

The Oxides of Uranium. Part VII. The Oxidation of Uranium Dioxide.*

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Uranium dioxide is oxidised by two distinct processes in the temperature ranges -130° to 50° and 130° to 180° , though in each case oxygen is absorbed into interstitial positions in the lattice. Between -130° and 50° , the oxygen absorbed increases as the logarithm of the time; the same law is followed at the same temperatures by solid solutions of uranium dioxide and thoria. The oxidation virtually ceases at temperatures below 50° at a composition which depends upon the surface area of the uranium dioxide. Between 130° and 180° the kinetic law followed is characteristic of a diffusion-controlled process but both the rate of reaction and, to some degree, the composition of the oxide finally formed depend upon the pressure. The reaction with nitrogen dioxide is much faster than the reaction with oxygen.

THE final products of the oxidation of uranium dioxide at moderate temperatures contain oxygen in interstitial positions in the original lattice and the course of the oxidation is not complicated by any abrupt phase change. Three processes of oxidation can be distinguished, taking place at different temperatures. The first proceeds rapidly at -183° , is probably confined to the surface, and consists of the adsorption of an oxygen molecule on at least 60% of the uranium atoms in the surface layer (Part V, *J.*, 1954, 3332). The second process can be followed at all temperatures from -130° to 50° on uranium dioxide itself and on those preparations of uranium dioxide-thorium dioxide mixed crystals which react with oxygen at -183° . Some results at 0° and 23° have already been recorded in Part V. More extensive results are presented below; it is shown that the extent of oxidation increases as the logarithm of the time of exposure to oxygen, and the effects of pressure and temperature are recorded. The third process occurs at measurable rates between 80° and 180° ; this was first studied by Alberman and Anderson (*J.*, 1949, S 303). They showed that the kinetics of oxidation in air at several temperatures could be satisfactorily accounted for by a simple diffusion law with an activation energy of 27 kcal./mole. They reported, however, that the reaction rate was not independent of the oxygen pressure at low pressures. The last section of the present work is concerned with the dependence both of the rate of oxidation and of the final composition reached on the ambient oxygen pressure at a number of temperatures. The reaction of nitrogen dioxide with uranium dioxide at similar temperatures was also studied, since this is equivalent to using atomic

* Part VI, preceding paper.

oxygen (Katz and Gruen, *J. Amer. Chem. Soc.*, 1949, **71**, 2106) and should illustrate the influence of surface reactions on the bulk oxidation.

EXPERIMENTAL

Apparatus.—The low-temperature oxidation process, in which the amounts of oxygen reacting were small, was followed in the constant-volume, variable-pressure apparatus used for chemisorption studies (Part V, *loc. cit.*). The amount of gas reacting was determined by measuring the rate of fall of pressure on a mercury manometer; the total pressure variation was not allowed to exceed 15% of the original pressure. Since the rate of reaction changed only slowly with pressure, such pressure variations had little influence on the rates observed. The uranium dioxide was contained in a silica bulb or U-tube, which could be immersed in suitable freezing mixtures. Temperatures below 0° were measured with a pentane thermometer.

Different techniques were used for following the high-temperature oxidation process at high and at low pressures. At pressures from 2 to 500 mm., the amount of gas reacting was measured in a constant-pressure, variable-volume apparatus. The pressure was maintained constant automatically to ± 0.2 mm. at the lower pressures, and to ± 2 mm. at the higher pressures, by arranging that the flow of mercury into the gas burettes was controlled by a valve activated by an electrical contact fused in a mercury manometer in the reaction system. Pressures below 10 mm. were actually measured on a manometer filled with Apiezon "A" oil. The uranium dioxide was weighed into a silica U-tube which was fused inside a wide silica tube in which liquids of suitable b. p. were refluxed, thus maintaining a constant temperature during the reaction period. Accurate measurements could be made with this apparatus, but the volume of gas to be handled became inconveniently large at pressures lower than 2 mm.

At lower pressures, the kinetics were followed by measuring the gain in weight of a 0.3 g. sample of uranium dioxide suspended in a silica bucket weighing 0.2 g. from a silica spring having an extension of 1 mm. per mg. Measurements of the extension of the spring were made with a travelling microscope to ± 0.02 mm. The accuracy obtainable by this method was not as high as the gas-volumetric measurements allowed, but it was sufficient to enable the main features of the kinetics to be determined, since the total weight gain in any experiment was ~ 4 mg. The silica bucket hung in the middle of a double-walled silica jacket, in the annular space of which liquids were refluxed during the kinetic experiments, and which could be surrounded by a furnace for high-temperature reduction and outgassing. During a kinetic experiment, oxygen from a cylinder streamed continuously past the sample, the pressure being controlled by a needle-valve on the inlet side and by a stopcock between the specimen and the pumps; the oxygen stream passed through a liquid-oxygen trap immediately before entering the reaction tube. The pressure was measured by a Pirani gauge which had been calibrated against a McLeod gauge. The outlet to the gauge was situated about 4 in. from the sample, on the downstream side, the connecting tube being of 2 cm. internal diameter. Measurements made with another gauge the same distance from the first showed that the pressure drop in this length of tubing under the conditions used was negligible; the gauge thus measured correctly the pressure of oxygen surrounding the sample under flow conditions.

The preparation of the gases used for reduction and gas-volumetric measurements has been described in Part V (*loc. cit.*). The oxygen used was either B.O.C. "Spectroscopically Pure" oxygen or was prepared by heating A.R. potassium permanganate and passing the gas through glass-wool, potassium hydroxide, and a liquid-oxygen trap. A nitrogen dioxide-oxygen mixture was generated by heating dry lead nitrate crystals to 400–450°, after first outgassing them at 150°.

Uranium Dioxide Preparations.—Full details of the preparation and characterisation of the uranium dioxide specimens used have been given in Part V (*loc. cit.*). For convenience, the mean particle diameters, \bar{d} , as determined by gas-adsorption methods, are repeated here :

Specimen	B1	C3	H	R	CA	B50
\bar{d} (in μ)	0.45	0.41	1.0	2.3	2.3	0.053

RESULTS

Section 1. Low-temperature Oxidation.

