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A THERMODYNAMIC DATA PROGRAM INVOLVING
PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 16

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F. A. AITKEN
M. G. ADAMSON
S. K. EVANS
T. E. LUDLOW

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**A THERMODYNAMIC DATA PROGRAM
INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES**

Quarterly Report No. 16
May 1, 1971 – July 31, 1971

E. A. Aitken S. K. Evans
M. G. Adamson T. E. Ludlow

Approved:

H. W. Alter, Manager
Nuclear Technology & Applications Operation

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ABSTRACT

Work progress is reported in the continuing scope of work related to vaporization of urania in urania-plutonia solid solutions, oxygen activities at high temperatures, oxygen redistribution in a temperature gradient, Pu/U segregation and sodium-fuel interactions.

1. INTRODUCTION

This quarterly report is the sixteenth in a series which describes experiments directed toward understanding plutonia segregation in urania-plutonia solid solutions and in fast reactor environments through a knowledge of its thermodynamic behavior. In the fifteenth quarterly (GEAP-12210) the progress of several experiments which have a bearing on plutonia segregation was described. In addition the thermodynamic aspects of the sodium-fuel reaction product were studied. Continued progress in these areas is described in this report.

2. THERMAL GRADIENT EXPERIMENTS WITH EXCESS SODIUM

The second series of thermal gradient experiments planned to investigate the reaction tendencies of sodium with mixed oxide fuel was in an advanced stage of fabrication at the end of the report period. A 1000-hour anneal in a temperature gradient with sodium reservoirs at 500, 700, and 900°C is scheduled to begin early in the next quarter.

Mixed oxide pellets of nominal 1.93 stoichiometry required for this second series of experiments were fabricated using the concepts discussed by Lindemer and Bradley.¹ The required pellets were prepared using normal cold press and sinter techniques. The stoichiometry was adjusted to the lowest possible value (approximately 1.96) in dried N₂-6% H₂. The adjusted pellets were then placed in a molybdenum furnace boat divided into six sections with 3 fuel pellet sections alternating with 3 sections containing chunks of graphite. The boat thus prepared was then sintered for 2-1/2 hours in He-8% H₂ at approximately 1550°C. The resulting oxygen to-metal ratio was 1.938 ± 0.006 .

3. OXYGEN MIGRATION IN (U, Pu)O₂ SYSTEMS

Planning is under way to fabricate a fixture for performing experiments in a radial temperature gradient. A preliminary design has been established and actual fabrication of the fixture will begin during the next quarter.

4. A THEORETICAL STUDY OF PLUTONIUM-URANIUM SEGREGATION IN MIXED OXIDE FUELS

The investigation of uranium and plutonium redistribution in nuclear fuels is of particular interest because of its influence on fuel center temperatures, axial power distributions and the Doppler coefficient of reactivity in fast reactors. The first two factors are likely to result in a penalty in the maximum allowable power rating of a typical LMFBR oxide fuel. In the past few years plutonium enrichment towards the fuel center has frequently been observed as a result of detailed examinations of irradiated fuel elements and, more recently, evidence for axial relocation has been obtained. As a starting point in this study we chose to consider radial U-Pu segregation (redistribution) in mixed (U, Pu) oxide fuels from a theoretical standpoint, with constant reference to actual measurements of steady state U/Pu distributions wherever these data were available. Radial effects were treated before axial effects because thus far they have been measured more frequently and it is presently felt that radial redistribution is a shorter term phenomenon

than the less localized axial relocation. Ultimately it is intended to explain both variants with a common model. Emphasis has been given to fuels which do not undergo center melting at any stage during irradiation in a fast neutron flux because this not only simplifies the theoretical approach but it is not expected that a LMFBR oxide fuel ever should operate in the molten state.

