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THERMAL STABILITY OF ZIRCONIA- AND
THORIA-BASE FUELS

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by

Carl A. Alexander
Julius S. Ogden
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THERMAL STABILITY OF ZIRCONIA- AND THORIA-BASE FUELS

Carl A. Alexander, Julius S. Ogden, and George W. Cunningham*

Vapor densities and/or dissociation pressures of urania, thoria, zirconia, ThO₂-8 and -20 w/o UO₂, and ZrO₂-20 and -50 w/o UO₂ were obtained in the range from 2000 to 3000 K by the transpiration technique. The urania-zirconia system exhibited marked positive deviation from ideality, indicative of a strong tendency toward immiscibility. The urania-thoria system was found to behave almost ideally. On the basis of the vapor pressures of urania and of thoria and the activity values it would be expected that compositions containing 1 m/o or more of urania would volatilize by preferentially losing urania. A composition containing slightly less than 1 m/o urania should prove to be the congruently subliming composition.

Oxygen dissociation pressures were determined for stoichiometric UO₂ and for a composition on either side of the stoichiometric one. At 2360 K, UO_{2.03} ± 0.01, UO_{2.00} ± 0.01, and UO_{1.97} ± 0.01 exhibited oxygen dissociation pressures of 1×10^{-7} , 4.3×10^{-10} , and 3×10^{-12} atm, respectively. From determinations of vapor density and measurements of oxygen pressure, pressure-temperature-composition relationships were established for urania over a small range of compositions encompassing UO_{2.00}.

INTRODUCTION

In the use of fuels of two components or more there is always the probability that compositional changes may occur which are detrimental to the efficient operation of the reactor. A knowledge of the magnitude of transport mechanisms under various thermal conditions can make it possible to estimate these effects for various geometries and power levels and in this manner may help in the obtainment of optimum performance from a fuel loading.

In the present investigation vaporization characteristics of pure urania, thoria, and zirconia were determined, as well as those of two urania-thoria and urania-zirconia compositions. Vaporization characteristics of urania were examined in some detail since uranium-bearing species are responsible for nearly all the mass transport which may occur in the oxide system.

EXPERIMENTAL PROCEDURE

Apparatus

The transpiration technique was employed to determine vapor density and/or dissociation pressure as a function of temperature and composition. While use of mass

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spectrometric and Knudsen effusion devices can be applied with good success in investigations of transport phenomena, such dynamic techniques work best for univariant systems where their superior speed and ease of detection make them a more logical choice than transpiration. In cases where compositional changes can occur the quasistatic transpiration method is generally more applicable. In special cases where one of the components of the system is a condensable gas whose pressure can be controlled and/or detected, the transpiration technique is especially applicable in that another degree of freedom of the system can be controlled.

The specific apparatus employed in this investigation was composed of a gas mixing, metering, and purification system; a furnace to heat the charge coupled with a condenser to collect the vapor; and, finally, a moisture detector and total volume flow indicator.

The gases employed were either high-purity argon or hydrogen or a combination which could be mixed in batches of 50 liters so that a known partial pressure of hydrogen could be employed in a run. The gases, either from the tank or from the gas storage flask, were dried and oxygen was removed by passing them over hot calcium hydride which was maintained in a stainless steel tube appended to the apparatus. This treatment reduced both oxygen and water vapor concentration to the background level of the mass spectrometer. The dried oxygen-free gas could then be directed into the apparatus or could be switched to a saturator maintained in a Dewar flask. In this manner controlled amounts of water vapor could be added to the gas flow. Experiments performed with no charge present in the apparatus indicated that the gas can be saturated at -77°C , heated to 2000 K , cooled, the water removed, and a value obtained for the vapor pressure of water within 10 percent of the handbook value.

