without any combination with oxygen, but no case could be discovered in which the two gases combined without a reaction taking place between the sulphur dioxide and the metallic oxide or other substance.

(5) The most striking instance of this surface action is afforded by manganese peroxide, some 20 per cent. of the sulphur dioxide being converted into sulphur trioxide. If the materials are carefully dried by means of phosphorus pentoxide, no combination takes place, as even after standing for several days no alteration in volume can be detected. By drying the mixture, combination of manganese dioxide and sulphur

dioxide is thus prevented, as is also the surface action of the oxide which brings about the union of sulphur dioxide and oxygen.

(6) When sulphur dioxide and oxygen are passed over heated platinised pumice, combination diminishes as the materials are more completely dried, and can be made very small. Hitherto it has been generally held that the "contact action" of platinum could bring about combination even in the absence of any impurity, but this does not appear to be the case in the present instance.

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