

CCX.—*The Intermediate-compound Theory of Heterogeneous Catalysis. An Attempt at a Quantitative Investigation of the Range of Validity of this Theory for the Reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ on a Copper Catalyst.*

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THE intermediate-compound theory is almost as old as the study of heterogeneous catalysis itself. Suggested by De la Rive (*Pogg. Ann.*, 1839, **46**, 489; 1841, **54**, 386) in 1839, it was much used until comparatively recently in the interpretation of catalytic phenomena, particularly by Sabatier and his co-workers. At one point its success appeared to be so overwhelming that McLeod (*B.A. Report*, 1892, 663) was led to state that "these catalytic actions are happily being explained (in terms of intermediate compounds) one after another so that soon the name itself will become obsolete." During the last ten years, however, the study of catalysis has been completely revolutionised by Langmuir (*Trans. Faraday Soc.*, 1922, **17**, 607). His theory, which may be called the activation theory, elaborated and modified by Rideal, Hinshelwood, and others, has

been so successful that it has tended to displace the older theory, which had become discredited owing to its indiscriminate application over too wide a range, necessitating the postulation of improbable intermediate compounds; in fact, Hinshelwood ("Kinetics of Chemical Change in Gaseous Systems," 2nd Edn., p. 22) has concluded that "intermediate compound formation between molecules of the gas and the catalysing surface is not usually a helpful hypothesis."

It is, however, certain that some catalytic reactions proceed, in part at least, through the formation of an intermediate compound. For instance, in the reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ on a copper catalyst at 200° , if we assume cuprous oxide to be the intermediate compound, then the catalysis will proceed in the following way: $2\text{Cu} + \text{O} \longrightarrow \text{Cu}_2\text{O}$, $\text{Cu}_2\text{O} + \text{H}_2 \longrightarrow 2\text{Cu} + \text{H}_2\text{O}$. Now, since both the oxidation of copper and the reduction of its oxide by hydrogen take place at measurable and commensurate speeds at 200° , a part of the water resulting from the catalysis must be formed through the medium of the oxide. Arguments of this type are the chief support of the intermediate-compound theory; and, when these appear to be invulnerable, as in the present instance, it is often implied that the whole catalysis is accounted for. The purpose of this investigation is to find out how far this interpretation provides a quantitative description of the catalysis over the temperature range of $140\text{--}250^\circ$.

The reaction has been studied by Bone and Wheeler (*Phil. Trans.*, 1906, A, 206, 1), working at pressures of several hundred mm. and temperatures of about 400° . They noticed that independent oxidation of the catalyst always took place. From the kinetics of the system, they concluded that the catalysis was not dependent upon the formation of an intermediate compound, but that reaction occurred between oxygen activated at the catalyst surface and hydrogen. Pease and Taylor (*J. Amer. Chem. Soc.*, 1922, 44, 1637) have also investigated this problem, using a streaming method in which the hydrogen-oxygen mixture was passed over the granulated catalyst, and the water formed removed by absorption from the gas stream. They worked at atmospheric pressure and at temperatures between 100° and 200° with gas mixtures which contained not more than 5% of oxygen. The kinetics of the catalysis under these experimental conditions are very complicated, so it was not possible to elucidate them quantitatively; they show that, even with gas mixtures containing so little oxygen, independent oxidation of the copper in general takes place. These authors were able to prove, however, that their results were not in agreement with the hypothesis of a purely activation catalysis, and they

suggested that they were not inconsistent with the view that all the water was formed through the oxide as an intermediate compound. The possibility of a mixed activation and intermediate-compound catalysis was not disposed of.

Earlier work on the oxidation of copper (Wilkins and Rideal, *Proc. Roy. Soc.*, 1930, *A*, **128**, 394; Wilkins, this vol., p. 330) has demonstrated that at pressures below 10 mm. the rate of oxidation of the metal in the activated condition is dependent upon the rate at which oxygen reaches the cuprous oxide surface. The rate of fall of pressure for the oxidation in a closed system is given by

$$- dp/dt = kp \dots \dots \dots (1)$$

where k is a constant. The results indicate that the cuprous oxide surface is almost completely free from adsorbed oxygen. The rate of reduction of films of cuprous oxide formed on activated copper in a closed system and at pressures of the order of 10^{-2} mm., and under conditions such that the water formed is immediately removed from the reaction chamber, is described by an equation of the same type. In this case it appeared that the rate of reduction was dependent upon the rate at which hydrogen evaporated into the body of the oxide (Wilkins, *loc. cit.*). It was, however, clear that the oxide surface could only be very sparsely covered with adsorbed hydrogen. Further, comparison of the two reactions showed that the rate of oxidation was much greater than the rate of reduction. The observations of Bone and Wheeler and of Pease and Taylor on the independent oxidation of copper during its catalysis of mixtures of hydrogen and oxygen are, therefore, such as would have been expected.

