504. *The Oxides of Uranium. Part IX.* The Decomposition of Carbon Monoxide on Uranium and Thorium Dioxides.*

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The decomposition of carbon monoxide, yielding carbon and carbon dioxide, takes place much faster on urania than on thoria at 500—900°. Carbon is deposited on urania up to a limit which depends on the surface area of the urania but not on temperature. The chemisorptive capacity of urania for oxygen is decreased and oxygen is lost from the solid oxide as carbon is deposited. The addition of a little carbon dioxide to the carbon monoxide is sufficient to inhibit the decomposition; carbon dioxide is chemisorbed on urania below 200°.

CARBON monoxide decomposes rapidly at 500° on iron, nickel, and cobalt catalysts; the product consists largely of free carbon if the gas contains some carbon dioxide, and carbon deposition is negligible above 750°.[1] Bankloh and Henke reported that urania did not catalyse the decomposition of carbon monoxide,[2] and this was apparently confirmed by results reported earlier in this series.[3,4] Carbon monoxide was used at 450—750° to reduce urania to the stoicheiometric composition, without any evidence of contamination by carbon being found. Urania which was reduced in carbon monoxide showed the same chemisorption and oxidation behaviour as urania reduced in hydrogen and one sample that had been prepared by reduction of a higher oxide with carbon monoxide had a very low carbon content (<0·03 mg./g.).

Edgington and McConnell found that the chemisorptive capacity of urania for oxygen decreased after exposure to a stream of very pure carbon monoxide at 1 atm. pressure for up to 50 hours.[5] Their specimens contained appreciable quantities of carbon. We have studied the deposition of carbon on urania and both confirmed and extended their work on the effects of this carbon on the surface properties and reactivity of the urania: carbon is not deposited on urania under the conditions of reduction with carbon monoxide, normally used in the earlier researches, in which the gas in contact with the solid contained a little carbon dioxide. A few experiments were carried out on thoria.

EXPERIMENTAL

Flow Experiments.—Carbon monoxide from a cylinder was passed through a liquid-oxygen trap, copper gauze at 500°, and another liquid-oxygen trap, and led over weighed specimens of oxide (1—2 g.) in silica U-tubes at about 100 c.c./min. Two or three silica U-tubes were sometimes placed in series, each in a separate furnace; two or three specimens could thus be exposed to the gas stream for different times. A reduction treatment preceded each run; the urania was treated with a static atmosphere of 30 cm. of carbon monoxide for 30 min. at 500°, or with 10—15 cm. of hydrogen for 30 min. at 600°, followed by pumping at 650—750°.

The carbon deposited on the oxide was estimated by heating it in a slow flow of oxygen at 750°, collecting the carbon dioxide in a trap at −183°, and measuring its volume with the

[1] Taylor, *J. Iron Steel Inst.*, 1956, **184**, 1.
[2] Bankloh and Henke, *Metallwirtschaft*, 1940, **19**, 463.
[3] Roberts, *J.*, 1955, 3939.
[4] Anderson, Roberts, and Harper, *ibid.*, p. 3946.
[5] Edgington and McConnell, unpublished work, A.E.R.E., Harwell.

trap at $-80°$; any water formed could subsequently be measured with the trap at room temperature.

Circulating-gas Experiments.—For apparatus, see Fig. 1. The all-glass pump was based on an earlier design [6] further developed in these laboratories by P. C. Davidge. An iron rod was sealed between springs inside a glass piston which was a sliding fit inside a " Veridia " tube of accurate dimensions. The barrel was mounted vertically and the piston was moved by supplying direct current alternately to two solenoids. A system of glass valves made the gas flow unidirectional, and rates of 200 c.c./min. were easily obtained.

The gas passed over the oxide in a U-tube, and then through a trap which could be cooled. The volumes of all parts of the apparatus were determined by comparison with a standard volume, so the quantity of gas in the system could be calculated after measurement of the pressure on the constant-volume manometer. The trap could be evacuated independently of the main apparatus, and its contents measured after warming to $-80°$ or room temperature.

