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WITH HYPOSTOICHIOMETRIC PLUTONIUM DIOXIDE
AT HIGH TEMPERATURES

by

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ABSTRACT

Vapor pressures and vapor compositions in equilibrium with a hypostoichiometric plutonium dioxide condensed phase have been calculated for the temperature range $1500 \leq T \leq 4000$ K. Thermodynamic functions for the condensed phase and for each of the gaseous species were combined with an oxygen-potential model which we extended into the liquid region to obtain the partial pressures of O_2 , O, Pu, PuO and PuO_2 . The calculated oxygen pressures increase very rapidly as stoichiometry is approached. At least part of this increase is a consequence of the exclusion of Pu^{6+} from the oxygen-potential model. No reliable method was found to estimate the importance of this ion whose existence has not been established in the oxide system and whose effects might be expected to increase greatly with temperature, similar to those of U^{6+} in the uranium/oxygen system. As a result of large oxygen potentials at high temperatures, extremely high total pressures that produced unreasonably high vapor densities were calculated. The highest temperature for which meaningful results could be calculated was therefore limited to 4000 K, and the range of oxygen-to-metal ratios was limited to 1.994 to 1.70. These calculations show that vapor in equilibrium with hypostoichiometric plutonium dioxide is poorly approximated as PuO_2 for most of the temperature and composition range of interest. In addition, the vapor is much more oxygen-rich than the condensed phase with which it is in equilibrium. The limitations of this approach and the implications of these calculations for the technologically important $(U,Pu)O_{2-x}$ system are also discussed.

1. INTRODUCTION

One of the most important thermophysical properties of reactor fuel in reactor safety analysis is vapor pressure, for which data are needed for temperatures above 3000 K. We have recently completed an analysis of the vapor pressure and vapor composition in equilibrium with the hypostoichiometric uranium dioxide condensed phase [1], and we present here a similar analysis for the plutonium/oxygen (Pu/O) system.

Defect models of various kinds have been proposed for plutonium dioxide. The characteristics of these models have been summarized by Rand and Potter [2].

The process we have followed is identical with the one we used previously for the uranium/oxygen (U/O) system [1] and is summarized by the procedure that is shown in Fig. 1. Thermodynamic functions for the gas-phase molecules were obtained previously [3] from experimental spectroscopic data and estimates of molecular parameters. The functions for the condensed phase have been calculated from an assessment of the available data including the heat capacity as a function of temperature [4]. The oxygen potential is found from extension into the liquid phase of a model that was derived for the solid phase. Thus, we have all the information needed to apply the procedure outlined in Fig. 1.

In this paper we describe: (1) the gas-phase thermodynamic functions; (2) the condensed-phase thermodynamic functions; (3) the oxygen potential (and the phase boundaries that are consistent with it); and (4) the resulting vapor pressure and composition as functions of temperature and of the composition of the condensed phase.

2. METHODS

2.1 General

The methods we have used to calculate the vapor pressures and vapor compositions at high temperatures are the same as those used previously [1] for

the U/O system. The total pressure, $p(\text{total})$, in equilibrium with a PuO_{2-x} condensed is

$$p(\text{total}) = p(\text{O}) + p(\text{O}_2) + p(\text{PuO}) + p(\text{PuO}_2) \quad (1)$$

where only the neutral species are considered. The oxygen-to-plutonium molar ratio in the gas phase, $R(\text{gas})$ is

$$R(\text{gas}) = \frac{p(\text{O}) + 2p(\text{O}_2) + p(\text{PuO}) + 2p(\text{PuO}_2)}{p(\text{Pu}) + p(\text{PuO}) + p(\text{PuO}_2)} \quad (2)$$

The set of partial pressures given by Eq. (1) must satisfy equilibria among themselves and with the condensed phase. Of the several possible choices of independent equilibria, the following set is a convenient one:

where c represents the condensed phase and g represents the gas phase.

