*The Oxides of Uranium. Part V.** *The Chemisorption of Oxygen on* UO_2 *and on* UO_2–ThO_2 *Solid Solutions.*

By L. E. J. Roberts.

[Reprint Order No. 5302.]

Oxygen is rapidly chemisorbed by freshly reduced surfaces of uranium dioxide at −183°, and also by surfaces of mixed crystals of uranium dioxide and thorium dioxide if these surfaces are prepared by crushing macrocrystalline samples. One oxygen molecule reacts with a single U^{4+} site in the primary act of chemisorption. At least half the U^{4+} ions in the surface layers react with oxygen and only about 30% of the occupied sites become vacant on high-temperature evacuation. There is evidence that Th^{4+} ions concentrate preferentially in the surface layers of some mixed-crystal preparations.

Uranium dioxide is commonly prepared by reduction with hydrogen or carbon monoxide at high temperatures, and the oxide so prepared can be shown to be $UO_{2.0}$ as closely as analytical accuracy permits. The oxide is oxidised readily in air at temperatures between 100° and 180°, taking up additional oxygen to a composition at least $UO_{2.25}$ without any change in the original fluorite crystal structure except a slight contraction of the unit cell (Anderson and Alberman, *J.*, 1949, S 303). The oxygen enters interstitial positions in the uranium dioxide lattice without the nucleation of a new phase at low temperatures, and the surface area remains unchanged as oxidation proceeds (Anderson and Roberts, to be published). It has been found that the solution of oxygen in uranium dioxide commences at temperatures even lower than the 27 kcal./mole activation energy of the bulk oxidation hitherto studied would lead one to expect; uranium dioxide preparations that have been exposed to air at room temperature always contain oxygen in excess of the stoicheiometric formula, in amounts proportional to their specific surface area. The present work is concerned with a chemisorption of oxygen on uranium dioxide, which is practically instantaneous even at −183°, and which must therefore occur with zero or very low activation energy. The study was extended to include uranium dioxide–thorium dioxide mixed crystals in order to discover the effect on the surface reaction of diluting the sites capable of reacting with oxygen, presumably the U^{4+} ions in the crystal surface, with Th^{4+} ions which would not be expected to react, because of their inability to donate electrons.

Experimental

Uranium Dioxide Preparations.—The preparation and properties of the uranium dioxide specimens used are listed below. Starting materials were " AnalaR " uranyl nitrate or the very pure grade of " ammonium diuranate " available in the atomic energy project. The preparations were characterised by: (i) *X*-Ray diffraction patterns, all of which showed the lines expected for the dioxide, with a cube cell edge of 5·457 ± 0·002 k.X.U. and a theoretical density of 10·96 g./c.c. The effective crystallite diameter, $\bar{a}$, was estimated from the half-width of the *X*-ray lines by comparison with a well-crystallised sample of particle size $\sim 2{\cdot}5\ \mu$, the calculations being made by Jones's methods (*Proc. Roy. Soc.*, 1938, *A*, **166**, 16). (ii) The real density as measured with helium. (iii) The mean particle diameter, $\bar{d}$, calculated from the specific surface area as measured by B.E.T. analysis applied to the physical adsorption isotherms of nitrogen at −196° or of oxygen at −183° (Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309).

Key to designation of UO_2 *specimens.*

B1. Prepared by reducing the trioxide with hydrogen at 650°. Density 10·84 g./c.c., $\bar{d} = 0{\cdot}45\ \mu$, $\bar{a} = 0{\cdot}22\ \mu$.

C3. Prepared by reducing triuranium octoxide with carbon monoxide at 700°. Density 10·90 g./c.c., $\bar{d} = 0{\cdot}41\ \mu$, $\bar{a} = 0{\cdot}38\ \mu$. The particles were therefore probably single crystals.

H. A pure grade of commercial dioxide. Density 10·15 g./c.c., $\bar{d} = 1{\cdot}0\ \mu$, $\bar{a} = 0{\cdot}18\ \mu$. The low density and high d/a ratio suggested that the microstructure was complicated, each particle being probably composed of a large number of crystallites.

---

* Part IV, preceding paper.