This earlier work leads us to suppose that, when a mixture of oxygen and hydrogen is admitted to a copper catalyst at a pressure of about 10^{-2} mm., during the catalysis oxidation of the catalyst will occur and a film of oxide will be built up which will ultimately cover its surface. Moreover, once this stage is reached the oxidation of the copper and the reduction of the oxide will proceed independently of each other at rates given by equations of the type (1). The assumption of the independence of these two reactions is justified, since it has been shown that they both leave the oxide surface effectively bare. In order to permit equation (1) to be applied over the whole reaction, we shall discuss the case in which the gas mixture is admitted to a catalyst which has been already superficially oxidised. The rates of fall of the pressure of oxygen and of hydrogen are respectively

$$- dp_{O_2}/dt = kp_{O_2} \dots \dots \dots (2a)$$

and

$$- dp_{H_2}/dt = k_1 p_{H_2} \dots \dots \dots (2b)$$

where p_{O_2} and p_{H_2} are the partial pressures of the corresponding gases at time t . Integrating, we have

$$p_{O_2} = p_{O_2}'e^{-kt} \text{ and } p_{H_2} = p_{H_2}'e^{-k_1t}$$

where p_{O_2}' and p_{H_2}' are the corresponding initial partial pressures. If the catalysis is of the intermediate-compound type already considered, the only reactions occurring in the system are the oxidation and reduction. If, then, no other reaction takes place, the total pressure (P) in the system is given by

$$P = p_{O_2} + p_{H_2} = p_{O_2}'e^{-kt} + p_{H_2}'e^{-k_1t} \quad . \quad . \quad . \quad (3)$$

We have, therefore, a means of testing the range of validity of the intermediate-compound theory quantitatively.

EXPERIMENTAL.

In order to test equation (3), the following method was employed. A copper catalyst was alternately oxidised and reduced until it had reached a steady state of activation, and the value of k was determined by oxidising it at a pressure of about 10^{-2} mm. It was then partially reduced in hydrogen at a pressure of the same order, and from the results k_1 was calculated. To this oxidised copper catalyst, a mixture of oxygen and hydrogen in known proportion was admitted, and the total pressure in the system measured as the catalysis proceeded. In most cases, k and k_1 were now redetermined. From the values of these coefficients and the known initial partial pressures, the theoretical values of P were calculated by using equation (3) and compared with the observed values.

Apparatus.—A reaction vessel, heated in a suitable vapour bath, was connected to a liquid-air trap which served to prevent the entrance of mercury and also to freeze out the water formed during the reactions. The long tube emerging from the other side of the trap was furnished successively with (i) a side tube to a McLeod gauge, (ii) a tap T_1 , (iii) another tap T_2 , (iv) a connexion to a large bulb, (v) a third tap T_3 ; the remote end of the tube then passed to connexions with the pumps and with a gas burette. For the catalysis, hydrogen and oxygen were mixed in known proportion in the gas burette and passed over into the space between the taps T_1 and T_3 . The tap T_2 was then closed and the large bulb pumped out. The gas remaining between T_1 and T_2 was expanded into the bulb and the fraction left in this portion of the tube was admitted into the reaction vessel. By adjusting the amount of gas put into the burette and the number of expansions from the section of tube into the bulb, it was possible to obtain mixtures of oxygen at suitable pressures, and at the same time to ensure that the composition remained the same as that measured in the burette.

The gases were prepared by the methods already described (Wilkins and Rideal, *loc. cit.*; Wilkins, *loc. cit.*). The mixtures of oxygen and hydrogen of the composition $2\text{H}_2 + \text{O}_2$ were obtained directly by the electrolysis of baryta solutions.

The catalyst was a sheet of pure electrolytic copper foil 1 sq. dm. in area. It was carefully cleaned in the way described before (Wilkins and Rideal, *loc. cit.*).