If we know the oxygen pressure, $p(\text{O}_2)$, from the oxygen potential, the required partial pressures may be obtained from Eqs. (3)-(6), in sequence, using the following relationships:

$$\ln p(\text{O}) = 1/2 \ln p(\text{O}_2) - \Delta G_f^\circ(\text{O})/RT \quad (7)$$

$$\ln p(\text{PuO}_2) = \frac{x}{2} \ln p(\text{O}_2) + [\Delta G_f^\circ(\text{PuO}_{2-x}, \text{c}) - \Delta G_f^\circ(\text{PuO}_2, \text{g})]/RT \quad (8)$$

$$\ln p(\text{PuO}) = [\Delta G_f^\circ(\text{PuO}_2, \text{g}) - \Delta G_f^\circ(\text{Pu}, \text{g})]/RT - 1/2 \ln p(\text{O}_2) + \ln p(\text{PuO}_2) \quad (9)$$

$$\ln p(\text{Pu}) = [\Delta G_f^\circ(\text{PuO}_2, \text{g}) - \Delta G_f^\circ(\text{Pu}, \text{g})]/RT - \ln p(\text{O}_2) + \ln p(\text{PuO}_2) \quad (10)$$

2.2 Thermodynamic Functions of the Gases

To apply Eqs. (1-10) the free energies of formation, ΔG_f° , for all gaseous species as a function of temperature are required. Tabulated data were fit by a least-squares procedure to derive an analytical equation for ΔG_f° of each vapor species. For the plutonium oxide vapor species, the data calculated from spectroscopic data [3] were used; for O(g) and O₂(g), the JANAF data [5] were used; and for Pu(g), data from the compilation of Oetting et al. [6] were used. The coefficients of the equations for ΔG_f° of the gaseous species are included in Table 1.

2.3 Oxygen Potential for Solid PuO₂

Considerable attention has been devoted to the temperature and composition dependence of the oxygen potential, $\Delta \bar{G}^\circ (O)$, for the solids PuO_{2-x} and (U,Pu)O_{2-x} [2] and many models of the oxygen potential have been proposed [7-15]. We have chosen the model devised by Blackburn [11] for solid PuO_{2-x} for three reasons: (1) It fits the available experimental data reasonable well [11], (2) It has a small number of adjustable parameters for which a physical basis can be provided, and (3) The model is analogous to the one that has been successfully applied to the UO_{2-x} system [1]. This model for the solid phase assumes the following equilibrium between oxygen gas and the ions in the lattice:

From this equilibrium the oxygen pressure may be determined:

$$\ln p(\text{O}_2) = 4 \ln (\text{Pu}^{4+})/(\text{Pu}^{3+}) + 2 \ln (\text{O}^{2-}) + \ln K_s \quad (12)$$

where the parentheses indicate ionic concentration (in moles per mole of Pu) and K_s is the equilibrium constant for Eq. (11):

$$K_s = \frac{(Pu^{3+}) p(O_2)}{(Pu^{4+})^4 (O^{2-})^2} \quad (13)$$

Blackburn also included in his model an equilibrium between trivalent and divalent plutonium. Because our interest lies principally in the region for which $x < 0.1$, the divalent ion concentration is relatively unimportant [16].

In addition to Eq. (12), we have the following equations for conservation of plutonium and charge, respectively:

$$(Pu^{4+}) + (Pu^{3+}) = 1 \quad (14)$$

and

$$2(Pu^{4+}) + 1.5 (Pu^{3+}) = (O^{2-}) \quad (15)$$

Substitution of $(O^{2-}) = 2 - x$ into Eqs. (14) and (15) gives $(Pu^{4+}) = 1 - 2x$ and $(Pu^{3+}) = 2x$; thus, Eq. (12) becomes

$$\ln p(O_2) = 4 \ln [(1 - 2x)/2x] + 2 \ln (2 - x) + \ln K_s \quad (16)$$

To evaluate K_s , Balckburn assumed $\ln K_s = A_s + B_s/T$, where T is the absolute temperature, and A_s and B_s are constants characteristic of PuO_{2-x} (5) that are consistent with the data of Alexander [17], Atlas and Schlehman [7], Markin and Mever [18], Woodley [19], Javed [20], Tetenbaum [21], and Blackburn [22]. This evaluation gave $B_s = -101600$ and $A_s = 20.8$. We have compared the oxygen potentials calculated used Eq. (16) and these parameter values with more recent unpublished data of Tetenbaum [23] and have found good agreement.