The urania specimens were reduced at the start of each experiment by circulating carbon monoxide at $500°$, with the trap at $-183°$. The reduction was orders of magnitude faster than the rate of carbon deposition at $500°$, and at the end of the reduction stage the pressure of the carbon monoxide became approximately constant. Reduction took less than 30 min. at $500°$. Carbon deposition was studied by measuring out a volume of carbon monoxide and circulating it for a known time with the oxide specimen at a given temperature. In some

Fig. 1. *Apparatus used for circulating-gas experiments.*
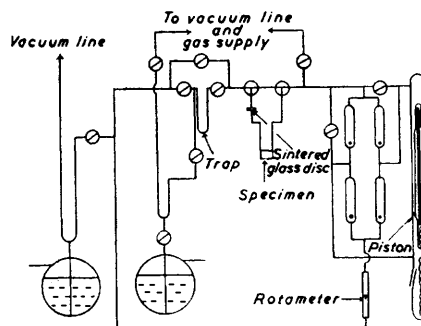
experiments, the carbon dioxide was continuously removed from the gas stream by cooling the trap with liquid oxygen, and the amount formed estimated from time to time by isolating the trap, evacuating, and warming. In other experiments, the carbon dioxide was not continuously removed, but was collected at the end of an experiment by evacuating the circulating system through the cooled trap. A technique that removed more than 99% of the carbon dioxide from the gas was to circulate for 10 min. with the trap at $-183°$, and finally to evacuate slowly through the trap, the evacuation being controlled with a stopcock so that the gas flowed through the trap at low pressure.

The carbon in an oxide specimen was determined by circulating pure oxygen over the hot oxide, with the trap cold, until the pressure became constant, and measuring the carbon dioxide produced.

Adsorption and Oxidation Experiments.—The adsorption and oxidation characteristics of some urania samples were determined after carbon deposition without exposure to air. Chemisorption of oxygen at $-183°$ was determined as the difference between two adsorption isotherms at $-183°$ which were measured before and after pumping at $-80°$; [7] the second isotherm was assumed to represent physical adsorption and was analysed by the B.E.T. equation to give a value of V_m, the volume of gas in c.c. at N.T.P. in a physically adsorbed monolayer of oxygen at $-183°$.

The rates of reaction with oxygen at $18°$ and subsequently at $142°$ were determined in a constant-volume apparatus by measuring the rate of fall of pressure, again without exposure of the urania to air after depositing carbon.

Materials.—Two samples of urania were used, both prepared from U_3O_8 which had been made from the pure grade of " ammonium diuranate " available in this Establishment. One

[6] Brenschede, *Z. phys. Chem.*, 1936, **178**, 74.
[7] Roberts, *J.*, 1954, 3332.

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sample (C3) had been prepared by reduction with carbon monoxide at 700°, and the other (C4) by reduction with hydrogen at 760°. The characteristics of these preparations respectively were: density, 10·90, 10·76 g./c.c.; mean particle size, 0·41, 0·47 micron; mean crystallite size, 0·38, 0·53 micron. Probably most of the particles were single crystals.[8]

Two samples of thoria were prepared by heating a pure grade obtained from Thorium Ltd. to about 1000° in air.

RESULTS

Rate of Reaction.—The amount of carbon deposited on urania is plotted against time of exposure to carbon monoxide at various temperatures and pressures in Figs. 2 and 3; the carbon content is expressed as the volume (c.c. at N.T.P./g.) of carbon dioxide produced upon subsequent oxidation. The results at 1·1 atm. pressure (Fig. 2) are those of flow experiments; pre-reduction was usually carried out with hydrogen and the carbon was directly determined; a fresh oxide sample was used for each run. Specimen C4 was used for all experiments except one series (broken curve) at 500° on C3. The flow rate was about 100 c.c./min.; markedly

Fig. 2. *Deposition of carbon on urania from carbon monoxide at* 1·1 *atm. pressure.*

A, 750°; *B,* 700°; *C,* 500° (C3); *D,* 650°; *E,* 500°.
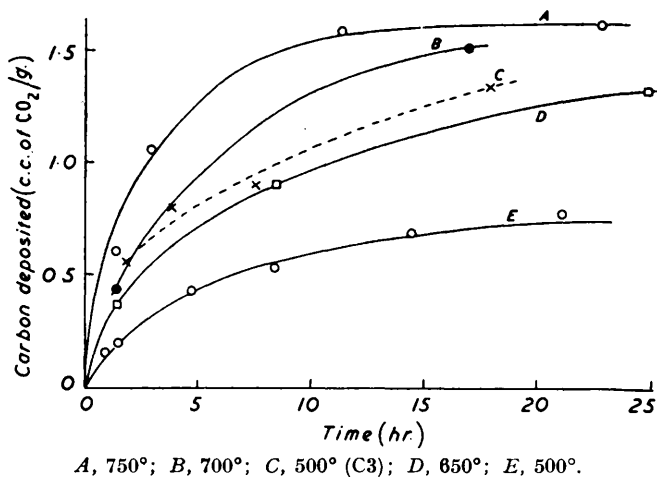
less carbon was deposited when the flow rate was reduced to about 20 c.c./min. Results at lower pressures (Fig. 3) were obtained both in flow and in circulation experiments. Specimen C4 was used throughout and the flow experiments were conducted exactly as at 1·1 atm.

