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Abstract

The volatility of $UO_{2 \pm x}$ and the phase relations in the uranium-oxygen system were studied using thermogravimetric techniques. Chemical reactions describing the loss of uranium from $UO_{2 \pm x}$ at temperatures between 1100 and 2200°C in oxygen pressures between approximately 10^2 and 10^{-6} torr are proposed. The uranium-bearing vapor species above $UO_{2 \pm x}$ appears to be $UO_4(g)$. Evidence supporting the existence of $UO_4(g)$ included the volatilization of material with an oxygen-to-uranium ratio of 4 during the decomposition of UO_{2+x} $(0.2 > x > 0)$ to near-stoichiometric UO_2 in vacuum above 1500°C and the dependence of the evaporation rate of the uranium dioxide on the oxygen pressure between 1200 and 1500°C.

The equilibrium oxygen pressures over compositions between $UO_{2.02}$ and $UO_{2.63}$ in the UO_{2+x} and U_3O_{8-y} regions and over the boundary between these phases were measured between 1000 and 1600°C. The equilibrium oxygen-to-uranium ratio of $UO_{2 \pm x}$ was less than 2 above 1700°C in vacuum.

Introduction

Gas-cooled reactors containing all-ceramic fuel elements operating above 1000°C without the aid of a metallic cladding are currently under consideration as a means of providing improved reactor performance. In an oxide-base gas-cooled reactor, uranium dioxide would be used for a portion of the fuel. The volatility of UO_2 and the phase relations in the uranium-oxygen system are of interest to predict and understand the migration and loss of fuel and the compatibility with coolant gases and gas contaminants. This information would also aid in understanding the behavior of fuel elements which contain UO_2 in a metallic can and operate with high center-line temperatures.

Ackerman et al.[1] measured the vaporization of UO_2 by effusion cell techniques at temperatures from 1300 to 2500°C in vacuum and concluded that UO_2 vaporizes congruently. Ackerman and Thorn[2] state that the thermodynamic properties of $UO_3(g)$ preclude this species from significantly contributing to the volatility of UO_2 in vacuum at high temperatures. Cordefunke,[3] however, used the available thermodynamic information to show, through calculations, that $UO_3(g)$ is the predominant vapor phase over UO_2 below 2000°C in low oxygen pressures (7.6×10^{-4} to 7.6×10^{-6} torr). Transpiration experiments were used by Ackerman et al.[4] to measure the vapor pressure of the gaseous uranium oxide at temperatures and in oxygen pressures where U_3O_{8-y} is stable. The relation of the uranium oxide pressure to the oxygen pressure and other considerations indicated they were monitoring the reaction

$$\frac{1}{3}\, U_3O_8(s) + \frac{1}{6}\, O_2(g) \rightarrow UO_3(g) \ . \qquad (1)$$

The transpiration technique was also employed by Alexander[5] to measure the $UO_3(g)$ pressure above U_3O_{8-y} in oxygen pressures between 7 and 760 torr. He equated the $UO_3(g)$ pressures measured above U_3O_{8-y} in controlled oxygen pressures with the $UO_3(g)$ pressure measured in the

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[1] Raymond J. Ackerman, Paul W. Gilles, and R. J. Thorn, "High-Temperature Thermodynamic Properties of Uranium Dioxide," J. Chem. Phys. 25(6), 1089–97 (1956).

[2] R. J. Ackerman and R. J. Thorn, "Vaporization Properties of Thorium, Uranium and Plutonium Metals and Oxides," pp 445–64 in Proceedings of the Symposium on Thermodynamics of Nuclear Materials held by the International Atomic Energy Agency in Vienna, 21–25 May 1962.

[3] E. H. P. Cordfunke, "Volatile Oxides of Some Important Materials Used in Nuclear Technology," pp 465–75 in Proceedings of the Symposium on Thermodynamics of Nuclear Materials held by the International Atomic Energy Agency in Vienna, 21–25 May 1962.

[4] R. J. Ackerman, R. J. Thorn, Carl Alexander, and Marvin Tetenbaum, "Free Energies of Formation of Gaseous Uranium, Molybdenum, and Tungsten Trioxides," J. Phys. Chem. 64, 350–55 (1960).

[5] Carl Albert Alexander, Vapor-Solid Equilibria in the Uranium Oxide-Oxygen System, University Microfilms, Inc., Ann Arbor, Michigan, Dissertation presented in partial fulfillment of the requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University (1961).

U_3O_{8-y}-UO_{2+x} region where decomposition of U_3O_{8-y} provided the oxygen to form $UO_3(g)$ to establish the equilibrium oxygen pressure over the two solid phase region. Alexander was unable to control the oxygen pressures well enough to verify the reaction

$$UO_{2+x} + \frac{1-x}{2} O_2 \rightarrow UO_3(g) \quad . \tag{2}$$

However, he found that the equilibrium constant for

$$UO_2 + H_2O \rightarrow UO_3 + H_2 \tag{3}$$

was compatible with the available thermodynamic information. Alexander used his data in conjunction with information from other investigators to draw a pressure-temperature-composition diagram for uranium oxides.

The phase relations in the uranium-oxygen system have been studied much more extensively than the volatility, and the results of previous investigations have recently been thoroughly reviewed.[6] The potential use of UO_2 at temperatures above 1800°C has generated interest in the region of substoichiometry, UO_{2-x}. Rothwell[7] identified uranium metal in UO_2 heated above 1800°C in vacuum and inert gases and presented arguments for the existence of a substoichiometric phase whose composition is dependent on oxygen pressure and temperature. Aitken et al.[8] also observed metallic uranium in UO_2 heated above 2000°C and reports that in hydrogen at 2400°C the oxygen-to-uranium ratio of the UO_{2-x} is dependent on the amount of weight loss and has a lower limit of 1.88.

This study describes the volatility of $UO_{2\pm x}$ at temperatures between 1000 and 2200°C in various oxygen pressures and the equilibrium oxygen pressures in the UO_{2+x} and U_3O_{8-y} regions and over mixtures of these phases.

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[6] J. Belle (ed.), Uranium Dioxide: Properties and Nuclear Applications, Naval Reactors, Division of Reactor Development, United States Atomic Energy Commission, 1961.

[7] E. Rothwell, High Temperature Substoichiometry in Uranium Dioxide, United Kingdom Atomic Energy Authority, AERE-R3897 (1961).

[8] E. A. Aitken, H. C. Brassfield, and J. A. McGurty, "Characteristics of Substoichiometric Urania," paper presented at the American Nuclear Society Meeting, Salt Lake City, Utah, June 1963.

Experimental

Figure 1 schematically describes the thermogravimetric (TGA) equipment used during this study. An automatic recording analytical balance was enclosed in a stainless steel bell jar. Calibration of the instrument with standardized weights using a 10-mv recorder for readout indicated the balance-recorder combination was accurate to within ±1%.

Furnacing and Temperature Measurement

Specimens were suspended from the balance at the midpoint of the heating element. An alumina tube (shown in Fig. 1) protected and isolated the refractory-metal heating element during the experiments in oxygen. Top and bottom radiation shields were constructed with sapphire rods and alumina disks. The temperature was measured with a Pt vs Pt—10% Rh thermocouple situated 1/4 in. below the specimen; repeated checks with a standard thermocouple established that this configuration monitored the sample temperature within ±5°C. When the Al_2O_3 firing tube was used, the temperature was limited to 1550°C to protect the vacuum seals and to minimize possible tube failures.

The alumina tube was removed for experiments in vacuum, inert, and reducing environments at temperatures to 2200°C. Then the sample was suspended directly inside the heating element, and the sample temperature responded rapidly to very rapid heating-element temperature changes. This ability to reach 1800 to 2000°C in less than 1 min was used to avoid reactions at low temperatures. Although the heating element was exposed to all reaction products when the Al_2O_3 tube was removed, this disadvantage was necessary to achieve the desired heating and cooling rates. Samples could be quenched from 2000 to 800—900°C in 20 to 30 sec by cutting the power to the heating element. The temperature of the sample and sample holder above 1500°C was measured optically. The optical pyrometer and associated sight glasses were calibrated with a National Bureau of Standards tantalum filament bulb; the temperatures are estimated to be accurate within ±20°C up to 1800°C and ±30°C above 1800°C.

Tantalum and occasionally molybdenum were used for heating elements and radiation shields. Power was controlled by manually varying the input voltage to a 21 kva stepdown transformer (output 15 v at 1400 amp).