The substitution of $(Pu^{3+}) = 2x$ into Eq. (16) creates a mathematical problem in the first term for the special case of $x = 0$ and a physical problem for all small values of x . We considered this problem in detail in the report ANL-CEN-RSD-82-1 [16]. Because of this problem at $x = 0$, we limit our discussion and numerical calculations to cases with $x > 0.005$.

In the oxygen-potential model that was used for the U/O system [1], two equilibria for the solid were considered. One of these equilibria is analogous to Eq. (11) and the other involved the U^{6+} ion. We are unaware of evidence for the existence of the Pu^{6+} ion in the oxide system. No PuO_3 molecule was identified in the matrix-isolatin studies [24] although, with similar experimental methods, the UO_3 molecule was easily observed [25]. No evidence for PuO_3 has been reported in mass spectrometric studies [26]. However, the existence of the Pu^{6+} ion has been established by the observation of the hexafluoride [27]. We have, therefore, not included any Pu^{6+} .

2.4 Oxygen Potential for Liquid PuO_2

To extend the oxygen-potential model from the solid phase to the liquid phase, we assume that the model for the solid defined by Eqs. (11-16) applies to the liquid with new values of the model parameters. Therefore, we must find a new equilibrium constant K_l that is analogous to K_s . We have considered several methods of evaluating the model parameters (the equation that gives K_l as a function of temperature) from the available data.

The model for the liquid phase may be obtained by analogy with the the solid phase. Equation (11) may be rewritten as

The equilibrium constant for this reaction is given by

$$-RT \ln K = \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (18)$$

An analogous equation may be written for the liquid counterpart of Eq. (17) so that an equation like Eq. (18) is valid for the liquid as well. The difference between ΔG° and Eq. (18) and ΔG° for its liquid analog becomes

$$\Delta(\Delta G^\circ) = 2 \Delta H_m^\circ (Pu_2O_3) - 4 \Delta H_m^\circ (PuO_2) - T [2 \Delta S_m^\circ (Pu_2O_3) - 4 \Delta S_m^\circ (PuO_2)] \quad (19)$$

where ΔH_m° and ΔS_m° are the enthalpy and entropy of fusion, respectively of the indicated compound.

If we assume $\ln K = A + B/T$ for the liquid as well as for the solid, then:

$$(A_l - A_s) + (B_l - B_s)/T = \Delta(\Delta G^\circ)/RT \quad (20)$$

If we assume the enthalpy and entropy of fusion are independent of temperature, we may compare Eq. (19) with Eq. (29) to obtain

$$\Delta A = A_l - A_s = [2 \Delta S_m^\circ (\text{Pu}_2\text{O}_3) - 4 \Delta S_m^\circ (\text{PuO}_2)]/R \quad (21)$$

and

$$\Delta B = B_l - B_s = -[2 \Delta H_m^\circ (\text{Pu}_2\text{O}_3) - 4 \Delta H_m^\circ (\text{PuO}_2)]/R \quad (22)$$

The enthalpies and entropies of fusion that are required for evaluation of Eqs. (21) and (22) may be estimated for PuO_2 and Pu_2O_3 in a manner analogous to that for UO_2 [1]. A reasonable estimate for the entropy of fusion was found [1] to be $1.4nR$ (n is the number of atoms per molecule, and R is the gas constant), that we obtain $\Delta A = -2.8$. The value of ΔB depends on the melting points.

2.5 The Phase Boundaries

Our interest in the phase diagram is solely to define the method by which the calculation of the partial pressures should be done. Because (1) there are only small effects on the total pressure and vapor composition as a result of small changes in the phase boundaries; and (2) the range of T and x values for which the method of calculation will be affected is small, there is little need to have an accurate phase diagram. It is more important for our purpose to use a phase diagram that is consistent with our method and our choice of parameter values.