The furnace which contained the reaction chamber and condenser was constructed as a high-vacuum vessel and could be evacuated to 10^{-8} torr at ambient temperature; after several hours of pumping a pressure of 10^{-7} torr at 2000°C could be obtained with the reaction chamber and condenser in the furnace. Connecting tubes were of refrigeration-grade copper and were periodically heated with a torch to insure that outgassing would not be significant. A mass spectrometer attached to the system at 10^{-7} torr indicated the major residual gas to be hydrogen, followed in intensity by CO and, finally, H_2O . The H_2O level was about 5×10^{-9} torr and the total amount of organic vapors passing through the traps was about 1×10^{-9} torr.

The reaction chamber itself was a hollow tungsten cylinder across the bottom of which was placed a porous tungsten disk. A tungsten tube was welded coaxially to the hollow cylinder and was connected below the furnace hot zone to a water-cooled gas inlet for the carrier gas. The porous disk served to prevent the charge from falling down this inlet tube, and also was considered to be an aid in distributing the carrier gas.

The condenser was also made of tungsten tubing and the tip was beveled and ground to form a nearly gastight fit with the reaction chamber. A slight leakage out around the condenser was allowed; this flow was never more than 1 percent of the total carrier gas flow. Analysis of the carrier gas indicated that any backflow of gas by diffusion into the condenser was less than the sensitivity of the mass spectrometer. Temperature was determined optically by sighting the blackbody at the intersection of the condenser and reaction chamber. The apparatus is shown in Figure 1.

Cooled gas that had deposited its condensable vapor somewhere along the thermal gradient in the condenser could be directed either to a magnesium perchlorate weighing

FIGURE 1. SCHEMATIC SHOWING FURNACE DETAILS OF TRANSPIRATION APPARATUS

tube or to a moisture monitor. All the data reported herein are based on the use of the magnesium perchlorate tube, since the reproducibility of the moisture monitor was not sufficiently good to allow thermodynamic calculations. The electrolysis type of moisture monitor was the kind that employed two flow rates. The monitor was first operated on the low flow rate to establish the "error" current produced by electrolysis of the water formed by the catalytic combination of the excess hydrogen with the atomic oxygen set free by electrolysis of the original water present in the sample gas. Once this is established and set to zero the flow rate is then doubled and the new reading now is compensated for the reaction. This is a special problem encountered with gas containing water vapor and either hydrogen or oxygen. The problem with the unit employed in the current investigation was that the differences obtained were small compared to the correction factor for the error current. In some cases the instrument read below zero for the moisture level.

The limitation of the magnesium perchlorate tube did not markedly affect the experimental program. Taking a typical oxygen dissociation pressure of 5×10^{-9} atm at 2500 K, the equilibrium constant for the reaction $\text{H}_2\text{O}(\text{g}) = \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$ is 5.4×10^{-3} . With hydrogen at a pressure of about 1 atm as the carrier gas the partial pressure of water vapor is 1.3×10^{-2} atm. For a typical run with a carrier gas flow rate of 15 cm³ per min at STP and a run duration of 2 hr, 1800 cm³ of hydrogen would be collected. Applying Dalton's Law, $1.3 \times 10^{-2}/1 = x/1800 \text{ cm}^3$, and about 23.4 cm³ of water vapor would be collected at STP, or slightly more than 1.8 mg of water would be collected. In general, a run three times this long would be made so that about 5 mg of water would be collected. The magnesium perchlorate trap can be weighed to within ± 0.2 mg, thus the error in weighing is of the order of ± 5 percent for a given determination. On runs where several liters of carrier gas were to be collected a wet test meter was employed. For short runs the gas volume was determined by a water displacement method. Calibration of the wet test meter by the displacement method indicated an agreement of ± 0.5 percent on volumes corrected to STP.

Assays

The urania collected in the condenser was removed with nitric acid washes and analyzed fluorimetrically⁽¹⁾.

Zirconia could be removed with sulfuric acid to which was added about 5 percent hydrofluoric acid. A considerable quantity of tungsten was also removed and the spectrochemical analysis was performed after removal of the tungsten. The zirconia analysis has not been previously reported in the literature; the method involves use of barium sulfate as a carrier and the determination of zirconia as an impurity in barium.