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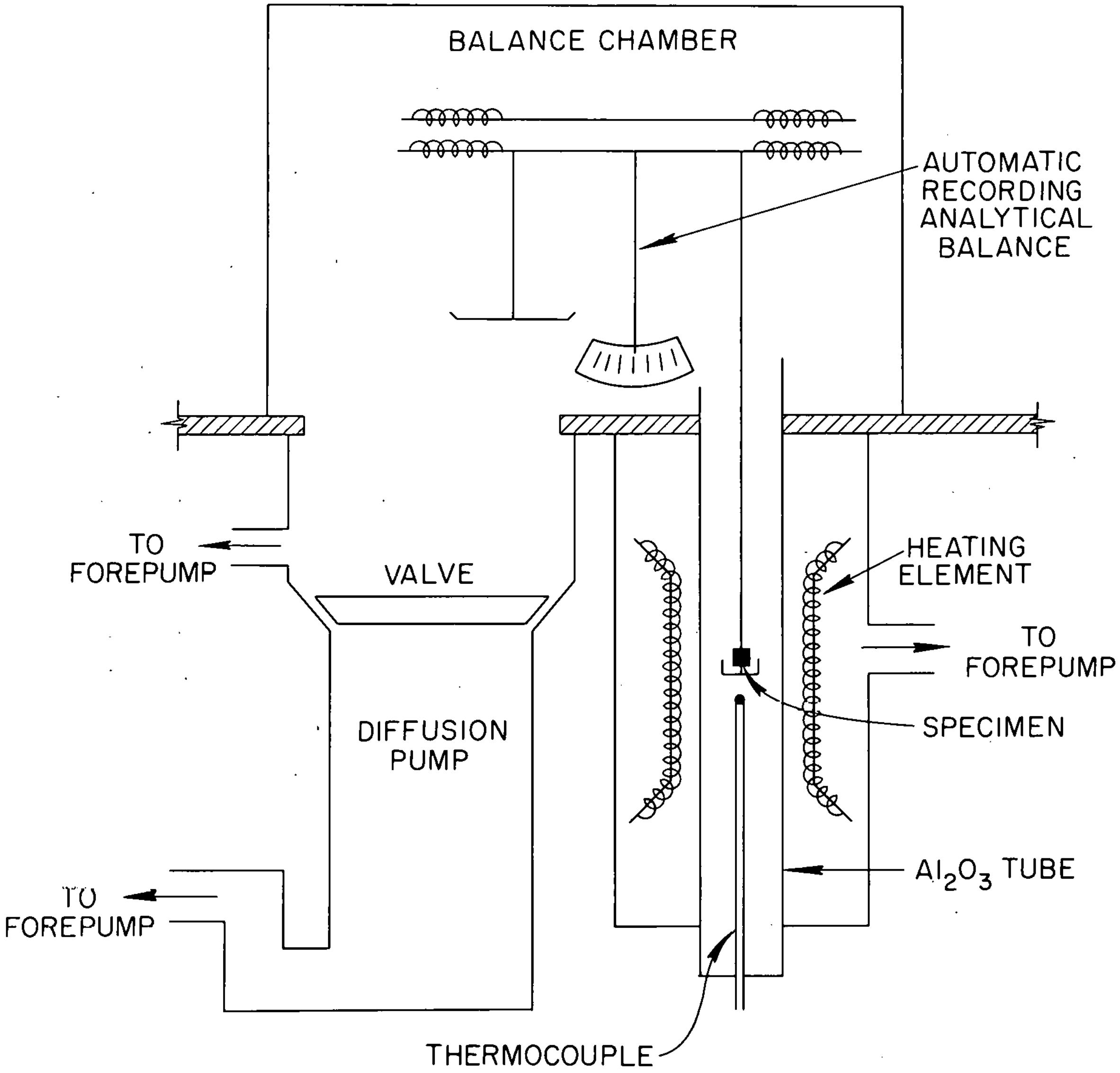

Fig. 1. Thermobalance Suitable for Use in Vacuum and Controlled Atmospheres.

Vacuum and Controlled-Atmosphere System

The vacuum-producing elements consisted of a 6-in. diffusion pump and associated mechanical pumps. Pressure-sensing instruments included Alphatron, thermocouple, ion, and McLeod gages and a mercury manometer. The vacuum gages were located in the roof of the bell jar. System pressures measured at the cold port were 5 to 8×10^{-6} torr at 1500°C with the alumina tube installed and 1 to 2×10^{-5} torr at 2000 to 2200°C with the alumina tube removed. The ultimate system pressure at room temperature was 1 to 2×10^{-6} torr. Neoprene O-rings and bell jar seals were used between metal parts of the system. Silicone-rubber O-rings were used for seals to the alumina tube.

Controlled pressures of oxygen between 5×10^{-4} and 50 torr were used. The low pressures were obtained by bleeding small amounts of gas through a controlled leak or small-bore capillary into the balance chamber with the vacuum pumps operating. The pressure was controlled by adjusting both the vacuum valves and the rate of gas admission. The measured system pressure with the gas leak operative was at least 10 and normally 50 to 100 times the pressure obtained after pumping several minutes with the leak closed. Pressures greater than 1 torr were obtained by evacuating the system, flushing, and bleeding in the desired gas pressure.

The gas pressure determination at the sample site is subject to several corrections. These include a vacuum gage correction for the response to different gases and a large thermomolecular flow correction that must be applied at low pressures where the mean free path of the gas approaches the diameter of the alumina tube or refractory-metal heating element. Roberts and Walter,[9] in their research on the uranium-oxygen system, reviewed the necessity for the latter correction and graphically presented the thermomolecular flow corrections which fit their experimental results. Since their furnace configuration was similar to the one used in this study, their thermomolecular flow corrections were employed. The relative response of the vacuum gages to oxygen was obtained from data supplied by the gage manufacturers.

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[9] L. E. J. Roberts and A. J. Walter, "Equilibrium Pressures and Phase Relations in the Uranium Oxide System," J. Inorg. Nucl. Chem. 22, 213–29 (1961).

Materials

Uranium oxides from a variety of sources were employed during this study. "Ammonium diuranate" (ADU) calcined at 800°C provided a fine powder containing about 1% of volatiles and having an oxygen-to-uranium ratio between 2.1 and 2.2.[10] A typical impurity analysis of the UO_{2+x} powder derived from ADU is given as follows:

Element	Content (ppm)	Element	Content (ppm)
Be	< 1	Cr	10
Ni	10	Ca	50
Si	80	B	< 1
Li	< 0.2	Al	10
Na	4	Cd	< 0.1
Mg	4	Co	< 1
Fe	100	V	< 1
Cu	10	Mn	5

The U_3O_8 was made by heating the ADU-derived powder in air at 800°C until the weight was constant. An oxide virtually free of volatiles was obtained by crushing dense hydrogen-fired $UO_{2.00}$ pellets and slowly oxidizing the resultant powder in air at temperatures below 200°C until a uniform oxygen-to-uranium ratio of about 2.1 was achieved. An electrically fused oxide with an oxygen-to-uranium ratio close to 2.00 was also used.[11]

A $(Th,U)O_2$ solid solution was formed by mechanically mixing the individual powders and sintering at 1750°C in hydrogen. The ThO_2 was obtained by calcining thorium oxalate in air at 650°C. The major metallic impurities in this oxide were less than 100 ppm each of Ca, Al, and Si.

Oxygen-to-Uranium Ratio Determinations

The oxygen-to-uranium ratios of both starting materials and specimens were routinely determined by heating 1-g samples in air to form U_3O_8 and following the weight increase with a thermal balance. The

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[10] Supplied by the Y-12 Chemical Development Department, Union Carbide Nuclear Division, Oak Ridge, Tennessee.

[11] Supplied by the Spencer Chemical Company, Kansas City, Missouri.

weight change was monitored to ±0.1 mg, which corresponds to a change of ±0.002 in the oxygen-to-uranium ratio. Allowance for instrument error and for some uncertainty in correcting for the "chimney effect" in the furnace leads to a total estimated uncertainty of ±0.005 in the oxygen-to-uranium ratio. The oxygen-to-uranium ratios determined by ignition to U_3O_8 in air were checked periodically by the polarographic determination of the U(VI) content. The oxygen-to-uranium ratios determined by these different techniques normally differed by less than 0.004.

