LII.—*Third Report to the Chemical Society on "Researches on some Points in Chemical Dynamics."*

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§ 1. *Determination of Relations existing between Rate of Reduction of Copper Oxide by Hydrogen, Time, and Temperature.*

It was incidentally shown in Reports I and II that when determinations are made of the amounts of oxygen removed from various metallic oxides at temperatures somewhat above the "points of initial action" (as found by periods of exposure to the action of reducing agents of some minutes only) numbers are obtained constituting the data for the construction of curves giving by inspection the ratios between the deoxidation taking place at varying temperatures in a given time (15 minutes say) and the temperatures themselves. Evidently by carrying out analogous experiments at constant temperatures for varying times, the other conditions of the experiments being as nearly as possible identical, other curves would be obtained giving the ratios between the amounts of deoxidation at given temperatures and the times requisite to produce these amounts of deoxidation. These two sets of curves can obviously be combined so as to form a curved surface related to three planes mutually at right angles, so that the lengths of the perpendiculars let fall upon these three planes from any given point on the surface shall represent respectively a given amount of deoxidation and the time and temperature requisite to produce that deoxidation under otherwise constant conditions.

Planes cutting this surface and parallel to one of the three given primary planes will then give intersections representing the curves for deoxidation and temperature, time being constant; other planes parallel to a second of the three primary planes will similarly give intersections representing the second set of curves for deoxidation and time, temperature being constant; whilst planes parallel to the third of the three primary planes will give intersections representing curves indicating the relative times and temperatures requisite to produce given constant amounts of deoxidation.

Given a series of curves indicating for various times $T_1, T_2, T_3 \dots$

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(constant for each curve) the relation between deoxidation and temperature, the curved surface can be drawn and the second and third sets of curves deduced therefrom. Or, given a series of curves indicating for various temperatures $t_1, t_2, t_3 \dots$ (constant for each curve) the relations between deoxidation and time, the curved surface can similarly be drawn and the first and third sets of curves thence deduced. As at first sight it appeared to be, for various reasons, more convenient to observe the curves of the second kind than those of the first, this mode of arriving at the curve-surface was adopted.

The use of paraffin, air, or other analogous baths, even when fitted with Page's mercurial regulator* (which we found to work far better than any other kind tried), was found to be far less convenient for obtaining sensibly constant temperatures for considerable periods of time than the employment of vapour-baths obtained by heating uniform substances in cohobating arrangements; such substances as glacial acetic acid, turpentine hydrocarbon, aniline, naphthalene, mercury, &c. (purified when requisite by previous fractional distillation), were therefore employed in nearly every one of the observations made. For temperatures above 100° Page's regulator was found to have the disadvantage that, after some hours or days' use, the mercury volatilised in sensible quantity, thus lowering its level and allowing more gas to pass, and consequently raising the temperature of the bath in which it was immersed: even at 85° this action was noticeable after a week or two. The exact temperature of the vapour-bath used was taken by means of thermometers carefully compared with a Kew-standardised thermometer, the upper part of the stem of which was carefully calibrated so as to give a table of readings based on the Kew-standardisation up to 100° C. In some cases the temperature rose slightly through oxidation (as with aniline) or volatilisation of more volatile portions; but the errors due to this cause were but slight, and moreover were distributed over the whole curve traced out and included in the other general sources of error through the mode of observation of the different points adopted.

In order to obtain numerical values comparable with one another, it was necessary that each experiment should be made under as nearly as possible constant conditions (save as to time and temperature), especially as regards rate of hydrogen supply, quantity and physical condition of the metallic oxide, amount of surface exposed, &c., &c. Several hundred grams of oxide of copper were prepared from electrolytic copper by solution in nitric acid, filtration, evaporation to dryness, and heating to redness in quantities of about 20 grams at a time in a well-covered platinum crucible, the ignition being finally completed over a gas blowpipe. Not until the whole series of experiments

* This Journal, 1876, 1, p. 24.

was nearly completed was it found that this last operation might have introduced a complicating circumstance. At a temperature near a white heat an ordinary platinum crucible becomes sensibly pervious to reducing gases (probably hydrogen), so that if a mass of pulverulent copper oxide be heated over a gas blowpipe flame for half an hour or more that portion of the copper oxide in contact with the platinum becomes notably reduced, so much so as sometimes to be distinctly red and to give off copious red fumes on moistening (after cooling) with nitric acid. That this is not due to the infiltration of reducing gases from the lid of the crucible is shown by the circumstance that it takes place even if a perforated lid be employed, furnished with a tube delivering into the crucible a rapid current of air or carbon dioxide, whilst if a porcelain crucible be used instead of a platinum one, the reduction is practically stopped entirely, even though no stream of air or carbon dioxide be used. Fortunately in the preparation of the oxide of copper required for the curve determinations the ignition over the blowpipe was not carried on for more than a few minutes, so that the amount of reduction introduced was but slight; it was, however, appreciable, for the products of the several portions thus ignited, after pulverisation in a clean porcelain mortar, sifting through a very fine brass sieve and thoroughly intimate intermixture, gave the following numbers:—

1.2415 gram reduced with hydrogen at a red heat till constant			
lost 0.2455 gram.....	=	19.77	per cent.
1.1540 „	lost 0.2275	=	19.71 „
1.1740 „	„ 0.2285	=	19.64 „
	Mean ..	<u>19.71</u>	„
Taking Cu = 63.5, calculated amount			
for CuO		<u>20.12</u>	„

whence a distinct deficiency in oxygen is noticeable. Moreover, on boiling with slightly acid ferric chloride, ferrous chloride was formed; on titration with permanganate numbers were obtained corresponding with those got by reduction in hydrogen, thus—

0.8570 gram required permanganate cor-			
responding to 0.00417 oxygen	=	0.47	per cent.
1.1135 gram required permanganate cor-			
responding to 0.00524 oxygen	=	0.47	„
0.6190 gram required permanganate cor-			
responding to 0.0031 oxygen	=	<u>0.50</u>	„
	Mean	<u>0.48</u>	„

hence the percentage of oxygen originally present is 19.74, this being the value of x when $\frac{x + 0.48}{100 + 0.48} = \frac{20.12}{100}$. These results correspond to the formula $\text{Cu}_{40}\text{O}_{39} = 38\text{CuO}, \text{Cu}_2\text{O}$.

Calculated for $\text{Cu}_{40}\text{O}_{39}$.	Found.	
	Mean from reduction in H. 19.71	Mean by titration. 19.74

The hydrogen employed was prepared from commercially pure granulated zinc and hydrochloric acid, being used direct from the generator after passing through **U**-tubes containing pumice stone soaked in caustic potash and silver nitrate. In order to obtain an equable stream of gas delivered as nearly as possible at a constant rate the gas was passed through a bubble arrangement consisting of a bottle half full of sulphuric acid and provided with a doubly perforated cork through which passed two glass tubes, one dipping under the sulphuric acid, one not doing so. By means of a Bunsen's screw clamp worked by a lever some inches long placed on a stout nonvulcanised india-rubber tube between the bubbler and the **U**-purifying tubes it was found tolerably easy to regulate the rate of bubbling of the gas through the acid to any required speed, 100 bubbles per minute being that finally adopted. In order to obtain anything like uniformity it was found indispensable to have no liquid potash or silver nitrate solution at the bottom of the **U**-tubes, and to have a tolerably constant back pressure of some ten inches of water in the hydrogen generator (consisting of two reservoirs united by an india-rubber tube between tubulations at their bases), easily obtained by elevating the acid reservoir on a stand. In order to determine how much hydrogen corresponded to a given rate of bubbling a number of preliminary experiments were needed. It was found that only rough results could be obtained by collecting the hydrogen delivered over water, because the bubbling up through the pneumatic trough affected the size of the bubbles in the bubbler, wherefore a gas-measuring arrangement was constructed on the principle of the gas reservoir of a gas-works, the bell being a graduated glass tube immersed in a wider tube, the bottom of which was closed by a doubly perforated cork, so that by turning suitable taps either water could be let into the cistern part of the arrangement from a reservoir at a higher level, or water could be run out, and thus the pressure in the bell kept almost exactly atmospheric, whether gas was allowed to enter it or to leave it. By means of this arrangement it was found that the size of the bubbles in the bubbler was not affected by small variations of pressure. Whether the water in the cistern stood an inch or two higher than that in the bell during

collection, an inch or two lower, or fluctuated, no perceptible difference was caused in the size of the bubbles; a marked alteration in their size, however, was produced by the interposition between the bubbler and the measuring arrangement of the narrow glass **U**-tubes containing copper oxide at the bend used in all the experiments. A considerable diminution in the size of the bubbles was thus caused, which diminution moreover was not constant, varying with the packing of the pulverulent copper oxide according as it was shaken down more or less. On an average it was found that 100 bubbles per minute, at a temperature of 15° , corresponded to a delivery of 16.14 c.c. at 15° and 760 m. per minute when no copper oxide **U**-tube was inserted, but that 16 per cent. less, or 13.5 c.c., were passed per 100 bubbles when the **U**-tube was inserted between the bubbler and collecting apparatus. When the copper oxide was very closely packed indeed the diminution rose to about 30 per cent., and when it was very loose (as when it was partially reduced in hydrogen and not shaken down) the diminution was as low as 5 per cent.; but, under the conditions obtaining in the majority of the experiments, it was close to 16 per cent.; so that the rate of delivery of gas was on an average very close to 13.5 c.c. at 15° and 760 m., or 12.5 c.c. normal = 0.00112 gram per minute. It is specially noticeable that the size of the bubbles was largely influenced by the rate at which they passed. Thus the following table gives the average results of a large number of accordant experiments from which a mean curve was deduced; in these the bubbler was directly connected with the measuring apparatus, no **U**-tube with copper oxide being between them:—

Time of passage of 100 bubbles.	c.c. of hydrogen at 15° and 760 m. per 100 bubbles.	
	Difference.	
50 seconds	16.70	—
55 "	16.40	0.30
60 "	16.14	0.26
65 "	15.91	0.23
70 "	15.70	0.21
75 "	15.50	0.20
80 "	15.32	0.18
85 "	15.15	0.17
90 "	15.00	0.15
95 "	14.87	0.13
100 "	14.76	0.11
105 "	14.67	0.09
110 "	14.60	0.07
120 "	14.55	0.05
125 "	14.51	0.04
130 "	14.48	0.03
135 "	14.46	0.02
140 "	14.45	0.01

Similar results were obtained, as described in § 2, with carbon oxide.

The experiments were conducted as follows:—A number of precisely similar **U**-tubes were constructed of quill tubing, the bottoms being bent into regular semicircular curves of about $\frac{1}{4}$ -inch radius, measured on the inner side of the curve; one end of the **U**-tube was bent over to a right angle, and slightly drawn out to admit of more easy connection by an india-rubber tube with the bubbler. A quantity of copper oxide was measured out in a platinum spoon fixed to a glass handle sufficient to just fill the semicircularly curved bottom of the **U**-tube; this was introduced by means of a small funnel (kept along with the spoon, under a shade to protect from dust). This quantity of oxide of copper averaged 1.15 gram, and was in every experiment very close to that weight (save in some observations made specially to test the influence of varying amounts of copper oxide). The quantity introduced was known by weighing the empty tube and the tube after introduction; or more simply, in view of the rest of the experiment, by weighing the tube filled with hydrogen, and covered with tightly fitting india-rubber caps beforehand, then introducing the oxide of copper, and filling again with hydrogen, and weighing again. The weighed **U**-tube being attached to the india-rubber tube connected with the bubbler, and the hydrogen stream regulated to the exact speed of 100 bubbles per minute, the **U**-tube was plunged into the vapour-bath, and the time noted. The vapour-bath in most of the experiments consisted of a copper bottle, into the mouth of which fitted a cork perforated with four holes, and cut in two by a vertical cut passing through two of them; these two halves of the cork embraced the two limbs of the **U**-tube, which just fitted into the two holes thus sliced asunder; the other two perforations (one in each half of the severed cork) served to insert a thermometer into the vapour-bath, and for the adaptation of a long tube to condense the vapour and act as a cohobator. This arrangement permitted of a rapid entrance or withdrawal of the **U**-tube from the vapour-bath, whilst yet enabling a tolerably vapour-tight cork junction to be made at the mouth of the copper bottle. When the required time of exposure had elapsed the **U**-tube was withdrawn, cooled down as quickly as possible with the hydrogen passing through it, and finally closed with the india-rubber caps and quickly weighed.