Thoria was removed with sulfuric acid and analyzed calorimetrically⁽²⁾.

Residues from runs were analyzed polarographically and by oxidation to constant weight (U_3O_8) in order to determine O/U ratios. In addition, some metallographic mounts were optically estimated and compared with the oxidized values as a check on the amount of free metal. In general, the results were within ± 0.01 in the O/U ratio.

(1) References at end of text.

Technique

Preparations were made for a run by placing the charge in the reaction chamber and inserting the condenser. The furnace was then rapidly heated to the desired temperature; about 15 min was required for the furnace to reach 2000 C. Once the required temperature was attained, the pressures of the gas in the reaction chamber and in the furnace were adjusted so that the gas pressure of the furnace was lower than that in the reaction chamber by about 5 torr. A provision existed so that the gas to be employed in the run could flow over the charge in a reverse direction in order that the charge and gas could become equilibrated prior to the run. Pellets were crushed; that material retained by a 20-mesh screen was used as the charge. Size was not critical, with the exception that material too fine would either fall through the porous plate or could become entrained in the gas. If the particles were too large there was the danger of having an insufficient vaporizing surface and also a possible lack of equilibration between the surface and the interior. Experimentally, it was found that about 20 min was required for equilibration when large differences existed between the equilibrium O/U ratio and that of the starting composition. This observation was made on the basis of runs performed after various times at reverse flow over the material prior to the beginning of the run.

The run was begun by reversing the flow and diverting the gas to the magnesium perchlorate trap and to the collector. After the prescribed amount of gas passed through the condenser the run was terminated by stopping the gas flow and shutting off the furnace. The furnace cooled to below red heat in less than a minute.

The system volume has been limited by use of 1/8-in. -ID tubing so that there is no appreciable volume of gas accessible to the charge during this cool-down period. It is considered that no detectable change in the O/U ratio occurs during this period.

After removal of the condenser the charge was removed for compositional assay, and the condenser was analyzed for total mass of the metal. The volume of carrier gas at STP can be calculated, and the mass of water calculated as a volume of STP. The partial pressure of water vapor is calculated with the use of Dalton's Law. Knowledge of the initial hydrogen content of the carrier gas and the temperature at which the run was performed permits calculation of the oxygen pressure from the equilibrium constants⁽¹⁾ for $\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O}$, as has been previously described.

The assay of the amount of metal collected can be utilized to calculate the total pressure of metal-bearing species if it is assumed that dimers or higher polymers are absent. This again is calculated from Dalton's Law written in general form,

$$\sum_{x=0}^n \text{pressure RO}_x / 1 = \Sigma \text{ moles R} / \Sigma \text{ moles carrier gas} + \Sigma \text{ moles R. In the present}$$

study the Σ moles R appearing in the denominator is very much less than the moles of carrier gas and can be neglected, and the equation also assumes the total system pressure to be 1 atm. Corrections are made to STP so that this relation may be applied.

The total pressure of the uranium or other metal-bearing species as well as the oxygen pressure having been determined, use can be made of available free energies to

establish the order of importance of various species to the vaporization process. On the basis of spectroscopic studies⁽³⁾ and other investigations^(4, 5), values exist for the free energy of formation of UO and UO_3 . With the use of the oxygen pressure and total pressure of the uranium-bearing species in an iterative process where the assumption is made that the total pressure comprises first one then another gaseous species, the major species can quickly be established. When corrections are made for the minor species and subtracted from the initial value, the process quickly converges to at least two-place accuracy, which is considered to be better than the limits on existing data.

These equilibrium constants are given in Figures 2 and 3, expressed in terms of $\text{UO}_2(\text{g})$ and $\text{O}_2(\text{g})$. Plots such as these presuppose a knowledge of the free energy of formation of gaseous UO_2 ; however, similar plots can be made using condensed UO_2 and in this manner the free energy of the gas can be determined. The present investigation as well as a previous effusion study lead to a value for free energy of formation for gaseous UO_2 in agreement to about 2 kcal per mole. The homogeneous equilibrium constant is somewhat easier to manipulate and is necessary for the evaluation of the effect of composition on vaporization.