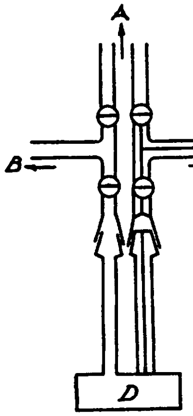
B50. Prepared by reducing the trioxide with carbon monoxide at 480°. $\bar{d} = 0{\cdot}053\ \mu$, $\bar{a} \sim 0{\cdot}05\ \mu$.

R. Prepared from specimen H by sintering at 2200° in a vacuum furnace, breaking the sintered pellet in a percussion mortar, and finely grinding the crystalline, glistening product in an agate mortar. The vacuum furnace was described by Alberman (*J. Sci. Instr.*, 1950, **27**, 280). The density was 10·85 g./c.c., $\bar{d} = 2{\cdot}3\ \mu$, $\bar{a} > 1\ \mu$. The particles were probably broken single crystals.

CA. Prepared from sample C3 by sintering at 2000° and crushing. $\bar{d} = 2{\cdot}3\ \mu$, $\bar{a} > 1\ \mu$.

Mixed-crystal Preparations.—Uranium dioxide and thorium dioxide form a continuous series of mixed crystals (Slowinski and Elliot, *Acta Cryst.*, 1952, **5**, 768). Two types of preparation were used. The first series of mixed crystals was prepared by coprecipitating the hydroxides from a mixed nitrate solution, drying, and reducing the product with carbon monoxide at 1200—1400°. Full details of these preparations are given in Part IV of this series (*loc. cit.*). The second series was made from the first by sintering at 1800—2100° and crushing the large crystals formed. All the precipitations were well-crystallised and had the expected apparent cell edge, which was a linear function of composition.

FIG. 1. *Adsorption bulb.*



A, to gas supply and pumps.
B, to McLeod gauge.
C, to mercury manometer and gas burette.
D, Adsorbent.

Adsorption Apparatus.—Measurements of gaseous adsorption could be made in two pressure ranges. A constant-volume mercury manometer was used for pressures above 10 mm., and read to ±0·2 mm.; a modified McLeod gauge measured pressures from 5×10^{-2} mm. to 6 mm. with an accuracy of ±2% above 0·1 mm. The powdered sample was contained in a " Vitreosil " U-tube, of which one limb was 1-mm. silica capillary and the other 5-mm. tubing. The capillary limb was connected by a cone-socket joint to the Pyrex capillary line joining the gas burette and constant-volume manometer, while the 5-mm. limb was connected through 5-mm. Pyrex tubing to the McLeod gauge. The arrangement is shown in Fig. 1. The high- and low-pressure measuring systems could be used independently on any one sample. During low-temperature adsorption measurements, the silica holder was surrounded by liquid oxygen or liquid nitrogen to a height of 2 in. above the sample bulb. At low pressures, the thermal gradient was thus carried by a 5-mm. diameter tube, and no thermomolecular flow corrections had to be applied to the pressure measurements so long as the pressure was >0·1 mm. The accuracy of the adsorption measurements varied according to the surface area of the adsorbent, being greater for the larger surface areas, but was judged to be generally better than ±3%. The temperature of the liquid-air baths was measured with an oxygen vapour-pressure thermometer.

B.O.C. " Spectroscopically Pure " oxygen and nitrogen were used without further purification. Hydrogen for reduction was obtained from a cylinder, and passed over hot platinised asbestos and through potassium hydroxide and magnesium perchlorate tubes. Carbon monoxide was obtained either by the action of sulphuric acid at 120° on formic acid or from a cylinder, and in each case was passed through potassium hydroxide, a liquid-oxygen trap, copper foil at 500°, potassium hydroxide, and a second liquid-oxygen trap. B.O.C. " Spectroscopically Pure " helium was used for determining the volumes of the gas leads and adsorption bulbs, and when used at low temperatures was first purified by passage through a charcoal trap at −195°. Taps were lubricated with Apiezon Grease " L " or " N " or with Dow Corning High Vacuum Silicone Lubricant if the taps were liable to get warm. Joints were made with Apiezon " W " wax.