Results and Discussions

Volatility of $UO_{2\pm x}$, Qualitative

The volatility of $UO_{2\pm x}$ $(0.2 > x > 0)$ was investigated first by heating powders and pressed (unsintered) pellets to temperatures above 1500°C at a system pressure of 10^{-5} to 10^{-6} torr. The characteristic thermogravimetric behavior of $UO_{2.186}$ heated between 1500 and 1600°C is shown in Fig. 2. The loss of material could not be attributed to the two logical causes — the loss of interstitial oxygen because the weight change was too large (approximately 9 wt % of the starting material) or the congruent vaporization of UO_2 because UO_2 was present when the reaction apparently ceased. The results of experiments designed to investigate this behavior are presented in Table I and indicate that UO_{2+x} under the described environmental conditions decomposes to produce a volatile phase with a composite oxygen-to-uranium ratio of 4 and a condensed phase with an oxygen-to-uranium ratio close to 2.00. The oxygen-to-uranium ratio of the volatile material was calculated by simple material balance considerations using the oxygen-to-uranium ratio of the starting and final UO_{2+x} and assuming no reaction with the residual gases present in the evacuated system. Many reactions may be proposed to describe these experimental results since the composition of the gas was not determined. Two potential reactions that will be considered are:

$$UO_{2+x}(s) \rightarrow \left(1 - \frac{x}{2}\right) UO_2(s) + \frac{x}{2} UO_3(g) + \frac{x}{4} O_2(g) \tag{4}$$

$$UO_{2+x}(s) \rightarrow \left(1 - \frac{x}{2}\right) UO_2(s) + \frac{x}{2} UO_4(g) \quad . \tag{5}$$

Table I. Experimentally Determined O/U Ratio of Volatile Material Escaping from UO_{2+x} ($0.2 > x \geq 0$) During Heating at a Pressure of 10^{-5} to 10^{-6} torr

Experiment No.	Temperature (°C)	O/U Ratio of UO_{2+x} Initial	O/U Ratio of UO_{2+x} Final	Weight Loss (%)	O/U Ratio of Volatile Material[a]
VF-4	1720	2.186	2.011	8.7	4.2
VF-7	1570	2.186	2.006	9.1	4.0
VF-13	1610	2.081	2.011	2.7	4.1
VF-87	1530	2.120	2.011	4.5	4.3
VF-90	1520	2.101	2.008	4.8	3.9
VF-91	1570	2.101	2.002	5.4	3.6
VF-92	1525	2.101	2.028[b]	3.0	4.1
VF-104	1540	2.140	2.002	6.2	4.2
VF-106	1800	2.160	1.998	9.0	3.9
VF-107	1800	2.160	1.995	9.2	3.8

[a] Determined by calculating the quantity of uranium and oxygen in the specimens before and after the experiment, subtracting to find the amount of uranium and oxygen lost, and converting this loss to an atomic ratio.

[b] Reaction stopped prior to completion.

The following precautions were employed to ensure that the loss of material described in Fig. 2 was not some spurious result associated with a specific material, experimental technique, or combination of reactions:

1. The temperature was raised from about 1000°C (where virtually no reaction takes place) to between 1500 and 1800°C in 20 to 30 sec to avoid reactions at intermediate temperatures.

2. The starting material was obtained from several different batches of low-calcined ADU-derived UO_{2+x} powder, as well as UO_{2+x} powder produced by a low-temperature oxidation of crushed UO_2 pellets.

3. One experiment (VF-92) was intentionally stopped before completion. Although the oxygen-to-uranium ratio of the residual material did not reach the value of about 2.005 associated with the experimental

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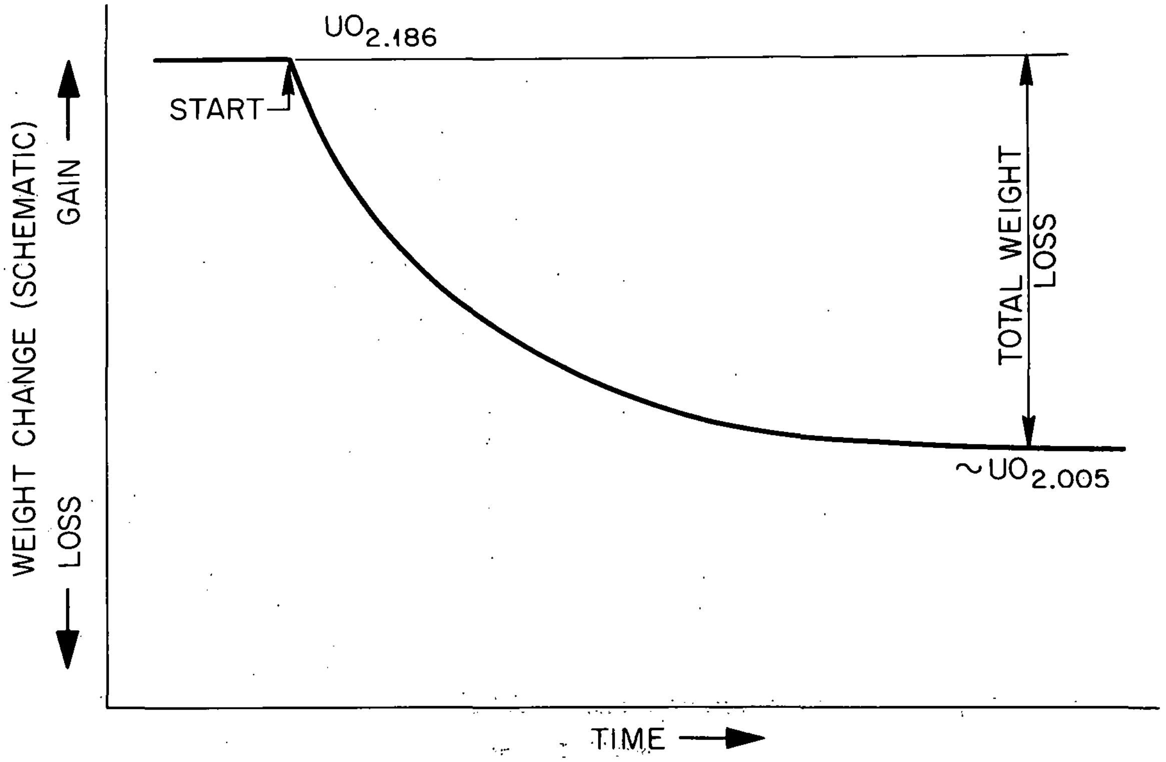

Fig. 2. Thermogravimetric Behavior of $UO_{2.186}$ at 1500 to 1600°C and a Pressure of 10^{-5} to 10^{-6} torr.

environment, the oxygen-to-uranium ratio of the volatile remained close to 4. Thus it is improbable that this ratio results from a fortuitous combination of sequential reactions.

4. Each automatically recorded weight change amounted to several hundred milligrams and was checked manually on an analytical balance.

In subsequent discussions $UO_4(g)$ will be used to describe the loss of material from UO_{2+x}; this is done to facilitate writing reactions and with the knowledge that the results in Table I do not provide conclusive evidence for the existence of a UO_4 gas molecule. (The results in Table I can be explained by the loss of any combination of uranium and oxygen atoms or molecules whose bulk composition has an oxygen-to-uranium ratio of 4, although reaction (4) or (5) would appear to be the best interpretation.)

The oxygen-to-uranium ratios of the volatile material liberated from UO_{2+x} in vacuum, measured at various temperatures, are:

Reaction Temperature (°C)	Oxygen-to-Uranium Ratio of Volatile Material
1000	∞
1200	~ 10
1400	~ 5
1500–1800	4

It is apparent that the constant ratio at 1500 to 1800°C (Table I) does not occur at temperatures below 1500°C. At 1000°C the reduction in oxygen-to-uranium ratio in vacuum is predominantly through the slow loss of oxygen and thus the oxygen-to-uranium ratio of the escaping material approaches infinity. Measurable loss of uranium from UO_{2+x} was observed at temperatures as low as 1125°C. The simultaneous loss of uranium oxide molecules and oxygen appears to occur at temperatures below 1500°C.

Two experiments were performed at a temperature of 1600°C in vacuum using U_3O_8 powder as the starting material. The total weight loss for U_3O_8 was very close to that predicted by the reactions:

$$UO_{2.67}(s) \rightarrow UO_{2.23}(s) + 0.22\ O_2(g) \qquad (6)$$

$$UO_{2.23}(s) \rightarrow 0.885\ UO_{2.0}(s) + 0.115\ UO_4(g)\ . \qquad (7)$$

The TGA pattern for U_3O_8 showed two distinct processes — a very rapid initial weight loss associated with the loss of oxygen to form cubic $UO_{2.23}$, reaction (6), and a period of slower weight loss similar to Fig. 2 resulting from reaction (7).

The results of experiments performed at 1500 to 1600°C, listed in Table I and schematically represented in Fig. 2, suggested that the weight loss accompanying the decomposition of UO_{2+x} ceased when the oxygen-to-uranium ratio of the condensed phase approached 2.00. Figure 3 illustrates the behavior observed at 1800°C and establishes that the loss of weight from UO_{2+x} $(0.2 > x > 0)$ in vacuum actually takes place by two processes: (1) an initial weight loss (caused by the loss of material with a composite oxygen-to-uranium ratio of 4) that occurs during the reduction in the oxygen-to-uranium ratio to the value associated with the environment, and (2) a continuous loss of a uranium-oxygen compound(s) that proceeds much slower than the first reaction and occurs without a change in the oxygen-to-uranium ratio of the residual phase. The second process was difficult to detect at 1500 to 1600°C and had very little effect on the results presented in Table I because the rate of weight loss was very low.