A correction was found to be necessary as to the time of exposure; some few seconds or more elapsed before the bend of the **U**-tube rose up to the temperature of the vapour-bath; an estimate as to this time was obtained by noticing how long it took a thermometer to rise to within a degree or two of its stationary temperature. On the other hand, the tube and contents did not cool down instantaneously below

the temperature at which reduction could take place on withdrawal from the bath; so that reduction was actually going on for a slightly longer period than that during which the **U**-tube was in the bath, after correction for the time taken to heat up the **U**-tube. An allowance of a few seconds more or less, according to the temperature, was made for this, the usual mode of combining both corrections being to note the time at which a thermometer introduced simultaneously with the **U**-tube reached to a point a few degrees below its stationary temperature, and to expose for the required time after this, removing the **U**-tube at the end of the time; it being considered that the deficiency in reduction, owing to the tube being not quite heated up on first taking the time, was about balanced by the slight amount of reduction going on during cooling after removal from the bath. It is true that a slight degree of uncertainty as to the true average times of exposure is unavoidable; but the error due to this cause is small compared with other sources of discrepancy.

One point essential to discover, first of all, was whether the hydrogen stream was thoroughly heated up to the temperature of the vapour-bath before coming in contact with the copper oxide. It was found that when the **U**-tube was of such length that 4 to 5 inches were inside the cork in the vapour, the hydrogen was perfectly brought to the temperature of the bath in passing through the heated upper part of the tube; this was shown by fixing two thermometers, one inside the vapour-bath, one inside the **U**-tube, containing no copper oxide, with the bulb as near the bend as possible. Series of readings of both thermometers were then taken, both when no hydrogen was passed, and when the usual current or a more rapid one was employed. On contrasting the average of a dozen readings of each thermometer it was found that precisely the same temperature difference was registered by the two thermometers in each case, which could not have been the case had the hydrogen been cooler than the vapour when it reached the thermometer inside the **U**-tube. Even with a hydrogen stream of double the normal rate (*i.e.*, double 12.5 c.c. per minute at 0° and 760), the gas was completely heated up to the temperature of the bath before reaching the bend.

An opposite kind of error to that which would have been occasioned by deficient heating up of the hydrogen is apt to be introduced by the circumstance that during reduction of copper oxide by hydrogen an evolution of heat takes place on the whole; and consequently when action has commenced, the temperature of the partially reduced copper oxide may rise above that of the bath owing to this development of heat. Such a rise is not likely to be great when the copper oxide is in a narrow tube, as the extra heat would be quickly carried off by conduction, and especially by the escaping hydrogen and steam. In

order to gain some information as to whether this development of heat was appreciable, readings were taken as above with two thermometers (one in the **U**-tube, one in the vapour-bath) firstly before any hydrogen current was turned on, nextly, whilst the average current of 12.5 c.c. normal was passing, the bend of the **U**-tube having been filled with copper oxide previously. In this way it was found in a vapour-bath of naphthalene that whilst the difference of scale-readings of the two thermometers was 2.35° (average of 20 readings of each thermometer), when no hydrogen current was passing, it was 2.44° (average of 10 readings) during the period when from 20 to 50 per cent. of the oxygen present was being removed from the copper oxide, and also 2.44° (average of 10 readings) during the periods when 50 to 80 per cent. was being removed. As shown below these periods correspond to the most rapid removal of oxygen, whilst the naphthalene bath temperature is almost the highest tried, again corresponding to most rapid deoxidation; even under these circumstances, however, the extra development of heat was only sufficient to heat the issuing hydrogen and steam up to 0.09°C. higher than the bath temperature. As shown in § 2 similar experiments with carbon oxide led to an analogous result; only in this case, as more heat is developed during reduction by carbon oxide than by hydrogen, the extra development of heat caused a greater difference between the two thermometers, not exceeding 0.25° however.

The **U**-tubes containing partially reduced oxide of copper were necessarily weighed as soon as possible, *i.e.*, as soon as they had cooled down to the temperature of the air. Under these conditions a tube of the size used (made from some 14 inches length of quill tubing) weighs less by some two milligrams than it would do if kept (in dry air) for an hour or two and then weighed, owing to the non-immediate re-absorption of the film of air condensed on its surface, and partially removed by heating.* In order to avoid this source of error

* Although the fact has been repeatedly pointed out that the weight of a recently heated vessel (*e.g.*, a crucible), weighed when just cold, is perceptibly less than its weight after standing an hour or two (even over sulphuric acid) owing to the slow recondensation on the surface of an air-film, yet as many experimenters seem to be unaware of the extent of the possible errors thus introduced, it may be as well to point out that the weight of an ordinary small Berlin porcelain covered crucible may differ 1, 2, or even 3 milligrams, according as it is weighed immediately after cooling, or after standing, so as again to take up the air-film. In organic analysis this point is of importance, as the heat radiated from the combustion furnace on to the potash bulbs will often expel sufficient air-film to make them weigh 1 or 2 milligrams less than their weight after standing an hour or two (of course with caps on). It is convenient to warm and then cool again the bulbs just before filling them with potash, and taking the first weighing: by this means the condition of the air-film before and a few minutes after the combustion is rendered practically the same.

the **U**-tube was always heated, and then cooled again before filling with hydrogen to take the weight of the empty tube, so that the condition of the air-film should be as nearly as possible the same at every weighing. A tube that had been used once was always carefully cleaned out with hot nitric acid before being used again, to avoid the possibility of particles of partially reduced substance adhering to it, and perchance causing, by contact action, reduction to commence earlier than it would otherwise have done.

The first experiments made led to the conclusion (borne out by subsequent results) that reduction of copper oxide by hydrogen does not always commence at once, but that in certain cases (*i.e.*, below a certain temperature) a certain amount of time must elapse before the action commences, and a yet longer time before it attains a constant rate, *i.e.*, before it ceases increasing in rate. The following experiments, however, lead to the curious result that in many cases, when the action has once started, allowing the substance to cool down and to stand for a sufficient length of time to take a weighing does not interfere noticeably with the rate of action on putting back again into the vapour-bath. This is not invariably the case, however, a distinct retardation being noticeable by interrupting the action when it takes place at temperatures below a certain limit, and even above this limit a retardation is still noticeable, if some hours elapse before the **U**-tube is put back again into the bath, *e.g.*, when an experiment is interrupted over night and resumed next morning. Accordingly the observations made may be grouped into two kinds, *viz.*, those where the exposure was carried out for a given time without an interruption, and those where the exposure was interrupted once or more; these latter observations were obtained by simply replacing the **U**-tube in the bath after the first weighing for the uninterrupted observation had been made, and going on for a fresh period of exposure, and so on; at temperatures above 160° the uninterrupted observations and the interrupted ones do not differ from one another more than those of the first kind do amongst themselves, so that on taking a sufficiently large number of observations, the mean curve-values deduced from each set are practically identical. In other words, whether the oxide of copper be exposed for a time T at one operation, or for a series of times $t_1, t_2, t_3, \dots$ jointly equal to T , makes no material difference, provided firstly that the temperature is not below the limit of about 160° , and secondly, the intervals elapsing between the periods t_1 and t_2 , t_2 and t_3 , $\dots$ do not exceed some ten minutes or so.

Thus the following numbers were obtained in a vapour-bath of aniline, the average corrected temperature throughout the series of Obviously weighings to less than half a milligram are utterly superfluous in all such cases.

[illegible]

Fig 1.

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observations being 184.5° , and the actual temperature at any given stage of any given experiment not being so much as 1° above or below the average, and generally within 0.25° of the average. The numbers represent the percentages of oxygen lost, the percentage originally present being 19.74 (*i.e.*, complete reduction equals a loss of 19.74 per cent.). The numbers placed in the same vertical column were all obtained with the same portion of oxide of copper, so that in each column the figure corresponding to the shortest time exposure is an "uninterrupted observation," and those corresponding to longer exposures are "interrupted observations," the period of interruption in each case being ten minutes or so, just enough to cool down thoroughly and weigh.

The annexed diagram (Fig. 1) represents these results, the thin line connecting the points deduced from uninterrupted observations, and the thick one those obtained from the interrupted observations; the numerals at the points represent the numbers of observations furnishing the points respectively as averages. It is evident from inspection of the curve, and of the preceding table giving the isolated observations themselves, that the mean curves deducible from the uninterrupted and interrupted observations are practically identical. The dotted line represents this mean curve, and the following table the average values thence reckoned.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
0	0	0	0	0
5	0.06	0.06	0.06	0.012
10	0.19	0.13	0.07	0.026
15	0.46	0.27	0.14	0.054
20	0.93	0.47	0.20	0.094
25	1.62	0.69	0.22	0.138
30	2.50	0.88	0.19	0.176
35	3.56	1.06	0.18	0.212
40	4.71	1.15	0.09	0.230
45	5.92	1.21	0.06	0.242
50	7.18	1.26	0.05	0.252
55	8.48	1.30	0.04	0.260
60	9.81	1.33	0.03	0.266
65	11.16	1.35	0.02	0.270
70	12.49	1.33	-0.02	0.266
75	13.76	1.27	-0.06	0.254
80	14.93	1.17	-0.10	0.234
85	15.95	1.02	-0.15	0.204
90	16.73	0.78	-0.24	0.156

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
95	17·34	0·61	—0·17	0·122
100	17·84	0·50	—0·11	0·100
105	18·27	0·43	—0·07	0·086
110	18·65	0·38	—0·05	0·076
115	18·99	0·34	—0·04	0·068
120	19·30	0·31	—0·03	0·062
150	19·50	0·20	—	0·007
180	19·65	0·15	—	0·005

From the general sigmoid character of the curve, it is evident that the rate of reduction during the first five minutes is so small as to be practically inappreciable, and that it then gradually increases to a maximum, after which it gradually decreases until complete reduction is attained. It might be supposed that the apparent minute amount of action during the first few minutes is not real, but is simply due to the retention in the oxide of copper of all, or almost all, of the water formed by the reaction, thus preventing any large loss of weight from being noticed. That this is not so, however, was shown in two ways; firstly, on titrating with permanganate (after solution in ferric chloride) the copper oxide after various short exposures during which no large loss of weight had taken place, no greater amount of reduction could be detected than that indicated by loss of weight; and secondly, on heating the slightly reduced substances to redness in a current of pure dry nitrogen (evolved from potassium nitrite and ammonium chloride), a chloride of calcium tube being attached, neither loss in weight of the oxide of copper, nor gain in weight of the chloride of calcium tube could be detected, clearly showing that no water was retained by the oxide of copper. Whether the reduction took place at as low a temperature as 130° , or at higher temperatures, and whether 5, 50, or 99 per cent. of the oxygen present had been removed, this same negative result was found, viz., that no measurable amount of moisture was retained by the copper oxide. Out of many experiments, the details of which it is unnecessary to quote, only one indicated a weighable amount of moisture as being retained, and this single case was where 3·1 per cent. of loss of weight (out of 19·74 per cent. of the oxygen originally present) had been occasioned by heating for several hours at 130° ; even in this solitary instance, however, the loss of weight of the copper oxide on ignition in nitrogen, and the gain in weight of the chloride of calcium tube were each only 0·5 milligram, a quantity hardly greater than the possible weighing errors through air-films, &c., and only corresponding to 0·04 per cent. on the weight of oxide of copper

employed (1.150 gram). In no other experiment was either the loss of the one or the gain of the other greater than 0.25 milligram, *i.e.*, greater than the possible weighing error.

