

Exchange Reactions of Solid Oxides. Part III. Magnesium Oxide.*

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Exchange of ^{18}O between the surface of magnesium oxide and oxygen gas has been studied over the temperature range $370\text{--}510^\circ$, oxygen pressures of 1—14 cm. being used. The rate of exchange and the amount of exchangeable oxide surface depend on the previous outgassing treatment of the oxide. The exchange process has an activation energy of approx. 3 ± 2 kcal. mole $^{-1}$ above $420\text{--}450^\circ$ (depending on temperature of outgassing) and 34 ± 2 kcal. mole $^{-1}$ below this temperature. An alternative treatment of the kinetics gives E for the high-temperature process of 7.7 ± 2 kcal. mole $^{-1}$ and for the lower temperature range approximately 36 ± 2 kcal. mole $^{-1}$. Rates of adsorption of oxygen by magnesium oxide at pressures near 10^{-3} cm. show that at low pressures the initial adsorption has an activation energy of about 14 kcal. mole $^{-1}$, but it is not possible with certainty to extrapolate to higher pressures and the nature of the rate-determining step in the two exchange processes remains uncertain.

EARLIER papers (Houghton and Winter, *Nature*, 1949, **164**, 1130; Winter, *J.*, 1950, 1170; Winter, *Discuss. Faraday Soc.*, 1950, **8**, 231; Houghton and Winter, "Mass Spectrometry," Inst. of Petroleum, 1952, p. 127) have described the technique used to study the exchange of ^{18}O between enriched oxygen gas and finely-divided oxides: some discussion has also been given of the kinetics of the process. This paper reports a detailed investigation of the exchange with magnesium oxide: a study has been made of the effect upon the kinetics of varying the time and temperature of outgassing, the temperature of the exchange reaction, and the oxygen pressure. It must be emphasised that this work is concerned with the initial rapid exchange reaction, associated with the surface of the oxide (Houghton and Winter, *Nature*, *loc. cit.*). A few of these observations have been given elsewhere, and the earlier values for velocity constants in some cases differ slightly from those now quoted; this is due to a more careful evaluation of α_0 and α_∞ (see *idem*, *ibid.*). In an attempt to identify the rate-determining step in the exchange, some measurements of the rate of adsorption of oxygen are reported here.

EXPERIMENTAL

Materials.—Magnesium oxide was of "AnalaR" purity, made by igniting the carbonate in air at 800° for *ca.* 4 hr. The oxygen, containing about 1.2% of ^{18}O , was prepared by electrolysis and was from the same stock as that used in earlier work; normal oxygen used for adsorption measurements was obtained by heating "AnalaR" potassium permanganate *in vacuo*; the first 10% of gas was rejected, and a middle fraction collected after passage through a trap cooled to -78° . Helium used in the adsorption experiments was from the British Oxygen Company, spectroscopically pure, and was passed through a trap at -78° before use.

Results.—Experiments designed to show the effect of time and temperature of outgassing, and pressure of oxygen, p_{O_2} , in the reaction system, are summarised in Tables 1—3. It is evident that the rate of reaction at a fixed temperature is strongly dependent upon the first two variables, but is not very sensitive to p_{O_2} . In the later work these three conditions were kept approximately constant in order to study the effect of reaction temperature upon the rate constant, k_0 , and the exchangeable surface oxygen, n_s (atoms/g. of oxide). These experiments are summarised in Table 4 and Figs. 1 and 2, and yield the following rate equations, where X and X' refer to the left-hand portion of the upper and the lower curve in Fig. 2 respectively and Y and Y' to the right-hand portions.

$$X, k_0 = 0.15 \exp(-2400/RT) \quad \dots \quad (1)$$

$$Y, k_0 = 4.25 \times 10^9 \exp(-35,400/RT) \quad \dots \quad (2)$$

$$X', k_0 = 0.12 \exp(-3000/RT) \quad \dots \quad (3)$$

$$Y', k_0 = 1.62 \times 10^8 \exp(-33,000/RT) \quad \dots \quad (4)$$

* *J.*, 1950, 1170, 1175, are regarded as Parts I and II.