Results.—Two series of experiments were carried out with hydrogen-oxygen mixtures of the compositions $2\text{H}_2 + \text{O}_2$ and $\text{H}_2 + \text{O}_2$. Examples of the results obtained are given in the tables. They show that, in general, equation (3) is not obeyed: P (calc.) is greater than P (obs.), the difference, Δ , increasing as the reaction proceeds. In all cases the time is expressed in minutes and the pressure in hundredths of a millimetre.

t .	P (obs.).	$p_{\text{O}_2}'e^{-kt}$.	$p_{\text{H}_2}'e^{-k_1t}$.	P (calc.).	Δ .
Mixture $2\text{H}_2 + \text{O}_2$. Temp. 142° . $k = 0.027$; $k_1 = 0.0014$.					
0	9.35	3.12	6.26	9.35	—
0.67	9.08	3.06	6.25	9.31	0.25
3.05	8.58	2.87	6.24	9.11	0.53
8.10	7.92	2.51	6.19	8.70	0.78
11.00	7.75	2.31	6.16	8.47	0.71
15.15	7.36	2.07	6.13	8.20	0.84
19.70	7.01	1.84	6.10	7.94	0.93
24.35	6.75	1.61	6.06	7.64	0.91
32.10	6.41	1.31	6.00	7.31	0.90
37.25	6.17	1.14	5.94	7.08	0.91
44.0	5.88	0.95	5.88	6.83	0.95
55.00	5.56	0.71	5.81	6.52	0.96
72.6	5.09	0.41	5.65	6.06	1.09

Mixture $2\text{H}_2 + \text{O}_2$. Temp. 142° . $k = 0.019$; $k_1 = 0.0014$.					
0	9.40	3.13	6.27	9.40	—
0.60	9.00	3.09	6.27	9.36	0.36
3.95	8.74	2.90	6.24	9.14	0.40
9.05	8.30	2.64	6.19	8.83	0.53
16.30	7.85	2.30	6.13	8.43	0.58
26.57	7.25	1.89	6.04	7.93	0.68
37.75	6.68	1.53	5.94	7.47	0.79
48.2	6.18	1.26	5.86	7.12	0.94
60.3	5.76	1.00	5.75	6.75	0.99
70.5	5.31	0.82	5.68	6.50	1.19
85.6	4.97	0.62	5.56	6.18	1.21

Mixture $\text{H}_2 + \text{O}_2$. Temp. 142° . $k = 0.0169$; $k_1 = 0.0043$.					
0	18.90	9.45	9.45	18.90	—
1	18.21	9.29	9.41	18.70	0.49
4	16.90	8.83	9.29	18.12	1.21
7	16.02	8.40	9.17	17.57	1.55
13	15.15	7.59	8.94	16.53	1.38
19	13.82	6.85	8.71	15.56	1.74
28	12.50	5.89	8.38	14.27	1.77
37	11.16	5.06	8.06	13.12	1.96
46	9.85	4.34	7.75	12.09	2.21
55	8.70	3.73	7.45	11.18	2.48

t .	P (obs.).	$p_{O_2}'e^{-kt}$.	$p_{H_2}'e^{-k_1t}$.	P (calc.).	Δ .
Mixture $H_2 + O_2$. Temp. 190° . $k = 0.156$; $k_1 = 0.022$.					
0	18.60	9.30	9.30	18.60	—
1	15.81	7.94	9.10	17.04	1.23
3	12.52	5.82	8.70	14.52	2.00
5	10.41	4.26	8.32	12.58	2.17
7	8.80	3.13	8.26	11.39	2.59
9	7.55	2.29	7.62	9.91	2.36
11	6.45	1.67	7.30	8.97	2.52
15	4.65	0.90	6.68	7.58	2.93
19	3.52	0.48	5.85	6.33	2.81
23	2.74	0.26	5.60	5.86	3.12
27	2.17	0.13	5.32	5.45	3.28
Mixture $H_2 + O_2$. Temp. 203° . $k = 0.176$; $k_1 = 0.034$.					
0	17.50	8.75	8.75	17.5	—
1	15.40	7.36	8.46	15.81	0.41
3	12.51	5.16	7.90	13.06	0.55
5	10.28	3.61	7.38	10.99	0.71
7	8.39	2.55	6.90	9.45	1.06
9	7.20	1.80	6.49	8.29	1.09
11	5.40	1.26	6.03	7.29	1.89
13	4.35	0.89	5.64	6.53	2.18
15	3.61	0.63	5.26	5.89	2.28
17	2.90	0.44	4.92	5.36	2.46
Mixture $H_2 + O_2$. Temp. 250° . $k = 0.414$; $k_1 = 0.151$.					
0.0	20.5	10.25	10.25	20.5	—
0.5	17.5	8.3	9.5	17.8	0.3
2.0	12.9	4.4	8.9	13.3	0.4
4.0	8.6	2.0	5.6	7.6	-1.0
6.0	5.8	0.9	4.2	5.1	-0.7
8.0	3.9	0.4	3.1	3.5	-0.4
10	2.5	0.2	2.3	2.5	—
12	1.8	0.1	1.7	1.8	—

The discrepancy between the theoretical and the observed values of P is considerable and (except at 250°) is much too large to be attributed to experimental error; in fact, in order to account for the observed values of P at 142° , the constants k and k_1 would need to be increased by about 100%. At 250° , however, the values of P (obs.) and P (calc.) agree within the limits of the experimental error, which, at this temperature, are very large owing to the rapidity of the reactions and also to the sintering of the surface.