Experimental Procedure.—The experiments essentially consisted of a comparison of adsorption isotherms of oxygen at −183° on " reduced " and " oxidised " surfaces of UO_2 and of the mixed crystals.

Reduction was carried out by streaming small volumes of hydrogen or carbon monoxide through the adsorption bulb at temperatures of 500—700°. The specimen was pumped out between each dose of reducing gas and the reduction continued until the amount of water or carbon dioxide that could be frozen out of the issuing gas had fallen to a constant low value. The specimen was then normally pumped out at 50° above the temperature of reduction until the system held a pressure <1 μ when isolated from the pumps, which generally took about 30 min. The specimen was then cooled in liquid oxygen for 1—2 hr., or for at least 30 min. if about 1 cm. of purified helium was added to aid the attainment of thermal equilibrium. The helium was pumped off, oxygen admitted, and adsorption measurements commenced. Equilibrium was apparently established in a few minutes if the gas pressure was higher than 1 cm.; equilibrium times were of the order of 30 min. if the pressure was lower than 1 mm.

After this determination of the oxygen adsorption isotherm on a "reduced" surface, the sample was either (*a*) pumped at $-183°$ for $\frac{1}{2}$—1 hr. and at $-80°$ for 10 min., or (*b*) allowed to oxidise at 0° or 23° until the rate of oxidation became low, and then outgassed for 5 min. at 0° or 23°. The sample was then cooled to $-183°$ as before, and a second adsorption isotherm of oxygen at $-183°$ determined; this was the isotherm characteristic of an "oxidised" surface. Any variations of this procedure are discussed with the results. All the gas adsorbed during the determination of the second isotherm could be recovered by warming the adsorbent to 25°. Adsorption on the oxidised surface was therefore taken to be physical adsorption only. If the isotherm on the oxidised surface had not been determined in a pressure range suitable for treatment by the B.E.T. equation, the isotherm was redetermined at relative pressures (p/p_0) of $\sim 0{\cdot}02$ to $0{\cdot}15$. In some cases, the physical adsorption of nitrogen was measured in the same pressure range at $-196°$.

The B.E.T. equation was used in the simple form:

$$\frac{p/p_0}{V(1 - p/p_0)} = \frac{p/p_0}{V_mC} + \frac{C - 1}{V_mC}$$

where V is the volume of gas adsorbed at a relative pressure p/p_0, V_m is the monolayer volume, and C a constant related to the heat of adsorption.

RESULTS AND DISCUSSION

The adsorption of oxygen on the reduced surfaces at $-183°$ and at any pressure was greater than on the oxidised surfaces, except in the case of some of the mixed crystals, which is discussed below. Two typical isotherms are shown in Fig. 2. It was clear that chemisorption occurred on the reduced surfaces at $-183°$; it was complete within a few minutes of admitting oxygen, and this time was probably due only to the dimensions of the apparatus; the amount chemisorbed at $-183°$ showed no signs of increasing in several hours' exposure. At higher temperatures an additional, time-dependent reaction occurred. A plot of the total amount of oxygen reacting at 0° against time of exposure for three samples of the C3 specimen is shown in Fig. 3: oxygen was admitted to the reduced surface at 0° in two cases, and in the third case was admitted first at $-183°$ and subsequently at 0°. The amounts reacting are divided by $V_m(N_2)$, the amount of nitrogen required to form a physically adsorbed monolayer calculated from the B.E.T. equation in order to correct for small differences in surface area introduced during the high-temperature reduction process. The results showed that the total attack at 0° was the sum of two processes, one of which was complete at $-183°$.

The amounts chemisorbed were calculated by direct subtraction of the isotherm relating to the oxidised surface from that determined on the reduced surface, as in Fig. 2. If the oxygen had been pumped off at $-183°$ and $-80°$ after the first isotherm and the second determined immediately, the two curves were accurately parallel over the whole pressure range ($p/p_0 = 10^{-4}$ to 10^{-1}). If oxidation at higher temperatures had occurred before the determination of the physical adsorption isotherm, the two isotherms were parallel at higher pressures ($p/p_0 = 10^{-2}$ to 10^{-1}), as in Fig. 2, but some divergence occurred at relative pressures below 10^{-3}, the apparent amount chemisorbed being larger at lower pressures. This effect seemed to be due to a change in the heat of physical adsorption of oxygen on the oxidised surface caused by the high-temperature oxidation. Such a change would particularly affect the physical adsorption isotherm at low relative pressures; around $p/p_0 \sim 0{\cdot}1$, where a physically adsorbed monolayer would be nearly complete, small changes in heats of adsorption would affect the isotherm less.

