The Oxides of Uranium. Part VI. The Chemisorption of Reducing Gases on Uranium and Thorium Dioxides.*

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Carbon monoxide is chemisorbed by uranium dioxide and by thoria at temperatures below 20°. There is mutual interference between the adsorption of oxygen and carbon monoxide on uranium dioxide at low temperatures. The adsorption of carbon monoxide by uranium dioxide at higher temperatures is small. Hydrogen is not appreciably chemisorbed by uranium dioxide below 400°, but at higher temperatures an activated adsorption occurs and high surface coverages can be attained. The results are discussed in terms of the numbers and the nature of the adsorption sites available.

URANIUM DIOXIDE adsorbs oxygen at $-183°$; a large fraction of the available surface is covered by a chemisorbed layer, about 75% of which is stable at temperatures up to room temperature (Part V *). Additional oxygen is adsorbed into the uranium dioxide lattice at temperatures above $-80°$, and the final result of oxidation is the production of interstitial anions. This type of chemisorption is different from the activated adsorption of oxygen on other oxidisable oxides such as cuprous oxide, where oxidation leads to the production of cation vacancies (Garner, Stone, and Tiley, *Proc. Roy. Soc.*, 1952, *A*, **211**, 472). The adsorption of carbon monoxide and of hydrogen on uranium dioxide provides further comparisons with chemisorption phenomena on other oxides. In addition, the effect of adsorbed carbon monoxide and hydrogen on adsorption of oxygen by uranium dioxide, and the effect of adsorption of oxygen on the subsequent adsorption of carbon monoxide yield information about the nature of the adsorbing centres in each case. The adsorption of carbon monoxide on thoria was also studied in order to obtain comparable data on adsorption of carbon monoxide on an oxide of the same structure as uranium dioxide but which is inert to oxygen and in which the cations cannot easily change their valency.

EXPERIMENTAL

The adsorption apparatus used for the bulk of this work was the constant-volume, variable-pressure apparatus described in Part V (*loc. cit.*). Some experiments were also performed in a constant-pressure, variable-volume apparatus. Desorbed gases were analysed for carbon dioxide and water by passing them through a U-tube cooled to $-183°$ or $-80°$, and subsequently allowing any condensed material to expand into an evacuated volume where the pressure could be determined, a manometer filled with Apiezon "A" oil being used.

The details of the preparation of the various samples of uranium dioxide are given in Part V, together with their density, mean particle size, and mean crystallite size. The samples used in this work were B1 and C3, prepared by reduction of higher oxides with hydrogen and with carbon monoxide respectively, and R, prepared by heating a pure commercial dioxide to 2200° in a vacuum, crushing the sintered mass, and then treating it with hydrogen. These were all well crystallised samples with particle diameter of 0·45, 0·41, and 2·3 μ, respectively.

Thoria was prepared from a pure sample of the carbonate, supplied by Thorium Limited, by heating it in air to 1000° and in vacuum to 2000°, and crushing it.

RESULTS

Adsorption of Carbon Monoxide by Uranium Dioxide.—Curves I and II of Fig. 1 are adsorption isotherms at $-183°$ of carbon monoxide on uranium dioxide samples B1 and C3. Sample B1 had been treated with hydrogen at 700° and pumped at 740°; sample C3 had been reduced with carbon monoxide at 700° and pumped at 750°. The amounts adsorbed are expressed as V/V_m, V being the volume of gas adsorbed and V_m (both in c.c. at N.T.P.) the quantity of oxygen required to form a monolayer of physically adsorbed oxygen at $-183°$, as calculated by

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* Part V, *J.*, 1954, 3332.

applying the B.E.T. equation to the physical adsorption of oxygen on these samples after low-temperature oxidation (Part V). After the determination of the carbon monoxide isotherms at −183°, the samples were pumped at −183° for 1 hr., by which time the rate of gas evolution was immeasurably small, and the isotherms redetermined at −183°; the results are plotted as curve III in Fig. 1. Curve III is parallel to the isotherms determined on a clean surface, but uniformly lower. If the carbon monoxide was removed at higher temperatures, at −120° or −80°, and the isotherm redetermined at −183°, parallel curves intermediate between curves I and II were obtained. Pumping at 250° removed all adsorbed carbon monoxide and the original isotherms, I or II, could be accurately reproduced.

