XLV.—*The Kinetics of the Reduction of Cuprous Oxide. Part I. The Reduction at Low Pressures: with an Appendix giving the Results of Further Experiments on the Oxidation of Copper at Low Pressures.*

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Previous work on the reduction of the oxides of copper (Wright, Luff, and Rennie, J., 1879, **35**, 475; Pease and Taylor, *J. Amer. Chem. Soc.*, 1922, **43**, 2179, etc.) has shown that the reaction is autocatalytic. It is, therefore, generally accepted that the reduction occurs at the oxide–metal interface. Pease and Taylor also showed (compare Palmer, *Proc. Roy. Soc.*, 1923, *A*, **103**, 444), in the case of the reduction by hydrogen, that the water formed inhibited further attack on the oxide.

The work now to be described relates to the kinetics of the reduction with respect to hydrogen, and the experiments have been carried out solely on systems possessing a cuprous oxide–copper interface constant in area. The conditions have been further simplified in that the complicating effect of the water formed has been eliminated by freezing it out in liquid air. The method of attack, both experimentally and theoretically, is essentially that employed in the earlier study of the kinetics of the oxidation of copper (Wilkins and Rideal, *Proc. Roy. Soc.*, 1930, *A*, **128**, 394; Wilkins, *ibid.*, p. 407) and attention was first directed, therefore, to the reduction at low pressures. In the appendix a few experiments are described in which the oxidation was studied over a far lower pressure range than that used in the earlier work.

EXPERIMENTAL.

Copper was used in the form of electrolytic foil in pieces 1 sq. dm. in area. After being carefully cleaned according to the method described in the earlier papers (*loc. cit.*), the copper was alternately oxidised and reduced, first at 305° and then at 183°, until a steady state of activation had been reached. It was assumed that during the reduction of an oxidised specimen so prepared, the interfacial area copper–cuprous oxide remained effectively constant.

Oxygen was obtained by the action of heat on pure potassium permanganate; and hydrogen by the electrolysis of baryta, traces of oxygen being removed by hot copper.

Since the water formed in the reduction was removed, the rate of the reduction could be followed conveniently by measurement of the fall of pressure in a closed system containing the oxidised copper and hydrogen. The apparatus used consists of a reaction chamber surrounded by a suitable vapour bath. To this is attached the liquid-air trap which serves the double purpose of removing the water from the system and protecting the cuprous oxide surface from poisoning by traces of mercury vapour. The experimental pressures, which were of the order of 10^{-2} mm., were measured on a McLeod gauge. The gas-generating systems and the pumps, which consisted of a Langmuir double-stage diffusion pump backed by a Hyvac, could be separated from the remainder of the apparatus by a mercury cut-off.

Results.—It is found that the relation between pressure and time may be described accurately over the whole temperature range by the equation $\log p_0/p = kt$, where p_0 is the initial pressure of hydrogen in the system, and p the pressure at time t. This agreement is shown in Table I, in which t is given in mins. and p in mm. × 10^{-2}.

TABLE I.

Temp. of reduction 250°.

t.	p obs.	p calc.
0	15·71	15·96
2	11·80	11·89
4	8·90	8·81
6	6·55	6·53
8	4·81	4·84
10	3·45	3·50

Temp. of reduction 220°.

t.	p obs.	p calc.
0	14·21	14·39
3	12·05	12·25
6	10·50	10·52
9	9·00	8·97
12	7·60	7·62
15	6·43	6·46
18	5·30	5·46

Temp. of reduction 210°.

t.	p obs.	p calc.
0	15·15	15·07
3	12·75	13·07
6	11·35	11·30
9	9·93	9·87
12	8·68	8·65
15	7·62	7·55
18	6·52	6·61
21	5·60	5·66
24	4·82	4·96

Temp. of reduction 183°.

t.	p obs.	p calc.
0	8·53	8·53
3	7·26	7·41
6	6·45	6·50
9	5·83	5·73
12	5·05	5·01
15	4·48	4·50
21	3·40	3·39
24	3·00	2·95
30	2·15	2·28

Temp. of reduction 144°.