For the theoretical treatment the assumption has been made that the prevailing mechanism of U-Pu segregation in noncenter-melted oxide fuel with a high radial temperature gradient is preferential evaporation/condensation and that this is restricted to fuel at temperatures in excess of approximately 1900°K. An attempt will be made to justify this assumption by presenting arguments for the elimination of alternative mechanisms. What follows is essentially a chronological description of our attempts to date to formulate a working model along the lines mentioned above. This is prefaced by a general review of the principal mechanisms that have already been proposed to account for the radial U-Pu segregation observed in irradiated mixed oxide fuels. In this review the alternative solid state thermal diffusion mechanism (so-called Soret Effect) is critically examined and original ideas about the preferential evaporation/condensation mechanism are also outlined. Utilization of vapor pressures data in the thermodynamic model necessitated a critical assessment of measured and calculated partial pressures over the U-Pu-O system; this takes the form of a digression in which comparisons are made between measured vapor pressures from different investigators and also between the measured pressures and calculated pressures. As a result of this assessment several discrepancies in both the measured partial pressure data and the high temperature thermodynamic data for the various metal-bearing vapor species have come to light.

To illustrate the nature of the radial U-Pu segregation we are attempting to model, two "idealized" steady-state radial Pu/U + Pu profiles have been drawn in Figure 1. These profiles represent the general behavior observed with center-melted (dashed line) and noncenter-melted (solid line) fuels. Figures 2 and 3 show some actual measured radial Pu/U + Pu profiles in center-melted (GE E1J series; O:M = 1.94, 1.97, 2.00) and noncenter-melted (GE F2C) mixed oxide fuels, respectively. These results have been reported in detail in the GE Sodium-Cooled Fast Ceramic Reactor Development Program Quarterly Reports, GEAP-10028-36 and -37.

Review of Proposed Mechanisms. The following table summarizes the principal mechanism (and variants) that have been proposed to account for radial U/Pu segregation effects in mixed oxide fuels:

PRINCIPAL MECHANISMS FOR U/Pu SEGREGATION

Type	Phase(s)	Details, Variations, etc.
1. (a) Thermal Diffusion (Soret Effect)	Solid (1)	(i) Volume Diffusion (Bulk Effect) (ii) Surface Diffusion (in Migrating Bubbles) (iii) Electrorefining (Thermal EMFs)
(b) Micro Segregation	Solid (1) ↓ Solid (2)	{ Simultaneous Pu Enrichment and O:M Reduction in Hot Fuel Center Assists Precipitation of Pu-rich Phase on Cooling
2. Differential Evaporation-Condensation	Solid (1) ⇕ Vapor (1)	(i) In Migrating Pores and Bubbles (ii) Distillation Along Interconnected Pores and Cracks
3. Noncongruent Melting-Freezing (Zone Refining)	Solid (1) ⇕ Liquid (1)	{ Prediction of Pu Enrichment at Fuel Center assumes "Normal Freezing" after Extended Operation with a Molten Center (Partitioning $\propto$ O/Pu)

Mechanism 1(a) is the solid state Soret effect in which uranium and plutonium cations are believed to undergo thermal diffusion when their mobilities become sufficiently high ($T > 2200^{\circ}\text{C}$).² Mechanism 1(b) accounts for the fine scale U-Pu segregation which has been observed in the central regions of some irradiated hypostoichiometric mixed oxide fuels (center-melted and noncenter-melted).³ This purely local effect is believed to be a *consequence* of bulk radial transport of both the metallic and non-metallic fuel components. Mechanism 2 involves preferential evaporation and vapor transport of metal-bearing species either along cracks or porosity channels within the fuel or inside closed pores and bubbles migrating up the temperature gradient. Mechanism 3 describes the zone refining that occurs when the central regions of the fuel undergo a cycle of melting and freezing. Although we have chosen to confine our attention to mechanism 2, it is appropriate to first briefly review some aspects of the liquid-solid zone refining mechanism (3) and then critically examine mechanism 1(a).

Mechanism 3 (Zone Refining). Measurements of the solidus and liquidus temperatures in the U-Pu-O system⁴ indicate that center melting in a $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{2-x}$ fuel will result in Pu enrichment of the liquid phase at all compositions in the range $0 < x \leq 0.08$. It is evident from the shape of the phase diagrams shown in Figure 4 that the degree of enrichment will increase as O:M decreases. Since oxygen redistribution in initially hypostoichiometric fuels tends to reduce center (O:M) even further, the final Pu enrichment should be greater than indicated. It will be recalled from Figure 2 that the greatest Pu enrichment was measured in the fuel with lowest O:M (1.94). Consideration of the normal (equilibrium) freezing behavior of mixed oxide at the center of a fuel pin, based on the known phase equilibria, confirms that the Pu concentration in the resulting *solid* will increase to a maximum at the center (as observed). This mechanism will certainly be dominant in fuels which operate almost continuously with molten centers and probably also will exert a strong influence in fuels which undergo short excursions above the melting point (especially near end-of-life). The unusual shape of the liquidus curves for hypostoichiometric mixed oxides deserves some comment. A possible explanation for the double inflection on the measured liquidus curves for O:Pu ≤ 1.90 is that there may be more than one condensed phase over a certain range of Pu concentration (*i.e.*, the liquidus is intersected by a 1-to 2-solid phase boundary).