Curve IV of Fig. 1 is a typical isotherm of physically adsorbed oxygen on an oxidised surface of uranium dioxide; curve IV is quite different in shape from curves I, II, or III, particularly at low pressures. This point is further illustrated in Fig. 2, in which curves II and IV are the low-pressure parts of the same isotherms in Fig. 1, plotted on a magnified pressure scale. The value of V/V_m found by the extrapolation of curve II to low pressures agrees well with the value found, by the subtraction of curve III from curve II, to be the amount of carbon monoxide that could not be pumped off sample C3 at −183°. This would be a function of the pumping speed and of the diameter of the arms of the sample holder. For comparison, 85% and 90% of a physically-adsorbed monolayer of nitrogen were removed by pumping under identical conditions for 45 min. and 2·5 hr. respectively at −196°. It seems reasonable to conclude, from the results in Fig. 2 and from the dimensions of the apparatus, that pumping at −183° removed carbon monoxide until the gas pressure fell to 10^{-5}—$10^{-6}p/p_0$.

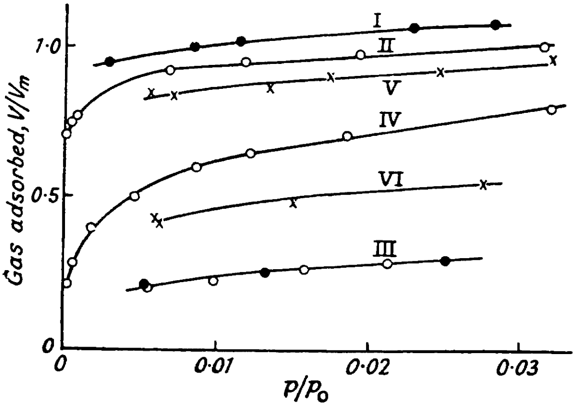

FIG. 1. *The adsorption of carbon monoxide and of oxygen on uranium dioxide at* −183°.

Curves I and II—carbon monoxide adsorption on reduced uranium dioxide; III—repeats of I and II after pumping at −183°; V—carbon monoxide adsorption on oxidised uranium dioxide; VI—repeat of V after pumping at −183°; IV—physical adsorption of oxygen on oxidised uranium dioxide.

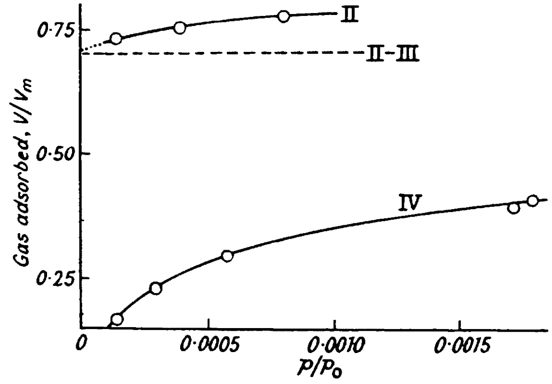

FIG. 2. *The adsorption of carbon monoxide and of oxygen at low pressures by uranium dioxide at* −183°.

Curve II—carbon monoxide adsorption on reduced uranium dioxide; IV—physical adsorption of oxygen on oxidised uranium dioxide; II—III—by subtraction of curves in Fig. 1.

Appreciable adsorption of carbon monoxide occurred at higher temperatures, where physical adsorption would be very small. Curves I and II of Fig. 3 are adsorption isotherms of carbon monoxide on specimen B1 in the reduced state, curve I being determined at −78° and curve II at +23°. Adsorption of carbon monoxide at these temperatures on C3 was similar but slightly smaller.

The adsorption of carbon monoxide at temperatures above room temperature was small.

A specimen of C3, which had been reduced in carbon monoxide at 600°, pumped at 680° until clean, and then exposed to 6 cm. pressure of carbon monoxide, adsorbed $<1\%$ of V_m at 680° and about 8% of V_m at 275°; the adsorption fell on raising the temperature again and the gas contained no measurable quantity of carbon dioxide at the end of the experiment.