General Procedure.—Each sample had to be reduced to stoichiometric uranium dioxide before each oxidation experiment. Reduction was carried out either with hydrogen or with carbon monoxide at temperatures between 500° and 750°, and the sample was subsequently

outgassed at temperatures 50° above the reduction temperature. A partially fresh surface might be exposed each time by this treatment, because of the tendency of uranium dioxide containing excess of oxygen to form ordered phases at temperatures below 500° (Anderson and Alberman, *loc. cit.*). Ideally, therefore, the surface area should have been measured after each reduction. This was often done, but it was found that a series of reductions carried out on the same sample after successive slight oxidations caused only small changes in surface area, and, in what follows, the surface area is assumed not to change during such series of experiments. The errors introduced by this assumption should be small; for example, one sample decreased in area by 6% after seven cycles involving oxidation at temperatures below 30° and reduction at 500° , and four such cycles reduced the surface area of another sample by 10%.

The reaction of the reduced uranium dioxide with oxygen at the desired temperature and pressure was studied either at once or after exposure to oxygen at -183° , and pumping off the gas not adsorbed at -183° and at -78° . The total reaction at higher temperatures can be

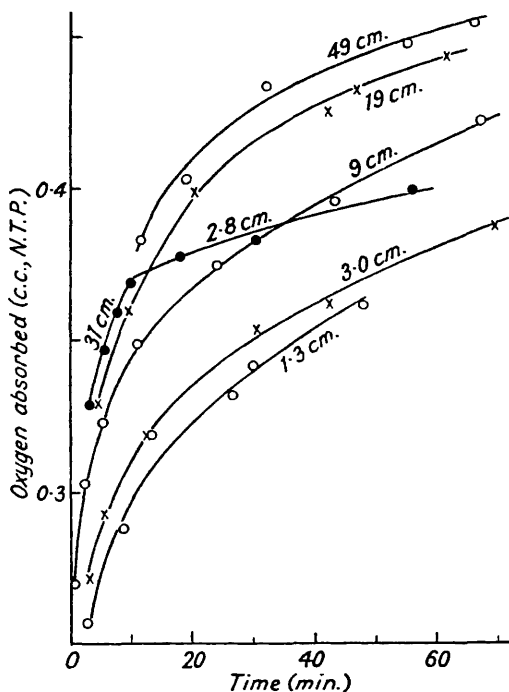


FIG. 1. Oxidation of uranium dioxide at 19° and at various pressures.

regarded as the sum of two quantities, a constant amount of oxygen chemisorbed even at -183° , and an amount characteristic of the higher temperature, the pressure of oxygen, and the time of reaction (see Fig. 3 of Part V of this series).

Oxygen could be admitted directly to samples of uranium dioxide at temperatures up to 50° if the particle size was 0.4μ or larger. Specimens having mean particle diameters of 0.05μ reacted pyrophorically if exposed directly to oxygen at 0° , but oxidised normally if exposed first at -80° , presumably because the heat evolved due to the rapid reaction at 0° on a reduced surface of large area could not be conducted away sufficiently rapidly. Specimens of particle size 0.4μ reacted pyrophorically if exposed in the reduced state to oxygen at 150° .

No differences in reaction rates were found between specimens reduced in hydrogen and those reduced in carbon monoxide. Hydrogen is adsorbed on uranium dioxide at high temperatures, while carbon monoxide is not (Part VI, *loc. cit.*). A direct comparison was made between the absorption of oxygen at 0° and 10–12 cm. pressure on one sample of specimen C3, no. 50, which had been reduced with carbon monoxide and another, no. 65, which had been heated in hydrogen and had adsorbed 0.3 c.c. of hydrogen/g. After correction for a small difference in surface area, the results were as follows :

Time of reaction (min.)	0.55	1.85	32
Oxygen absorbed, sample 50 (c.c./g.)	0.37	0.40	0.50
Oxygen absorbed, sample 65 (c.c./g.)	0.32	0.335	0.42

Chemisorption of a considerable quantity of hydrogen thus caused a rather small decrease in the amount of oxygen absorbed at 0°. The effect on the reaction with oxygen of the small amounts of hydrogen that might have been left on the surface after reduction with hydrogen and high-temperature outgassing would therefore not be serious.

The Logarithmic Law.—Results obtained with specimen R at 19° and at pressures from 1.3 to 49 cm. are plotted in Fig. 1. The amount of oxygen reacting in a given time increased with increasing pressure, though the effect was rather small. However, suddenly dropping the pressure from 31 cm. to 2.8 cm. in one run, after the reaction had been proceeding for 10 min., caused a notable decrease in the rate of reaction, and raising the pressure from 3.0 to 13 cm. in another run after 70 min. caused some acceleration. The effect of pressure was thus not only an initial effect. The amount of oxygen absorbed in each case increased as the logarithm of the time of exposure, as is shown in Fig. 2, where the results of Fig. 1 are replotted against the logarithm of the time.

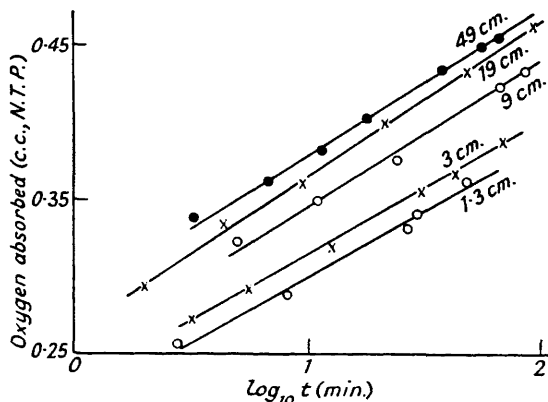


FIG. 2. Logarithmic plot for oxidation of uranium dioxide at 19°.

A logarithmic kinetic law was followed over the whole range in which the low-temperature process could be studied. If the fundamental equation is written

$$dc/dt = Ke^{-pc} \dots \dots \dots (1)$$

where c is the amount of oxygen absorbed in time t , and K and p are constants, then, if $c = 0$ at $t = 0$

$$c = (1/p) \ln (Kpt + 1)$$

If $Kpt \gg 1$, $c = (2.3/p) (\log_{10} Kp + \log_{10} t)$, and the constants p and K can be evaluated from a plot of c against $\log t$.

In order to facilitate the comparison of results on different specimens, the quantity $(V - V_0)/V_m$ was plotted against $\log_{10} t$; V is the total quantity of oxygen reacting in t min., V_0 the amount of oxygen chemisorbed at -183° , and V_m the amount of oxygen required to form a single, physically-adsorbed monolayer on the specimen studied at -183° , as determined by application of the B.E.T. equation. The methods used in the evaluation of V_0 and V_m are discussed fully in Part V (*loc. cit.*). Essentially, $(V - V_0)/V_m$ represents the amount of oxygen absorbed by the time-dependent process studied here on a constant area of each specimen of uranium dioxide. The values of the constants K and p of the logarithmic law which were found in this way are recorded in Table 1, together with the values of $(V - V_0)/V_m$ reached in 30 min., which illustrate the magnitude of the amounts of oxygen reacting.