Mechanism 1a (Soret Effect). Schumacher and co-workers observed cation segregation in out-of-pile thermal diffusion experiment with $\text{UO}_2\text{-CeO}_2$ ⁵ and $\text{UO}_2\text{-PuO}_2$ ^{6,7} mixtures and they attempted to interpret the nonsteady-state results in terms of a solid state Soret effect using Wirtz's kinetic interpretation² for the heat of transport, Q^* . A curve fitting procedure was used to derive values of Q^* that provided the best agreement with the experimental data; for $\text{UO}_2\text{-PuO}_2$ mixtures these values ranged from 35 to 58 kcal/mole. In this treatment the flux of plutonium in the applied temperature gradient was taken to be

$$J_{\text{Pu}} = -D \left[\left(1 + \frac{C_{\text{Pu}}}{C_{\text{U}}} \right) \nabla C_{\text{Pu}} - \frac{\alpha}{T} C_{\text{Pu}} \nabla T \right]$$

where $D = D_0 e^{-E_{\text{act}}/RT}$ (chemical diffusion of Pu); $\alpha = \text{thermal diffusion factor} (= T \times "S" = Q^*/RT)$ and $C = \text{concentration}$, and the mass balance was described by the "equation of continuity" $\nabla \cdot J_{\text{Pu}} + \partial C_{\text{Pu}}/\partial t = 0$. It should be mentioned that the initially stoichiometric mixed oxide specimens used in these experiments were reduced to significantly hypostoichiometric compositions during the high temperature anneals (by tungsten) and there was clear evidence of evaporative loss of material from the hottest regions. Chasanov⁸ has performed similar experiments with both $\text{UO}_2\text{-CeO}_2$ and $\text{UO}_2\text{-PuO}_2$ and concluded that the small effects observed are due primarily to vaporization processes. In view of this disagreement it is appropriate to examine the so-called Soret effect at somewhat greater depth.

Generally, when thermomigration in a two component system is based on exchange of two chemical species by vacancy movement, we can write:⁹

$$Q_{12}^* = Q_2^* - \frac{D_1}{D_2} Q_1^*$$

where 1 and 2 denote the solvent and solute, respectively, and Q_{12}^* is the net heat of transport for an exchange process such as that between Pu and U ions. We can see that Q_{12}^* should become vanishingly small when chemical differences vanish. In fact, in dilute solutions of PuO_2 in UO_2 (i.e., a *pseudo* binary system) D_U and D_{Pu} are known to be nearly identical in the temperature range 2000 to 2400°C.^{10,11} A proper treatment of solid state thermal diffusion requires inclusion of irreversible thermodynamic quantities which cannot be readily predicted from simple kinetic parameters such as activation energies.¹² Thus the differences in Q^* between pure PuO_2 and pure UO_2 are more difficult to assess than diffusion coefficients. Since both of the species under consideration have similar ionic radii and masses these properties should not contribute to differences in Q^* — however, if the system becomes significantly nonstoichiometric, valence differences could produce a substantial effect as a result of specific interactions between oxygen sublattice defects and the cation sublattice. These interactions, which would produce a nonideal solid solution and a Soret effect with Pu migration up the temperature gradient, are most likely to occur in markedly hypostoichiometric mixed oxide. Preferential migration of plutonium up the temperature gradient could also result from any electrical potential gradients developed in hypostoichiometric mixed oxide due to differences in the fluxes of oxygen atoms and the associated (charged) vacancies; this would only occur at very high temperatures where electrical conduction is principally ionic. Although a Soret effect may operate in highly hypostoichiometric mixed oxide at very high temperatures it would be practically impossible to observe this using any conceivable experimental arrangement because at the temperatures needed to mobilize the U and Pu ions ($\geq 2500^\circ\text{K}$) the vapor pressures of metal-bearing species above the specimen are always sufficiently high for (noncongruent) vapor transport to occur (see Figure 5). (Of course, if a 100% dense specimen could be made this problem possibly could be circumvented). Since most fuel compositions of practical interest approach stoichiometry towards end-of-life it seems unlikely that the Soret effect, if indeed such an effect exists in $\text{U}_{1-y}\text{Pu}_y\text{O}_{2+x}$ plays a significant role in the U/Pu segregation observed in irradiated FCR fuels.