The oxygen-to-uranium ratios given in Table I for the volatile material leaving during experiments VF-106 and -107 were determined during the initial rapid weight loss process; this was essentially all of experiment VF-106 and the portion of experiment VF-107 to point A, Fig. 3. The oxygen-to-uranium ratio of the condensed phase did not change during the constant rate (second step) process. This is apparent because the oxygen-to-uranium ratio of the residues obtained from these two experiments was the same, although the specimen in VF-107 eventually lost much more weight than the specimen in VF-106.

Experiment VF-109, Fig. 3, was performed in vacuum using an electrically fused oxide with an oxygen-to-uranium ratio of 2.00 as the starting material. A constant rate of weight loss similar to the second step of the loss from $UO_{2.160}$ (VF-107) was evident. Experiment VF-111 was performed using the same material and initial conditions as VF-109. The initial behavior was identical with the earlier experiment. However, at point B carbon monoxide at a pressure of 0.2 to 0.3 torr was admitted to

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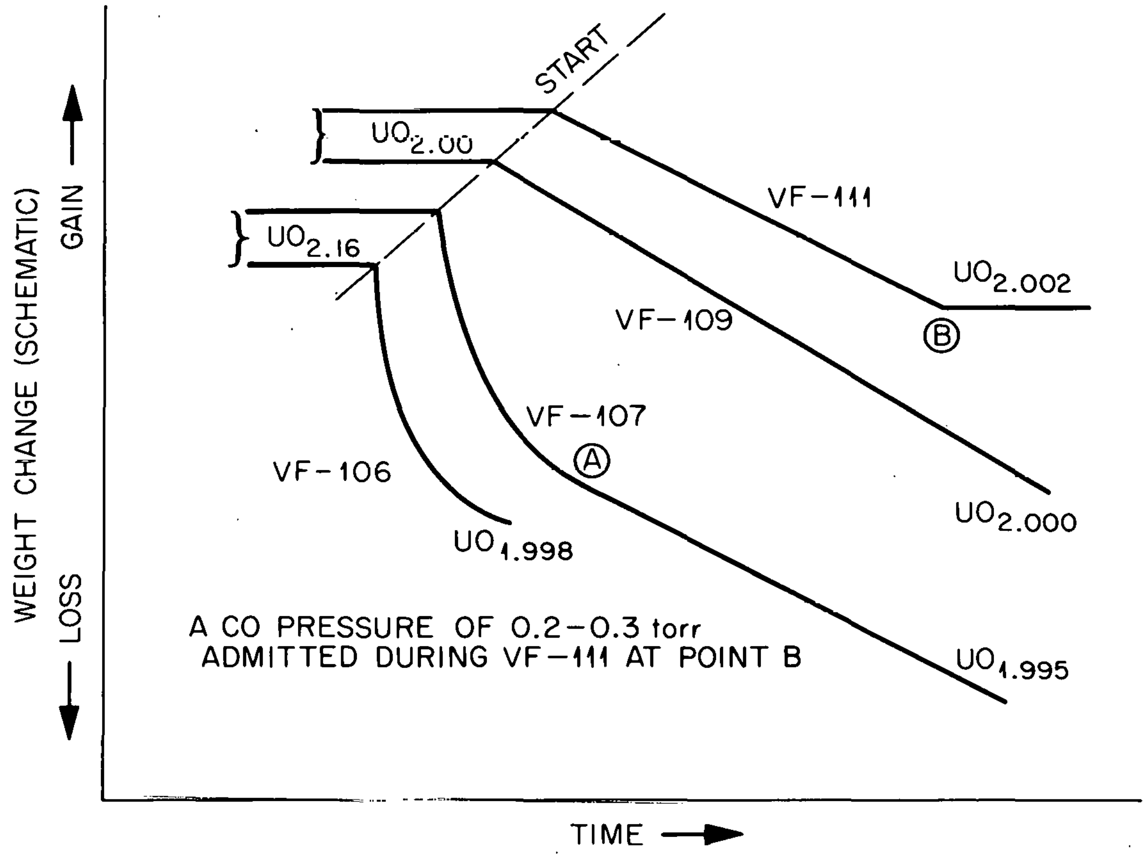

Fig. 3. Thermogravimetric Behavior of $UO_{2.00}$ and $UO_{2.16}$ at 1800°C and a Pressure of 10^{-5} to 10^{-6} torr.

the furnace chamber. The slope of the weight loss curve then rapidly decreased and the loss essentially stopped. This suggests that the loss of material normally attributed to the direct vaporization of $UO_{2.00}$ is, in reality, some type of oxidation or decomposition reaction.

It had been naively anticipated early in this investigation that changes in composition of UO_{2+x} in varying oxygen pressures could be studied by merely equating observed weight changes to changes in the oxygen content. Figure 4 schematically represents the thermogravimetric behavior of UO_{2+x} at 1300°C in an oxygen pressure of 0.10 torr. The weight increased initially as a result of the oxidation of $UO_{2.008}$. Then the weight decreased continuously at an essentially constant rate that showed no indication of terminating during the experiment. The volatilization of a uranium oxide was indicated by the magnitude of the weight loss and the presence of a condensate in the cooler regions of the furnace. The oxygen-to-uranium ratios of two specimens heated for different times under these conditions are presented in Table II and shown at points A and B in Fig. 4. These values, 2.189 and 2.181, agree within the experimental error and show that the oxygen-to-uranium ratio of the solid phase remains constant during this process. The behavior depicted in Fig. 4 was observed in many experiments performed at various temperatures and oxygen pressures where UO_{2+x} is the stable phase.

Table II. Behavior of UO_{2+x} at 1300°C in an Oxygen Pressure of 0.10 torr

Experiment No.	Initial O/U Ratio	Duration of Heating (hr)	Weight Loss (%)	Final O/U Ratio
VF-116	2.008	16.0	12	2.189
VF-117	2.008	1.5	1	2.181

Two reactions are proposed to describe the loss of material from UO_{2+x} in low oxygen pressures after the equilibrium oxygen-to-uranium ratio is established:

$$UO_{2+x}(s) \rightarrow zUO_4(g) + (1 - z)UO_{2+x-\alpha}(s) \tag{8}$$

$$(1 - z)UO_{2+x-\alpha}(s) + \frac{\beta}{2}\,O_2(g) \rightarrow (1 - z)UO_{2+x}(s) \quad , \tag{9}$$

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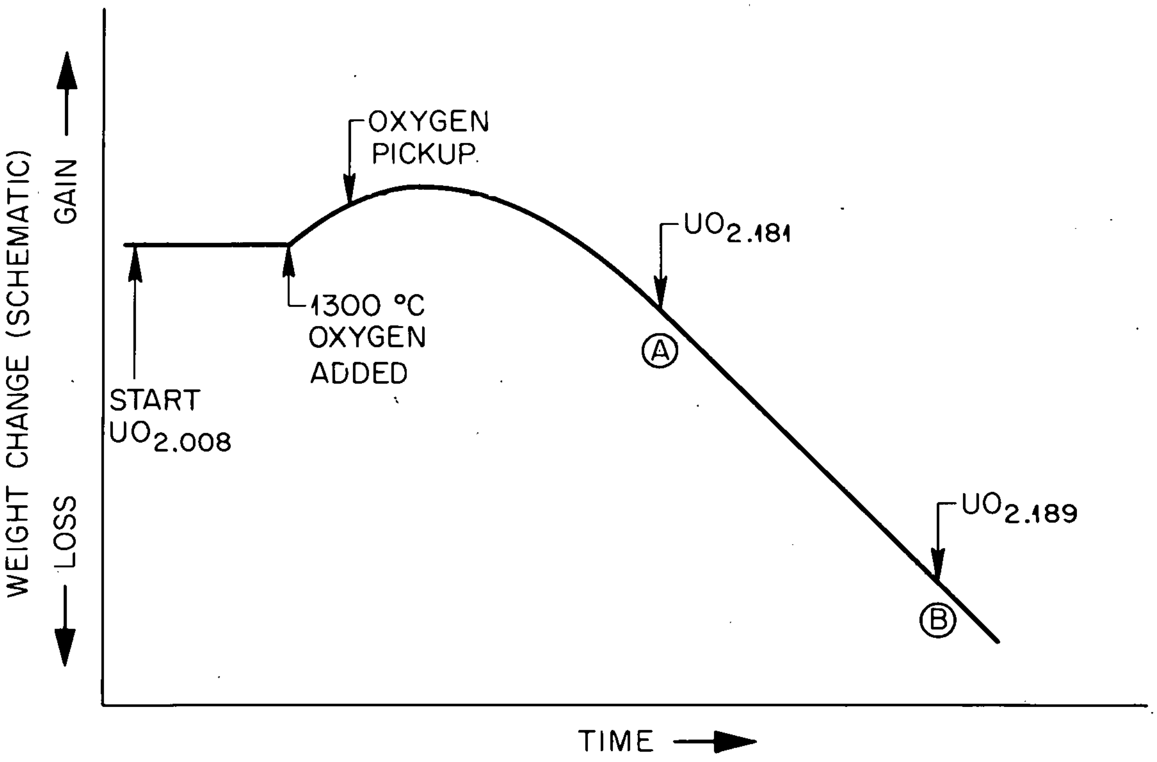

Fig. 4. Thermogravimetric Behavior of $UO_{2.008}$ at 1300°C in an Oxygen Pressure of 0.10 torr.

where

$$\alpha = \frac{z(2 - x)}{1 - z}$$

$$\beta = z(2 - x) \quad .$$

Reactions (8) and (9) may be added to yield reaction (10)

$$UO_{2+x}(s) + \frac{2 - x}{2} O_2(g) \rightarrow UO_4(g) \quad . \tag{10}$$

This interpretation is based solely on the decomposition of UO_{2+x} in vacuum which yields a volatile material with a bulk oxygen-to-uranium ratio of 4. It should be noted that the thermogravimetric behavior of UO_{2+x} at 1300°C in oxygen at a pressure of 0.10 torr is similar to the behavior of $UO_{2.00}$ at 1800°C in a system pressure of 10^{-5} to 10^{-6} torr.