These equations are of the usual general form $k_0 = A \exp(-E/RT)$: there is some uncertainty as to the exact values of A and E , owing to the scatter of the results; the figures given above are the most probable values and the limits are given in Table 5.* This uncertainty is

TABLE 1. Dependence of k_0 and n_s upon time of outgassing.

p_{O_2} (mm.)	Outgassing conditions		Exchange reaction		k_0 , min. ⁻¹	$n_s \times 10^{-20}$
	Time (hr.)	Temp.	temp.			
75	14½	540°	442°		0.0276	5.88
75	{ 18	540	{ 442		0.0340	6.88
77	{ + 7	445	{ 475		0.0278	6.95
79	{ 18	540	{ 475		0.0403	8.91
142	{ +24	475	{ 533		0.118	7.95
92	1½	537	537		0.0365	10.2

TABLE 2. Effect of temperature of outgassing upon k_0 and n_s .

p_{O_2} (mm.)	Temp.		Outgassing time (hr.)	k_0 , min. ⁻¹	$n_s \times 10^{-20}$	$k_0 n_s \times 10^{-20}$
	Outgassing	Exchange				
56	866°	460°	14	0.158	0.283	0.0447
89	748	461	13.8	0.087	1.70	0.149
85	640	459	13	0.045	2.99	0.135
87	600	463	14	0.042	3.96	0.167
69	540	459	17	0.0256	4.48	0.115
—	510	462	14	0.0155 *	6.90 *	0.107 *
76	866	388	13.8	—	0.183	—
101	540	388	14	0.00648	3.25	0.0211
62	510	388	14	0.00215	4.45	0.00957

* Interpolated.

TABLE 3. Dependence of k_0 and n_s upon p_{O_2} .

p_{O_2} (mm.)	Temp.		Outgassing time (hr.)	k_0 , min. ⁻¹	$n_s \times 10^{-20}$
	Outgassing	Exchange			
41	510°	491°	14	0.0139	8.23
80	510	491	14	0.0160	8.15
83.5	510	493	14	0.0169	6.85
88	492	492	14	0.0149	—
147	492	492	14	0.0178	—
59	540	386	14½	0.0076	3.15
11.7	540	386	14	0.0069	5.15
101.5	540	388	14	0.0065	3.25
11.5	540	450	14	0.0383	6.30
67.5	540	450	15½	0.0324	—

regrettable but is due, we believe, to the extreme sensitivity of the oxide to the outgassing conditions; we were unable to control the temperature of the furnace to better than $\pm 5^\circ$ overnight. Recent work by Dr. J. A. Barnard upon zinc oxide (Thesis, London, 1952, and Part IV), which is more sensitive, has shown that by close control of the temperature (better than $\pm \frac{1}{2}^\circ$ overnight) the scatter of the k_0 results is much reduced: it may be remarked, however, that the scatter of values of n_s (cf. Fig. 1) is not removed.

To provide an alternative measure of surface, low-temperature (78° K) nitrogen adsorption isotherms were measured for samples of the oxide which had been subjected to various outgassing treatments; these results are given in Table 6, calculated according to both the Harkins-Jura (*J. Chem. Phys.*, 1943, 11, 430) and the Brunauer-Emmett-Teller (B.E.T.) (*J. Amer. Chem. Soc.*, 1938, 60, 309) method. There is little difference between the surface areas given by the two theories, and we shall use the B.E.T. figures in discussion. Other results are given in Table 9.

* The method of least squares was applied to the results, giving equal weight to T and $\log k_0$; the limits were obtained from the quadratic mean error (cf. Whittaker and Robinson, "The Calculus of Observations," Blackie, Glasgow, 1946, p. 246).

TABLE 4. *The effect of exchange reaction temperature on k_0 and n_s for magnesium oxide at constant outgassing temperature.*

