LX.—*Second Report to the Chemical Society on "Researches on Some Points in Chemical Dynamics."*

By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

In the first report it was shown that when oxide of copper and ferric oxide are reduced by the three agents, carbon oxide, hydrogen, and amorphous carbon, the temperatures at which reduction first becomes perceptible, after a time varying from a few minutes to half an hour or so, depend firstly on the physical condition of the metallic oxide employed and, in the case of carbon, on that of the carbon; and secondly on the amount and character of the heat disturbance ensuing during the reaction, the rule being uniformly noticeable in comparable cases that the greater, algebraically speaking, is the heat evolution (*i.e.*, the greater the actual evolution if the heat disturbance be of + sign, and the less the heat absorption if the heat disturbance be of − sign), the lower is the temperature of initial action. Moreover, it has been shown that the temperatures at which these three agents first begin to act on cuprous oxide are no further removed from those at which they begin to act on various forms of cupric oxide than may be reasonably supposed to be due to difference in physical state; this being a particular case of the above rule, since the heats of combustion of copper to Cu_2O and to CuO are practically the same (calculated per equal amounts of oxygen consumed).

In order to see if these rules are also obeyed by other metallic oxides, experiments have been made, as described below, with different kinds of oxides of various other metals; the determinations were made in the main in the same way as those described in the first report, the chief differences being that, in determining the temperatures of initial action of carbon oxide, the paraffin bath was mostly discarded, the air-bath arrangement described in the first report as employed in certain cases for temperatures above 250°, being used instead, as more convenient; and that in some cases the criteria adopted as to the temperatures at which action commenced were, for reasons dependent on the nature of the oxides examined, different from those employed in the case of the oxides of copper and iron; thus in many cases, especially with hydrogen, the temperature of initial action was determined by finding at what temperature a perceptible loss of weight first took place after 15 minutes or more exposure to the reducing agent; in some instances (with super oxides) the loss of oxygen was arrived at by boiling the substance with hydrochloric acid, receiving the evolved chlorine in potassium iodide solution, and titrating the iodine liberated; by comparing the numbers thus found before exposure and after, the amount of oxygen removed was readily deducible (this method is referred to briefly, hereafter, as the "iodine process"). In some instances samples of amorphous carbon, prepared from carbon oxide by ferric oxide, but different from the specimen used in the first report, were employed, wherefore the corrections for amount of occluded gases are not always the same; and in a few cases a bath of sulphur vapour was employed instead of a melted solder bath with test pieces of metal when a temperature of about 420° was required.

§ 1. Oxides of Iron Lower than Ferric Oxide.

(A.) *Ferrous Oxide.*

It has been shown by Lowthian Bell (*Chemical Phenomena of Iron Smelting*, p. 28), that when a mixture of equal volumes of carbon oxide and dioxide is passed over ferric oxide at a red heat, reduction goes on until about one-third of the oxygen in the ferric oxide is removed; whilst, conversely, spongy metallic iron heated in the same gaseous mixture to the same temperature, becomes oxidised to an extent indicating an addition of about two-thirds of the quantity of oxygen requisite to form ferric oxide; in other words, that whether metallic iron or ferric oxide be originally employed, the resultant substance is an oxide of composition tolerably close to that indicated by FeO.

A quantity of this stable oxide was prepared by passing equal volumes of carbon oxide and dioxide (prepared from oxalic acid and sulphuric acid) over pure ferric oxide at a bright red heat, for eight hours. After cooling down in a stream of the mixed gases, 1·3680 gram of the product gave 1·4870 Fe_2O_3, whence the composition was nearly that indicated by FeO; in order to make sure that the action had gone on as far as possible the whole was well intermixed, and heated again to a bright red heat in the same gaseous mixture for eight hours more. After cooling, 1·0425 gram gave 1·1360 Fe_2O_3,

	Calculated.		Found.	
	For Fe_2O_3.	For FeO.	After 1st 8 hours.	After 2nd 8 hours.
Fe =	70·00	77·78	76·09	76·28

whence scarcely any change had been produced during the second eight hours. The substance finally obtained contained a perceptible amount of occluded gases; on heating in a Sprengel vacuum it behaved in just the same way as carbon, *i.e.*, on heating to a given temperature gas was given off for a few minutes, and the evolution then ceased ; on raising the temperature to another limit, more gas came off for a short time, and then entirely ceased coming off; whilst on further raising the temperature the same result again occurred. The following amount of gas was extracted per gram of substance :—

At 360° (in mercury vapour)......	1·83	c.c. at 0° and 760 mm.
360—420° (up to melting point of zinc)	1·50	,, ,,
420—460° (antimony thoroughly melted)	0·67	,, ,,
	4·00	

Of this gaseous mixture, 12·5 per cent. was absorbed by potash, the remainder being almost wholly carbon oxide ; whence it results that the composition by weight of the ultimate product was—

Iron	76·28
Occluded $CO + CO_2$....	0·53
Oxygen (by difference)..	23·19
	100·00

Or, omitting the occluded gases, the composition approximated to FeO, being much more nearly $Fe_{16}O_{17} = 14FeO,Fe_2O_3 = 13FeO,Fe_3O_4$.

	Calculated.		Found.
	For FeO.	For $Fe_{16}O_{17}$.	
Iron	77·78	76·71	76·68
Oxygen......	22·22	23·29	23·32
	100·00	100·00	100·00

No iron in the metallic form was present, as on digesting with boiled water and iodine, no trace of iron was dissolved out.

The action of carbon oxide on this substance, when examined as described in the first report, was found to be imperceptible at all temperatures below 270° ; at 275° the baryta-water just began to grow turbid after 3—4 minutes' passage of gas, and at 290° it became very turbid after the passage of only a few bubbles of gas.

In order to find out how far determinations by loss of weight would agree with those made with baryta-water as a test of initial action, 0·794 gram was heated in a narrow **U**-tube containing the oxide at the bend, with a plug of glass wool in front of the oxide, to prevent any mechanical loss of particles by the current of carbon oxide, which was passed through the tube heated by an air-bath. No appreciable loss of weight was observed below and up to 270°; at 280° the loss after 15 minutes was 0·0025 = 0·31 per cent. Hence both the baryta-test and the loss of weight experiment indicated about 275° as the temperature of initial action; but as gases containing CO_2 were expelled at this temperature on heating in a Sprengel vacuum, it is possible that the turbidity of the baryta-water and the loss of weight were partly due to this cause, although not wholly, inasmuch as the gas expelled on heating to 360° in a Sprengel vacuum, corresponded to only 0·24 per cent. by weight, and hence the amount expelled at 280° would have been less than this, and consequently less than the 0·31 per cent. lost on heating in carbon oxide for 15 minutes. To settle this point definitely the experiment was repeated, a current of pure nitrogen (from ammonium chloride and potassium nitrite) being substituted for carbon oxide. After passing through baryta-water for 15 minutes, the effluent gas produced a trace of turbidity in baryta-water, the substance being heated to 290—300°; the amount of occluded gas expelled, however, was so minute that no perceptible loss of weight was produced in 1·4330 gram of substance, the loss being less than 0·25 milligram, and hence less than 0·02 per cent. The same result was found on heating to 320° in a current of nitrogen for 15 minutes; no appreciable loss of weight occurred either in this case or in another experiment in which air was substituted for nitrogen, the temperature being kept at 300° or 15 minutes.

It hence results, firstly, that about 275° is the true temperature of initial action of CO on the ferrous oxide used; and secondly, that the gas occluded by the ferrous oxide is removed far more rapidly by heating *in vacuo* for a short time than in air or nitrogen; *i.e.*, gases do not under all circumstances act as vacua to one another.

The temperature of initial action of hydrogen was determined by the loss of weight process; the weighings were always made with the tube full of hydrogen, the exit end being first closed by a tightly fitting india-rubber cap, and the entrance end being then disconnected from the hydrogen generator and rapidly closed in the same way; it was found that with due care entrance of air could always be avoided, so that no error was introduced by the displacement of hydrogen by the heavier air. In this way no loss of weight was noticeable after 15 minutes' action at various temperatures below 300°, or at that temperature.

At 310° 0·9200 gram lost in 15 minutes 0·0010 gram = 0·11 per cent.

At 360° (boiling mercury) 0·7460 lost in 15 minutes 0·0100 gram = 1·34 per cent.

At 360° (boiling mercury) 0·7460 lost in 30 minutes 0·0160 gram = 2·14 per cent

A visible condensation of moisture was observed in the last two experiments; that the small loss of weight in the first experiment was not due to the removal of occluded gases, is evident from the circumstance above mentioned, that on heating in a current of nitrogen for 15 minutes at 320° no appreciable loss of weight occurred.

Hence 305° may be taken as the temperature of initial action of hydrogen on this ferrous oxide.

In order to determine the temperature of initial action of carbon, 0·6 gram of the oxide and 0·3 of carbon (from CO) were ground together in an agate mortar and treated as described in the first report. The following numbers were obtained, the amounts of gas collected being given in c.c. at 0° and 760 mm.:—

Range of temperature	Up to 360°	360—440°	440—460°
Time of heating in minutes..	30	15	15
Carbon dioxide collected	0·6	—	1·5
Other gases	1·2	—	2·8
Total gas collected	1·8	2·5	4·3
Gas occluded by ferrous oxide	1·1	2·0	2·0
Ditto by carbon............	0·3	0·4	0·4
Total gas due to occlusion ...	1·4	2·4	3·2
Gas due to reduction of FeO.	0·4	0·1	1·1

Up to 440° the expulsion of gas was fitful, going on for a short time on raising the temperature, and then stopping till the temperature was again raised; in short, the gas collected was simply that due to occlusion. At 450° and upwards, however, a slow regular evolution of gas was observed, whence the temperature of initial action may be taken as being 450°.

It results from these experiments that the temperatures of initial action of carbon oxide, hydrogen, and carbon are situated respectively at near 275°, 305°, and 450°, following the same order as that observed with ferric oxide and the oxides of copper.

(B.) *Ferroso-ferric Oxide.*

Magnetic oxide of iron was prepared from the rolling mill scales of boiler plate manufacture by finely powdering, sifting, and digesting with a solution of iodine in potassium iodide to dissolve out particles of metallic iron; about 0·3 per cent. of metal was thus extracted; the whole was then quickly filtered and washed successively with water, alcohol, and ether, and exposed to the air. The oxide thus obtained gave the following numbers on analysis, 1·55 per cent. of SiO_2 being subtracted; the ferrous iron was determined by titration with permanganate:—

	Calculated for Fe_3O_4.		Found.
Fe as FeO	24·14		24·17
Fe as Fe_2O_3	48·28		48·76
O................	27·58	(by diff.)	27·07
	100·00		100·00

On heating to redness in a Sprengel vacuum, no gas was given off.

The action of carbon oxide was found to begin at 200° by the baryta-water test, CO_2 being copiously formed at 215°.

Hydrogen caused no loss of weight at temperatures below and up to 280°.

At 300° 1·3640 gram lost in 15 minutes 0·0010 gram = 0·07 per cent.