The vapor species liberated from UO_{2+x} could not be identified by analyzing the condensate scraped from cool radiation shields and furnace walls. X-ray diffraction analysis of condensates produced during the vacuum experiments indicated the material was UO_{2+x} with oxygen-to-uranium ratios under 2.02; condensates collected from runs performed in varying oxygen pressures consisted of UO_{2+x}, U_3O_{8-y}, or mixtures of these phases. Apparently the transient vapor species decomposes on condensation to form the equilibrium solid for the prevailing conditions. Attempts at mass-spectrometric verification of the presence of $UO_4(g)$ over decomposing UO_{2+x} were inconclusive. The UO_3, UO_2, UO, and U ions were readily identified when UO_{2+x} was heated on a platinum filament in the mass spectrograph.

Volatility of $UO_{2\pm x}$, Quantitative

The vapor pressure of $UO_{2\pm x}$ was measured by observing the rates of evaporation from 96%-dense wafer-shaped UO_{2+x} specimens having an initial oxygen-to-uranium ratio of about 2.00 and a geometric surface area of 4 cm^2. The wafers were heated to temperatures between 1600 and 2200°C at a pressure of 10^{-5} to 10^{-6} torr. These data are presented in Fig. 5 along with the results obtained from a preliminary experiment with a dense solid-solution $(U,Th)O_2$ pellet containing 50 wt % of each oxide. The vapor pressures were obtained using the conventional expression

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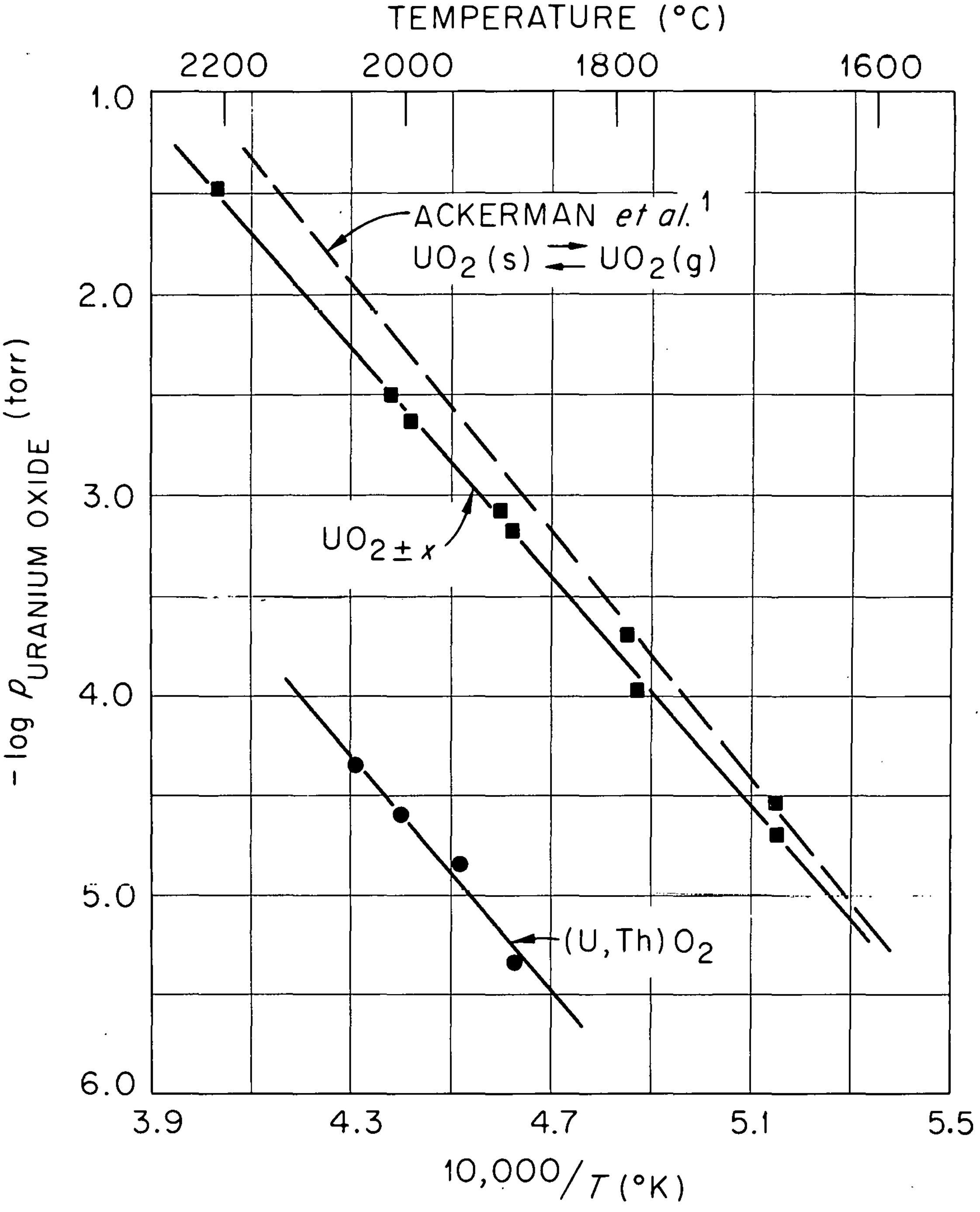

Fig. 5. The Pressure of the Uranium Oxide Vapor (Measured at a Pressure of 10^{-5} to 10^{-6} torr) vs Temperature for $UO_{2\pm x}$ and a $(U,Th)O_2$ Solid Solution Containing 50 wt % of Each Oxide.

$$P(\text{torr}) = 17.14\ G\ (T/M)^{1/2} \quad , \tag{11}$$

where

G = the rate of weight loss in $g/cm^2 \cdot sec$

T = the absolute temperature,

M = the molecular weight of the vaporizing material.

The following assumptions were used:

1. The geometric surface is the evaporating area.

2. The surface of the solid-solution $(U,Th)O_2$ pellet was 50% inert ThO_2.

3. The experiments were measuring the loss of material with a molecular weight of 270 (molecular weight of UO_2), since the composition of the wafer remained close to $UO_{2.00}$.

The $(U,Th)O_2$ experiments show that the addition of 50 wt % ThO_2 to UO_2 reduces the volatility of UO_2 at least a hundredfold. It should be noted that the solid solution was obtained by reacting mechanically mixed powders in hydrogen at 1750°C, and a very small amount of free (unreacted) UO_2 could produce the observed vaporization from this specimen. Figure 5 also includes the vapor pressure data reported as the congruent vaporization of UO_2 by Ackerman et al.[12] It is interesting that Ackerman's data, determined by effusion cell experiments, are in basic agreement with the present evaporation rate data. This agreement implies that the present experiments are measuring the same process as the earlier effusion cell work. However, other results in this study suggest that the loss of material from compositions close to $UO_{2.00}$ at 1800°C at a pressure of 10^{-6} torr is an oxidation process and not congruent vaporization. The oxidation reaction may be approximated as either

$$UO_2(s) + \frac{1}{2}\,O_2(g) \rightarrow UO_3(g) \quad , \text{ or} \tag{12}$$

$$UO_2(s) + O_2(g) \rightarrow UO_4(g) \quad . \tag{13}$$

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[12] Raymond J. Ackerman, Paul W. Gilles, and R. J. Thorn, "High-Temperature Thermodynamic Properties of Uranium Dioxide," J. Chem. Phys. 25(6), 1089–97 (1956).

The agreement between the evaporation rate and effusion cell information suggested that the pressure of the uranium-oxygen vapor species (determined by evaporation rates) could be measured as a function of oxygen pressure to distinguish between reactions (12) and (13) as the probable oxidation process.