p_{O_2} (mm.)	Temp. Out-gassing	Temp. Exchange reaction	Out-gassing time (hr.)	k_0 min. ⁻¹	n_s $\times 10^{-20}$	p_{O_2} (mm.)	Temp. Out-gassing	Temp. Exchange reaction	Out-gassing time (hr.)	k_0 min. ⁻¹	n_s $\times 10^{-20}$
76.6	510°	507°	14	0.0194	10.6	67.9	540°	491°	16	0.0360	5.35
83.5	510	493	14	0.0169	6.85	76.9	540	475	18	0.0278	6.95
79.7	510	492	14	0.0160	8.15	72.1	540	462	13.5	0.0256	2.76
78.4	510	473	14	0.0150	7.46	69.0	540	459	17	0.0256	4.48
56.3	510	454	14	0.0159	5.4	67.5	540	450	15.5	0.0324	3.51
62.1	510	450	14	0.0163	5.76	74.9	540	442	14.5	0.0276	5.91
76.2	510	424	14	0.00804	5.40	78.1	540	419	13.5	0.0281	3.15
65.0	510	402	14	0.00347	5.20	78.0	540	403	14	0.0149	3.72
63.2	510	401	13.3	0.00293	3.35	56.1	540	397	14.5	0.0111	3.70
62.1	510	388	14	0.00215	4.45	59.3	540	386	14.5	0.00760	3.15
62.4	510	382	15	0.00148	6.26	100.0	540	382	13.5	0.00680	—
62.6	510	381	14	0.00132	5.07	61.6	540	368	14.5	0.00344	4.15
62.2	510	370	13.8	0.00112	5.00						

TABLE 5. *Accuracy of Arrhenius plots.*

Line	A	E	Line	A	E
X	0.022—1.0	2.4 ± 2.8	X'	0.036—0.42	3.0 ± 1.8
Y	(2.76—6.53) × 10 ⁹	35.4 ± 0.6	Y'	3.2 × 10 ⁷ —1.0 × 10 ⁹	33.0 ± 2.2

TABLE 6. *The surface areas of oxides by low-temperature nitrogen adsorption.*

Outgassing conditions Time (hr.)	Temp.	B.E.T.*		Harkins-Jura	
		C	m. ² /g.	A	m. ² /g.
32	400°	22.5	62.3	282.3	68.2
48	400	27.8	62.0	283.3	68.3
64	400	29.4	61.5	260.8	65.6
16	500	29.4	61.5	260.8	65.6
14.5	835	44.3	21.8	33.96	23.7

* The area of the nitrogen molecule is taken to be 16.2 Å².

TABLE 7.

p_{O_2} (mm.)	Outgassing conditions		Exchange reaction		k_0 , min. ⁻¹
	Time (hr.)	Temp.	temp.	temp.	
—	18	540°	540°	540°	0.033 *
76.6	14	507	507	507	0.0194
87.7	14	492	492	492	0.0149
80.2	14	480	480	480	0.00924
86.4	14	444	444	444	0.00364

* Interpolated from Fig. 2.

TABLE 8. *Oxygen adsorption rates.*

Expt. No.	T	10 ⁴ × Initial oxygen pressure, cm.	(dn_g/dt) _{t=0} †	Expt. No.	T	10 ⁴ × Initial oxygen pressure, cm.	(dn_g/dt) _{t=0} †
A1	432°	10.8	0.30	A8	388°	10.6	0.19
A3	484	9.8	0.73	A9	416	11.2	0.24
A4	470	11.0	0.60	A11	412	10.8	0.23
A5	386	10.6	0.20	A2 *	432	9.0	0.45
A6	456	10.5	0.38	A10	416	27.0	0.42
A7	456	12.5	0.37	A12	486	20.2	1.05

* Run A1 allowed to come to equilibrium (24 hr.), final pressure being 2.3 × 10⁻⁵ cm., and another dose of oxygen added; this gave an equilibrium pressure of 3.3 × 10⁻³ cm. after 24 hr.† To convert to atoms min.⁻¹ g.⁻¹ multiply by 3.07 × 10¹⁶.

TABLE 9.

Outgassing temp.	Surface area, m. ² g. ⁻¹		Outgassing temp.	Surface area, m. ² g. ⁻¹		Outgassing temp.	Surface area, m. ² g. ⁻¹	
	B.E.T. at 78° K	Exchange at 460° C		B.E.T. at 78° K	Exchange at 460° C		B.E.T. at 78° K	Exchange at 460° C
866°	15.8	} 2.86	640°	33.9	} 30.2	600°	34.4	40.0
	21.8			32.2			540	38.6
748	36.7	17.2			510	61.5	69.7	

