

240. *Studies of the Exchange Reactions of Solid Oxides. Part II. The Exchange of Oxygen between Water Vapour and Certain Metallic Oxides.*

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Experiments are reported on the exchange of ^{18}O between water vapour and $\gamma\text{-Al}_2\text{O}_3$, ThO_2 , and TiO_2 ; the amount of exchange is discussed in relation to the water content and the surface area (as determined by nitrogen-adsorption isotherms) of the powders.

THIS work was prompted by a wish to study the nature of certain catalytic reactions using ^{18}O , and we examined first the dehydration and dehydrogenation of alcohols upon alumina and thoria. Clear-cut results could not be obtained, however, because of the extreme ease of the exchange of oxygen between water vapour and the oxide; preliminary experiments demonstrating this exchange, and its general characteristics are reported here. Because of the relatively large amounts of water required for analysis the technique used to study the reaction is somewhat crude; it is intended later to repeat and extend the work by using very much smaller quantities of water which, after reaction, will be equilibrated isotopically with carbon dioxide, and the carbon dioxide analysed by mass spectrometer. Such facilities were not available at the start of this work, but should now permit a detailed examination of the kinetics of the reaction. It may be noted that in experiments similar to those reported below we found that deuterium was very labile on the surface of alumina. Thus D_2O vapour exchanged rapidly with the H_2O associated with the alumina, while the hydrogen in ethylene suffered ready exchange with the hydrogen in alumina at 300° .

EXPERIMENTAL.

Materials.—The heavy-oxygen water was some residual material of relatively low enrichment previously prepared in these laboratories by fractional distillation; it was normalised with respect to deuterium by repeated equilibration with ammonium chloride. The oxides were those used in Part I.

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Method.—The exchange reaction was followed by determining the density of the water to $\pm 0.5 \gamma d$ by the semi-micro-flotation method of Briscoe *et al.* (*J.*, 1934, 1207; 1937, 1492) ($1 \gamma d \equiv 1$ part in 10^6 of density).

25 G. of the oxide were weighed into a glass tube and confined, so as to fill the cross section of the tube, between two plugs of glass wool. The tube was connected at each end through a standard ground joint to a cold trap and then to the main vacuum line and pumping system; the portion of the tube containing oxide was surrounded by an electrically-heated furnace. The oxide was heated to the temperature of the experiment and pumped for 8 hours to a pressure of 10^{-4} mm. of Hg or less; the water evolved was collected in a trap cooled to -78° and weighed. 1 ml. of heavy-oxygen water was then distilled *in vacuo* to and fro over the oxide, the density being determined from time to time, until no further rapid exchange took place. Eight such distillations, taking about 4 working days, each distillation taking about 4 hours, were sufficient in all cases. The treatment with the water was then continued for a further 14 distillations in order to determine the extent of the slow exchange (cf. below).

The apparent surface areas of the oxides were found by measuring the adsorption isotherms of nitrogen at 76°K. , upon samples outgassed for at least 8 hours at the temperatures of the exchange reactions. In calculating the surface areas both the Harkins-Jura and the Brunauer-Emmett-Teller equation were employed; excellent plots were obtained, and the two methods agreed well (to within 1%) in all cases, provided that the constant in the first equation was taken as 4.06 and the area occupied by the nitrogen molecule as 15.1 \AA.^2 for the B.E.T. equation; these values were therefore used by us and they are in general agreement with those found necessary by other workers. The results are summarised in the table.

Expt.	Oxide.	Temp.	Water content,* g./25 g. of oxide.	Excess density of H_2^{18}O , $\Delta \gamma d$.			Surface area, $\text{m.}^2/\text{g.}$
				Initi- ally.	After 8 distillns.	After 22 distillns.	
1	Al_2O_3	20°	0.526	105.2	52.6	52.6	86.0
2	"	100	0.361	"	62.2	62.2	95.0
3	"	200	0.158	"	55.4	52.7	94.3
4	"	400	0.160	"	47.1	39.6	94.5
5	ThO_2	120	0.078	"	83.5	82.8	3.85
6	TiO_2	120	—	"	62.2	62.0	7.20

* At the temperatures given in col. 3; obtained by the difference between the water content found by igniting the oxide in air to constant weight, and the water distilled off during the evacuation.

DISCUSSION.