The gas-circulating experiments to determine reaction rates were conducted with continuous removal of the carbon dioxide from the gas stream and the variation of gas pressure with time was recorded. The calculation of the amount of carbon deposited was made by assuming that the ratio (CO_2 produced : CO lost) for any stage in the reaction was that determined in other experiments (see below) at the same temperature. Then, by material balance,

Carbon deposited = (CO lost) − (CO_2 produced) for that time interval

The errors in such a procedure are cumulative and tend to be large because the amount of carbon monoxide lost was less than 10% of the total amount in the system. The figures for carbon deposited in any time interval were therefore corrected by multiplying by the ratio (C found : C calculated), where " C found " is the carbon determined by analysis at the end of the run and " C calculated " is the sum of the amounts of carbon deposited in the various time-intervals, as calculated from the amount of carbon monoxide lost. Two or three such experiments were carried out at each temperature; the results were in fair agreement and averaged values are plotted in Fig. 3. The results were compatible with those of the flow experiments and good agreement was directly established at 700° and 0·45 atm.

The rate of deposition of carbon increased regularly with both pressure and temperature. Comparison of the initial rates of reaction at 750°, 700°, and 650° shows that the rate is more

[8] Anderson, Harper, Moorbath, and Roberts, A.E.R.E. C/R 886.

nearly proportional to the first power of the pressure than to any other simple-power law and this is also found to be so when the rates at different pressures at 750° are compared at times of equal carbon deposition. The reaction becomes so slow below 650° and below 1 atm. that no firm statement can be made. At any one pressure, the rate increases regularly with temperature and there is no sign that the rate reaches a maximum in the temperature range studied. The form of the kinetic curve was always that of a reaction proceeding to a definite limit and the maximum amount of carbon deposited seemed to be independent of the rate of deposition. The maximum amounts of carbon deposited in different long runs were: C4: 900°, 0·45 atm., 1·61 and 1·62 c.c. CO_2/g.; 750°, 1·1 atm., 1·62 c.c./g.; 790°, 0·45 atm., 1·84 c.c./g.; C3: 900°, 0·45 atm., 1·89 c.c./g.

The rate of deposition of carbon at 500° was faster on specimen C3 than on C4 (Fig. 2), in accordance with the larger surface area of C3. The rate of deposition on the same area of

FIG. 3. *Deposition of carbon on urania from carbon monoxide at low pressures.*
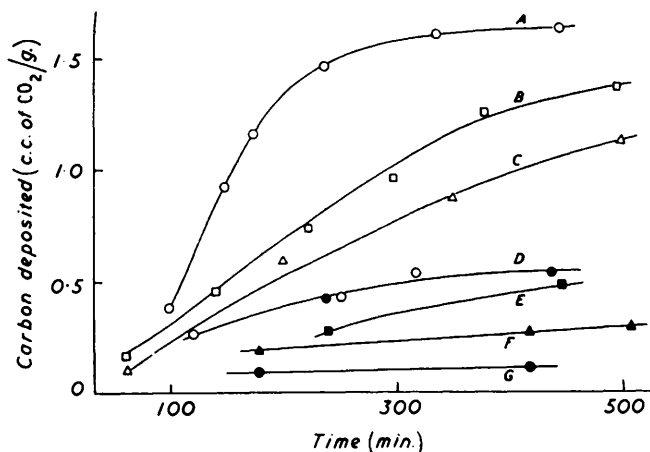
Open symbols: circulating-gas experiments; full symbols: flow experiments.
A, 900°, 0·45 atm.; *B*, 800°, 0·45 atm.; *C*, 750°, 0·45 atm.; *D*, 700°, 0·45 atm.; *E*, 650°, 0·64 atm.;
F, 650°, 0·31 atm.; *G*, 500°, 0·31 atm.

thoria was much lower. The results on two specimens of thoria are in Table 1, together with the values of V_m; the amount of carbon deposited is expressed as c.c. of CO_2 collected on analysis. The ratio (volume of CO_2 collected) : V_m (Table 1), which is a measure of the carbon deposited per unit surface area, can be compared with the values for urania C4, for the same temperature, pressure, and duration of experiment, in the last column; the reaction proceeded 3—7 times faster on urania than on the same area of thoria.