To accomplish this, UO_2 wafers were continuously weighed in oxygen pressures controlled between 10^{-3} and 10^{-1} torr at temperatures between 1215 and 1515°C. Under these conditions, reaction (12) or (13) could proceed to the right. However, the reverse reaction, the condensation of the uranium oxide vapor on the $UO_2(s)$ surface and disproportionation to UO_2 and O_2, which would be proceeding at a rate equal to the loss of UO_3 or UO_4 at equilibrium, is negligible because the oxide vapor species rapidly leaves the sample site at these low pressures and condenses in a cool region of the furnace. This analysis neglects the geometry of the system and any reflection of vapor molecules back to the surface of the specimen. However, the rate of weight loss of the wafer should at least provide a relative measure of the pressure of the uranium oxide vapor phase at varying temperatures and oxygen pressures and, hopefully, an approximation of the absolute pressure. If the rate of weight loss of the specimen is proportional to the square root of the oxygen pressure, reaction (12) is valid; if the loss is directly proportional to the oxygen pressure, reaction (13) describes the process.

Table III presents the pressure of the uranium oxide vapor species calculated from the rate of weight loss using Eq. (11). Values of the exponent, α, reported in the last column of Table III should ideally be 0.5 or 1.0, depending on whether reaction (12) or (13) is being monitored in the experiments. Since the value of the exponents are near 1.0, these results offer strong support for using reaction (13) in describing the loss of uranium from UO_{2+x} in the presence of oxygen. It is possible to formulate other vapor species and to write additional reactions in which the pressure of the uranium oxide vapor would be directly proportional to the oxygen pressure. However, these reactions require compounds at least as speculative as $UO_4(g)$.

To confirm the validity of using gas-solid reaction rates to approximate equilibrium pressures, molybdenum was heated under conditions

Table III. The Relation of Oxygen Pressure and the Pressure of the Metal-Oxide Vapor Phase Determined During Evaporation Rate Experiments

Experiment No.	Solid Phase	Temperature (°C)	Oxygen Pressure[a] (torr) P_{O_2}	Metal-Oxide Vapor Pressure[b] (torr) P_{MO_x}	The Exponent, α, Relating the Oxygen and Metal-Oxide Pressure[c]
			$\times 10^{-3}$		
VF-160	UO_{2+x}	1215	3.8	8.4×10^{-6}	0.82
			30	4.5×10^{-5}	
VF-153	UO_{2+x}	1315	4.0	1.6×10^{-5}	1.1
			31	1.4×10^{-4}	
VF-152	UO_{2+x}	1415	4.5	6.4×10^{-5}	1.0
			32	5.1×10^{-4}	
VF-159	UO_{2+x}	1515	1.5	6.8×10^{-5}	0.85[d]
			4.0	1.6×10^{-4}	0.97
			29	1.2×10^{-3}	1.0
VF-155	Mo wire	1215	6.4	2.1×10^{-5}	1.4[d]
			35	2.3×10^{-4}	1.4
			52	4.1×10^{-4}	1.5
VF-156	Mo plate	1215	4.3	8.7×10^{-6}	1.6
			28	1.6×10^{-4}	

[a] The oxygen pressure was maintained by a controlled leak and the tabulated pressure has been corrected for the Alphatron vacuum gage response and thermomolecular flow.

[b] The pressure of the uranium oxide vapor phase was calculated using Eq. (11).

[c] The exponent, α, was calculated from the relation $K_p = \frac{P_{MO_x}}{(P_{O_2})^\alpha} = \frac{P'_{MO_x}}{(P'_{O_2})^\alpha}$ since the equilibrium constant is fixed at a given temperature (neglecting changes in the activity of the UO_{2+x} phase resulting from small changes in composition).

[d] The exponent, α, may be calculated for any two sets of pressures. The first and third values were calculated for the first two and last two sets of data, respectively; the center exponent was determined using the first and third pressure relations.

similar to the UO_2 wafers. The predominant reaction describing the oxidation of molybdenum is

$$Mo + \frac{3}{2} O_2(g) \rightarrow MoO_3(g) \quad , \tag{14}$$

so the pressure of the MoO_3 (rate of weight loss) should be proportional to the 3/2 power of the oxygen pressure. The results of heating a molybdenum wire possessing a surface area of about 3 cm^2 and a plate with a surface area of about 10 cm^2 at 1215°C in different oxygen pressures are also included in Table III. These data indicate the exponent of the oxygen pressure averages about 1.5 as predicted by reaction (14). This confirms that equilibrium pressures may be estimated using gas-solid reaction rates as long as the pressures are low.

Certain difficulties and necessary assumptions associated with these oxidation-vaporization experiments are noted below.

1. It was not possible to extend the oxygen pressures much above 0.05 torr and maintain a sufficiently constant exponent for the oxygen pressure (constant Kp). The loss of the metal-oxide vapor (UO_4 or MoO_3) in oxygen pressures above 0.1 torr was not large enough to maintain the relation that was valid at oxygen pressures less than 0.05 torr. It appears that at oxygen pressures above 0.1 torr molecular collisions retard the removal of the metal-oxide molecules from the sample site and prevent the use of evaporation rates to approximate equilibrium pressures.

2. In the UO_2 experiments, it was assumed that the activity of the condensed phase (UO_2 wafers) remained constant (unity), even though the composition of the wafers must change with oxygen pressure. All the experiments were performed using the UO_{2+x} phase. At 1515°C, where the increase in the oxygen-to-uranium ratio from the starting value of about 2.00 would occur most readily, the equilibrium oxygen-to-uranium ratio in an oxygen pressure of 0.03 torr is only 2.05. At 1215°C the increase in the oxygen-to-uranium ratio of sintered UO_2 is sluggish, but the equilibrium oxygen-to-uranium ratio in an oxygen pressure of 0.03 torr is about 2.16. The changes in weight of the wafers resulting from increasing the oxygen-to-uranium ratio were too small to affect the determination of the rates of weight loss.

The data presented in Table III are displayed graphically in Fig. 6 with the assumption that reaction (13) is valid. The top two lines express the UO_4 pressure as a function of temperature in oxygen pressures of about 30 and 4×10^{-3} torr. A single point for the UO_4 pressure at 1515°C and an oxygen pressure of 1.5×10^{-3} torr is also plotted. The bottom line is the equilibrium constant for reaction (13) and was obtained by dividing the pressure of the UO_4 by the oxygen pressure. The equation (obtained graphically) expressing the $UO_4(g)$ pressure as a function of temperature and oxygen pressure is

$$\log P_{UO_4} = \frac{-13,510}{T(°K)} + 6.20 + \log P_{O_2} \quad . \qquad (15)$$

This equation should be applicable for temperatures between 1100 and 1500°C and oxygen pressures that maintain the composition of the condensed phase close to UO_2. However, when Eq. (15) is extrapolated to the temperature range of the "vapor pressure" measurements shown in Fig. 5, the measured uranium oxide pressure corresponds to an oxygen pressure well above the observed system pressure. Thus it appears that either the residual oxygen pressure in the neighborhood of the specimen at 1800°C is not measured by a vacuum gage at a cold port, or that congruent vaporization is chiefly responsible for the volatility of $UO_{2\pm x}$ in vacuum at 1800°C in spite of the evidence suggesting this is an oxidation process.

Phase Relations

The relation of oxygen pressure, temperature, and composition in a portion of the uranium-oxygen system is presented in Fig. 7. The two-phase region in which UO_{2+x} and U_3O_{8-y} coexist in equilibrium (represented by a line on the pressure-temperature diagram) was established by several different experimental techniques. In the thermogravimetric experiments, powder specimens of UO_{2+x}, U_3O_{8-y}, or both were successively heated and cooled in oxygen at a fixed pressure and the weight change was observed as a function of temperature. Although it was necessary to compensate for the continuous volatilization of material, the rate of oxidation of UO_{2+x} or oxygen evolution from U_3O_{8-y} as the sample crossed the two-phase region was rapid enough to permit positive recognition of the event.

