

Exchange Reactions of Solid Oxides. Part V. Dissociation of Molecular Oxygen at Oxide Surfaces : Magnesium Oxide and Zinc Oxide.*

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The reaction $^{18}\text{O}_2 + ^{16}\text{O}_2 \rightleftharpoons 2^{18}\text{O}^{16}\text{O}$, taking place on the surface of zinc oxide and magnesium oxide, has been studied at temperatures such that oxygen exchange with the surface did not occur. For magnesium oxide the equilibration reaction has $E = 6.5 \pm 0.5$ kcal. mole⁻¹, and varies as $(p_{\text{O}_2})^{1.0}$; it is much faster than the oxygen-exchange reaction and it is concluded that adsorption-desorption cannot be rate-determining steps in the latter. For zinc oxide the equilibration reaction has $E = 22 \pm 1.0$ kcal. mole⁻¹ below 215° and 8.5 ± 1.0 kcal. mole⁻¹ above this; the rate varies as $(p_{\text{O}_2})^{1.0}$ throughout. By comparison with earlier observations upon oxygen adsorption and exchange it is concluded that the latter figure for E refers to migration of oxygen atoms over the oxide surface, and the former to the adsorption and desorption of oxygen.

THE earlier papers in this series (*J.*, 1950, 1170, 1175; Parts III and IV *; see also *Discuss. Faraday Soc.*, 1950, 8, 231; *Nature*, 1949, 164, 1130) have been concerned with the kinetics of ¹⁸O exchange between gaseous oxygen and the surface layer of oxygen ions of various oxides. The oxides fully examined, *viz.*, Cr₂O₃, MgO, and ZnO, exhibit the same general phenomena: there is one exchange reaction at high temperatures (above about 400—450°) with a low apparent activation energy (0—8 kcal. mole⁻¹) and another at lower temperatures with an apparent activation energy of 25—40 kcal. mole⁻¹. Owing to the difficulty of measuring the rates of adsorption and desorption, and in two cases the small amount of adsorption, at pressures similar to those used in the exchange experiments (Cr₂O₃ will be considered in more detail in another paper), it has not been possible to determine the nature of the rate-determining steps in the exchange reactions, although tentative identifications have been made. The exchange step involves dissociation of the oxygen molecule, either at the moment of exchange or earlier, during the adsorption stage; no direct measurements of this process have been attempted hitherto. The work now reported consists essentially of studies on the rate of equilibration of a mixture of ¹⁶O₂ and ¹⁸O₂ molecules, exposed to samples of the oxides used in the exchange work: $^{16}\text{O}_2 + ^{18}\text{O}_2 \rightleftharpoons 2^{16}\text{O}^{18}\text{O}$; the temperatures used were such that isotopic exchange with the oxide surface did not occur.

In practice, a mixture of pure ¹⁸O₂ and ¹⁶O₂ was not used; instead a 1:1 mixture of normal oxygen and a fully equilibrated sample containing *ca.* 30% of ¹⁸O was exposed to the oxide, and the reaction followed by watching the approach of the 32/36 mass ratio to the equilibrated figure corresponding to *ca.* 15% of ¹⁸O.

EXPERIMENTAL

Materials.—The oxides used were from the same well-mixed batches which were prepared for use in the exchange reactions: fresh samples were used for each experiment. Gaseous oxygen containing about 30% of ¹⁸O was prepared by thermal diffusion, using a hot-wire column, from oxygen obtained by electrolysis of water containing about 12% of ¹⁸O. Normal oxygen was made by heating potassium permanganate, as described in Part III (*J.*, 1954, 1509).