EXPERIMENTAL RESULTS

Vapor pressures of the pure oxides are given in Figures 4, 5, and 6, and the experimental values on which these and the following curves are based are included in the Appendix. Since knowledge of the behavior of urania is essential to an understanding of both the thorium-uranium and the zirconium-uranium systems, its vaporization and dissociation characteristics were examined in some detail. Dissociation pressures were determined at three different O/U ratios and are shown in Figures 7, 8, and 9. A somewhat different technique was employed in determining UO_2 as compared with that previously discussed. No hydrogen was employed and the O_2 pressure was calculated from the equilibrium ratio of UO_3/UO_2 . The composition UO_2 was about as oxidizing a composition as could be employed with this apparatus without forming condensed-phase tungsten oxides in the apparatus. O/U ratios of the condensed phases were determined by oxidation to U_3O_8 .

Zirconia-Base Compositions

The partial pressures of urania and zirconia were determined for ZrO_2 -20.3 w/o UO_2 and ZrO_2 -49.7 w/o UO_2 compositions. The experimental fit of the urania data is shown in Figures 10 and 11. Within the precision of the data, ZrO_2 appeared to be present at the same level as pure zirconia at similar temperatures. A calculation of $p\text{UO}_2(\text{solution})/p\text{UO}_2(\text{pure})$ would indicate that this system deviates positively from ideality. At temperatures below 2120 C it was not possible to detect a difference in the partial pressure of urania between the nominal 20 w/o urania and nominal 50 w/o urania unless the 20 w/o composition was first preheated to at least 2300 C and held at this temperature for about 0.5 hr. This apparent higher volatility was probably due to metastability or inhomogeneity, as would be indicated from the phase-equilibria investigation. Had the phase diagram not been available⁽⁶⁾, it would have been concluded that

FIGURE 2. EQUILIBRIUM CONSTANTS FOR THE REACTION
 $\text{UO(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{UO}_2\text{(g)}$

FIGURE 3. EQUILIBRIUM CONSTANTS FOR THE REACTION
 $\text{UO}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{UO}_3\text{(g)}$

FIGURE 4. VAPOR PRESSURE OF UO_2 FIGURE 5. VAPOR PRESSURE OF ZrO_2

FIGURE 6. VAPOR PRESSURE OF ThO_2

FIGURE 7. OXYGEN DISSOCIATION PRESSURE OF $\text{UO}_{2.03 \pm 0.01}$

FIGURE 8. OXYGEN DISSOCIATION PRESSURE OF $UO_{2.00 \pm 0.01}$

FIGURE 9. OXYGEN DISSOCIATION PRESSURE OF $UO_{1.97 \pm 0.01}$

FIGURE 10. PARTIAL PRESSURE OF UO_2 OVER ZrO_2 -20 W/O UO_2

FIGURE 11. PARTIAL PRESSURE OF UO_2 OVER ZrO_2 -50 W/O UO_2

both these compositions were in a two-condensed-phase field. The homogenizing at higher temperature appeared to result in a true equilibrium rather than a surface depletion or some other kinetic phenomenon because of the independence of vapor pressure from flow rate. The activity of urania at a temperature of 2500 K is plotted in Figure 12. The standard state is the vapor pressure of pure UO_2 at this temperature.