The results were reasonably reproducible as between the various specimens; the one general trend noted was that the rates of reaction of oxygen with specimen R were usually lower than with other specimens. It had previously been found (Part V, *loc. cit.*) that the chemisorption of oxygen per unit surface of specimen R was also lower than normal. The logarithmic law was found to hold for amounts of gas reacting of from $0.05V_m$ to about $2V_m$ and for times of reaction ranging from 100 to 1000 min. The constant p of equation (1) decreased regularly as the temperature increased. The results on specimen R at 19° showed that the value of p was not much, if at all, dependent on pressure—as is illustrated by the straight-line plots in Fig. 2 being nearly parallel. The pressure dependence was due to the rise in the value of K as the pressure was increased. The values of K at a given pressure certainly decreased as the

temperature was lowered, although the K values were in general more variable than the p values. This is probably due to $\log Kp$ being estimated from the absolute amount of oxygen absorbed in a given time, once p had been determined from the slope of a logarithmic plot, and the value of K therefore depends on the conditions during the first moments when oxygen was admitted to the samples: results might be vitiated by local rises in temperature due to too rapid admission of gas or by lack of thermal equilibrium. Some such effect probably explains the extremely high K value found with specimen H at -113° .

TABLE 1. *Low-temperature oxidation of uranium dioxide.*

$$(V - V_0)/V_m = (2.3/p) \log Kp + (2.3/p) \log t \text{ (min.)}$$

Specimen	Reduction conditions	Oxidation at :		$(V - V_0)/V_m$ at		$\log_{10} Kp$	K
		Temp.	Pressure (cm.)	30 min.	p		
H	H ₂ , 500°	-138°	(1.2)	0.065 *	59	0.17	0.025
		-113	(2.3)	0.21 *	43	2.50	7.3
		-79	3.2	0.23	28	1.27	0.67
		-66	4.5	0.29	19.2	0.95	0.46
		-42	10.5	0.46	18.2	1.34	1.2
		-19	9.7	0.54	14.5	1.88	5.2
		0	11	0.62	13.7	2.14	10.1
B1	H ₂ , 580	-66	5	0.29	23.3	1.35	0.96
		-19	10	0.54	14.2	1.84	4.9
		0	5	0.75	10.1	1.83	6.7
C3	CO, 580	0	17	0.45	13.1	1.72	4.0
		0	13	0.71	10.1	1.65	4.4
		0	12	0.50	13.4	2.31	15.2
		25	5	—	9.2	—	—
		51	12	1.40	5.6	1.84	12.4
CA	CO, 700	0	6	0.56	11.7	1.37	2.0
R	H ₂ , 530	-66	6.5	0.19	35.7	1.55	1.0
		-21	7.5	0.33	20.6	1.49	1.5
		0	7	0.49	13.9	1.42	1.9
		19	49	0.66	9.3	1.53	3.7
		19	19	0.64	8.6	1.20	1.8
		19	9	0.56	9.9	1.00	1.01
		19	3	0.50	10.3	1.00	0.97
		18.5	1.3	0.47	10.2	0.85	0.69
B50	CO, 480	-78	16	—	(98)	—	—

* Corrected for physical adsorption.

The results found with specimen B50, which had a very large specific surface, were anomalous. Oxygen was admitted at -78° after first saturating the surface with oxygen at -183° and pumping the oxygen away at -183° , -78° , and 20° . An initial large absorption was followed by a very slow reaction ($p = 98$) for about 30 min., after which time the reaction rate increased and the p value found (33) was much the same as was found when using the preparations of larger particle-size at the same temperature.

Oxidation of UO₂-ThO₂ Solid Solutions.—The oxidation of these solid solutions at low temperatures also followed a logarithmic law. The constants K and p are recorded in Table 2.

TABLE 2. *Low-temperature oxidation of U_xTh_{1-x}O₂ preparations.*

$$\text{Equation : } (V - V_0)/V_m = (2.3/p) \log_{10} Kp + (2.3/p) \log_{10} t \text{ (min.)}$$

$$\text{Oxidation conditions : } (V - V_0)/V_m \text{ at } t = 30 \quad (V - V_0)/V_0$$

x	Temp.	Pressure (cm.)	$(V - V_0)/V_m$ at $t = 30$		p	$\log_{10} Kp$	K
0.90	0°	10	0.57	1.26	15.7	2.20	10.0
0.82	0	7	0.53	1.27	15.8	2.17	9.3
0.82	23	8	0.73	2.15	9.3	1.50	3.4
0.66	0	6	0.37	1.20	15.3	0.97	0.60
0.66 C.C.	0	9	0.33	0.97	20.1	1.40	1.2
0.50 C.C.	0	7	0.26	0.96	22.8	2.00	4.4
0.24 C.C.	0	6	0.053	0.35	(90)	(0.57)	(0.04)
0.24 C.C.	23	6	0.14	0.95	38	0.88	0.20
0.15 C.C.	23	4	0.0075	0.068	115	0.46	0.025

In order to compare the amounts of oxygen reacting at 0° and at 25° with the amounts chemisorbed at -183° , values of $(V - V_0)/V_0$, as well as of $(V - V_0)/V_m$, at $t = 30$ min. are recorded in Table 2. Comparative values of $(V - V_0)/V_0$ for uranium dioxide can be read off from Table

1, since in this case $V_0 \sim 0.5V_m$. The preparations denoted "C.C." had been prepared by crushing macrocrystalline sintered pellets of the solid solutions. All specimens were reduced with carbon monoxide at $\sim 600^\circ$ immediately before the oxidation measurements were begun.

The ratio $(V - V_0)/V_0$ decreased sharply when the mixed crystals were dilute in uranium—the amount of reaction in a given time at 0° or 23° decreased more rapidly than the amount of surface reaction. The p values found were roughly constant and comparable with those for uranium dioxide until the mole fraction of uranium dioxide in the solid solution became lower than 0.66, when p increased. The K values were again more variable, but in general decreased as the mole fraction of uranium dioxide decreased.