Oxygen Adsorption Measurements.—The apparatus used was constructed from Pyrex glass and was of conventional design, comprising two McLeod gauges, covering the range 10^{-1} to 10^{-6} mm. (all pressures are expressed in mm. of Hg), a mercury manometer for measuring pressures above 10^{-1} mm., a dosing system, and bulbs containing pure dry oxygen and helium. The adsorption vessel was of approximately the same size as that used for the exchange reactions: the apparatus was interconnected with taps lubricated with Apiezon vacuum grease, and was evacuated through a cold trap at -78° with a two-stage mercury diffusion pump backed by a rotary oil-pump. Dead-space determinations were made by using helium, and included measurements of the equivalent dead-space of the adsorption vessel, loaded with oxide, at all temperatures used. In the latter case the pressure of helium was adjusted to be approximately that of the oxygen at equilibrium in the adsorption measurements; the connecting tubing was of 7 mm. internal diameter, and it was established by calculation that under these conditions of measurement corrections due to possible thermal transpiration were negligible. Fresh lots of oxide were used for each experiment.

The procedure was to outgas the oxide sample (usually 1 g.) overnight at 540° , as in the exchange experiments; if the vacuum in the morning was satisfactory ($<10^{-6}$ mm.) the oxide was isolated from the pumps and cooled to the desired temperature; when the temperature had been steady for about 20–30 min. the adsorption was begun: if the morning pressure was too high the experiment was abandoned. Preliminary work showed that the amount of adsorption was very small, amounting to about $6\text{--}9 \times 10^{17}$ atoms/g., or about 0.1% of the exchangeable surface, at 485° , and 6 cm. upon 20 g. of magnesium oxide outgassed for 6 days to an ultimate pressure of 8×10^{-6} mm., at 535° : this corresponds to a pressure drop in the system of about 0.1 cm. in 6 cm.: under these conditions the adsorption appeared complete in less than 10 min. A similar experiment at 388° showed adsorption at 6 cm. pressure to be complete in, at the most, 5 min. It was, therefore, not possible to measure rates of adsorption at these pressures; such experiments were performed in the region of 10^{-2} – 10^{-3} mm. Observations were made at constant volume by expanding a known quantity of oxygen from the gas-dosing system into the adsorption volume and measuring the pressure on one or other of the McLeod gauges after suitable time intervals. Most adsorptions were followed to equilibrium, but the process obeyed unambiguously no simple law, and it was most convenient to evaluate $(dn_g/dt)_{t=0}$, the initial uptake rate (n_g in atoms/g. of oxide): these figures are given in Table 8. From these results a plot of $\log [(dn_g/dt)_{t=0}]$ yields an apparent activation energy of about 13.8 kcal. mole $^{-1}$. It is seen that in this pressure range the rate is roughly proportional to pressure (cf. expts. A3 and A12, and A9 and A10); also from expts. A1 and A2 the surface is not covered after the adsorption of 2.0×10^{17} atoms/g., since at least a further 1.5×10^{17} atoms/g. can be readily taken up at about the same pressure, in fact at an initial rate greater than that of the first adsorption on the freshly-outgassed oxide.

It is noteworthy that the rate of bombardment of the surface of 1 g. of oxide (taken as 62 m. 2 from the B.E.T. results of Table 6) at 456° is about 8.6×10^{25} molecules/min. at a pressure of 10^{-3} cm., according to simple kinetic gas theory: multiplication of this by the factor $\exp(-13,800/RT)$ gives approximately 1.25×10^{21} atoms per g. per min., which is roughly 10^5 times the observed rate of adsorption at this temperature.

It was established that the rate of desorption from a partly-covered surface was slow. For instance, after the adsorption on 20 g. of oxide at 6 cm. pressure at 485° , the furnace temperature was raised to 540° , and the oxide evacuated for 15 min.; at the end of this time the pressure during pumping was 4×10^{-3} mm., and when the pumps were cut off the pressure rise in the adsorption system during 3 min. corresponded to a desorption rate of 3.4×10^{15} atoms per g. per min. After a further 2 hours' pumping the corresponding figures were 6×10^{-4} mm. and 5.4×10^{14} atoms per g. per min.