Adsorption of Carbon Monoxide on Oxidised Uranium Dioxide Surfaces.—Uranium dioxide preparations that had adsorbed oxygen were still capable of chemisorbing carbon monoxide at low temperatures by a process very similar to that described above but the amount chemisorbed was smaller. The specimen of B1 previously studied was exposed to oxygen at −183°, and the oxygen pumped off at −183° and briefly at room temperature. The carbon monoxide isotherm at −183° determined after this treatment is shown as curve V in Fig. 1; the adsorption is less than on a reduced surface (I). The sample was pumped at −183° for 1·5 hr. and the isotherm redetermined: curve VI of Fig. 1 was obtained. A greater proportion of the adsorbed gas was removed by pumping at −183° than in the case of the reduced specimen, and the volume that could not be removed by pumping at −183° fell from $0{\cdot}77V_m$ to $0{\cdot}40V_m$. Chemisorption also occurred on oxidised surfaces at higher temperatures; curves III and IV of Fig. 3 show the adsorption of carbon monoxide at −78° and +23·5° respectively on sample B1 after the adsorption of oxygen; the adsorption was about half that occurring on the reduced oxide under the same conditions. All the adsorbed carbon monoxide was removed by pumping at room temperature.

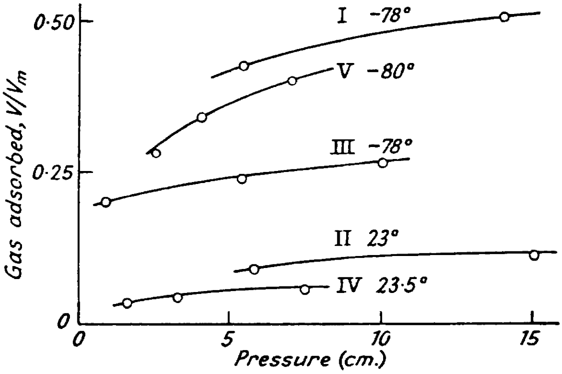

FIG. 3. *Adsorption of carbon monoxide on uranium dioxide and on thoria.*

Curves I and II—carbon monoxide adsorption on reduced uranium dioxide at −78° and 23°; III and IV—carbon monoxide adsorption on oxidised uranium dioxide at −78° and 23·5°; V—carbon monoxide adsorption on thoria at −80°.

The effect on the adsorption of carbon monoxide at −183° of progressively larger amounts of oxygen on the surface was studied in a series of experiments in which measured amounts of oxygen were allowed to be adsorbed on sample C3 and carbon monoxide isotherms determined after each addition. The volume of carbon monoxide that could not be pumped away at −183° (V_{CO}) was measured by repeating the −183° isotherm after pumping for 1—2 hr. at −183°.

TABLE 1.

Temp. of oxidation	Temp. at which O_2 removed	Total O_2 reacted (c.c., N.T.P.)	V_{CO} (c.c., N.T.P.)	Temp. of oxidation	Temp. at which O_2 removed	Total O_2 reacted (c.c., N.T.P.)	V_{CO} (c.c., N.T.P.)
—	—	0	0·470	—	—	0	0·268
−183°	−183° and 20°	0·136	0·328	−183	−183 and 20°	0·074	0·190
−183	−183 and −80	0·285 (V_O)	0·242	−183	−183 and 20	0·175 (V_O)	0·115
				20	20	0·665	0·062
—	—	0	1·15	120	20	2·11	0·062
−183	−183 and 20	0·76 (V_O)	0·60	120	110	3·49	0·083
				110	−80	4·19	0·068

The carbon monoxide was then finally removed by pumping for about 1 hr. at room temperature. The samples were also normally pumped at room temperature after the oxygen additions. Finally, one specimen was exposed to oxygen at higher temperatures, so that bulk oxidation occurred, and V_{CO} again measured. The results are collected in Table 1. Pumping times at the higher temperatures recorded in col. 2 were only a few minutes.

The maximum oxygen adsorption at −183° is denoted by the symbol V_O in col. 3; oxygen adsorbed at higher temperatures in excess of V_O is accommodated in interstitial positions in the lattice. The last results in Table 1 refer to B1; they are the results taken from Fig. 1.

The amounts of oxygen recorded in col. 3 have not been corrected for small losses due to reaction with carbon monoxide at room temperature.

It is evident from Table 1 that adsorption of quantities of oxygen less than $0{\cdot}5V_0$ caused V_{CO} to decrease by the same amount. Thus, in the first example, V_{CO} decreased by 0·142 c.c. when 0·136 c.c. of oxygen was adsorbed and, in the second, the adsorption of 0·074 c.c. of oxygen lowered V_{CO} by 0·078 c.c. Addition of more oxygen caused V_{CO} to decrease further, but by an amount quantitatively less than the amount of oxygen added. By the time V_0 of oxygen had been adsorbed, V_{CO} had been lowered by 68%, 87%, and 72% of V_0, in the three cases in Table 1. Bulk oxidation of the uranium dioxide lowered V_{CO} to about half the V_{CO} value characteristic of a surface on which V_0 of oxygen was adsorbed.

