Exchange Reactions of Solid Oxides. Part VII. Chromic Oxide, Nickel Oxide, and Ferric Oxide.*

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The rates of isotopic exchange between gaseous oxygen and the oxide surface, and of the equilibration of molecular oxygen catalysed by the oxide, have been examined by use of the technique described in earlier papers. On all three oxides the exchange and equilibration reactions occur at the same speed; the studies were performed mainly at $P_{O_2} \approx 6$ cm. and the approximate temperature ranges and apparent activation energies, in kcal. mole^{-1}, are: Fe_2O_3, 290—400°, $E = 19 \pm 2$, rate $\propto P_{O_2}^{1\cdot0}$; NiO, 390—590°, $E = 35 \pm 2$; rate independent of P_{O_2}; Cr_2O_3, 270—530°, $E = 32 \pm 2$ below 430° and 1—2 above, both rates independent of P_{O_2}. The rates of adsorption of oxygen on these oxides obey the Elovich equation, with the activation energy for adsorption rising in a roughly linear manner from ~ 0 at zero coverage to ~ 35 (NiO, Cr_2O_3) or >12 (Fe_2O_3) at saturation. The rates of adsorption are proportional to P_{O_2} over the whole range, but the saturation coverages, in terms of the total exchangeable surface, are small. It is concluded that the exchange–equilibration reaction is in all cases (but for Cr_2O_3 only below 430°) a measure of the rate of adsorption-desorption of oxygen; above 430° on Cr_2O_3 either the rate of migration of chemisorbed oxygen or that of surface defects in the solid is rate-determining. Limited mobility of chemisorbed oxygen on the surface of NiO at 250—300° has been directly demonstrated.

The semiconductivities of the oxides have been measured over the same temperature range in oxygen at various pressures and *in vacuo*: no direct correlation has been found between semiconductivity and isotopic exchange or oxygen adsorption.

The total surfaces of the oxides determined by oxygen exchange, by B.E.T. isotherm, and, in the case of Fe_2O_3, by adsorption of Fe^{3+} from aqueous solution, are compared: good agreement is obtained between the various methods.

THE techniques described in Parts I—VI * have been used to examine in detail the interaction of gaseous oxygen and the oxides Cr_2O_3, NiO, and Fe_2O_3; since these oxides adsorb appreciable amounts of oxygen at temperatures and pressures approaching those of interest

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* Parts I—VI, *J.*, 1950, 1170, 1175; 1954, 1509, 1517, 1522; 1955, 2726.

here, it has been possible to study the kinetics of adsorption and to relate them to the exchange and equilibration reactions. The dependence of the semiconductivity of the oxides upon oxygen pressure and upon the degree of outgassing has been studied. The oxide most thoroughly studied was chromic oxide and this work is described in the greatest detail, since the behaviour of this oxide was generally typical; work on the other oxides is presented in an abbreviated form, except for some observations upon the determination of the surface area of Fe_2O_3 by use of radioactive iron. The symbols, where undefined, are those used in earlier papers.

EXPERIMENTAL

(a) *Materials.*—Cr_2O_3 was prepared by controlled ignition of " AnalaR " CrO_3 in a stream of dry air (Bevan, Shelton, and Anderson, *J.*, 1948, 1729); two preparations were used, made from different batches of CrO_3. NiO was prepared by ignition of the carbonate in air at 850° for 6 hr.: B.D.H. carbonate of low cobalt and iron content was used. Fe_2O_3 was prepared by reaction of ferric chloride solution with aqueous ammonia, followed by copious decantation and washing, and ignition in air at 500° (cf. Gregg and Hill, *J.*, 1953, 3945; Hill, Ph.D. Thesis, London, 1950).

Enriched, non-equilibrated, and normal oxygen were as previously described (*J.*, 1954, 1522).

(b) *Adsorption Experiments.*—Adsorption isotherms were studied in the apparatus used for earlier work (*J.*, 1954, 1509), pressures being measured on two McLeod gauges and a mercury manometer; rates of adsorption were studied in a constant-pressure apparatus similar to that of Taylor and Strother (*J. Amer. Chem. Soc.*, 1934, **56**, 586); at low pressures this apparatus was actuated by a Pirani gauge instead of a mercury manometer. Certain rates of adsorption were measured under constant-volume conditions. Nitrogen adsorption isotherms for B.E.T. area calculations were determined at liquid-nitrogen temperatures in an apparatus like Gregg and Sing's (*J. Phys. Colloid Chem.*, 1951, **55**, 592).

(c) *Exchange and Equilibration.*—The kinetics were studied as in earlier work (*locc. cit.*).

(d) *Electrical Conductivity.*—The stainless steel conductivity " cell " was of the same design as that of Jacobs (*J. Sci. Instr.*, 1953, **30**, 204): the pellet was made by compression in a stainless-steel press and was outgassed for some days (as noted under each oxide) at about 510° before the commencement of observations; 2—12 v D.C. was applied to opposite faces of the pellet, and the current measured on a sensitive galvanometer (sensitivity 5×10^3 mm. μA^{-1} at 1 m.). It was noted at each oxygen pressure whether the pellet obeyed Ohm's law and whether conductivity at each point was independent of the direction of current flow. Readings were taken at random, with both rising and falling temperature, to confirm absence of drift.

(e) *Radioactive-iron Experiments.*—These refer to only one oxide and are discussed in detail under Fe_2O_3.

(f) *General.*—Temperatures above room temperature were continuously controlled to $\pm\frac{1}{2}$° by an electronic controller actuated by a platinum-resistance coil wound directly on to the silica tube of the furnace, under the heater windings.

Results.—(*a*) Cr_2O_3. The exchange reaction rate for Sample B was independent of outgassing temperature over the range 395—630° and of P_{O_2} over the range 2·5—8·6 cm. (Table 1). The plot of $\log_{10} (k_0 n_s)$ against $10^5/T$ for Samples A and B is shown in Fig. 1; the two preparations are seen to be very similar, despite the fact that they were made from different batches of CrO_3 and that the work on Sample A was done some years ago at Imperial College with different equipment. We shall consider mainly the results obtained from Sample B, since most of the adsorption and conductivity work was done on this, and for this preparation Fig. 1 gives an apparent activation energy for exchange and equilibration of 32 ± 2 kcal. mole⁻¹ below 430°, and of 1—2 kcal. mole⁻¹ for exchange above this temperature. Change of n_s with temperature is shown in Table 2.