Hence, if oxidation had occurred at 0° or above, the physical adsorption was determined only at the higher relative pressures; when it was necessary to determine the amount chemisorbed at low pressures, because the amount was small, the temperature of the specimen was not raised above $-80°$ between the two isotherms. Direct comparisons of the amounts chemisorbed by determining the physical adsorption isotherm at high pressures (*a*) after pumping at $-80°$ and (*b*) after bulk oxidation gave results in agreement within 5%.

Chemisorption on Uranium Dioxide.—The volume of oxygen (V_0 c.c., N.T.P.) chemisorbed at $-183°$ on various samples of uranium dioxide is recorded in Table 1, together with the essential details of the treatment of the sample before the isotherms were determined, and the values of $V_m(O_2)$, the volume of oxygen at N.T.P. required to form a monolayer of physically adsorbed oxygen on the surface of the sample, as calculated by the B.E.T. equation from the oxygen isotherm on the oxidised surface. Since $V_m(O_2)$ was determined after oxidation at very low temperatures, the value was characteristic of the surface upon which chemisorption had occurred. Changes in the extent of the adsorbing surface of a particular sample occurred only during the high-temperature reduction processes, and were probably connected with the tendency of the oxidised uranium dioxide samples to split into two phases of constant composition ($UO_{2\cdot0}$ and U_4O_9) at temperatures a little below those at which rapid reduction occurred (>450°). Increases in surface area due to particle division on high-temperature annealing have been observed. The final surface after any reduction was then the result of two competing processes: particle division and the sintering of some of the smaller particles, which was shown in separate experiments to occur at all temperatures above 500°. Hence the surface on which chemisorption took place was at least partly a fresh surface in each experiment, even on the same specimen of UO_2.

FIG. 2. *Adsorption of oxygen at* $-183°$ *on reduced and oxidised surfaces of uranium dioxide.*

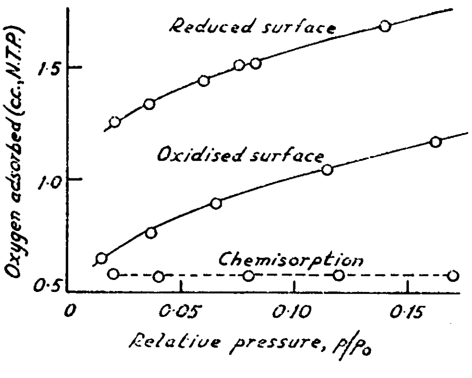
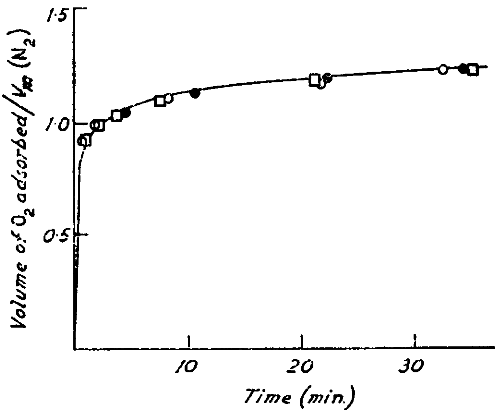


FIG. 3. *Oxygen absorption by uranium dioxide at* 0°.



□ Oxidation at 0° and 17 cm. pressure after chemisorption at $-183°$; $V_m(N_2) = 0{\cdot}373$ c.c./g.

○ Oxidation at 0° and 12 cm. pressure; $V_m(N_2) = 0{\cdot}404$ c.c./g.

● Oxidation at 0° and 12 cm. pressure; $V_m(N_2) = 0{\cdot}410$ c.c./g.