At 360° (mercury vapour) 1·163 gram lost in 15 minutes 0·0050 gram = 0·43 per cent.

At 360° (mercury vapour) 1·163 gram lost in 30 minutes 0·0150 gram = 1·29 per cent.

Hence about 290° may be taken as the temperature of initial action.

With amorphous carbon the following numbers were obtained, the experiments being conducted precisely as described in the first report.

Temperature	360°	360—420°	420—440°	440—460°
Time in minutes	30	15	15	15
CO_2 produced	—	—	—	2·0
Other gases	—	—	—	0·8
Total gas	·25	·5	·75	2·8
Gas due to occlusion	·3	·4	·7	0·8
Gas due to reduction	Nil	Nil	Nil	2·0

Hence 450° may be taken as the temperature of initial action.

On comparing the foregoing results with those obtained with ferric oxide prepared by ignition processes described in the first report, the following numbers are obtained as the temperatures of initial action:—

Reducing agent.	Ferric oxide.		Ferroso-ferric oxide.	Ferrous oxide.
	From ignition of $FeSO_4$.	From ignition of precipitated Fe_2O_3.		
Carbon oxide	202	220	200	275
Hydrogen	260	245	290	305
Carbon (from CO)	430	430	450	450

from which it appears that the difference in temperature of initial action of each reducing agent is hardly greater than may reasonably be ascribed to difference in physical texture due to differences with modes of preparation of the different oxides; that is, the oxides of iron, like those of copper, are first acted on by the three reducing agents, carbon oxide, hydrogen, and carbon at sensibly the same temperatures when in the same physical states, whatever the composition of the oxides; whence it probably results that the heats of combustion of iron to FeO, to Fe_3O_4, and to Fe_2O_3, are sensibly the same (calculated per equal amount of oxygen combined), just as the heats of combustion of copper to Cu_2O, and to CuO are sensibly the same (Andrews). That this is so is indicated by the values obtained by Julius Thomsen as the "heat of formation" of ferrous and ferric hydrate from iron, oxygen, and water (*Jahresbricht*, 1873, p. 81), viz., 68280 for FeO,H_2O, and 191130 for F_2O_3, $3H_2O$, or 68280, and 63710 per 16 grams of oxygen: it is noticeable that the heat of formation of the lower oxide is somewhat, but not much, greater than that of the higher one, whence the heat evolution during reduction of the first must be slightly less than that during reduction of the second; whilst accordingly, if there is any noticeable difference between the temperatures of initial action of reducing agents on FeO and on higher oxides, it is in the direction indicated by the thermal rules arrived at from the previous experiments, the FeO requiring a slightly higher temperature than the other oxides.

In the case of ferroso-ferric oxide the presence of small quantities of silicate, titanate, &c., and the denser texture produced by fusion, appears to raise considerably the temperatures of initial action of these three agents; thus the following numbers were obtained with New Zealand iron-sand picked out by a magnet after crushing and well washing to get rid of particles of dust, &c., and finally powdering finely in an agate mortar. Neither carbon oxide nor hydrogen had any action whatever on the iron-sand at the temperature of boiling mercury; both, however, acted at the temperature of boiling sulphur, weight being lost, and CO_2 being formed on passing CO over the ore at that temperature, and a yet greater loss of weight ensuing when hydrogen was used instead of carbon oxide.

1·256 gram heated in CO for 15 minutes in sulphur vapour lost 0·0030 = 0·24 per cent.

A copious precipitate was formed in baryta-water by the exit gas.

1·0995 gram heated in H for 15 minutes in sulphur vapour lost 0·0035 = 0·32 per cent.

1·0995 gram heated in H for 30 minutes in sulphur vapour lost 0·0105 = 0·95 per cent.

It was found impracticable to obtain accurately the temperatures of initial action in these two cases; it does not follow that because at about 420° hydrogen acts somewhat more energetically than carbon oxide, therefore the initial temperature of action of hydrogen is below that of carbon oxide; for it has been noticed in other cases that the loss of weight on heating in CO to a temperature somewhat above the point of initial action takes place more slowly than in hydrogen under analogous conditions, a circumstance probably connected with the superior lightness and diffusibility of hydrogen: moreover, the following experiment indicates that the initial action of CO is really manifested at a lower temperature than that of hydrogen. A gram of finely powdered iron-sand was introduced into each of two similar tubes holding about 4 c.c., one of which was filled with CO and carefully sealed, and the other similarly filled with hydrogen and sealed: both tubes were then heated in mercury vapour for three hours. After cooling no deposition of moisture was apparent in the hydrogen tube, and no absorption took place on opening the tube under mercury; whence evidently no action had here taken place. With the other tube, however, action had evidently taken place; for on opening the tube no absorption ensued, but 25 per cent. of the contained gas had become converted into CO_2, being absorbed by potash, and precipitating baryta-water.

It is noteworthy that an analogous result as regards the effect of long continued heating to a temperature somewhat below the point of initial action as deduced from experiments lasting a few minutes only has been observed with other metallic oxides: thus cupric oxide prepared from ignition of the nitrate is not visibly acted on by pure CO during 5 to 10 minutes at temperatures below 125°; but if a large quantity of this substance be sealed up with CO and heated to 100° for several hours, a copious production of CO_2 ensues. Thus in two experiments in each of which 5 grams of this cupric oxide were sealed up with about 30 c.c. of CO, the following numbers were obtained:

After 8 hours at 100°, gas contained 70 per cent. of CO_2.
" 72 " " " 90 "

It is to be remarked, however, that the conditions were not precisely the same in the experiments for a few minutes at 125°, and those for several hours at 100°, irrespective of temperature difference: for in the first case a stream of gas at the ordinary pressure was employed, whilst in the second the pressure was increased to about $\frac{4}{3}$ atmosphere since the tubes were filled and sealed *cold*, and then heated to 100°; some experiments on the absorption of CO_2 by lead monoxide (§ 3A) indicate that increase of pressure is correlative with an alteration in rate of chemical action in such cases.

In connection with these points, we are endeavouring to obtain the data for the construction of curves representing the correlations between the deoxidation taking place with given oxides and reducing agents, the time of action, and the temperature and pressure, the other conditions being as far as possible the same.

On heating the iron-sand with carbon (from CO) it was evident that in this also a higher temperature was requisite before action commenced than with the other samples of iron oxides: the following numbers were obtained:—

Temperature	360°	360—420°	420—460° antimony well melted.	460° to about 500°, fully red-hot in daylight.
Time in minutes......	30	15	15	15
Carbon dioxide formed	—	—	—	1·8
Other gases ,,	—	—	—	0·7
Total gas formed	·25	·5	about ·7	2·5
Gas due to occlusion..	·3	·4	·8	about 0·8
Gas due to reduction..	Nil	Nil	Nil	1·7

No continuous evolution of gas took place until the temperature was considerably higher than the fusion point of antimony, so that 480° at least may be taken as temperature of initial action.

The temperatures obtained with this iron-sand then are—

Carbon oxide	Between 360° and 420°.
Hydrogen..........	Ditto, but higher than with CO.
Carbon (from CO) ..	About 480°.

§ 2. Oxides of Manganese.

It has just been shown that in the case of iron and copper the temperature of initial action (during some 5—30 minutes) of carbon oxide, hydrogen, and carbon, are practically the same whatever oxide of the metal examined be employed, provided the physical state is about the same; whilst coincidently the heat evolved in converting a given quantity of oxygen into any one oxide of either metal severally is practically equal to that evolved in the formation of any other oxide of the same metal. *A priori* it would seem unlikely that the heats of formation of the higher oxides of metals, which like manganese form superoxides decomposed by heat alone and not corresponding to stable well-defined series of salts would be as great as the heats of formation of the lower oxides of these metals respectively; whilst, as shown by J. THOMSEN (*Jahresbericht*, 1873—80), the heat of formation of manganous hydrate, $MnO.H_2O$, is far greater in proportion to the oxygen employed than that of hydrated manganese dioxide, $MnO_2.H_2O$, the values being 94,770 and 116,280 respectively, or 94,770 and 58,140 per 16 grams of oxygen. It should hence result, if the rules hitherto traced out connecting the initial temperature at which an action of the form—

$$AB + C = A + BC$$

takes place be generally applicable, that the action of a given reducing agent on manganese dioxide begins to take place at a lower temperature than that at which the reducing action on the lower oxide is first noticeable. To see if this is the case, the following experiments were made, from which it clearly results that the thermic rule applies here also:—

(A.) *Precipitated Manganese Dioxide.*

Two specimens of manganese dioxide were prepared by precipitation processes; the first, by adding to solution of pure manganese chloride excess of caustic soda, adding bromine to supersaturation, leaving the solution at rest for 48 hours, and filtering off after repeated washings by decantation; the second, by boiling potassium permanganate solution with dilute nitric acid, and thoroughly washing on a glass-wool filter. Jet-black and somewhat glossy substances were obtained after drying at 100°; neither product, however, was pure manganese dioxide; for, in addition to water of hydration, a certain amount of an oxide lower than MnO_2 was present in each. Thus the following analytical numbers were obtained:—

I. *Specimen prepared by Bromine process.*—0·3615 gram heated with hydrochloric acid, and the vapours received in potassium iodide solution liberated iodine equal to 65·5 c.c. of decinormal iodine solution (titrated by thiosulphate), corresponding to 0·0524 oxygen = 14·49 per cent.

0·3885 gram corresponded to 70·9 c.c. = 0·05672 oxygen = 14·59 per cent.

0·7030 gram ignited over a gas blowpipe left 0·6110 gram of residual oxide; this, however, contained somewhat more oxygen than Mn_3O_4, since on titration by the iodine process it corresponded to 73·9 c.c. of decinormal iodine = 0·0591 gram oxygen = 9·67 per cent., whilst had it been Mn_3O_4, it would only have corresponded to 53·4 c.c. of decinormal iodine = 0·0427 oxygen = 6·99 per cent.; the amount of MnO present, therefore, was 0·6110 — 0·0591 gram = 0·5519 gram = 78·51 per cent.

0·3420 gram was heated in a current of air for several hours to 200° till perfectly constant in weight; the loss of weight was 0·0240 gram = 7·02 per cent. That no material portion of this loss was due to the evolution of oxygen was shown by titrating the residue by the iodine process, when it represented 60·7 c.c. of decinormal iodine = 0·0486 gram oxygen = 14·21 per cent. reckoned on the undried substance, or practically the same as that found before heating to 200°.