TABLE 1. Cr_2O_3 (B) : *Variation of exchange rate with pressure.*

Temp. Outgassing	Temp. Reaction	$\log_{10} (kn_s)$	P_{O_2}	Temp. Outgassing	Temp. Reaction	$\log_{10} (kn_s)$	P_{O_2}
630°	394°	18·710	2·5	630°	394°	18·701	8·6
,,	,,	18·722	4·4	510	,,	18·708	6·0
,,	,,	18·720	5·9	395	395	18·690	6·0

TABLE 2. Cr_2O_3: *Influence of temperature on n_s.*

Temp. Outgassing	Temp. Reaction	$\log_{10} n_s$	Temp. Outgassing	Temp. Reaction	$\log_{10} n_s$	Temp. Outgassing	Temp. Reaction	$\log_{10} n_s$
Sample A.						Sample B.		
387°	386°	20·297	455°	441°	20·310	630°	320°	19·898
455	323	20·288	527	527	20·342	,,	358	19·895
,,	345	20·283	567	345	20·283	,,	394	19·904
,,	365	20·301	600	367	20·107	,,	447	20·004
,,	391	20·238	,,	374	20·199	,,	485	20·135
,,	410	20·299				,,	522	19·959

A study of the equilibration reaction on Sample B showed that this occurred at the same rate as the exchange reaction, as is seen from Fig. 1, where several points from the equilibration runs are plotted and fall closely on the line drawn through the exchange rates for $E = 32 \pm 2$ kcal. mole^{-1}. Equilibration runs at temperatures above 430°, the inflexion temperature in the Arrhenius plot for the exchange reaction, were not possible as the rate was too great for accurate measurement.

A typical adsorption–desorption isotherm on Sample A at 395° is shown in Fig. 2, and in Fig. 3 are shown some rates of adsorption and of exchange, at corresponding temperatures and pressures. As in the exchange experiments, the oxide was outgassed at 520° overnight, isolated, cooled to the required temperature, and then put into contact with the required amount of oxygen; the fall of pressure with time in the constant volume was then recorded, and from the results the quantity adsorbed, expressed as a percentage of the equilibrium value, was calculated. On this basis the rate of adsorption is much greater than the rate of exchange at all temperatures but during desorption appreciable hysteresis occurs. In order to provide more precise information the rates of adsorption on Sample B were determined at constant pressure, mainly at $P_{O_2} = 5{\cdot}9$ cm., and at temperatures from 135° to 240°, which gave rates suitable for measurement. It was found that the uptake, q, followed the law

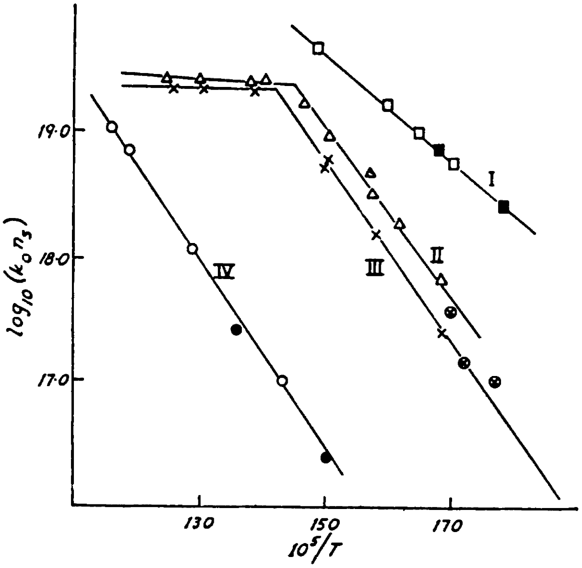


FIG. 1. *Exchange and equilibration experiments.*

- □ ■ Exchange and equilibration on Fe_2O_3, outgassed at 450°; $P_{O_2} = 5{\cdot}7$ cm.
- △ Exchange on Cr_2O_3 (A), outgassed at various temperatures between 385° and 520°; $P_{O_2} = 6{\cdot}5$ cm.
- × ⊗ Exchange and equilibration on Cr_2O_3 (B), outgassed at 630°; $P_{O_2} = 6$ cm.
- ○ ● Exchange and equilibration on NiO, outgassed at 605°; $P_{O_2} = 6$ cm.

$$dq/dt = a \exp(-bq) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(cf. Elovich and Zhabrova, *J. Phys. Chem. U.S.S.R.*, 1939, **13**, 1761, 1775; Taylor and Thon, *J. Amer. Chem. Soc.*, 1952, **74**, 4169; Porter and Tompkins, *Proc. Roy. Soc.*, 1953, **217**, *A*, 529).

Integration of eqn. (1) yields (cf. Porter and Tompkins *loc. cit.*):

$$q = \frac{1}{b}\left\{\ln\left(t + \frac{\exp(bq_0)}{ab}\right) + \ln ab\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

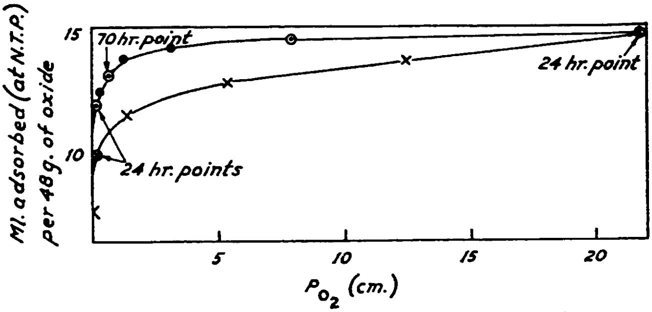
where q_0 = amount instantaneously adsorbed when $t = 0$.