Oxygen Adsorption after Carbon Monoxide Adsorption.—A sample of B1 uranium dioxide that had adsorbed carbon monoxide at −183° and had been pumped at −183°—therefore retaining $V_{CO} = 0{\cdot}77V_m$, from Fig. 1—was exposed to oxygen at 183°; the isotherm measured is curve I in Fig. 4. The oxygen was pumped away for 30 min. at −183°, and the isotherm measured again—curve II in Fig. 4 is a plot of the results. The adsorption was very low compared with that of oxygen on a pumped, reduced surface (curve III) or with the physical adsorption of oxygen on the same surface after oxidation (curve IV). Curves I and II are not strictly parallel, but they illustrate that all except 0·1—0·15V_m of the oxygen adsorbed on a surface saturated with carbon monoxide could be removed by pumping at −183°, whereas a clean surface chemisorbed 0·51V_m of oxygen.

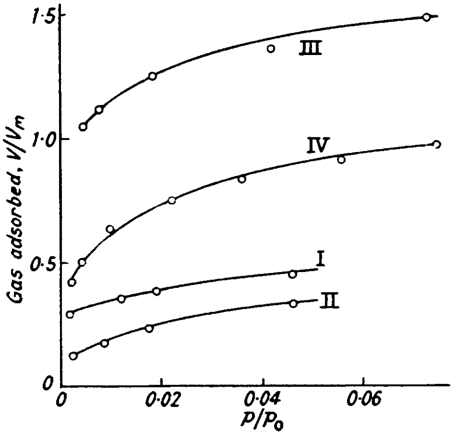

FIG. 4. *The effect of carbon monoxide adsorption on the adsorption of oxygen by uranium dioxide at* −183°.

Curves III and IV—adsorption of oxygen on reduced and oxidised uranium dioxide. Curve I—oxygen adsorption after chemisorption of carbon monoxide at −183°. Curve II—repeat of I after pumping at −183°.

TABLE 2.

Sample	Total O_2 adsorbed or reacted (c.c., N.T.P.)	Conditions in CO : Temp.	Time	Pumping temp.	CO_2 found (c.c., N.T.P.)
R.61	0·136	20°	1·5 hr.	20°	0·0065
	V_O = 0·285	20	96 ,,	20	0·0157
	1·22	19·5	17 min.	19·5	0·0254
		,,	+17 ,,	,,	0·010
		,,	+20 ,,	,,	0·005
		,,	—	120	0·0256
R.60	0·074	20	30 ,,	20	0·00
	V_O = 0·175	20	16 hr.	20	0·00
	0·665	20	45 min.	20	0·025
	2·11	20	60 ,,	20	0·021
				120	<0·005
	3·49	20	16 hr.	20	0·047

Reaction of Carbon Monoxide with Adsorbed Oxygen.—During the experiments recorded in Table 1, the partially oxidised uranium dioxide samples were frequently allowed to remain in contact with carbon monoxide at room temperature for varying periods of time after the determination of the isotherms at −183°. The gas was gently circulated over the sample during this time and then analysed for carbon dioxide. The amount of reaction was very small; the results are given in Table 2. With only the oxygen adsorbed at −183° on the sample, carbon monoxide removed in one experiment ~3% and in another <1% of the surface oxygen. After bulk oxidation had occurred, amounts of carbon dioxide corresponding to ~10% of the oxygen on the surface were found after long periods of exposure to carbon monoxide at 20°. At the end of the experiments on sample R.61 (Table 2), an equimolar mixture of carbon monoxide and oxygen was circulated at 8 cm. pressure over the sample for 24 min. at 20°; only 0·001 c.c. of carbon dioxide was found, but 0·014 c.c. of carbon dioxide was recovered by heating the sample to 120°.

