XXXIII.—*A Contribution to the History of the Oxides of Manganese.*

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It has long been known that oxides of manganese, when heated to redness in air, either evolve or absorb oxygen, so as constantly to leave a residual oxide of the composition Mn_3O_4 . Some years ago, Schneider found that when the ignition is made in pure oxygen, the residue consists of Mn_2O_3 .†

This result differs from what might have been expected; for we

* See the interesting criticism of the binary theory by M. Dumas in his "*Leçons sur la Philosophie Chimique*," delivered in 1836, from which I cannot refrain from quoting the following passage :—"J'insiste sur ce raisonnement, car je ne trouve pas d'autres faits à opposer au système soutenu par Davy et M. Dulong: Ainsi la question n'est pas irrévocablement vidée. D'un moment à l'autre, il est possible que cette théorie se relève triomphante, appuyée par quelque découverte qui lui donnera une force nouvelle. Mais jusqu'à présent je suis d'avis qu'elle doit être repoussée, en raison de cette multitude innombrable d'êtres inconnus qu'elle suppose. Si seulement j'en voyais naître une partie . . . j'aurais moins de répugnance à croire à l'existence du reste."—*Leçons sur la Philosophie Chimique*, par M. Dumas, p. 292. Ed., Bruxelles, 1839.

† Poggeudorff's *Annalen*, cvii, 605.

do not know of any chemical action exerted by nitrogen on the oxides of manganese or on free oxygen, and, therefore, one might have thought that air would act simply like dilute oxygen, and produce the same oxide.

To explain the result of Schneider's experiment, we must suppose either that artificially made oxygen differs in some respects from that in the atmosphere, or what is more likely, that the proportion of oxygen in the residue depends on the *tension of the oxygen* in which the original oxide was heated, as well as on the temperature to which it was exposed.

Accepting this latter explanation, we say that, at a red heat, in presence of oxygen of the tension of one atmosphere, the oxide Mn_2O_3 , being the most stable under these conditions, is formed, while at the same temperature, with oxygen of the tension of only one-fifth of an atmosphere, the oxide Mn_3O_4 is the most stable, and hence it is produced. This leads to the question,—What oxides will be formed when oxygen of intermediate tensions is employed? Will there be a continuous series of oxides corresponding to a continuous series of oxygen tensions under which they have been formed?

These questions seemed to me to merit an experimental investigation, and that the more, because the results of such an inquiry would be a small contribution to our as yet very imperfect knowledge of the laws which govern the influence of physical conditions on chemical reactions.

In a preliminary series of experiments, pure binoxide of manganese, prepared by heating the nitrate, was heated to dull redness in a combustion-tube, whilst in the first experiment, a current of nitrogen, in the second, one of air, and in the third, one of oxygen, was kept passing over it. After weighing the residual oxide, it was again heated under the same conditions as before, and then weighed a second time. Finally, by ignition in a current of hydrogen, it was reduced to protoxide, which was also weighed.

The following Table contains the results—

TABLE I.

No. of Exp.	Gas employed.	Weight of the oxide after		Weight of MnO.	Composition of Oxide = MnO_x
		1st heating = P.	2nd heating = P'.		
1	Nitrogen ..	0.7984 grm.	0.7971	0.7184	{ from P ; $x = 1.494$ from P' ; $x = 1.486$ $x = 1.517$ $x = 1.527$
2	Air	0.891 "	0.891	0.798	
3	Oxygen ..	1.084 "	1.084	0.969	

From these data it will be seen that in each of the three experiments, Mn_2O_3 was obtained. This fact led me to think that Schneider, in heating an oxide of manganese in pure oxygen, obtained the sesquioxide, only on account of his having performed his experiments at about the same temperature that I employed, at which air, and even nitrogen, gives the same result as oxygen.

The second series of experiments showed, however, that the oxide Mn_2O_3 is stable when heated in oxygen, even at a higher temperature than would suffice in presence of air to reduce it to Mn_3O_4 . In this series of experiments, pure binoxide of manganese, in a porcelain or platinum boat, was placed within a porcelain tube, and the whole heated to bright redness for about an hour, while a current of dry nitrogen or oxygen, or a mixture of the two, was passing over it. The oxide was then analysed as before, by igniting in hydrogen and weighing the protoxide left. Most of the experiments were conducted under the ordinary atmospheric pressure, but in a few, the tension of the gas in which the MnO_2 was heated, was diminished below one atmosphere by con-

TABLE II.

