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SOME ASPECTS OF THE HIGH TEMPERATURE VAPORIZATION BEHAVIOR AND VALENCE EFFECTS IN ACTINIDE-OXIDE RARE-EARTH-OXIDE SYSTEMS

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Some Aspects of the High Temperature Vaporization Behavior and Valence Effects in Actinide-Oxide Rare-Earth-Oxide Systems*

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ABSTRACT

The vaporization behavior of the neodymium sesquioxide phase has been studied as a function of oxygen partial pressure in the temperature range from 2155 to 2485 K. Oxygen potentials for the U-Nd-O system, where Nd/(U + Nd) = 0.1 and 0.2 are higher than those obtained with unalloyed urania. A significant increase in oxygen potential occurs when cerium is incorporated into the lattice of the U-Pu-O system for actinide ratio of Pu/(U + Pu) = 0.2 and cerium-to-metal ratio Ce/(U + Pu + Ce) = 0.05. Measurements of oxygen potential at 2050 K above hypostoichiometric U-Pu-O compositions having plutonium-to-metal ratios ranging from 0.15 to 0.30 indicate that for a given plutonium valence, the oxygen potential is dependent on the plutonium-to-metal ratio. Total pressures of actinide-bearing species estimated from our experimental oxygen potentials and the free energies of formation of the gaseous and condensed phases are in good agreement with those obtained from analysis of sublimates collected during transpiration experiments.

INTRODUCTION

A knowledge of the high temperature thermodynamic properties of actinide-oxide and rare-earth-oxide systems is of importance in understanding the behavior of fast breeder reactor oxide fuels. Of particular interest are the oxides of neodymium and cerium, which are major rare-earth products. In accordance with the theme of this Colloquium, this paper will review selected studies at Argonne National Laboratory, previously published and recent work, involving the high-temperature vaporization behavior of actinide-oxide and rare-earth-oxide systems. Because of space limitations, only the highlights of these studies will be emphasized.

Nd_2O_3 and U-Nd-O Systems

The vaporization behavior of the neodymium sesquioxide phase has been studied[1] as a function of oxygen partial pressure in the temperature range from 2155 to 2485 K by means of a transpiration technique. The agreement between the total pressure of neodymium-bearing species derived from the weight loss of samples and from analysis of sublimates in the condenser tube was very good. For the assumed reaction $Nd_2O_3(s) = 2NdO(g) + 1/2\ O_2(g)$, the third-law heat of reaction was found to be $\Delta H^\circ_0 = 361.1 \pm 1.1$ kcal/mol. The heat of formation and the dissociation energy of NdO(g) derived from this study were $\Delta H^\circ_f(NdO,g,0\ K) = -33.7 \pm 0.6$ kcal/mol and $D^\circ_0\ (NdO,g) = 7.42 \pm 0.1$ eV, respectively. The dissociation energy of NdO(g) is in accord with the approximate value expected from the variation of gaseous monoxides and heats of sublimation of rare-earth metals as a function of atomic number. The value for the heat of formation of NdO(g) derived from this study appears to be more in line with the variation in the heats of formation of the rare earth monoxides as one goes from lanthanum to lutetium than does the heat of formation value of -36.9 kcal/mol given by Ames et al.[2] in their 1967 assessment.

Oxygen potentials over the U-Nd-O system, where Nd/(U + Nd) = 0.1 and 0.2, have been investigated[3] at 2250 and 2350 K. Typical results at 2250 K are shown in Figure 1. It is seen that oxygen potentials for the U-Nd-O system are higher (and therefore more oxidizing) than those obtained with unalloyed urania.[4] The oxygen potential also increases with increasing Nd/(U + Nd) ratio at a fixed O/M ratio. With the neodymium assumed to be in the trivalent state, the higher oxygen potential obtained for Nd/(U + Nd) = 0.2 at a fixed O/M ratio can be attributed to an increase in the average valence of uranium. The introduction of neodymium into the fluorite lattice also has a strong effect on the magnitude of the partial entropy and enthalpy of solution of oxygen in these compositions.