Adsorption of Carbon Monoxide on Thoria.—A specimen of thoria was pumped at 750° and carbon monoxide isotherms were determined at −183°, again after pumping at −183°, and at −80°; V_m was determined by using oxygen at −183°. The two −183° isotherms were practically identical with the corresponding isotherms on B1 uranium dioxide, curves I and III of Fig. 1, and V_{CO}, the amount not removable by pumping at −183°, was $0{\cdot}78V_m$. The −80° isotherm is plotted as curve V in Fig. 3. It is evident that carbon monoxide is chemisorbed on thoria by a process very similar to its chemisorption on a reduced uranium dioxide. The thoria sample used chemisorbed only ~3% of V_m of oxygen at −183° after treatment with carbon monoxide at 700°.

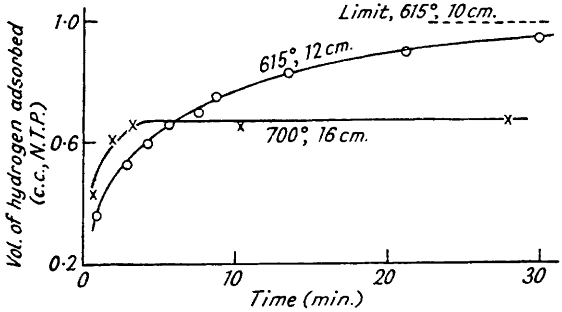

FIG. 5. *The rate of hydrogen adsorption on uranium dioxide at* 615° *and* 700°.

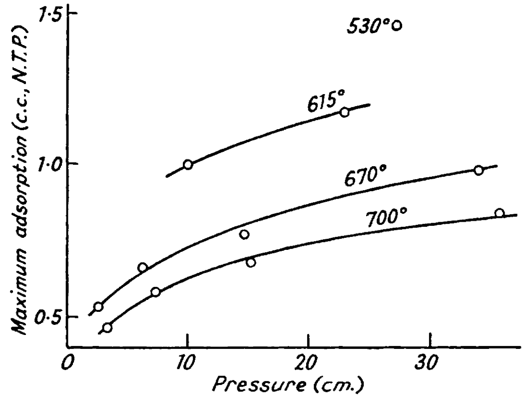

FIG. 6. *Hydrogen adsorption on uranium dioxide.*

Adsorption of Hydrogen by Uranium Dioxide.—A small adsorption of hydrogen occurred on reduced uranium at −183°:

Hydrogen pressure (cm.)	1·68	4·28	8·15
Hydrogen adsorbed (as V/V_m)	0·109	0·192	0·287

All the adsorbed hydrogen was recovered by warming to room temperature. No adsorption could be measured at 23° up to 25 cm. pressure.

Adsorption of hydrogen on reduced uranium dioxide proceeded at measurable rates above 470°. The quantity of hydrogen adsorbed on sample B1 at 615° and at 700° is plotted as a function of time in Fig. 5; the adsorbent had been reduced in hydrogen and pumped at 750° before these experiments. The adsorption apparently reached a final value in about 40 min. at 615° and in about 4 min. at 700°. The adsorption at 615° was shown to be pressure dependent. The rate of adsorption increased with increasing temperature: an approximate activation energy of 35 kcal./mole was calculated by comparing the rates of adsorption at half the saturation adsorption at 615° and 700°. The hydrogen was slowly desorbed as such when the temperature was raised above 700°. The volume-calibration of the " Vitreosil " specimen bulb used was checked with helium at 700° and no loss of helium could be detected in 30 min.

The same specimen of B1 uranium dioxide was again out-gassed at 750°, and hydrogen adsorption followed to apparent saturation at various pressures at 700° and 670°. The maximum amounts adsorbed are plotted in Fig. 6 : the 615° results are taken from the previous experiment. The single result at 530° was determined after 16 hr. at 530°. Approximate values for the heat of adsorption can be calculated if the system is assumed to be in equilibrium ; values vary from 30 to 40 kcal./mole. Further adsorption occurred upon cooling to 475° and 415°. The final amount adsorbed was 1·94 c.c., or $1{\cdot}3V_m$, where V_m was measured as usual with oxygen at −183°.

In other experiments, the amounts of hydrogen adsorbed at low temperatures increased after exposure to hydrogen at high temperatures and repeated temperature cycling caused the total adsorption to increase slowly. The adsorption on one specimen of sample R increased from 0·24 c.c. to 0·55 c.c. after five heating cycles between 500° and 750°, the specimen being held at the lower temperatures for about 16 hr. and at the higher temperatures for 0·5—1·5 hr. Some water—0·05 c.c.—was recovered at the end of the experiment, leaving 0·50 c.c. as the maximum amount of hydrogen adsorbed ; during the hydrogen treatment, V_m decreased from 0·46 to 0·30 c.c. A similar effect was observed on one specimen of sample C3. The adsorption at 460° increased from 0·55 to 0·85 c.c. after 3 heating cycles between 460° and 760° ; no water was found in the hydrogen at the end of the experiment and V_m (nitrogen value) had decreased from 0·93 to 0·84 c.c.