In all our runs [exp $(bq_0)]/ab$ was zero within experimental error, so that $q_0 \approx 0$ (which was confirmed by runs at 10^{-3} mm. of O_2); and straight lines were obtained by plotting q against $\log_{10} t$; from the slopes and intercepts, a and b were evaluated for each temperature and pressure. From eqn. (1) we have

$$\ln r_s = \ln a - bq \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $r_s = dq/dt$; under our conditions experiments in which ^{18}O was adsorbed up to $\theta \approx 0{\cdot}4$, followed by normal oxygen, established that the rate of desorption was negligible, at least up to $\theta \approx 0{\cdot}8$—$0{\cdot}9$ (where $\theta = q/q_\infty$); thus values of r_s from eqn. (3) should be reasonably correct. By using eqn. (3) values of $\log_{10} r_s$ were found at $P_{O_2} = 6$ cm., at different temperatures for $\theta = 0$, 0·22, 0·67, and 0·89; these were plotted against $1/T$ for constant θ, and the apparent activation energy for adsorption, E_a, found at each value of θ; q_∞ did not vary by more than 8% over the temperature range. The results are summarised in Table 3; reasonably straight lines were obtained in the $\log_{10} r_s$–$1/T$ plots, except that the values for $\theta = 0$ (*i.e.*,

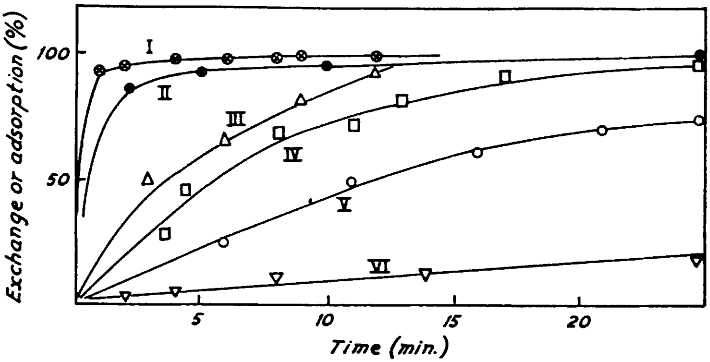
FIG. 2. *Adsorption–desorption of oxygen on* Cr_2O_3 (*A*) *at* 395° : *oxide outgassed at* 520°.



× Adsorption. ● Desorption.

Circled points refer to readings 24—70 hr. after changing P_{O_2}; remainder to readings taken after 3—4 hr.

FIG. 3. *Adsorption and exchange on* Cr_2O_3 (*A*) *outgassed at* 520°.



Curve I : Adsorption of oxygen at 365—492° (approximate combined curve).
Curve II : Adsorption of oxygen at 325°.
Curves III—VI : Exchange at 493°, 391°, 365°, and 323°, respectively.

TABLE 3. *Adsorption of oxygen on* Cr_2O_3 (B).

		$\log_{10} (r_s)$ *			
Temp. (°K)	$10^5/T$	$\theta = 0$	$\theta = 0{\cdot}22$	$\theta = 0{\cdot}67$	$\theta = 0{\cdot}89$
514	194·5	3·210	2·606	1·407	0·809
465	215	3·043	2·134	0·315	−0·594
433	231	2·876	1·732	−0·530	−1·674
408	245	3·204	1·683	−1·394	−2·933
E_a, kcal. mole⁻¹		~0	9·0	25·3	33·5

* Arbitrary units; to convert to atoms $min.^{-1}$ $g.^{-1}$ add 21·670.

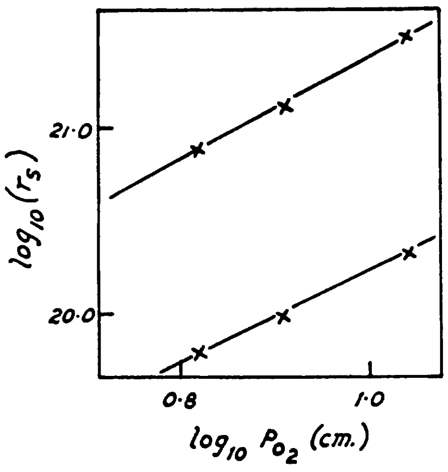
effectively $\log_{10} a$) show some scatter; this is not unexpected in view of the extrapolations involved. A plot of E_a against θ shows that E_a varies linearly from $\sim$0 at $\theta = 0$ to $\sim$35 kcal. mole^{-1} at $\theta \approx 1$. The pressure dependence of r_s was studied at 160° by doing runs at $P_{O_2} = 3{\cdot}5$, 5·9, and 12·3 cm.; the results are summarised in Fig. 4 for $\theta = 0{\cdot}67$ and 0·89; it is evident that r_s is directly proportional to P_{O_2} at these coverages; here also there was some scatter of values at $\theta = 0$: the figures for 3·5 cm. are the mean of the three runs given in Table 4.

TABLE 4. *Adsorption of oxygen on* Cr_2O_3 (B).

		$\log_{10}(r_s)$			
Run	q_∞ *	$\theta = 0$	$\theta = 0{\cdot}22$	$\theta = 0{\cdot}67$	$\theta = 0{\cdot}89$
1	51·5	2·417	1·340	−0·860	−1·937
2	60·7	2·293	1·306	−0·715	−1·702
3	60·0	2·543	1·453	−0·778	−1·868

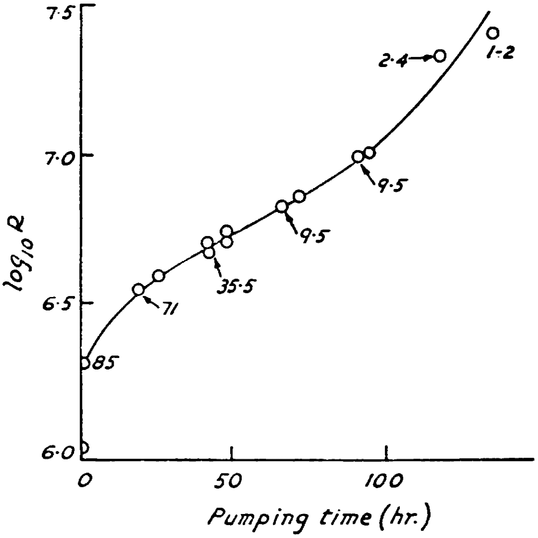
* Ml. of O_2 measured at 17° and 3·5 cm., adsorbed on 10 g. of oxide at 160°; *i.e.*, q_∞ (Runs 2 and 3) $\approx 1{\cdot}4 \times 10^{19}$ atoms g.$^{-1}$

FIG. 4. *Rate of oxygen adsorption on* Cr_2O_3 (*B*), *outgassed at* 520°: *variation of* r_s *with* P_{O_2} *at* 160°.