The enriched oxygen prepared by thermal diffusion was shown by analysis to be in isotopic equilibrium; thus the % of ¹⁸O was the same, whether calculated from the 32/34, 34/36, or 36/32 ratios: this indicated no separation of mass 34 from 36 in the column, showing that the reaction $^{18}\text{O}_2 + ^{16}\text{O}_2 \rightleftharpoons 2^{18}\text{O}^{16}\text{O}$ occurred readily on the platinum-rhodium and nichrome wires used at temperatures near 1000° (cf. Clusius and Dickel, *Naturwiss.*, 1943, 31, 210). A stock was prepared of oxygen consisting of a mixture of equal volumes of the normal gas and

* Parts III and IV, preceding papers.

that containing ca. 30% of ^{18}O : this mixture was kept in a black-painted glass bulb in case incident light caused equilibration, and no equilibration was detected at room temperature in six months. The mixture, analysed in the mass spectrometer, had a highly abnormal 32/36 ratio, as can be seen from the following figures, which refer to an approximately 1:1 mixture of normal and of 30.7% ^{18}O : 32/36 ratio before equilibration = 14.83, after equilibration 27.50 (Calc., 27.46). With a constant galvanometer deflection of some 15,000 cm. for mass 32 the above figures imply a fall in the mass 36 deflection from about 1000 cm. to less than 550 cm.; this fall is measurable to better than $\pm 0.2\%$, but observations taken during kinetic runs are not likely to be correct to better than $\pm 1\%$.

Method.—The experimental procedure was exactly that used in the exchange work; a suitable weight (usually 1—3 g.) of oxide was outgassed overnight at a temperature used in the exchange work, viz., 540° (MgO) and 630° (ZnO). In the morning the final vacuum was checked and if satisfactory the sample was isolated from the pumps and cooled to the desired temperature, and the requisite amount (usually ca. 5 ml., N.T.P.) of non-equilibrated oxygen admitted. A record of the change with time of the 32/36 (and in some cases 32/34) ratio was taken by drawing off oxygen continuously through a leak into the ion source of the mass spectrometer and following the change in 32:34:36 peak heights. The reaction system was of similar design to that used in the oxygen-exchange experiments (see Part I, *J.*, 1950, 1170); the reaction vessel used, however, was of silica. The mass spectrometer was a 60° sector Nier-type instrument, with the circuits of Graham, Harkness, and Thode (*J. Sci. Instr.*, 1947, 24; 119), and very similar to that used in earlier work, but had an all-metal analyser tube. Ion currents corresponding to the various masses were measured by a galvanometer and shunt system; masses were brought into focus by manual voltage scanning.

A few very slow reactions were performed in a modified apparatus in which a small Töpler pump was interposed between the reaction vessel and the leak to the mass spectrometer. After suitable time intervals most of the oxygen was withdrawn from the reaction vessel and forced into a small volume attached to the leak until the pressure was high enough for accurate analysis, and after measurement the oxygen was returned to the reaction vessel. This procedure was adopted to avoid excessive loss of oxygen from the reaction system; by this means runs of several days' duration were carried out with no detectable change in oxygen pressure; the time taken to perform the measurements was negligible when compared with the total reaction time.

Kinetics.—As expected for an isotopic reaction, it was found that the fall of the 36-mass peak to the equilibrium value followed a first-order law, thus

$$-dx/dt = k_e'x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x is the excess abundance of mass 36, at time t , above the equilibrium value; there was a similar rise in the mass 34 abundance but this was followed in detail in only a few runs.

We use the notation of other papers in this series, viz., $n_g/2$ = no. of oxygen gas molecules introduced into the reaction system at $t = 0$; w = wt. (g.) of oxide used; $C_g/2$ = no. of molecules of oxygen adsorbed on 1 g. of oxide at equilibrium at the pressure of the reaction, p_{O_2} ; n_s = no. of atoms of exchangeable oxygen in the oxide surface per g.; p_{O_2} = pressure of oxygen gas (in mm. Hg); k_A , k_M , k_E , k'' are rate constants; k_e' is the experimental rate constant for the equilibration [cf. eqn. (1)]; and k_0 is a rate constant of the exchange reaction, and is defined in earlier papers (*Discuss. Faraday Soc.*, 1950, 8, 231; Part III, *J.*, 1954, 1509).