No.	Nature of atmosphere.	Tension* in atmospheres of.			Weight of Oxide of Manganese.	Weight of MnO obtained from it.	Composition of Oxide being $MnOx$.
		N.	O.	N + O.			
1	Oxygen	0	1	1	0.9500	0.8491	1.527
2	Nitrogen.....	1	0	1	0.4269	0.3993	1.307
3	Air	0.79	0.21	1	0.7485	0.6935	1.352
4	Equal vol. of air and oxygen	0.40	0.60	1	0.6559	0.5879	1.513
5	Nitrogen.....	1	0	1	0.3942	0.3670	1.329
6	Oxygen	0	1	1	0.8738	0.7844	1.506
7	Air	0.79	0.21	1	0.6163	0.5672	1.384
8	1 vol. oxygen, 2 vol. air ...	0.53	0.47	1	0.7465	0.6687	1.516
9	Vacuum of air	0.013	0.003	0.016	1.0256	0.9505	1.350
10a	{ 1 vol. of oxygen, 5 vol.	0.66	0.34	1	0.7571	0.6821	1.488
10b	{ of air				0.9038	0.8098	1.515
11a	{ Mixture of oxygen and				0.6756	0.6265	1.348
11b	{ nitrogen, both arti-	0.81	0.19	1	0.3426	0.3180	1.343
	{ ficially made						
12	Oxygen of low tension ...	0	0.17	0.17	0.9062	0.8412	1.343
13	Oxygen of low tension ...	0	0.027	0.027	0.6769	0.6292	1.336
14	Oxygen of low tension ...	0	0.16	0.16	0.6333	0.5876	1.345
15	{ 15 vol. of air, 1 vol. of }	0.74	0.26	1	0.8172	0.7362	1.488
16	{ oxygen	0.74	0.26	1	0.8658	0.7736	1.529

* The tensions given do not pretend to be more than rough approximations to the real values.

necting the exit-end of the porcelain tube with a large bell-jar, within which the pressure was diminished, and kept constant by means of an air-pump. The preceding Table gives the result of eighteen experiments carried out in this manner.

It will be seen that, in each of the experiments, the number of the equivalents of oxygen ($O = 8$), combined with one of manganese ($Mn = 27.5$), was very near either to $1\frac{1}{2}$ or to $1\frac{1}{3}$, that is to say, either Mn_2O_3 , or Mn_3O_4 was produced, and *intermediate oxides were not formed*. These two oxides which were formed are easily distinguished, the sesquioxide being black, while the oxide, Mn_3O_4 , is brown. In a few cases, a large quantity of the brown oxide was obtained, side by side, *but not mixed*, with a small quantity of the black sesquioxide; but the amount of the latter was never sufficiently great to make the composition of the whole, *as given in the table*, differ materially from Mn_3O_4 . In all cases in which Mn_3O_4 was obtained, the partial tension of the oxygen lay between 0 and 0.21 atmospheres. As is stated in the Table, some of the experiments were made with nitrogen (Nos. 2 and 5), and some with air (Nos. 3, 7, 9) of different pressures. Others were performed with oxygen of low tension (Nos. 12, 13, 14), or with a mixture of artificial oxygen and nitrogen (Nos. 11a and 11b). In those experiments which gave Mn_2O_3 , the tension of the oxygen lay between 0.26 and 1 atmosphere. Oxygen tensions between 0.21 and 0.26 atmospheres did not occur in this series; still we can assert with a high degree of probability, that the function expressing the relation between the *composition* of an oxide of manganese, formed at a bright red heat in an atmosphere of oxygen, and the tension of that oxygen, is *discontinuous*, ~~or~~ that Mn_2O_3 is formed whenever the tension exceeds, and Mn_3O_4 , whenever it is below, a *certain definite limit*.