FIGURE 12. THERMODYNAMIC ACTIVITY IN $\text{ZrO}_2\text{-UO}_2$ AT 2500 K

The activity is not strongly dependent upon temperature; hence, this figure is representative of the system behavior. The activity of ZrO_2 was calculated from the UO_2 activity by means of the Gibbs-Duhem relation, $d \ln a_1 = -N_2/N_1 d \ln a_2$. The integration was carried out both by a planimeter and by square counting. Essentially the same curve was obtained in both cases. Examination of the curve generated for ZrO_2 verifies the experimental observation that the activity of ZrO_2 is very nearly unity, even at 50 w/o UO_2 , and that there are no attractive forces between ZrO_2 and UO_2 at any composition. The nearly horizontal nature of the curve at the high-zirconia end, coupled with its intrinsic low vapor pressure, would indicate that the system may be considered as a volatile component in a nearly completely inert matrix (at least at the high-zirconia end).

Thoria-Base Compositions

Two thoria-urania compositions were run and are shown in Figures 13 and 14. The compositions contained 7.97 w/o UO_2 and 20.3 w/o UO_2 . Thoria, like zirconia, was found to be at nearly unit activity. The positive deviation from ideality observed for urania-zirconia was not observed for thoria-urania, where near ideal behavior was noted. An activity curve, Figure 15, is sketched for this system but because of the

FIGURE 13. PARTIAL PRESSURE OF UO_2 OVER ThO_2 -20 W/O UO_2

FIGURE 14. PARTIAL PRESSURE OF UO_2 OVER ThO_2 -8 W/O UO_2

limited range of compositions investigated no mathematical treatment has been made. Some negative deviation from ideality can be observed in this temperature range, although there is evidence that at lower temperatures the system is essentially perfectly ideal. This could be predicted from consideration of the nearly identical crystal structures.

FIGURE 15. THERMODYNAMIC ACTIVITY IN $\text{ThO}_2\text{-UO}_2$ AT 2500 K

The metastability encountered in urania-zirconia was not observed in this system; thus, chances are better that a homogeneous material can be obtained by use of urania-thoria rather than urania-zirconia. In addition, the thoria-urania system exhibits better thermal stability against transport. At 20 w/o urania, the urania transport rate would be three times higher in zirconia-urania than in thoria-urania; thus, a significant reduction in volatility would be obtained by use of thoria-base solid solution.

DISCUSSION AND CONCLUSIONS

On the basis of the above data it would be expected that thoria-base fuels would be somewhat more stable than zirconia-base fuels, but at center-line temperatures, massive transport of urania could occur, at least until a steady-state condition was established. This steady state would depend on the power generation and the geometrical configuration of the core, as well as the composition of the fuel.

Since urania is responsible for the transport and would be the prime cause of compositional or configurational changes, the variation of volatilization as a function of

temperature and composition has been computed. These data were obtained from cross plots of the curves given earlier in this report. Because of the wide variation in composition in the gas phase, graphical representation would not show in detail the composition changes in the solid; hence, the data are arranged in Tables 1 through 4 as four isotherms.

Two significant features can be seen from such a presentation: (1) a minimum exists in the total pressure over the urania and this minimum shifts to lower O/U ratios at higher temperatures, and (2) at O/U ratios of 2.03 or lower, neither atomic nor molecular oxygen are of importance in mass-transport considerations and contribute less than 5 percent to the transport. The oxygen pressures, although small, may cause serious interactions with cladding, especially under conditions where the fuel volume is very much greater than the cladding volume.

One simplification was made in computing these tables; the partial pressure of UO_2 does not change as a function of composition. There would be a slight change but this is a matter of only several percent over the composition range covered in these tables.

The thermodynamics consistency of the uranium-oxygen system can be evaluated by representing all the high-temperature data available on a plot of the partial molal free energy of oxygen versus composition. Such a plot is shown in Figure 16, which is based on Figure 8 of a paper by Aitken, Brassfield, and Fryxell⁽⁹⁾. The two-phase data of Ackermann, et al.⁽¹⁰⁾, were used to calculate the oxygen pressure for uranium saturated with urania. An extrapolation of 100 deg of the isopeistic determination of the two-phase boundary was made and indicated with a dashed line. The data obtained in the current investigation appear to be in general accord with that of other investigators. The difficulty in such determinations can be seen by observing the large changes in partial molal free energy that occur for small compositional changes, especially in the neighborhood of $\text{UO}_{2.00}$, where these data indicate that a point of inflection occurs.