TABLE 1. *Decomposition of carbon monoxide on thoria.*

Oxide	V_m (c.c./g.)	Conditions	Time (min.)	Temp.	c.c. of CO_2/g.	$\dfrac{\text{c.c. of } CO_2/g.}{V_m}$	$\dfrac{\text{c.c. of } CO_2/g. \text{ of } UO_2}{V_m}$
Th/0	0·90	Flow, 1·1 atm.	180	505°	0·03	0·033	1·0
		,,	180	650	0·21	0·23	1·8
		,,	360	650	0·46	0·51	2·5
		,,	180	745	0·65	0·73	3·2
Th/1	0·50	Circulating, 0·4 atm.	320	850	0·40	0·80	3·8

Stoicheiometry of the Reaction.—The results of experiments in the gas-circulating apparatus in which the carbon dioxide was continuously removed from the gas stream are collected in Table 2. The calculated value for the carbon deposited, expressed as before as c.c. of CO_2, is the difference between the total volumes of carbon monoxide lost and carbon dioxide formed. The actual amounts of carbon found by analysis after each experiment are given in column 9; the results in parentheses were obtained after the circulation of CO–CO_2 mixtures under

conditions in which it is unlikely that carbon is either deposited or removed (see below). The agreement between the calculated and observed values for carbon is reasonable in view of the likely errors in the measurement of volumes of carbon monoxide; the total amount of carbon monoxide was in all cases about 100 c.c. at N.T.P. at 0·4—0·45 atm. The errors in two runs (C4/9 and C4/21) were noticeably higher than the average.

TABLE 2. *Gas-circulating experiments with trap at* −183°.

Run	Weight (g.)	Temp.	Time (min.)	CO lost (c.c., N.T.P.)	CO₂ found (c.c., N.T.P.)	CO₂/CO	Carbon calculated (c.c. of CO₂)	Carbon found (c.c. of CO₂)	Oxygen lost (c.c./g.)
C4/9	3·702	650°	172	1·4	0·73	0·52			
			350	2·1	0·84	0·40			
			330	2·0	0·90	0·45			
			852	5·5	2·47		3·0	1·33	0·16
C4/8	3·644	750	175	5·5	3·31	0·60			
			175	2·4	1·40	0·58			
			420	4·9	2·45	0·50			
			770	12·8	7·16		5·6	5·36	0·25
C4/10	3·464	800	66	2·1	1·53	0·73			
			95	2·8	1·84	0·66			
			75	2·5	1·17	0·47			
			88	2·2	1·14	0·52			
			141	1·8	0·89	0·49			
			175	0·6	0·30	0·50			
			640	12·0	6·87		5·1	5·34	0·22
C4/4	3·461	790	290	7·4	4·03	0·55			
			435	8·4	4·83	0·58			
			725	15·8	8·86		6·9	(6·37)	0·36
C4/21	3·543	900	38	1·4	1·51	1·08			
			80	3·0	1·92	0·64			
			85	4·3	2·14	0·50			
			215	3·3	2·00	0·61			
			418	12·0	7·57		4·4	(5·74)	0·26
C4/18	3·457	900	450	12·2	7·10	0·58	5·1	(5·57)	0·22
C4/2	4·769	750	520	13·1	7·10	0·54	6·0	5·07	0·21
C4/14	4·051	700	345	5·4	3·19	0·59	2·2	—	—
Th1/2	5·926	850	320	—	4·23	—	—	2·38	0·155

In every case except one (C4/9), the volume of carbon dioxide collected was greater than half the volume of carbon monoxide lost, and the decomposition cannot be represented simply by the formula $2CO \longrightarrow C + CO_2$. Extra oxygen must have been obtained from the oxide. The amount can be estimated from the difference between the volume of carbon dioxide collected during the experiment and the volume obtained on analysis for carbon; both these volumes were comparatively small and were accurately measured. Half this difference is the volume of oxygen lost from the oxide, listed in the last column of Table 2. The low value for the volume of carbon monoxide lost recorded for run C4/9 is clearly due to the difficulty of measuring accurately such small changes in the volume of carbon monoxide.