DISCUSSION

(a) *Adsorption Studies.*—It is interesting to compare the rates of exchange (at ~ 6 cm.) with those of adsorption (at $\sim 10^{-3}$ cm.) at temperatures 456° and 388° , which fall respectively in the regions of low and high activation energy for the exchange reaction. The initial rate of exchange, v_0 , atoms per g. per min., may readily be shown to be given by

$$v_0 = n_g/w (-d\alpha/dt)_{t=0} = n_0 k_e/w (\alpha_0 - \alpha_\infty)$$

where k_e is the experimental first-order rate constant, $n_g/2$ is the number of oxygen molecules in the gas phase, and α_0 and α_∞ are the ^{18}O abundances of the gas respectively

at the beginning and the end of the reaction. The initial rate of adsorption, $v_a = -(dn_g/dt)_{t=0}$ (cf. Table 8), and if this process is rate-determining, the maximum possible initial exchange rate would be $(\alpha_0 - \beta_0)v_a$, where β_0 is the initial ^{18}O content of the oxide. For these two temperatures, with oxide outgassed at 540° , $v_0 = 1.1 \times 10^{17}$, $(\alpha_0 - \beta_0)v_a = 1.1 \times 10^{14}$ (456°), and $v_0 = 2.6 \times 10^{16}$, $(\alpha_0 - \beta_0)v_a = 5.6 \times 10^{13}$ (388°) atoms per g. per min. Since adsorption must precede exchange, we conclude that measurements of initial adsorption rates at low pressures on to an outgassed surface can tell us little about the rate-limiting factors in the exchange process at several cm. pressure. It may be remarked that at 388° , where adsorption (at 6 cm.) appeared complete in <5 min., the exchange, similar proportions of oxide and oxygen being used, had a time of half-change of 62 min.; the corresponding figures for 456° were <10 and 17.3 min. However, the accuracy of these adsorption-rate measurements was low. It is unfortunately not possible to measure adsorption rates over a range of pressures from 10^{-3} to 6 cm. so as to determine the pressure dependence of the process, but assuming $v_a \propto p_{\text{O}_2}$, the values of $(\alpha_0 - \beta_0)v_a$ become 3.4×10^{17} (388°) and 6.6×10^{17} (456°), which are both greater than the corresponding v_0 figures.

It must be noted that the validity of a comparison of these figures with the values of v_0 given above is doubtful since, apart from the long extrapolation involved in assuming $v_a \propto p_{\text{O}_2}$, the oxide surface is undoubtedly heterogeneous, as shown by the change of n_s with temperature (cf. Table 4 and Fig. 1), and indicated also by the very low coverage ($\sim 0.1\%$) of the exchangeable surface, which is itself roughly equal to the B.E.T. area) at 6 cm. It is probably best to conclude that the adsorption studies do not allow us to reject either adsorption or desorption as possible rate-determining steps in the exchange process, although it is probable that adsorption is not the slow stage.

(b) *Exchange Reaction.*—Some discussion has been given elsewhere of the kinetics of this process (Houghton, Thesis, London, 1952; Houghton and Winter, *op. cit.*; Winter, *loc. cit.*), but some recapitulation and extension is convenient here, the notation of an earlier paper (Winter, *Discuss. Faraday Soc.*, 1950, 8, 231) being used.

We may generalise the approach used there by assuming that the velocity of exchange, v atoms min.^{-1} , will be proportional to the product of a function $f(C_g)$ of the surface coverage with oxygen, and a function $\phi(n_s)$ of the exchangeable surface. Then

$$v = -n_g(d\alpha/dt) = k_2 n_g (\alpha - \alpha_\infty) \quad \dots \dots \dots (5)$$

$$= w k_1 f(C_g) \phi(n_s) (\alpha - \beta) \quad \dots \dots \dots (6)$$

and remembering that the ^{18}O content of the reaction system remains constant,

$$(\alpha_0 - \alpha_\infty)n_g = w n_s (\alpha_\infty - \beta_0) \quad \dots \dots \dots (7)$$

we have finally

$$k_0 n_s = k_1 f(C_g) \phi(n_s) = n_s k_2 [(\alpha_\infty - \beta_0)/(\alpha_0 - \beta_0)] \quad \dots \dots \dots (8)$$

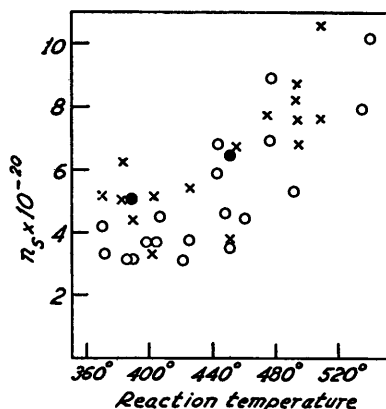
which may be compared with eqns. (2)—(11) of the paper given above.