t.	p obs.	p calc.
0	13·83	13·50
3	13·11	13·09
6	12·90	12·91
13	12·49	12·50
20	12·03	12·10
25	11·83	11·80
30	11·50	11·55
35	11·27	11·28
40	11·07	11·04

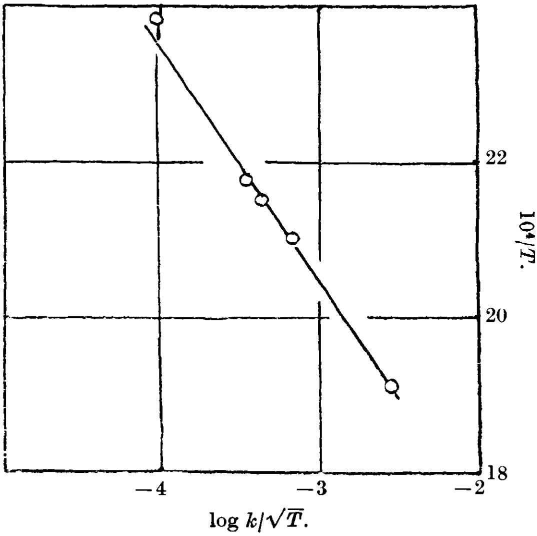
Heat of activation. The relation between k and T was measured by using a piece of copper which had been oxidised to such an extent that it was possible to carry out all the reduction experiments required on the same specimen. In this way it was hoped that the possibility of a change in the properties of the oxide surface during the series of the experiments would be reduced to a minimum. The values of the velocity coefficient k and of the absolute temperature T are related by the equation

$$d \log (k/\sqrt{T})/dT = Q/RT^2 \quad . \quad . \quad . \quad . \quad (1)$$

This equation was tested by plotting the linear expression obtained by integration (see Fig. 1).

As a mean of two independent measurements, the "heat of activation" Q was found to be 18,000 cals., a value which is surprisingly large compared with the figure of 10,000 cals. for the corresponding "heat of activation" for the oxidation.

FIG. 1.



Discussion.

In the earlier study of the oxidation of copper (*loc. cit.*) it was suggested that the oxidation could be considered as the sum of the four consecutive processes : (*a*) the condensation of oxygen at the oxide–oxygen interface, (*b*) the evaporation of the oxygen from this interface into the body of the oxide, (*c*) the diffusion of oxygen through the oxide layer, and (*d*) the reaction between oxygen and copper. The experimental work confirms this analysis in considerable detail (Wilkins, *Phil. Mag.*, 1931, **11**, 422). If the cuprous oxide–hydrogen system is dissected in the same way, it would appear to consist of six consecutive reactions : (*a*) the condensation of hydrogen at the oxide–hydrogen interface, (*b*) the evaporation of hydrogen from this interface into the body of the oxide, (*c*) the diffusion of hydrogen through the cuprous oxide, (*d*) the reaction between hydrogen and cuprous oxide at the oxide–metal interface, (*e*) the diffusion of water from the reaction centre through the oxide layer, and (*f*) the desorption of water. It is the purpose of this work to determine which of these reactions controls the rate of the reduction under different experimental conditions.

Continuing the analogy between the copper–oxygen and the cuprous oxide–hydrogen systems, we may expect, if the pressure of hydrogen is sufficiently low, that the rate of the reduction will be controlled by the rate of the process (*a*). As before, for the reduction in a closed system the rate of fall of hydrogen pressure is given by

$$-dp/dt = kp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and therefore,

$$\log_e p_0/p = kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is the equation found experimentally.

This hypothesis is, however, not entirely satisfactory when we attempt to explain why the heat of activation of the reduction is so much greater than that of the oxidation. Further, it fails to explain why the rate of the reduction is less than that of the oxidation. For example, the value of k_{203° for the reduction was in one case 0·0339, whereas an oxidation carried out on the same sample of oxidised copper gave $k_{203^\circ} = 0{\cdot}176$. It seems evident, therefore, that the rate of reduction is not determined by the chance that a hydrogen molecule condenses on a " locker-stelle " in the cuprous oxide surface, for if this were true, owing to the fact that the diameter of the hydrogen molecule is less than that of the oxygen molecule, the rate of the reduction should be greater and its temperature coefficient less than the corresponding values for the oxidation.