The results of experiments in which carbon dioxide was not removed from the gas stream are in Table 3. The original composition of the gas is given in columns 4 and 5, and the carbon dioxide content of the gas at the end of the run in column 8. The total pressure of gas was in all cases 0·4—0·5 atm. The carbon on the oxide is given in column 3; the second figure listed for each run is the carbon determined by analysis at the end of the experiment, and is accurate, while the first is the carbon estimated to be present at the start of the experiment from the results of a previous deposition run, and is liable to considerable error for the reasons already

discussed. The amount of oxygen lost from the solid, calculated as before, is recorded where possible in the last column.

TABLE 3. *Gas-circulating experiments with trap at room temperature.*

| Run | Weight (g.) | Carbon on oxide (c.c. of CO_2) | Original gas | | Temp. | Time (min.) | Final gas CO_2 (c.c.) | Oxygen lost (c.c./g.) |
			CO (c.c.)	CO_2 (c.c.)				
C4/11	3·886	0	117	0	800°	330	0·92	
			135	0	,,	250	1·62	
			116	0	,,	108	0·62	
			125	0	,,	180	1·01	
			121	0	,,	150	0·67	
		3·72				1018	4·84	0·15
C4/13	3·767	0	110	0	800	780	0·74	
			109	0·74	,,	240	0·76	
		0·26				1020	0·76	0·067
C4/3	3·244	0	106	0	730	310	0·92	
			140	0	,,	288	0·78	
		0·087				598	1·70	0·24
C4/19	3·759	0	90	2·60	800	270	2·91	
		0·03						0·040
C4/14	4·051	(2·2)	116	0	750	405	0·58	
			123	0·54	,,	320	1·03	
			121	1·03	,,	210	1·13	
		3·69	133	0	,,	235	0·43	
C4/6	3·013	(4·3)	110	0	740	335	0·04	
			94	4·12	,,	416	4·32	
		3·8	100	4·32	,,	206	3·95	
C4/21	3·543	(4·4)	97·5	18·42	750	115	17·87	(−0·078)
			93·5	17·87	,,	100	17·81	
		5·74	86·7	17·81	,,	122	17·84	
C4/23	5·781	(1·3)	~100	3·57	850	60	3·14	(−0·04)
			~100	3·12	,,	270	3·11	
			~100	3·11	,,	120	3·07	
CO circulated at 850° with trap at −183°; 2·61 c.c. of CO_2 collected.								
		3·90	100	2·61	850	90	2·23	(−0·033)
C4/17	4·481	(5·6)	0	65·9	750	278	61·9	
		2·23						
Th1/3	5·926	0	121	0	850	26	1·45	
		0·05	126	1·45	,,	125	1·48	0·118
Th1/5	5·926	0	128	3·93	850	140	5·17	0·105
		0·01						

In the first three experiments in Table 3, pure carbon monoxide was circulated over a freshly-reduced, clean specimen of oxide. The apparent rate of decomposition was far lower than it had been when the carbon dioxide formed was continuously removed, and the result of C4/13 indicated that the reaction stopped when the carbon dioxide concentration had reached a limiting value, which varied in different experiments from 0·5 to 1·2% of the total gas. Very little carbon was deposited when a larger concentration of carbon dioxide was initially added to the carbon monoxide (C4/19).

A similar result was obtained when pure carbon monoxide was circulated over an oxide holding some carbon (C4/14); carbon dioxide production continued up to a gas content of 0·93%, by which time the reaction had practically stopped, but removal of the carbon dioxide and circulation of fresh carbon monoxide led again to the production of more carbon dioxide.

Circulation of gas mixtures containing more than 4% of carbon dioxide seemed to remove little or no carbon, which would cause the carbon dioxide content of the gas to fall. This was investigated in detail by using two specimens, one of which had been " saturated " with carbon

(C4/21), while the other (C4/23) held about half this amount. Loss of carbon dioxide occurred the first time a mixture rich in carbon dioxide was circulated over these specimens, but no change occurred during subsequent runs. Circulation of pure carbon monoxide, with removal of the carbon dioxide produced, regenerated a surface that would react with a little carbon dioxide. Continuous removal of carbon was clearly not taking place. The loss of carbon dioxide during the first runs following carbon deposition is then due to oxidation of the oxide by carbon dioxide rather than to the removal of carbon; the amounts of oxygen gained by the oxide, on this assumption, are given in parentheses as a " negative loss " in the last column of Table 3.