It may be noticed in this connection, that the spongy copper obtained after 3—4 hours' heating to 184.5° , and that produced at somewhat higher temperatures in shorter periods (*e.g.*, 50—60 minutes at 256°), was so nearly perfectly reduced, that on further heating to redness in hydrogen, it only lost 0.1 to 0.2 per cent. in weight; reduction to such a stage that no further loss occurred on heating to redness in hydrogen was, however, never brought about, even after 6—8 hours' heating at 184.5 , or a little higher. Of the small quantity of weight further lost at a red heat, doubtless a portion was due to occluded hydrogen; the quantity of hydrogen obtained as such on Sprengel-pumping at a red heat from a gram or two of this copper was however so minute as to be wholly immeasurable, less than 0.1 c.c. of total gas being obtained, and this apparently consisting only of air. According to Graham (*Trans. Roy. Soc.*, 1866, 432), and Thudichum and Hake (this Journal, 1876, ii, 251), from 0.01 to 0.08 c.c. of hydrogen are obtainable per gram of compact metallic copper reduced on the surface by hydrogen after superficial oxidation (as in the preparation of copper for organic analysis). Since, however, quantities of water, corresponding to considerably larger amounts of hydrogen, have been shown by Melsens (*Ann. Chim. Phys.*, 1843, [iii], 8, 205); Lietzenmayer (*Deut. Chem. Ges. Ber.*, 1878, 306); and Johnson (this Journal, 1876 [i], 178, and 1879 [i], 243), to be formed by heating such reduced copper in dry air, it seems highly probable that the non-withdrawal of hydrogen in more than minute quantity by Sprengel-pumping at a red heat is due, not to the hydrogen not being there, but to its acting on the small quantity of unreduced copper oxide present (probably disseminated through the mass of metal), and consequently escaping as water. In just the same way, if iron oxide be almost but not quite completely reduced at a bright red heat by carbon oxide, and cooled down in a current of that gas, a spongy metal containing occluded carbon oxide will be obtained; on Sprengel-pumping this, however, and gradually heating, much carbon dioxide is pumped out, as well as carbon oxide, the former being doubtless formed by the reaction of the latter on the small quantity of iron oxide still present; just as in the experiments described in Parts I and II, on the reduction of metallic oxides by free carbon, the gas pumped out on Sprengelising the mixture, and heating till reduction commenced, consisted usually of little save carbon dioxide, the carbon monoxide presumably first formed being instantly further oxidised by the metallic oxide present.

It would naturally be expected that at temperatures higher than 184.5° , the rate of reduction would be more rapid than that observed

at this temperature; in order to see if analogous sigmoid curves represent the character of the action at higher temperatures, the above experiments were repeated twice, using in the first case a vapour-bath of naphthalene, to which a little of a high boiling fluid distillate from citronella oil had been added, to make the volatilised portion sufficiently fusible to avoid all risk of choking up the condensing tube by deposition of solid naphthalene; and in the second instance the hydrocarbon of cubeb oil separated by fractional distillation. The average vapour temperatures in these two cases were respectively 210° (corrected) and 256.5° (corrected), the actual temperature differing but little from these numbers in every observation. The following values were obtained:—

Time in minutes.	At 210° .									Averages.	
	Percentage loss of oxygen.									Uninterrupted.	Interrupted.
5	0.12	—	—	—	—	—	—	—	—	0.12	—
10	—	0.58	0.73	—	—	—	—	—	—	0.65	—
15	1.34	—	1.81	1.39	—	—	—	—	—	1.39	1.57
20	—	—	3.28	—	2.60	—	—	—	—	2.60	3.28
25	—	5.28	4.94	—	—	3.86	—	—	—	3.86	5.11
30	6.04	—	—	6.78	—	—	6.46	—	—	6.46	6.41
40	—	12.05	—	—	—	—	—	12.88	—	12.88	12.05
45	14.09	—	—	13.96	—	—	12.04	—	—	—	13.36
50	—	—	—	—	—	—	—	—	14.50	14.50	—
55	—	—	—	17.45	—	—	15.83	—	—	—	16.61
60	—	—	—	—	—	—	—	—	17.63	—	17.63
65	—	—	—	19.28	—	—	—	—	18.59	—	18.93
70	—	19.50	—	—	—	—	—	—	—	—	19.50

Time in minutes.	At 256.5° .									Averages.	
	Percentage loss of oxygen.									Uninterrupted.	Interrupted.
3	0.60	—	—	—	—	—	—	—	—	0.60	—
3½	—	0.77	—	—	—	—	—	—	—	0.77	—
5	—	—	1.12	—	—	—	—	—	—	1.12	—
8	3.71	—	—	—	—	—	—	—	—	—	3.71
10	—	4.09	—	4.84	3.41	—	—	—	—	4.12	4.09
15	—	—	7.75	—	—	5.85	—	—	—	5.85	7.75
20	—	11.00	—	10.55	—	—	10.40	—	—	10.40	10.77
25	—	—	13.96	—	—	11.70	13.89	13.42	—	13.42	13.18
30	—	17.13	16.98	17.04	—	15.74	—	—	16.96	16.96	16.72
35	—	19.16	—	—	—	18.32	18.56	—	—	—	18.68
40	—	—	—	—	—	—	—	18.94	19.34	—	19.14
45	—	—	—	—	19.61	—	—	—	—	—	19.61

Fig. 2.

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Curves Nos. 1 and 2 (thick continuous lines) in the diagram (Fig. 2) represent these average results, the curve marked No. 3 being the corresponding mean curve obtained at 184.5° . The straight sloping line to the left marked "limit" indicates the limit to which the curves all tend, this being the line that would be traced out did deoxidation commence at the first instant and go on at such a rate that every trace of hydrogen was converted into steam. To reduce 1.15 gram of copper oxide containing 19.74 per cent. of oxygen would require 24.2 minutes' passage of a stream of hydrogen conveying 12.5 c.c. of hydrogen (at 0° and 760 m.) per minute.

The following values are deduced from these average curves:—

Time in minutes.	Percentage loss.	At 210° .		Percentage loss per minute during each consecutive 5 minutes.
		Difference.	2nd difference.	
0	0	0	0	0
5	0.10	0.10	0.10	0.020
10	0.50	0.40	0.30	0.080
15	1.35	0.85	0.45	0.170
20	2.80	1.45	0.60	0.290
25	4.70	1.90	0.45	0.380
30	6.95	2.25	0.35	0.450
35	9.40	2.45	0.20	0.490
40	11.85	2.45	0	0.490
45	14.00	2.15	—0.30	0.430
50	15.55	1.55	—0.60	0.310
55	16.70	1.15	—0.40	0.230
60	17.65	0.95	—0.20	0.190
65	18.57	0.92	—0.03	0.184
70	19.49	0.92	—0	0.184

Time in minutes.	Percentage loss.	At 256.5° .		Percentage loss per minute during each consecutive 5 minutes.
		Difference.	2nd difference.	
0	0	0	0	0
5	1.10	1.10	1.10	0.22
10	3.80	2.70	1.60	0.54
15	6.95	3.15	1.45	0.63
20	10.45	3.50	0.35	0.70
25	13.70	3.25	—0.25	0.65
30	16.50	2.80	—0.45	0.56
35	18.50	2.00	—0.80	0.40
40	19.20	0.70	—1.30	0.14
45	19.60	0.40	—0.30	0.08

Evidently the curves for $184\cdot5^{\circ}$, 210° , and $256\cdot5^{\circ}$, are all of the same general character; before drawing deductions from them, the results obtained at temperatures below $184\cdot5^{\circ}$ must be considered. In order to obtain them experiments similar to the preceding ones were carried out in vapour-baths giving lower temperatures, viz., in cajeputol vapour giving an average temperature of 175° (corrected); hydrocarbon from oil of turpentine, 160° (corrected); a petroleum distillate, 150° (corrected); fusel oil, 130° (corrected); glacial acetic acid, 118° (corrected); and water, 100° ; the first four of these substances were subjected to several fractional distillations before use, so as to obtain substances of as nearly as possible constant boiling points.

One point in connection with these values is noteworthy; whereas at $184\cdot5^{\circ}$ and upwards, the values obtained never showed any very marked discrepancy or inconsistency, but always approached reasonably close to a mean value; it occasionally happened at temperatures lower than $184\cdot5^{\circ}$ that irregularities were observed of this kind, that whilst the majority of the observations agreed fairly together, giving a mean value the probable error of which was but small, now and then the copper oxide was not acted upon at all for a considerably longer period than that observed in the other cases, and consequently gave, when action did at length commence, numbers not agreeing with the mean curve deduced from the accordant observations, but close to a curve parallel with this mean curve, and lying to its right hand, as the curves are drawn in the diagram; in other words, an abnormal prolongation of the period during which the action was so slight as to be imperceptible was noticed in some few instances. At 175° and 160° these irregular observations were comparatively rare; but below 160° they were so frequent as to prevent any concordance at all between the results.

The following values were obtained in nine accordant experiments at 175° :—

Time in minutes.	Percentage loss of oxygen.										Averages.	
											Uninterrupted.	Interrupted.
10	0	—	—	—	—	—	—	—	—	—	0	—
15	—	0·07	0·12	—	—	—	—	—	—	—	0·09	—
20	0·27	—	—	—	—	—	—	—	—	—	—	0·27
25	—	0·31	—	—	—	—	—	—	—	—	—	0·31
30	0·54	—	0·73	0·82	—	—	—	—	—	—	0·82	0·63
35	—	0·75	—	—	1·65	0·86	—	—	—	—	1·25	0·75
40	—	—	—	—	2·37	—	—	—	—	—	—	2·37
45	1·59	—	2·15	—	3·33	—	1·75	—	—	—	1·75	2·36
60	3·92	—	—	5·11	5·55	—	—	4·94	—	—	4·94	4·86
65	—	—	—	—	—	5·32	—	—	—	—	—	5·32
75	7·11	—	7·85	—	8·11	—	7·40	—	—	—	—	7·62
80	—	—	—	—	9·01	—	—	—	—	—	—	9·01
90	10·14	—	—	—	—	—	10·35	9·88	11·64	11·64	11·64	10·12
95	—	—	11·64	—	—	—	—	—	—	—	—	11·64
105	—	—	—	—	—	—	—	12·47	14·32	—	—	13·39
120	—	—	—	—	—	—	16·24	15·37	17·04	—	—	16·22
140	—	—	—	—	—	—	18·87	—	—	—	—	18·87

In two other observations a marked retardation was noticed; in one at the end of 60 minutes the loss was only 0·43 per cent. instead of 4·51 per cent., as indicated by the mean curve deduced from the preceding nine experiments; in the other the losses at 50, 55, and 60 minutes respectively were 0·21, 0·34, and 0·61 per cent., instead of 2·79, 3·61, and 4·51, as indicated by the mean curve.

Rejecting these two abnormal results, the above figures yield a mean curve, which is traced on the diagram, and marked No. 4.

From this the following values are obtained:—

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
0	0	0	0	0
5	0	0	0	0
10	0	0	0	0
15	0·06	0·06	0·06	0·012
20	0·18	0·12	0·06	0·024
25	0·37	0·19	0·07	0·038
30	0·64	0·27	0·08	0·054
35	1·00	0·36	0·09	0·072
40	1·47	0·47	0·11	0·094
45	2·07	0·60	0·13	0·120
50	2·79	0·72	0·12	0·144
55	3·61	0·82	0·10	0·164

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
60	4.51	0.90	0.08	0.180
65	5.47	0.96	0.06	0.192
70	6.48	1.01	0.05	0.202
75	7.53	1.05	0.04	0.210
80	8.61	1.08	0.03	0.216
85	9.71	1.10	0.02	0.220
90	10.81	1.10	0	0.220
95	11.89	1.08	-0.02	0.216
100	12.93	1.04	-0.04	0.208
105	13.90	0.97	-0.07	0.194
110	14.78	0.88	-0.09	0.176
115	15.58	0.80	-0.08	0.160
120	16.32	0.74	-0.06	0.148
125	17.01	0.69	-0.05	0.138
130	17.66	0.65	-0.04	0.130
135	18.28	0.62	-0.03	0.124
140	18.88	0.60	-0.02	0.120

Five observations at 160° gave the following accordant results:—

Time in minutes.	Percentage loss of oxygen.					Averages.	
						Uninterrupted.	Interrupted.
20	0	—	—	—	—	0	—
30	—	0.08	—	—	—	0.08	—
40	0.29	—	—	—	—	—	0.29
50	—	0.69	—	—	—	—	0.69
60	1.06	—	1.25	—	—	1.25	1.06
90	3.93	4.58	5.02	—	—	—	4.51
120	7.69	—	8.36	—	—	—	8.02
150	10.95	12.89	11.39	10.93	—	10.93	11.74
180	14.28	—	13.20	14.15	—	—	13.88
210	—	16.69	15.28	16.75	17.01	17.01	16.23
240	—	—	17.32	—	—	—	17.32
270	—	—	18.66	—	—	—	18.66
300	—	—	19.22	—	—	—	19.22