The solidus, the liquidus, the oxygen-potential model for the solid Pu/O system, and the oxygen-potential model for the liquid Pu/O system each depend upon the temperature and the composition. Because the oxygen-potential model has a greater effect on the vapor pressure and composition at high temperature

than do the solidus and liquidus, we have fixed the functional forms and the parameter values for the oxygen-potential model. We choose the IAEA solidus [28] and determine the liquidus that is consistent with it and twith the two parts of the oxygen-potential model. Calculated liquidus, which is based on the liquid model parameters, is very close to the IAEA liquidus [28].

The phase diagram that we shall use to define the method of calculation is given in Fig. 2. The regions are defined by:

Region I: One-phase solid; $T < 2416$ K; $0.005 < x < 0.30$

Region II: One-phase solid; $2416 < T < 2701$; $0.005 < x < x_s$

Region III: Solid and liquid phases: $2416 < T < 2701$; $x_s < x < x_\ell$

Region IV: One liquid phase; $T < 2701$; $x_\ell < x < 0.30$

Region V: One liquid phase: $2701 < T < 5000$; $0.005 < x < 0.3$

The solidus, which is the one recommended by the IAEA, [27] may be represented by the following equation for $2416 < T < 2701$ K:

$$x_s = 9.577 - 6.333 \times 10^{-3} T + 1.032 \times 10^{-6} T^2 \quad (23)$$

The liquidus, which is consistent with Eq. (23) and the two parts of the oxygen-potential model, may be represented by the following equation for $2416 < T < 2701$ K:

$$x_\ell = 5.108 - 2.534 \times 10^{-3} T + 2.378 \times 10^{-7} T^2 \quad (24)$$

2.6 Thermodynamic Functions of the Condensed Phases

Tabulated thermodynamic functions for the condensed phases of plutonium dioxide and a detailed description of their calculation are given elsewhere. The ΔG_f° (PuO_2, C) is represented by the equation given in Table 1. The ΔG_f° values were calculated using standard thermodynamic relations and the data given below.

The phase-transition temperatures for Pu and PuO₂, which were used, are given in Table 2.

The heat capacity function for the solid phase is from Fink [4]. It assumes one solid phase for PuO₂. Fink points out that while (U,Pu)O₂, UO₂ and ThO₂ have solid-solid phase transitions, the available data for PuO₂ [4] makes it impossible to determine the existence of a phase transition for PuO₂. If additional high-temperature measurements indicate the presence of a solid-solid phase transition, the heat capacity of PuO₂ between the phase transition and 2701 K may be significantly higher.

The heat capacity for liquid PuO₂ has been estimated as 96 J mol⁻¹ K⁻¹. In this estimation, the details of which are given elsewhere [16], the liquid heat capacity is assumed to have no electronic contribution. If an electronic contribution is found by experiment to be present, the liquid heat capacity would be increased by about 40%.

The free energy of formation of the hypostoichiometric condensed phase $\Delta G_f^\circ(\text{PuO}_{2-x}, c)$, can be calculated at any temperature from the free energy of formation of PuO₂(c) and the oxygen potential using the following relationship:

$$\Delta G_f^\circ(\text{PuO}_{2-x}, c) = \Delta G_f^\circ(\text{PuO}_2, c) - \frac{RT}{2} \int_0^x \ln p(\text{O}_2) dx' \quad (25)$$

This relationship, which is applicable provided that no phase boundaries are crossed at T between $x = 0$ and $x = x'$, arises from the Gibbs-Duhem equation and has been successfully used for U/O system [1].

The evaluation of the integral in Eq. (25) differs from the corresponding integral for the U/O system because of the differences in the oxygen-potential models. In particular, the neglect of Pu⁶⁺, but not U⁶⁺, leads to the problem that $\ln p(\text{O}_2)$ for the Pu/O system becomes infinite as x goes to zero. However, the integral in Eq. (25) remains finite and has been evaluated [16].

