

239. *Studies of the Exchange Reactions of Solid Oxides. Part I. The Exchange of Oxygen Isotopes between Gaseous Oxygen and Certain Metallic Oxides.*

By E. R. S. WINTER.

Preliminary experiments are reported on the exchange of ^{18}O between gaseous oxygen and $\gamma\text{-Al}_2\text{O}_3$, ThO_2 , TiO_2 , and ZnO . It is shown that the reaction consists of an initial rapid exchange, followed by a slow process. A more detailed study of the exchange with $\gamma\text{-Al}_2\text{O}_3$ shows that the rapid process follows first-order kinetics, is independent of the oxygen gas pressure over the range 35—600 mm., and has an activation energy of 37.3 ± 0.5 kcal.

THE only experiments showing by isotopic methods the lability of the surface oxygen atoms of solid oxides are those of the Japanese workers, Morita *et al.* (*Bull. Jap. Chem. Soc.*, 1938, **13**, 357,

601, 656; 1939, 14, 9, 520; 1940, 15, 1, 37, 71, 119, 166, 226, 298) and some observations by Brandner and Urey (*J. Chem. Physics*, 1945, 13, 351). In the Japanese work attention was principally directed towards the (qualitative) study of the exchange reaction, catalysed by oxides, between oxygen and water vapour (although the exchange of ^{18}O between oxygen and Mn_2O_3 - MnO_2 mixtures was made the subject of a separate study; Morita, *ibid.*, 1939, 14, 520; 1940, 15, 1). Morita showed that exchange of ^{18}O between the two gases became rapid at temperatures usually of the order of 500–700°, depending on the oxide used, and that exchange with the manganese oxides was appreciable at 400°. Brandner and Urey found in the course of a kinetic investigation of the (heterogeneous) reactions:



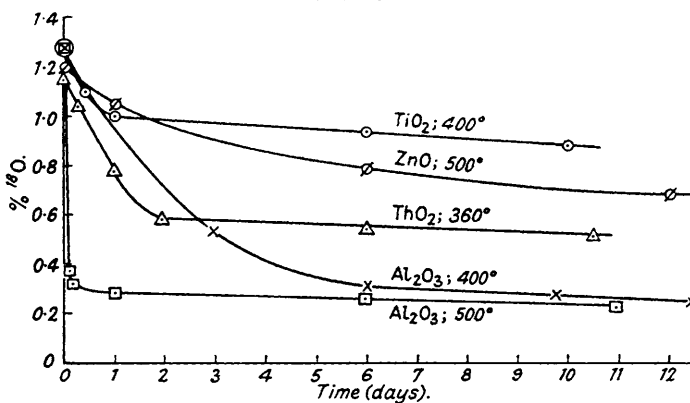
that exchange of ^{18}O occurred between carbon dioxide and a quartz vessel at 900°, but they did not pursue the matter further.

Much indirect evidence for the lability and reactivity of specially prepared oxides towards certain gases may be cited from the literature upon heterogeneous catalysis: the work of Garner *et al.* upon zinc, manganese, chromium, copper, and zinc oxides is particularly instructive in this respect (Garner, *J.*, 1947, 1239, and papers there cited; Garner, Gray, and Stone, *Proc. Roy. Soc.*, 1949, A, 197, 294). Information may also be obtained from recent studies of the dependence of the semi-conductivity of oxides on the pressure and nature of the gas with which they are in contact (Bevan, Shelton, and Anderson, *J.*, 1948, 1729; Anderson, Faraday Society Discussion on the Physical Chemistry of Process Metallurgy, 1948, 163).

EXPERIMENTAL.

Materials.—The alumina was a sample of γ - Al_2O_3 , type H, supplied by Messrs. Peter Spence, Ltd.; the zinc oxide was prepared by precipitation of the hydroxide, according to the method of Taylor and Sickman (*J. Amer. Chem. Soc.*, 1932, 54, 602); the thoria and titania were samples of reagent-grade material of unknown history. The oxygen contained about 1.2% of ^{18}O and was prepared by electrolysis of water enriched in ^{18}O , the gas being passed over palladized asbestos, dried, and collected over mercury; it contained about 0.2% of an impurity giving rise to mass 28 in the mass spectrometer. The impurity was not removed by prolonged heating of the gas at 400–600° in contact with the oxides and so was presumably nitrogen. Search was made by the mass spectrometer for other impurities up to mass 70, and none was found in a detectable amount (0.001%).