Upper line : $\theta = 0{\cdot}67$; $r_s \propto (P_{O_2})^{1\cdot10}$.
Lower line : $\theta = 0{\cdot}89$; $r_s \propto (P_{O_2})$.

FIG. 5. *Change of semiconductivity of* Cr_2O_3 *on long outgassing at* 532°.



Figures on curve represent pressures (10^{-6} mm.). Initial pressure 1·70 cm.

In order to confirm that $E_a \approx 0$ at $q \approx 0$, 0·1 g. of the oxide was outgassed at 520° and the rates of adsorption of small quantities of oxygen at low pressures were determined, under constant volume conditions, the Pirani gauge being used to follow pressure changes. At 85° and at 103° and mean pressures of 2×10^{-3} mm. the initial rates of adsorption were $2{\cdot}4 \times 10^{20}$ and $2{\cdot}7 \times 10^{20}$ atoms g.$^{-1}$ min.$^{-1}$, which correspond to rates of roughly $7{\cdot}5 \times 10^{23}$ at $P_{O_2} \approx 6$ cm., assuming $r_s \propto P_{O_2}$. Clearly, at these temperatures $E_a \approx 0$ at $\theta \approx 0$; also the initial rate of $7{\cdot}5 \times 10^{23}$ atoms g.$^{-1}$ min.$^{-1}$ is within a power of 10 of that found at higher temperatures and pressures by long extrapolation (Table 3), which is reasonable agreement.

For most of the adsorption work the same 20-g. sample of oxide was employed; the oxide was outgassed at 520° for 18—42 hr. between each run. Preliminary experiments were carried out on a 10-g. sample at 160° and 3·5 cm. pressure to ensure that the reproducibility of the oxide properties was satisfactory between one run and the next. The results are given in Table 4. Although the quantity of oxygen adsorbed at saturation (24 hr.), q_∞, increased appreciably between the first and subsequent runs, all three gave substantially the same values for log a and for log r_s at corresponding coverages: this was confirmed by repeated runs on the 20-g. sample at the completion of the work reported in Table 3. Additional confirmation was provided by running two exchange experiments on portions of oxide which had been used for the adsorption work; satisfactory agreement was obtained (within 7%) of $(k_0 n_s)$ with values found using fresh lots of oxide. The saturation coverage at 406° and 6·0 cm. was about 1·3 × 10^{19} atoms of oxygen per g. : at 321° and 6·0 cm. the coverage was 1·25 × 10^{19} atoms per g.

The B.E.T. surface areas were found in the usual way and call for no comment; an area of 16·2 Å^2 was assumed for the nitrogen molecule; the values found were 30·0 m.^{2} g.$^{-1}$ for Sample A and 14·2 m.^{2} g.$^{-1}$ for Sample B, both specimens being outgassed overnight at 520° before measurement. The n_s values for these two samples were roughly 1·8 × 10^{20} and 8 × 10^{19} atoms g.$^{-1}$ (Table 2).

The semiconductivity experiments are summarised in Figs. 5 and 6, Fig. 5 showing the decrease of conductivity on prolonged outgassing at a fixed temperature of 532°, and Fig. 6 the change of activation energy, E_σ, for semiconduction with degree of outgassing and with oxygen pressure. When thoroughly outgassed, or in an atmosphere of hydrogen, $E_\sigma = 35 \pm 2$ kcal. mole^{-1}, but at $P_{O_2} > 0{\cdot}01$ cm., $E_\sigma \approx 11$ kcal. mole^{-1}. Under conditions such that the activation energy is constant at ~11 kcal. mole^{-1}, the semiconductivity increases with P_{O_2} roughly according to $\sigma \propto P_{O_2}^{1/12}$. In all this work the pellets appeared to obey Ohm's, law and the resistance was independent of the direction of current flow : the work in hydrogen was carried out last.

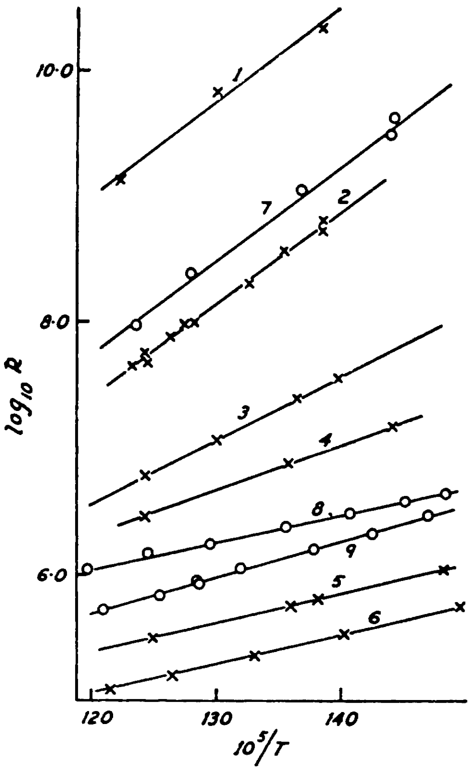


FIG. 6. *Semiconductivity of* Cr_2O_3*—variation with temperature and* P_{O_2}.

× Pellet No. 1, pumped first for 5 days at 532°.
○ Pellet No. 2, pumped first for 2 days at 532°.

Curve 1, $P_{H_2} = 1{\cdot}1$ cm., $E_\sigma = 36$ kcal.
Curve 2, $P_{O_2} < 10^{-6}$ mm., $E_\sigma = 35$ kcal.
Curve 3, $P_{O_2} = 4{\cdot}7 \times 10^{-2}$ mm., $E_\sigma = 24$ kcal.
Curve 4, $P_{O_2} = 10^{-1}$ mm., $E_\sigma = 17$ kcal.
Curve 5, $P_{O_2} = 4{\cdot}6 \times 10^{-1}$ mm., $E_\sigma = 11$ kcal.
Curve 6, $P_{O_2} = 219$ mm., $E_\sigma = 11$ kcal.
Curve 7, $P_{O_2} = 3{\cdot}5 \times 10^{-5}$ mm., $E_\sigma = 37$ kcal.
Curve 8, $P_{O_2} = 0{\cdot}14$ mm., $E_\sigma = 10$ kcal.
Curve 9, $P_{O_2} = 120$ mm., $E_\sigma = 13$ kcal.