It would be expected that the existence of pores could lead to a vapor transport mechanism which would cause localized changes in composition and which may possibly be a driving force for pore or bubble migration. This, again, would be a function of density, the nature of the "pore phase", temperature gradients, and composition.

While the oxygen pressure is not a major mechanism by which mass can be transferred it can be expected that the existence of a temperature gradient will result in a composition gradient. From Figure 16 it can be seen that the fluorite phase of urania can exist through a variation in oxygen pressure of twenty orders of magnitude. If a center-line temperature of 2750 K and a composition of $\text{UO}_{1.96}$ are considered, then the equilibrium oxygen pressure would be about 2×10^{-10} . At all points accessible to this oxygen pressure O/U ratios higher than 1.96 will exist at lower temperatures. This oxygen pressure also affords a driving force for diffusion and offers a suggestion that if a material with a lower O/U ratio were placed in the center of a fuel rod it should be possible to eliminate the driving force for diffusion to the cladding. In this manner, by preselection of compositions, it may be possible to direct the activity gradient of oxygen away from the cladding, thus greatly prolonging cladding life under operating conditions.

TABLE 1. URANIA PRESSURE VERSUS COMPOSITION AT 2750 K

O/U Ratio		Pressure, atm					
Solid	Gas	Total	O ₂	O	UO ₂	UO	UO ₃
2.03	2.70	2.4×10^{-3}	1×10^{-4}	1×10^{-4}	8×10^{-4}	7×10^{-7}	1.5×10^{-3}
2.02	2.57	1.7×10^{-3}	3×10^{-6}	7×10^{-5}	8×10^{-4}	1×10^{-6}	9×10^{-4}
2.01	2.36	1.2×10^{-3}	8×10^{-7}	4×10^{-5}	8×10^{-4}	2×10^{-6}	4×10^{-4}
2.00	2.20	1.0×10^{-3}	2×10^{-7}	2×10^{-5}	8×10^{-4}	5×10^{-6}	2×10^{-4}
1.99	2.10	9.0×10^{-4}	3×10^{-8}	7×10^{-6}	8×10^{-4}	1×10^{-5}	9×10^{-5}
1.98	2.02	8.7×10^{-4}	5×10^{-9}	3×10^{-6}	8×10^{-4}	3×10^{-5}	4×10^{-5}
1.97	1.93	8.8×10^{-4}	9×10^{-10}	1×10^{-6}	8×10^{-4}	7×10^{-5}	1×10^{-5}
1.96	1.80	1×10^{-3}	2×10^{-10}	5×10^{-7}	8×10^{-4}	2×10^{-4}	7×10^{-6}

TABLE 2. URANIA PRESSURE VERSUS COMPOSITION AT 2500 K

O/U Ratio		Pressure, atm					
Solid	Gas	Total	O ₂	O	UO ₂	UO	UO ₃
2.03	2.69	1.7×10^{-4}	6×10^{-7}	1×10^{-5}	6×10^{-5}	7×10^{-8}	1×10^{-4}
2.02	2.49	1.1×10^{-4}	1×10^{-7}	4×10^{-6}	6×10^{-5}	2×10^{-7}	5×10^{-5}
2.01	2.36	9.2×10^{-5}	3×10^{-8}	2×10^{-6}	6×10^{-5}	3×10^{-7}	3×10^{-5}
2.00	2.16	7.1×10^{-5}	5×10^{-9}	1×10^{-6}	6×10^{-5}	8×10^{-7}	1×10^{-5}
1.99	2.04	6.7×10^{-5}	9×10^{-10}	4×10^{-7}	6×10^{-5}	2×10^{-6}	5×10^{-6}
1.98	1.97	6.6×10^{-5}	2×10^{-10}	2×10^{-7}	6×10^{-5}	4×10^{-6}	2×10^{-6}
1.97	1.87	7.1×10^{-5}	3×10^{-11}	8×10^{-8}	6×10^{-5}	1×10^{-5}	8×10^{-7}
1.96	1.67	9.0×10^{-5}	7×10^{-12}	3×10^{-8}	6×10^{-5}	3×10^{-5}	3×10^{-7}

