

Exchange Reactions of Solid Oxides. Part IV. Zinc Oxide.*

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The exchange of ^{18}O between the surface of zinc oxide and oxygen gas has been studied over the temperature range $367\text{--}630^\circ$, with oxygen pressures from 1 to 25 cm. The rate of exchange and the amount of exchangeable oxide surface depend on the previous outgassing of the oxide. The exchange rates are dependent upon $(p_{\text{O}_2})^{1.0 \pm 0.1}$ over the whole temperature range and have $E = 0.5 \pm 1$ kcal. mole $^{-1}$ at high temperatures and 27.5 ± 1.0 kcal. mole $^{-1}$ at lower: the change of mechanism occurs at 510° for oxide outgassed at 580° , and at 415° for oxide outgassed at 630° . It is not possible to identify with certainty the rate-determining step in the exchange, but it is probable that the exchange reaction proper has $E = 27.5$ kcal. mole $^{-1}$ and that the other figure refers to surface migration of adsorbed oxygen. Semi-conductivity measurements on this preparation of zinc oxide gave $E = 27.5$ kcal. mole $^{-1}$ at $p_{\text{O}_2} = 60$ mm.

As an extension of earlier work (*J.*, 1950, 1170, 1175, and Part III *) we have studied the exchange of ^{18}O between zinc oxide and ^{18}O -enriched oxygen gas. Zinc oxide was chosen since more is known about its semi-conductivity properties than is the case with the other oxides so far examined. The exchange kinetics are formally similar to those found for magnesium oxide (Part III), except that the rate increases markedly with increase of oxygen pressure; in an effort to elucidate the mechanism of the exchange, measurements were undertaken of the adsorption of oxygen on zinc oxide and of the semiconductivity of the oxide. The symbols used in this paper have the same significance as in Part III.

EXPERIMENTAL

Materials.—The enriched oxygen, containing some 1.2% excess of ^{18}O , was prepared as before (Part III). Normal oxygen was obtained by heating "AnalaR" potassium permanganate. Spectroscopically pure neon was from the British Oxygen Co. Nitrogen for the B.E.T. measurements was taken from a cylinder and passed through concentrated sulphuric acid, over heated copper, and finally through a trap at -78° into the adsorption apparatus. The zinc oxide was made by burning 99.99% zinc in air.

Exchange Experiments.—The experimental method has been described in Part I (*J.*, 1950, 1170); samples of about 3 g. of oxide with about 5 ml. (N.T.P.) of oxygen gave reasonable changes in ^{18}O content. The technique was improved by using an electronic device to control the furnace temperature and by recording the temperature at 30-sec. intervals throughout most runs, including the outgassing period, with a Cambridge thread recorder so operated as to be sensitive to changes of $<0.5^\circ$. The controller, working off a platinum-resistance thermometer wound on the furnace tube, kept the temperature constant to within $\pm 0.5^\circ$ overnight.

Adsorption Measurements.—B.E.T. isotherms were obtained in the usual manner, nitrogen being used as the adsorbate, at 78°K : the oxide was first outgassed overnight at temperatures from 150° to 630° .

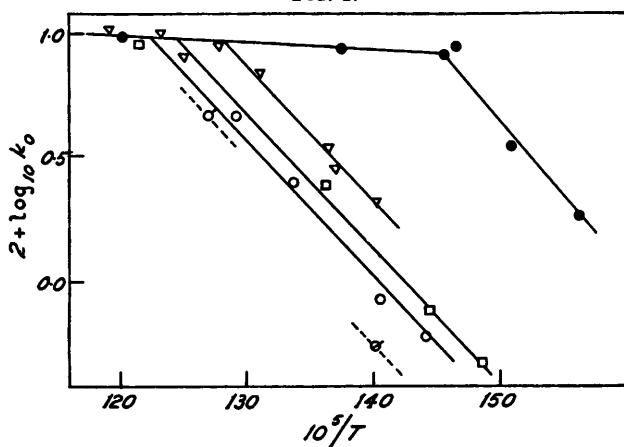
Oxygen-adsorption measurements were carried out in a constant-volume apparatus of conventional design. Pressures from 10^{-3} to 15 mm. were measured by McLeod gauge: at the upper end of this range a correction was applied for the pressure exerted by the system on the open limb of the gauge. Pressures above 15 mm. were read on a wide-bore U-tube manometer with the aid of a cathetometer. Oxide samples (30 g.) were subjected to the same pretreatment, by outgassing for 16 hr. at a steady elevated temperature, as was used in the exchange experiments: if the limiting pressure reached during the outgassing was $>10^{-6}$ mm. the run was discarded. After completion of the oxygen adsorption, the system was re-evacuated, and the volume calibration performed at the same temperature, neon being used.