Vacuum Treatment after Partial Oxidation.—The oxygen absorbed at low temperatures was mobile above 100° . A sample of specimen C3 was oxidised for 30 min. at 0° , pumped at 170° for 2 hr., and oxygen again admitted at 0° , whereupon the oxidation followed the same course as initially on the reduced sample, the rate being about 0.9 of the initial rate. Again, a rapid absorption of oxygen occurred in the first 20 min. upon re-admission of oxygen to a sample (H) which had been pumped at 120° for 3 hr. after oxidation for 100 min. at 0° .

The same mobility did not occur at 25° . A sample of C3 was oxidised for 23 min. at 25° and then pumped at 25° for 3 hr. Oxygen was readmitted at the same pressure (~ 5 cm.) at 25° :

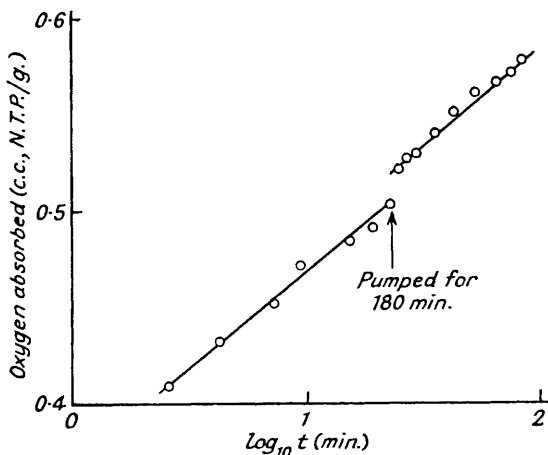


FIG. 3. The effect of interrupting oxidation at 23° by pumping at 23° .

a small adsorption, 0.02 c.c./g., occurred in the first minute, after which the oxidation continued as if there had been no interruption. The results are plotted in Fig. 3, in which the total oxygen absorbed is plotted against the total time of exposure to oxygen. The same result was obtained when oxidation at 23° was interrupted by the 16 hours' pumping at 23° . A similar, small effect was observed when oxidation at -113° was interrupted by 30 min. in vacuum at 20° .

These results indicate that the oxygen which has reacted does not leave the position it first occupied at 25° , but that it migrates away from the original position at temperatures above 100° , so that more can be absorbed into the same sites.

Limit of the Low-temperature Process.—The amounts of oxygen absorbed when a sample of C.3 was held in 12–20 cm. of oxygen and the temperature raised in stages from 0° — 23° — 51° — 88° — 124° are plotted in Fig. 4. Raising the temperature from 23° to 51° , after a long time of exposure to oxygen at 23° , caused only slight additional oxidation, but rapid acceleration of oxidation followed when the temperature was raised to 88° and to 124° . The oxidation above 88° was due to a different process, which was negligibly slow below 51° ; this is the high-temperature process for which results are given in Section 2 (below).

It was clear from the results shown in Fig. 3, and from an extrapolation of the logarithmic plot of the oxidation of C.3 at 51° , that the low-temperature process could lead to the absorption of at least 1.0 c.c. of oxygen per g. of specimen C.3, or about $2.5V_m$. Since $V_0 \sim 0.5V_m$, the limit reached by $(V - V_0)$ is $\sim 2V_m$, or $4V_0$. A similar result was found on analysing small particle-size preparations, such as B.50, after exposure to air. These preparations were oxidised regularly and slowly if exposed to oxygen first at -183° , then at -78° , and then at slowly rising temperatures to room temperature. After finally standing in a desiccator at room temperature for 1–2 weeks, the composition was $\text{UO}_{2.16}$ — $\text{UO}_{2.18}$: about 6.6 c.c. (N.T.P.) of oxygen had been

absorbed per g. Since, for these samples, $V_m \sim 2.5$ c.c./g., oxygen had been adsorbed by the "logarithmic," low-temperature oxidation process to $\sim 2.2V_m$, or $4V_o$.

Density Changes following Low-temperature Oxidation.—Work to be reported elsewhere has shown that the densities of uranium dioxide preparations oxidised at temperatures of 80—150° increase regularly and almost linearly with the amount of oxygen absorbed. These results refer essentially to high-temperature oxidation. Oxidation at low temperatures leads to composition changes too small to cause detectable density differences unless the particle size is very small. The methods of density measurement outlined in Part IV of this series (*J.*, 1954, 3324) were modified to allow for vacuum handling of highly reactive preparations, and the results

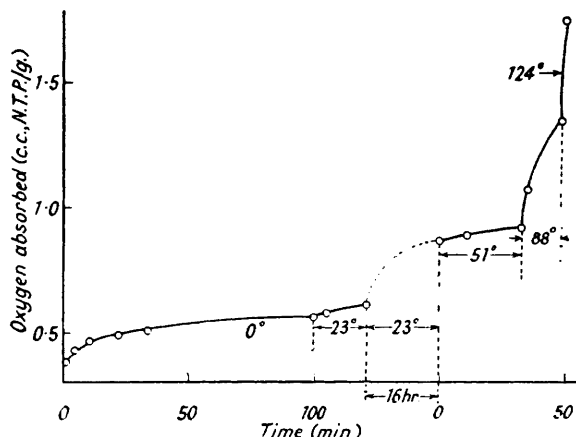


FIG. 4. Continued oxidation of uranium dioxide at increasing temperatures.

obtained are given below. The temperature of oxidation was always -78° at first and it was gradually raised to room temperature; too rapid oxidation led to the nucleation of a U_3O_8 -like phase even at room temperature. The surface areas of the preparations used were ~ 11 sq.m./g.

Sample	Density, as as reduced (g./c.c.)	Density (g./c.c.) after oxidation at -183°	Density (g./c.c.) after oxidation at -78° and 20°	Final composition	Measuring fluid
B.50	10.82	—	10.66	$UO_{2.18}$	Toluene
	10.99		10.66		
B.55	10.79	10.47	10.53	$UO_{2.18}$	Toluene
L.16	10.99	10.35 *	10.78	$UO_{2.15}$	Helium

* This value may be low.

Before each density determination, the samples were outgassed at 20—50°. After oxidation at -183° , the oxygen was removed first at -183° and then at -78° , to prevent further oxidation occurring. The second sample, the density of which was determined with toluene, had to be heated to 100° under toluene to complete the outgassing; the third sample was never heated above 50°.

The density decreased upon oxidation at -183° ; further oxidation at low temperatures caused an increase in density. The X-ray diffraction patterns of the final oxidised products were those of a slightly distorted UO_2 -structure, with a contracted unit cell.

Section 2. High-temperature Oxidation.