2.7 Ions

The ionization potentials of each vapor species given in Table 3 are similar to their counterparts in the U/O system [1]. Ionization was shown to be of minor importance for the U/O system in the temperature and composition ranges of interest. Furthermore, the results obtained from the oxygen-potential model along indicate that the vapor composition for the Pu/O system will be as oxygen-rich or more oxygen-rich than that for the U/O system. A very oxygen-rich equilibrium vapor gives less ionization because of the relatively high ionization potentials of O and O₂. Thus we conclude that ionization may be neglected for the temperature and composition ranges of interest and have not included ionization effects in our calculations.

3. RESULTS

The partial pressures of O, O₂, Pu, PuO, and PuO₂ were calculated as functions of T ($1500 \leq T \leq 4000$ K) and x ($0.005 \leq x \leq 0.30$), with particular emphasis on $0.005 \leq x \leq 0.10$. Preliminary calculations to 5000 K yielded unreasonably high oxygen pressures and vapor densities such that an upper temperature limit of 4000 K was selected. Tables presenting selected results are given in ANL-CEN-RSD-82-1 [16].

The calculated composition of the vapor in equilibrium with a PuO_{1.96} condensed phase, which is a typical composition for a reactor fuel, is shown in Fig. 3. Below 2652 K, which is the temperature at which PuO begins to melt, the vapor is PuO₂ with varying amounts of PuO, O, and O₂. Above 2668 K, which is the liquidus temperature for PuO_{1.96}, the vapor is almost entirely O₂ with some O. None of the plutonium-containing species makes an appreciable contribution to the total pressure at high temperatures. Even the vapor in equilibrium with PuO_{1.90}, which is shown in the bottom part of Fig. 3, is largely O₂ and O at temperatures above 3000 K.

An alternative way to view the oxygen enrichment of the vapor relative to the condensed phase, is to calculate the oxygen-to-plutonium ratio of the gas, $R(\text{gas})$, with Eq. (2). The Pu/O ratio of the gas phase exceeds that of the condensed phase with which it is in equilibrium by such a larger amount that a plot of $R(\text{gas})$ vs. the condensed-phase O/Pu is of little value. Like the U/O system, this oxygen enrichment of the vapor relative to the condensed phase is increasing with temperature. One implication of these results is that the condensed-phase and vapor-phase compositions will depend upon the extent of vaporization of a sample with overall composition given by $\text{O/Pu} = 2 - x$.

The temperature dependences of the total pressures in equilibrium with the condensed-phase composition $\text{PuO}_{1.90}$, $\text{PuO}_{1.96}$, and $\text{PuO}_{1.994}$ are compared in Fig. 4. The differences shown in Fig. 4 are due to the differences in oxygen pressures for the different compositions.

4. DISCUSSION AND CONCLUSIONS

4.1 Comparison to the U/O System

In comparing the results of these calculations with those for the corresponding U/O system, the major difference is the very high oxygen pressures calculated for the plutonium oxides. Some of these data are compared in Table 4 for $T = 2100$ and 4000 K. The oxygen pressures in equilibrium with PuO_{2-x} at 4000 K are higher than those in equilibrium with UO_{2-x} by factors ranging from about 10^6 to 10^3 for oxygen-to-metal ratios ranging from 1.98 to 1.90 . Although these ratios are quite large, an examination of comparable data at 2100 K, where experimental oxygen potentials are available, shows ratios over the same composition range that vary by 10^{20} to 10^8 . Thus, the oxygen potentials for the two materials are actually getting closer as the temperature increases.

The high oxygen pressures for equilibrium with PuO_{2-x} at 4000 K relative to those at UO_{2-x} should not be at all surprising when compared with available experimental data.

Another significant comparison between the two systems concerns the partial pressures of the metal dioxide molecules. These pressures are relatively insensitive to the condensed-phase composition and are quite similar in the plutonia and urania systems. Calculated metal dioxide vapor pressures are compared in Table 5 for $O/M = 1.96$.