From (1) the rate of reaction (equilibration) in the system, in atoms min.^{-1} , is

$$v = -n_g(dx/dt) = n_g k_e'x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which we may equate to

$$k'' w f'(C_g) \phi'(n_s) x$$

where k'' is the rate constant of the equilibration reaction, and $f'(C_g)$ and $\phi'(n_s)$ are unknown functions of the adsorbed layer and of the oxide surface; so that

$$n_g k_e' = k'' w f'(C_g) \phi'(n_s) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now a similar argument applied to the exchange reaction gave

$$k_0 n_s = k' f(C_g) \phi(n_s) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

[cf. Part III, *J.*, 1954, 1509; eqn. (8)].

From equations (3) and (4) it follows that if the rate-determining process in the measured exchange reactions is the same as that of the equilibration reactions, then

$$k_0 n_s = n_g k_e' / w \quad \dots \quad (5)$$

and since dissociation and recombination should be at least as rapid as exchange, $k_0 n_s$ should never be greater than $n_g k_e' / w$ at a given temperature. Since it is difficult to separate the exchange and equilibration reactions when both are proceeding simultaneously, the latter has been studied at temperatures low enough for the exchange reaction to be neglected, and the results extrapolated to higher temperatures by means of the Arrhenius plot (cf. Fig. 3).

Results.—The highest reaction temperature used in this work was 311°; it was first established that even at 500° the empty reaction vessel itself did not cause equilibration; thus after 40 min. at this temperature the 32/36 ratio changed by less than 1.5%, while at 100° less than 0.3% change occurred in a week: this degree of reactivity was negligible compared with that of the oxides. The inert character of the reaction vessel was again confirmed at the end of this series of experiments.

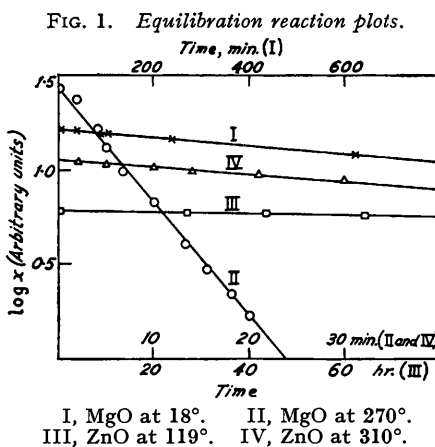


FIG. 2. Dependence of reaction rate upon pressure of oxygen.

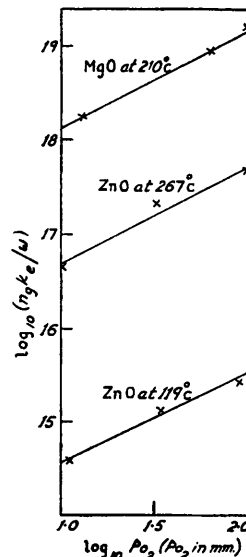


Fig. 1 shows a few plots of $\log x$ against t for the equilibration reaction on both oxides, providing experimental evidence for the use of eqn. (1). Fig. 2 shows the variation of $n_g k_e' / w$ with oxygen pressure for the two oxides; it is evident that in both cases this function is directly proportional to p_{O_2} over the pressure range 1—10 cm. It was shown in Part III (*loc. cit.*) that, for the exchange reaction with MgO, $n_s k_0$ is approximately independent of p_{O_2} , and in Part IV it was found that $n_s k_0$ varied as $(p_{O_2})^{1.0}$ for ZnO over the pressure range 1—15 or 20 cm. The exchange kinetics of Parts III and IV were determined at a pressure of oxygen of ca. 6 cm. and the equilibration runs for ZnO are plotted in Fig. 3b in the form $\log_{10} (n_g k_e' / w p_{O_2})$ against $10^5/T$, where T is the reaction temperature, and in Fig. 3a are plotted also $\log_{10} (n_s k_0 / p_{O_2})$ against $10^5/T$ for the exchange reaction, the results used being those of the earlier paper: the results for MgO are plotted in the form $\log_{10} (n_g k_e' / w)$ and $\log_{10} (n_s k_0)$ in Fig. 3a, since all equilibration runs for this oxide were done at $p_{O_2} = 6$ cm. (except those of Fig. 2).