Mechanism 2 (Evaporation-Condensation). The idea that independent transport of the several gaseous metal-bearing species which volatilize from $\text{U}_{1-y}\text{Pu}_y\text{O}_{2+x}$ in an operating fuel will take place down the appreciable radial pressure gradients that are developed and ultimately lead to U-Pu segregation in the solid phase was first suggested by Markin and Rand.¹³ In a first attempt to model real fuel behavior using this idea of noncongruent evaporation/condensation it was assumed that the gas phase would be in thermodynamic equilibrium with the solid at each point along the temperature (and pressure) gradient in *both* variants of the mechanism, i.e., free flow through open pores and pore/bubble migration.¹⁴ The condition for steady-state in the system was chosen to be $\Delta(\text{Pu}/\text{U}) = 0$ (i.e., a balance in the flows of uranium- and plutonium-bearing gases down the temperature gradient) and the corresponding Pu/U ratios in the solid at various temperatures were calculated using Raoult's law. With this treatment both variants of the vapor transport mechanism should yield the same solid composition gradient; however in practice, pore/bubble migration is restricted to the columnar grain growth region of the fuel whereas the open pore transport mechanism can also operate in somewhat lower temperature regions of the fuel. Application of this model requires knowledge of the various vapor pressures as functions of temperature and fuel composition and, based on a method suggested by Markin and Rand,¹³ a computer code (VAPRES) was written to provide this information. Initial calculations¹⁴ were performed with erroneous thermodynamic data and consequently misleading results were obtained.

Vapor pressures were recalculated using an ideal solid solution model for $\text{U}_{1-y}\text{Pu}_y\text{O}_{2+x}$ i.e., $\text{UO}_{2+x}\text{-PuO}_2$ and $\text{UO}_2\text{-PuO}_{2-x}$, employing the best (assessed) thermodynamic data available for this system.¹² Individual vapor pressures thus calculated were in excellent agreement with Markin and Rand's original calculations. Figure 5 illustrates the O/M variations of the individual vapor pressures over $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{2+x}$ at 2500°K and also show the dependence of the total Pu/total U partial pressure ratio in the vapor as a function of O/M (curves A and B). (Curve B was calculated using an alternative value for one of the thermodynamic parameters¹⁶). It may be noted that at this particular temperature the Pu/U ratio in the gas only equals that in the solid (0.25) when $(\text{O}/\text{M})_g \cong 1.96$.

Before latest results on the development of the vapor transport model are described the validity of the calculated vapor pressures will be examined in the light of recent effusion cell/mass spectrometric measurements on the $\text{U}_{1-y}\text{Pu}_y\text{O}_{2+x}$ systems at high temperatures.^{15,17}

An Assessment of Measured Partial Pressures and Thermodynamic Data for the Metal-Bearing Vapor Species over $\text{U}_{1-y}\text{Pu}_y\text{O}_{2+x}$. Ohse and Olsen,¹⁶ and Battles, *et al.*,¹⁵ have made individual determinations of the vapor pressures of the various metal-bearing species in the hypostoichiometric region using the Knudsen cell/mass spectrometric

technique. Dean, *et al.*,¹⁷ made *total* vapor pressure measurements only for both hypo- and hyperstoichiometric material ($\sim 50\%$ Pu) using a Knudsen cell method. Comparisons of the measured vapor pressures at various selected compositions and temperatures with vapor pressures calculated (Rand-Markin model) using VAPRES for the same conditions are made in Tables 1, 2 and 3. In both the studies of Ohse and Olsen, and Battles, *et al.*, there is generally

TABLE 1. Measured and Calculated Vapor Pressures Over $U_{0.80}Pu_{0.20}O_{2-x}$ at 2240°K
(experimental data of Battles, *et al.*,¹⁵)

(The figures in parentheses are the calculated values)