Another experiment, however, furnished numbers indicating a considerable retardation in the commencement of the action; in 60, 90, and 150 minutes the losses were respectively 0.18, 1.83, and 7.39 per cent., or close to those representing a curve parallel to that deduced from the above five experiments, but shifted to the right

through a space representing about 30 minutes. Neglecting this abnormal experiment the above numbers furnish the mean curve marked No. 5 in the diagram, from which the following figures are deduced:—

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 30 minutes.
20	0	—	—	—
30	0·08	0·08	0·08	0·003
40	0·28	—	—	—
50	0·64	—	—	—
60	1·20	1·12	1·04	0·037
90	4·50	3·30	2·18	0·110
120	8·05	3·55	0·25	0·118
150	11·60	3·55	0	0·118
180	14·15	2·55	—1·00	0·085
210	16·00	1·85	—0·70	0·062
240	17·30	1·30	—0·55	0·043
270	18·35	1·05	—0·25	0·035
300	19·30	0·95	—0·10	0·032

At temperatures below 160° the length of time which elapsed before any perceptible amount of reduction took place was much greater than the corresponding periods observed at 160° and upwards; and, moreover, on repeating observations considerable irregularities and discrepancies were noticed, so that it was impossible to obtain any numbers concordant enough to allow of a mean curve being deduced. Thus at 150° (in a bath of a petroleum distillate separated by repeated fractional distillation) the following numbers were obtained in four experiments:—

Time in minutes.	Percentage loss of oxygen.			
20	0	—	—	—
40	0	—	—	—
60	0	0·42	—	—
90	—	—	0	—
120	0	4·38	—	—
180	0·08	9·88	—	0·26
240	—	15·48	—	—
300	—	18·57	—	—

The second of these experiments, yielding by far the highest numbers, corresponds to a curve lying considerably below No. 5 (that obtained at 160°).

Similarly the following numbers were obtained in four experiments at 130° (in a fusel oil vapour-bath) :—

Time in minutes.	Percentage loss of oxygen.			
60	0	—	—	—
180	0.17	0.13	—	—
240	—	—	0.26	—
270	1.71	—	—	—
360	3.48	0.26	—	0.43

The first of these experiments corresponds to a curve lying far below all the curves obtained at higher temperatures. In none of several experiments at 118° (glacial acetic acid) and 100° (water) was any reduction noticeable even after seven hours' uninterrupted exposure, *i.e.*, the period during which no action is perceptible exceeds seven hours at these temperatures.

No doubt the discrepant results occasionally observed as above described at 160° and 175° , and nearly always found at somewhat lower temperatures, arise from alteration in the physical texture of the copper oxide produced by continued exposure to heat during the period before any perceptible amount of action is noticed; as an illustration of the effect thereby produced in delaying the action the following figures are instructive. In three experiments made at 184.5° the copper oxide was heated just before use to a temperature short of redness in a porcelain crucible over a rose Bunsen burner, and weighed into the U-tube immediately after cooling, the rest of the experiments being performed precisely as before. In one of these three instances the numbers obtained approximated tolerably closely to the mean curve values above stated; in the second case a distinct retardation in the action was noticeable, and in the third case a very marked retardation was produced.

Time in minutes.	Percentage loss of oxygen.			Value from mean curve.
30	1.71	1.32	—	2.50
60	7.26	6.27	0.78	9.81
90	17.74	—	5.58	16.73
120	19.39	16.20	8.12	19.30
180	—	19.23	—	19.65

In two other experiments the copper oxide was heated in the U-tube in a current of air for some 15 minutes to 184.5° ; the air current was then shut off, and the hydrogen current substituted, when the following numbers were obtained, clearly showing that the physical state of the copper oxide was materially influenced by the

previous heating in the current of air, a very marked retardation being produced in each case:—

Time in minutes.	Percentage loss of oxygen.		Value from mean curve.
5	0	—	0·06
10	0	—	0·19
15	0·05	—	0·46
20	0·11	—	0·93
30	0·16	0·05	2·50
60	—	0·20	9·81
120	—	5·83	19·30
180	—	15·60	19·65

Similarly, a portion of the copper oxide heated to below redness just before use, and then exposed at 160° as before, gave the following results:—

Time in minutes.	Percentage loss of oxygen.	Value from curve.
180	0	14·15
360	0·17	19·65
Complete reduction.		

indicating a very great amount of retardation.

On comparing together the five mean curves deduced as above described for the temperatures 256·5, 210, 184·5, 175 and 160° respectively, some noteworthy conclusions are deducible.

(1.) In all five cases for a length of time which is the shorter the higher the temperature, the action is so slight as to be almost or quite imperceptible, after which it goes on at an accelerating rate until a maximum rate is attained, when it again diminishes, owing doubtless to the admixture of reduced copper with the unaltered copper oxide; *i.e.*, the curves exhibit points of contrary flexure. In each case the point of contrary flexure corresponds to the removal of about half of the oxygen originally present. This non-instantaneous development of maximum action is the more marked the lower the temperature, being more particularly observable at 160° and lower temperatures still; it is evidently a case of the “chemical induction” studied by Bunsen and Roscoe (*Phil. Trans.*, 1857) in the case of the action of bromine water on tartaric acid, and the analogous “photochemical induction” observed when light acts on a mixture of chlorine and hydrogen.

(2.) The rates of increase in rate of action during the lower parts of the curve, and those of increase in rate of retardation during the latter halves, are not uniform throughout; during the lower halves whilst the rate of action increases continually, the increment in the

rate first increases from 0° to a maximum, and then decreases again to zero, when the point of contrary flexure is arrived at. Similarly, during the latter halves, the decrement in the rate of action increases in magnitude from 0 at the point of contrary flexure to a maximum, and then again decreases to 0 when complete reduction is arrived at. These variations are evident from the inspection of the columns headed "2nd Difference" in the mean curve tables given above. This may be otherwise put thus: the radius of curvature is at first infinite, and then decreases to a minimum, after which it again increases to infinity at the point of contrary flexure; it then changes its sign, decreases to a minimum of opposite sign to that of the first minimum, and finally again increases to infinity when perfect reduction is accomplished.

(3.) Between the commencement of the action and its end no sudden abrupt alteration in curvature is noticeable; especially no marked sudden alteration in curvature is noticeable when half the oxygen is removed, corresponding to the formation of Cu_2O ; save that this point lies near to the point of contrary flexure, as might be expected, since after reduction to Cu_2O further reduction would produce metallic copper, which by partially covering up the unaltered oxide would tend to diminish the rate of action.

(4.) Whilst the duration of the period during which no action is perceptible is, as above stated, shorter the higher the temperature, the rates of increase in the rate of action during the first half and of decrease in rate of action during the second half, are greater the higher the temperature, as is also the maximum rate of reduction arrived at. the values of the maximum rates of reduction are:—

At 160°	0.118 per cent. of oxygen per minute (out of		
	19.74 per cent. originally present).		
„ 175	0.220	„	„
„ 184.5	0.270	„	„
„ 210	0.490	„	„
„ 256.5	0.700	„	„
Maximum possible	0.779	„	„

It is evident that the method above described for obtaining these curves is attended with a certain amount of experimental error, and that in consequence the mean curves deduced cannot be regarded as more than fair approximations. The chief sources of error are the uncertainty in the exact amount of hydrogen delivered by 100 bubbles, even when these pass exactly in the minute, and the chances of difference in amount of action from differences in the packing of the powdered oxide in the bend of the U-tube; whilst these errors are of such a kind as to be largely capable of elimination by taking a

numerous series of observations and averaging, they are yet sufficiently great to render it desirable to obtain, if possible, another check on the curve values. Accordingly a number of experiments were made with the object of directly checking these values by determining the ratio between the volume of hydrogen actually converted into steam, and that escaping unchanged at different periods of the reduction. Since the amount of copper oxide used in each experiment averaged 1.150 gram, and the average rate of supply of hydrogen was 12.5 c.c. normal = 0.00112 gram per minute, the average percentage of oxygen which could have been removed per minute by perfect conversion of the whole of the hydrogen into steam was $\frac{0.00112 \times 8}{1.150} \times 100 = 0.7791$.

Hence if x be the percentage of oxygen removed per minute at any period of the action, $\frac{x}{0.7791}$ will be the fraction representing the ratio of the hydrogen oxidised to steam to the total amount employed, *i.e.*, the quantity of hydrogen employed being 100, the amount oxidised will be $\frac{x}{0.7791} \times 100 = 128.3 \times x$.

Thus, at the periods when the maximum rates of action were attained, the amounts of hydrogen oxidised were respectively—

At 160	$128.3 \times 0.118 = 15.1$	per 100 of hydrogen employed.
„ 175	$128.3 \times 0.220 = 28.2$	„ „
„ 184.5	$128.3 \times 0.270 = 34.6$	„ „
„ 210	$128.3 \times 0.490 = 62.8$	„ „
„ 256.5	$128.3 \times 0.700 = 89.8$	„ „

In order therefore to obtain a check on the values of x deducible from the above mean curves, it is only required to determine the diminution in the bulk of a given quantity of hydrogen passed through the U-tube at the normal rate for a given time. By determining the amount of oxygen removed from the copper oxide at the beginning and end of the experiment, and taking the mean of the two amounts, a tolerably close approximation is obtained to the point on the curve corresponding to the mean value of x during the experiment, especially when the amounts of oxygen removed before and after the observation do not differ very largely.

The first experiments in this direction were made by passing hydrogen through the U-tube from one graduated vessel to another, so as to determine directly the diminution in volume brought about during the action; the results, however, were not at all sharp, owing to the great difficulty in making the current of gas pass regularly at anything approaching to the normal rate of 12.5 c.c. per minute. The following numbers obtained at 210°, with currents not far removed from the

normal one, however, approximate sufficiently to those calculated from the values of x deduced from the mean curve for 210° to bear out the general correctness of the character of the curve as regards its shape:—

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of hydrogen oxidised to H_2O .	
		Observed.	Calculated from formula $128.3 \times x$.
6.0	0.42	47.1	53.9
8.2	0.47	57.8	60.3
9.0	0.48	67.9	61.6
9.6	0.49	55.4	62.8
13.0	0.46	50.5	59.0
14.45	0.40	44.5	51.3
15.05	0.35	35.1	44.9
16.5	0.25	32.9	32.1

Much better results were obtained by operating in the way by which the data for the mean curve values were obtained, and collecting the hydrogen that escaped at the far end in the gas works reservoir-like apparatus above described; the quantity of hydrogen converted into water was known by calculation from the loss of weight of the copper oxide during the experiment; adding this to the quantity collected at the far end, the total amount employed was known. Thus for instance, in one experiment at 256.5° the following data were obtained: 1.164 gram of copper oxide exposed in the U-tube for 12 minutes lost 0.061 gram = 5.24 per cent.: on further exposure for 8 minutes more, it further lost 0.067 gram = 5.75 per cent., making a total loss of 10.99 per cent. During this 8 minutes, the gas not oxidised collected at the far end amounted to 18.0 c.c. normal: whilst 0.067 gram of oxygen represents 0.008375 gram hydrogen = 93.8 c.c. normal. Hence $93.8 + 18.0$ c.c. = 111.8 c.c. were passed in 8 minutes, or 13.97 c.c. per minute; and of this $\frac{93.8}{111.8} = 83.9$ per cent. was oxidised to water. The loss of oxygen at the commencement of this observation being 5.24 per cent., and that at the end 10.99, the mean loss may be taken as 8.12 per cent.; the value of x corresponding to this, obtained by interpolation from the numbers in the table given above for the mean curve for 256.5° , is 0.652: whence $128.3 \times 0.652 = 83.6$, the calculated percentage from the mean curve, agreeing with the number just found, 83.9 per cent., more closely than might have been anticipated, especially as the hydrogen current was somewhat more rapid than the normal one, viz., 13.97 c.c. per minute, instead of 12.5 c.c. In a similar way the following numbers were obtained in other experiments:—

At 256.5°.

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of hydrogen oxidised to H_2O .	
		Observed.	Calculated from formula $128.3 \times x$.
3.0	0.46	61.4	59.0
4.4	0.57	74.3	73.1
8.1	0.65	83.9	83.4
10.8	0.70	88.5	89.8
13.7	0.65	80.8	83.4
17.75	0.46	59.4	59.0

At 210°.