DISCUSSION

Considering first the case of MgO, it was concluded in Part III that the following three stages could be rate-determining in the exchange reaction: (1) adsorption-desorption, (2) migration of ad-atoms on the surface, and (3) exchange proper. It was also shown that it was unlikely that adsorption was a slow step although the evidence on this point was not

unequivocal; the surface coverage at the exchange temperatures was very small (*ca.* 0.1%) so that (2) could well be a slow stage. The present observations show conclusively that adsorption-desorption involving dissociation of the oxygen molecule is faster than any step we have hitherto measured in the exchange reaction. Thus the equilibration rate measured here at 275° is slightly faster than the exchange reaction at the same pressure at *ca.* 500° (see also Fig. 4). It seems reasonable to decide, in view of this evidence and the argument presented in Part III, that the "exchange reaction" at high temperatures (> *ca.* 420°) with a low activation energy is limited by process (2), while the "exchange reaction" below *ca.* 420° is the true exchange process, involving replacement of lattice oxygen by ¹⁸O-enriched ad-atoms. It is not possible to determine with certainty the true activation energies of any of these processes since, as we indicated in Part III, all the experimentally determinable quantities, $n_s k_0$, $n_g k_e' / w$, etc., contain unknown functions of C_g (and probably of n_s) and the variation of C_g with temperature at these pressures (*ca.* 6 cm.) cannot be measured with sufficient accuracy. We may note, however, that the activation energy of ($n_g k_e' / w$) under our conditions is 6.5 ± 0.5 kcal. mole⁻¹; the direct dependence of this reaction upon oxygen pressure is consistent with an adsorption-desorption process involving dissociation. It was found in Part III that the adsorption of oxygen on this oxide, as measured by the initial rate of adsorption at pressures near 10⁻³ cm., had $E = 13.8$ kcal. mole⁻¹; this value is unlikely to hold at pressures around 6 cm., since the surface is undoubtedly heterogeneous, as shown by the variation of n_s with temperature. We have already indicated (Part III) that it is impossible in isotopic reactions of the present type to distinguish between adsorption and desorption as rate-determining steps.

Our observations thus permit the following conclusions to be drawn regarding the processes occurring on MgO. Adsorption-desorption involving equilibration occurs on certain sites, with an apparent $E = 6.5 \pm 0.5$ kcal. mole⁻¹; the equilibration involves dissociation of the oxygen molecule, but the sites are not saturated in the temperature range 17–275° since the reaction rate increases directly as the oxygen pressure. From the adsorption sites a proportion of the ad-atoms migrate over the surface ($E = 7.7 \pm 2.0$ kcal. mole⁻¹; Part III); in the temperature range where this process controls the exchange the surface concentration of mobile ad-atoms is independent of oxygen pressure (exchange rate pressure-independent). The mobile ad-atoms exchange with oxygen ions in the surface when they reach suitable exchange sites; the apparent activation energy of the exchange process proper, involving a switch of electrons from one oxygen nucleus to another, or from an appropriate defect to the ad-atom, is 36 ± 1.0 kcal. mole⁻¹, but because of the influence of the non-exponential term this process is only rate-determining below 420°. In considering this picture we note that Becker *J. Phys. Chem.*, 1953, 57, 153) records that Ashworth has detected with the electron-field emission microscope twin nuclei on tungsten at room temperature in the presence of oxygen; these nuclei appear suddenly on the tungsten surface, gyrate rapidly around each other, and usually disappear simultaneously, but sometimes separate (? dissociate) and wander off independently. Since only single nuclei were observed in the presence of argon, the twin nuclei might well be adsorbed oxygen molecules, which are moderately mobile over the surface and sometimes dissociate. On the other hand, our observations could equally well arise if adsorption-desorption occurred at fixed sites, the ad-atoms remained relatively immobile, and $E = 7.7$ kcal. mole⁻¹ referred to the mobility of suitable lattice defects, but such immobility of adsorbed oxygen is in our opinion most unlikely (cf. de Boer "Dynamical Character of Adsorption," O.U.P., 1953).