X-ray analysis of several U-Nd-O solid solution compositions, where Nd/(U + Nd) = 0.1, showed only a single-phase, face-centered-cubic structure, and a decrease in lattice parameter with increasing oxygen content. The contraction in lattice parameter is in accord with expectations, because to maintain electrical neutrality, the uranium valence must increase from its value of 4+ at the composition O/M = 1.95 when the condensed phase is oxidized toward the stoichiometric composition. A decrease in lattice parameter was observed for Nd/(U + Nd) = 0.2 at a fixed O/M ratio. The reason for the discrepancy between our results and the higher lattice parameter values observed by Wadier _et al._[5] for this system has not been resolved.

U-Pu-O and U-Pu-Ce-O Systems

The postulate of Markin and McIver,[6] namely, that oxygen potentials for the U-Pu-O system are a function only of the valence of the metal whose oxidation state is changing, has frequently served as a convenient basis for intercomparison of oxygen potential measurements made on materials having different Pu/(U + Pu) ratios. Thus for hypostoichiometric U-Pu-O, oxygen potential is a function of the plutonium valence, and for hyperstoichiometric compositions, oxygen potential is a function of the uranium valence. This postulate was based on interpretations of their low-temperature (1173-1373 K) galvanic-cell measurements on U-Pu-O compositions having Pu/(U + Pu) ratios of 0.11, 0.15 and 0.30. Because of the scatter in their data, it is difficult to establish rigorously the dependency of oxygen potential on actinide valency.

Our recent measurements of oxygen potential at 2050 K above hypostoichiometric U-Pu-O compositions having plutonium-to-metal ratios ranging from 0.15 to 0.30 are given in Figures 2 and 3. The results (good to about ±2 kcal) show that oxygen potentials increases with increasing Pu/(U + Pu) ratio at a fixed O/M ratio. From Fig. 3, where oxygen potential is plotted versus plutonium valency, the results indicate that for a given plutonium valence, the oxygen potential is dependent on the plutonium-to-metal ratio, increasing with increasing Pu/(U + Pu) ratio; thus, our results are not in accord with the Markin-McIver postulate. It should be noted that measurements of Chilton and Kirkham[7] at Windscale with hyperstoichiometric U-Pu-O compositions in the temperature range from 1518 to 1823 K also show that oxygen potential is dependent on the U/(U + Pu) ratio at a given uranium valence.

Measurements of oxygen potential as a function of O/M ratio have been carried out at 2050 K over the U-Pu-Ce-O system, with an actinide ratio Pu/(U + Pu) = 0.2 and a cerium-to-metal ratio of Ce/(U + Pu + Ce) = 0.05. Oxygen-to-metal ratios of the residues were obtained by means of the McNeilly-Chikalla method.[8] The results are shown in Fig. 4. For comparison, oxygen potential values obtained with the U-Pu-O system at 2050 K comparison, oxygen potential values obtained with U-Pu-O systems at 2050 K (see above) are included in the figure. It is apparent that a significant increase in oxygen potential occurs when cerium is incorporated into the lattice of the U-Pu-O solid-solution system.

Estimated values of the valence of U, Pu, and Ce ions in the compositions investigated are given in Table I, and are based on the reducibility of these ions being in the sequence Ce $\gg$ Pu > U. A sharp increase in the valence of cerium occurs in the region in which the composition of the oxide mixture exceeds O/M = 1.975 and approaches O/M = 2.00; at the latter composition, the valences of Ce, Pu, and U are all 4+.