General Procedure.—Specimens H and C.3 oxidised at convenient rates at temperatures of 130—180°, and were the only ones used in this study. Since the reaction of fully-reduced preparations with oxygen at these temperatures was pyrophoric, the high-temperature reaction had to be preceded by partial oxidation at low temperatures. Even then, a pyrophoric reaction would result if the reaction rate became too high. Thus, samples of specimen C.3 oxidised regularly at all pressures at 155° after 30 min. in oxygen at 30°, but the reaction was pyrophoric at high pressures at 165°, though the reaction was regular at low pressures at 165°. The particle size of specimen H was double that of C.3, and specimen H oxidised regularly at all pressures at 183° after 30 min. in oxygen at 30°.

It proved impossible to obtain reproducible results on samples from a bottle of specimen H

which had been exposed to air at room temperature for some years. Consequently, it was necessary to reduce each sample with carbon monoxide at 500–700°, and then to oxidise it under standard conditions at low temperatures before each high-temperature run: 30 min. in 12 cm. of oxygen at 30° were the usual conditions when using the gas-volumetric apparatus, and 30 min. in air at room temperature when using the silica-spring apparatus for low-pressure work. The samples were pumped out at room temperature and not pumped at the higher temperature for more than a few seconds before the high-temperature reaction was started. When using the gas-volumetric apparatus, oxygen at the required pressure was admitted as soon as the uranium dioxide sample attained the required temperature, the time of admission being taken as zero time; readings could be taken within 1 min. When using the silica-spring apparatus, the gas flow was adjusted to give the necessary pressure while the sample was at room temperature, and the sample was then heated, the time of reaching the required high temperature being taken as zero time; this procedure did not allow of such detailed study of the initial 10 min. of the reaction.

Reduction at high temperatures following bulk oxidation had more effect on the surface area than reduction following only low-temperature oxidation. Consequently, it was found more satisfactory to use a fresh uranium dioxide sample for each run than to use one sample with successive reductions. All the results quoted below were obtained by using one sample per run. However, a preliminary series of experiments made with one sample of specimen C.3

FIG. 5. Oxidation of uranium dioxide (H) at various pressures at 183°.

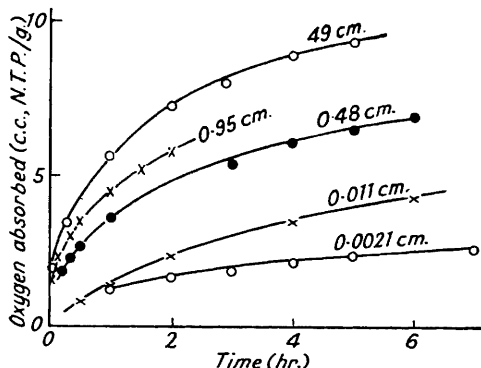
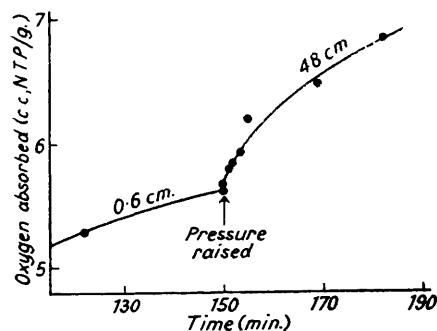


FIG. 6. The effect of raising the pressure on the rate of oxidation of uranium dioxide at 155°.



at various pressures from 3 to 48 cm. at 154° showed that the pressure had a definite effect on the rate of reaction. At the end of this series, the same sample was mixed with twice its weight of pure thoria, and the kinetic runs were repeated in exactly the same way at 12 and 48 cm. at 154°. The addition of the inert thoria made no difference to the rates of reaction. The particular geometry of the sample holder therefore had no effect on the course of the reaction.

The surface areas of the samples used were in many cases determined at the end of the oxidation by gas-adsorption methods, using nitrogen at -196° or krypton at -183° or at -196° . The surface areas of only 4 samples in 27 varied by more than 11% from average values characteristic of specimens C.3 and H; the kinetic constants given below were therefore not corrected for surface-area variations. Results reported elsewhere showed that no change of surface area occurred as oxidation proceeded.

Effect of Pressure on Oxidation Rate.—Some of the results obtained with specimen H at 183° and pressures of oxygen from 0.002 cm. to 49 cm. are shown in Fig. 5; these results illustrate the dependence of oxidation rate on pressure which was quite generally found on both specimens at all the temperatures studied; it can also be seen that the pressure had to be varied by some powers of 10 before the general trend was definitely established.

The rate of oxidation changed quickly when the pressure was altered. The result of raising the pressure to 48 cm. after one sample of C.3 had oxidised for 150 min. at 0.6 cm. is shown in Fig. 6: the rate of oxidation suddenly increased by a factor of about 8. A sample of specimen H was oxidised for 105 hr. at 183° and 0.48 cm., after which time the rate of oxidation had fallen to 0.01 c.c./g./hr. and the total absorption was 12.5 c.c./g. ($\text{UO}_{2.30}$); the pressure was then raised to 24 cm. and a further 0.5 c.c./g. was absorbed in 5 hr. A sudden decrease in

pressure caused an abrupt drop in reaction rate. The oxidation rate of a sample of C.3 dropped by a factor of 5 when the pressure was lowered from 48 to 0.5 cm. after 52 minutes' reaction at 155°, and a similar change in pressure caused the oxidation rate of a sample of H to drop by a factor of 7 after 4.7 hours' reaction at 183°.

Many of the experiments were continued until the oxidation rate became zero—until no measurable absorption of oxygen occurred in 24 hr. The limiting compositions reached were to some extent a function of pressure. The compositions and a brief description of the X-ray characteristics of the final products are given in Table 3. The compositions quoted include the small amount of oxygen absorbed in the first low-temperature oxidation; the sign > means that oxidation had nearly but not quite stopped. The UO₂ structure is described as α ; in the course of oxidation, the diffraction lines broadened in the sense of a contraction of the unit cell, until the β structure was reached: this is the cubic U₄O₉ phase. Oxidation much beyond the composition UO_{2.25} led to tetragonal structures, eventually to the γ'' structure. The relationships between the α , β , and γ'' structures is discussed elsewhere by Anderson (to be published). In general, the structures of the final products of oxidation were those characteristic of the composition reached, irrespective of the temperature and of the rate of oxidation.