Zinc oxide shows a more complicated state of affairs, the Arrhenius plot for the equilibration reaction showing a break at *ca.* 215°, and the process having an apparent activation energy of 22 ± 1 kcal. mole⁻¹ below this temperature and 8.5 ± 1.0 kcal. mole⁻¹ above 215°. The higher-temperature line on extrapolation passes satisfactorily through the "high-temperature" exchange reaction points; all processes measured on this oxide vary directly as the oxygen pressure. It seems clear that the process with $E = 8.5 \pm 1.0$ kcal. mole⁻¹, which is rate-determining in the exchange measurements above 415° for oxide outgassed at 630°, is the surface migration of ad-atoms, which implies that

the oxygen molecule is adsorbed at one site, dissociates, and its component atoms migrate over the surface, undergoing exchange on the way, to other sites where they recombine with other atoms and are desorbed; defect migration appears not possible here because of the pressure-dependence of the process. The "exchange reaction" below 415° , of $E = 27.5 \pm 1.0$ kcal. mole⁻¹ (cf. Part IV), appears to be the true exchange reaction; note, however, that when plotted as $k_0 n_s$, the activation energy becomes 40 ± 2 kcal. mole⁻¹, owing to the change of n_s with temperature. The equilibration reaction below 215° , of $E = 22 \pm 1$ kcal. mole⁻¹, we believe to refer to the adsorption-desorption process: in this connection it is significant that the adsorption measurements in the range 420 – 520° outlined in Part IV, when separated so far as possible from the reaction with zinc exposed during the outgassing treatment (see Part IV), yield rates which have $E = 15 \pm 6$ kcal. mole⁻¹, and are within a factor of 5 to 10 of those calculated from the slope of the line *AB* in Fig. 3*b*. In the circumstances, the agreement must be regarded as satisfactory, especially since not every act of adsorption and desorption would be expected

Figs. 3*a* and 3*b*. Summary of exchange and equilibration results.

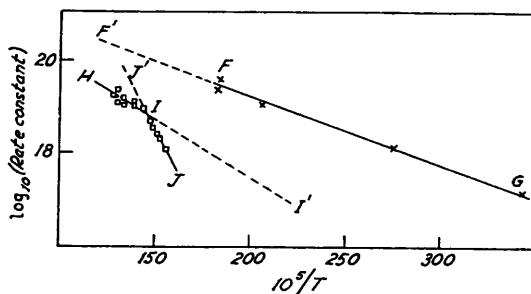


Fig. 3*a*: MgO, outgassed for ca. 16 hr. at 540° .
 ×, Equilibration. □, Exchange (Part III).

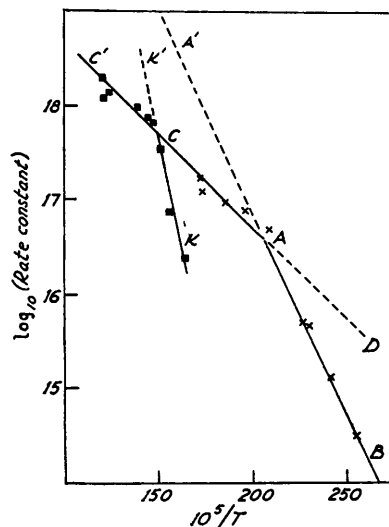


Fig. 3*b*: ZnO, outgassed for ca. 16 hr. at 630° .
 ×, Equilibration. ■, Exchange (Part IV).

to lead to equilibration. Since all processes on this oxide increase directly as the oxygen pressure, it appears that the coverage is small over the whole range of experimental conditions, insofar as saturation is not reached up to at least 15–20 cm.