These percentages are close to those required for the formula—

$$Mn_{11}O_{20},4H_2O = 7MnO_2,2Mn_2O_3,4H_2O.$$

	Calculated.		Found.		
11MnO	781	78·33		78·51	
O_9	144	14·45	14·49		14·59
$4H_2O$	72	7·22		7·02	
$7MnO_2,2Mn_2O_3,4H_2O$	997	100·00			

II. *Specimen prepared from Permanganate.*—0·7510 gram ignited over a large Bunsen lamp left of residue 0·6620 gram; on repeating the ignition the residue slightly *gained* in weight, now weighing 0·6650 gram; whilst after heating almost to whiteness for 15 minutes over the gas blowpipe, the crucible being surrounded by a clay jacketting furnace, it weighed 0·6545 gram. Even this final product, however, was not Mn_3O_4, inasmuch as 0·6485 gram of it treated by the iodine process corresponded to 69·1 c.c. of decinormal iodine = 0·05528 oxygen, or 8·52 per cent.; whilst Mn_3O_4 requires 6·99 per cent. Since, however, the product of the last heating contained 100 — 8·52 per cent. of MnO = 91·48 per cent., the original dioxide employed contained $\frac{0·6545}{0·7510} \times 91·48$, or 79·73 per cent. of MnO.*

1·6725 gram in Fresenius and Will's apparatus gave by the

---

* In connection with these numbers and those obtained previously with the first specimen of precipitated MnO_2, indicating that the composition of the oxide obtained by igniting MnO_2 is variable, and contains more oxygen than Mn_3O_4, it is noticeable that the products obtained by strongly calcining in the air manganese carbonate and manganese monoxide, MnO, exhibit similar peculiarities. *Vide infra* § 2, C, D, and E.

oxalic acid process 1·4070 CO_2, representing 0·2558 oxygen = 15·29 per cent.

0·1965 gram corresponded to 37·6 c.c. of decinormal iodine when titrated by the iodine process = 0·03008 oxygen = 15·31 per cent.

0·5435 gram heated to 200° in a current of dry air lost 0·0230 gram, a drying tube attached gaining 0·0250 (hence, as with the first specimen, no oxygen was expelled at 200°, for otherwise the loss of weight would have *exceeded* the water collected; it is shown below that no oxygen was evolved on heating this specimen in a Sprengel vacuum to any temperature short of 260°).

0·5165 gram lost at 200° 0·0230 gram.

These percentages are close to those required for the formula—

$$Mn_{21}O_{39},5H_2O = 15MnO_2,3Mn_2O_3,5H_2O.$$

	Calculated.		Found.		
$21MnO$	1491	79·78		79·73	
O_{18}.....	288	15·41	15·29		15·31
$5H_2O$	90	4·81	4·23	4·60	4·45
$15MnO_2,3Mn_2O_3,5H_2O$.	1869	100·00			

Comparing this formula with that arrived at for Specimen I, $7MnO_2.2Mn_2O_3.4H_2O$, it is at once evident that Specimen No. II contains a somewhat smaller quantity of oxide lower than MnO_2 than is present in No. I. For this reason Specimen II (prepared from permanganate) was chosen for the subsequent experiments detailed below; the point of initial action of hydrogen being determined by loss of weight, the substance was rendered anhydrous by heating to 200° in a current of dry air for some time, no further loss of weight ensuing on continuing the heating for an hour.

Carbon oxide was found to act vigorously on the anhydrous oxide at temperatures below 60°, whilst even at the ordinary temperature CO_2 was slowly formed, the issuing gases forming a perceptible precipitate in baryta-water; a tube containing about 20 c.c. of pure CO, and about 1·5 gram of the manganese dioxide was sealed up, and left to itself for 10 days at Christmas in a room without a fire (temperature probably from — 10° to + 10°). When opened the gases contained 32·1 per cent. of CO_2.

It is noteworthy that the non-dehydrated oxide (dried only at 100°) acted in just the same way, and not apparently any more vigorously; the other specimen of dioxide (prepared by the bromine process) behaved in precisely the same way, a perceptible precipitate being formed in baryta-water by passing pure CO over it for two or three minutes at a temperature of about 18°.

To determine the temperature at which hydrogen first began to act, weighed quantities of the dioxide dried at 200° were heated in a slow current of hydrogen precisely as above described. No loss of weight was produced by heating for 15 minutes to any temperature below and up to 140°.

0·2920 gram heated to 150° for 15 minutes lost 0·0015 gram = 0·51 per cent.

On further heating to 170° for 15 minutes this lost in addition 0·0040 gram = 1·37 per cent.

And on further heating to 190° for 15 minutes this lost in addition 0·0085 gram = 2·91 per cent.

Hence the temperature of initial action lies between 140 and 150°, and therefore is near 145°.

In another similar experiment no loss occurred at 140°, 0·48 per cent. at 150° for 15 minutes, and a further loss of 2·91 per cent. on again heating to 190° for 15 minutes.

As a further check on these numbers 0·3060 gram were heated in hydrogen to 160° for 30 minutes, whereby the loss in weight was 0·0070 gram = 2·29 per cent.

On titrating the "available oxygen" in the residue by the iodine process it was found to represent 51·9 c.c. of decinormal iodine = 0·04152 gram oxygen = 13·57 per cent. reckoned on the original substance. As the substance originally yielded by the same process 16·04 per cent., the loss of oxygen during reduction was 2·47 per cent., which agrees very fairly with the loss of weight determination.

The determination of the temperature of initial action of carbon was complicated by the circumstance that although no oxygen was evolved on heating to 200° in air, yet on heating in a Sprengel vacuum to temperatures below 360° oxygen was continuously evolved. Experiments were therefore made simultaneously with the manganese dioxide alone (0·6 gram), and the same quantity of dioxide mixed with half its weight of carbon (from CO) in the same way as those previously described with metallic oxides mixed with carbon. The following values were obtained, each pair of simultaneous experiments being exactly alike in all respects save the presence of carbon :—

(1.) Heated in mercury-vapour (360°) for 30 minutes: gas evolved reduced to 0° and 760 mm.—

	Dioxide alone.	Dioxide and carbon.
CO_2..........	Nil	7·9 c.c.
Oxygen	3·5 c.c.	0·1
Other gases ..	trace	
Total gas	3·5	8·0

(2.) Heated in air-bath to 270° for 30 minutes—

	Dioxide alone.	Dioxide and carbon.
CO_2..........	Nil	2·3
Oxygen	0·7	0·1
Other gases ..	Nil	
Total gas	0·7	2·4

(3.) Heated in air-bath to 250° for 30 minutes—

	Dioxide alone.	Dioxide and carbon.
Total gas evolved..	Nil	0·15

just that due to occlusion by the carbon.

It hence results that at a temperature between 250° and 270°, and therefore very close to 260°, this form of manganese dioxide first begins to evolve oxygen *in vacuo*, and that the action of carbon thereon is also first manifested *in vacuo* at the same temperature. That the carbon does actually act is shown by the circumstances, firstly, that in presence of carbon no free oxygen was evolved, but only carbon dioxide; and secondly, that the amount of oxygen present in the CO_2 thus formed is considerably greater in each case than that evolved in the free state in the companion experiments respectively. Thus reckoned per gram of manganese dioxide employed, the oxygen eliminated was—

	Temperature.	Evolved as CO_2.	Evolved as free O.
Exp. (I) ..	360°	0·0187 gram = 1·87 p. c.	0·0083 gram = 0·83 p. c.
„ (II) ..	270°	3·0054 „ = 0·54 „	0·0016 „ = 0·16 „

The ratios of the oxygen evolved as CO_2 and as free O in these two experiments are (since carbon dioxide occupies the same space as the oxygen contained therein)—

$$(1.)\quad \frac{7{\cdot}9}{3{\cdot}5} = 2{\cdot}26 \text{ to } 1 \text{ at } 360^\circ$$

$$(2.)\quad \frac{2{\cdot}3}{0{\cdot}7} = 3{\cdot}28 \text{ to } 1 \text{ at } 270^\circ$$

whence it would seem that the reducing action of carbon increases less rapidly from 270 to 360 than does the tendency to evolve oxygen in the free state, the increase in the former case being from 2·3 to 7·9 or from 1 to 3·43, and that in the latter from 0·7 to 3·5 or from 1 to 5·0.

On the whole, then, the temperatures of initial action of carbon oxide, hydrogen, and carbon on this manganese dioxide are—

CO	Below 15°
Hydrogen	Near 145°
Carbon............	„ 260°

or in the same relative order as that hitherto found with iron and copper oxides.

(B.) *Pyrolusite.*

A sample of finely crystallised compact pyrolusite was found on qualitative analysis to contain practically nothing but manganese, oxygen, water, and SiO_2; especially no more than traces of iron or other reducible metallic oxides were present. At 200° this substance did not become anhydrous, although it lost a little moisture; on analysis the substance dried at 200° till perfectly constant in weight gave the following numbers:—

1·4330 gram gave 0·0070 SiO_2 = 0·49 per cent.

1·1860 gram ignited in a current of dry air communicated to a calcium chloride tube 0·0420 gram H_2O.

1·2530 gram, by Fresenius and Will's process, gave 1·078 CO_2 = 0·1960 oxygen.

0·3230 gram, by the iodine process, corresponded to 63·7 c.c. of decinormal iodine = 0·05096 O.

				Mean.
SiO		0·49		0·49
H_2O		3·54		3·54
O................	15·64		15·78	15·71
MnO (by difference)				80·26
				100·00

On calculating these numbers into percentages reckoned on the material excluding the 0·49 per cent. of SiO_2, they are found to agree with the formula $Mn_{30}O_{56}$, $5H_2O$ = $22MnO_2,4Mn_2O_3,5H_2O$,

	Calculated.		Found.
30MnO	2130	80·81	80·66 (by difference)
O_{26}	416	15·78	15·78
$5H_2O$	90	3·41	3·56
$22MnO_2,4Mn_2O_3,5H_2O$..	2636	100·00	100·00

so that the natural pyrolusite had a composition closely resembling the precipitated manganese dioxide (prepared from permanganate), so far as ratio between manganese and oxygen is concerned, the anhydrous substances being indicated respectively by—

Pyrolusite, $22MnO_2,4Mn_2O_3 = 11MnO_2,2Mn_2O_3$,
Precipitated dioxide, $15MnO_2,3Mn_2O_3 = 10MnO_2,2Mn_2O_3$,

each being practically manganese dioxide, but actually containing somewhat less oxygen than pure MnO_2. The pyrolusite, however, parted with only minute quantities of combined water at 200°, the water of hydration being only expelled at a higher temperature, whilst the water of hydration in the precipitated dioxide (not removed at 100°) was practically all lost at 200°).

The action of carbon oxide was not noticeable at any temperature below and up to 85°. At 87° a slight turbidity was produced in baryta-water on passing the gas for some few minutes, and at 95° the reducing action was very manifest.

Hydrogen did not begin to act at any temperature below and up to 180°, no loss of weight being occasioned after 15 minutes' exposure.

At 200° 1·1705 gram lost in 15 minutes 0·0005 gram = 0·04 per cent.

At 210° 1·1545 gram lost in 15 minutes 0·0075 gram = 0·17 per cent.

At 210° 1·1895 gram lost in 30 minutes 0·0075 gram = 0·63 per cent.

At 220° 1·1700 gram lost in 15 minutes 0·0100 gram = 0·85 per cent.

Hence the temperature of initial action lies between 180° and 200°, and therefore is near 190°.