When the final composition was known, it was possible to fit the kinetic results to the simple equation for diffusion into spheres used by Alberman and Anderson (*loc. cit.*), *viz.*,

$$\frac{C}{C_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \cdot \frac{Dt}{a^2}\right) \dots \dots \dots (2)$$

where C is the oxygen absorbed at time t , C_{∞} the maximum amount absorbed at $t = \infty$, a the radius of the particles, assumed to be spheres, and D the apparent diffusion constant. The equation can be tested by plotting C/C_{∞} against t/t_1 , where t_1 is the time when $C = 0.5C_{\infty}$. The theoretical curve was closely followed by samples of C.3 at 154° up to $C = 0.9C_{\infty}$, at all pressures, and by samples of H at 183° up to $C = 0.6C_{\infty}$. Values of D were calculated from t_1 ,

TABLE 3. Final products of oxidation.

Specimen	Temp.	Press. (cm.)	Final composition (O atoms/U atoms)	X-Ray characteristics	
H	184°	49	2.36	Tending to γ''	
	182	45.7	—	—	
		0.45	2.28	—	
	183	0.48	2.31	—	
		24	> 2.32	—	
	183	3.1	2.32	β , some γ''	
	184	0.60	2.22	$\alpha - \beta$	
	182	0.011	2.27	Distorted β	
	182	0.0021	> 2.21	α , contracting	
	173	0.011	2.21	$\alpha +$ contracted α	
	C.3	154	48	2.38	γ''
		155	0.6	—	—
48			> 2.37	—	
155		3.2	2.36	γ''	
154		1.0	2.29	β , no γ	
154		1.0	2.26	β , poorly cryst.	
153		48	—	—	
155		0.5	2.24	—	
		0.49	2.26	β , poorly cryst.	
154		0.0135	2.24	β , ? γ	
154		0.0020	2.27	β	
143		0.0135	2.24	—	

since, from equation (2), $Dt/a^2 = 3.02 \times 10^{-2}$ when $C = 0.5C_{\infty}$. Values of D so found are listed in col. 6 of Table 4; a was assumed to be 0.5μ for specimen H, and 0.2μ for specimen C.3.

Not all the experiments could be followed to completion, because of the slow oxidation rates. It was found, however, that a parabolic law

$$C = K\sqrt{t} + A \dots \dots \dots (3)$$

was accurately followed at all temperatures and pressures up to a composition of UO_{2.10}. A plot of equation (3) for specimen C.3 at five pressures at 155° is shown in Fig. 7. Values of K and A are listed in cols. 4 and 5 of Table 4; C was measured in c.c. (N.T.P.)/g., and t in minutes. The values of the intercept A were rather variable, as might be expected since they depend

on the length of time of heating after the initial low-temperature oxidation before high-temperature measurements were started and, although conditions were standardised so far as possible, variations must have occurred.

The values of K showed, at all temperatures, a general dependence on pressure, and the apparent D values also decreased at low pressures. The general trend is well established by the results in Table 4, although exact values of the kinetic constants were difficult to determine,

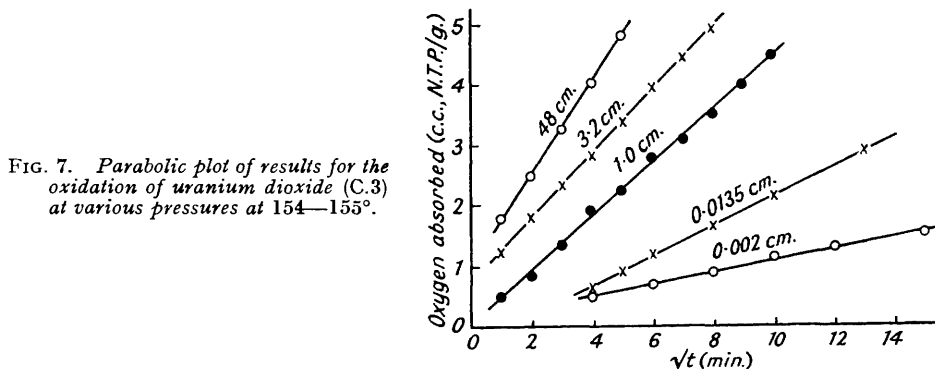


FIG. 7. Parabolic plot of results for the oxidation of uranium dioxide (C.3) at various pressures at 154–155°.

particularly at the lowest pressures reached. The times taken for specimens C.3 and H respectively to reach a given value of C/C_∞ under the same conditions were usually in the ratio 1 : 5, in good agreement with the prediction, from equation (2), that $t \propto 1/a^2$ when C/C_∞ is constant, which leads to a predicted ratio of 1 : 6.

TABLE 4.

Specimen	Temp.	Press. (cm.)	K	A	$10^{15} D$ (cm. ² /sec.)	Specimen	Temp.	Press. (cm.)	K	A	$10^{15} D$ (cm. ² /sec.)
C.3	164.5°	12	0.82	0.45	—	H	184°	48	0.65	0.7	—
	164.5	3.2	0.69	1.0	—		183	49	0.70	0.4	—
	164.5	1.0	0.57	0.9	—		184	49	0.73	0.4	8.9
	163.3	0.0135	0.25	0	—		182	46	0.59	0.4	—
	154	48	0.80	0.9	2.50		183	3.1	0.40	0.7	5.2
153.4	48	0.62	0.5	—	—		183	0.95	0.47	0.8	—
155	3.2	0.53	0.8	1.52	—		184	0.60	0.29	1.5	7.7
154	1.0	0.43	−0.2	0.83	—		183	0.48	0.40	0.4	4.8
154	1.0	0.45	0	0.83	—		183	0.20	0.37	0.75	—
155	0.6	0.40	0.2	—	—		182	0.011	0.26	0	1.9
155	0.49	0.39	0.8	1.67	—		182	0.0021	0.11	0.8	—
154	0.0135	0.24	−0.2	0.37	—		173.4	0.0135	0.16	−0.2	1.2
154	0.0023	0.10	0.1	—	—		165	48	0.41	0.2	—
154	0.0020	0.20	−0.3	0.15	—		165	48	0.44	0.0	—
143.4	0.0135	0.19	−0.1	0.22	—		165	49	0.45	0.15	—
							165	6.4	0.265	0.1	—
131	48	0.35	0.4	—	—		165	1.0	0.26	0.35	—
131	48	0.24	0.1	—	—		165	1.0	0.32	0.3	—
131	12.2	0.25	0.25	—	—		163	0.30	0.22	1.1	—
131	1.1	0.21	0.30	—	—		163	0.011	0.12	−0.25	—
							155	48	0.42	−0.3	—
							153	48	0.29	0.05	—
							154	0.97	0.22	0.35	—
							155	0.25	0.17	0.2	—
Oxidation in $\frac{1}{2}$ atm. of O ₂ -NO ₂ mixture :											
C.3	155	—	1.44	0.8	—	C.3	131	—	0.64	0.8	—