The processes on zinc oxide are a little difficult to visualise in detail: it appears that adsorption and desorption occur first on an array of active and relatively closely-packed sites ($E \approx 22$ kcal. mole⁻¹), this process leading also to equilibration (*A'AB*, Fig. 3*b*). As the temperature is raised the coverage of these sites increases, as does the speed of equilibration, until the maximum speed possible on these sites is reached at *A*; thereafter the rate of equilibration (and, at higher temperatures, of exchange) is governed by the rate of migration ($E \approx 8.5$ kcal. mole⁻¹) of ad-atoms across the surface to less accessible desorption sites.

We may summarise our findings with reference to Fig. 3: (i) *F'FG* (MgO) and *A'AB* (ZnO) — adsorption-desorption

$$\text{Rate} = k_A f_A(C_g) \phi_A(s)$$

$$f_A(C_g) \propto p_{O_2} \text{ for both oxides}$$

$\phi_A(s)$ is some function of the surface; possibly equal to the number of suitable sites per g.

(ii) *HII'* (MgO) and *C'CAD* (ZnO)—migration of ad-atoms or possibly of surface defects (MgO); surface migration of oxygen (ZnO) :

$$\text{Rate} = k_M f_M(C_g) \phi_M(s)$$

with the same remarks as above for $\phi_M(s)$; $f_M(C_g) \propto p_{O_2}$ for ZnO but independent of p_{O_2} for MgO.

(iii) *J'IJ* (MgO) and *K'CK* (ZnO)—the true exchange reaction

$$\text{Rate} = k_E f_E(C_g) \phi_E(s)$$

with the same remarks as for the previous case for $f(C_g)$ and $\phi(s)$.

It is not possible to say whether any of the three $f(C_g)$ or $\phi(s)$ terms are the same: hitherto we have used $\phi(n_s)$ instead of $\phi(s)$ but the latter formulation, being more general, seems preferable.

We have insufficient evidence to determine the mechanism of the adsorption stage leading to dissociation; *i.e.*, whether the act of adsorption involves dissociation (which

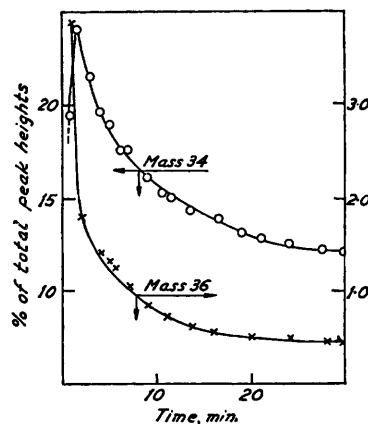


FIG. 4. Exchange reaction using non-equilibrated oxygen. MgO at 385°.

seems most likely) or whether this is promoted by bombardment from the gas phase; neither can we say whether on dissociation both oxygen atoms become mobile or if one is bound to the lattice as suggested by Garner *et al.* (*Discuss. Faraday Soc.*, 1950, 8, 246) for cuprous oxide. Speculation about the exact nature of the exchange step is unprofitable at present; the significant point is the demonstration of appreciable mobility of the surface oxygen in crystalline oxides.

Fig. 4 provides direct evidence that the equilibration reaction is much faster than the exchange reaction on MgO; *i.e.*, it gives justification for the extrapolation of *GF* to *F'* in Fig. 3*a*. Fig. 4 shows the 34- and 36-mass peaks as percentages of the total oxygen molecule peaks during the early stages of an *exchange* reaction in which a 1 : 1 mixture of normal and *ca.* 30% ^{18}O oxygen was used. It is seen that in the first 3–4 min. the 36 peak abundance drops very rapidly to around the equilibrium value for *ca.* 15% ^{18}O (*viz.*, 2% of total peaks) while in the same time the 34 peak abundance *rises* to a value near the equilibrium value (*viz.*, 25% of total peaks) before beginning to fall owing to the effect of the exchange reaction. Several such runs have been performed on both oxides in order to check the validity of the technique and argument used in this work; no anomalies were found.

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