FIG. 1.



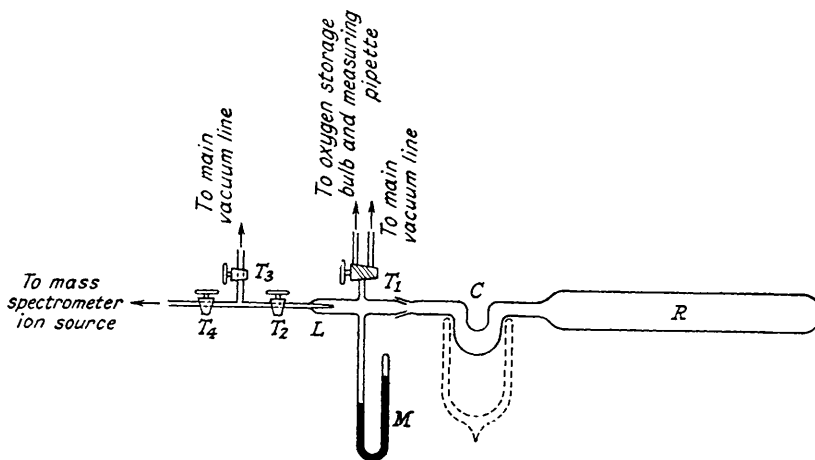
Method.—Analyses of ^{18}O content were performed on gaseous oxygen by using a 60° Nier-type mass spectrometer, incorporating the circuits of Graham, Harkness, and Thode (*J. Sci. Instr.*, 1947, 24, 119). Two methods were used to follow the reaction. In the preliminary work the oxide was weighed and transferred to a clean Pyrex tube of about 80-ml. capacity, fitted with a tap and standard ground joint; the tube was placed in the furnace, attached to the vacuum line, and outgassed in a vacuum of 10^{-6} mm. of Hg or better for some 16 hours. The tube was then connected to a Töpler pump through which the necessary amount of heavy oxygen was added; samples of the gas were withdrawn by means of the Töpler pump from time to time, transferred to sample tubes, and sealed off. The sample tubes were each provided with a drawn-out capillary tip, which could be broken as required inside a conventional vacuum seal-breaker attached to the gas-inlet line of the mass spectrometer. In general, the reaction tube contained 1–2 g. of oxide and was filled with oxygen at a pressure usually of 10–35 cm. of Hg at room temperature; each sample tube was of about 3-ml. capacity and was filled with oxygen at a pressure of about 16 cm. of Hg, also measured at room temperature. This method was convenient in that it left the mass spectrometer available for other work while the reactions were proceeding, and it enabled the

exchange reactions to be examined in a qualitative manner; it suffered from the disadvantage that the reacting system did not remain constant throughout any run, as oxygen was withdrawn in appreciable quantity for analysis.

For this reason the results obtained by this technique are presented in graphical fashion only, in Fig. 1; the curves have not been corrected for the oxygen withdrawn for analysis during the runs.

For the detailed examination of the kinetics of the exchange reactions, the system shown in Fig. 2 was constructed. The sample of oxide (generally 1–2 g.) was confined in *R* (made of Pyrex glass or silica), which was surrounded by the furnace; *C* was a cold finger kept at -78° which served to condense any volatile impurities in the reaction system. Evacuation of the oxide and the introduction of a measured quantity of enriched oxygen gas was achieved through the three-way tap T_1 ; the pressure of oxygen in the system during the exchange reactions was measured on the manometer *M*. *L* was a capillary leak, such that with a pressure of 5–8 cm. of Hg on one side, and with taps T_2 and T_4 open, the pressure of gas drawn through into the mass spectrometer was about 10^{-5} mm. of Hg in the ionisation region; this pressure provided peaks at masses 32 and 34 ($^{16}\text{O}_2$ and $^{18}\text{O}^{18}\text{O}$) of sizes suitable for accurate analysis of the ^{18}O isotope abundance. The three taps T_2 , T_3 , and T_4 provided a lock so that the volume between T_2 and *L* could be pumped out without affecting the vacuum in the mass spectrometer, *i.e.*, so that *R* and *C* could be readily removed and a fresh sample of oxide put in. The distance from *R* to the capillary leak *L* was constructed of 1-cm. bore tubing to reduce to a minimum (< 10 secs. at the gas pressures used) the time of diffusion of oxygen from the reaction region to *L*. The capillary leak was made by pulling down sharply in a hot flame a piece of Pyrex capillary tubing of about $\frac{1}{2}$ -mm. bore. The leak was tested to give single bubbles of air (about 2 or 3 per second) when dipped under ether and subjected to a pressure of

FIG. 2.