1.5	0.19	25.6	24.4
3.5	0.31	40.9	39.8
8.2	0.47	59.8	60.3
9.5	0.49	62.4	62.8
11.7	0.49	62.3	62.8
18.3	0.19	25.5	24.4

At 175°.

0.27	0.031	2.7	3.9
0.47	0.043	5.6	5.5
2.0	0.117	13.0	15.0
2.9	0.147	18.3	18.9
6.6	0.202	21.4	25.9
8.4	0.215	29.4	27.6
9.9	0.220	29.6	28.2
12.1	0.215	28.7	27.6
16.0	0.152	24.6	19.5

The observed percentages of hydrogen oxidised to water, and those calculated from the mean curve values agree quite as closely as could be expected, considering the difficulty of keeping up an equable hydrogen current whilst the action was going on, and the unaltered gas was being collected at the far end. As a general rule, when the observed percentage falls below that calculated, the hydrogen current was a little more rapid than the normal one of 12.5 c.c. per minute, and *vice versa*; as might be expected, *à priori*, since with the slower current the hydrogen was relatively a longer time in contact with copper oxide, and therefore was presumably more completely oxidised, and *vice versa* with the more rapid current. In none of the above experiments, however, was the hydrogen current very different from the normal one.

That a hydrogen current more rapid than the normal one causes

absolutely a larger amount of reduction of copper oxide in a given time (although the amount of hydrogen oxidised is less relatively to the total amount employed), is shown by the following numbers obtained at 184.5° with a stream of nearly double the normal current, the other conditions being the same as before.

Time in minutes.	Percentage loss with rapid current.	Loss with normal current deduced from the mean curve.
20	2.08	0.93
40	13.22	4.71

Lessening the weight of copper oxide employed might be expected to produce the same result as increasing the speed of the hydrogen current; the following figures obtained at 184.5° show that this is the case, the increase in rate of reduction being greater the smaller the weight of copper oxide used; the hydrogen current in all these cases was the normal one.

Weight of copper oxide used in grams.	0.992	0.972	0.929	0.9215	0.8525	0.8245	Values deduced from mean curve.
Percentage loss after							
20 minutes	—	1.90	1.88	—	2.17	2.42	0.93
30 „	—	5.67	4.84	—	—	—	2.50
35 „	6.14	—	—	—	7.68	—	3.56
40 „	—	—	—	6.18	—	9.33	4.71
45 „	—	—	10.76	—	—	—	5.92
75 „	—	—	—	17.68	—	—	13.76
85 „	—	—	—	19.15	—	—	15.95

Conversely, the opposite effect was produced to some extent by increasing considerably the weight of copper oxide employed: thus with 1.7645 gram of copper oxide the following numbers were obtained at 184.5° with a normal hydrogen current:—

			Values from mean curve (obtained with 1.15 gram).
Percentage loss after 20 minutes..	0.73		0.93
„ „ 40 „ ..	3.74		4.71

When the above five mean curves are employed to generate a surface as described in the earliest portion of this report, and sections of this surface are made so as to generate the two other classes of curves there described (*viz.*, those illustrating the connections between the amounts of deoxidation produced in a given time at various temperatures, and those indicating the relations between the times and tem-

peratures required to produce a given amount of deoxidation), the following numbers are obtained:—

Amounts of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	Temperatures.				
	160°.	175°.	184·5°.	210°.	256·5°.
5	0	0	0·06	0·10	1·10
10	0	0	0·19	0·50	3·80
15	0	0·06	0·46	1·35	6·95
20	0	0·18	0·93	2·80	10·45
25	0·03	0·37	1·62	4·70	13·70
30	0·08	0·64	2·50	6·95	16·50
35	0·16	1·00	3·56	9·40	18·50
40	0·28	1·47	4·71	11·85	19·20
45	0·44	2·07	5·92	14·00	19·60
50	0·64	2·79	7·18	15·55	—
55	0·89	3·61	8·48	16·70	—
60	1·20	4·51	9·81	17·65	—
65	1·61	5·47	11·16	18·57	—
70	2·15	6·48	12·49	19·49	—
75	2·73	7·53	13·76	—	—
80	3·32	8·61	14·93	—	—
85	3·91	9·71	15·95	—	—
90	4·50	10·81	16·73	—	—
95	5·09	11·89	17·34	—	—
100	5·68	12·93	17·84	—	—
105	6·27	13·90	18·27	—	—
110	6·86	14·78	18·65	—	—
115	7·45	15·58	18·99	—	—
120	8·05	16·32	19·30	—	—
125	8·64	17·01	—	—	—
130	9·23	17·66	—	—	—
135	9·82	18·28	—	—	—
140	10·41	18·88	—	—	—
150	11·60	—	—	—	—
180	14·15	—	—	—	—
210	16·00	—	—	—	—
240	17·30	—	—	—	—
270	18·35	—	—	—	—
300	19·30	—	—	—	—

*Lengths of Time in Minutes required to produce given Amounts of
Deoxidation at different Temperatures.*

Percentages of oxygen removed (19·74 per cent. originally present).	Times.				
	At 160°.	At 175°.	At 184·5°.	At 210°.	At 256·5°.
1	57	35	20	13	5
2	67	44	27	17	7
3	77	51	32	20	9
4	86	57	37	23	11
5	95	62	41	26	13
6	103	67	45	28	14
7	111	72	49	30	15
8	120	77	53	32	17
9	128	82	57	34	18
10	136	86	60	36	19
11	145	90	64	38	21
12	155	95	68	40	22
13	166	100	72	42	24
14	178	106	76	45	26
15	193	112	80	48	27
16	210	118	85	52	29
17	233	125	92	57	31
18	260	133	102	62	34
19	291	142	115	67	39

§ 2. *Determination of Relations existing between Rate of Reduction of
Copper Oxide by Carbon Oxide, Time, and Temperature.*

The results above described show that the particular temperature at which the action of hydrogen on copper oxide (prepared by calcining the nitrate) is first perceptible, depends to a notable extent on the length of time allowed for the observation with the particular sample employed; for example, if ten minutes be taken as the time of observation, the "temperature of initial action" deducible from the preceding observations would be about 180°, since no loss of weight was experienced at 175° in ten minutes, whilst 0·19 per cent. was lost at 184·5°: if, however, fifteen minutes were allowed for the observation, the "temperature of initial action" would be taken as about 167°, since a slight loss was experienced during that time at 175°, but none at 160°. Similarly, if thirty minutes' time were allowed, the temperature of initial action would be taken as below 160°, whilst with longer periods still yet lower temperatures would be deduced.

It is evident also from the preceding observations, that apparently trifling circumstances may so affect the physical condition of the metallic oxide examined, that no action at all may be noticed in a given

time sufficient under other conditions to bring about a considerable amount of action: thus, simply heating the copper oxide and allowing it to cool before use, largely extends the duration of the period during which no perceptible amount of action takes place. From these circumstances it appears that the results obtained in Reports I and II are, in some cases at any rate, open to the objection that the non-occurrence of action at any given temperature with any given metallic oxide, cannot be held to substantiate completely the rule deduced that the temperature of initial action is, *cæteris paribus*, the lower the greater (algebraically speaking) is the heat evolution occurring during the reaction; for the time of observation in each case was only some few minutes, rarely more than a quarter of an hour; whence, not only were numbers obtained at the temperatures of initial action probably considerably different from those that would have been obtained had the duration of the observations been longer, but also the negative results observed below certain temperatures might have been due to something abnormal about the physical state.

It is, therefore, highly desirable to check the conclusions arrived at from these short-time observations in another way: and this it seems probable can be done at any rate in certain instances by determining the character of the curves obtainable with different metallic oxides under the reducing influence of hydrogen and carbon oxide under uniform condition; if the reaction is influenced by the amount of heat that would be developed by its occurrence in such a way that the greater (algebraically) is this heat development the more readily does the action take place (which is the essential idea embodied in the rule arrived at in Reports I and II, which for shortness may be referred to as the *dynamic rule*), it should result that the rate of reduction arrived at when the action is once started must be greater the greater the heat evolution: for example, under constant conditions as to temperature and general circumstances, the reduction of copper oxide by carbon oxide should go on more rapidly when once started than the reduction by hydrogen. It is, however, by no means inconceivable that the rate of action may be modified by certain circumstances and conditions which it is not possible to equalise in the two cases; for instance, the differences in diffusive power, viscosity, surface attraction to the metallic oxide, &c., &c., naturally existing between the two gases, may so influence the rate of action as to wholly interfere with the verification of the dynamic rule in this way; since these causes, if operative at all, are *à priori* more probably inclined to facilitate the reducing action of the hydrogen than of the carbon oxide, it would seem that, although the establishment of the circumstance that the rate of reduction by carbon oxide is greater than that by hydrogen, would considerably strengthen the evidence on behalf of the dynamic rule, the non-establishment of

this circumstance would not necessarily furnish an argument against the correctness of this rule.

It being, therefore, of interest to examine these points experimentally, the experiments above detailed were repeated with precisely the same conditions with the exception of the particular temperatures employed and of the use of carbon oxide instead of hydrogen as reducing agent. It has been already shown in Part II (p. 511), that when copper oxide from calcined nitrate is heated to 100° for some hours in an atmosphere of carbon oxide, CO_2 is formed in quantity, although the mere passage of the gas over the metallic oxide for a few minutes develops no CO_2 at temperatures below 125° ; whence it appears probable that the phenomenon observed with hydrogen also occurs with carbon oxide, viz., that a certain length of time is requisite for the action to commence, this period of incubation, so to speak, varying in duration inversely with the temperature.

Considerable difficulty was experienced in producing anything like an equable current of carbon oxide: the gas, prepared from ferrocyanide of potassium and sulphuric acid, and purified as described in the previous reports, was stored in a gasometer over water, and when required for use was passed first through a bubbling apparatus to enable the bubbles to be counted, then through a red-hot tube containing charcoal, and finally through two potash-bulbs to absorb the carbon dioxide produced from the admixture of air necessarily present to some extent. The bubbling apparatus was filled with sulphuric acid to dry the gas, and prevent the formation of hydrogen in the red-hot tube from the reaction of the water vapour on the red-hot charcoal. The size of the bubbles was found to be seriously affected by the height of the water column forcing the gas out of the gasometer, being about 10 per cent. less when the water pressure was two feet than when it was three feet: as with hydrogen (§ 1) the quantity of gas delivered per 100 bubbles was considerably less when the gas passed slowly than when it passed more quickly: thus for instance, the following numbers were obtained with two different bubbling apparatus:—

<i>Apparatus A.</i>		<i>Apparatus B.</i>	
Time of passage of 100 bubbles in seconds.	c.c. of gas at 0° and 760 per 100 bubbles.	Time of passage of 100 bubbles in seconds.	c.c. of gas at 0° and 760 per 100 bubbles.
35	7.9	50	18.7
50	7.0	60	17.5
60	6.8	100	16.3
125	6.4		

Another source of difficulty arose from the circumstance that the gas employed, being collected and stored over water, was never abso-

lutely free from admixed air, so that after passing through the red hot tube containing charcoal, small quantities of nitrogen were mixed with it. The average composition of the gas (after passing through the red-hot tube and potash bulbs) was found to be 96 per cent. of carbon oxide and 4 of nitrogen; other gases were carefully sought for, especially hydrocarbons, but no evidence of their presence obtained, saving that in one or two instances the numbers obtained pointed to the presence of a little cyanogen, and in one or two others of a minute quantity of free hydrogen. Neither of these gases, if present, would have interfered with the results found even had they been present in much larger quantity than that suspected to be present (1 or 2 per cent.): for the reducing action of hydrogen at most of the temperatures employed is so small as to be practically, if not entirely, imperceptible in the time of exposure allowed; whilst direct experiments made with cyanogen (prepared by heating mercuric cyanide) showed that the same is true for that gas also: to this point and other allied ones we hope to return in a future paper. The actual gas currents employed were so regulated as to pass on an average 13.0 c.c. of carbon oxide containing nitrogen or 12.5 c.c. of pure CO per minute measured at 0° and 760 m.