Pure carbon dioxide did remove some carbon from a carbon-loaded oxide (C4/17); 4 c.c. of CO_2 was lost in 278 min. at 750°, and the subsequent analysis for carbon gave a figure 3·4 c.c. lower than the amount calculated to have been deposited. This amount is well outside the usual error on the calculated amount of carbon deposited.

The results of two experiments on thoria are recorded at the end of Table 3. Carbon deposition was inhibited by the presence of about 1% of carbon dioxide, though it proceeded normally if the carbon dioxide was removed, as shown by the last experiment in Table 2. The rapid production of carbon dioxide at first, associated with considerable loss of oxygen from
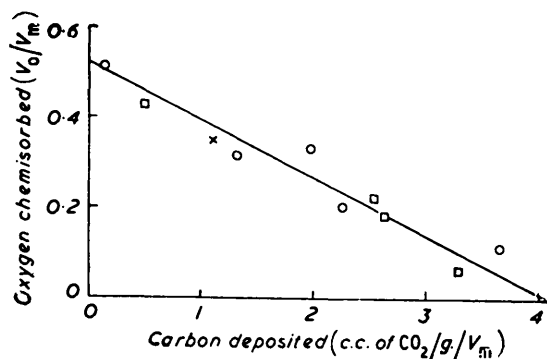

Fig. 4. *The effect of carbon deposition on urania on the chemisorption of oxygen at* −183°.

O, C3;   □, C4;   ×, reactive UO_2 from Edgington and McConnell.

the oxide, is due to these samples' not being given the prior reduction that the urania samples received (see p. 2480).

Reaction on Silica.—Blank runs on the empty silica container were carried out from time to time to check the purity of the carbon monoxide and the extent of the decomposition on the silica walls. Carbon monoxide was circulated for between 4 and 6 hr., with the silica at 700—850° and the trap cold. The highest amount of carbon dioxide collected was 0·11 c.c. from 121 c.c. of carbon monoxide, and the smallest amount was 0·04 c.c. from 120 c.c. of carbon monoxide. Some water was also found—about double the amount of carbon dioxide—presumably formed from hydrogen impurity in the carbon monoxide. A mixture of 2·538 c.c. of carbon dioxide and about 100 c.c. of carbon monoxide was circulated through a silica tube at 850° for 2 hr.; 2·524 c.c. of carbon dioxide was recovered at the end. The reaction with silica was therefore negligible under all conditions.

Carbon Dioxide–Urania Reaction.—The adsorption of carbon dioxide was studied with a sample of urania C4 which had been reduced with carbon monoxide as usual. A slow adsorption occurred at low temperature, 0·135 c.c./g. being adsorbed in 14 hr. at 25° and 13 cm. pressure, and 0·123 c.c./g. in 2 hr. at 100° and 13·8 cm. All the gas was recovered by heating above 200° and no adsorption could be measured at 500°, 650°, or 800°.

Oxidation might have occurred, to form carbon monoxide, without change in gas volume. To check this, 89 c.c. of carbon dioxide were circulated for 5 hr. over 3·25 g. of urania C4 at 750° after the usual reduction period. The carbon dioxide was pumped off and the degree of oxidation assessed by circulating pure carbon monoxide for 30 min. at 650°, after which 0·72 c.c. of carbon dioxide was found in the gas. The oxygen absorption by the urania from the carbon dioxide was therefore 0·11 c.c./g., and this is a maximum value, since it would have included any carbon dioxide formed in the initial stages of the usual carbon deposition process (see above).

Chemisorption and Oxidation Properties.—The results plotted in Fig. 4 illustrate the decrease

in the chemisorption of oxygen at $-183°$ on urania that occurs as carbon is deposited. V_0/V_m is the ratio of the oxygen chemisorbed at $-183°$ to the volume of oxygen in a physically-adsorbed monolayer, and the carbon content is expressed as c.c. of CO_2/g. divided by V_m to refer the results on different samples to the same surface area of oxide. Carbon was deposited under flow conditions at $500°$ in most cases and $650°$ in others on C3 and C4. The values of V_m varied considerably amongst themselves, those for C3 samples varying from 0·37 to 0·43 c.c./g. and for C4 from 0·30 to 0·33 c.c./g. with one of 0·41 c.c./g.; this variation is almost certainly due to the particle division which occurs when a partially-oxidised sample of urania is heated before the first reduction treatment.[4] Also plotted in Fig. 4 is one (unpublished) result obtained by Edgington and McConnell [5] on a very reactive sample of urania, having $V_m = 3·9$ c.c./g.