Total Pressures of Uranium- and Plutonium-Bearing Species Above U-Pu-O Systems

In the earlier studies[2] of oxygen potentials over the U-Pu-O system in the temperature range from 2150 to 2550 K, a limited number of measurements were also made of the total pressure of actinide-bearing species.[8] The actinide-bearing sublimates were collected inside a tungsten condenser tube and subsequently dissolved by repeated washings with hot, concentrated nitric acid. These solutions were analyzed for uranium and plutonium by means of standard analytical techniques. The total pressure of uranium- and plutonium-bearing species derived from the chemical analyses and transpiration measurements are given in Table II. The total pressures of these species can also be estimated from our experimental oxygen potential values and the free energies of formation of the gaseous and condensed phases.[3,10] The calculated pressures of uranium and plutonium species are shown in column 4. The agreement is very good between the experimental and calculated values for uranium pressures, and is reasonable between the experimental and calculated values for plutonium pressures. For comparison this table also includes actinide pressures calculated from the mass-effusion and mass-spectrometric measurements of Battles et al.,[11] and Ohse and Olson.[12] The data of Ohse and Olson were for compositions of Pu/(U + Pu) = 0.15; these data were recalculated to enable comparison with data obtained with Pu/(U + Pu) = 0.2. The agreement between the various sets of measurements is reasonable.

A limited number of measurements of sample weight losses were also made during the course of the transpiration measurements, and from these, the total pressures of actinide-bearing species were estimated. On the basis of mass spectrometric measurements[11,12] the average molecular weight of the gaseous species was assumed to be 270 over the compositions ranging from O/M = 1.93 to 1.95, with UO_2(g) being the predominant species above the condensed phase. The results are also given in Table II. The agreement between the values of total pressure of actinide-bearing species derived from analysis of the sublimate and those derived from weight-loss measurements is very good. Thus, it appears that weight-loss measurements on this system can serve as a basis for approximating the total pressure of actinide-bearing species over the U-Pu-O system. Finally, the agreement between the calculated values of total actinide pressure derived from oxygen potential measurements and those derived from the various procedures indicated in Table II is good.

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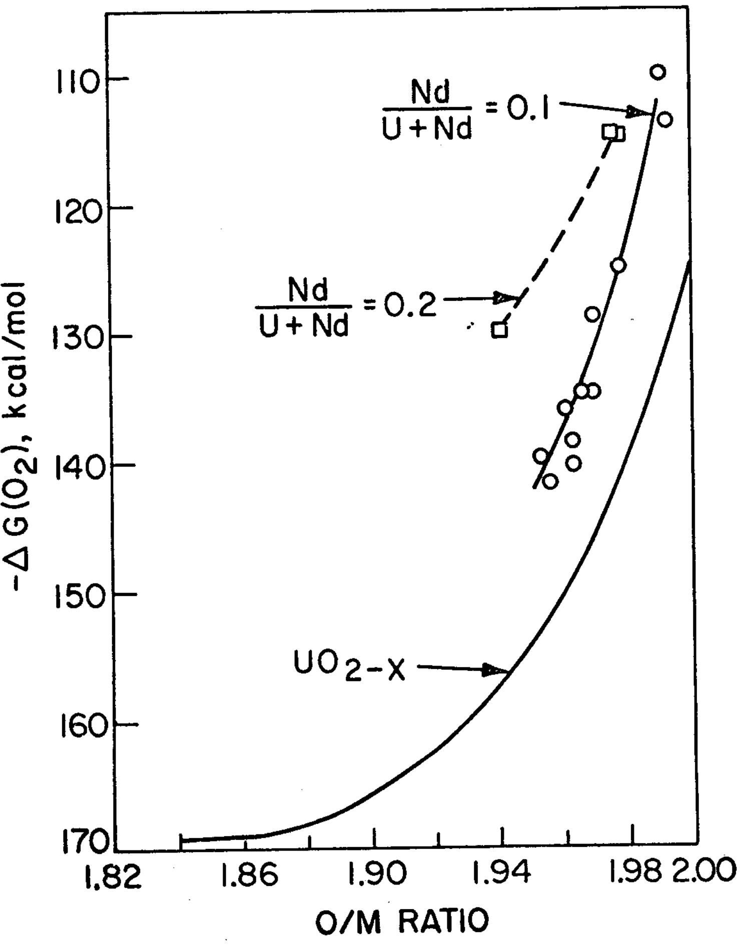
110
120
130
140
150
160
170
$-\Delta\bar{G}(O_2)$, kcal/mol
1.82
1.86
1.90
1.94
1.98
2.00
O/M RATIO
$\frac{Nd}{U+Nd} = 0.1$
$\frac{Nd}{U+Nd} = 0.2$
UO_{2-X}

Figure 1. Oxygen Potential as a Function of O/M Ratio for U-Nd-O and UO_{2-x} Systems at 2250 K.