The sums of partial pressures of the metal-bearing species behave similarly. This result would not have been easily predicted because each of the partial pressures is sensitive to $p(\text{O}_2)$, which is shown by the equilibria given in Eqs. (3-6). Some comparisons of these pressures are shown in Table 6 again for the $O/M = 1.96$ case.

The conclusions based on the data in Tables 5 and 6 are reflections of the fact that the dioxide, in the range of temperature and compositions being considered, is an important metal-bearing species.

A consequence of the extreme sensitivity of oxygen pressure to stoichiometry for small values of x in PuO_{2-x} is the fact that the total pressures changes by a factor of about 10^3 in going from $\text{PuO}_{1.98}$ to $\text{PuO}_{1.90}$ at 4000 K. In contrast, the corresponding factor for the U/O system is approximately 2.

The observation that the total pressure of the Pu/O system is much more sensitive to the condensed-phase composition than is that of the U/O system was pointed out in Section 3.

It is important to consider the complex nature of the vapors in both oxide systems. Any analysis which considers only the dioxide partial pressures, or approximates the total pressures as a dioxide pressure, will be seriously in error.

4.2 Implications for Mixed Oxides

Because the oxygen potentials for the liquid plutonium oxide were as high, some preliminary calculations were performed for the mixed $(U,Pu)O_{2-x}$ system. Calculations were done by simultaneously solving the equations for the oxygen potentials of the Pu/O and U/O systems as described by Blackburn [11]. These results showed that even though the Pu/O system has an oxygen pressure larger than that for the comparable U/O system (same composition and temperature) by a factor of 10^4 or 10^5 , the mixed oxide containing 20% plutonium has oxygen pressures only slightly greater than those for urania. Moreover, the pressure differences between the urania and mixed-oxide systems decreased as the temperature increased.

It appears that the presence of U^{6+} , for which there is no counterpart in the Pu/O system, is responsible for preventing the oxygen pressures from increasing as rapidly in the mixed system as in the plutonia system. Although considerable additional effort is needed to calculate reliable total pressures, our preliminary results indicate that the oxygen partial pressures in equilibrium with the mixed oxide will not differ drastically from those in equilibrium with urania.

4.3 Uncertainties and Limitations

The limitation of our calculations to temperatures less than 4000 K is a consequence of excessive oxygen partial pressures, which are, in turn, the result of the oxygen-potential model or the model parameters that are used. Uncertainties in the gas-phase thermodynamic functions are not important, and the uncertainties in the condensed-phase thermodynamic functions are not limiting. These unrealistically high oxygen pressures may be partially attributable to the lack of experimental data on a Pu^{6+} state (or other higher

valence states). Furthermore, high-temperature experimental data are required to test the model employed here and, if necessary, modify it. If this problem with the oxygen-potential model is solved, then the limiting source of error would be the condensed-phase thermodynamic functions.

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Table 1. Coefficients of the Equations ΔG_f° (in $\text{kJ}\cdot\text{mol}^{-1}$) = $A + BT + CT^2 + DT^3 + E/T + F\cdot\ln(T)$. (T represents 298.15 K.)

Species	T-range, K	A	B	C	D	E	F
O (g)	T -1400	252.36	-6.2747×10^{-2}	-1.3294×10^{-6}	---	-527.69	---
	1400-6000	259.03	-6.7710×10^{-2}	-1.6525×10^{-8}	---	-3747.4	---
Pu (g)	1000-3605	260.58	-7.9957×10^{-2}	-2.4343×10^{-6}	---	12715	6.8126
	3605-6000	0.0	---	---	---	---	---
PuO (g)	1000-3605	-106.88	-6.4867×10^{-2}	3.4979×10^{-6}	---	---	---
	3605-6000	-452.62	3.0418×10^{-2}	3.6209×10^{-6}	---	---	---
PuO ₂ (g)	1000-3605	-481.09	2.1026×10^{-2}	2.3283×10^{-6}	---	---	---
	3605-6000	-783.92	8.9630×10^{-2}	7.6581×10^{-6}	-2.9487×10^{-10}	---	---
PuO ₂ (c)	913-2701	-1060.9	2.0521×10^{-1}	-6.0130×10^{-6}	---	---	---
	2701-3605	-918.62	1.3644×10^{-1}	---	---	---	---
	3605-6000	-1241.0	2.1943×10^{-1}	-2.0882×10^{-6}	-8.9622×10^{-11}	---	---