Discussion.

The immediate deduction from the experimental results is that oxygen and hydrogen react more rapidly than is to be expected from equation (3). Two general hypotheses may be put forward to explain this fact. The first assumes that when the oxidation of copper and the reduction of the oxide occur at the same time and at the same interface they promote each other. This possibility is suggested by an earlier investigation of Palmer (*Proc. Roy. Soc.*, 1923, *A*, **103**, 444), who measured the rate of oxidation of a supported copper film by determining the change in its electrical

conductivity, and was thus able to follow the rate of oxidation of copper in a mixture of oxygen and hydrogen. The gas pressures used were of the order of several hundred millimetres, and moreover, the water vapour formed by the reduction of the oxide by hydrogen was not removed from the system. The results of these experiments showed that copper was oxidised at a greater rate in mixtures of oxygen and hydrogen than in pure oxygen. It has not been possible to confirm this work: details of these experiments will be published later, but it may be stated here that the rate of oxidation of copper in hydrogen-oxygen mixtures at a pressure of the order of those used by Palmer either with or without the removal of water vapour is always very much slower than the rate in pure oxygen.

The second general hypothesis assumes that the excess formation of water vapour is due to a second catalytic process, which may be either of the intermediate-compound or of the activation type. Now, G. P. Thomson (*Proc. Roy. Soc.*, 1930, *A*, **128**, 649), using the electron camera, has demonstrated that the oxide formed on copper at low temperatures is cuprous oxide. This would suggest that cupric oxide is the intermediate compound: $\text{Cu}_2\text{O} + \text{O} \longrightarrow 2\text{CuO}$; $2\text{CuO} + \text{H}_2 \longrightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$. Pease and Taylor (*loc. cit.*) have shown, however, that scarcely any formation of water takes place catalytically when hydrogen and oxygen mixtures are passed over cupric oxide at 200°. The hypothesis of a second intermediate-compound catalysis is consequently ruled out.

We therefore assume that the excess formation of water vapour over the amount required by equation (3) is due to an activation catalysis at the cuprous oxide surface. With the experimental data available, it is not possible to test this theory quantitatively, for the solution of any set of kinetic equations deducible from this hypothesis demands a knowledge of the separate values of p_{O_2} and p_{H_2} throughout the whole course of the reaction, and we propose to continue the investigation in an apparatus designed for this purpose. Although the evidence in favour of the theory is, therefore, negative in character, it is not without interest to interpret the existing data in terms of it. These permit a rough comparison to be made of the relative amounts of water formed by the intermediate-compound and the activation catalysis. The rate of the former is equal to the rate of the reduction, and the amount of water formed is given very roughly from the figures in the fourth column of the tables. This will represent the maximum possible value, since the partial pressure of hydrogen is always less than that calculated from equation (2b), owing to the existence of the activation catalysis. The amount of water formed in the latter catalysis is

roughly measured by the value of Δ : this is a minimum value for reasons analogous to those given above. Hence, we conclude that at 142° the activation catalysis preponderates; as the temperature is raised the intermediate-compound catalysis appears to become more and more important until at 250° it is greater than the activation catalysis. This result is perhaps to be expected, since on the surface there are two reactions competing for the oxygen, *viz.*, the oxidation of copper and the surface reaction between oxygen and hydrogen. If the temperature coefficient of the oxidation is greater than that of the activation catalysis, then the latter would become of decreasing importance as the temperature is raised. This interpretation is not, we believe, inconsistent with the experimental results of Pease and Taylor.

We conclude, therefore, that the catalysis by copper of the reaction between hydrogen and oxygen to form water is in part an intermediate-compound catalysis occurring through the formation of cuprous oxide, and in part an activation catalysis at the cuprous oxide film formed on the copper.

Summary.

A quantitative method has been devised to test the validity of the intermediate-compound theory of heterogeneous catalysis for the reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ on an activated copper catalyst. It is found that when copper is heated in an atmosphere of hydrogen and oxygen, the reaction taking place exceeds that calculated on the assumption that only oxidation of the copper and reduction of the oxide are occurring in the system, and this excess reaction is attributed to the formation of water in an activation catalysis at the cuprous oxide surface. At 142° , the lowest temperature at which the reaction was studied, the activation catalysis preponderates, but as the temperature is raised it becomes of decreasing importance, and at 250° the intermediate-compound catalysis appears to account for practically the entire reaction. This phenomenon is to be expected, since there are two reactions competing for the oxygen in the system.

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