Conductivity Determinations.—Pellets of oxide were prepared by compression (5 ton in. $^{-2}$), and measurements made in the cell described by Jacobs (*J. Sci. Inst.*, 1953, 30, 204), a microammeter and a known potential source being used: standard resistances were used to check the accuracy of the figures obtained. The pellet was placed in the cell, which was then sealed

* Part III, preceding paper.

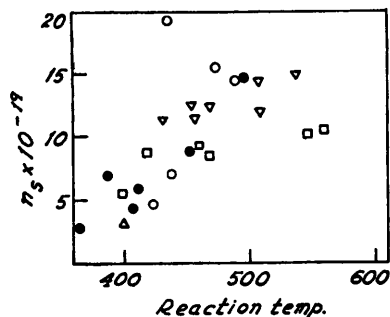
to the vacuum-line and evacuated overnight at 560°, precautions being taken to ensure that the zinc which distilled out from the pellet did not short-circuit the cell. During outgassing the resistance fell from several megohms to $\sim 80\Omega$. Oxygen was admitted until the pressure was 60 mm., whereupon the resistance rose very rapidly to several megohms and became steady. The temperature was lowered, and the resistance altered as rapidly as the temperature to the

FIG. 1.



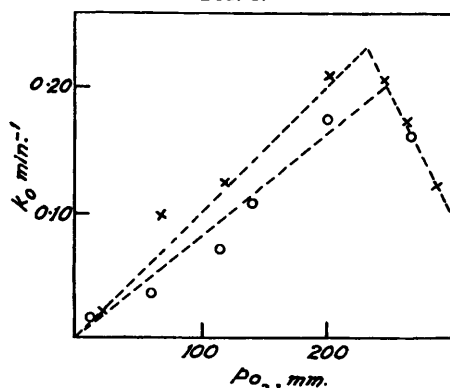
●, ▽, □, ○, ○, ○ : Outgassed at 630°, 580°, 570°, 550°, 545°, and 530°, respectively.

FIG. 2.



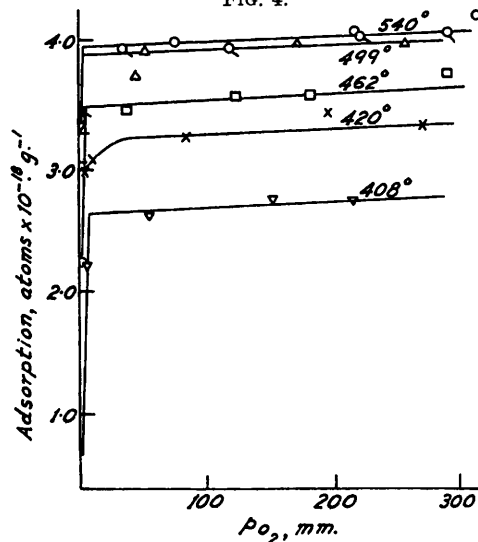
△, ●, ▽, □, ○ : Outgassed at 698°, 630°, 580°, 570°, and 550°, respectively.

FIG. 3.



× : Outgassed at 630°; reaction at 560°.
○ : Outgassed at 570°; reaction at 474°.

FIG. 4.



○, ○, □, ▽, △, × : Outgassed at 560° and 522°, respectively.

new equilibrium value; in this way the resistance of the pellet was measured over the range 560—450°.