The Cr_2O_3 as prepared for this work, *i.e.*, after being heated to ~520° in dry air and cooled in air, contained a detectable proportion of chromium in a higher valency state; this was estimated by allowing 1 g. of the oxide to react with acidified potassium iodide solution, centrifuging off the oxide, and titrating the liberated iodine with N/50-thiosulphate (cf. Weller and Voltz, *J. Amer. Chem. Soc.*, 1954, **76**, 4695) : similar estimations were made upon 1-g. samples which had been outgassed in high vacuum (*ca.* 10^{-6} mm.) for long peroids, and it was found, as expected, that the oxidising power falls off continuously, but the decrease, amounting only to some 50% in 194 hours' pumping, is not nearly so pronounced as the fall in conductivity on outgassing shown in Fig. 5. These experiments are not very relevant to the main object of the present paper, but will be reported in detail later in another connection.

For the purpose of this set of experiments, the 1-g. samples were sealed in separate tubes to a common vacuum line and sealed off one by one; for titration, the tubes were broken under the surface of the potassium iodide solution so that the outgassed oxide did not come into contact with the air until it had reacted. An aqueous extract of the original oxide sample, tested with diphenylcarbazide (cf. Feigl, "Spot Tests—Inorganic Applications," p. 162, Elsevier, 1954), gave a strong reaction for chromate.

(*b*) NiO. Only a limited amount of exchange and equilibration work has been done with this oxide. It has been established that, for samples outgassed at 605° overnight: (*a*) n_s is about 10^{20} atoms g.$^{-1}$, varying slowly with reaction temperature from $1{\cdot}1 \times 10^{20}$ at 570° to $6{\cdot}3 \times 10^{19}$ at 486°; (*b*) equilibration and exchange occur at the same speed; (*c*) the apparent activation energy of the exchange–equilibration reaction is 35 ± 2 kcal. mole^{-1}; (*d*) the latter reaction is independent of P_{O_2} over the range 1·5—10·0 cm. The results are not quoted in detail, but the Arrhenius plot is given in Fig. 1 together with those of the other oxides. Over the temperature range covered there is no sign of the abrupt change of slope in the Arrhenius plot that was found with Cr_2O_3 (and MgO and ZnO; Parts III and IV, *locc. cit.*).

The adsorption experiments yielded results very similar to those obtained with Cr_2O_3; for instance, the rate of adsorption follows the same law [eqns. (1) and (2) above], with E_a rising (at 400—460°) from about 0 at zero coverage to about 38 ± 3 kcal. mole^{-1} at saturation at 6 cm. oxygen pressure. The pressure dependence of the rate of adsorption was not studied in detail, but it was found that, at very low coverages in the pressure range 2×10^{-3} to 2×10^{-2} mm., the rate is directly proportional to P_{O_2}. The saturation oxygen coverage at 407° and 5·7 cm. was about $1{\cdot}3 \times 10^{18}$ atoms g.$^{-1}$. The B.E.T. (N_2) surface was 5·5 m.^{2} g.$^{-1}$.

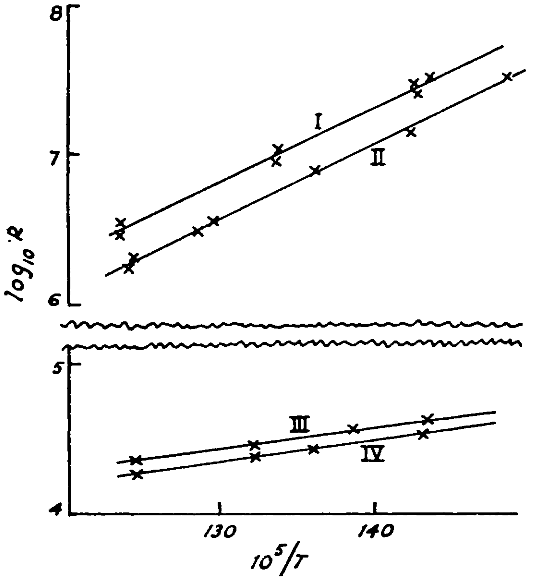


FIG. 7. *Semiconductivity of* NiO*—variation with temperature and* P_{O_2}*: pumped first for* 2 *days at* 520°.

Curve I, $P_{O_2} = 2 \times 10^{-5}$ mm., $E_\sigma = 22$ kcal.
Curve II, $P_{O_2} = 10^{-4}$ mm., $E_\sigma = 22$ kcal.
Curve III, $P_{O_2} = 3{\cdot}6$ cm., $E_\sigma = 7$ kcal.
Curve IV, $P_{O_2} = 14{\cdot}8$ cm., $E_\sigma = 7$ kcal.

The semiconductivity phenomena, very similar to those of Cr_2O_3, are summarised in Fig. 7; E_σ varies from 23 ± 2 kcal. mole^{-1} in a high vacuum to 7 ± 1 kcal. mole^{-1} in presence of oxygen. This oxide is not so regular in its behaviour as Cr_2O_3, some lack of reproducibility being experienced; in a few cases the resistance depended on the direction of current flow and in this event the mean resistance has been recorded: the uncertainty was never more than 10%. In the presence of oxygen the pellet acquired a surface layer containing excess of oxygen, becoming grey-black in contrast to the grey-green of the evacuated oxide.

(*c*) Fe_2O_3. The exchange and equilibration reactions (see Fig. 1) occur at the same speed, and $E \approx 19 \pm 2$ kcal. mole^{-1}; n_s is approximately constant at $\sim 6{\cdot}5 \times 10^{20}$ atoms g.$^{-1}$ at 300—400°. In contrast to the other two oxides, the rate of exchange–equilibration is directly proportional to $P_{O_2}^{1{\cdot}0}$ at 1·7—10·2 cm.