To find out whether there is really such a limit, and if so to determine its position, I undertook a third series of experiments, which, for the sake of comparison, were made as uniform as possible. In each experiment the bioxide of manganese was placed in a platinum boat, which was itself placed on a strip of platinum foil, and by means of this introduced into the porcelain tube. (The same tube and boat were used in all the experiments). The tube was subjected to the strongest heat of a Hofmann's gas furnace for about half an hour, while a current of oxygen and nitrogen, mixed in exactly known proportions, was sent through it. The boat was then quickly withdrawn from the tube and allowed to

cool. As this required only a very few minutes, no appreciable quantity of Mn_2O_3 could be formed at the temperatures conducive to its formation. The oxide was then weighed and analysed by determining the amount of Mn_3O_4 which it gave when ignited in a current of air partially deprived of its oxygen. The mixtures of oxygen and nitrogen which I employed were made from air and oxygen.

The air was collected in a glass gasometer over water, which had been previously saturated with air at the temperature of the laboratory. Its volume was determined by measuring the water which it displaced, and its temperature was assumed to be that indicated by a thermometer hung up close to the gasometer, while its tension was made equal to that of the surrounding atmosphere. In some experiments, the temperature was taken more carefully by plunging the whole gasometer into a water-bath of a constant known temperature, until equilibrium of temperature was established. The oxygen was measured out in a small glass gasometer, which was entirely immersed in a water-bath of known and constant temperature. The tension of the gas was in most cases made equal to that of the atmosphere, by originally collecting it under a higher pressure, and after establishing the desired temperature, allowing the excess of the gas to escape through a layer of water from 1 to 2 mm high. Lastly, the oxygen was transferred to the air-gasometer by displacing it with water, through which oxygen had been previously passed for some time. The gaseous mixture was displaced by water previously saturated with air, and before entering the porcelain tube, it passed first through a soda-lime, and then through a chloride of calcium tube, to free it from carbonic acid and water.

The volume of the oxygen formed in all cases only about one-twentieth of that of the air, and hence any error in measuring the proportions of oxygen and air, gave rise to a comparatively small error in estimating the proportion of oxygen in the mixture. For the same reason, the absorptiometric exchange between the gaseous mixture and the water could not change the composition of the former to any appreciable extent.

In determining the composition of the mixtures, one volume of air was assumed to contain 0.2093 vol. of oxygen. The following experiments were carried out in the manner described:

TABLE III.

The following abbreviations are used in the sequel :—

V for volume in litres, and P for pressure in inches of mercury of a gas.

t for temperature in centigrade degrees.

Q for volumes of oxygen in 100 vols. of gaseous moisture.

p for partial pressure of the oxygen prevailing during the experiment.

B for height of barometer in inches.

W for weight in grammes.

EXPERIMENT 17.

*Air.** $V = 10.90$ } P the same in both cases.

*Oxygen.** $V = 0.50$ } t not observed.

As the temperatures of both gases were about the same, Q is approximately = 24.4.

B during ignition = 29.68; hence $p = 7.24$.

The greater part of the oxide obtained was brown, a small portion of it black.

W of oxide obtained = 1.0716.

W after reduction to $Mn_3O_4 = 1.0683$.

Therefore its composition :

Mn_3O_4	..	..	0.9739	} grammes.
Mn_2O_3	..	..	0.0977	

EXPERIMENT 18.

Air. $V = 10.91$; $t = 12.2$, $P =$ that of atmosphere = B .

Oxygen. $V = 0.35$; $t = 9.5$, $P = B + 1.2$.

Hence $Q = 23.5$.

B during ignition was not observed; taking it = 30, p becomes = 7.05.

W of oxide obtained = 1.8884.

W after reduction to Mn_3O_4 was = 1.8880.

Loss of oxygen = 0.0004, corresponding to 0.0118 of Mn_2O_3 ; the rest consisted of Mn_3O_4 .

* In this as well as in the following experiments, the V and P given for air and oxygen refer to the moist gases.

EXPERIMENT 19.

Air. $V = 10.91$; $t = 13.3$; $P = 29.92$.

Oxygen. $V = 0.54$; $t = 10.3$; $P = 30.5$.

Hence $Q = 24.7$; B during ignition = 29.84 ; hence $p = 7.38$.

Weight of oxide obtained, 0.9030 .

After reduction to Mn_3O_4 , 0.8626 .

Hence its composition: MnO 1.557 ; *i.e.*, Mn_2O_3 .

EXPERIMENT 20.

Air. $V = 12.77$; $t = 10.5$ } P the same in both cases.
Oxygen. $V = 0.490$; $t = 83$ }

Hence $Q = 23.9$, and as B during ignition = 29.46 , we have
 $p = 7.04$.