In order to prove that the trifling loss of weight at 200—210° was not due to expulsion of combined water, a similar experiment was made with air instead of hydrogen; no loss of weight at all occurred. Moreover, whilst, as just stated, on heating 1·1895 gram in hydrogen to 210° for 30 minutes the loss of weight was 0·0075 gram = 0·63 per cent., on further examining by the iodine process, 0·3530 gram of the reduced substance, representing 0·3555 of the unreduced substance, it corresponded to 66·0 c.c. of decinormal iodine = 0·0528 oxygen = 14·85 per cent. As the original substance contained oxygen = 15·71 per cent., the loss on heating in hydrogen is 0·86 per cent., which fairly agrees with the loss of weight determination.

The temperature of initial action of carbon was determined in the manner above described, simultaneous experiments being made with 0·6 gram of the dioxide, and the same weight of dioxide mixed with half its weight of carbon. The following numbers were obtained:—

Temperature.	Pyrolusite alone.	Pyrolusite and carbon.
At 360° for 30 minutes	No gas evolved.	0·2 c.c. (due to occlusion).
At 420° for 15 minutes	CO_2 .... Nil Oxygen .... 0·6 Other gases trace 0·6	CO_2 .... 6·5 Oxygen .... } 0·2 Other gases .... } 6·7

Hence between 360° and 420°, say at 390°, is the temperature at which reduction by carbon and evolution of free oxygen on heating alone in a Sprengel vacuum both commence, the former action being at 420° very much more powerful than the latter.

The temperatures of initial action, then, are—

Carbon oxide	87°
Hydrogen	Near 190
Carbon................	„ 390

again following the usual order.

(C.) *Manganoso-manganic Oxides.*

With the object of preparing the oxide, Mn_3O_4, the usual process employed in the quantitative estimation of manganese was tried, perfectly pure manganous chloride being precipitated by sodium carbonate, and the resulting manganous carbonate thoroughly washed, dried, and calcined for two hours at a pretty bright red heat with frequent stirring. The brown-red powder obtained, however, did not possess the desired composition, but corresponded much more closely to $Mn_5O_7 = Mn_3O_4, Mn_2O_3$.

0·6005 gram, treated by the iodine process, corresponded to 62·4 c.c. of decinormal iodine = 0·04992 oxygen.

0·4385 gram corresponded to 46·0 c.c. = 0·0368 oxygen.

Calculated.						Found.	
For Mn_3O_4.			For Mn_5O_7.				
$3MnO$..	213	93·01	$5MnO$..	355	91·73		
O......	16	6·99	O_2	32	8·27	8·31	8·39
Mn_3O_4..	229	100·00	Mn_5O_7..	387	100·00		

Another specimen of manganous carbonate furnished analogous results; the product of several hours' calcination at a full red heat over a large Bunsen burner finally contained of "available oxygen" 8·52 per cent.

By long-continued strong ignition over a powerful gas blowpipe, especially in a capsule surrounded with a clay-jacketting furnace, the substances thus prepared lost in weight, forming ultimately substances closely approximating to Mn_3O_4; thus the product of the heating of the second sample above described for three successive periods of 10 minutes each became almost constant in weight and then gave these numbers:—

0·483 gram, titrated by the iodine process, corresponded to 42·8 c.c. of decinormal iodine = 0·03424 oxygen = 7·09 per cent.

5·533 gram, titrated by the iodine process, corresponded to 47·1 c.c.

= 0·03768 oxygen = 7·07 per cent.; calculated for Mn_3O_4, 6·99 per cent.

Another specimen similarly treated finally contained 7·13 per cent.

The action of carbon oxide, hydrogen, and carbon on each of the above two substances was tried with the following results:—

(I.) Manganoso-manganic oxide, containing 8·31—8·39 per cent. of available oxygen, corresponding nearly to $Mn_5O_7 = Mn_3O_4,Mn_2O_3$.

The action of carbon oxide was first noticeable at 97° by the baryta test, the action being well defined at 110°.

Hydrogen caused no loss of weight in 15 minutes at any temperature up to and including 230°.

At 250°, 0·5575 gram lost 0·0025 gram in 15 minutes = 0·44 per cent.

At 300°, 0·4345 gram lost 0·0035 gram in 15 minutes = 0·80 per cent.

At 320°, 0·3165 gram lost 0·0045 gram in 15 minutes = 1·42 per cent.,

whence the action commenced between 230° and 250°, or at about 240°.

With carbon from CO the following numbers were obtained, 0·6 gram being heated with 0·3 of carbon as usual.

Temperature	360°	30—400° zinc not melted but softened	400—420° zinc just melted
Time in minutes........	30	15	15
CO_2 formed............	—	—	3·7
Other gases............	—	—	0·1
Total gas evolved	0·25	0·4	3·8
Gas due to occlusion....	0·3	0·4	0·4
Gas due to reduction....	Nil	Nil	3·4

Hence about 410° may be taken as the temperature of initial action of carbon, that of hydrogen being 240°, and that of carbon oxide being 97°, *i.e.*, the order is the usual one.

(II.) Manganoso-manganic oxide, containing 7·07 to 7·09 per cent. of available oxygen, corresponding nearly to Mn_3O_4.

By the baryta test the action was first noticeable at 240°, being well marked at 260°; on attempting to corroborate these results by loss of weight, however, no noticeable difference in weight was perceptible after 15 minutes' heating at any temperature lower than that of boiling mercury, at which temperature 2·14 per cent. was lost in 15 minutes and 3·90 in 30 minutes. That this imperceptible variation in weight (observed at 200°, 300°, and 320°) was due to absorption of part of the CO_2 formed so as about to compensate for the loss of oxygen, is rendered highly probable by the following experiment:—0·5 gram of the manganese oxide was sealed up in a tube containing 8·0 c.c. of CO; the tube was then heated to 250° for 3 hours, and after cooling opened under mercury, the mercury rushed in filling the tube all but 2·0 c.c., of which 0·5 c.c. was absorbed by caustic potash. Hence the CO_2 formed by action at 250° had been, to a large extent, absorbed with formation of manganese carbonate; on adding dilute nitric acid to the particles of manganese oxide after the experiment effervescence was distinctly noticeable.

Hence 240° is the temperature of incipient action of CO as nearly as could be determined, but it is not at all improbable that this temperature is a little too high, the non-evolution of CO_2 at temperatures below 240° being due to its retention by the manganese oxide; the action at these lower temperatures, however, could only have been very faint, *no gain* in weight being observable.

Hydrogen brought about no loss of weight in 15 minutes at any temperature up to and including 250°.

At 260° 0·2480 gram lost in 15 minutes 0·0005 gram = 0·20 per cent.

At 280° 0·2480 gram further lost in 15 minutes 0·0020 gram = 0·80 per cent.

At 300° 0·1600 gram lost in 15 minutes 0·0055 gram = 3·44 per cent.

At 300° 0·1600 gram lost in 30 minutes 0·0085 gram = 5·31 per cent.

At 360° 0·3500 gram lost in 15 minutes 0·0200 gram = 5·71 per cent.

On sealing up in a tube about 8 c.c. of hydrogen with 0·5 gram of the manganese oxide, and heating to 250° for 3 hours, a slight absorption of hydrogen was noticeable on opening the tube, about 10 per cent. having disappeared. In a precisely similar companion-experiment in mercury vapour, however, the action was much more decided, for on opening the tube under mercury, the mercury rushed up and filled the whole tube.

Hence 255° is the temperature of incipient action, as nearly as it can be fixed.

On heating 0·6 gram of the Mn_3O_4 with 0·3 of carbon from CO, the following values were obtained:—

Temperature	360°	360—420°	420—440° Zinc melted. Antimony not melted.
Time in minutes	30	15	15
CO_2 formed	—	—	5·9
Other gases	—	—	0·1
Total gas evolved	0·25	0·4	6·0
Gas due to occlusion	0·3	0·4	0·4
Gas due to reduction	Nil	Nil	5·6

Hence about 430° is the temperature of initial action of carbon.

(D.) *Manganous Oxide.*

On heating precipitated manganese dioxide to redness for several hours in a platinum boat in a gentle stream of hydrogen, it lost weight rapidly at first, becoming of a greenish-grey colour, and subsequently more slowly, gradually becoming more and more green in shade; finally a substance of an emerald green tint was obtained, resembling oxide of chromium, but of a somewhat lighter and brighter shade. On heating this product for several hours to a full red heat in hydrogen, no further loss of weight ensued, and precisely the same result was obtained on substituting carbon oxide for hydrogen; whence it is evident that the points of initial action of carbon oxide and hydrogen on the green substance lay considerably above 500—600°.

That this green substance was pure MnO was shown by determining the increase of weight on roasting for some time in the air at a red heat, and also determining the "available oxygen" in the superoxide thus formed by the iodine process: sensibly equal values were obtained, which could not have been the case had the green substance contained manganese and oxygen in any different proportion than that indicated by MnO.

	Gram.		Per cent.
0·2655 gram roasted for three-quarters of an hour at a full red heat in a small platinum capsule gained in weight	0·0240	=	9·04
On igniting over the blowpipe for five minutes it further gained	0·0010	=	0·37
On further calcining at full red heat for three-quarters of an hour it further gained	0·0035	=	1·32
	0·0285		10·73

0·2915 gram of the roasted product, corresponding to 0·2633 of original green oxide, when titrated by the iodine process, corresponded to 34·4 c.c. of decinormal iodine = 0·02752 gram of oxygen = 10·45 per cent. calculated on the original green oxide, or sensibly the same percentage as that found by direct weighing.

It is worthy of note, in passing, that the gain in weight, had M_3O_4 been formed by the roasting, would only have been $\frac{16}{3 \times 71} = 7·51$ per 100 of MnO; the actual gain 10·45—10·73 corresponds to the composition $Mn_{15}O_{22} = Mn_3O_4,6Mn_2O_3$, which requires 10·52 per 100.

On mixing 0·6 gram of the green monoxide with half its weight of carbon from CO, and heating in a Sprengel vacuum to various temperatures from 360° up to a full red heat continued for half an hour (the tube being almost collapsed), only 1·0 c.c. of gas was obtained, that due to occlusion by the carbon employed being, as nearly as could be estimated, exactly the same, 1·0 c.c. Moreover, the gas came off fitfully on raising the temperature from stage to stage, and not continuously. Hence the point of initial action of carbon also lies upwards of 500—600°.

On comparing the temperatures of initial action of carbon oxide, hydrogen, and carbon on these different kinds of manganese oxides, it is at once noticeable that, whilst in every case the first reducing agent begins to act at a lower temperature than the second, and the second than the third, the several temperatures of initial action are notably higher the less the oxygen in the manganese oxide.