The amount of oxygen chemisorbed was remarkably independent of all factors except the extent of the adsorbing surface. The last column in Table 1 gives the values of the ratio $V_0/V_m(O_2)$, the amount of oxygen chemisorbed per standard area of surface. All V_0/V_m values were between 0·3 and 0·9, independent of the temperature at which the uranium dioxide had originally been produced or at which reduction took place before chemisorption, of which reducing gas was used, and of whether the preparation consisted of broken crystals (CA and R) or of dioxide as prepared by reduction of a higher oxide. Some systematic variations in $V_0/V_m(O_2)$ values occurred. The average value of V_0/V_m for those preparations which had never been in hydrogen (C3, CA, and B50) was 0·64 and for the two in closest agreement (C3 and CA) 0·55, while the average V_0/V_m value for those reduced with hydrogen (B1, H, and R) was 0·45. This difference can be ascribed to a change in surface properties following upon the chemisorption of hydrogen, It has been found that uranium dioxide is capable of chemisorbing hydrogen in quantites at least sufficient to form a complete monolayer by an activated process that occurs rapidly above 550°. It is difficult to remove the hydrogen quantitatively even at considerably higher temperatures, and the pumping conditions employed here after reduction by hydrogen may well have been insufficient to remove all chemisorbed gas. A direct test

TABLE 1.

UO_2 sample	Treatment of sample: before 1st isotherm	before 2nd isotherm	V_0, c.c./g.	$V_m(O_2)$, c.c./g.	V_0/V_m
C3	CO, 580°	O_2, 0°	0·220	0·403	0·55
	CO, 700	Pumped −80	0·183	0·321	0·57
	CO, 580	Pumped −80	0·210	0·403	0·52
CA	CO, 700	O_2, 0	0·0295	0·052	0·57
	CO, 700	O_2, 0	0·0300	0·057	0·54
B50	CO, 480	Pumped −80	2·30	2·71	0·85
	CO, 480	O_2, 20	2·40	2·69	0·86
B1	H_2, 550	O_2, 22	0·185	0·332	0·56
	H_2, 740	O_2, 22	0·168	0·332	0·51
	H_2, 530	O_2, 22	0·146	0·320	0·46
	H_2, 500	O_2, 22	0·171	0·311	0·55
H	H_2, 500	O_2, 0	0·065	0·139	0·47
	H_2, 550	O_2, 22	0·059	0·133	0·45
R	H_2, 500	O_2, 23	0·0262	0·069	0·38
	H_2, 500	O_2, 22	0·0238	0·062	0·39
	H_2, 700	O_2, 22	0·0148	0·051	0·29

TABLE 2. *Adsorption of oxygen on uranium dioxide at* −183° *following chemisorption of hydrogen.*

Sample	Hydrogen chemisorbed, c.c./g.	Temp. at which H_2 removed	V_0, c.c./g.	$V_m(O_2)$, c.c./g.	V_0/V_m
B1	0·23	22°	0·151	0·332	0·46
	0·42	22	0·146	0·332	0·44
	—	740	0·185	0·332	0·56
C3	0·34	200	0·165	0·354	0·47

TABLE 3.

Sample	Reduction conditions	V_0, c.c./g.	Pumping conditions after O_2 chemisorption: Time	Temp.	V_1, c.c./g.	V_1/V_0
B1	H_2, 550°	0·185	30 min.	22°	0·034	0·18
			30 ,,	140	0·050	0·27
			30 ,,	400	0·060	0·33
R	H_2, 700	0·0148	3 hr.	25	0·0051	0·33
			24 ,,	25	0·0033	0·21
			1 ,,	150	0·0033	0·21
C3	CO, 580	0·220	16 ,,	25	0·0078	0·035
			2 ,,	170	0·043	0·20
$U_{0·82}Th_{0·18}O_2$	CO, 750	0·290	16 ,,	25	0·060	0·21