Table 2. Important Transition Temperatures for
the Plutonium Dioxide Condensed Phase

T, K	Phase Transition	Reference
395	Pu(α)--Pu(β)	Oetting <u>et al.</u> [6]
480	Pu(β)--Pu(γ)	Oetting <u>et al.</u> [6]
588	Pu(γ)--Pu(σ)	Oetting <u>et al.</u> [6]
730	Pu(σ)--Pu(σ')	Oetting <u>et al.</u> [6]
752	Pu(σ')--Pu(ϵ)	Oetting <u>et al.</u> [6]
913	Pu(ϵ)--Pu(ℓ)	Oetting <u>et al.</u> [6]
2701	PuO ₂ (s)--PuO ₂ (ℓ)	Aitkin and Evans [25]
3605	Pu(ℓ)--Pu(g)	Calculated fromn data in [6]

Table 3. Ionization Potentials (IP) of the Molecules and Atoms in Equilibrium with a Plutonium Dioxide Condensed Phase
(1 eV·molecule⁻¹ = 23.06 kcal·mol⁻¹ = 96.48 kJ·mol⁻¹)

Species	IP, eV	Reference
Pu	5.83	Report NSRDS-NBS 34 [30]
PuO	6.2 ± 0.5	Blackburn et al. [31]
PuO	9.4 ± 0.5	Blackburn et al. [31]
O	13.61	Moore [31]
O ₂	12.07	Huber and Herzberg [32]

Table 4. Comparison of the Calculated Partial Presures (in MPa)
of O_2 at 2100 K and 4000 K for the U/O and Pu/O Systems

T, K	System	x = 0.02	x = 0.04	x = 0.06	x = 0.08	x = 0.10
2100	UO_{2-x}	3.4×10^{-18}	8.0×10^{-19}	3.3×10^{-19}	1.8×10^{-19}	1.3×10^{-10}
	PuO_{2-x}	1.2×10^{-8}	7.2×10^{-9}	1.2×10^{-9}	3.0×10^{-10}	9.8×10^{-11}
4000	UO_{2-x}	3.5×10^{-3}	1.9×10^{-3}	1.1×10^{-3}	7.1×10^{-4}	4.7×10^{-4}
	PuO_{2-x}	1.8×10^3	92	15	3.9	1.3

Table 5. Comparison of the Partial Presures (in MPa) of the Dioxides in Equilibrium with the Hypostoichiometric (L/M = 1.96) Dioxides of Plutonium and Uranium

T, K	$p(\text{PuO}_2)$	$p(\text{UO}_2)$
2000	3.8×10^{-8}	1.2×10^{-8}
3000	1.0×10^{-3}	1.0×10^{-3}
4000	6.2×10^{-2}	7.8×10^{-2}

Table 6. Comparison of the Sums of Partial Presures (MPa)
of Metal-Species for the Pu/O and U/O Systems

T,K	PuO _{1.96}	UO _{1.96}
2000	3.9×10^{-8}	3.4×10^{-8}
3000	1.0×10^{-3}	1.1×10^{-3}
4000	6.2×10^{-2}	1.7×10^{-1}

LIST OF FIGURES

<u>No.</u>	<u>Title</u>
1	Procedure for calculation of vapor pressures from spectroscopic data.
2	Phase diagram of the plutonium/oxygen system.
3	Vapor compositions in equilibrium with a $\text{PuO}_{1.96}$ condensed phase (top) and a $\text{PuO}_{1.90}$ condensed phase (bottom).
4	Log of total pressure (MPa) in equilibrium with $\text{PuO}_{1.994}$, PuO and $\text{PuO}_{1.90}$.

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Figure 1 Scheme for calculating vapor pressures and compositions from spectroscopic data.

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Fig. 4