Oxidation with Nitrogen Dioxide.—Oxidation for a long period of specimen C.3 at 131° and at 155° in an oxygen-nitrogen dioxide mixture gave a highly oxidised product containing structures other than fluorite. However, the initial periods of the reaction—until a composition UO_{2.26} was reached, which took 5.5 hr. at 131° and 1.3 hr. at 155°—were apparently similar to the oxidation with oxygen at these temperatures, and the products showed a poorly crystalline

U_4O_9 X-ray diffraction pattern. Weight gain due to adsorption of nitrogen dioxide was corrected for by pumping at 155° at the end of each experiment and subtracting the weight decrease found from the overall weight gain: the adsorption was small at 155° . Adsorption of nitrogen dioxide was so extensive at 100° that the kinetics of oxidation could not be followed, a similar result to that obtained by Katz and Gruen (*loc. cit.*). The parabolic constants, K , determined from the corrected kinetic curves are recorded at the bottom of Table 4. The rate of oxidation was at least twice as large in $\frac{1}{2}$ atm. of a nitrogen dioxide-oxygen mixture as in $\frac{1}{2}$ atm. of oxygen at the same temperature.

DISCUSSION

The low-temperature and high-temperature processes represent two quite distinct modes of oxidation; it is easy to show that the high-temperature process would not proceed at measurable speeds below about 70° , since the activation energy is too high. Either there are two mechanisms by which oxygen can enter the uranium dioxide lattice or a different final state is reached at low and high temperatures.

The changes in density and X-ray characteristics as oxidation proceeds by the high-temperature process (80° to 180°) show that oxygen enters interstitial positions in the uranium dioxide lattice (Alberman and Anderson, *loc. cit.*; Anderson and Roberts, to be published). The study of the similar oxidation of solid solutions of uranium dioxide and thorium dioxide (Part IV, *loc. cit.*) suggests that the factors which limit the amount of oxygen that can enter the uranium dioxide lattice in this way are essentially geometrical.

The X-ray and density evidence obtained on small-particle preparations which oxidised to a considerable extent by the low-temperature process suggest that the final products closely resemble oxides of the same composition obtained by high-temperature oxidation of large-particle specimens. The broad diffraction lines caused by the small crystallite size render exact comparison of the X-ray patterns difficult, but the unit cell does tend to contract as oxidation proceeds. The density also rises as low-temperature oxidation proceeds, although when oxygen is first admitted to a reduced uranium dioxide, the density falls. The results given above suggest that this fall in density is associated with the formation of the first chemisorbed layer of oxygen, complete at -183° . The adsorption of a layer of oxygen on the surface of uranium dioxide would be expected to cause a decrease in density; a quantitative calculation cannot be made accurately until the state in which the oxygen is adsorbed is known, as well as the distribution on the surface. Nevertheless, the density decrease may be approximately calculated if the chemisorbed layer is assumed to be equivalent to a layer of O^- ions, of diameter 2.8 \AA , covering the surface of each particle. The density of a uranium dioxide particle of 500 \AA diameter would then fall by 3.3% owing to chemisorption; further inclusion of $\sim 0.140/VO_2$ interstitially would cause a density rise of 0.9% , and the overall result of oxidising a uranium dioxide preparation of this particle size to $UO_{2.18}$, if all the extra oxygen except the surface oxygen entered interstitial positions, would be a fall in density of $\sim 2.4\%$, a prediction which is close to the observed values. If the extra oxygen were accommodated by the creation of cation vacancies, the density would continue to fall as oxidation proceeded, and the density of $UO_{2.18}$ would be about 10% below that of $UO_{2.00}$.

Low-temperature oxidation would then appear to lead to the filling of interstitial positions by oxygen in much the same way as high-temperature oxidation. The interstitial positions filled seem to be those nearest the surface, since the limiting compositions reached before oxidation becomes extremely slow are dependent not on gross composition but on surface area, the limiting amount of oxygen entering the lattice being $\sim 2.2V_m$. The high-temperature oxidation comes to an end when each unit cell accommodates 1–1.5 extra oxygen atoms. If each unit cell near the surface provides 1 interstitial position which can be filled by low-temperature oxidation, then the number of such positions in one layer is $0.28V_m$, if the area of an oxygen molecule, used to measure V_m , is assumed to be 16.4 \AA^2 . Then the penetration below the surface of the oxygen that enters by the low-temperature process is $2.2/0.28 = 8$ unit cells, or 44 \AA . Further, the regeneration of the absorptive capacity for oxygen at low temperatures by heating in vacuum to temperatures above 100° also indicates that low-temperature oxidation occurs only near the

surface, and that further oxidation can occur only when the oxygen that has entered the lattice receives enough energy to permit migration into the interior.

The formation of a thin film ($\sim 50 \text{ \AA}$) of oxidised uranium dioxide near the surface, at temperatures too low for normal migration of oxygen through the lattice, is reminiscent of the formation of thin films of oxides on metals at temperatures too low for normal migration of metal ions through the oxide layer. This has been explained by Mott and Cabrera (*Reports Progr. Phys.*, 1949, **12**, 163) as being due to the high electrostatic field set up between the metal and the adsorbed oxygen ions, which accelerates the outward motion of the positive metal ions through the oxide film if the film is thin. Some similar mechanism may be operative here, accelerating the inward motion of the negative oxygen ions. Mott and Cabrera showed that, in certain circumstances, this mechanism may lead to a logarithmic kinetic law. Consideration of the electrostatic field set up between the surface and the interior of a *p*-type semiconductor upon adsorption of an electron-accepting molecule, which increases the concentration of positive holes near the surface, has been shown by Engell and Hauffe (*Z. Elektrochem.*, 1953, **57**, 762) to lead to a logarithmic relation of the form of equation (1), but where *C* is the amount chemisorbed at time *t*. Their treatment cannot be directly applied to our case, where the chemisorption is rapid and constant and the oxygen reacting by the logarithmic law penetrates into the solid. There is in any case the difficulty that any such explanation would seem to predict that, as long as the chemisorbed layer remains intact, some inward motion of the interstitial oxygen should continue as long as the oxidised film is very thin. This does not seem to be the case. Even though at least 70% of the chemisorbed layer is stable to evacuation at 20° (Part V, *loc. cit.*), the results of experiments in which the logarithmic oxidation at 20° was interrupted by long periods of pumping (at $\sim 10^{-4}$ mm.) at 20° showed that the interstitial oxygen had not left its original positions; if inward migration had continued in the absence of oxygen in the gas phase, then an accelerated reaction would have occurred when oxygen was re-admitted.