showed that the chemisorption of hydrogen lowered the V_0/V_m value for subsequent oxygen chemisorption. The results of two experiments in which $V_0/V_m(O_2)$ values were determined in the usual way on surfaces of uranium dioxide that had chemisorbed known quantities of hydrogen and then been outgassed at temperatures sufficiently low, so that none of the hydrogen was removed, are given in Table 2. It is apparent that the $V_0/V_m(O_2)$ value characteristic of a hydrogen-covered surface is 0·46—0·48, and that prolonged pumping at 740° causes the $V_0/V_m(O_2)$ value to rise to 0·57, in agreement with values found after reduction by carbon monoxide (Table 1). This gas is not chemisorbed at high temperatures to anything like the extent that hydrogen is. A small chemisorption was observed, reaching, at constant pressure, a maximum of ~8% coverage at ~250°, and falling to barely measurable amounts above 600°. No carbon dioxide was formed when the monoxide was left in contact with a fully reduced C3 sample for 10 hr. at temperatures between 670° and room temperature.

It seems fair to conclude that the $V_0/V_m(O_2)$ values on specimens reduced by carbon monoxide were characteristic of " clean " uranium dioxide surfaces. It is not clear why the $V_0/V_m(O_2)$ ratio rose to 0·9 on the B50 sample, but this is probably due to the highly disordered, " active " nature of the surface of this specimen, which had been made at relatively low temperatures (480°), consisted of very small particles, of about 500 Å diameter, and was poorly crystalline. The other anomaly is the values below 0·4 which were determined on one of the crushed crystal samples (R), though the other crushed crystal sample (CA) showed normal behaviour. It is possible that sample R had been " poisoned " more extensively by hydrogen, or that the crystals had cleaved in a different way when crushed, to expose less active surfaces.

The chemisorbed layer formed at $-183°$ remained complete so long as the dioxide was in contact with oxygen, *i.e.*, the second or physical adsorption isotherm on any one sample remained essentially unchanged whether oxidation occurred at 0°, 25°, or 135°. (These results are not recorded in Table 1 since only the low-pressure parts of the isotherms were determined.) The results in Table 1 show that no additional chemisorption took place on readmitting oxygen to a uranium dioxide surface that had been exposed to oxygen at $-183°$ and then pumped at $-80°$. But some additional chemisorption did occur when the chemisorbed layer was pumped at higher temperatures. The results are collected in Table 3. The V_0 values were determinated as before from $-183°$ isotherms on the freshly reduced and fully oxidised surfaces, and the V_1 values quoted are the additional chemisorption found after the oxygen had been removed from the original chemisorbed layer at $-183°$ and $-80°$ and the uranium dioxide sample pumped at the temperature shown in Col. 3 of Table 3; V_1 was calculated by subtracting the $-183°$ isotherm on the fully oxidised surface from that obtained after the given pumping treatment. The experiments are quoted in chronological order, and it is clear that a certain amount of oxygen can be lost from surface sites at 25° whatever the previous history of the specimen, so long as bulk oxidation has been avoided. The results on the three samples of uranium dioxide are in reasonable quantitative agreement for the experiments in which the evacuation was carried out at 140—170°, when about 25% of the original chemisorbed layer was lost from the surface sites. Only about 33% was lost even on heating to 400°. One result on an 82 mole-% uranium dioxide–thorium dioxide mixed crystal is included in Table 4; the behaviour was very similar to that of uranium dioxide itself.

The surface oxygen is far less mobile than the previous bulk oxidation studies might suggest. Anderson and Alberman (*loc. cit.*) found that the bulk oxidation proceeded with an activation energy of 27·5 kcal./mole between 100° and 180°, which they ascribed to the energy required to move an oxygen atom from one interstitial position to the next in the uranium dioxide lattice. From their measured diffusion coefficients it can be calculated that each uranium atom should travel a mean distance inwards of 40 Å in 30 min. at 175°, and this conclusion is borne out by the fact that uranium dioxide which has reacted with oxygen at 0° for 30 min. and then been pumped for a short time at 150° absorbs more oxygen at nearly the same rate as it initially did when next exposed to oxygen at 0°.