10 cm. of Hg. A leak of this specification, used with oxygen behind it at 5–8 cm. of Hg pressure, gives suitable peak sizes in the mass spectrometer. Leaks can readily be made in this manner with a fine-drawn portion only some 2–3 mm. long; they are easily selected by the bubble test to work at pre-determined gas pressures. This method of construction and testing, for details of which the author is indebted to Dr. R. L. Graham, is much preferable to that described by Harris (*J. Sci. Instr.*, 1948, 25, 417).

With this system the procedure used was to place the oxide sample in *R* and outgas it by heating it to the desired temperature and pumping through T_1 , with T_2 and T_3 open and T_4 shut, to a vacuum of 10^{-5} mm. of Hg or better, for some 16 hours. If required, the temperature of the furnace was then rapidly reduced to that at which the exchange reaction was to be studied. The enriched oxygen gas was introduced, in known amount, through T_1 , T_3 was shut, and T_4 opened. A continuous slow drain of oxygen from the reaction zone passed through *L* into the mass spectrometer and a record was taken of decrease of the ^{18}O content with time. The amount of oxygen taken off in this way for analysis was in all cases no more than 10^{-4} g. per hour and was usually no more than 10^{-5} g.; most runs were complete in 4 hours, and about 10^{-2} g. of oxygen was normally present in the reaction system, so that errors due to sampling during the runs were negligible. It is to be noted that, although the mass spectrometer will give ^{18}O contents correct to ± 1 or 2 parts in 1000 of the figure measured (Whalley, Winter, and Briscoe, *Trans. Faraday Soc.*, in the press), yet accuracy of this order cannot be expected here. This is because the normal method of analysis involves the measurement and averaging of a number of abundance ratios, so as to eliminate random fluctuations in the mass spectrometer tube and its electronic circuits; in the present work the sample is continually changing so that only a very few ratios, and often only one, can be obtained for each experimental point. Inspection of the results has indicated that even so the ^{18}O contents are almost always consistent among themselves to 1 part in 100 or better.

Kinetics.—The exchange with $\gamma\text{-Al}_2\text{O}_3$ was selected for study. The exchange obeys first-order kinetics (cf. Mackay, *Nature*, 1938, 142, 997) as is shown by Fig. 3 where $\log_{10} (^{18}\text{O}_t - ^{18}\text{O}_\infty)$ is plotted against t (minutes); $^{18}\text{O}_t$ is the % of ^{18}O in the gas being analysed at time t after the start of the experiment, and $^{18}\text{O}_\infty$ is the ^{18}O content when the reaction is complete. The evaluation of $^{18}\text{O}_\infty$ is not free from uncertainty since, as is seen from Figs. 1 and 4, there is a slow drift downwards of ^{18}O content after the first reaction has finished. The procedure adopted is clear from Fig. 4; the line *AB* is projected

back to C, and the mean of the ^{18}O contents at B and C taken as the infinity value. The velocity of the exchange reaction is independent of the oxygen gas pressure, over the limited range which can be studied by the present technique, as is shown by Table I. Table II presents results obtained at six temperatures which yield an activation energy of 37.3 ± 0.5 kcal. It is interesting that the run at 400° shown in Fig. 1 and performed at a pressure of about 60 cm. of Hg yields a k_0 value of approximately 2.5×10^{-6} min.^{-1} ; this value falls very close to the activation-energy plot based on the values in Table II, so the rate appears to be independent of oxygen pressure from 3.5 to 60 cm. of Hg. The calculation of k_0 is given in the next section.

FIG. 3.

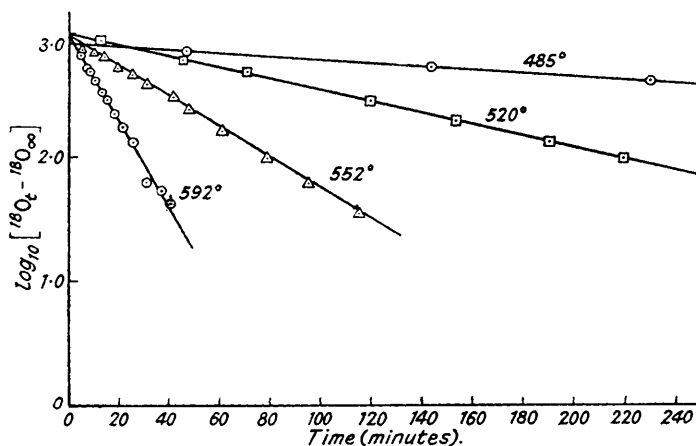


FIG. 4.