DISCUSSION

The adsorption of nitrogen on reduced or oxidised surfaces of uranium dioxide at −196° is very similar to that of oxygen on an oxidised surface at −183°, and such adsorption is therefore physical adsorption. The boiling point and molecular size of carbon monoxide are close to those of oxygen and nitrogen, and the physical adsorption of carbon monoxide at −183° should be similar to that of oxygen at −183° at the same relative pressure. The carbon monoxide isotherms actually measured (Figs. 1 and 2) therefore indicate chemisorption. The amount of carbon monoxide that cannot be pumped away at −183° (V_{CO}) will be taken as the amount chemisorbed at that temperature. The much smaller adsorption at −80° and at −23° shows that the heat of adsorption falls rapidly with increasing surface coverage. Approximate values of the heats of desorption may be calculated from the following equation (see Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw Hill Co., New York, 1941, p. 353) :

$$\text{Rate of desorption} = C\,\frac{\boldsymbol{k}T}{\boldsymbol{h}}\cdot\frac{f^{\ddagger}}{f}\,e^{-E/\boldsymbol{R}T}$$

where C is the surface coverage and $f = f^{\ddagger}$. Times of half desorption of 10 min. are obtained with $E = 6$ kcal./mole at −183° and with $E = 21$ kcal./mole at 20°. Since the pumping speeds in the apparatus used would be low at low pressures, it is probable that V_{CO} comprises gas adsorbed with desorption energies of from 20 to 4 kcal./mole. It is unlikely that any of this gas is adsorbed in a second layer, but it is not certain that V_{CO} can be equated to complete surface coverage, since the heat of adsorption may fall to ~4 kcal./mole before all sites are occupied. A similar low-energy chemisorption of carbon monoxide on thoria was observed.

The depression of the adsorption of carbon monoxide on uranium dioxide by prior adsorption of oxygen, and of oxygen adsorption by prior adsorption of carbon monoxide, may be some evidence that both are adsorbed on the same sites, and it is very probable that adsorption of oxygen takes place on uranium sites. Studies of the adsorption of oxygen on mixed crystals of uranium and thorium dioxides (Part V, *loc. cit.*) confirmed that oxygen adsorption occurred only on uranium sites, where electrons could be donated to the oxygen. The type of carbon monoxide chemisorption studied here can take place on thoria and therefore does not depend on electron-donation to the adsorbed gas. A similar reversible, low-temperature chemisorption of carbon monoxide has been reported on zinc oxide (Garner, *J.*, 1947, 1239), on cuprous oxide (Garner, Stone, and Tiley, *Proc.*

Roy. Soc., 1952, *A*, **211**, 472), and on nickel oxide (Dell and Stone, *Trans. Faraday Soc.*, 1954, **50**, 501). The heat of adsorption is 26 kcal./mole on nickel oxide and 20 kcal./mole on zinc oxide; the heat of adsorption on cuprous oxide is 21 kcal./mole at 10% coverage, falling rapidly with increasing coverage. Adsorption on cuprous oxide is accompanied by electron donation from the gas to the substrate (Garner, Gray, and Stone, *Proc. Roy. Soc.*, 1949, *A*, **197**, 294) and the adsorption is held to occur on metal sites; 60% of the available metal sites are occupied at low pressures at —183° (Garner, Stone, and Tiley, *loc. cit.*). The marked lowering of the physical adsorption, as well as the chemisorption of oxygen on uranium dioxide by the previous adsorption of a chemisorbed layer of carbon monoxide at —183° (Fig. 4) is reminiscent of the depression of the adsorption of krypton on cuprous oxide by a partial layer of carbon monoxide, chemisorbed by a low-temperature process (Stone and Tiley, *Nature*, 1951, **167**, 654); carbon monoxide adsorbed in this fashion presumably alters the polarising properties of the surface, and subsequent physical adsorption of any gas resembles " second-layer " rather than " first-layer " adsorption.