Pressure (log ₁₀ atm) of	O/M		
	1.96	1.98	2.00
UO =	-7.65 (-7.50)	-8.03 (-7.93)	-8.8 (-8.69)
UO ₂ =	-5.15 (-5.36)	-4.8 (-5.36)	-4.77 (-5.36)
UO ₃ =	-6.2 (-6.06)	-5.4 (-5.63)	-4.33 (-4.86)
PuO =	-6.0 (-5.98)	-6.25 (-6.20)	-6.65 (-6.67)
PuO ₂ =	-6.6 (-6.66)	-6.25 (-6.45)	-5.90 (-6.15)
(ΣO) _A =	-8.26 (-7.75)	-7.72 (-7.32)	-7.12 (-6.55)
(ΣO) _B =	-6.87	-6.32	-5.73
(Pu/U) _g =	0.17 (0.244)	0.056 (0.146)	0.023 (0.051)

Note: The "measured" values (ΣO)_A and (ΣO)_B were actually computed by Battles, *et al.* from measurements of the UO₂/UO₃ and PuO/PuO₂ pressures, respectively, via the gas phase equilibria: $UO_2 + 1/2 O_2 = UO_3$ and $PuO + 1/2 O_2 = PuO_2$. Both "measured" and "calculated" oxygen pressures are for *total* oxygen, *i.e.*, $p_O + p_{O_2}$.

TABLE 2. Measured and Calculated Vapor Pressures Over $U_{0.85}Pu_{0.15}O_{2-x}$ at 2108°K
(experimental data of Ohse and Olsen¹⁶)

(The figures in parentheses are the calculated values)

Pressure (log ₁₀ atm) of	O/M	
	1.969	1.992
UO ₂ =	-6.06 (-6.18)	-5.98 (-6.18)
UO ₃ =	-6.80 (-6.83)	-6.04 (-6.11)
PuO =	-6.88 (-6.87)	-7.70 (-7.26)
PuO ₂ =	-7.25 (-7.60)	-7.12 (-7.26)
O =	-8.92 (-8.70)	-8.00 (-7.95)
(Pu/U) _g =	0.182 (0.207)	0.0465 (0.076)

Note: The "measured" value of p_O was actually calculated using experimental data for p_{PuO} , p_{PuO_2} , p_{UO_2} and p_{UO_3} , and using an adjusted value of $\Delta G_f (PuO_2)_g$.

TABLE 3. Measured and Calculated (Total) Vapor Pressures Over $U_{0.50}Pu_{0.50}O_{2\pm x}$ at 1814°K (experimental data of Dean, *et al.*¹⁷)

Pressure (log ₁₀ atm)		O/M		
		1.95	2.00	2.05
ΣU	=	-8.25[UO ₂] (-8.415)	-7.8[UO ₃] (-7.24)	-6.5[UO ₃] (-4.20)
ΣPu	=	-8.5[PuO/PuO ₂] (-8.625)	-8.55[PuO ₂] (-8.85)	-8.35[PuO ₂] (-8.88)

Note: The "measured" values are actually *total* vapor pressures, the species shown inside the square brackets following this figure is the major vapor species. The "calculated" values (in parentheses) are calculated *total* pressures.

fair to good agreement between the measured and calculated pressure of individual metal-bearing vapor species for hypostoichiometric compositions. However, it is interesting that the rather small individual discrepancies compound to produce discrepancies as high as 100% between the experimental and calculated values of $(\Sigma p_{Pu}/\Sigma p_U)_{gas}$. There are rather serious inconsistencies in the data of Blackburn, *et al.*, as evidenced by the disagreement between their calculated oxygen pressures for given sets of conditions (see Table 1). Other possible sources of error are the thermodynamic parameters or the model for UO_2 - PuO_2 solid solutions used in their calculations; the former is considered rather unlikely since it would require errors as high as 12-13 kcalories in the free energies of formation of $(PuO)_g$ and $(PuO_2)_{gas}$, or $(UO_2)_{gas}$ and $(UO_3)_{gas}$. Ohse and Olsen only obtained consistency between their PuO/PuO_2 and UO_2/UO_3 pressure data by using a modified value for $\Delta G_f(PuO_2)_g$ in their calculations. The foregoing two sets of workers disagree by ca. 0.04 in the O:M ratio at which $(Pu/U)_g \equiv (Pu/U)_s$ at given temperature (*i.e.*, the quasi-congruently evaporating composition). This is unlikely to be due to the slightly different Pu contents used in these two studies. Discrepancies between the measured and calculated UO_3 pressures are evident in all three studies at the stoichiometric composition, and Dean, *et al.*, find very serious discrepancies for hyperstoichiometric material (see Table 3) which they attributed to the use of incorrect (extrapolated) $\Delta \bar{G}_{O_2}$ data for $U_{1-y}Pu_yO_{2+x}$ at high temperatures. There are known to be pitfalls in using linearly-extrapolated $\Delta \bar{G}_{O_2}$ versus T data for hyperstoichiometric material at temperatures above ca. 1200°C¹⁸ but the observed discrepancies are in the opposite direction to that required by Dean, *et al.*