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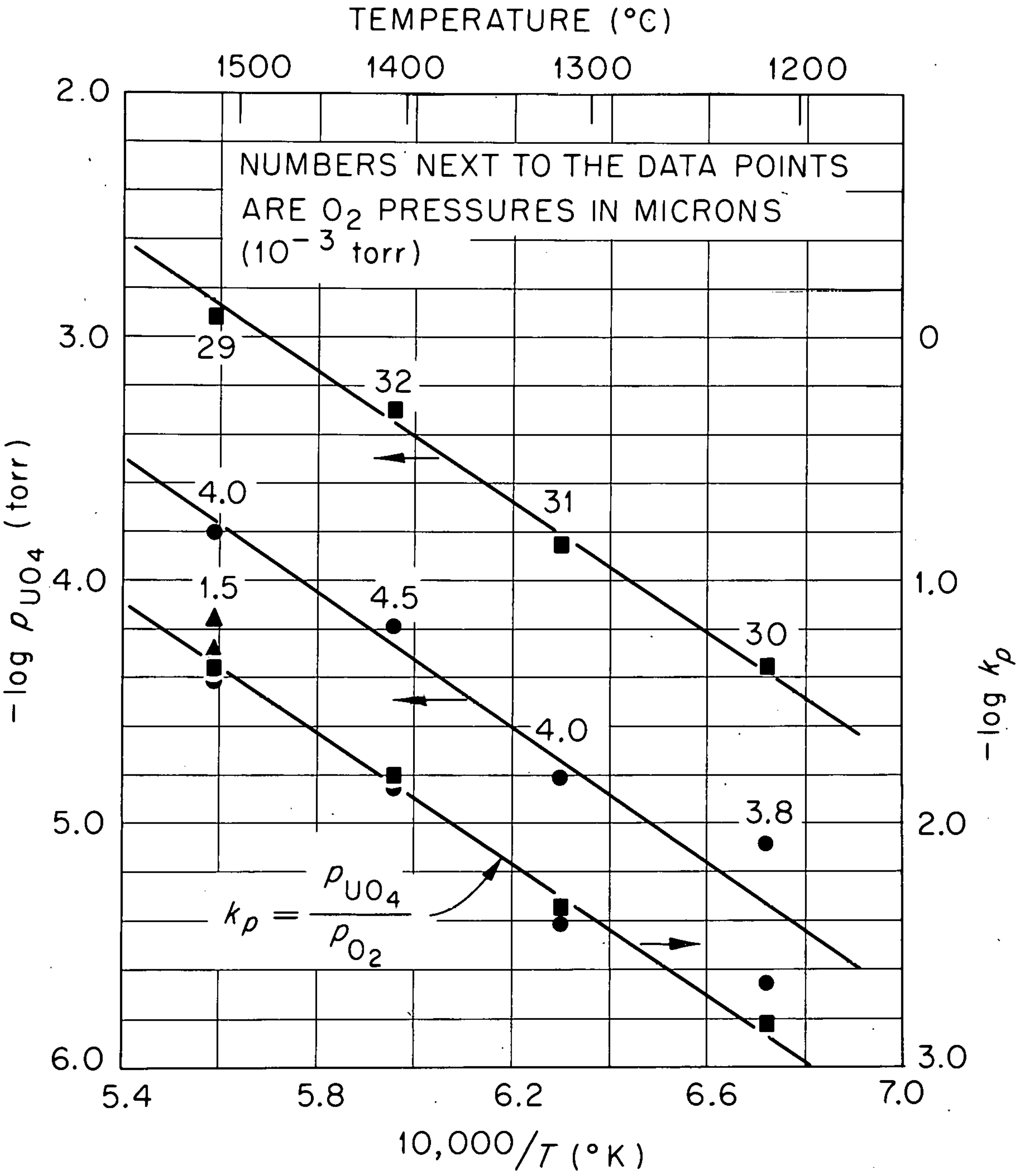

Fig. 6. The Relation of the Pressure of UO_4(g) to the Oxygen Pressure Assuming the Reaction $UO_2(s) + O_2(g) \rightleftharpoons UO_4(g)$ Is Valid.

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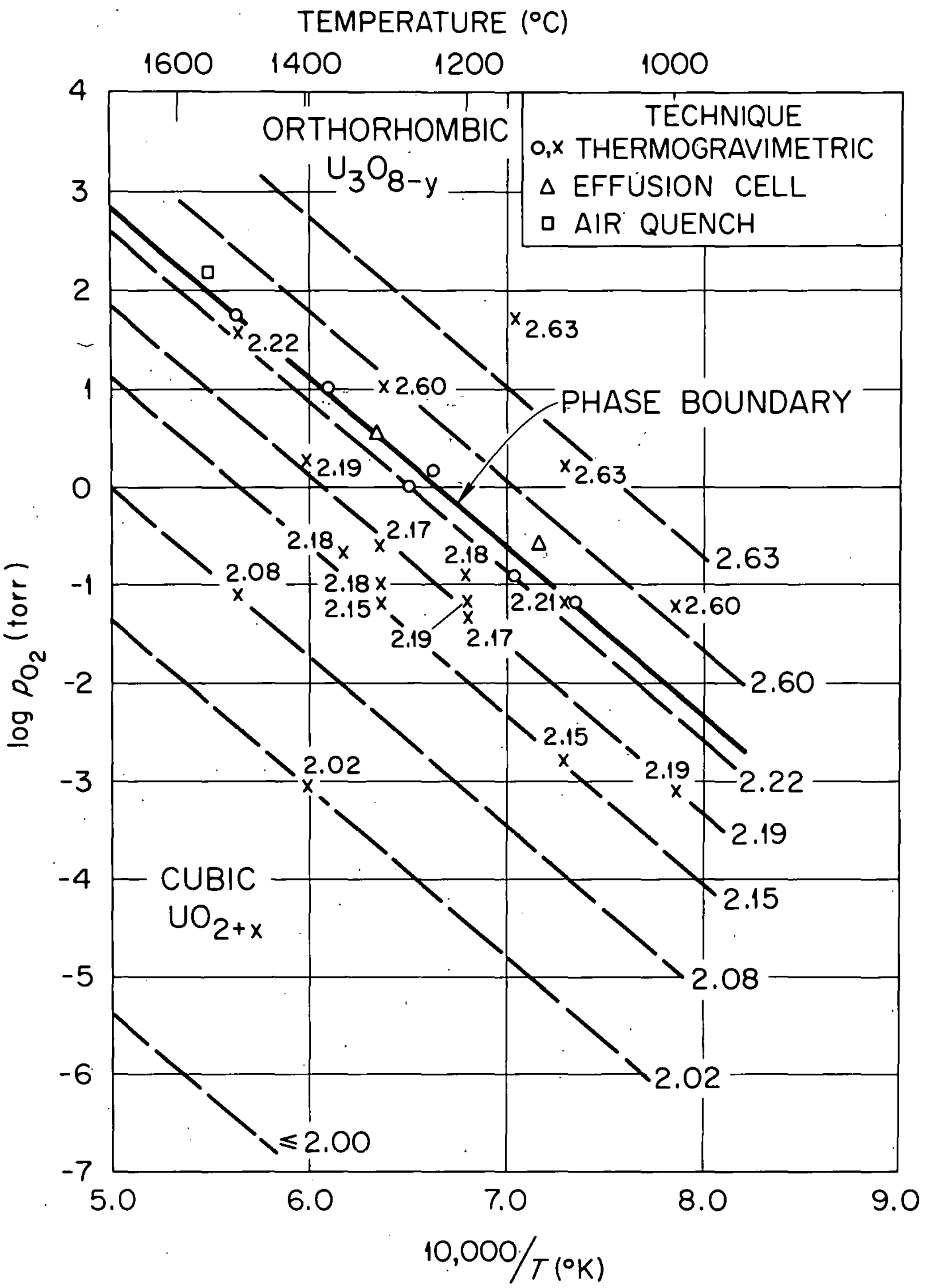

Fig. 7. The Relation of Oxygen Pressure and Temperature to Compositions Between $UO_{2.00}$ and $UO_{2.63}$ in the Uranium-Oxygen System.

The effusion cell results shown in Fig. 7 were obtained by heating U_3O_8 in a platinum cell at a system pressure of 10^{-6} torr. A very rapid initial weight loss was observed, which agreed quantitatively with reaction (6). The oxygen pressure was calculated using the equation

$$P_{torr} = 17.14 \frac{G'}{AKt} \left(\frac{T}{M}\right)^{1/2} \quad , \qquad (16)$$

where G′ denotes the actual loss of weight in grams occurring in t seconds through an orifice of A cm^2; K is a correction for the thickness of the wall containing the orifice and is related to the wall thickness and orifice diameter (a value for K of 0.89 was used for an orifice 40 mils in diameter cut in platinum 10 mils thick); the remaining symbols have the standard meanings. The high-temperature point on the UO_{2+x}-U_3O_{8-y} phase boundary was obtained by heating small wafers of U_3O_{8-y} in air to successively higher temperatures and dropping them into dry ice. X-ray diffraction analysis of the quenched samples indicated that U_3O_{8-y} reverts to cubic UO_{2+x} at 1550°C and above in air.