Results.—Oxygen exchange. Values of k_0 and n_s were obtained as previously described; the kinetic runs gave good first-order plots. It is seen from Figs. 1 and 2 that for zinc oxide the variations of k_0 and n_s with both reaction and outgassing temperature are very similar to the behaviour of magnesium oxide; if anything, zinc oxide is more sensitive to outgassing conditions than the latter oxide, but this is masked in the present results because of the closer temperature control exerted here. However, a plot of $\log k_0 n_s$ against $10^5/T$ shows considerably more scatter than Fig. 3 of Part III, although showing the same general characteristics. Activation energies from Fig. 1 are 0.5 ± 1 kcal. mole⁻¹ for the high-temperature region, and

27.5 \pm 1 kcal. mole⁻¹ for the lower temperatures. Fig. 3 shows that k_0 depends strongly upon the pressure of oxygen used; for this reason the experiments of Fig. 1 were done at pressures between 50 and 75 mm. A few results at lower pressures (\sim 10 mm.) showed that n_s has no systematic variation with pressure. A plot of $\log k_0$ against $\log p_{O_2}$ from Fig. 3 was made and showed that $k_0 \propto (p_{O_2})^{1.0 \pm 0.1}$ up to the point of inflexion which occurs for both temperatures at about 220 mm. The fall of k_0 at higher pressures is believed to be because the rate of diffusion through the leak into the mass spectrometer was becoming the slow stage; this would explain why the fall takes place at about the same p_{O_2} and k_0 at two different reaction temperatures. An alternative explanation may be that the inflexion points represent the onset of changes in the adsorbed state; *i.e.*, changes in C_g , completion of one layer of adsorbed oxygen, etc., but this is most unlikely to be occurring at the same pressure at two widely different temperatures, where the activation energies of the exchange reaction are so different. Some experiments illustrating the importance of standardising the time of outgassing are summarised in Table 1, and the results of a few poisoning experiments are given in Table 2; the effect of incomplete outgassing (time or pressure) is significant, and all experiments with the exception of these were conducted under a strict routine of outgassing for 16 hr. to a pressure $<10^{-5}$ mm.: if the pressure at the end of 16 hr. was too high the run was discarded. It will be recalled that magnesium oxide shows a similar sensitivity to pretreatment (Part III, *loc. cit.*), but that, whereas k_0 for the latter increases with increasing outgassing time, yet in the case of zinc oxide a decrease is observed. Like magnesium oxide, our specimen of zinc oxide shows clear evidence of heterogeneity (cf. Fig. 2).

TABLE 1. Effect of time of outgassing on rate of exchange.

Temp.	Time (hr.)	Run	k_0 ,	$10^{-20}n_s$,	Temp.	Time (hr.)	Run	k_0 ,	$10^{-20}n_s$,
	of outgassing	temp.	min. ⁻¹	atoms g. ⁻¹		of outgassing	temp.	min. ⁻¹	atoms g. ⁻¹
(a) Low-temperature region					(b) High-temperature region				
580°	4	457°	(not 1st order)	0.91	570°	4	540°	0.127	1.37
580	16	457	0.0336	1.16	570	4½	540	0.139	1.04
580	60	457	0.0294	1.27	570	16	540	0.0927	1.20

TABLE 2. Poisoning experiments.

Expt. No.	Outgassing temp.	Run temp.	k_0 , min. ⁻¹	k_0 , min. ⁻¹
				(Interpolated from Fig. 1)
Heated with benzene				
1	565°	470°	0.0571	0.0368
Heated with water				
2	565	478	0.0695	0.0394
Heated in 10^{-2} mm. of air overnight				
3	630	560	0.650	0.0927
4	630	398	0.0840	0.0476
5	630*	475	0.0682	0.090
6	630*	387	0.00494	0.036

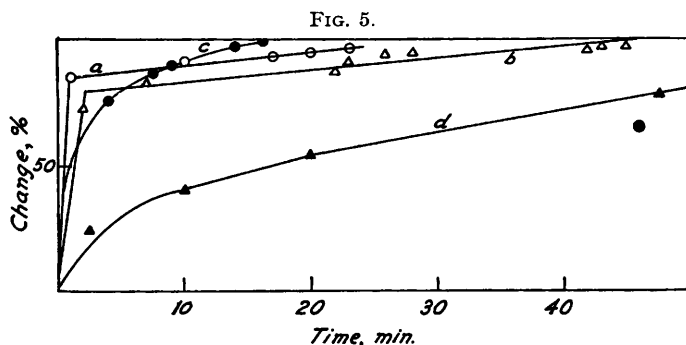
* In these two experiments the oxide, after outgassing, was treated with 6 cm. of O₂ for *ca.* 7 hr. and then re-evacuated at 630° overnight before the rate of exchange was measured.