It is thus seen that $k_0 n_s$ may be a more important function than k_0 ; only when the term $f(C_g)\phi(n_s)$ contains n_s as a simple factor will it be correct to use k_0 : a brief discussion of some possible cases when the use of k_0 is justified has been given elsewhere (Winter, *loc. cit.*); a more detailed argument has been developed by Houghton (Thesis, London, 1952). In any case it must be remembered that neither k_0 nor $k_0 n_s$ is likely to be identical with the true rate constant k_1 , and activation energies calculated from the variation with temperature of these two functions will include the effect of temperature upon $f(C_g)$ and $\phi(n_s)$.

Possible rate-determining processes in the exchange are (a) adsorption of oxygen molecules, (b) dissociation of adsorbed molecules to ad-atoms, (c) diffusion of adsorbed atoms or molecules over the oxide surface, into surface cracks, pores, etc., (d) exchange proper, which must involve electron transfer between adsorbed oxygen and lattice oxygen or suitable lattice defects, (e) recombination of ad-atoms to molecules, (f) desorption of oxygen molecules, and (g) gaseous diffusion through the powdered oxide. Now processes (a) and (f) involve only van der Waals forces; it has been established (Winter, unpublished work) that at liquid-oxygen temperatures *physical* adsorption and desorption of oxygen on

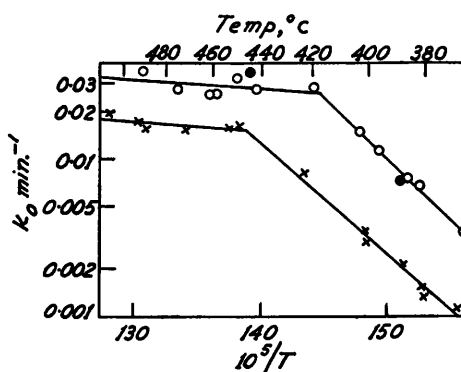
the magnesium oxide used in this study are rapid, being complete in less than a minute at oxygen pressures of 2–30 cm. We can, therefore, eliminate these as possible rate-determining steps at the much higher temperatures of the exchange reaction. We discard process (g) because exchange reactions in which the oxide was packed moderately firmly into a platinum boat gave the same rate constants as runs wherein the oxide was loosely spread over the bottom of the reaction vessel: this was confirmed for both slow and fast exchange rates. In addition, if (g) were rate-determining, the temperature dependence of k_0 (or $k_0 n_s$) should be that of the gaseous self-diffusion coefficient, *i.e.*, proportional to T^n , where $0.5 < n < 1$; as noted above, the rate constants show an exponential dependence upon T^{-1} . A plot of $\log k_0$ or $\log k_0 n_s$ against $\log T$ in the region of low E gave a curve, from which it was obvious that $n \gg 1$. It is not possible to reject (c), particularly since, as we have already noted, the coverage at 6 cm. pressure is quite sparse. No unambiguous evidence upon this point was obtainable from the measurements of rates of adsorption of oxygen. It is, however, unlikely that the process of high activation energy is one of surface diffusion, although it is possible the high-temperature reaction, of low E ,

FIG. 1.



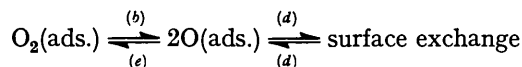
- × Outgassed at 510° c; $p_{O_2} = 6-8$ cm.
- Outgassed at 540° c; $p_{O_2} = 6-8$ cm.
- Outgassed at 540° c; $p_{O_2} = 1.1$ cm.

FIG. 2.