Most of the oxide obtained was brown, a small part was black.

W of oxide = 0.8222 .

After reduction to Mn_3O_4 it was 0.8217 .

The 0.0005 of oxygen lost correspond to 0.0148 of Mn_2O_3 ; the rest, 0.8074 , consisted of Mn_3O_4 .

EXPERIMENT 21.

Air. $V = 11.41$; $t = 15.8$ } P the same in both cases.
Oxygen. $V = 0.503$; $t = 12.2$ }

Hence $Q = 24.3$, and as B during ignition = 21.52 , therefore,
 $p = 7.17$.

Most of the oxide was black, a small portion only being brown.

W of oxide = 1.1745 .

After reduction to Mn_3O_4 it was 1.1417 .

Hence composition :

$$Mn_3O_4 = 0.2035.$$

$$Mn_2O_3 = 0.9710.$$

EXPERIMENT 22.

Air. $V = 11.90$ } P and t exactly the same in both cases.
Oxygen. $V = 0.499$ }

Hence $Q = 24.1$, and as B during ignition = 29.32 , therefore
 $p = 7.07$.

W of oxide obtained 0.8648 .

After reduction to Mn_3O_4 it was 0.8643 .

The 0.0005 of oxygen lost correspond to 0.0148, of Mn_2O_3 , the rest consisted of Mn_3O_4 .

EXPERIMENT 23.

Air $V = 11.7$ } t and P the same in both cases.
Oxygen $V = 0.499$ }

Hence $Q = 24.2$, and as B during ignition = 29.54, $p = 7.14$.

W of oxide = 0.6513.

After reduction to $\text{Mn}_3\text{O}_4 = 0.6281$.

Therefore composition, $\text{MnO}_{1.510}$ i.e. Mn_2O_3 .

EXPERIMENT 24.

Air $V = 14.54$ } P and t the same in both cases.
Oxygen $V = 0.502$ }

This mixture was employed three times under different pressures.

Experiment a.—The tension of the mixture was made greater than that of the atmosphere by forcing it, after coming out of the porcelain-tube, through a layer of water, 4.5 inches deep. B during ignition = 29.96, hence $p = 7.14$.

This time the binoxide of manganese, previous to being heated in the mixture of oxygen and nitrogen, was converted into Mn_2O_3 by ignition in pure oxygen.

Experiment b.—The oxide obtained in experiment a was heated in the same gas as before, but this time without increasing its pressure beyond that of the atmosphere $B = 29.95$, therefore $p = 7.06$.

Experiment c.—The oxide obtained in experiment b was heated in the same mixture of N and O as before; the tension of the latter, however, was brought down below that of the atmosphere by sending it from the porcelain tube into a large bolt-head, within which the pressure was diminished and kept constant by sucking. The difference between this pressure and that of the atmosphere was measured by means of a water-manometer. The height of the latter was kept as near as possible to 5.5 inches. $B = 29.9$; hence $p = 6.95$.

At last the oxide from experiment c was reduced to Mn_3O_4 in the ordinary way.

The composition of the oxides obtained in these three experiments is given in the following table:—

Weight of Mn_2O_3 employed = 1.1852.

Exp.	p .	W. of Oxide.	Composition.
a.	7.14	1.1842	$\text{Mn}_{1.503}$.
b.	7.06	1.1842	$\text{Mn}_{1.503}$.
c.	6.95	1.1469	1.0463 of Mn_3O_4 * and
After reduction to Mn_3O_4		1.1435	0.1006 of Mn_2O_3 .
			Mn_3O_4 .

It is seen that, under the oxygen tension of 7.06, Mn_2O_3 was not decomposed, while under the oxygen tension of 6.95 it was for the most part reduced to Mn_3O_4 . Under the conditions prevailing in experiment 24, therefore, the point of discontinuity above spoken of seems to correspond very nearly to an oxygen-pressure of 6.95 inches.

EXPERIMENT 25.

Air. $V = 14.00$ } t and P of both gases the same.
Oxygen. $V = 0.407$ }

The same mixture was employed under two different pressures.

In *Experiment a*, the tension of the mixture of nitrogen and oxygen was made to exceed that of the atmosphere by 6.8 inches of water-pressure. $B = 30.03$, therefore $p = 7.07$.