Adsorption measurements. (a) B.E.T. Samples of zinc oxide outgassed overnight at 570° and at 630° gave B.E.T. areas of 5.30 and 5.25 m.² g.⁻¹, respectively; a sample outgassed overnight at 150° gave an area of 6.35 m.² g.⁻¹. Good B.E.T. plots were obtained; an area of 16.2 Å² was assumed for the nitrogen molecule (cf. Part III, *loc. cit.*).

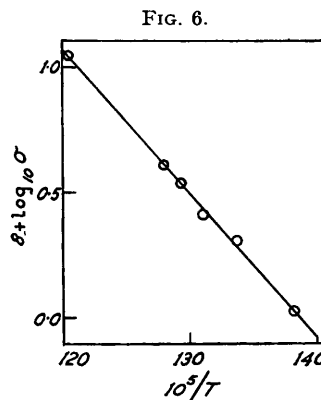
(b) *Oxygen-adsorption experiments.* The adsorption isotherms are given in Fig. 4: the amount of gas taken up at equilibrium is independent of outgassing temperature and substantially independent of pressure above \sim 25 mm.; this uptake is rapid at all temperatures studied, 70% or more being complete in no more than 2 min., and once equilibrium is reached, usually in less than an hour, no further change occurs even after 72 hr. The adsorption is irreversible since after 16 hr. pumping at 460° of a sample which at this temperature had reached adsorption equilibrium with 310 mm. oxygen, no further uptake is detectable at 337 mm. oxygen pressure: this experiment would have detected an adsorption of 2×10^{17} atoms g.⁻¹, which corresponds to about 0.5% of the B.E.T. surface. However, if the temperature of the sample is raised, oxygen is taken up until the higher-temperature isotherm is reached: the reverse process does not occur. It appears clear that at any rate the greater part of the adsorption is chemisorption, probably mainly on to metallic zinc exposed during the

outgassing treatment. In this connection it is noteworthy that the oxide used contained significant amounts of unoxidised metal; this was not apparent on microscopic examination but at the end of each outgassing treatment a zinc mirror had distilled on to cool portions of the reaction tube just outside the furnace: it is probable, particularly in view of the method of preparation, that many of the oxide particles contained small cores of metal. Since the amount of chemisorption often increases at lower temperatures, adsorption on an oxygenated surface was sought at 260° and at 200° but none was found; the oxide was here pumped overnight at 550° and treated with 89 mm. of oxygen at that temperature until adsorption was complete, pumped hard, and cooled to 200° (or 260°), whereat further oxygen was added; no adsorption (to $\pm 2 \times 10^{17}$ atoms g^{-1}) was detectable up to 257 mm.

The rate of adsorption was followed by taking pressure measurements at intervals during the uptake of the first dose of oxygen; in these experiments the initial pressure was about 10 mm., falling to between 0.5 and 5.0 mm. at equilibrium. On examining the results it was at once apparent that the initial very rapid adsorption was a different process from the slow disappearance of the last 10–20%. Attempts to separate the two processes, by assuming various mechanisms and adopting different methods of extrapolation to zero time, were not successful, the resulting rate constants showing considerable scatter. We therefore shall not consider the results in detail here; two typical experiments are shown in Fig. 5, together with two exchange-reaction curves determined under similar experimental conditions.



Curves *a* and *b*, adsorption of oxygen, outgassed at ca. 565°.
Curves *c* and *d*, exchange of oxygen, outgassed at 570°
Reaction temperatures: *a*, 540°; *b*, 462°; *c*, 550°; *d*, 461°.



Conductivity determinations. The results are shown in Fig. 6, and fit an equation of the form $\sigma = A \exp(-E/RT)$, where σ is the conductivity, $A = 2.00$ mhos, and $E = 27.5$ kcal. mole⁻¹. Recorded values for E for this oxide vary widely, but the recent work of Hogarth (*Z. physikal. Chem.*, 1951, *A*, **198**, 30) gives a value of 26.4 kcal. mole⁻¹ in the temperature range 560–640°, at a p_{O_2} of ca. 50 mm.