Experiments were first made to see if the current of gas was heated up to the temperature of the air-bath by passing through one heated limb of the U-tube employed before reaching the bend where the copper oxide lay: these were carried out in precisely the same way as those described in § 1 with hydrogen for a similar purpose, and with the same result, viz., no cooling effect on a thermometer was produced by the carbon oxide stream, proving that it was completely heated up. Similar experiments were also made, as with hydrogen, to see if the heat developed during reduction sensibly affected the temperature of the partially reduced copper oxide, with the following results, the temperature being 184.5° , i.e., the highest employed: during the period of reduction between 3 and 13 minutes' exposure, the average scale-reading difference of the two thermometers was 0.73° , the thermometer exposed to the CO stream being the lowest: between 13 and 24 minutes the average difference was 0.57° ; and between 24 and 35 minutes it was 0.68° : the difference when no current at all passed, or when the current was passing, but no copper oxide was in the U-tube, was 0.80° ; so that in the first, second, and third of these three periods, the temperatures of the issuing gases were raised, 0.07° , 0.23° and 0.12° respectively: the middle period corresponds to the period of most rapid reduction, the whole of the oxygen being removed in less than 45 minutes. Practically, therefore, the development of heat during reduction, although perceptibly greater than that observed with hydrogen, was too small to produce any material heating of the copper oxide.

Owing to our stock of the particular sample of copper oxide used for the previous experiments being not very great, we were unable to perform as many experiments at each temperature as would have been desirable for the exact determination of the mean curves, since the experimental errors through inequality in the gas current were probably greater than was the case with hydrogen; the following numbers, however, exhibit quite sufficient accordance to enable fair approximations to mean curves to be drawn; since these were obtained with the same volume of gas per minute (12.5 c.c. normal), whilst the reducing powers of equal volumes of the two gases are equal, the carbon oxide figures are directly comparable with those obtained with hydrogen; the same average weight of copper oxide, 1.15 gram, was used in every experiment.

At temperatures of 130° and upwards, the curves deduced from interrupted observations, and those from uninterrupted ones, coincided, showing that under these circumstances interrupting the reduction for a few minutes so as to cool and weigh did not interfere with the action subsequently: but below 130° it was found that the results of interrupted experiments were always below those obtained by uninterrupted observations. It is specially noticeable that the great irregularities in action noticed with hydrogen at temperatures between 130° and 160° did not manifest themselves with carbon oxide at corresponding temperatures (*i.e.*, 100° to 130°), the effect of interruption being allowed for; probably this arises from the lower temperatures not affecting the physical condition of the copper oxide during the earliest part of the exposure, so much as was the case in the hydrogen experiments at the somewhat higher temperatures.

The following numbers were obtained:—

At 184.5°.

Time in minutes.	Percentage loss of oxygen.										Averages.	
											Uninterrupted.	Interrupted.
1½	0.43	—	—	—	—	—	—	—	—	—	0.43	—
2½	—	1.65	—	—	—	—	—	—	—	—	1.65	—
5	2.87	3.61	2.91	—	—	—	—	—	—	—	2.91	3.24
10	—	7.08	5.77	5.11	4.61	—	—	—	—	—	4.86	6.42
15	10.50	—	8.90	—	8.45	8.68	—	—	—	—	8.68	9.28
20	—	—	12.10	10.48	—	—	12.50	—	—	—	12.50	11.29
25	15.63	—	—	—	14.89	14.01	—	13.04	—	—	13.04	14.84
30	18.10	—	—	—	—	—	17.42	16.35	18.89	—	18.89	17.29
35	19.62	—	—	—	—	—	—	18.26	—	—	—	18.94
40	—	—	—	—	—	—	19.44	—	—	—	—	19.44

At 160°.

Time in minutes.	Percentage loss of oxygen.										Averages.	
											Uninterrupted.	Interrupted.
2½	0·45	0·40	—	—	—	—	—	—	—	—	0·42	—
5	2·08	1·58	1·13	—	—	—	—	—	—	—	1·13	1·83
10	—	4·44	—	2·95	—	—	—	—	—	—	2·95	4·44
15	8·08	—	—	—	9·13	—	—	—	—	—	9·13	8·08
20	—	10·21	9·06	8·85	—	10·13	12·69	—	—	—	11·41	9·37
25	13·08	—	—	—	—	—	14·78	—	—	—	—	13·93
30	—	—	—	14·32	17·30	—	16·34	15·91	—	—	15·91	15·98
35	17·92	—	—	—	—	—	—	17·73	16·62	16·62	16·62	17·82
40	19·36	—	—	—	17·87	—	—	18·94	18·01	—	—	18·54
45	—	—	—	19·61	—	—	—	—	—	—	—	19·61

At 130°.

5	0·08	0	0	—	—	—	—	—	—	—	0·03	—
10	0·69	1·35	—	—	—	—	—	—	—	—	—	1·02
15	2·91	—	4·22	2·86	—	—	—	—	—	—	2·86	3·56
20	6·04	5·32	—	—	5·54	—	—	—	—	—	5·54	5·68
25	8·09	—	8·46	—	—	6·42	—	—	—	—	6·42	8·27
30	11·83	10·12	—	9·98	—	—	13·09	—	—	—	13·09	10·64
35	14·22	—	11·89	—	—	—	—	—	—	—	—	13·05
40	16·18	14·37	—	—	13·60	—	—	14·37	—	—	14·37	14·72
45	—	—	14·32	—	—	15·98	18·07	—	—	—	—	16·12
50	—	17·53	—	—	—	—	—	18·12	18·22	18·22	—	17·82
60	—	18·26	—	—	18·19	—	—	—	18·91	—	—	18·45
65	—	—	—	—	18·45	—	—	—	—	—	—	18·45
70	—	19·39	—	—	—	—	—	—	—	—	—	19·39

On plotting these values for three temperatures, 184·5°, 160°, and 130° respectively, as was done for the corresponding hydrogen values (§ 1), it is evident that the mean curves deducible from the interrupted and uninterrupted observations practically coincide: from these curves the following values are deduced: the curves themselves are shown in Fig. 2, being marked A, B, and C respectively (dotted lines):—

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 5 minutes.
5	2·90	2·90	2·90	0·580
10	6·35	3·45	0·55	0·690
15	9·85	3·50	0·05	0·700
20	12·90	3·05	—0·45	0·610
25	15·40	2·50	—0·55	0·500
30	17·55	2·15	—0·35	0·430
35	19·60	2·05	—0·10	0·410

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At 160°.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 5 minutes.
5	1.80	1.80	1.80	0.360
10	4.50	2.70	0.90	0.540
15	7.35	2.85	0.15	0.570
20	10.20	2.85	0	0.570
25	12.80	2.60	-0.25	0.520
30	14.70	1.90	-0.70	0.380
35	16.40	1.70	-0.20	0.340
40	18.02	1.62	-0.08	0.324
45	19.61	1.59	-0.03	0.318

At 130°.

5	0.03	0.03	0.03	0.006
10	1.13	1.10	1.07	0.220
15	3.45	2.32	1.22	0.464
20	5.85	2.40	0.08	0.480
25	8.25	2.40	0	0.480
30	10.55	2.30	-0.10	0.460
35	12.70	2.15	-0.15	0.430
40	14.60	1.90	-0.25	0.380
45	16.00	1.40	-0.50	0.280
50	17.05	1.05	-0.35	0.210
55	17.80	0.75	-0.30	0.150
60	18.40	0.60	-0.15	0.120
65	18.92	0.52	-0.08	0.104
70	19.39	0.47	-0.05	0.094

The rate of supply of carbon oxide in these experiments being the same as that of hydrogen in the previous ones (12.5 c.c. at 0° and 760 m., capable of removing 0.7791 per cent. of oxygen from 1.15 gram of copper oxide per minute), the limit to which the curves gradually tend as the temperature rises is the same as that existing with the hydrogen curves, viz., the straight slanting line to the left in Fig. 2 (marked "limit").

Below 130° the results of interrupted experiments no longer coincided with those of uninterrupted observations; thus the following values were obtained at 118° and 100°, clearly showing that the greater the number of interruptions, the less is the total amount of reduction brought about in a given time.

At 118°.

Time in minutes.	Percentage loss of oxygen.						Uninterrupted observations only.
5	0	—	—	—	—	—	0
10	0·13	—	—	—	—	—	0·13
15	—	1·39	—	—	—	—	1·39
20	1·87	—	—	—	—	—	—
30	3·91	4·95	6·19	—	—	—	6·19
50	7·98	10·46	—	13·13	—	—	13·13
70	11·46	14·12	15·14	15·67	15·73	—	15·73
90	13·23	15·91	18·13	—	—	18·78	18·78
105	—	16·60	—	—	—	—	—
120	14·81	17·35	19·35	—	—	—	—
135	—	18·00	—	—	—	—	—
165	—	18·60	—	—	—	—	—
195	—	18·96	—	—	—	—	—

At 100°.

Time in minutes.	Percentage loss of oxygen.										Uninterrupted observations only.
30	0	0	—	—	—	—	—	—	—	—	0
45	—	—	0·17	—	—	—	—	—	—	—	0·17
60	0	0	—	0	0·18	—	—	—	—	—	0·09
75	—	—	0·48	—	—	1·26	—	—	—	—	1·26
90	0	0·07	—	—	—	—	1·30	—	—	—	1·30
120	0·13	—	—	—	—	—	—	7·72	—	—	7·72
150	0·35	—	—	—	—	—	4·35	10·86	—	—	—
180	—	—	—	—	—	—	—	—	11·93	—	11·93
210	—	—	—	—	—	—	5·91	15·54	—	—	—
240	—	—	—	—	—	—	6·44	—	—	17·10	17·10

At 83—84°.

Time in minutes.	Percentage loss of oxygen.						Uninterrupted observations only.
60	0	—	—	—	—	—	0
120	—	0·69	—	—	—	—	0·69
180	—	—	0·86	—	—	—	0·86
240	—	—	—	0·69	—	—	0·69
360	—	—	—	—	—	2·44	2·44

The curves marked D, E, and F (Fig. 2, dotted lines), represent the

mean curves deduced from the uninterrupted observations only. The following values are deduced from these mean curves :—

At 118°.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 10 minutes.
10	0.15	0.15	0.15	0.015
20	2.60	2.45	2.30	0.245
30	6.20	3.60	1.15	0.360
40	10.00	3.80	0.20	0.380
50	12.50	2.50	-1.30	0.250
60	14.50	2.00	-0.50	0.200
70	16.10	1.60	-0.40	0.160
80	17.50	1.40	-0.20	0.140
90	18.80	1.30	-0.10	0.130

At 100°.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 20 minutes.
20	0	0	0	0
40	0.03	0.03	0.03	0.0015
60	0.10	0.07	0.04	0.0035
80	1.25	1.15	1.08	0.0575
100	3.50	2.25	1.10	0.1125
120	6.20	2.70	0.45	0.135
140	8.80	2.60	-0.10	0.130
160	10.90	2.10	-0.50	0.105
180	12.70	1.80	-0.30	0.090
200	14.30	1.60	-0.20	0.080
220	15.75	1.45	-0.15	0.0725
240	17.10	1.35	-0.10	0.0675

At 83—84°.

Time in minutes.	Percentage loss.	Difference.	Percentage loss per minute in each consecutive hour.
60	0	0	0
120	0.30	0.30	0.005
180	0.65	0.35	0.006
240	1.00	0.35	0.006
300	1.45	0.45	0.0075
360	2.40	0.95	0.016

On comparing together these six curves they are found to present almost exactly the same characteristics as the corresponding curves above described obtained with hydrogen. The existence of "chemical

induction" to an extent varying inversely with the temperature is evident; each curve rises gradually to a point of contrary flexure, when the rate of action is a maximum, the only noticeable difference between the hydrogen curves and those obtained with carbon oxide being that whilst with the former the point of contrary flexure lies close to the point representing a removal of half the oxygen present, with the latter it lies sensibly lower down, at a point corresponding to a removal of from two-fifths to three-sevenths of the oxygen present. This difference, doubtless, is due to the more easy permeability of the film of reduced copper or of cuprous oxide on the surface of the particles by hydrogen than by carbon oxide, owing to the greater diffusive power of the former. The rates of reduction (percentage loss of oxygen per minute) arrived at when the action is most rapid, corresponding to the points of contrary flexure, are:—

At 184.5°		0.70 per cent. of oxygen removed per minute	
		out of 19.74 per cent. originally present.	
„ 160	0.57	„	„
„ 130	0.48	„	„
„ 118	0.38	„	„
„ 100	0.135	„	„
Possible maximum	0.779	„	„

When these curves are employed to construct a surface as described in § 1, the following numbers are obtained by taking sections of this surface in the manner there referred to.