Although the ideal solid-solution calculated model for single phase $U_{1-y}Pu_yO_{2\pm x}$ is probably over-simplified, and there probably are shortcomings in some of the input thermodynamic data,[†] it is equally evident that there are many unresolved inconsistencies in the measured vapor pressure data. Apart from the numerous instrumental and calibration problems associated with the Knudsen cell/mass spectrometric technique there is also the more general criticism that it is necessarily *dynamic* and as such may prevent the establishment of true equilibrium vapor pressures over a complex noncongruently evaporating system, such as $U_{1-y}Pu_yO_{2\pm x}$. It is quite possible that any one or some combination of these factors may account for the observed experimental inconsistencies. Results of recent transpiration experiments conducted on UO_{2+x} and $U_{1-y}Pu_yO_{2\pm x}$ under conditions of constant oxygen potential suggest that the mixed oxide is in fact behaving ideally in the temperature range of 1300 to 1500°C.¹⁹ It is partially for this reason, and partially because of reservations concerning the Knudsen cell/mass spectrometric technique, that we have adopted the calculational approach to obtaining vapor pressures. It is acknowledged nevertheless that this method will probably yield erroneous results at temperatures above 2500°K (and also at highly nonstoichiometric compositions) and that relatively small uncertainties in the free energy values used in the calculations can produce rather large fluctuations in the calculated value of $(\Sigma Pu/\Sigma U)_{gas}$.

[†]For example, free energies of formation are only reliable up to ca. 2500°K (max.) and $\Delta \bar{G}_{O_2}$ data to ca. 1500°K (O:M > 2) or ca. 1750°K (O:M < 2). Battles has obtained an expression for $\Delta G_f(PuO_2)_g$, based on recent work on the PuO systems,²² which differs appreciably from both Ohse and Olsen's¹⁵ and Ackerman, Faircloth and Rand's²³ value.

Development of the Vapor Transport Model. Our first conception of this model¹³ was outlined earlier. For nonstoichiometric oxide fuels an additional assumption was required, namely that the radial O:M gradient would be defined by a constant H_2/H_2O ratio corresponding to the over-all O/M of the fuel (and the radial temperature gradient). This was equivalent to settling the heat of transport of oxygen equal to approximately -50 kcal/mole. On the basis of results from some out-of-pile thermal diffusion experiments performed on $U_{1-y}Pu_yO_{2-x}$ ¹⁹ this Q^* value was modified to -10 kcal/mole. The resulting radial O/M gradients for a series of fuel compositions in a typical low (power-rating) radial temperature gradient are shown in Figure 6. Plots of the gas phase composition (expressed as $(Pu/U)_g$) versus temperature for several of these fuel compositions are shown in Figure 7; these refer to "zero time" for U-Pu redistribution and illustrate the relative vapor and solid compositions as a function of radius. The solid composition profile correspondin to a constant Pu/U ratio in the gas phase ($\equiv 0.25$) for a fuel with over-all O/M = 2.005 is drawn as a dashed line. The fact that this does not bear any resemblance to measured Pu/U + Pu profiles in irradiated fuels indicated that the original assumption that $(Pu/U)_{gas} = \text{constant}$ describes the steady-state condition is probably in error. Several alternative (constant) values of $(Pu/U)_g$ were tried but no improvement in the matching between the predicted and measured Pu profiles was obtained. Figure 8, in which the measured Pu/U + Pu profile on a noncenter-melted transverse section of GE fuel pin F3B has been drawn together with the corresponding (calculated) oxygen (O/M) gradient and gas phase composition profile, confirms the inadequacy of the relation $\Delta(Pu/U)_g = 0$ for describing steady-state conditions. It is quite obvious that, at steady state, $(Pu/U)_g$ is not constant across the high-temperature portion of the fuel.