Owing to the relatively small amount of oxygen adsorbed and to the slow rate of attainment of equilibrium it was not possible to measure rates of oxygen adsorption at pressures of several cm. on this oxide. At $P_{O_2} \lessapprox 2$ mm. (mainly at 10^{-2}—10^{-3} mm.) the rate of adsorption measured at 85—250° on oxide outgassed at 500° follows the same law as on the other two oxides, with $E_a \approx 0$ at $q \approx 0$, rising to at least 12 kcal. mole^{-1} near "saturation" at $P_{O_2} = 1{\cdot}5$ mm.* and

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* The saturation value for q is inaccurate since not only did q increase slowly during 24 hr. at 1·5 mm., but q also showed a slow increase with increasing P_{O_2}.

appears to be proportional to P_{O_2}. " Saturation " at 4 cm. pressure at 277° corresponds to an adsorption of about $5{\cdot}6 \times 10^{17}$ atoms g.$^{-1}$: the B.E.T. (N_2) surface area is 33·5 m.^{2} g.$^{-1}$.

An attempt was made to measure the surface area of the oxide by exchange of iron between the surface and ferric chloride solution containing Fe-55/59. No exchange was detected but it proved possible to perform the desired measurement by following the adsorption of radioactive iron from solution. The radioactive iron, obtained from A.E.R.E., Harwell, was diluted with iron carrier to give a N/10-solution of ferric chloride with a count in a liquid counter of 12,000—15,000 min.$^{-1}$. For several such solutions, adjusted to different pH's with hydrochloric acid or ammonia, the iron content was determined by titration with permanganate by the Zimmermann–Reinhardt method; 15 ml. of these solutions were agitated in stoppered tubes for 24 hr. with 0·1 g. of Fe_2O_3 in a rotary shaker, and the iron content and radioactive count found in 10 ml. of the clear supernatant liquid obtained by centrifugation. The results are shown in Table 5.

TABLE 5. *Stability of* Fe_2O_3 *at various* pH.

pH	1·1	1·15	1·28	1·50	1·94	2·2
Change of Fe^{3+} content (%) in solution in 24 hr.	+392	+14	−1	−8	−18	−24

There was no significant loss of radioactivity from the solution when the oxide was dissolving (*i.e.*, below about pH 1·2) but the loss of Fe^{3+} from solution found analytically above pH 1·2 was parallel to the loss of radioactive iron. 0·1-g. lots of the oxide were shaken at *ca.* 18° for varying times with ferric chloride solution adjusted to a chosen pH 2·2, determined by glass electrode and a commercial pH meter, and the total iron content and the radioactivity of the solution determined : the results, given in Table 6, show that an exact parallelism exists between iron lost from the solution by adsorption on the powdered oxide and the loss of radioactive iron determined by counting: assuming that the adsorption isotherm reaches equilibrium when ~40% of the iron in solution has been adsorbed, we find that this corresponds to about $5{\cdot}3 \times 10^{20}$ atoms of Fe per g. of oxide.

TABLE 6. *Adsorption on* Fe_2O_3 *at* pH 2·2.

Time (hr.)	Loss of Fe from solution (%) : Radioactive	Titration	Time (hr.)	Loss of Fe from solution (%) : Radioactive	Titration
$\frac{1}{3}$	6·4	0·9	$51\frac{1}{3}$	31·0	29·8
1	11·9	11·7	113	36·1	36·9
$20\frac{1}{3}$	23·7	26·1			

The semiconductivity measurements were less reproducible than for the other oxides; conductivity is high *in vacuo* (48 hr. at 500°) with $E_\sigma \approx 2$, and falls rapidly with increasing P_{O_2}; E_σ at $P_{O_2} \approx 0{\cdot}5$ mm. upwards $\approx$ 22 kcal. mole^{-1}.

DISCUSSION

The semiconductivity measurements were undertaken to see whether any relation exists between the activation energies characteristic of this property and those found for the exchange reactions. No such relation was detected but the experiments merit discussion. The work was performed with D.C. voltages; as it is now well known that a correct interpretation of such work in terms of semiconductivity theory is difficult owing to the great influence of high (or low) conductivity surface states on the pellet conductivity, a wide frequency range should be used (cf. Henisch, *Phil. Mag.*, 1951, **42**, 734; Verwey, Reading Conference on Semi-Conductors, 1950, Butterworths, 1952, p. 151; Volger, *Phys. Rev.*, 1950, **79**, 1023). It is therefore noteworthy that our measurements agree in general with recent results of other workers using the same technique; thus, with E_σ in kcal. mole^{-1} : Cr_2O_3, present work 35 and 11; Bevan, Shelton, and Anderson (*loc. cit.*) 32 and 7—14; Chaplin, Chapman, and Griffiths (*Proc. Roy. Soc.*, 1954, **224**, *A*, 419) ~31 and 14: Fe_2O_3, present work ~2 and 22; Bevan, Shelton, and Anderson 8·5 and 25; Morin (*Phys. Rev.*, 1951, **83**, 1005) — and 25 (A.C. measurement) : NiO, present work 23 and 7; Morin (*ibid.*, 1954, **93**, 1199) 23 and ~10 (A.C. and D.C.); Hogarth (*Proc. Phys. Soc.*, 1951, **64**, *B*, 691) "green" ~22, "black" ~11; Parravano (*J. Chem. Phys.*, 1955, **23**, 5) — and 9. In this list the first figure of each pair refers to measurements in a high vacuum or in hydrogen, and the second to measurements in several cm. of air or oxygen :

they are for roughly the same temperature ranges as ours. Our results are very similar to those of Anderson *et al.*, and the slow drift of conductivity of Cr_2O_3 on prolonged pumping (Fig. 5) is like that recorded by them for ZnO (cf. also Bevan and Anderson, *Discuss. Faraday Soc.*, 1950, **8**, 238); we have found, as expected, the same effect with NiO and Fe_2O_3. All three oxides, when fully reduced (*i.e.*, evacuated thoroughly at ~500°), can adsorb small quantities of oxygen at low pressure without any effect on the conductivity. When the quantity adsorbed became sufficient to change the conductivity it was noted that the addition of a charge of oxygen causes an immediate change in resistance, followed by a slow drift to equilibrium. On all three oxides at around 400° and pressures of 10^{-2}—10^{-3} mm. the equilibrium takes an hour or more to be attained, but is fairly rapidly reached at 500° (cf. Bevan and Anderson, *loc. cit.*). This effect may well be due to a slow redistribution of the adsorbed oxygen over the interior surface of the compressed pellet: in this connection it was noted that the NiO pellet, after a series of measurements in oxygen, had a blackened surface, the interior remaining grey-green, but the blackening did not extend fully under areas covered by the tightly-clamped platinum electrodes. Clearly, true equilibrium was never attained in the presence of oxygen with this material and therefore possibly not in the case of the others: this probably did not affect the limiting values for E_σ, which were reproducible from one pellet to another, in several cm. of oxygen and in a vacuum or hydrogen, but may have altered the intermediate figures and the absolute values of resistance recorded, but in the present context these are not important.