- × Outgassed at 510° c; $p_{O_2} = 6-8$ cm.
- Outgassed at 540° c; $p_{O_2} = 6-8$ cm.
- Outgassed at 540° c; $p_{O_2} = 1.1$ cm.

is diffusion-controlled (cf. Tompkins, *Trans. Faraday Soc.*, 1950, **46**, 569; Patterson, *ibid.*, 1953, **49**, 802). Pending the completion of work now in progress, we postpone discussion of (c), and are left with (b), (d), and (e):



The experimental work presented here does not allow us to choose between (b-e) and (d) as rate-determining steps. If we assume, as seems reasonable, a rapid attainment of the steady state among the adsorbed species, reactions (b) and (e) become indistinguishable, and the apparent activation energy of the exchange reaction, when this is controlled by (b)(e), will, in the usual way, reflect the change with temperature of the equilibrium between $O_2(\text{ads.})$ and $O(\text{ads.})$. Thus, considering this case, if we assume the rate of dissociation is proportional to the stationary concentration of $O_2(\text{ads.})$ and that the equilibrium lies well to the right (as is very probable since the lifetime of O_2 on the surface at these temperatures is likely to be much less than that of an oxygen atom), then

$$k_{(b)}C_g\gamma = k_{(e)}C_g^2(1-\gamma)^2 \quad \dots \quad (9)$$

where C_g is the total concentration of adsorbed oxygen (atoms and molecules) expressed as atoms/g. of oxide, and $k_{(b)}$, $k_{(e)}$, are the corresponding rate constants. We have already assumed $k_{(b)} \gg k_{(e)}$, so that the degree of association, γ , of the oxygen is small, and

$$k_{(b)}C_g\gamma \approx k_{(e)}C_g^2 \quad \dots \quad (10)$$

Then it follows from eqn. (8) that

$$k_{(e)}C_g^2 = n_s k_0 = n_s k_e [(\alpha_\infty - \beta_0)/(\alpha_0 - \beta_0)] \quad \dots \quad (11)$$

where k_e is the experimental first-order rate constant of the exchange reaction. If we further assume $C_g \propto n_s$, then (11) reduces to

$$k_{(e)}'C_g = k_0 \quad \dots \quad (12)$$

For the case when (d) is rate-determining, we have the result (Winter, *loc. cit.*)

$$k_{(d)}C_g = k_0 \quad \dots \quad (13)$$

Note that in the derivation of eqn. (13) no assumption is needed regarding the relation between C_g and n_s .

We may note also that the exchangeable oxygen, n_s , in the oxide surface (in atoms/g. of oxide), is given by eqn. (7), thus

$$n_s = (n_g/w) (\alpha_0 - \alpha_\infty)/(\alpha_\infty - \beta_0) \quad \dots \quad (14)$$

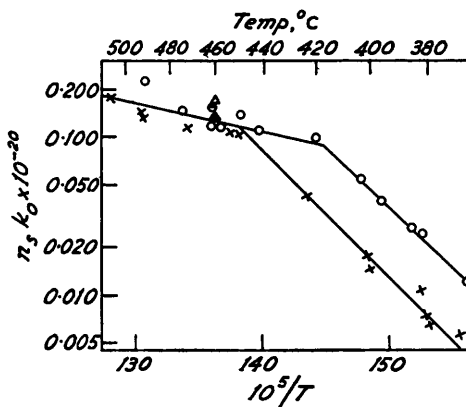


FIG. 3. x, O, Δ, ▲, ●: Outgassed at 510°, 540°, 600°, 640°, and 748° c, respectively.

The experimental figures are presented in Fig. 2 in terms of k_0 , and in accordance with the above analysis there is clear evidence of two processes, the characteristics of which are shown in Table 5.

It may be noted that if (b)-(e) is rate-determining and C_g is not proportional to n_s , then $\log k_0 n_s$ and not $\log k_0$ should be used in the Arrhenius plot; if this is done with the data of Table 4, Fig. 3 results, in which the distinction between the two outgassing temperatures disappears for the high-temperature process and its activation energy is now 7.7 ± 2 kcal. mole⁻¹; the activation energy for the lower-temperature region is not much changed, being 37.6 ± 2 and 35.9 ± 1 kcal. mole⁻¹ for outgassing temperatures of 510° and 540°, respectively.

There are a number of other interesting points arising from the above kinetic analysis: thus the rate constants are not very dependent upon the oxygen pressure (Table 3), which may mean that in spite of the sparse coverage of the surface, the active sites are effectively saturated at pressures of 1 cm. upwards; *i.e.*, that C_g is virtually independent of p_{O_2} above 1 cm. up to the highest pressure used, *viz.*, 14.7 cm.