(ANL-308-3689)

Figure 2. Oxygen Potentials over Hypostoichiometric U-Pu-O Compositions at 2050 K

(308-77-44)

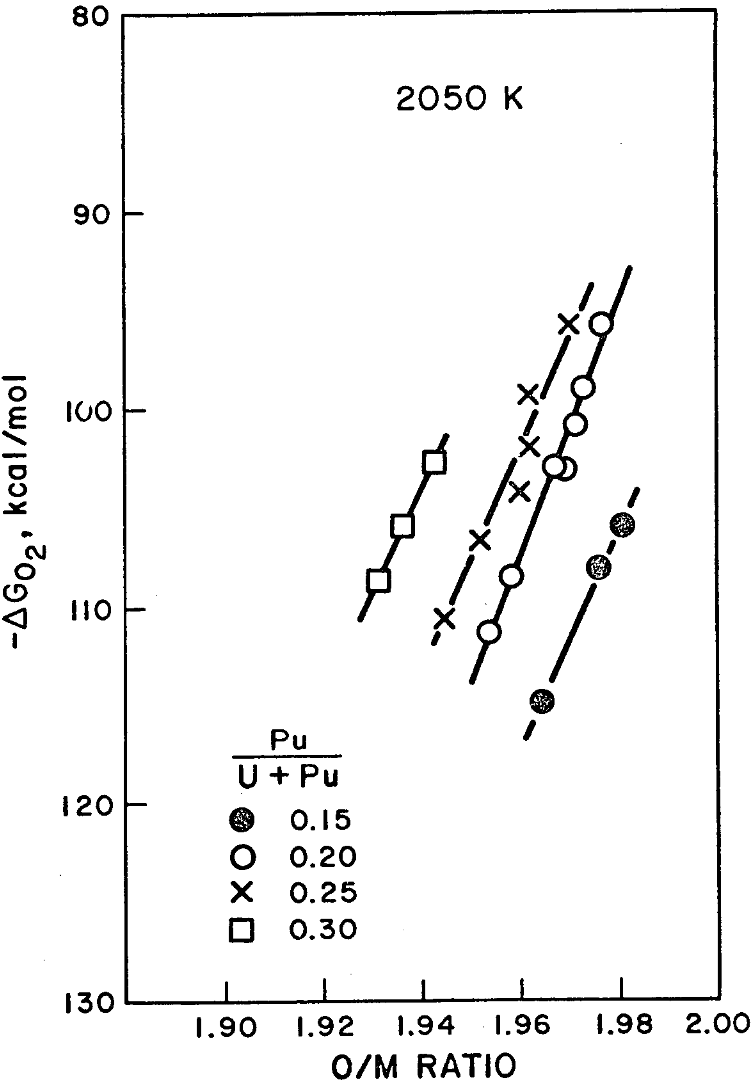
2050 K
80
90
100
110
120
130
$-\Delta\bar{G}_{O_2}$, kcal/mol
$\frac{Pu}{U + Pu}$
● 0.15
○ 0.20
× 0.25
□ 0.30
1.90
1.92
1.94
1.96
1.98
2.00
O/M RATIO

Figure 3. Oxygen Potentials vs. Plutonium Valence for Hypostoichiometric U-Pu-O Compositions at 2050 K.