TABLE 3. URANIA PRESSURE VERSUS COMPOSITION AT 2250 K

O/U Ratio		Pressure, atm					
Solid	Gas	Total	O ₂	O	UO ₂	UO	UO ₃
2.03	2.58	4.3×10^{-6}	7×10^{-9}	3×10^{-7}	2×10^{-6}	6×10^{-9}	2×10^{-6}
2.02	2.32	2.9×10^{-6}	1×10^{-9}	1×10^{-7}	2×10^{-6}	2×10^{-8}	8×10^{-7}
2.01	2.20	2.6×10^{-6}	3×10^{-10}	7×10^{-8}	2×10^{-6}	3×10^{-8}	5×10^{-7}
2.00	2.09	2.3×10^{-6}	5×10^{-11}	3×10^{-8}	2×10^{-6}	7×10^{-8}	2×10^{-7}
1.99	1.97	2.3×10^{-6}	8×10^{-12}	1×10^{-8}	2×10^{-6}	2×10^{-7}	9×10^{-8}
1.98	1.84	2.5×10^{-6}	1×10^{-12}	4×10^{-9}	2×10^{-6}	5×10^{-7}	3×10^{-8}
1.97	1.67	3.0×10^{-6}	2×10^{-13}	2×10^{-9}	2×10^{-6}	1×10^{-6}	1×10^{-8}
1.96	1.50	4.0×10^{-6}	7×10^{-14}	1×10^{-9}	2×10^{-6}	2×10^{-6}	7×10^{-9}

TABLE 4. URANIA PRESSURE VERSUS COMPOSITION AT 2000 K

O/U Ratio		Pressure, atm					
Solid	Gas	Total	O ₂	O	UO ₂	UO	UO ₃
2.03	2.61	1.2×10^{-7}	1×10^{-10}	7×10^{-9}	5×10^{-8}	2×10^{-10}	6×10^{-8}
2.02	2.32	7.3×10^{-8}	7×10^{-12}	2×10^{-9}	5×10^{-8}	9×10^{-10}	2×10^{-8}
2.01	2.07	5.9×10^{-8}	1×10^{-12}	7×10^{-10}	5×10^{-8}	2×10^{-9}	6×10^{-9}
2.00	1.93	5.8×10^{-8}	2×10^{-13}	3×10^{-10}	5×10^{-8}	6×10^{-9}	2×10^{-9}
1.99	1.86	6.1×10^{-8}	3×10^{-14}	1×10^{-10}	5×10^{-8}	1×10^{-8}	1×10^{-9}
1.98	1.63	8.1×10^{-8}	6×10^{-15}	5×10^{-11}	5×10^{-8}	3×10^{-8}	5×10^{-10}
1.97	1.42	1.2×10^{-7}	1×10^{-15}	2×10^{-11}	5×10^{-8}	7×10^{-8}	2×10^{-10}
1.96	1.20	2.5×10^{-7}	2×10^{-16}	9×10^{-12}	5×10^{-8}	2×10^{-7}	8×10^{-11}

FIGURE 16. PARTIAL MOLAL FREE ENERGY OF OXYGEN IN URANIA AT 2400 C

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APPENDIX

EXPERIMENTAL VALUES

APPENDIX

EXPERIMENTAL VALUES

The actual experimental values upon which the curves and tables in the text were based are given in Tables A-1 through A-10.