Before constant $(Pu/U)_g$ was completely eliminated as a viable condition for steady-state another factor was considered. Evidence has recently been obtained that the heat of transport of oxygen in hypostoichiometric mixed oxide approaches zero at temperatures in excess of $1600^\circ C$ ²⁰ — in other words, the O/M gradient in the columnar grain region of an irradiated nonstoichiometric mixed oxide fuel may be very small or nonexistent. Figure 9 shows some calculated $(Pu/U)_g$ profiles for $U_{0.80}Pu_{0.20}O_{1.978}$ fuel with various assumed oxygen gradients (*i.e.*, Q^* values from 0 to -50 kcal/mole). The curves for $Q^* = 0$ (A refers to this condition at temperatures above $2000^\circ K$, B assumes $Q^* = 0$ over-all) predict a steadily decreasing Pu enrichment from the fuel center out to the $2000^\circ K$ isotherm — a trend which is in general agreement with observation. Also shown on this diagram is a $(Pu/U)_g$ profile calculated (with $Q^* = -10$ kcal/mole) using the alternative value for $\Delta G_f(PuO_2)_g$ recommended by Ohse and Olsen.¹⁵ This profile predicts Pu depletion at the fuel center rather than Pu enrichment and illustrates the sensitivity of $(Pu/U)_{calculated}$ to the value of a particular thermodynamic parameter.

Consideration was given to an alternative description of "steady-state" for U and Pu. Figure 10 shows the large (total) pressure gradients of metal-bearing species generated across two typical fuel compositions (O:M = 1.968 and 2.005); if paths for vapor flow are available within the fuel such gradients should result in significant distillation of U and Pu down the temperature gradient. Vapor pressure calculations (VAPRES) indicate that the large pressure gradients will be maintained throughout the life of the fuel thus resulting in a permanent net "Downhill" flow of U and Pu. Under these nonequilibrium conditions a reasonable condition for the establishment of a steady U:Pu gradient in the solid might be that the solid attempts to reach a quasi-congruently evaporating composition at each point across the fuel. Thus, assuming a constant O:Pu gradient exists across the fuel during its operation (*i.e.*, $Q^* = \text{const.}$, or is a known function of T and, hence, radius), the problem would reduce to calculating the Pu:U ratio in the solid which, at given values of O:Pu and temperature, corresponds to congruent evaporation (*i.e.*, $(Pu/U)_s \equiv (Pu/U)_g$). In practice, for a given temperature, there is only one value of O:Pu at which this can occur (regardless of $(Pu/U)_s$); at all other O:Pu ratios evaporation would result in continuous enrichment or depletion of plutonium. Clearly quasi-congruent evaporation in a fixed O:Pu gradient cannot be a general condition for steady-state in a mixed oxide fuel system. In the situation just described it is probable that the oxygen gradient will no longer be described by a single Q^* value since the metal-bearing vapor species themselves will constitute a (temperature dependent) oxygen transfer path. It is also probable that U:Pu composition gradients built up in the solid as a result of vapor transport will induce counter-flows of these species back through the solid (volume diffusion down concentration gradients). Under such circumstances it is hardly surprising that a purely equilibrium thermodynamic approach cannot provide a quantitative description of U:Pu segregation. We are thus forced to conclude that a model accommodating the dynamic aspects of mass transport is necessary to accomplish this.