Hence at least 70% of the chemisorbed oxygen is far more firmly bound to the surface sites than is oxygen than has already entered the uranium dioxide lattice. This conclusion is supported by some preliminary measurements of the heat of adsorption of oxygen at $-183°$, which may be as high as 50 kcal./mole on a clean dioxide surface, and which falls as the surface layer becomes completed.*

Chemisorption on Uranium Dioxide–Thorium Dioxide Mixed Crystals.—The chemisorption of oxygen at $-183°$ was measured on a series of mixed crystals in the same manner as on uranium dioxide; all the reductions were carried out with carbon monoxide. The results are shown in Fig. 4, $V_0/V_m(O_2)$ values being plotted against the composition of the crystals, expressed as moles % of uranium dioxide. There was a profound difference

---

* The author is indebted to Mr. J. D. M. McConnell for this information and for permission to mention it before publication.

between the behaviour of mixed crystals as reduced at 1200—1400° and of crushed crystals. Chemisorption per unit surface on the crushed crystals was a roughly linear function of the uranium content at least down to 15 moles % of uranium dioxide, while chemisorption on the samples as reduced fell to very low values below 57 moles % of uranium dioxide.

This difference was further illustrated by comparing the amount of oxidation occurring at 0° or 23° for the various specimens. The quantities of oxygen absorbed in the first 30 min. are collected in Table 4; after 30 min., the rate of oxidation became slow (Fig. 2). Longer times are recorded in Table 4 for the slower reactions. Pressures of oxygen were between 3 and 11 cm. The quantities recorded (V) do not include the oxygen chemisorbed at −183°. The $V/V_m(O_2)$ ratios are recorded in order to make a valid comparison of reaction rates. The rate was at least a factor of 10 higher on the crushed crystals having low uranium concentrations than on the reduced samples.

These results imply that Th^{4+} ions had been preferentially concentrated in the surface layer or layers of the reduced mixed crystals in the dilute uranium range. Surfaces that had been generated by crushing large crystals almost certainly contained a representative fraction of the U^{4+} and Th^{4+} cations, which must, from the crystallographic evidence, be randomly distributed throughout the bulk of the crystals. The preferential concentration of Th^{4+} ions in the surface of the reduced specimens could be a consequence of the equilibrium surface at 1300° not containing a random selection of cations, or it may have occurred during the coprecipitation process that was the first stage in the manufacture of these solid solutions.

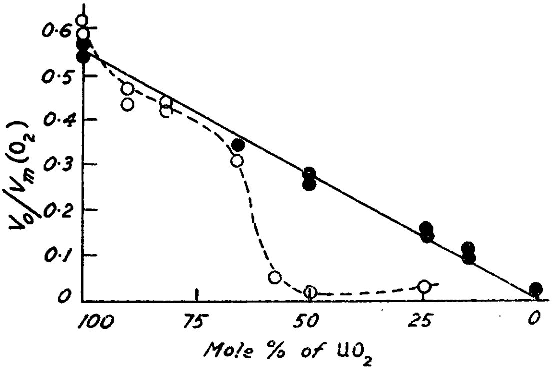


FIG. 4. *The chemisorption of oxygen at −183° on mixed crystals of uranium dioxide and thorium dioxide.*

● Crushed crystal preparations.
○ As reduced preparations.

The linear dependence of $V_0/V_m(O_2)$ on the mole-fraction of uranium dioxide, for surfaces that almost certainly contained a random distribution of U^{4+} and Th^{4+} cations, suggests that the primary act of chemisorption of oxygen at −183° involves the interaction of an oxygen molecule with a single U^{4+} site. In a face-centred array of cations, each cation has 4 nearest cation neighbours and thus most U^{4+} cations in a 25 moles % solution and almost all in a 15 moles % solution would be surrounded by Th^{4+} cations; it is unlikely that direct co-operation between two U^{4+} sites could occur. It is not clear from these considerations alone how many electrons are effectively transferred to the oxygen, or whether the molecule of oxygen dissociates in the primary act of chemisorption or not.

Extent of Surface Coverage.—The extent of the adsorbing surface may be calculated from $V_m(O_2)$ or $V_m(N_2)$ if an area is assumed for a physically adsorbed molecule. The area of 16·2 Å^2 for the nitrogen molecule at −196° is usually taken as a standard. The area of the oxygen molecule at −183° may be calculated from the density of the liquid to be 14·1 Å^2, and the ratio $V_m(N_2)/V_m(O_2)$ should therefore 1/1·15. The mean of four determinations of this ratio on various UO_2 samples was 1/0·97, and, to facilitate comparison with other work, the effective area of the oxygen molecule will be assumed to be 16·7 Å^2. Measurements of surface area are in any case not generally considered accurate in the absolute sense to better than ±25%.