Amount of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	Temperatures.					
	At 83—84°.	At 100°.	At 118°.	At 130°.	At 160°.	At 184.5°.
5	No action at all in 70 minutes.	0	0	0.03	1.80	2.90
10		0	0.15	1.13	4.50	6.35
15		0	1.20	3.45	7.35	9.85
20		0	2.60	5.85	10.20	12.90
25		0	4.10	8.25	12.80	15.40
30		0.01	6.20	10.55	14.70	17.55
35		0.02	8.10	12.70	16.40	19.60
40		0.03	10.00	14.60	18.02	—
45		0.04	11.40	16.00	19.61	—
50		0.06	12.50	17.05	—	—
55		0.08	13.55	17.80	—	—
60		0.10	14.50	18.40	—	—
65		0.30	15.35	18.92	—	—
70		0.60	16.10	19.39	—	—

Lengths of Time in Minutes required to produce given amounts of Deoxidation at different Temperatures.

Percentage of oxygen removed (19·74 p.c. originally present).	Times.					
	At 83—84°.	At 100°.	At 118°.	At 130°.	At 160°.	At 184·5°.
1	240	78	13	9	3	2
2	340	88	18	12	5	4
3	—	96	22	14	7	5
4	—	104	25	17	9	6
5	—	112	28	19	11	8
6	—	119	31	21	13	9
7	—	126	33	23	15	11
8	—	134	35	25	16	12
9	—	142	37	27	18	13
10	—	151	40	29	19	15
11	—	161	43	31	21	16
12	—	172	47	33	23	18
13	—	183	52	35	25	20
14	—	195	57	38	28	22
15	—	208	63	41	31	24
16	—	222	69	45	34	26
17	—	238	75	50	37	28
18	—	—	82	57	40	31
19	—	—	92	66	44	34

As a check upon the approximate accuracy of these values, the volumetric experiments described in § 1 were repeated, using carbon oxide instead of hydrogen. The following numbers indicate that, as with hydrogen, a tolerable proof of the correctness of the curve values is thus obtainable. The values of x given below are deduced from the curve numbers just quoted, in precisely the same way as that employed with hydrogen, *i.e.*, they are the numbers corresponding in the tables of mean curve values to the rates of reduction per minute for the percentage loss of oxygen represented by the mean between the loss at the beginning of the observation and that at the end. The following numbers were obtained :—

At 130°.

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of CO converted into CO ₂ .	
		Observed.	Calculated from formula $128\cdot3 \times x$.
5·0	0·47	60·2	60·3
9·6	0·47	59·7	60·3
14·0	0·40	52·1	51·3
17·2	0·20	27·1	25·7
18·1	0·14	18·1	18·0

At 160°.

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of CO converted into CO ₂ .	
		Observed.	Calculated from formula $128.3 \times x$.
5.5	0.55	71.0	70.5
7.3	0.57	71.5	73.1
11.6	0.53	64.5	67.9
13.0	0.50	61.5	64.1
16.1	0.35	44.9	44.9

At 184—5°.

5.9	0.68	88.5	87.2
6.7	0.69	88.0	88.5
8.0	0.70	91.8	89.8
10.9	0.65	77.5	83.4
14.0	0.55	62.0	70.6

On comparing together the two surfaces thus described with carbon oxide and hydrogen, it is at once noticeable that *the former surface lies wholly outside the latter one*. This fact may be translated into the following proposition, which is evidently a large amplification of the rule deduced in Parts I and II from experiments, lasting a few minutes only (viz., that the reducing action of carbon oxide first becomes manifest at a lower temperature than that of hydrogen):—"When the reducing action of a given amount of carbon oxide, exerted in a given time on a given quantity of copper oxide, is compared with that exerted by the equivalent quantity of hydrogen (one fourteenth of its weight, or an equal bulk when measured under the same conditions) in the same time, on the same quantity of copper oxide, and under the same conditions throughout, the former is always greater than the latter; whilst the period of time required to produce a given amount of deoxidation by the carbon oxide, the temperature being constant throughout, is less than that required with the hydrogen; and the temperature requisite to produce a given amount of deoxidation in a given time is less with the carbon oxide than with the hydrogen." Further, if the rates of deoxidation attained when certain definite amounts of oxygen have been removed be compared in the two cases when the reduction is effected by carbon oxide and by hydrogen, the temperature being the same in each case, the rate in the former case is uniformly greater than that in the second. Thus at the temperature of 184.5°, the following figures are obtained:—

Percentage loss of oxygen at end of experiment.	Rate of deoxidation (percentage loss per minute) attained to at end of experiment.	
	With hydrogen.	With carbon oxide.
3·0	0·195	0·59
6·0	0·245	0·68
9·0	0·265	0·70
12·0	0·27	0·63
15·0	0·23	0·52
18·0	0·09	0·42

Similarly, at 160°, the following values are obtained :—

3·0	0·09	0·44
6·0	0·11	0·55
9·0	0·12	0·57
12·0	0·11	0·53
15·0	0·08	0·38
18·0	0·04	0·32

and so on for other temperatures, the results being deducible by interpolation from the tables given above.

It does not seem to follow necessarily in every case that when the "dynamic rule" is true (that in comparable cases action during a few minutes becomes first manifested at a lower temperature the greater the algebraic value of the heat evolution occurring during the action), these extensions of it will also be true; for it is easily conceivable that the rate at which the action goes on after being once started, is influenced by various circumstances besides the amount of heat generated in the action; thus physical differences in the reducing agents may exist which it is impossible to equalise in different cases (*e.g.*, difference in density, and consequently in rate of diffusion; differences in the surface attraction for the metallic oxide, condensibility therein or thereon, &c., and so on), and these differences may possibly in some cases influence the rate at which the action proceeds so largely as to overpower the influence of the heat evolution [that the differences in diffusive power, &c., between hydrogen and carbon oxide do affect the rate at which reduction goes on, has been already indicated by the fact that the points of contrary flexure in the carbon oxide curves lie lower down than those in the hydrogen curves.] Similarly, analogous physical differences in the gaseous products of reduction (*e.g.*, steam and carbon dioxide), may influence the rate at which the action proceeds. Again, in certain cases there may be a tendency more or less marked towards the setting up of chemical changes other than the simple deoxidation of form—

where B is oxygen, A B a metallic oxide, and C a reducing agent ; and these tendencies, even if not sufficiently strong to cause these other changes to take place to a measurable extent, may yet interfere with the occurrence of the simple deoxidation at as rapid a rate as it would have gone on at had these different tendencies not existed. Thus for example when oxides of iron are deoxidised by hydrogen, there is a more or less strongly marked tendency towards an inverse reaction of the nature of the following:—

i.e., towards a reoxidation of the metal and the formation of free hydrogen from the steam produced. Similarly, when carbon oxide is the reducing agent, there is an analogous tendency to an inverse reaction of the form—

and it does not necessarily follow that at any given temperature the influence of the first inverse tendency in reducing the rate of reduction by hydrogen is equal to the influence of the second inverse tendency in reducing the rate of reduction by carbon oxide.

Again, in the case of reduction of iron oxide by carbon oxide, there exists a more or less strongly marked tendency towards the setting up of a reaction of the form—

(Lowthian Bell, “Chemical Phenomena of Iron Smelting,” page 44, *et seq.*), *i.e.*, towards the occurrence of a chemical change, wholly different from the one of simple deoxidation, expressed by equation (2) ; and the existence of this tendency, even though it may not be sufficiently strong to cause the deposition of a weighable amount of carbon, is yet likely to diminish the rate at which the deoxidation of the iron oxide by carbon oxide would otherwise take place.

Yet again, with many metallic oxides there is more or less tendency for the oxide to combine with the carbon dioxide (perhaps whilst still nascent), so as to form a carbonate ; and this tendency, whether sufficiently strong to cause the formation of recognisable quantities of carbonate or not, must necessarily influence the rate of the action of the carbon oxide on the metallic oxide.

From considerations such as these, therefore, it results that it is not always possible to predict *a priori* what will be the relationships of the curved surfaces indicating the relations between deoxidation, time, and temperature in the case of any two reducing agents and a given metallic oxide, or between any two metallic oxides and a given reducing agent. This much can be deduced from the experiments described in Reports I and II, that the points where the surface just begins to

rise perceptibly above the basal plane probably correspond, for equal times, to lower temperatures in the case of the substances which evolve most heat (or absorb least) during their reaction ; and probably similarly correspond, for equal temperatures, to shorter times in these cases ; but it cannot be predicted with certainty that this must be the case, and still less that the one surface will lie wholly outside the other, the two never cutting ; this may be the case where disturbing influences are but small compared with the influence of the amount of heat generated during the reaction (copper oxide, with hydrogen and carbon oxide, seems to be an instance of this), but it may be otherwise when the disturbing influences are greater relatively ; from experiments now in progress on the character of the curve surfaces obtained with ferric oxide and hydrogen and carbon oxide, it seems probable that these surfaces are to some extent instances of the latter kind. The discussion of these, and other analogous results, will be referred to in a future report.

§ 3. *Experiments on the Reduction of Copper Oxide by Carbon Oxide and Hydrogen at comparatively Low Temperatures in Sealed Tubes.*

The experiments above described indicate that the lower the temperature the greater is the length of time which must elapse before the amount of reduction taking place becomes measurable, this being the case both when hydrogen and when carbon oxide is the reducing agent. The form of apparatus used did not conveniently lend itself to carrying out experiments for a longer period than some six or seven hours, so that in order to obtain information as to the relative amounts of time required to produce a measurable amount of reduction by hydrogen and by carbon oxide when these lengths of time were considerable, an entirely different mode of experimenting was adopted, consisting in sealing up the copper oxide in glass tubes in an atmosphere of the reducing gas (the tubes being heated to the required temperatures before finally sealing, to avoid any material variation in pressure in the different experiments), and then keeping at the required temperature for a given time, cooling, opening the tubes, and examining the copper oxide to see if reduction had taken place (and in the carbon oxide experiments examining the gas in the tube to see if carbon dioxide had been formed).

It is evident that the results of experiments made in this way could not be directly compared with those obtained in the U-tube apparatus ; for in the latter case a continuous current of reducing gas was perpetually passing over the copper oxide, and as shown above, the rate of reduction depends on the current speed (*cæteris paribus*) ; whilst the sealed tube experiments might be taken as a kind of limiting case of

the **U**-tube observations when the current speed was 0; so that of necessity it should result that reduction to a measurable extent should be brought about at a given temperature more quickly in the **U**-tube experiment than in the sealed tube observations. That this is so, the following results clearly prove; since, however, all the sealed tube experiments were conducted in the same way, the results obtained in this series of observations are strictly comparable among themselves. As will be seen on inspecting the results detailed below, the time required to produce a just measurable amount of action at a given temperature is considerably less in an atmosphere of carbon oxide than in one of hydrogen.

The sealed tubes employed were about 5 to 6 inches long, and held 10—15 c.c.: a piece of carefully cleaned and dried glass tubing having been drawn out to a capillary tube at one end, and this end blocked with a plug of glass-wool, about 0.5 gram of copper oxide was introduced, and the other end drawn out to a similar capillary. By means of india-rubber tubes the glass tube was then connected with the exit pipe of a current of purified hydrogen (or carbon oxide) so as to displace the air, the gas being admitted at the end not plugged; the plugged end was then sealed by the blowpipe, and the india-rubber tube connecting the other end to the gas supply tightly clamped. The tube was then quickly transferred to the vapour-bath, the clamp just opened to allow the expanded gas to escape, and the projecting capillary tube sealed by the blowpipe. The vapour-baths employed were usually flasks containing a liquid of tolerably constant boiling point, and furnished with an inverted condenser; for some of the lower temperature observations, however, a water or paraffin-bath furnished with a Page's regulator was used, the sealed tubes being sunk nearly to the bottom of the warm fluid by a weight attached by a wire, in such a fashion that the tube could not get overheated by contact with the bottom of the bath, nor partially cooled by floating above its surface.