DISCUSSION

When we try to decide, from the work reported here, the exact nature of the rate-determining steps in the exchange reaction we are faced with a very similar situation to that found with magnesium oxide (preceding paper). Thus, by the same arguments we are left with processes (*b*), (*c*), (*d*), and (*e*) of that paper as possible rate-determining steps. With regard to (*c*)—migration of oxygen over the surface from the adsorption or desorption sites to exchange sites—we note that the n_s values from the exchange work are of the order of 10^{20} atoms g^{-1} , and assuming a surface of oxygen ions the B.E.T. figures give a value of about 6×10^{19} atoms g^{-1} ; the total oxygen adsorption is about $3-4 \times 10^{18}$ atoms g^{-1} at comparable temperatures to those used in the exchange studies, and this value undoubtedly includes a large contribution due to oxidation of metallic zinc. It appears that the coverage with oxygen is sufficiently sparse for surface migration to remain a possible rate-determining step.

In considering the surface exchange reaction [(*d*) of Part III] as possibly rate-determining, the fact that the apparent activation energy of the low-temperature exchange reaction is the same as that found for the conductivity might be thought significant. It could be postulated that the exchange sites are identical with (or at least closely connected

with, in position and number) the semiconductivity sites in the surface, which for zinc oxide are almost certainly interstitial zinc atoms, Zn_i (von Baumbach and Wagner, *Z. physikal. Chem.*, 1933, B, 22, 199; Bevan and Anderson, *Discuss. Faraday Soc.*, 1950, 8, 239). The exchange reaction could then be written



$O_{ads.}$ representing chemisorbed oxygen in isotopic equilibrium with the gas phase. The continuous formation and destruction of Zn_i at various points in or just beneath the surface would then account for the exchange's slowly spreading over the whole surface. This is an attractive hypothesis and may well be close to the truth, but in certain important respects it does not account for our observations. It has been shown (*idem, loc. cit.*) that the above equation accounts satisfactorily for the observed dependence of the semiconductivity, σ , upon oxygen pressure, p_{O_2} , at pressures above about 10^{-3} cm., thus $\sigma \propto p_{O_2}^{\frac{1}{2}}$, while $[Zn_i] \propto p_{O_2}^{-\frac{1}{2}}$, so that if we write the exchange rate as $\propto [Zn_i][O_{ads.}]$ it should be independent of p_{O_2} : our results (Fig. 3) show that $k_0 \propto (p_{O_2})^{1.0 \pm 0.1}$ (although, in fact, we have not directly demonstrated that the exchange mechanism is the same at any one temperature, over the whole pressure range studied). Since the exchange reaction on magnesium oxide, which exhibits no semiconductivity properties at these temperatures, occurs roughly as readily as on the semiconducting zinc oxide we incline to the view that there is no direct relation between exchange and conductivity, and conclude that the agreement between the two activation energies in the case of zinc oxide is probably fortuitous.

As in the case of magnesium oxide, we tentatively ascribe the exchange reaction of high E (27.5 kcal. mole $^{-1}$) to the true exchange reaction, and that with $E = 0.5 \pm 1.0$ kcal. mole $^{-1}$ to the migration of ad-atoms of oxygen over the oxide surface. Evidence in support of this assignment of mechanisms is given in Part V (following paper).

The experiments detailed in Table 2 are interesting, but little definite information regarding mechanisms can be drawn from them. It is seen that exposure to a high pressure of oxygen at 630° before exchange (Expts. 5 and 6) affects the reaction of low E hardly at all, but decreases that of high E very considerably; exposure to very low oxygen pressure increases the speed of both reactions. These observations are doubtless connected with the likelihood that (a) exposure to the lower oxygen pressure will lead to much less adsorption-desorption and exchange of oxygen, so that it is likely that less sintering occurs under these conditions—this could well lead to a more active surface—(b) the lower oxygen pressure would leave a higher concentration of Zn_i in and near the surface, and this may well increase the speed of any exchange process involving reaction of $O_{ads.}$ with Zn_i . It is known from the work of Bevan and Anderson (*loc. cit.*) that surface defects are largely frozen in the surface of zinc oxide below about $0.3T_m$ ($\approx 900^\circ$); if the rate of the exchange reaction of $E = 27.5$ kcal. mole $^{-1}$ is proportional to $[Zn_i]$ we would expect it to be increased by increasing the outgassing temperature (*in vacuo*) (provided the temperature was not too near 900° , so that no sintering occurred). This is in fact observed (cf. Fig. 1), the temperature at which change occurs to a high-temperature reaction of low E being 510° when outgassed at 580° , and 415° when outgassed at 630° ; similar observations were, however, made on magnesium oxide (cf. Part III, *loc. cit.*) in which the presence of Mg $_i$ has not been demonstrated so far as we know.

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