¹³ *Proposed "Dynamic" Vapor Transport Model.* Such a model is currently being developed to describe relocation of plutonium in irradiated mixed oxide fuels. The simplest version of this model is illustrated schematically in Figure 11. Metal-bearing gas phase species are assumed to flow continuously down the temperature/pressure gradient through free space in the fuel and the composition gradients thus created in the solid induce uranium and plutonium to diffuse down the resulting concentration gradients. In this model there is always a net flux of mass down the applied temperature gradient (via the vapor phase) and the condition for steady-state is defined by $\delta(Pu/U)_s/\delta t \rightarrow 0$ at a particular position, z , along the fuel section. The fuel sample is divided into a number of segments each of which is assigned fixed values of temperature, O:Pu, initial mass of fuel, and free space. The VAPRES program is used to calculate the gas compositions and individual vapor pressures above the fuel in each segment at fuel temperatures above 1800°K. In a given time interval δt quantities of vapor are transferred between segments S_i and S_{i+1} , all the way down the temperature gradient, and a complete cycle of calculations is made on a computer to determine the resulting changes in U and Pu concentrations in the solid. The quantities of material transferred between each segment, $\delta m_{i-1,i}$, in the given time interval are proportional to the partial pressure gradient $\partial P_{i-1,i}/\partial z$. A second cycle of calculations for the same time interval determines the effect of volume back-diffusion in the solid. This double cycle of calculations is reiterated until a steady Pu:U gradient is obtained in the solid. Concurrent with this approach an attempt is being made to formulate an exact analytical solution for the flux equations which arise in such a model. This requires a knowledge of (a) the rates of evaporation and condensation of the various species vaporized from $U_{1-y}Pu_yO_{2+x}$ as functions of temperature, composition and total pressure, and (b) the rate of fuel restructuring under specified irradiation conditions, i.e., bubble size, density (population) and velocity as functions of fuel radius.

Conclusions. Application of simple equilibrium thermodynamics concepts to the differential evaporation-condensation model of radial U-Pu segregation does not give a complete description of steady state in an irradiated mixed oxide fuel; however, it does allow prediction of whether there will be net depletion or enrichment of plutonium at the center of a particular fuel for given operating conditions. The exact degree of plutonium enrichment or depletion will depend on the dynamics of the mass transport process, a factor which is currently being incorporated into our model.

FIGURE 1. "IDEALIZED" RADIAL $Pu/U + Pu$ GRADIENTS; CURVE (a) REFERS TO A NONCENTER-MELTED FUEL, CURVE (b) REFERS TO A CENTER-MELTED FUEL.

FIGURE 2. RADIAL $Pu/U + Pu$ PLOTS FOR $U_{0.75}Pu_{0.25}O_{2-x}$ E1J SERIES—CENTER MELTS, PLUS TYPICAL MACROGRAPH OF MELTED FUEL SECTION.

FIGURE 3. RADIAL $Pu/(Pu + U)$ PLOTS FOR TWO SECTIONS FROM PIN F2C.

FIGURE 4. PHASE DIAGRAMS FOR $\text{UO}_2\text{-PuO}_2$ (MEASURED SOLIDUS AND LIQUIDUS CURVES).

FIGURE 5. "CALCULATED PARTIAL PRESSURES OF GASEOUS SPECIES OVER $U_{0.80}Pu_{0.20}O_{2\pm x}$ AT $2500^{\circ}K$ AS FUNCTIONS OF O/M ." (THE VARIATION OF TOTAL Pu PRESSURE TO TOTAL U PRESSURE IS ALSO SHOWN AS CURVES A AND B. THESE TWO CURVES REFER TO THE RIGHT HAND ORDINATE AND B WAS DRAWN USING OHSE AND OLSEN'S "MODIFIED" VALUE OF $\Delta G_f(PuO_2)_g$).

FIGURE 6. CALCULATED O/M PROFILES IN 920 - 2500°C.

FIGURE 7. CALCULATED $(Pu/U)_g$ GRADIENTS FOR $U_{0.80}Pu_{0.20}O_{2\pm x}$; 920–2500°C; $Q^* = -10$.

FIGURE 8. MEASURED AND CALCULATED GRADIENTS FOR F3B(3) ($Pu = 25\%$, $O/M = 2.005$, $T_{center} = 2500^{\circ}C$).

FIGURE 9. CALCULATED GAS COMPOSITION $U_{0.80}Pu_{0.20}O_{1.978}$; 920–2500°C; DIFFERENT ASSUMED HEATS OF TRANSPORT FOR OXYGEN.

FIGURE 10. TOTAL PRESSURES AND GAS COMPOSITIONS AFTER "O" REDISTRIBUTION IN $U_{0.80}Pu_{0.20}O_{2\pm x}$ (RADIAL $\nabla T = 920-2500^\circ C$).

FIGURE 11. MASS TRANSPORT MODEL FOR $U_{1-y}Pu_yO_{2\pm x}$.

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