	Manganese dioxide.		Manganoso-manganic oxide.		Manganous oxide.
	Precipitated.	Pyrolusite.			
Composition by analysis of substance regarded as anhydrous	Mn_7O_{13}	$Mn_{15}O_{28}$	Mn_5O_7	Mn_3O_4	MnO
Physical texture......	Fine powder, amorphous	Very compact, crystalline	Fine powder, amorphous	Fine powder, amorphous	Amorphous
Carbon oxide	Below 15°	87°	97°	240°	No action at 600°
Hydrogen	Near 145°	Near 190°	Near 240°	255°	Ditto
Carbon.............	„ 260°	„ 390°	„ 410°	430°	Ditto

(E.) *Composition of the Oxide of Manganese formed by Ignition in Air of Higher and Lower Manganese Oxides.*

In the preceding sub-sections A, C, D, numbers have been quoted showing that the substances formed by the calcination at a full red heat (over a good Bunsen burner in a thin platinum capsule) of manganous oxide, manganous carbonate, or manganese dioxide, contain much more oxygen than that due to the formula Mn_3O_4. In the case of the product from manganous carbonate, half-an-hour's intense ignition over a gas blowpipe caused the expulsion of oxygen and the reduction to an oxide nearly approaching to Mn_3O_4; but in the case of manganese dioxide, conversion into Mn_3O_4 was not so nearly effected, a larger surplus of oxygen always remaining. In other experiments not quoted above, precisely similar results were obtained: thus prolonged ignition did not convert the pyrolusite employed above into Mn_3O_4, whilst another specimen of MnO roasted in the air over a Bunsen burner became a brown oxide containing 8·17 per cent. of oxygen. All the numbers obtained indicated a composition lying between Mn_3O_4 and Mn_2O_3, many of them being close to those required for the formula Mn_5O_7 or Mn_3O_4,Mn_2O_3.

Dittmar has already shown (this Journal, 1864, 294) that when manganese dioxide is ignited in air at the ordinary pressure or in a mixture of oxygen and nitrogen, in which the oxygen tension is near to that in the air (0·21 atmosphere), the oxide ultimately formed is extremely variable in composition between these limits; when, however, the oxygen tension exceeds 0·26 atmosphere, the product approximates more or less closely to Mn_2O_3, and when it falls below about 0·19 atmosphere, the product is nearer to Mn_3O_4. Thus on ignition in air at the ordinary pressure (tension of oxygen 0·21 atmosphere), Dittmar obtained in two experiments oxides MnO_x, in which $x = 1·352$ and 1·384 respectively; the first corresponding to $4M_3O_4,M_2O_3 = Mn_{14}O_{19} = MnO_{1·357}$; the second to $3Mn_3O_4,2Mn_2O_3 = Mn_{13}O_{18} = MnO_{1·385}$; and on ignition in mixtures of oxygen and nitrogen in which the oxygen-tension was between 6·87 and 7·38 inches (0·23 to 0·25 atmosphere), sometimes Mn_3O_4, sometimes Mn_2O_3 predominated in the product.

The following experiment well illustrates the influence of difference of temperature on the oxide of manganese formed under otherwise constant conditions as to oxygen-tension, when that tension is 0·21 atmosphere. About 1½ gram of manganous carbonate was calcined for an hour over a large Bunsen burner in a thin platinum capsule; the product was then roasted for some hours over the same burner, being weighed at intervals; finally the whole was strongly ignited over a blast gas furnace, and again weighed at intervals. The following numbers were obtained:—

	Gram.		Per cent.
1·4095 gram of the product of the calcination for one hour gained on further calcination for two hours	0·0055	=	0·39
After two hours more the further gain was	0·0040	=	0·29
,, ,, ,, ...	0·0035	=	0·24
Total gain ..	0·0130		0·92

	Gram.		Per 100 of original substance.
The product was then ignited for ten minutes over the blast gas lamp, and lost	0·0125	=	0·89
Ignited ten minutes more lost further....	0·0065	=	0·46
,, ,, ,, ...	0·0040	=	0·28
Total loss..	0·0230		1·63

The product of the last heating was found on titration to contain 7·08 per cent. of available oxygen (Mn_3O_4 requires 6·99 per cent.), whence the substance ultimately produced by the first series of calcinations over the Bunsen burner contained in 100 + 1·63 parts, 7·08 + 1·63 of "available oxygen" = 8·52 per cent., corresponding to $2Mn_3O_4,3Mn_2O_3$, which requires 8·58 per cent.

From these experiments, it results that in the quantitative estimation of manganese the usual directions of the text books to precipitate as carbonate and ignite until there is no further gain in weight may lead to serious errors, if, as is usual, an ordinary large Bunsen lamp be employed for the ignition, it being assumed that the end product is Mn_3O_4; whilst if the manganese be precipitated as hydrated peroxide and ignited, the same result may be brought about. Either a prolonged exposure of the substance to the highest temperature of a good gas blowpipe is essential to convert it into something approaching to Mn_3O_4, or preferably the "available oxygen" in the weighed calcined substance must be determined, and the true amount of MnO present thence deduced by subtraction from the total weight. The MnO present may also be obtained by prolonged heating in hydrogen at a bright red heat until weight is no longer lost, and weighing the residue. The error produced by reckoning the roasted product just described containing 8·52 of oxygen as Mn_3O_4, would amount to an over estimation of manganese to the extent of about 16 parts in the thousand, = 1·6 per cent.; for every 100 − 8·52 = 91·48 of MnO, really present would be estimated as 100 — 6·99, or 93·01 parts.

A curious phenomenon was observed with a specimen of nearly pure MnO prepared as just described, by reduction in a crucible at a bright red heat by hydrogen. After cooling down in an atmosphere of hydrogen (the crucible being plunged into a jar of CO_2 to extinguish the flame), the product was of a tolerably fine green underneath, with a brownish film on the surface; on standing exposed to the air for a couple of days under a shade, the film became black and much thicker, whilst an increase in weight of 3·93 per cent. took place, indicating a spontaneous absorption of oxygen. Nothing of the kind was observed with pure MnO, prepared by long-continued heating of the dioxide in a boat in a current of hydrogen, until no further loss of weight ensued even after several hours' further heating; no gain in weight or alteration in appearance ensued even after several days' exposure to air. Another specimen of not quite perfectly reduced MnO, just resembling the first in appearance, was kept over sulphuric acid for a fortnight, without altering in appearance or weight; it was then freely exposed to the air under a shade for a few days without noticeable alteration; at the end of a week, however, the brownish film had become sensibly darker and thicker, and an increase of weight to the extent of 1·06 per cent. had taken place.

§ 3. OXIDES OF LEAD.

In extension of the preceding experiments with the oxides of manganese, the following observations were made with various lead oxides:—

(A.) *Monoxide.*

Pure lead nitrate was recrystallised and ignited at first gently, and afterwards somewhat more strongly, but without fusion, until no more fumes of oxides of nitrogen were evolved. On heating the product with pure sulphuric acid, no fumes were evolved capable of acting on potassium iodide and starch; and on boiling with hydrochloric acid, and passing the vapours into potassium iodide and starch, only a trace of blue coloration was formed, showing that the lead oxide was practically free from any higher oxide. Moreover, on dissolving 0·9515 gram in glacial acetic acid, adding pure sulphuric acid, evaporating the poured off fluid to dryness, and weighing the total lead sulphate formed, 1·2920 gram of $PbSO_4$ were obtained.

	Calculated.			Found.
Pb	207	92·83		92·77
O	16	7·17	(By difference)	7·23
PbO	223	100·00		100·00

On heating this oxide in carbon oxide, it was found that a permanent change of tint from reddish-yellow to slatey-grey ensued, when even only a very minute amount of reduction had taken place, this change of colour being accompanied by the production of a perceptible turbidity, when the partially reduced substance was dissolved in hot acetic acid (the original substances dissolved to an almost perfectly clear fluid under the same conditions). This change of colour was faintly noticeable at temperatures somewhat below those at which any appreciable formation of CO_2 or loss of weight was first discernible, and, therefore, was presumably a more delicate test of incipient reduction than these criteria, especially as it was not produced at all at any temperature when air was substituted for carbon oxide. Thus, on leading pure carbon oxide over the lead oxide for 15 minutes at a time, no change of colour took place at 155°, or below, whilst a slight change was noticeable at 160°, and a more decided alteration of tint at 170°, and much greater ones at 180° and 190° respectively. The loss of weight in 15 minutes at 160°, however, and also at 180° was less than 0·25 milligram on about 1·5 gram of substance, or less than 0·02 per cent.; whilst no appreciable turbidity was produced in baryta-water by the effluent gases. At 190° the loss of weight first became perceptible in 15 minutes, 1·228 gram losing 0·0010 gram = 0·08 per cent., the baryta test first giving a perceptible turbidity at this temperature, a very decided action being noticeable at 200°. It hence results that the temperature of incipient action during 15 minutes, as determined by the colour test, is about 160°, whilst that from the loss of weight and the baryta test lies between 180° and 190°, say at 185°. This circumstance suggests the possibility that the nascent CO_2 formed by slight action at 160°, was absorbed by the PbO, forming $PbCO_3$, so as to prevent any action on baryta-water; the fact that there was *no appreciable gain* in weight in 15 minutes, however, proves that such action, if occurring at all, was extremely slight. That the heated PbO could take up CO_2 when not in a nascent condition, although not very readily, was proved by passing CO_2 over the PbO for 15 minutes at 200°, when no alteration in weight whatever ensued; after one hour's passage of gas no alteration in weight had taken place, but after four hours' passage, 1·750 gram of PbO increased in weight 0·0020 = 0·12 per cent.; the resulting product effervesced perceptibly with dilute nitric acid, whilst the original oxide did not do so. It is especially noteworthy that the slow absorption of CO_2 by PbO at 200° thus manifest is greatly quickened by increase of pressure; thus about 2·5 grams of the same PbO was sealed up in a tube containing 10 c.c. of CO_2 at the ordinary temperature, and was then heated to 200° for four hours. On opening the tubes under mercury, the mercury rushed up, and *completely filled the tube*, indicating perfect absorption, whence it would seem that the increased pressure (about $\frac{5}{3}$ atmosphere) obtaining at first caused the action to commence sooner, and that it went on, after being once started, so thoroughly as to render the tube vacuous, the amount thus absorbed representing about 0·0195 gram of CO_2 = 0·78 per cent. of the weight of the PbO employed. (*Vide* § 6.)

On heating the PbO in hydrogen, no alteration in tint was noticeable after 15 minutes' action at any temperature below and up to 185°, at 190° a faint change was noticeable after 15 minutes, and at 200° the change was much more decided in 15 minutes. No loss of weight was noticeable at 190° in 15 minutes, but at 200°,—

1·900 gram lost in 15 minutes 0·0010 = 0·05 per cent.
" " 30 " 0·0020 = 0·10 "

Hence, manifestly, 190—195° is the temperature of initial action, both colour test and loss of weight test nearly agreeing: whence it is evident that the difference between the values for the point of initial action of CO found above by these two tests (160° and 185° respectively), is really due to the retention by the PbO of part of the first traces of CO_2 formed at the lower temperature, thus preventing any perceptible loss of weight being perceptible, and diminishing the turbidity produced in baryta-water by the issuing gas below the point at which it is readily recognisable.