There is an alternative hypothesis which is more satisfactory. If the pressure of hydrogen is not low enough to satisfy the conditions of the hypothesis discussed above, it is clear that an adsorption layer will be built up at the oxide surface. When this occurs the rate of reduction will be determined not by the rate of condensation at the oxide surface, but by the rate of evaporation of the adsorbed hydrogen into the body of the oxide. Since the pressure is low, we may expect the amount adsorbed to be proportional to the pressure, and therefore the rate of evaporation and consequently the rate of reduction will be proportional to the pressure. The hypothesis gives in this way the required relation (see equations 2 and 3) between pressure and time. Further the heat of activation is to be identified with the heat of evaporation of hydrogen into cuprous oxide.

We may conclude from the difference between the kinetics of the oxidation and reduction at low pressures that hydrogen is adsorbed on cuprous oxide much more strongly than oxygen.

Appendix.

Further Experiments on the Oxidation of Copper at Low Pressures.—The experiments on the low-pressure oxidation of copper which led to the development of the equation (3) were carried out over a pressure range of approximately 2—10 mm. In order to substantiate the interpretation of the kinetics of this reaction advanced in the earlier paper, it was essential to show that it applied to the oxidation at still lower pressures. The apparatus built for the study of the reduction at low pressures provided a convenient opportunity for carrying out this work. The results obtained satisfy equation (3) accurately, as shown by Table II, in which the units employed are the same as in Table I.

TABLE II.

Temp. of oxidation 144°.

t.	p obs.	p calc.
0·33	8·95	8·81
3·00	8·31	8·32
5·60	7·87	7·94
8·62	7·48	7·52
12	7·02	7·03
15	6·65	6·65
19·2	6·19	6·14
23	5·74	5·70
27·5	5·25	5·22
32·5	4·73	4·75

Temp. of oxidation 183°.

t.	p obs.	p calc.
0	19·1	19·1
3	16·5	16·3
6	13·7	13·8
9	11·8	11·8
12	9·9	10·1
15	8·5	8·6
18	7·4	7·4
21	6·2	6·3
24	5·5	5·4

Temp. of oxidation 206°.

t.	p obs.	p calc.
0	14·25	14·75
2	10·50	10·54
4	7·81	7·60
6	5·40	5·35
8	3·85	3·78
10	2·45	2·51

Temp. of oxidation 218°.

t.	p obs.	p calc.
0	5·80	5·75
2·2	3·20	3·20
4·25	1·65	1·50
6·20	0·89	0·89
8·50	0·42	0·42
10·70	0·24	0·21

In order to complete the test of the identity of the kinetic processes at the low pressures of this work with those of the earlier work at 2—10 mm., it was necessary to investigate the effect of temperature. It is found that the results satisfy the equation (1), and moreover, the value of Q is calculated to be 9,600 cals., which agrees well with the value of 10,000 ± 1,000 cals. previously obtained. We may therefore conclude that the results of these experiments substantiate completely those found earlier.

Summary.

The reduction of cuprous oxide has been studied at low pressures under such experimental conditions that the area of the copper–cuprous oxide interface is effectively constant, and the water formed during the reduction is removed instantly from the reaction vessel.

The rate of the reduction can be described by the equation $\log_e p_0/p = kt$, where p_0 is the initial pressure of hydrogen, and p the pressure at time t; k is a constant. This result can be explained if it is assumed that the rate of the reduction is dependent upon the rate at which hydrogen can evaporate from the adsorbed layer at the cuprous oxide surface into the body of the oxide.

The heat of activation of the reaction is 18,000 cals., which, on the above hypothesis, is to be identified with the heat of evaporation of adsorbed hydrogen into cuprous oxide.

The earlier work on the oxidation of copper at low pressures has been extended to measurements at pressures of the order of 10^{-2} mm.

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