Our conductivity results for Cr_2O_3 (Figs. 5 and 6), taken with the results of other workers mentioned above (cf. also Weisz, Prater, and Rittenhouse, *J. Chem. Phys.*, 1953, **21**, 2236), confirm the view that (subject to the uncertainty introduced by the surface states, which uncertainty will not disappear until much higher temperatures where very rapid oxygen exchange between gas and solid may occur) in the presence of oxygen this oxide is a *p*-type conductor, containing a (surface) excess of oxygen as O^-_{ads} or O^{2-}_{ads} and a proportion of its (surface) chromium in a 4- or 6-valent state. In hydrogen or other reducing atmosphere, or if thoroughly outgassed, the oxide probably passes through an intrinsic state to become an *n*-type conductor, possibly containing excess of metal. Similarly Fe_2O_3 is an *n*-type conductor while NiO is of *p*-type: the mechanism of semiconduction in these two oxides is uncertain (Morin, Parravano, *locc. cit.*).

We refer now to the remainder of the experimental work, and assume that the conclusions of the adsorption experiments can be applied over the whole of the temperature range used in the exchange–equilibration work. It appears that on Cr_2O_3 and NiO the exchange–equilibration reaction as measured is the rate of adsorption–desorption of oxygen (the reaction of $E \approx 2$ above ~430° on Cr_2O_3 will be considered later): the same probably applies to Fe_2O_3 but here the adsorption results are not conclusive enough to be sure of this. Thus we can say that on exposure to oxygen the freshly-outgassed oxide adsorbs the gas (forming almost certainly O^-_{ads}, with consequent change in conducting properties) with an activation energy for adsorption, E_a, which rises approximately linearly with coverage from zero to about 35 kcal. mole^{-1} (for Cr_2O_3 and NiO, and probably ~20 kcal. mole^{-1} for Fe_2O_3) at saturation when $P_{O_2} = 6$ cm.; at the same time the activation energy for desorption, E_d, must fall similarly from some value $\nless 35$ kcal. mole^{-1} * (say $\nless 20$ for Fe_2O_3) until at saturation $E_a = E_d$. The rate of desorption then governs the observed rate of exchange–equilibration.

The fact that $r_s \propto P_{O_2}^{1\cdot0}$ for an adsorption process which is almost certainly dissociative presents no difficulty when it is noted that the coverages, in terms of fractions of the total surface, n_s, are all small around 6 cm., *viz.*, 15% (Cr_2O_3), 1—2% (NiO), 0·1% (Fe_2O_3).

In the case of Cr_2O_3 and NiO, the surface is effectively saturated with oxygen well below 6 cm., so that the exchange–equilibration reaction is pressure-independent; on Fe_2O_3 the latter reaction is directly proportional to P_{O_2} and it is considered that the coverage is still increasing over the range 1·7—10·2 cm., although this could not be directly demonstrated owing to the small amount of oxygen adsorbed on this oxide, and, as noted earlier, the slowness of approach to equilibrium.

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* Garner reports a value of 37 for the initial heat of adsorption of oxygen on oxidised Cr_2O_3 at room temperature (Trapnell, "Chemisorption," Butterworths, 1955, p. 142).

In order to account for oxygen exchange with the whole surface, although adsorption occurs on only a small fraction, it is evident that either the adsorbed oxygen (O^-_{ads}) or the defects promoting adsorption are mobile in the surface. In the light of present knowledge it is not possible to say for certain which species is the more mobile; certainly above ~430° in the case of Cr_2O_3 the mobility of one species becomes rate-determining in the exchange (Fig. 1).

Some evidence pointing to distinctly limited mobility of adsorbed oxygen on NiO at temperatures rather lower than those used in the exchange–equilibration experiments (Fig. 1) was obtained as follows: 10 g. were outgassed overnight at 540°, isolated, cooled to 200°, and exposed for 10 min. at this temperature to 2 cm. of the non-equilibrated oxygen mixture. The gas left unadsorbed was recovered by Töpler pump, and the quantity adsorbed determined. The oxide was pumped for 30 sec. and then isolated from the back line and connected directly to the ionisation region of the mass spectrometer, by-passing the leak, so that all gas evolved from the oxide passed through the ionisation region and was analysed for masses 32, 34, and 36. There was no appreciable oxygen pressure over the oxide at 200°, and the temperature was raised fairly quickly in stages. Evolution of oxygen began at 220°, and was sufficient for analysis at 250°, 6 min. after the commencement of heating and 21 min. from the first adsorption; 3 min. later, at 300°, the gas evolved contained 4·8% of ^{18}O and *was not equilibrated.* Had the adsorbed gas exchanged with all the available oxide surface (the n_s value of ~10^{20} atoms $g.^{-1}$ obtained in higher-temperature exchange experiments being used) the ^{18}O content of the gas evolved should have been well below 0·30%: the value of 4·8% corresponds to exchange with 0·26% of the surface, or approximately two surface oxygen atoms exchanged for every one adsorbed (~$1·8 \times 10^{18}$ O atoms adsorbed; ~$3·8 \times 10^{18}$ O atoms in the surface suffered exchange). This experiment demonstrates clearly that at 250—300° the adsorbed oxygen is only able to exchange with (on the average) two nearest neighbour surface oxygen ions; there is no surface mobility of adsorbed gas leading to equilibration, which indicates that somewhere in the 90° temperature range between the exchange–equilibration reactions of Fig. 1 and this experiment it should be possible to separate the exchange and the equilibration reactions.