TABLE A-1. UO_2

Temperature, K	UO_2 Pressure, atm
2940	3.52×10^{-3}
2930	3.78×10^{-3}
2840	2.24×10^{-3}
2780	1.12×10^{-3}
2620	1.98×10^{-4}
2500	5.01×10^{-5}
2420	2.58×10^{-5}
2360	9.98×10^{-6}
2340	6.24×10^{-6}
2280	3.84×10^{-6}
2210	1.28×10^{-6}
2090	2.28×10^{-7}
2000	1.79×10^{-7}

TABLE A-2. ZrO_2

Temperature, K	ZrO_2 Pressure, atm
2820	1.00×10^{-5}
2740	7.60×10^{-6}
2720	4.02×10^{-6}
2700	4.25×10^{-6}
2640	2.20×10^{-6}
2620	1.91×10^{-6}
2590	8.20×10^{-7}
2580	1.25×10^{-6}
2520	4.22×10^{-7}
2360	4.14×10^{-8}
2160	1.79×10^{-9}

TABLE A-3. ThO_2

Temperature, K	ThO_2 Pressure, atm
2900	2.82×10^{-5}
2740	5.85×10^{-6}
2640	1.02×10^{-6}
2590	9.82×10^{-7}
2500	3.82×10^{-7}
2490	3.40×10^{-7}
2490	3.40×10^{-7}
2490	2.62×10^{-7}
2440	1.35×10^{-7}
2380	7.11×10^{-8}

TABLE A-4. OXYGEN DISSOCIATION PRESSURE
OF $\text{UO}_{2.03 \pm 0.01}$

Temperature, K	UO_2 Pressure, atm
2360	1.0×10^{-7}
2280	1.9×10^{-8}
2260	1.0×10^{-8}
2180	1.9×10^{-9}
2090	4.5×10^{-10}
2060	4.1×10^{-10}
1950	4.8×10^{-11}

TABLE A-5. OXYGEN DISSOCIATION PRESSURE
OF $\text{UO}_{2.00 \pm 0.01}$

Temperature, K	UO_2 Pressure, atm
2560	9.0×10^{-9}
2360	4.3×10^{-10}
2350	2.6×10^{-10}
2260	8.0×10^{-11}
2260	7.2×10^{-11}
2110	1.5×10^{-12}

TABLE A-6. OXYGEN DISSOCIATION PRESSURE
OF $\text{UO}_{1.97 \pm 0.01}$

Temperature, K	UO_2 Pressure, atm
2720	8.5×10^{-10}
2640	1.5×10^{-10}
2500	3.3×10^{-11}
2430	5.2×10^{-12}
2360	3.0×10^{-12}
2340	2.8×10^{-12}
2290	1.5×10^{-12}

TABLE A-7. ZrO_2 -20 w/o UO_2

Temperature, K	UO_2 Pressure, atm
2680	1.32×10^{-4}
2640	1.13×10^{-4}
2620	6.70×10^{-5}
2490	1.55×10^{-5}
2400	4.18×10^{-6}
2340	2.01×10^{-6}
2290	1.04×10^{-6}
2280	1.20×10^{-6}

TABLE A-8. ZrO_2 -50 w/o UO_2

Temperature, K	UO_2 Pressure, atm
2680	1.95×10^{-4}
2670	1.68×10^{-4}
2460	2.00×10^{-5}
2310	2.70×10^{-6}
2280	1.71×10^{-6}
2260	1.75×10^{-6}
2190	5.12×10^{-7}

TABLE A-9. ThO_2 -8 w/o UO_2

Temperature, K	UO_2 Pressure, atm
2740	3.00×10^{-5}
2670	9.05×10^{-6}
2720	1.30×10^{-5}
2590	3.25×10^{-6}
2480	9.50×10^{-7}
2380	4.45×10^{-7}
2340	1.51×10^{-7}

TABLE A-10. ThO_2 -20 w/o UO_2

Temperature, K	UO_2 Pressure, atm
2760	9.50×10^{-5}
2590	2.21×10^{-5}
2590	1.55×10^{-5}
2480	6.98×10^{-6}
2400	1.39×10^{-6}