Experiment b. Pressure of gaseous mixture = $B = 30.05$, hence $p = 6.96$. Under this pressure, the oxide obtained in experiment *a* was ignited. The composition of the oxides will be given below.

EXPERIMENT 26.

Air. $V = 14.02$ } P and t the same in both cases.
Oxygen. $V = 0.408$ }

Experiment a. In this mixture the oxide obtained in experiment 25 *b*, was heated. During the ignition $B = 30.02$, therefore $p = 6.95$.

Experiment b. 11.26 litres of the same mixture of nitrogen and oxygen as was used in experiment *a*, of the temperature of 14°C , were mixed with 1.00 litre of air of 8°C . P of both gases the same. In this mixture the oxide obtained in experiment *a* was ignited. B , during the ignition, 30.04, hence $p = 6.90$.

Experiment c. 8.75 litres, at 11°C ., of the same mixture of

* A small portion of the oxide was black; the greater part was brown.

nitrogen and oxygen as was used in experiment *b*, were mixed with 0.50 litres (at 8°) of air. *P* of both gases was the same. In this mixture, the oxide obtained in experiment *b* was heated. *B* during ignition = 30.05, therefore *p* = 6.87.

Experiment d.—The oxide obtained in experiment *c* was again ignited in the same mixture of nitrogen and oxygen *B* = 30.03, hence *p* = 6.87.

Experiment e.—The oxide obtained in *d* was reduced to Mn_3O_4 .

COMPOSITION OF OXIDES OBTAINED IN EXPERIMENTS 25 AND 26.

Exp.	<i>P</i> .	<i>W.</i> of oxide.	Composition.
25a	7.07	0.7982	$\text{MnO}_{1.505}$
25b	6.96	0.7982	$\text{MnO}_{1.505}$
26a	6.95	0.7953	0.0829 of Mn_3O_4 0.7124 of Mn_2O_3
26b	6.90	0.7982	$\text{MnO}_{1.505}$
26c	6.87	not determined	Mixture of brown and black oxide.
26d	6.87	0.7745	0.1184 of Mn_2O_3 0.6561 of Mn_3O_4
26e		0.7705	Mn_3O_4

In order to define approximately the range of temperatures within which the experiments of this series had been performed, a piece of aluminum and also a piece of pure silver were placed into the porcelain tube, and heated in the same manner as had been the case with the oxide of manganese. Twenty minutes after the tube had become thoroughly heated, the aluminum was found to be fused, but not the silver.

We see that sometimes pure Mn_2O_3 , sometimes pure Mn_3O_4 was formed, while in some cases both were obtained, side by side, not mixed; one of them, however, always greatly predominated in quantity.

Mn_2O_3 was formed alone or predominated in experiments :

	19	21	24a	23	25a	24b	25b	26b
<i>P</i> being respectively	7.38	7.17	7.14	7.14	7.07	7.06	6.96	6.90

Mn_3O_4 was formed alone or predominated in experiments.

	26d	24c	20	22
<i>P</i> being	6.87	6.95	7.04	7.07*

* Experiment 18 is not mentioned here, because in it the barometer was not observed during the ignition; also experiment 17 is omitted, because the high value of *P* deduced from it, makes me suspect some error committed in making the synthesis of the gaseous mixture.

These results seem to confirm the conclusions drawn from the second series of experiments. Experiments 24*b* and 24*c*, and also 26*b* and 26*d*, clearly show that, at a certain temperature, and in a certain atmosphere of nitrogen and oxygen, Mn_2O_3 will be stable, while a slight diminution in the tension of the oxygen, the other conditions remaining the same, will cause its reduction to Mn_3O_4 . The exact value of the limiting tension of the oxygen below which Mn_3O_4 , and above which Mn_2O_3 is formed, depends, no doubt, on the temperature to which the oxide of manganese is exposed. If we suppose that the function expressing this dependency is a *continuous one*, the apparently anomalous result of the third series of experiments, viz., that at oxygen-tensions contained between 6.60 and 7.07, either of the two oxides may be formed under *apparently* the same conditions, may be explained.

I cannot conclude without expressing my best thanks to Mr. Francis Jones, for his valuable assistance during the earlier part of this investigation.

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