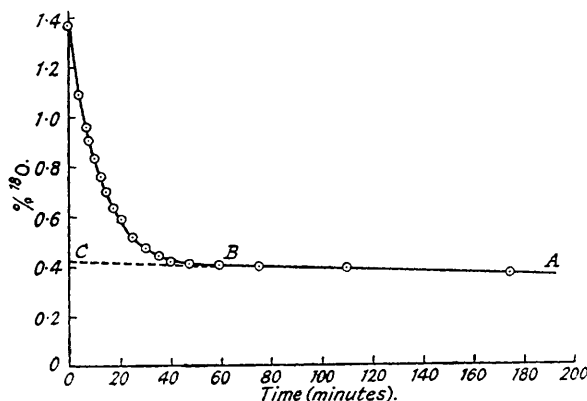


TABLE I.

Reactions at 548—556°: $\gamma\text{-Al}_2\text{O}_3$ outgassed for 16 hours at 590°.

Temp.	548°	553°	556°	556°
P_{O_2} (cm. Hg)	3.50	7.05	10.30	14.60
k_0 (min.^{-1})	0.0044	0.0049	0.0060	0.0059

TABLE II.

Reactions from 485° to 592°: $\gamma\text{-Al}_2\text{O}_3$ outgassed for 16 hours at 590°.

Temp.	$10^5/T$.	P (cm. Hg).	k_0 (min.^{-1}).	$\log_{10} k_0$.	Temp.	$10^5/T$.	P (cm. Hg).	k_0 (min.^{-1}).	$\log_{10} k_0$.
485°	132	6.85	0.00067	-3.174	553°	121.0	7.05	0.0049	-2.310
520	126.1	6.30	0.00194	-2.712	556	120.7	—*	0.00595*	-2.226*
548	121.8	3.50	0.0044	-2.356	592	115.6	7.00	0.0146	-1.837

* Mean of 2 runs, see Table I.

DISCUSSION.

The experiments presented in Figs. 1 and 4 demonstrate that the exchange with gaseous oxygen possesses the same characteristics as that with water vapour (see Part II), *viz.*, an initial rapid reaction followed by a slow drift which continues indefinitely. From the quantities of oxygen and oxide used (an approximate allowance being made for the gas withdrawn for analysis in the preliminary experiments, Fig. 1), we obtain the number of readily exchangeable atoms of oxygen, n'_s , per g. of oxide, using the equation

$$n'_s = \frac{n_g(^{18}\text{O}_0 - ^{18}\text{O}_\infty)}{w(^{18}\text{O}_\infty - 0.2)} \quad [\text{cf. equation (6)}]$$

where $^{18}\text{O}_0$ and $^{18}\text{O}_\infty$ are the initial and final ^{18}O contents of the gas expressed as %, and 0.2 is the ^{18}O content initially of the solid surface (assumed to be the normal ^{18}O abundance); n_g is the number of oxygen atoms in the amount of gas used, and w is the weight of oxide used. We assume here and in what follows that the ^{18}O content of the exchangeable part of the oxide surface becomes equal to that of the gas phase at equilibrium [cf. eqn. (7)]; this will be nearly enough true for our present purpose. These values of n'_s are compared in Table III with

TABLE III.

Oxide.	Exchangeable O, atoms/g. of oxide.		
	From H_2^{18}O exchange.	From $^{16}\text{O}^{18}\text{O}$ exchange.	From N_2 isotherms.
Al_2O_3	1.32×10^{21} (200°)	8.2×10^{20} (410°)	1.35×10^{21}
ThO_2	3.48×10^{20} (120°)	1.30×10^{21} (555°)	4.91×10^{19}
TiO_2	9.27×10^{20} (120°)	3.1×10^{20} (400°)	9.14×10^{19}