(ANL-308-77-46)

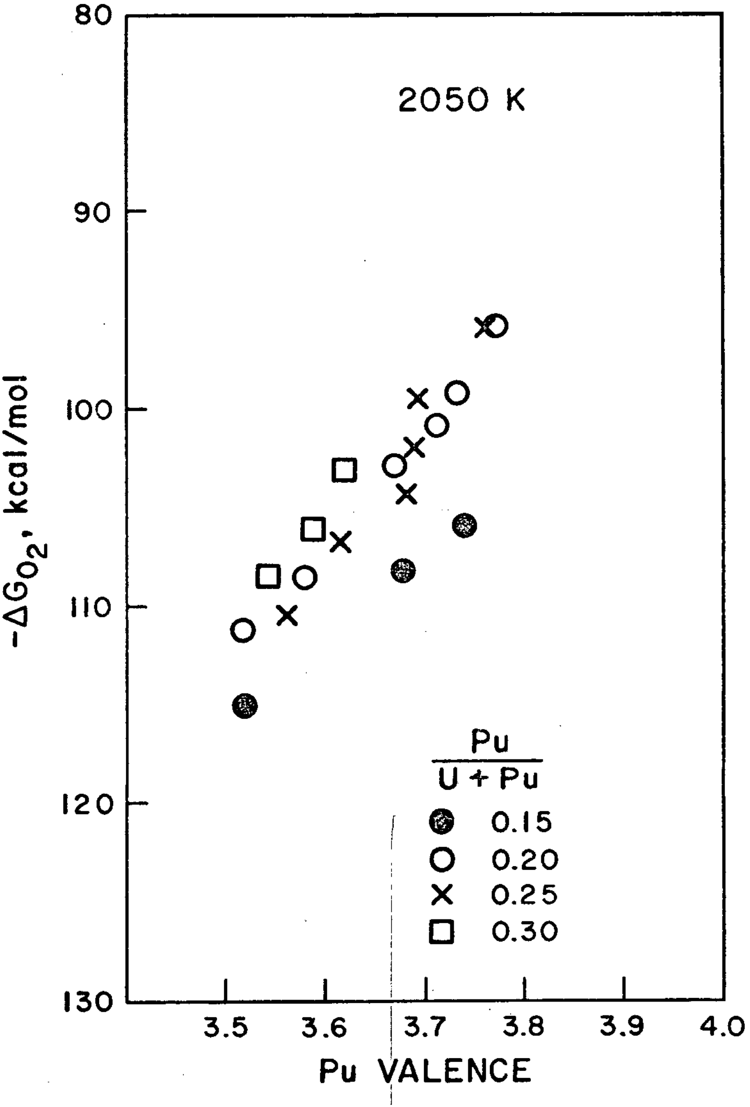
2050 K
80
90
100
110
120
130
$-\Delta\bar{G}_{O_2}$, kcal/mol
3.5
3.6
3.7
3.8
3.9
4.0
Pu VALENCE
$\frac{Pu}{U + Pu}$
● 0.15
○ 0.20
× 0.25
□ 0.30

Figure 4. Oxygen Potentials Over $U_{0.8}Pu_{0.2}O_{2-x}$ and $(U_{0.8}Pu_{0.2})_{.95}Ce_{0.05}O_{2-x}$ Compositions at 2050 K

(308-77-42)