A least-squares treatment was performed on all the experimental data relating the oxygen pressure and temperature in the two-phase region in which UO_{2+x} and U_3O_{8-y} coexist and the resultant equation, which applies between 1100 and 1600°C, is

$$\log P_{O_2}\ (\text{torr}) = \frac{-18{,}050}{T(°K)} + 11.99 \quad . \qquad (17)$$

This equation is in good agreement with the results of Roberts and Walters.[13]

The equilibrium compositions in the two single-phase regions, UO_{2+x} and U_3O_{8-y}, were normally determined by heating UO_{2+x} powder having an initial oxygen-to-uranium ratio near 2.00 to the desired temperature and admitting oxygen at controlled pressure (the typical TGA behavior is shown in Fig. 4). After a sufficient time had elapsed for the equilibration of the UO_{2+x} with oxygen (1 to 2 hr above 1300°C for all oxygen pressures used, and as long as 24 hr for low oxygen pressures at

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[13] L. E. J. Roberts and A. J. Walter, "Equilibrium Pressures and Phase Relations in the Uranium Oxide System," J. Inorg. Nucl. Chem. 22, 213–29 (1961).

temperatures below 1200°C), the specimen was brought to room temperature for the oxygen-to-uranium ratio determination. The technique of cooling the sample for analysis is critical. The oxygen pressure and temperature must be reduced together, ideally as shown along an isocomposition line in Fig. 7, to avoid measurable changes in weight resulting from rapid changes in oxygen composition during cooling. The composition limits of the cubic and orthorhombic phases may be estimated from Fig. 7 as 2.23 and 2.58, respectively. These values are somewhat lower than the generally reported values, possibly because some previous investigators failed to compensate for oxygen pickup during cooling. The temperature-oxygen-pressure relations, shown in Fig. 7, for compositions with oxygen-to-uranium ratios less than 2.08 are tentative because of the very few data points and the difficulties in controlling and measuring the oxygen pressures and in applying thermomolecular flow corrections. No effort was made to distinguish U_4O_{9-y} from UO_{2+x} in this study.

Figure 8 presents the final, and presumably equilibrium, oxygen-to-uranium ratios of the residual $UO_{2\pm x}$ obtained during experiments performed at a system pressure of 10^{-5} to 10^{-6} torr and temperatures between 1200 and 2200°C. All of the specimens heated at 1800°C and above were the dense wafer-shaped specimens, which were quenched to room temperature for oxygen-to-uranium ratio analysis. These data indicate the sub-stoichiometric UO_{2-x} phase forms in vacuum above 1700°C. Metallographic and x-ray diffraction examination of the specimen heated to 2000°C ($UO_{1.984}$) showed no obvious inclusions of uranium metal and a cell size of 5.4697 ± 0.0008 A.

Summary and Conclusions

At a system pressure of 10^{-5} to 10^{-6} torr, UO_{2+x} decomposed by several processes to reduce its oxygen-to-uranium ratio to values close to stoichiometry. At temperatures below 1100°C, this reduction took place solely through the loss of oxygen; at 1500°C and above, the volatile material had a composite oxygen-to-uranium ratio of 4. Between these temperatures the oxygen-to-uranium ratio of the volatile material produced during decomposition was greater than 4 and presumably a mixture

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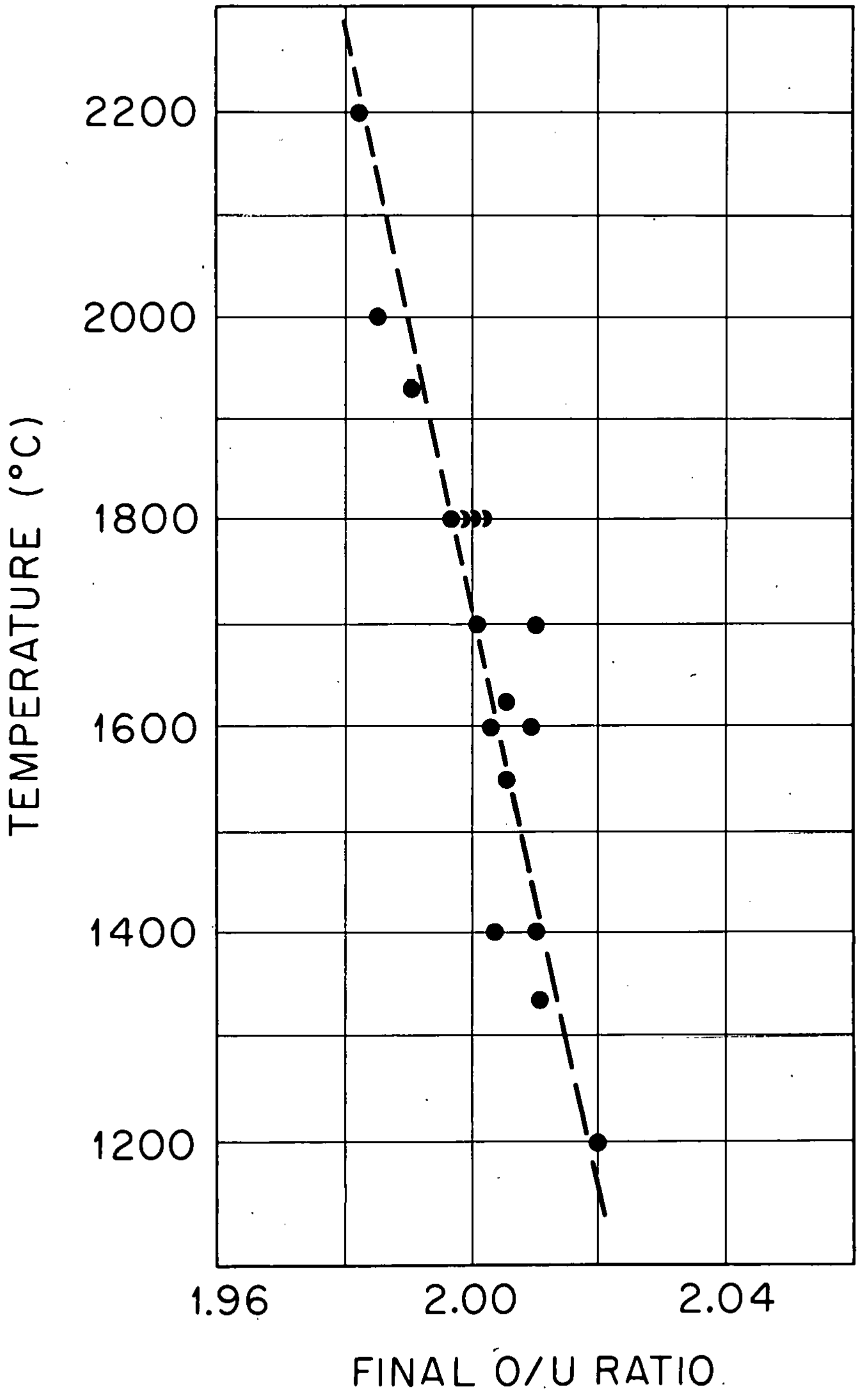

Fig. 8. The Final Oxygen-to-Uranium Ratio of $UO_{2\pm x}$ Heated Between 1200 and 2200°C at a Pressure of 10^{-5} to 10^{-6} torr.

of uranium oxide vapor and oxygen. The decomposition of U_3O_8 in vacuum proceeded in this manner after the evolution of oxygen transformed the solid phase to UO_{2+x}.

The rate of evaporation of near-stoichiometric UO_2 in vacuum (10^{-5} to 10^{-6} torr) was found to be in good agreement with published vapor pressure data.[14] However, in an experiment at 1800°C, the use of a small amount of carbon monoxide to reduce the residual oxygen pressure existing at a system pressure of 10^{-5} torr suppressed the evaporation of UO_2, indicating that an oxidation reaction was contributing to the observed evaporation.

The rate of evaporation from UO_{2+x} at 1200 to 1500°C was proportional to the oxygen pressure up to 0.03 torr and consistent with the reaction

$$UO_{2+x}(s) + \frac{(2-x)}{2} O_2(g) \rightarrow UO_4(g) \quad .$$

Equilibrium constants for this reaction were derived.

A phase diagram (Fig. 7) was constructed showing the relation of oxygen pressures between 10^{-3} and 10^{2} torr, compositions between $UO_{2.02}$ and $UO_{2.63}$, and temperatures between 1000 and 1600°C. The composition limits of the UO_{2+x} and U_3O_{8-y} phases in this temperature range were estimated to be 2.23 and 2.58, respectively. The oxygen pressure at which these solid phases coexist was found to depend on temperature according to

$$\log P_{O_2} \text{ (torr)} = \frac{-18{,}050}{T(°K)} + 11.99 \quad .$$

The oxygen-to-uranium ratio of $UO_{2\pm x}$ heated in vacuum decreased with increasing temperature and became less than 2 above 1700°C.

The results of all the volatility and phase relation experiments are best described by reactions that use $UO_4(g)$ as the uranium oxide vapor phase above $UO_{2\pm x}$. This consistent evidence is sufficient to question the continued usage of reactions that assign $UO_3(g)$ as the vapor species above $UO_{2\pm x}$.

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[14] Raymond J. Ackerman, Paul W. Gilles, and R. J. Thorn, "High-Temperature Thermodynamic Properties of Uranium Dioxide," J. Chem. Phys. 25(6), 1089–97 (1956).

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