Carbon first began to act at a considerably higher temperature, the following numbers being obtained with carbon from CO, and the sugar-charcoal described in the first report:—

	Sugar charcoal.			Carbon from CO.	
Temperature	360°	360—420°	420—450°	360°	360—420°
Time in minutes	30	—	—	30	15
CO_2 collected	—	—	23·4	—	27·8
Other gases	—	—	0·2	—	0·2
Total gas	0·5	0·55	23·6	0·3	28·0
Gas due to occlusion	0·5	0·53	0·6	0·3	0·5
Gas due to reduction	Nil	Nil	23·0	Nil	27·5

In the first case no action occurred until zinc was well melted and antimony was softening, so that about 435° is the temperature of initial action. In the second case, no gas was evolved until the temperature was very close to the melting point of zinc, when action began and went on rapidly, so that here about 415° is the temperature.

On the whole, then, the temperatures of initial action are:—

	By colour test.	By baryta and loss of weight tests.
Carbon oxide	160	185
Hydrogen..............	190	195
Carbon from carbon oxide	415	
Carbon from sugar......	435	

(B.) *Plumboso-plumbic Oxide.*

A finely-coloured specimen of commercial red lead was selected which yielded on qualitative analysis nothing but lead and oxygen, with a minute trace of organic dust, which led to the evolution of a small quantity of CO_2 on heating in a Sprengel vacuum. On analysis, this yielded numbers indicating a composition much nearer to $Pb_5O_6 = Pb_3O_4 + 2PbO$ than to Pb_3O_4.

1·000 gram gave 1·230 gram of $PbCl_2$ by moistening with HCl, and evaporating down till no more gain in weight was noticed, and finally heating to fusion.

0·664 gram left after ignition 0·6530 fused PbO.

0·500 gram titrated by the iodine process represented 8·85 c.c. of normal iodine = 0·00708 oxygen.

0·500 gram titrated by the iodine process represented 8·95 c.c. of decinormal iodine = 0·00716 oxygen.

	Calculated.		Found.		Mean.
5PbO	1115	98·59	98·67	98·35	98·51
O	16	1·41	1·42	1·43	1·43
Pb_5O_6	1131	100·00			99·94

Carbon oxide did not act on this substance below 200°; at this temperature a slight action was noticeable (baryta test), whilst at 215° the action was very evident. 1·880 gram heated to 205° in CO for 15 minutes lost 0·0015 gram = 0·08 per cent.

On heating in hydrogen no loss of weight was observed at 200° nor at 220°.

At 240° 2·112 gram lost 0·0045 in 15 minutes = 0·21 per cent.
" 250° 2·155 " " 0·0050 " " = 0·23 "

At 270° the residue from the preceding lost further 0·0080 in 15 minutes = 0·37 per cent.

Comparative experiments made with red lead alone (0·6 gram), and the same weight of red lead with half its weight of carbon (from CO), in the way described in § 2, gave the following results:—

Temperature.	Red lead alone.	Red lead and carbon.
At 200° for 15 minutes ...	No gas evolved......	0·2 c.c. (due to occlusion
250° ,, ,, ...	Ditto	0·25 c.c. (ditto)
300° ,, ,, ...	Ditto	0·3 c.c. (ditto)
360° (mercury vapour) for 15 minutes	Gas evolved for a few minutes only CO_2 .... 0·8 Other gases .... — 0·8	Gas continuously evolved Co_2 .... 2·9 Other gases 0·1 3·0

The evolution for a short time of CO_2 from the red lead alone was doubtless due, as above stated, to the presence of a trace of organic dust in the red lead; the non-evolution of free oxygen alone is noteworthy, a different result being obtained with lead dioxide (*infra*) as well as with the superoxides of manganese, nickel, and cobalt. The temperature of initial action of the carbon may be taken as 330° (mean of 300° and 360°, so that the order of reduction is the usual one:—

Carbon oxide	200
Hydrogen	230
Carbon	330

(C.) *Lead Dioxide.*

The red lead used in the preceding experiments was digested with dilute nitric acid for two days, and the residual puce oxide thoroughly washed and dried at 100°, and finally at 130°. On analysis it was found to be nearly indicated by the formula $Pb_{11}O_{21}$, which may be written $19PbO_2,Pb_3O_4$ or $10PbO_2,PbO$.

0·2000 gram titrated by the iodine process represented 15·2 c.c. decinormal iodine = 0·01216 oxygen.

0·2085 gram titrated by the iodine process represented 16·0 c.c. decinormal iodine = 0·0128 oxygen.

	Calculated.		Found.		Mean.
11PbO	2453	93·88			
O_{10}..........	160	6·12	6·08	6·14	6·11
$Pb_{11}O_{21}$	2613	100·00			

On ignition, 0·6980 gram lost 0·0475 gram = 6·80 per cent; whence it would appear that a few tenths per cent. of water were still present after drying at 130°; no loss of weight, however, took place on heating to 240°. On heating to redness in a Sprengel vacuum, no CO_2 was evolved.

Carbon oxide first began to act at 80° (baryta test), the action being well marked at 90°. 0·9655 gram at 100° for 15 minutes lost 0·0035 gram = 0·36 per cent.

Hydrogen did not begin to act at any temperature below and up to 135°.

At 150°, 1·365 gram lost in 15 minutes 0·0010 gram = 0·07 per cent.

At 170°, the residue further lost in 15 minutes 0·0050 gram = 0·36 per cent.

At 200°, 0·967 gram lost in 15 minutes 0·0120 gram = 1·24 per cent.
,, ,, ,, ,, 30 ,, 0·0270 ,, = 2·79 ,,

At 240°, the residue further lost in 15 minutes 0·0120 gram = 1·24 per cent.

Hence the action began at about 140°, and was so far energetic at 200—240° that in an hour almost the whole of the "available oxygen" was removed, 5·27 per cent. being lost out of 6·11 per cent.

As a check on this initial temperature determination, 1·2195 gram was heated to 140° in hydrogen for 30 minutes, when a loss of 0·0025 gram was observed = 0·20 per cent.

0·6090 of the residue, representing 0·6105 of original substance, on titration by the iodine process, corresponded to 45·5 c.c. decinormal iodine = 0·0364 oxygen = 5·96 per cent.

0·608 of the residue, representing 0·609 of original substance, corresponded to 45·5 c.c. of iodine = 0·0364 oxygen = 5·97 per cent.

Hence the mean "available oxygen" before heating in hydrogen being 6·11 per cent., and that after 5·96 per cent., the loss was 0·15 per cent., closely agreeing with the loss of weight determination.

The temperature of initial action of carbon from CO was found as above described, comparative experiments being made with the dioxide alone (0·6 gram), and the same weight of dioxide with half its weight of carbon.

Temperature.	Dioxide alone.	Dioxide and carbon.
Heated up to 150° for 15 minutes	No gas evolved	About 0·1 c.c. (due to occlusion)
At 200° for 15 minutes ..	Ditto	About 0·15 c.c. (ditto)
250° „ „ ..	Ditto	About 0·2 c.c. (ditto)
270° „ „ ..	Gas continuously evolved CO_2 .... Nil Oxygen .... 1·5 Other gases.. trace Total .. 1·5	Gas continuously evolved 3·0 c.c. } 0·2 „ 3·2 „
360° (mercury vapour)	Gas continuously evolved CO_2 .... Nil Oxygen .... 4·9 Other gases.. 0·1 5·0	Gas continuously evolved 8·3 c.c. } 0·2 „ 8·5

Hence about 260° (mean of 250° and 270°) may be taken as the temperature at which carbon first begins to act on lead dioxide, and at which this substance begins to decompose in a vacuum, evolving oxygen. As with manganese dioxide, § 2, the formation of CO_2 causes a much more rapid withdrawal of oxygen than takes place on simply splitting up; in each case the action increases with the temperature, being roughly about three times as great at 360° as at 270° in each instance.

On comparing together the temperatures of initial action of carbon oxide, hydrogen, and carbon on the above different oxides of lead, it is evident that the dioxide is much more readily reduced than the monoxide, or the plumboso-plumbic oxide, which, being formed at a low red heat, is presumably more akin to the monoxide as regards stability.

	Monoxide.	Plumboso-plumbic oxide.	Dioxide.
Composition by analysis	PbO	Pb_5O_6	$Pb_{11}O_{21}$
Carbon oxide	160—185	200	80
Hydrogen	190—195	230	140
Carbon (from CO)	415	330	260
Carbon from sugar	435	—	—

§ 4. OXIDES OF COBALT.

Commercially pure cobalt nitrate was dissolved in water, slightly acidulated, and treated with sulphuretted hydrogen; the filtrate was boiled with a little nitric acid, and treated with excess of ammonia; the clear filtered fluid deposited on standing a mass of red crystals of a cobalt-ammonium nitrate; these were collected, dried, and ignited, at first gently, and finally very strongly. A black light powder was left, consisting essentially of cobalt monoxide, but containing a small excess of oxygen; no trace of nickel was present therein, nor of any metal save cobalt: on reduction in hydrogen this black powder furnished in two experiments 77·62 and 77·70 per cent. of cobalt, or 77·66 per cent. as the mean, $Co_{16}O_{17}$ requiring 77·63 per cent. (Co = 59). In order to obtain pure CoO from this, Russell's process (this Journal, 1863, 51) was adopted, the oxide being strongly heated over a blast lamp in a current of CO_2. It was found difficult to prevent reducing gases from the flame passing inwards and effecting further reduction of the CoO when an ordinary crucible lid was employed; but by employing a sheet of platinum foil fitting pretty tightly *inside* the crucible, and perforated with a central hole for the CO_2 tube, and keeping up a rapid current of CO_2, this difficulty was easily overcome.

0·7000 gram of the oxide finally obtained gave 0·5510 metallic cobalt on reduction in hydrogen = 78·71 per cent.

Average found by Russell = 78·59 per cent.

Calculated for CoO (Co = 59) 78·67 per cent.

From the black oxide containing 77·66 per cent. of metal, the sesquioxide was prepared by dissolving in dilute nitric acid, adding pure potash in excess, and a considerable excess of bromine, and digesting in the cold for some days; the jet-black precipitate was then washed many times by decantation, collected on a glass-wool filter, thoroughly washed, and dried at 100°; as thus obtained, the oxide formed a light black powder, which lost a small percentage of water on heating to 200° in a current of dry air, but did not part with any trace of oxygen at that temperature. After thus finally drying at 200° it gave numbers agreeing with the composition $6(Co_2O_3,H_2O),CoO$.

0·2185 gram titrated by the iodine process was equivalent to 22·15 c.c. of decinormal iodine = 0·01772 gram oxygen.

0·4225 gram = 43·15 c.c. = 0·03452 gram oxygen.

0·7580 gram gave 0·4935 metallic Co = 0·6273 CoO (Co = 59).

	Calculated.		Found.		Mean.
13CoO	975	82·70	82·75		82·75
O_6	96	8·14	8·11	8·17	8·14
$6H_2O$	108	9·16			By diff. 9·11
$6(Co_2O_3,H_2O),CoO$	1179	100·00			100·00

As a check on these numbers, the water produced during reduction in hydrogen was determined—

0·8930 gram gave 0·3495 gram H_2O.
0·7580 „ „ 0·2960 „

	Calculated.	Found.	
Water present as H_2O. . . .	9·11	—	—
,, formed from CoO. .	19·86	—	—
,, ,, Co_2O_3	9·16	—	—
Total	38·13	39·14	39·05

Hence the substance dried at 200° was essentially monohydrated cobalt sesquioxide.