The rate of oxidation of C3 at higher temperatures was determined after deposition of carbon to a limiting value of 1·89 c.c. of CO_2/g. The oxidation at 4·7 cm. and $18°$ followed the normal logarithmic dependence on time [4] but the rate of reaction was about a quarter of that of the rate with carbon-free C3 specimens under the same conditions. The rate of oxidation at $142°$ and 3·5 cm. also followed the expected kinetic law,[4] and the results for the first 60 min. fitted the parabolic equation

$$V = 0·082\sqrt{t} + 0·09$$

where V is the volume of oxygen absorbed (c.c. of O_2/g.) in t min. This is again a factor of 3 or 4 slower than the rate of oxidation previously determined. Only 0·01 c.c. of carbon dioxide was found in the residual oxygen at the end of the experiment.

DISCUSSION

The results in Tables 2 and 3 establish that oxygen is lost from urania during the deposition of carbon. The CO_2 : CO ratios listed in Table 2 are admittedly not very accurate, but the general tendency is clear: more oxygen is lost from the oxide early in the reaction than later. The results of the first experiments in Table 3 show, however, that some deposition of carbon does occur in the early stages and the amounts of oxygen lost from the oxide tend to be higher the more carbon is deposited. The two processes, oxygen loss and carbon deposition, probably occur simultaneously but not at the same rates.

The two processes are linked. The decomposition stops when the carbon dioxide content of the gas is about 1%. This is not due to an equilibrium state's being reached, in which the rates of deposition and removal of carbon are equal, since there is no evidence that carbon is removed at any appreciable speed when gas mixtures containing much more carbon dioxide are circulated over carbon deposits, and the rate of removal of carbon was very slow compared with the rate of deposition from pure carbon monoxide, even when pure carbon dioxide was used. The loss of carbon dioxide that occurs the first time a CO–CO_2 mixture is circulated over urania holding appreciable carbon is more readily explained as being due to loss of oxygen from the carbon dioxide, replacing some of the oxygen lost from the oxide during the deposition of carbon. It seems clear that it is the re-adsorption of this small amount of oxygen which inhibits the further deposition of carbon; the decomposition is then controlled by an equilibrium involving oxygen, not carbon. Re-exposure to pure carbon monoxide results in reduction of the oxide again, and more carbon can be deposited (*e.g.*, C4/23, Table 3); subsequently, oxygen can again be adsorbed from a CO–CO_2 mixture. The fact that a little oxygen is lost from urania when a gas mixture containing as much as 2·9% of carbon dioxide is circulated before any carbon has been deposited (run C4/19, Table 3) indicates that the oxygen activity is higher initially than it is after oxygen has been removed and carbon deposited; this is inherently reasonable and in line with the other evidence that oxygen is removed predominantly in the early stages of the reaction. The total oxygen loss from urania during carbon deposition reached 0·26 c.c./g. on C4, the higher value in run C4/4 (Table 2) being almost certainly due to a high surface area value for this specimen as shown by the high

value for the carbon deposited. A single layer of O^{2-} ions in the surface of a urania sample having $V_m = 0.32$ c.c./g. would be about 0.42 c.c. of O_2/g.,[9] so that oxygen equivalent to 60% of a single layer is lost during carbon deposition. The amounts of oxygen which are sufficient to stop the reaction when re-absorbed at a later stage amount to less than 30% of the total oxygen loss.

The few results available indicate that oxygen equilibria also control the deposition of carbon on thoria. The thoria samples had no prior reduction treatment but were used after ignition in air. The comparatively large oxygen loss that rapidly occurred in carbon monoxide has been shown in other work to be entirely independent of the deposition of carbon and to comprise 10—20% of the oxygen in the thoria surface.[10] A corresponding loss of oxygen from urania would certainly have occurred during the prior reduction stage. The amount of oxygen lost from a thoria sample on which appreciable carbon had been deposited was higher than the amount that was quickly lost before carbon deposition began [cf. Th 1/2 (Table 2) with Th 1/3 and Th 1/5 (Table 3)] so that further oxygen is lost from thoria as carbon deposition proceeds.