The occurrence of low-temperature oxidation, by the same kinetic law, on all the uranium dioxide-thoria solid solutions which chemisorbed oxygen shows that the process is a general one characteristic of the lattice type and the interaction of uranium and oxygen. Adequate theoretical explanation must await data on the energetics of the various steps involved.

The High-temperature Process.—Perio (*Bull. Soc. chim. France*, 1953, 256) has argued that the oxidation of uranium dioxide at temperatures below 175° proceeds by formation of a skin of a tetragonal oxide, of composition $\text{UO}_{2.32}$. A recent study of the profiles of the *X*-ray lines of oxidised specimens of C.3 and H uranium dioxide (Anderson, to be published) shows, however, that they are compatible with a regular concentration gradient of interstitial oxygen being set up inside each particle, and that ordered structures, $\text{UO}_{2.25}$, $\text{UO}_{2.31}$, and $\text{UO}_{2.375}$, are formed during the later stages of oxidation. The final composition reached was dependent on the pressure (Table 3), though it was not a smooth function of pressure. In a large number of the experiments at lower pressures, the final composition was close to U_4O_9 ($\text{UO}_{2.25}$), and the *X*-ray pattern of the final product was that of a poorly-crystalline U_4O_9 . The final composition reached before oxidation became extremely slow at these temperatures may have depended on the ratio between the rate of oxidation and the rate of ordering of the interstitial oxygen, which would be a function of concentration and temperature. When the oxidation rate was slow, at low pressures, the U_4O_9 structure might have had a chance to form and the oxidation therefore stopped at this composition; other experiments showed that well-annealed U_4O_9 oxidised extremely slowly below 200°. When the rate of oxidation was fast, oxygen may have occupied random interstitial positions more quickly than the ordering process to U_4O_9 could take place, and one of the ordered tetragonal phases was formed. At very low pressures, the oxidation ceased at a composition below $\text{UO}_{2.25}$, and there was *X*-ray evidence that some unoxidised $\text{UO}_{2.0}$ remained; this seems to indicate that, in these cases, the oxidation was so slow that the ordered structure could be formed as a surface skin, inhibiting further oxidation.

The form of the kinetic law followed, and the fact that interstitial oxygen could diffuse away from the surface in the absence of oxygen in the gas phase as soon as the temperature

was raised above 100°, suggest that the high-temperature process was essentially diffusion-controlled, which was the view put forward by Alberman and Anderson (*loc. cit.*). However, for a diffusion-controlled reaction, not only should equation (2) be followed in every case, but, at any temperature, the values of D , the diffusion constant, should be the same at all pressures. This was not so; the values found for D (Table 4) decreased at low pressures. This result may be explained in one of two ways: (i) The surface concentration of mobile oxygen quickly comes to a value characteristic of the pressure at any temperature, but which is not equal to C_∞ , the limiting composition reached. In view of the discussion above of the ordering processes which probably determine the limiting composition, this is not unlikely. The D values are calculated from the time taken to reach $C = 0.5C_\infty$, and if C_∞ is not equal to the surface concentration controlling the diffusion process, the variation of D values with pressure is explained. Alternatively, (ii) the surface process may not always be rapid compared to diffusion. The overall rate of reaction may be determined partly by the rate at which a vacant interstitial site near the surface is occupied by oxygen from the gas phase, and be diffusion-controlled only in the sense that oxygen has to migrate into the interior before vacant sites near the surface can be regenerated. The process is then equivalent to diffusion with a variable surface concentration. At low pressures, the rate would be determined mainly by the rate of the surface reaction, whereas at high pressures, the slow stage would be diffusion into the interior.

The evidence seems to favour a process of type (i). Interstitial sites near the surface are rapidly filled even at low temperatures, and values obtained for the activation energy at different pressures, although rather variable, showed no definite dependence on pressure, which may point to the same diffusion process being rate-controlling at all pressures.

The diffusion equation, equation (2), reduces at small values of C/C_∞ to the parabolic form

$$C/C_\infty = K_1\sqrt{D}\sqrt{t}$$

where K_1 is a numerical constant. Hence the constant K of equation (3) is proportional to \sqrt{D} , and the apparent activation energy of the diffusion process may be calculated from the variation of K^2 with temperature. The results obtained are given below; averaged values of K for a given temperature were used.

Pressure (cm.)	48	12	1	0.25	0.013
E , kcal./mole (spec. H)	18	—	20	21	24
E , kcal./mole (spec. C.3)	27	25	22	—	14—18

These values for the activation energy, E , may be compared with the value of 27 kcal./mole reported by Alberman and Anderson (*loc. cit.*) and with the value of 24 kcal./mole calculated from the K values for the reaction with nitrogen dioxide. The E values showed no definite trend with pressure, as has been reported by Moore and Lee (*Trans. Faraday Soc.*, 1951, 47, 501) for E values calculated from parabolic constants for the oxidation of zinc, between 370° and 400°, which were also dependent on the pressure.

If the effective concentration of interstitial oxygen near the surface is indeed a function of pressure, then the large variation in K observed, more than a factor of 10 if the nitrogen dioxide experiments are included, would seem to require that C_∞ be lower than $0.25/U$ atom at low pressures, since the concentration of interstitial oxygen can never be greater than 1 O atom/ U atom. This suggests that the continuation of the oxidation up to the C_∞ values observed at low pressures, which was a very slow process, may be due to the ordering tendency discussed above, which would lead to interstitial atoms tending to occupy positions in neighbouring unit cells, thus denuding some areas of interstitial oxygen and enabling oxidation to proceed. This view is not incompatible with the eventual formation of a "skin" of U_4O_9 , which was proposed above to account for the diffraction patterns of the final products.

The kinetics of oxidation may therefore be controlled at different stages by different processes. Nevertheless, the experiments which involved rapid pressure changes while oxidation was proceeding showed that the oxidation, both at low and at high temperatures, was immediately sensitive to changes of pressure. It seems, therefore, that the concentration of oxygen which can potentially diffuse into the interior is reversibly pressure

dependent. At any temperature, the parabolic constant K was proportional to p^n , where n varied from 0.13 to 0.16 and was usually between 0.15 and 0.16. The surface concentration of oxygen which can migrate inwards therefore follows a Freundlich adsorption isotherm.

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