In titrating the copper oxide after the experiment allowance was, of course, made for the small quantity of permanganate required by the copper oxide itself previously to any further reduction, owing to its possessing the average composition not of pure CuO , but of $\text{Cu}_{40}\text{O}_{39}$ (§ 1). Owing to this correction being requisite and other unavoidable experimental errors, it was found impossible to determine accurately a subtraction of oxygen of much less than 0.00025 gram; but this quantity, corresponding to about .25 c.c. of the weak permanganate solution employed, and to about 0.05 per cent. of oxygen removed, could be recognised pretty readily; in most cases, however, the amount of reduction taking place, if measurable at all, greatly exceeded this limit. In the experiments with carbon oxide another test was

obtained by breaking off the ends of the sealed tube, and cautiously aspirating the gas through clear baryta-water to see if any carbon dioxide were formed. It very frequently happened that traces of turbidity were thus caused, even though no evidence could be obtained of any reduction on titration; but we are inclined to attribute this not so much to true reduction in an incipient stage as to the possible action of the oxygen of the trace of air present (as a film on the surface of the copper oxide and glass tube mechanically condensed thereon) on the carbon oxide, much as spongy platinum causes the combination of hydrogen and oxygen by condensing them within its pores. The capacity of the sealed tube being approximately known and the quantity of oxygen removed, the approximate percentage of reducing gas oxidised is readily calculated.

The following results were obtained:—

At 160° (corrected).

<i>Carbon oxide.</i>			<i>Hydrogen.</i>	
Time in minutes.	Percentage of oxygen removed determined by titration.	Baryta test for carbon dioxide.	Time in minutes.	Percentage of oxygen removed determined by titration.
5	0	—	25	0
10	0	—	35	0
15	0·28	copious	45	0
In this last experiment about 25 per cent. of the CO present was converted into CO ₂ .			60	0
			75	0
			88	0·59
			105	0·61
			125	0·12

At 130°.

15	0	—	120	0
25	0	—	180	0
30	0	—	255	0·05
40	0·64	copious	300	1·24
60	0·98	copious		
In these two last experiments about 60 and 85 per cent. of the CO present was converted into CO ₂ respectively.			In this last experiment about 94 per cent. of the hydrogen was converted into H ₂ O.	

At 108°.

Time in hours.	Percentage oxygen removed.	Baryta test.	Time in hours.	Percentage oxygen removed.
1	0	—	3	0
2	0	—	4	0
2·5	0	—	5	0
3	0	—	8	0
3·5	0	—	10	0
4·5	0	—	14	0·18
6	0	—	17	0·30
6·5	0·61	copious	18	1·07
7·0	0·84	copious	In this last experiment upwards of 90 per cent. of the hydrogen was oxidised to water.	

At 100°.

0·5	0	—	18	0
0·75	0	—	24	0
1·0	0	—	27·25	0
1·5	0	—	30	0·11
2·0	0	—	39	0·81
3·0	0	—	In this last experiment about 80 per cent. of the hydrogen was oxidised to H ₂ O.	
6·0	0	—		
7·0	0	—		
8·0	0·50	copious		
10·0	0·70	copious		

At 83—84°.

2·5	0	—	42	0
4·0	0	—	51	0
5·0	0	—	69	0
8·0	0	—	112	0
13·25	0·20	considerable	143	0
17·5	0·41	copious	167	0
21·0	0·76	copious	190	0·12
In these three last experiments, the amounts of CO converted into CO ₂ , were respectively about 15, 30, and 90 per cent. of the total quantity present.			216	0·07
			256	0·07
			292	0
			335	$\left\{ \begin{array}{l} a = 0·64 \\ b = 0·36 \end{array} \right.$

On comparing together these results, it is evident that in all cases they are fairly concordant, the only apparent exception being in the case of the experiments at 83—84° with the hydrogen tubes, when one experiment after 190 hours gave a notable amount of reduction, two after 216 and 256 hours respectively a lesser amount, but one after 292 hours no action at all. It is hence evident that the following

times may be taken as close approximations to the periods which elapsed in the different cases before reduction went on to an extent great enough to be measurable :—

Tempera- ture.	Carbon Oxide.	Hydrogen.
At 160° ...	Between 10 and 15 m., say 12 m.	Between 75 and 88 m., say 80 m.
„ 130 ...	„ 30 and 40 m., „ 35 m.	A little less than 255 m., „ 230 m.
„ 108 ...	„ 6 and 6·5 h., „ 6·25 h.	Between 10 and 14 h., „ 12 h.
„ 100 ...	„ 7 and 8 h., „ 7·5 h.	„ 27·25 and 30 h., „ 28 h.
„ 83—84.	Somewhat less than 13·25 h., say 11 h.	„ 167 and 190 h., „ 180 h.

That is to say, the length of time required to elapse before a measurable amount of reduction takes place, *is uniformly greater the lower the temperature with the same reducing agent and metallic oxide; and is less with carbon oxide than with hydrogen for the same temperature and metallic oxide.*

These time-values also illustrate the great effect which variation in current speed of reducing gas produces. As already indicated the sealed tube values may be taken as being the times requisite for a current speed of 0. The following table gives the relation between these times and those observed with the normal current of 12·5 c.c. per minute (§§ 1 and 2) in the **U**-tube experiments.

Tempera- ture.	Carbon Oxide.		Hydrogen.	
	Sealed tube.	U -tube.	Sealed tube.	U -tube.
160°	About 12 mins.	Less than 2·5 mins.	About 1·3 hrs.	About 0·5 hr.
130	„ 35 „	About 5 „	„ 3·9 „	„ 2 „
118	„ 6·25 hrs.	„ 8 „	„ 12 „	More than 7 „
100	„ 7·5 „	„ 40 „	„ 28 „	„ „ „
83—84 ...	„ 11 „	—	„ 180 „	—

It is noticeable that the difference seems to be more marked with carbon oxide than with hydrogen.

A check on the above observations made at 100° in hydrogen was obtained in another way. A piece of quill tubing some 30 inches in length was bent to a double right angle like a **U**, but with one limb much longer than the other; about a gram of copper oxide was introduced and shaken down to the middle part of the **U**, the limbs being vertical and pointing upwards. The air was then displaced by hydrogen, and the shorter limb sealed by the blowpipe, the india-

rubber tube connected with the other limb being clamped tight. As soon as the sealed-up end was cold, the oxide of copper was shaken to the sealed part, and the U-tube held so that the limbs pointed downwards; the sealed end was then passed through a hole in the cork of a flask containing boiling water and furnished with a condenser; the other end was then opened under mercury. After the first few seconds, when hydrogen rushed out at the open end owing to expansion, no perceptible alteration in the level of the mercury took place for 28 hours; but after 44 hours the mercury had risen some inches in the limb dipping under mercury, and continued steadily rising. The tube was marked at different points corresponding to the position of the mercury after various lengths of time, and when the experiment was finished, the tube was roughly calibrated by pouring in water from a burette, so as to determine the amount of diminution in bulk of the hydrogen owing to its conversion into steam and the condensation of this in the cooler part of the tube; the copper oxide was also titrated by permanganate after the end of the experiment. The following numbers were obtained, the diminution in bulk of hydrogen being calculated to weight of oxygen removed:—

After 28 hours, oxygen removed	= 0
„ 44 „ „	= 0.63 per cent.
„ 47 „ „	= 0.82 „
„ 50 „ „	= 1.04 „
Oxygen removed after 50 hours (by titration) ..	= 1.03 „

Judging from the rate at which the diminution of the hydrogen progressed, the action must have been first commenced after between 30 and 35 hours, about 29 hours being the time found in the sealed tube experiments.

§ 4. *Experiments carried out in an Atmosphere containing an excess of Reducing Agent.*

Some experiments were also made with a view to determine the rate at which deoxidation of copper oxide goes on under such conditions that the vessel containing the copper oxide always contained more reducing gas than would suffice for complete reduction. To effect this a weighed quantity (close to 0.2 gram) of copper oxide was dropped into a bulb-tube or spherical flask holding some 300 c.c. immersed in a vapour-bath of the required temperature, and after a given time the bulb and contents were removed from the vapour-bath, cooled down, and the partially reduced copper oxide was dissolved up in a measured quantity of slightly acid ferric chloride solution, diluted with water and titrated by permanganate. In order to avoid entrance

of air during the introduction of the copper oxide, the reduction thereof, and the cooling down of the whole, a current of the reducing gas employed was admitted into the bulb by a small glass tube fused through the side of the bulb and dipping downwards inside almost to the bottom, in such a position that as the experiment proceeded the steam or carbon dioxide formed must have been mostly displaced by the entering gas as fast as formed. This glass tube was curled round the bulb externally so that the entering gas should be thoroughly heated to the temperature of the vapour-bath before entrance. Into the mouth of the flask was fitted a cork carrying a thermometer and a thistle-funnel, down which the copper oxide was poured (the current of reducing gas being momentarily stopped) at a noted time when the thermometer indicated that the flask and contained gas had reached the temperature of the vapour-bath.

It was found, however, that no good concordant results were obtainable; the rate at which the reduction proceeded in hydrogen appeared to be variable with the rate at which the entering reducing gas passed over the surface, and in particular the period of time which elapsed before any appreciable amount of action took place varied considerably even when all the conditions were apparently the same or nearly so.

The reduction commenced visibly by the formation of a red speck amongst the little mass of copper oxide at the lowest part of the bulb; this quickly spread, becoming rapidly larger and larger until practically the whole mass became a reddish metallic powder, the progress of the action reminding one of the slow deflagration of a quantity of touch-paper, the reducing action being apparently propagated from particle to particle throughout the mass. For this reason the action went on for some seconds or more after removal of the bulb from the vapour-bath, and nothing like an accurate time-correction could be made.

A different specimen of copper oxide was employed in these observations owing to the former batch being used up. This was prepared in the same way, but was not ignited over the blowpipe; the nitrate, partially decomposed by heating in an open basin to below a red heat, was heated to redness in a combustion-tube in a current of air for some two hours. The product was affected by hydrogen at 184.5° in almost exactly the same way as the specimen used for the previous experiments, with only this slight difference, that the period of time elapsing before action commenced to an appreciable extent was somewhat longer, so that the curve traced out on repeating the U-tube experiments lay a little to the right hand of the mean curve deduced above from the experiments with the first batch. Thus the following numbers represent the difference:—

Time in minutes.	Percentage of oxygen removed.	
	New batch of copper oxide.	Old batch (from mean curve, <i>supra</i>).
20	0·79	0·93
40	3·78	4·71
80	12·33	14·93
110	18·03	18·65

This new batch of copper oxide was sensibly pure copper monoxide, CuO , as it was found to contain 20·05 per cent. of oxygen, and caused only a very small amount of reduction in dilute slightly acid ferric chloride solution on boiling therewith, the amount of oxygen deficiency from that corresponding to CuO , deduced on titration with permanganate being only 0·08 per cent.

With carbon oxide the results obtained were not so discrepant as with hydrogen. With the latter it often happened that in some experiments complete reduction was brought about in a time much less than that in which, in other experiments, no action at all took place, so that no curve-values could be deduced. With the former the following numbers were obtained at 130° and similar ones at other temperatures :—

Time in minutes.	Percentage of oxygen removed.
10	0
15	0
15	0
18	10·0
20	7·7
20	10·4
25	15·6
30	14·8
32	14·5
40	16·0
45	18·0
60	18·6

These numbers are sufficiently concordant to show that the curve line representing the reducing action in an atmosphere containing a surplus of carbon oxide over the amount required for complete reduction is of the same general character as that representing the action in the **U**-tubes in which the copper oxide was in contact during any given small period of time with only a small fraction of the quantity requisite for complete reduction : *i.e.*, for some time no action at all takes place; the action then commences and rapidly increases to a maximum rate, and then diminishes in rate until complete reduction is brought about.

In other words, chemical induction takes place whether the reducing agent or the metallic oxide be in excess.

Experiments are now in progress by one of us and Mr. A. E. Menke as to the rate at which oxidation of spongy metallic copper goes on when heated in a known current of air to various temperatures. It would seem from the results already arrived at that in this case there is no chemical induction at all. The action begins as soon as the temperature is attained by the tube containing the metal, and goes on at a rate which is a maximum at first and then gradually diminishes, doubtless owing to the covering over of the particles of metal with an increasing film of oxide.