This result is evidence that the oxygen which is removed from urania as carbon deposition occurs is not the last trace of interstitial oxygen which is not removed by the prior reduction treatment, since thoria would not be expected to contain any appreciable amount of interstitial oxygen. The abrupt change in reaction rate provided additional evidence; the prior reduction stage, involving removal of interstitial oxygen,[4] is very rapid at 600°, 1.8 c.c. of O_2/g. being removed in less than 15 min., while oxygen loss accompanying carbon deposition occurs for at least two hours at 800° and probably proceeds slowly for as long as carbon is being deposited. It seems likely that this oxygen loss is a surface, not a bulk, phenomenon.

The simplest hypothesis to explain the almost linear fall in chemisorptive capacity with carbon deposition (Fig. 4) is that the carbon is uniformly distributed over the surface. The differential heat of adsorption of oxygen at $-183°$, at low coverage, is not affected by the presence of some carbon on the surface,[11] so it appears that it is the number and not the nature of the adsorbing centres which is affected by carbon. The line drawn through the experimental points in Fig. 4 extrapolates to $V_0/V_m = 0.52$ with no carbon on the surface, in good agreement with other observations that $V_0/V_m = 0.50—0.56$ for urania samples of this type.[12] Also, the chemisorption of oxygen falls to zero at a carbon content of 4.1 c.c. of CO_2/V_m which is rather less than the corresponding figures for the maximum carbon deposition on urania, which are 4.7 and 4.9 c.c. of CO_2/V_m for samples C3 and C4 respectively, suggesting that deposition stops when the surface is nearly completely covered. The maximum number of surface uranium atoms per physically-adsorbed oxygen molecule is 1.3.[9] The maximum carbon deposition is thus equivalent to at least 3.8 carbon atoms per surface uranium atom, or 1.9 carbon atoms per surface oxygen atom, if the carbon is deposited evenly. This seems to be spatially possible, for the minimum diameter of a C_2 group in UC_2 is about 3.0 Å and the diameter of an O^{2-} ion in urania is about 2.7 Å.

The formation of a " surface carbide " might be possible under the conditions used even though the formation of bulk carbide is thermodynamically impossible.[13] The formation of a thin layer of carbon over the surface in this case may explain why the general features of the reaction are so different from those characteristic of the decomposition of carbon monoxide on metal catalysts, when bulk carbon can be formed.[1] The only conflicting observation is the light-grey colour of the thoria samples after carbon deposition, which would usually be taken as evidence for the formation of discrete particles

[9] McConnell and Roberts, " Chemisorption," Butterworths, London, 1957, p. 218.
[10] Roberts and Walter, unpublished work.
[11] Ferguson and McConnell, *Proc. Roy. Soc.*, 1957, *A*, **241**, 67.
[12] Roberts, *J.*, 1954, 3332.
[13] Heusler, *Z. anorg. Chem.*, 1926, **154**, 364.

of carbon or of thick, local deposits. However, it is not certain that all the deposition occurred in the same manner on the two oxides; the rate of reaction was much slower on thoria, and the thoria samples were of smaller particle size than the urania; there is other evidence for the deposition of free carbon on an " active " surface of thoria.[14]

A detailed explanation of the kinetics will not be attempted here because of the complex nature of the deposition reaction. The " autocatalytic " appearance of the early stages of the high-temperature runs (Fig. 3) may be due to a real acceleration of the carbon deposition as the oxide surface is stripped of oxygen, or it may be due to the difficulty of displacing carbon dioxide efficiently from the powder bed, which was 5 mm. thick, at high reaction rates. The kinetic curves in Fig. 2 approximate to the shape expected if the diminution in rate with time is due to the gradual occupation of a fixed number of suitable sites. The rate of deposition of carbon is approximately dependent on the first power of the pressure of carbon monoxide. This would be the case if the reaction were between carbon monoxide in the gas phase and adsorbed carbon monoxide, if adsorption equilibrium was quickly established. Adsorption of carbon monoxide on urania has been shown not to be extensive at the temperatures used here, but no results obtained now or previously rule out the possibility that carbon monoxide is quickly adsorbed on a few sites, and these might be oxygen vacancies, since the re-adsorption of as little as 8% of the oxygen in a surface layer was sufficient to stop the deposition of carbon in some cases.

[14] D'Eye and Sellman, A.E.R.E. C/R 1286.