(A.) *Cobalt Monoxide.*

The action of CO on the pure monoxide was found by the baryta-test to be first manifested at 155° after 3 or 4 minutes' passage of the gas; even at 170° and upwards, however, the action was not rapid, a copious production of turbidity in baryta-water by a few bubbles of issuing gas being only caused at about 180°. 0·8155 gram heated in CO to 155° for 15 minutes, lost 0·0010 gram = 0·12 per cent., no loss of weight being experienced at 100°, 120°, and 150° in 15 minutes in each case.

The action of hydrogen, on the other hand, was imperceptible at 155° and also at 160° after 15 minutes, but was quite noticeable at 170°; so that 165° may be taken as the temperature of initial action; distinctly above the temperature of initial action of CO, but only slightly above, when tested in the same way, by loss of weight.

0·8190	gram at	160°	lost in	15	minutes	Nil = 0
,,	,,	170°	,,	15	,,	0·0010 = 0·12 per cent.
0·9400	,,	180°	,,	15	,,	0·0030 = 0·32 ,,
,,	,,	,,	,,	30	,,	0·0080 = 0·85 ,,
,,	,,	,,	,,	45	,,	0·0105 = 1·12 ,,
0·9360	,,	210°	,,	15	,,	0·0075 = 0·80 ,,
,,	,,	,,	,,	30	,,	0·0105 = 1·12 ,,

With carbon (from CO) the following numbers were obtained, 0·6 gram of the oxide and 0·3 of carbon being employed as in all the other experiments:—

Temperature . . . . Time in minutes	360° 30	360—420° 15	420—440° 15	440—460° 15
CO_2 produced. . . . . Other gases	— —	— —	— —	11·1 0·9
Total gas . . . . Gas due to occlusion . .	0·3 0·3	0·4 0·4	0·6 0·7	12·0 0·8
Gas due to action	Nil	Nil	Nil	11·2

Hence about 450° is the temperature of initial action.

(B.) *Cobalt Sesquioxide.*

By the baryta-water test, the action of CO on the cobalt sesquioxide prepared as above described, was not only readily perceptible at the temperature of the laboratory, but also at 0°, and could even be distinctly noticed after two or three minutes' passage of gas in a freezing mixture at −11°.

Hydrogen, however, did not cause any loss of weight in the substance (dried till constant in a current of air at 200°) below 110°.

0·5380 gram at 100° for 15 minutes lost nil = 0.

0·5380 gram at 120° for 15 minutes lost 0·0005 = 0·55 per cent.

0·5380 gram further heated to 135° for 15 minutes lost further 0·0030 = 0·55 per cent.

0·6905 gram at 170° for 15 minutes lost 0·0785 = 11·36 per cent.

To make doubly sure that the loss at 120° was not due to the expulsion of water of hydration, 0·6285 gram were heated in hydrogen to 125° for 30 minutes, the loss of weight being 0·0030 gram = 0·48 per cent. On titrating the residue by the iodine process, it was found to be equivalent to 59·1 c.c. of decinormal iodine, corresponding to 0·04728 gram oxygen = 7·52 per cent.; as the original sesquioxide contained 8·14 per cent. of extra oxygen, the loss deduced from the titration is 8·14—7·52 = 0·62 per cent., agreeing as nearly as could be expected with the loss of weight determination, and clearly indicating that oxygen was actually removed.

The temperature of initial action of carbon was determined as described in § 2; it was found that, just as with manganese and lead dioxide, the temperature of initial action is practically identical with that at which oxygen is first evolved: the following values were obtained, 0·6 gram of Co_2O_3 being used in each case, alone in the first instance, mixed with 0·3 gram of carbon (from CO) in the second:—

At 200° for 15 minutes..	No gas evolved	0·1 c.c. evolved (due to occlusion by carbon)
At 250° for 15 minutes.	Nil................	0·15 c.c. evolved (due to occlusion)
At 270° for 15 minutes.	CO_2 evolved .. — Oxygen .... 5·2 c.c. Other gases .. 0·2 „ Total.. 5·4 „	5·0 c.c. 0·5 „ 0·2 „ 5·7 „

Hence about 260° is the temperature of initial action.

On contrasting the numbers obtained as above described with cobalt monoxide and sesquioxide, the same result is distinctly noticeable, as was observed with manganese oxides, viz., that each reducing agent respectively begins to act at a considerably lower temperature on the higher than on the lower oxide. Thus:—

	Monoxide.	Sesquioxide.
CO..............	155	Below −11°
H	165	110
Carbon	450	260

It may be noticed that the temperature of initial action of CO and H were determined on the cobalt oxide prepared by ignition of the cobalt-ammonium nitrate (indicated nearly by $Co_{16}O_{17}$), with the following results:—

Carbon oxide	120° (baryta-water test).
Hydrogen	195° (loss of weight test).

In this case the difference between the temperatures for CO and H is not so small as with the pure CoO, whilst the usual rule is obeyed that CO begins to act at a lower temperature than hydrogen.

§ 5. Oxides of Nickel.

Pure nickel oxide was prepared from commercially pure nitrate by acidulating and treating with sulphuretted hydrogen, boiling the filtrate with nitric acid and adding ammonia in large excess: to the blue clear filtrate clear solution of pure oxalic acid was added in quantity insufficient to neutralise completely; on standing, nickel oxalate separated; this was collected and washed, dried and ignited, and the residue moistened with nitric acid and again ignited. In this way an oxide was formed approximating to the monoxide, more closely indicated by $Ni_{20}O_{21}$ (Ni = 59); on reduction in hydrogen it furnished 77·80 per cent. of nickel, whilst $Ni_{20}O_{21}$ requires 77·83 per cent. This oxide contained no trace of cobalt, or of any other metal save nickel.

By Russell's process (this Journal, 1863, 51) the pure monoxide was prepared from this substance (by strong ignition over a blast amp in a crucible surrounded with a clay jacket): as with cobalt monoxide, it was found necessary to avoid entrance of reducing gases by employing a crucible lid fitting *inside* the crucible, with a current of carbon dioxide led in through a perforation in the lid.

0·6705 gram of the oxide finally obtained gave 0·5270 metallic Ni = 78·60 per cent.

Average found by Russell 78·59 per cent.

Calculated (Ni = 59) 78·67 per cent.

From the nickel oxide containing 77·80 of metal we attempted to prepare the sesquioxide in the same way as that employed for cobalt sesquioxide (§ 4), viz., by dissolving in nitric acid, adding excess of pure potash and a large excess of bromine, and digesting in the cold for some days: a jet-black powder was thus obtained which, after thorough washing by decantation and on a glass-wool filter, became constant in weight at 100°, forming a hydrated substance containing considerably less oxygen than Ni_2O_3; on heating to 150° it readily parted with oxygen, but none was evolved at 140°; the oxygen evolved at 150° contained a little CO_2, indicating the presence of organic matter in small quantity (taken up from the wash-water, &c.).

0·4740 gram of product, dried at 100° till perfectly constant in weight, was titrated by the iodine process and found equivalent to 20·55 c.c. of decinormal iodine = 0·01644 oxygen.

0·4810 gram = 20·9 c.c. of iodine = 0·01672 oxygen.

0·9355 gram gave 0·5440 metallic Ni = 0·6915 NiO.

These percentages approximate to $2Ni_2O_3,5NiO,12H_2O$.

	Calculated.		Found.	
9NiO	675	73·13	73·92	
O_2	32	3·47	3·47	3·48
$12H_2O$	216	23·40		
$2Ni_2O_3,5NiO,12H_2O$ ..	923	100·00		

So that this body was hydrated sesquioxide largely intermixed with monoxide.

(A.) *Pure Nickel Monoxide.*

The action of CO, as determined by baryta-water, was first manifest at 120°, being very evident at 130°.

Hydrogen caused no loss of weight below or at 215°.

At 225° 0·7310 gram lost in 15 minutes 0·0010 gram = 0·13 per cent.

At 250° 0·6515 gram lost in 15 minutes 0·0095 gram = 1·45 per cent.

At 270° 0·6420 gram lost in 15 minutes 0·0560 gram = 8·72 per cent.

Carbon (from CO) gave the following numbers, 0·6 gram of oxide and 0·3 of carbon being employed as in the other experiments :—

Temperature	360°	360—420°	420—440°	440—460°
Time in minutes	30	15	15	15
CO_2 evolved	—	—	—	3·8
Other gases evolved	—	—	—	0·2
Total	0·25	0·5	0·7	4·0
Gas due to occlusion	0·3	0·4	0·7	0·8
Gas due to action	—	—	—	3·2

Hence the temperatures of initial action of CO, H, and C are respectively about 120°, 220°, and 450°, or not very far from those found for the similarly prepared cobalt monoxide; it is noticeable that the nickel oxide containing 77·80 per cent. of metal ($Ni_{20}O_{21}$) gave as temperatures of initial action of CO and H respectively 180° and 215°, the action of the CO being but slow, even at 200°, so that only a few tenths per cent. were lost in half an hour at that temperature.

(B.) *Nickel Sesquioxide.*

The sesquioxide containing monoxide, above described, did not form CO_2 on leading CO over it at the ordinary temperature, but baryta-water began to be rendered turbid by the issuing gas at 30°, the action being well marked at 45°. Hydrogen caused no loss of weight at 60° or any temperature below that point.

At 70° 0·4935 gram lost in 15 minutes 0·0010 gram = 0·20 per cent.

At 90° 0·4935 gram further lost in 15 minutes 0·0060 gram = 1·21 per cent.

At 110° 0·4935 gram further lost in 15 minutes 0·0110 gram = 2·23 per cent.

So that about 65° is the temperature of initial action as deduced from the loss of weight test; to make sure that this loss of weight was really due to removal of oxygen and not of water of hydration, 0·5720 gram was heated to 80° for 50 minutes in a current of hydrogen, whereby a loss of weight took place of 0·018 gram = 3·15 per cent.

On titrating the residue by the iodine process it corresponded to 11·2 c.c. of decinormal iodine = 0·00896 oxygen = 1·56 per cent.; as the original substance yielded 3·48 per cent. of oxygen by titration, the loss of oxygen by reduction was 3·48 −1·56 = 1·92 per cent.

Hence oxygen was actually removed, the somewhat higher value found by loss of weight being doubtless due to loss of a little water in addition.

With carbon (from CO) the following numbers were obtained, 0·6 gram of the oxide being heated in one tube, and 0·6 gram of oxide with 0·3 of carbon in another tube simultaneously:—

	Nickel oxide alone.	Nickel oxide with carbon.
At 120° for 15 minutes	No gas evolved	Only a trace of gas, due to occlusion.
At 140° for 15 minutes	No gas evolved	Ditto.
At 150° for 15 minutes	A little gas evolved at first, and then a much slower steady evolution of oxygen.	Gas evolved continuously throughout the 15 minutes.
	CO_2 .... 1·6 cc.	4·2 c.c.
	Oxygen .... 1·7 „	0·2 „
	Other gases .. —	trace
	Total .... 3·3	4·4

As above stated, apparently a minute quantity of organic matter was contained in the nickel superoxide, giving rise to the evolution of CO_2 on heating alone; manifestly the evolution of oxygen and the temperature of initial action of carbon lie close together at near 145°.