It is evident from the table that, as in the exchange with gaseous oxygen (Part I), two processes occur; one resulting in an initial exchange which reaches equilibrium comparatively rapidly at all temperatures and which can readily be shown (by a simple calculation from the weights of oxide and heavy water present) to involve only a small fraction of the oxygen present in the sample of oxide used, and the other resulting in a very much slower exchange. The exchange with alumina is the most thoroughly studied and here it is seen that the slower process must have an appreciable activation energy since it decreases rapidly in rate as the temperature is lowered and becomes inappreciable, under the conditions used, at 100° . The cases of the other oxides are doubtless similar. There are at least two possible explanations of the observations: (a) The rapid process is an exchange of the surface oxygen ions of the oxide (plus perhaps the exchange of all or part of the water still left in the oxide), and the slow process is the exchange of the second layer of oxygen ions in the lattice. (b) The rapid process is an exchange of part of the surface ions, and the slow process represents the completion of the surface exchange, being the slow exchange of poorly-reactive parts of the surface, of Smekal cracks, capillaries, etc., and/or of partly poisoned surface. There is much evidence that the surface of a solid is by no means uniform in catalytic activity, so that the second explanation is quite plausible, but for the present we shall discuss our results in terms of the first hypothesis.

Before comparing the readily exchangeable oxygen with the surface area as measured by nitrogen adsorption we note that the water present in the $\gamma\text{-Al}_2\text{O}_3$ appears to be held in two ways; the more labile part is readily removed at 200° ; the more firmly bound water, amounting to 0.16 g./25 g. of alumina, is not removed at 400° . To eliminate any possible complication due to exchange with the labile water we discuss the results of Expt. 3 (see table). We see that during the final fourteen distillations, which took 7 days, the water density fell from 55.4 to 52.7 γd ; this corresponds to an exchange with 0.080 g. of oxygen from the oxide. The first eight distillations took four days and we may as a rough approximation say that if the slow reaction is due to diffusion of oxygen through the solid, the equivalent of 0.02 g. of oxygen which has exchanged with the water will in this time have diffused from the exchange zone and have been replaced by fresh oxygen of normal isotopic content. The rapid reaction shows as a fall in water density from 105.2 to 55.4 γd , which corresponds to exchange with 0.80 g. of oxygen; thus the corrected figure for rapidly exchangeable oxygen is roughly 0.78 g. per 25 g. of alumina. To calculate the surface area of $\gamma\text{-Al}_2\text{O}_3$ occupied by 0.78 g. of oxygen we assume

that the [100] planes of a cubic close-packed oxide lattice are those mainly exposed at the surface. (This is not, of course, an accurate picture, but will suffice for our rough calculations.) Under these conditions the area occupied by n oxygen ions is $4nr^2$, where r is the ionic radius, for which we take Pauling's value of 1.4 Å., and the area occupied by 0.78 g. of oxygen is then 2300 sq. m. The sample used weighed 25 g., so our calculation gives a surface of 92 sq. m./g. which agrees closely with the value of 94—95 sq. m. obtained from the nitrogen isotherms. In view of the crude nature of the foregoing calculation and the uncertainty as to what the B.E.T. or the Harkins-Jura treatment really tells us about the surfaces of solids, no important significance can be attached to the agreement obtained above without a considerable amount of further work.

Turning to Expts. 1 and 2, we find that the amount of exchangeable oxygen is 0.889 g. and 0.615 g., respectively, per 25 g. of oxide, while the difference in water content between the samples used is 0.165 g., corresponding to 0.147 g. of oxygen. Thus 0.147 g. of oxygen (as water), removed from the oxide by outgassing at 100°, reduces the exchangeable oxygen in the sample by 0.274 g. It therefore appears that each water molecule, present as labile water, facilitates the exchange of two oxygen atoms—its own and one in the surface of the alumina. An exchange mechanism involving the two hydrogen atoms is an attractive way of explaining this result, but the present work is not extensive enough to warrant detailed speculation. It is doubtless significant in this connection that the results given here show that ^{18}O exchange between water vapour and $\gamma\text{-Al}_2\text{O}_3$ occurs much more readily than the exchange between the oxide and oxygen gas reported in Part I.

It is noteworthy that the increase in surface area of 9 sq. m./g. obtained by outgassing the alumina at 100° instead of 20° is reversible and apparently closely associated with the loss of 0.165 g. of water. A quantity of oxide was outgassed at 20°, and possessed the normal surface area of 86 sq. m./g. The same sample was then outgassed at 100°, as in Expt. 2, and gave a surface area by nitrogen adsorption of 95 sq. m./g.; on exposure to water vapour for some time until water was no longer rapidly taken up, followed by outgassing as before at 20° (which treatment removed some water), a surface area of 86 sq. m./g. was again obtained.

A temperature of 120° was used for the experiments with thoria and titania in order to eliminate from the oxide any loosely adsorbed water, the temperature being chosen also so that, judging from the results on alumina, no significant amount of the slow exchange would occur. It is seen that the latter expectation was realised. By similar calculations to that outlined above it can be shown that the exchangeable oxygen in thoria corresponds to a surface of about 27 sq. m./g. and in titania to 73 sq. m./g. Thus in these cases there is only an order of magnitude agreement between the exchangeable surface and that deduced from the nitrogen isotherms.

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