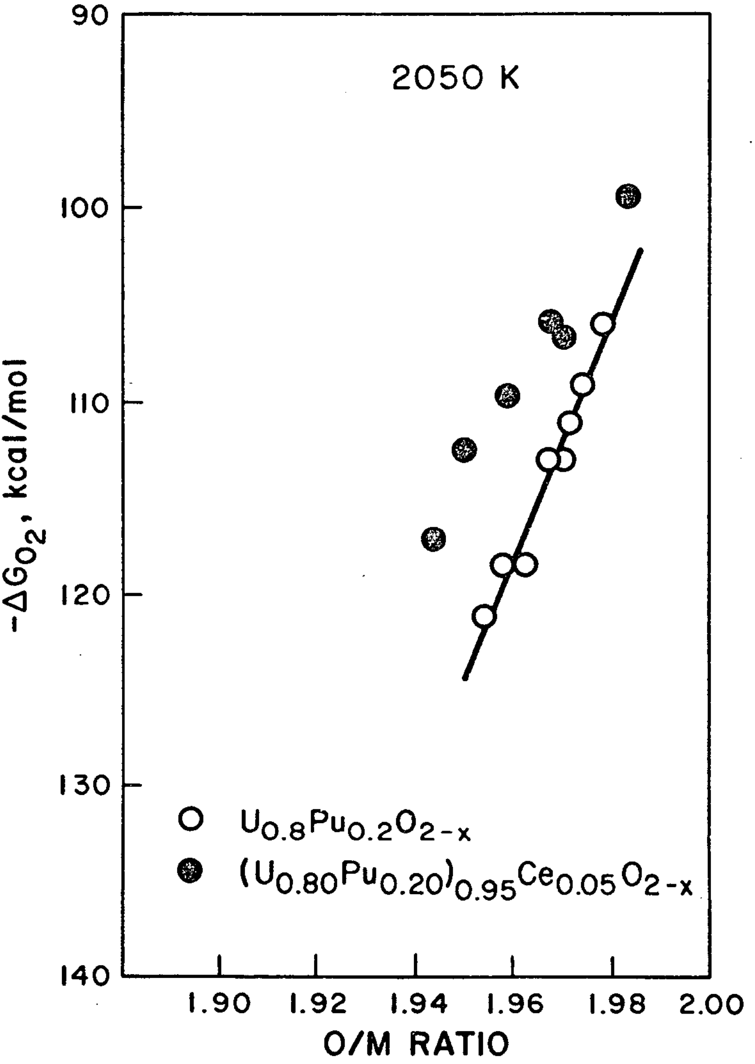
2050 K
90
100
110
120
130
140
$-\Delta\bar{G}_{O_2}$, kcal/mol
1.90
1.92
1.94
1.96
1.98
2.00
O/M RATIO
○ $U_{0.8}Pu_{0.2}O_{2-x}$
● $(U_{0.80}Pu_{0.20})_{0.95}Ce_{0.05}O_{2-x}$

Table I. Estimated Values for the Valence of U, Pu, and Ce Ions in U-Pu-Ce-O Solid-Solution Systems where Pu/(U + Pu) = 0.2 and Ce/(U + Pu + Ce) = 0.05.

O/M	U	Pu	Ce
1.943	+4	+3.66	+3
1.949	+4	+3.73	+3
1.958	+4	+3.82	+3
1.967	+4	+3.92	+3
1.970	+4	+3.94	+3
1.975	+4	+4	+3
1.981	+4	+4	+3.24

Table II. Calculated and Experimental Values for Total Pressures of Actinide-Bearing Species over $U_{0.8}Pu_{0.2}O_{2-x}$

			Transpiration			Mass Spec. & Mass Effusion	
T, K	$-\Delta G(O_2)$ kcal	O/M	Calc	Measured (Sublimate)		Battles et al.	Ohse & Olson
				-log p(U), atm			
2150	117.3	1.935	6.14	5.96		5.91	-
2150	105.3	1.951	6.04	5.92		5.80	-
2250	101.3	1.959	5.29	5.33		5.06	5.01
2450	105.1	1.928	4.39	4.47		(4.08)[a]	-
2450	107.5	1.922	4.43	4.38		(4.08)[a]	-
				-log p(Pu), atm			
2150	117.3	1.935	6.20	6.73		6.34	-
2150	105.3	1.951	6.54	6.62		6.40	-
2250	101.3	1.959	6.12	6.04		5.84	5.87
2450	105.1	1.928	4.65	5.15		(4.81)[a]	-
2450	107.5	1.922	4.54	4.94		(4.75)[a]	-
				$-\log p\ \Sigma[U(g) + Pu(g)]$, atm			
				Sublimate	Wt Loss		
2150	117.3	1.935	5.87	5.89	5.71	5.77	-
2150	105.3	1.951	5.92	5.84	5.73	5.70	-
2250	101.3	1.959	5.23	5.24	5.17	4.97	4.95
2450	105.1	1.928	4.20	4.39	-	(4.01)[a]	-
2450	107.5	1.922	4.18	4.27	-	(4.00)[a]	-

[a] Extrapolated.