The calculation of the number of U^{4+} sites in the surface is further dependent upon some assumption of the crystal planes that are outermost. The equilibrium surfaces and cleavage planes are likely to be planes of low index. The (100) planes, in the fluorite structure, consist alternately of O^{2-} and of U^{4+} ions; the (110) planes consist of both O^{2-} and U^{4+} ions and are electrically neutral. The area occupied by a U^{4+} ion is $a^2/2$ or 14·9 Å^2 in the (100) planes and $a^2/\sqrt{2}$ or 21 Å^2 in the (110) planes. The area per ion will increase for planes of higher indices. Thus the maximum number of U^{4+} ions per physically adsorbed oxygen molecule (16·7 Å^2) will be 1·12—0·80, *i.e.*, there cannot be more than about 1 surface U^{4+} ion per oxygen molecule physically adsorbed on UO_2. The value of 0·58 for the $V_0/V_m(O_2)$ ratio on UO_2 therefore implies that at least half the U^{4+} ions in the surface are active in chemisorbing oxygen at −183°, one oxygen molecule being assumed to react with one U^{4+} site. It is not possible to postulate particular sites for the chemisorption : virtually the whole surface is active. This type of chemisorption, taking place on the whole surface with zero or very low activation energy, differs from the chemisorption of oxygen on oxides such as cuprous oxide, which is an activated process, occurring slowly at room temperature, although at least a monolayer of oxygen may eventually be adsorbed (Garner, Stone, and Tiley, *Proc. Roy. Soc.*, 1952, *A*, **211**, 472). The case of uranium dioxide is more closely analogous to that of metals, which are covered by a chemisorbed layer of oxygen swiftly at −183° (Allen and Mitchell, *Discuss. Faraday Soc.*, 1950, **8**, 309; Brunauer and Emmett, *J. Amer. Chem. Soc.*, 1940, **62**, 1732); the similarity is possibly due to the ready availability of electrons in both cases.

TABLE 4. *The oxidation of* $U_xTh_{1-x}O_2$ *preparations at* 0° *and* 23°.

Preparation Type	x	Oxidation conditions			O_2 absorbed, V, c.c./g.	$V_m(O_2)$, c.c./g.	$V/V_m(O_2)$
		Temp.	Mean pressure, cm.	Time			
Crushed crystals	1·00	0°	7	30 min.	0·0332	0·0565	0·59
	0·66	0	9	,,	0·043	0·129	0·33
	0·50	0	7	,,	0·0134	0·051	0·26
	0·24	0	6	,,	0·0039	0·074	0·053
	,,	23	6	,,	0·010	0·070	0·143
	0·15	23	6	,,	0·00039	0·052	0·0075
As reduced	1·00	0	11	30 min.	0·27	(0·40)	0·67
	0·90	0	10	,,	0·59	1·04	0·57
	0·82	0	7	,,	0·33	0·65	0·53
	,,	23	8	,,	0·475	0·65	0·73
	0·66	0	6	,,	0·042	0·114	0·37
	0·57	23	3	,,	0·0004	0·021	<0·02
	0·50	23	4	48 hr.	<0·0005	0·035	<0·01
	0·24	23	5	16 ,,	<0·001	0·034	<0·03

The oxidation processes occurring at 0° and 25°, for which some results have been given, cannot be further surface processes; solution of oxygen in the uranium dioxide lattice must be involved, since the amounts of oxygen taken up in long times of exposure may be four times the amount chemisorbed at −183° and this is far too much to be accommodated on the surface on any reasonable model.

The author gratefully acknowledges help and criticism received from Dr. J. S. Anderson in the course of this work. He is indebted to Mr. D. N. Edgington for the mixed-crystal preparations and to Mr. E. A. Harper for the helium-density measurements.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, DIDCOT, BERKS.

[*Received, April* 13*th*, 1954.]