The figures recorded in Table 7 were obtained before the importance of standardising the outgassing temperature was realised; they indicate an apparent activation energy for k_0 of about 26.5 kcal./mole⁻¹. These experiments refer to temperatures at which the "true" activation energy, at constant outgassing temperature, is around 3 kcal. mole⁻¹ (cf. Table 4 and Figs. 1 and 3); it is likely that the difference reflects mainly an increase in the number (S_c) of reactive sites as the outgassing temperature is raised, thus we may write

$$k_0 = A \exp(-E/RT) = S_c Z_c \exp(-E/RT)$$

where A is the coefficient of intrinsic catalytic activity (cf. Schwab, *Z. physikal. Chem.*, 1929, **5**, B, 406; 1930, **9**, B, 265; *Trans. Faraday Soc.*, 1946, **42**, 689; Balandin, *Z. physikal. Chem.*, 1932, **19**, B, 451; Eckell, *Z. Elektrochem.*, 1933, **39**, 859; Cremer, *Z. physikal. Chem.*, 1929, **144**, A, 231; Storch, *J. Amer. Chem. Soc.*, 1935, **57**, 1395; Huttig, *Kolloid-Z.*, 1941, **98**, 263, and papers there cited), Z_c is the frequency factor for energy transfer between the reactant species, and S_c is the number of active sites on the catalyst surface. If this type of behaviour is typical, it indicates the great difficulty of properly interpreting heterogeneous catalytic phenomena. It is unfortunate in this connection that the figures given in Table 5 and eqns. (1)–(4) are not sufficiently accurate to show whether the increase in rate with outgassing temperature at constant reaction temperature is due to a change in A or in E . The values for k_0 at $\sim 460^\circ$ on samples outgassed at temperatures from 866° to 510° yield the Arrhenius equation $k_0 = 19.1 \exp(-10,900 \pm 700/RT)$, if it is assumed that k_0 properly refers to the high-temperature exchange reaction. Alternatively, if $k_0 n_s$ should be used, it is seen from the last column of Table 2 that the product rises to a flat maximum between outgassing temperatures of 550° and 750° , falling sharply at 866° . This is very similar to the effect found by Huttig (*Z. physikal. Chem.*, 1934, **171**, 83; *Z. anorg. Chem.*, 1935, **223**, 241; *Kolloid-Z.*, 1942, **98**, 6, 263) for the decomposition of nitrous oxide on spinels heat-treated at various temperatures. The sharp drop in reactivity, expressed as $k_0 n_s$, around 750° ($\sim 0.33 T_m$) is in agreement with the conclusions (Bevan, Shelton, and Anderson, *J.*, 1948, 1728) that surface defects become mobile between 0.3 and $0.5 T_m$, where T_m is the m. p. of the solid: the commencement of sintering is shown clearly by the results in Table 2 and the B.E.T. figures in Table 9.

The complexity of even the present, at first sight simple, reaction is further demonstrated by the heterogeneity of the oxide surface—as in the change of n_s with reaction temperature (Fig. 2) and with outgassing temperature (Table 2). The heterogeneity indicated in Fig. 2 may also be demonstrated and confirmed by allowing a sample to reach equilibrium with ^{18}O -enriched oxygen at a relatively low temperature, say 380° , and then quickly raising the furnace temperature by some 30° , whereupon a rapid exchange occurs with more of the oxide surface and a new equilibrium ^{18}O -content of the oxygen is established; this process may be repeated several times, but up to a reaction temperature of 507° , n_s is not more than 7% of the total oxygen in the oxide.

A comparison between the surface areas obtained from the B.E.T. plots and the n_s values obtained by exchange has been made by assuming that the surface of the magnesium oxide powder consists of a random distribution of the (111), (110), and (100) planes, then, a radius of 1.4 \AA being used for the oxygen ion, the average area occupied by an oxygen ion is 10.1 \AA^2 , and the surface area of the oxide is given in each case by $10.1 n_s \times 10^{-20} \text{ m.}^2/\text{g}$. Table 9 gives some typical results and shows that the two methods give comparable figures at outgassing temperatures of up to 640° , but diverge somewhat above this, until at 860° , when considerable sintering has occurred, the B.E.T. values are some 5–8 times those obtained from the exchange.

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