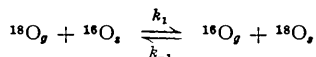
corresponding figures obtained from the water-vapour exchange experiments and the nitrogen-adsorption isotherms of Part II. (Zinc oxide is not considered here since the exchange reaction is very slow for this oxide, even at 500°; a detailed examination of zinc oxide is in progress and will be reported later.) It seems reasonable to ascribe the initial rapid exchange to reaction between adsorbed ^{18}O -enriched gas and surface oxygen ions, and the slower exchange to either or both of the following causes: (a) reaction with much less active parts of the surface such as stable and relatively complete crystal faces, or the surface exposed inside Smekal cracks, etc., or (b) to a slow diffusion of ions from the second layer in the solid to the surface, where exchange occurs. It is not possible at present to decide between these possibilities, but it is planned to measure the diffusion of ^{18}O into various oxides at higher temperatures so that the extent of diffusion at the lower temperatures considered here may be estimated. These diffusion measurements will themselves be of great interest apart from their application to the present problem.

The velocity constants k_e obtained directly from the plots of $\log_{10}(^{18}\text{O}_t - ^{18}\text{O}_\infty)$ against time are not absolute values: we may write

$$- da/dt = k_e(\alpha - \alpha_\infty) \quad \dots \quad (1)$$

where k_e is the experimental velocity constant, and the α terms refer to ^{18}O atom fractions in the gas phase.

We may regard the exchange reaction as essentially



and make the assumption that $k_1 = k_{-1}$, which will be very nearly true. The symbols O_g and O_s refer to the reacting species, of the gas and solid respectively, and need not for the present purpose be more closely identified.

The velocity of the exchange reaction is

$$v = -n_g \cdot da/dt = n_g k_e (\alpha - \alpha_\infty) \quad \dots \quad (2)$$

$$= k_1 w n'_s C_g [\alpha(1 - \beta) - (1 - \alpha)\beta]$$

$$= k_1 w n'_s C_g (\alpha - \beta) \quad \dots \quad (3)$$

where k_1 is the absolute velocity constant, C_g is the concentration of oxygen gas in the reaction zone, and β is the atom fraction of ^{18}O in the solid surface at time t .

If we assume that C_g does not change with the oxygen gas pressure (for example, if we suppose that C_g refers to a saturated chemisorbed layer of oxygen upon the oxide surface) we may put

$$v = k_0 w n'_s (\alpha - \beta) \quad \dots \quad (4)$$

The above equations assume that the reacting portion of the gas, C_g , is in isotopic equilibrium with the remainder.

At any time during the reaction

$$(\alpha_0 - \alpha)n_g = (\beta - \beta_0)n'_{i,w} \dots \dots \dots (5)$$

and at the end of the reaction

$$(\alpha_0 - \alpha_\infty)n_g = (\beta_\infty - \beta_0)n'_{i,w} \dots \dots \dots (6)$$

and we have already assumed that

$$\beta_\infty = \alpha_\infty \dots \dots \dots (7)$$

where α_0 and β_0 are the values of α and β when $t = 0$. Equations (2 and 4—7) yield

$$k_s = k_0(\alpha_0 - \beta_0)/(\alpha_\infty - \beta_0) \dots \dots \dots (8)$$

The results are given as values of k_0 , obtained from equation (8); k_0 is independent of the relative proportions of gas and solid present in the reaction system, and should be independent of the oxygen gas pressure, provided that the constancy of C_g , assumed above, is correct: the results show that this appears to be so over a wide pressure range for $\gamma\text{-Al}_2\text{O}_3$.

We cannot yet identify the process being measured, which in the case of $\gamma\text{-Al}_2\text{O}_3$ has an activation energy of 37.3 ± 0.5 kcal. The exchange must involve at least three steps: (a) adsorption of the gas, (b) exchange, (c) desorption: there is probably a dissociation into atoms between (a) and (b) and a corresponding recombination process between (b) and (c). Any of these stages may be rate-determining, and indeed the limiting reaction may depend on the temperature of observation; there are no data from other studies which enable any choice to be made with certainty, but a study of the rates of adsorption and desorption of oxygen is planned and should be valuable in this respect. Detailed discussion of the significance of the present results is reserved until this has been done.

Acknowledgment is made to Professor H. V. A. Briscoe for his interest and encouragement, to Imperial Chemical Industries Limited for financial assistance towards the expenses of maintaining the mass spectrometer, and to the Central Research Fund of London University for a grant for the purchase of equipment.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[Received, November 23rd, 1949.]