Hydrogen is not much adsorbed at —183° and what little adsorption there is may well be physical adsorption, since the adsorption falls to zero at room temperature. The high-energy, activated process by which hydrogen is adsorbed above 400° resembles the processes of hydrogen adsorption by many oxides and oxide catalysts (Garner, *loc. cit.*; Taylor and Shou Chu Liang, *J. Amer. Chem. Soc.*, 1947, **69**, 1306), though the adsorption on the well-crystallised samples studied here took place at higher temperatures than on the "active" surfaces of catalysts prepared at low temperatures. Hydrogen adsorption had only a small effect on the subsequent adsorption of oxygen (Part V) and other work shows that the effect of hydrogen on low-temperature oxidation processes is also small. These results are compatible with hydrogen adsorption taking place on oxygen sites. The relatively small adsorption of carbon monoxide on uranium dioxide at 200° may also take place on oxygen sites, with the formation of a carbonate complex, as occurs on other oxides (Garner, *loc. cit.*). The carbon monoxide and hydrogen are desorbed at high temperatures as such, not as carbon dioxide and water, because of the thermodynamic stability of uranium dioxide.

The maximum amounts of oxygen, carbon monoxide, and hydrogen adsorbed on the uranium dioxide samples used were $0{\cdot}5$—$0{\cdot}6V_m$, $0{\cdot}7$—$0{\cdot}8V_m$, and $1{\cdot}0$—$1{\cdot}6V_m$, respectively; V_m was always measured by physical adsorption of oxygen at —183°. These quantities represent very high surface coverages. On the assumptions that a physically adsorbed oxygen molecule occupies an area of 16·7 Å^2, equal to the usual nitrogen area, and that the planes having the highest density of U^{4+} ions—the (100) planes—are outermost, the number of U sites is 1·12 per physically-adsorbed oxygen molecule; this figure is reduced to 0·80 if the outermost planes are (110) planes. The minimum values for the surface coverage achieved by oxygen and by carbon monoxide at —183° are therefore 48% and 67% respectively if both are adsorbed as molecules. There are two O sites for each U site and an adsorption of $1{\cdot}3V_m$ of hydrogen amounts to at least 60% surface coverage if one molecule is adsorbed on each O site or to at least 120% if the adsorption is dissociative. Since dissociative adsorption seems probable in the case of hydrogen, these results may point to some penetration of hydrogen into the lattice, which may explain the slowly rising figures for total adsorption found in some experiments involving repeated temperature cycling; solution of hydrogen in the lattice of tungsten sulphide has been postulated by Friz (*Z. Elektrochem.*, 1950, **54**, 538).

The quantitative agreement between the lowering of the carbon monoxide adsorption and the initial amounts of oxygen adsorbed (Table 1) could be explained if carbon monoxide and oxygen are both adsorbed as molecules on the same sites. That the carbon monoxide adsorption is not lowered to the same extent by subsequent increments of oxygen up to the V_O limit is probably explicable by some of the last increments of oxygen, which are adsorbed with a lower heat of adsorption (J. D. M. McConnell, personal communication), being lost from the surface sites during the brief period of pumping at room temperature before carbon monoxide was admitted. It is known that additional chemisorption of oxygen can occur after treatment at room temperature and that oxygen can dissolve in the uranium dioxide lattice at room temperature. The results in Table 1 then suggest that 13—32% of the oxygen adsorbed at −183° is lost from the surface upon warming to 29°, on the assumption that the total number of sites available for oxygen and carbon monoxide adsorption remains constant. The further lowering of V_{CO} after bulk oxidation may mean that previously unoccupied sites are covered by oxygen after exposure to oxygen at 20° and above, or it may be a consequence of a change in surface energy levels due to interstitial positions in the lattice being filled with dissolved oxygen.

Some of the oxygen on the surface of uranium dioxide after bulk oxidation has occurred reacts slowly with carbon monoxide at 20° (Table 2). A reaction between carbon monoxide and adsorbed oxygen, with the extensive formation of carbonate complexes, has been found with other oxides (Garner, Stone, and Tiley, *loc. cit.*; Dell and Stone, *loc. cit.*). In the case of uranium dioxide, it is likely that only a fraction of the oxygen on the surface engages in such reactions, since the adsorption of carbon monoxide at 23° on a surface holding one layer of adsorbed oxygen was very small (curve IV, Fig. 3).

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