On contrasting the temperatures of initial action of CO, H, and carbon on these two nickel oxides, it is at once noticeable that they follow the same rule as with the oxides of manganese, lead, and cobalt, viz., that the higher oxide is first affected at a sensibly lower temperature.

	Pure monoxide.	Superoxide.
CO	120	30
H	220	65
C	450	145

§ 6. ABSORPTION OF CO AND CO_2 BY METALLIC OXIDES.

In § 2 it was incidentally noticed that when an oxide of manganese approximating in composition closely to Mn_3O_4 was heated to 250° for three hours in a sealed tube containing CO, a considerable absorption took place, manganous carbonate being formed together with a small quantity of free CO_2. This action may apparently be due to one or both of two slightly different causes; either the CO becomes directly united to the manganese superoxide forming carbonate, thus—

$$(1.)\quad Mn_3O_4 + CO = 2MnO + MnCO_3,$$

or the formation of carbonate takes place in two stages, the Mn_3O_4 being first reduced to MnO, thus—

$$(2.)\quad Mn_3O_4 + CO = CO_2 + 3MnO,$$

and the MnO thus formed subsequently combining with the CO_2 liberated, forming carbonate, thus—

$$(3.)\quad MnO + CO_2 = MnCO_3.$$

That certain anhydrous metallic oxides are capable of uniting with dry CO_2, forming carbonates, is a well-known fact; in § 3 it has been shown that in the case of PbO the absorption of CO_2 is facilitated by sealing up in a tube, and heating so that at first the tension of the CO_2 is greater than that of the atmosphere; for in two experiments in which PbO was heated to 200° for four hours in CO_2, in the one case in a gentle current of the gas, in the other in a sealed tube, the amounts of gas absorbed were respectively 0·12 and 0·76 per cent. of the weight of the PbO, the latter percentage being manifestly less than the PbO would have absorbed had the supply of CO_2 not been necessarily limited by the conditions of the experiment.

In order, if possible, to throw some light as to the true cause of the formation of manganous carbonate in the above-cited experiment, the following trials were made: that the reaction represented by equation (1) does not represent the whole chemical change is manifest from the presence of free CO_2 in residual gas.

(A.) Pure MnO was sealed up in a tube with pure CO_2 (about 0·8 gram of MnO and 10 c.c. of CO_2 being employed), and the whole heated to 250° for four hours. After cooling no inrush was perceptible on opening the tube under mercury, and no effervescence of the manganese oxide was perceptible on adding nitric acid; whence, apparently, reaction (3) did *not* take place; hence, if the second view above referred to be correct, the combination of MnO and CO_2 to form $MnCO_3$ must be greatly facilitated by both substances being in the nascent state.

(B.) Precipitated MnO_2 was sealed up in a tube with a quantity of CO insufficient to reduce the MnO_2 to Mn_3O_4 by the reaction—

$$3MnO_2 + 2CO = Mn_3O_4 + 2CO_2,$$

and the whole laid by for a fortnight in a cold room in winter time (temperature about 0—10° throughout). On opening the tube no inrush ensued, but on examination almost the whole of the CO was found to have been converted into CO_2; the manganese oxide formed did not effervesce with nitric acid. Hence the following reaction—

$$(4.)\quad MnO_2 + CO = MnCO_3,$$

parallel to equation (1) did *not* take place.

(C.) Precipitated MnO_2 was heated to 100° for three hours in a current of pure CO; reduction took place copiously, the loss in weight being 6·7 per cent., the residual oxide contained no trace of carbonate, but evolved chlorine on heating with hydrochloric acid. Here, again, reaction (4) did *not* take place.

Hence it results that there is no reason for supposing that the formation of $MnCO_3$ from Mn_3O_4 and CO is due to the direct combination of CO with a superoxide of manganese as indicated by equations (1) and (4); the more probable explanation being that equations (2) and (3) express the changes, (3) only taking place with *nascent* MnO and CO_2.

As the nascent state is not requisite for the combination of PbO and CO_2 to form $PbCO_3$ corresponding experiments were made with oxides of lead.

(D.) 2·5 grams of PbO were sealed up with 10 c.c. of pure CO at the ordinary temperature, and were then heated to 200° for four hours. On opening the tube an absorption of gas to the extent of 2 c.c. was observed, the residual gas being CO with no trace of CO_2; the lead oxide effervesced with nitric acid. In this case, therefore, every portion of CO_2 formed was absorbed by the lead oxide with formation of lead carbonate, thus—

$$(5.)\quad PbO + CO_2 = PbCO_3.$$

(E.) On repeating the last experiment with the red lead described above (§ 3) indicated by Pb_5O_6, 2·5 c.c. of gas were absorbed with formation of carbonate by 2·4 grams of red lead; 7·5 c.c. of gas left unabsorbed consisted of CO with no trace of CO_2; the residual lead oxide effervesced with nitric acid. Here, therefore, the carbonate may be supposed to be formed either by reduction to PbO and absorption of the CO_2 formed in accordance with equation (5), or by direct combination, thus—

$$(6.)\quad Pb_5O_6 + CO = 4PbO + PbCO_3,$$

this latter view, is however, rendered improbable by the result of the following experiment:—

(F.) 1·2 gram of the PbO_2 above described (§ 3) was heated in a sealed tube with about 10 c.c. of pure CO to 100° for four hours. On opening the tube no absorption was evident, and no effervescence of the resulting lead oxide was noticeable on treatment with nitric acid; 2 c.c. of free CO_2 were, however, formed. Hence it would appear to result (since the amount of reduction taking place was insufficient to reduce the PbO_2 to Pb_3O_4, and *à fortiori* insufficient to reduce it to Pb_5O_6 or PbO) that CO_2 is not absorbed by superoxides of lead under the conditions of these experiments, although it is readily absorbed by

PbO under these conditions. That this is so is made evident by the following two experiments:—

(G.) 1·2 grams of PbO_2 and about 10 c.c. of CO_2 were sealed up together, and heated to 100° for four hours. No trace of absorption nor of formation of lead carbonate was noticeable.

(H.) Precisely similar negative results as regards absorption and formation of carbonate were obtained on heating 2·5 grams of red lead and 10 c.c. of CO_2 to 200° for four hours.

On the whole, then, these experiments point to the conclusion that when a carbonate is formed by heating a manganese or lead superoxide in CO (which does not take place with all the superoxides of these metals, but at most only with those intermediate between monoxide and dioxide) the action that takes place is not a direct combination of CO and the superoxide, but is accomplished in two stages, monoxide being first formed, and this substance subsequently combining with the CO_2 thus produced, the combination taking place in the case of manganese only when the monoxide and CO_2 are nascent.

Another conclusion that may be drawn also is that the red lead indicated by the formula Pb_5O_6, was *a definite and distinct oxide of lead, and was not a mixture* of Pb_3O_4 and $2PbO$, as might be supposed; for in the latter case an absorption of CO_2 must have taken place in experiment (H).

§ 7. CONCLUSIONS.

From the results detailed in Parts I and II of these researches the following general conclusions may be drawn:—

(1.) Whilst differences in physical state are attended with correlative differences in the temperatures at which the actions of the reducing agents, CO, H, and C, on metallic oxides are first manifest (after periods not exceeding a few minutes up to 15 minutes or so), the variations in temperature of initial action thus observable are usually not so great as to interfere seriously with the drawing of certain inferences, especially when the substances compared are in approximately the same physical state, having been prepared by analogous processes.

(2.) In the case of the oxides of the metals iron and copper, which form different oxides, each corresponding with definite series of salts and other compounds, and stable (*i.e.*, not evolving oxygen) on heating, the temperature of initial action of a given reducing agent on all the oxides of any one metal is sensibly the same unless the difference in physical structure is very marked; this fact is clearly correlated with the sensible equality in heat-evolution by the union of a given quantity of oxygen with either of these metals respectively, whether the one or the other oxide be formed.

(3.) In the case of the oxides of the metals, manganese, lead, nickel, and cobalt, which form superoxides, not corresponding with definite series of salts and other compounds, and not stable on heating (*i.e.*, evolving oxygen when heated), the temperature of initial action of a given reducing agent on the superoxide of one of these metals is sensibly lower than that of the same agent on the stable monoxide of the same metal, even after making all probable allowance for difference in physical structure: in the case of manganese this fact is clearly related to the circumstance that the heat-evolution in uniting a given quantity of oxygen with the metal so as to form the superoxide, is sensibly less than the heat-evolution taking place when the monoxide is formed instead; probably, therefore, the same relationship also holds in the case of lead, nickel, and cobalt.

(4.) In no case out of many examined has any exception been found to the general rule, that the temperature of initial action (during a few minutes) of carbon oxide on a given metallic oxide is lower than that of hydrogen on the same sample of metallic oxide; and that the temperature of initial action of hydrogen is similarly lower than that of carbon on the same sample of metallic oxide. In some few cases, however, the differences between the temperatures of initial action of carbon oxide and of hydrogen are not very large.

(5.) In one or two instances at present examined, a long continued exposure of a metallic oxide to the action of a given reducing agent at a temperature some degrees lower than the temperature of initial action deduced from experiments lasting a few minutes only, will give rise to a sensible reduction of the metallic oxide, especially under an increased pressure in a sealed tube. It is therefore desirable that experiments should be made to find out how far the elements of time and pressure can be substituted for increase of temperature in such cases; on these points experiments are in progress. It is noticeable in this connection that in certain instances the rapidity of action of hydrogen appears to augment more rapidly with a slight rise of temperature than is the case in corresponding experiments with carbon oxide; a circumstance doubtless connected with the superior lightness and diffusibility of hydrogen.

(6.) In a large number of cases the rule holds that the greater (algebraically) the heat-evolution during the performance of a reaction of the kind indicated by the symbols—

$$AB + C = A + BC,$$

(when AB is a metallic oxide and C a reducing agent) the lower is the temperature at which this action is first manifested to a just measurable extent in the course of a few minutes. All the cases included in paragraph 4 and some of those in paragraph 3 of these conclusions, are special cases of this rule; whilst probably all the other cases included in paragraph 3 also come under the rule, although it cannot be said with certainty that they do, from want of determinations of the actual heat-evolutions, or of the data from which they can be calculated.

(7.) Whilst experimenting on the above points, it has incidentally been found that the products of ignition in air of manganese carbonate and of various oxides of manganese always contain more oxygen than Mn_3O_4, and can be reduced nearly to that composition, only by long continued heating over a powerful blast-lamp; and that in consequence serious errors are apt to be introduced into quantitative determinations of manganese unless special care be taken to avoid them.

(8.) Evidence has also been obtained, tending to show that under certain conditions carbon oxide can apparently combine directly with certain metallic superoxides to form carbonates; but that the reaction really takes place in two stages, viz., first, reduction to monoxide with formation of CO_2, and second, combination of monoxide with CO_2 to form carbonate.