A similar experiment in which the gas was adsorbed at 105° on Cr_2O_3 showed that, at ~300°, 40 min. after the adsorption had started and 20 min. after heating of the oxide was begun, the gas first evolved had undergone complete exchange and equilibration with the whole oxide surface. This result is not surprising since the exchange–equilibration reaction is of measurable speed around 300° (cf. Fig. 1): in the case of Cr_2O_3, therefore, the adsorbed oxygen is held too tenaciously at lower temperatures to permit this method of studying surface mobility.

The reason for the rate of oxygen chemisorption on these oxides obeying Elovich's equation (1) is uncertain. This relation may be derived in at least three ways: (1) assume a uniform surface, with interaction between the adsorbed molecules or atoms; (2) assume a non-uniform surface (these two cases are mentioned by Trapnell, *op. cit.*, p. 104); (3) assume a uniform semiconducting surface, with charge transfer between the surface and adsorbed gas, leading to the formation of an electrical double layer at the interface. Case (3) has been discussed in detail by Engel and Hauffe (*Z. Elektrochem.*, 1952, **56**, 366; 1953, **57**, 762; see also Aigrain and Dugas, *ibid.*, 1952, **56**, 363) who call it "the boundary-layer theory" ("die Randschichttheorie") of chemisorption: they have also applied their equations to certain reactions catalysed by oxides and to the rates of oxidation of metals under conditions where the simple Wagner mechanism does not apply. Engel and Hauffe (*loc. cit.*, 1953, p. 773) have investigated the kinetics of adsorption of oxygen on NiO from room temperature to 700° and find that Elovich's equation is obeyed, although below 300° the plots of q against log $(t + t_0)$ show a discontinuity in every case, which they attribute to the presence of two processes, chemisorption and lattice incorporation, the former being the slow process at 300° and above. They found it necessary to put $t_0 \approx 60$—220 sec., and suggest that E_0, the activation energy of the adsorption at zero coverage, is about 11—12 kcal. $mole^{-1}$; the B.E.T. area of their sample, determined with NiO at −78°, was 61 $m.^2$, presumably measured on the 62·9 g. of oxide used for the oxygen work, or about 1 m.^{2} g.$^{-1}$. It is satisfactory that our observations agree with those of Engel and Hauffe, insofar as the Elovich equation is concerned; the fact that we found E_0 and t_0 both ≈ 0 whereas the earlier workers did not may be due to differences in preparation. It appears that Engel and Hauffe's oxide was of much lower specific surface than ours, which would indicate a greater degree of sintering leading to a more uniform surface. We believe that the mechanism of oxygen adsorption on semiconducting oxides is due to a combination of cases (2) and (3), so that a sample with a highly non-uniform surface might well have $E_0 \approx 0$, whereas a well-sintered specimen may need an activation energy before appreciable quantities of oxygen are adsorbed. The accuracy of our adsorption experiments is not such (owing mainly to the nature of Elovich's equation) as to exclude the possibility in our case of $E_0 \approx 3$ kcal. mole^{-1}; also, the method whereby Engel and Hauffe arrive at a value of 11—12 is only approximate.

The presence of an electrical double layer on the oxide surface when oxygen is adsorbed is evident from the semiconductivity experiments, while some degree of non-uniformity is inevitable in oxide preparations of this type. Other oxides used by us, notably those of zinc and magnesium, possess a non-uniformity of surface which is readily demonstrated by the regular increase of n_s with the temperature of the exchange reaction, but, curiously, only nickel oxide, of the three oxides examined here, shows this effect over the temperature ranges studied. Some experiments on the mechanism of the reactions $2N_2O \longrightarrow 2N_2 + O_2$ and $2CO + O_2 \longrightarrow 2CO_2$, catalysed by these oxides, have shown, by use of ^{18}O, clear evidence of heterogeneity of surface in the case of NiO (Winter, unpublished work). Heterogeneity could probably be demonstrated also by oxygen-exchange reactions carried out at lower temperatures than those used in the present work.

The present results, together with those presented in Parts III—V (*locc. cit.*), demonstrate the rather surprising diversity in detail of behaviour towards oxygen of metallic oxides, and show how complicated may be the considerations controlling catalytic activity and electrical conductivity. The five oxides so far studied in detail comprise ZnO and Fe_2O_3 (both *n*-type conductors), NiO and Cr_2O_3 (*p*-type), and MgO [described as an insulator, but cf. Mansfield (*Proc. Phys. Soc.*, 1953, **66**, *B*, 612) and Lenpicki (*ibid.*, p. 281) who, using single crystals, examined the conductivity and thermoelectric power of MgO and concluded that it is a defect semiconductor containing excess of oxygen]: no two of these behave in exactly the same way, although the same basic reactions of dissociative chemisorption, surface migration, exchange, recombination and desorption of oxygen are undergone by each.

Finally, it is of interest to compare the surface areas deduced for these three oxides from the various studies reported here: Cr_2O_3 (A); B.E.T. (N_2) area of 30 m.^{2} g.$^{-1}$ corresponds to a calculated n_s of $\sim 3 \times 10^{20}$ atoms of oxygen g.$^{-1}$, a random exposure of crystalline faces being assumed; n_s observed was about $1·8 \times 10^{20}$ atoms g.$^{-1}$. Cr_2O_3 (B); B.E.T. area 14·2 m.^{2} g.$^{-1}$ corresponding to n_s (calc.) of $1·4 \times 10^{20}$ atoms g.$^{-1}$; n_s (obs.) $\approx 8 \times 10^{19}$ atoms g.$^{-1}$.

Similarly for NiO (in units of atoms g.$^{-1}$); B.E.T. $\gtrapprox 7 \times 10^{19}$; n_s (obs.) $\approx 9 \times 10^{19}$. For Fe_2O_3; B.E.T. $\gtrapprox 5 \times 10^{20}$ atoms per g. of oxygen, or $3·3 \times 10^{20}$ per g. of iron; n_s (obs.) $= 6·5 \times 10^{20}$ of oxygen; n_s deduced from the adsorption isotherm for iron from solution, $5·3 \times 10^{20}$ of iron.

In view of the three widely differing techniques used, involving a temperature range of some 650°, the agreement is remarkable.

Certain of the results given for Cr_2O_3 (A) were obtained with the help of Dr. G. Houghton at Imperial College; I am also indebted to colleagues here for the B.E.T. measurements.

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