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AUGUST 1969

A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 7

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E. A. AITKEN
S. K. EVANS

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NUCLEONICS LABORATORY
VALLECITOS NUCLEAR CENTER
GENERAL ELECTRIC
PLEASANTON, CALIFORNIA

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ABSTRACT

In the sixth quarterly report (GEAP-5777) the continuing scope of work related to measurement of liquidus-solidus transformations, vaporization of urania and oxygen redistribution in a temperature gradient was presented. Work progress is reported in these tasks. In addition, a possible mechanism for the appearance of a plutonium-to-uranium gradient in the high temperature regions of the fuel is presented and analyzed from existing thermodynamic data. The mechanism is based on preferential vaporization of uranium and plutonium species along a temperature gradient until a steady-state composition is achieved.

1. INTRODUCTION

This quarterly report is seventh in a series which described experiments directed toward understanding plutonium segregation in urania-plutonia solid solutions used in fast reactor environments. In the sixth quarterly report (GEAP-5777) the progress of several experiments which have a bearing on plutonium segregation was described. In this report, progress made in these areas is described. In addition, a particular mechanism of plutonia-urania segregation - preferential vaporization - is described and analyzed.

2. LIQUID-SOLID TRANSFORMATION

Relocation of the plutonium enclosure containing melting point determination equipment was completed late in the report period. The final series of melting capsules prepared last quarter will be run to complete this phase of the study.

3. DETERMINATION OF COMPONENT ACTIVITIES

The determination of uranium activity in a solid solution is being carried out with a transpiration apparatus, with air and CO/CO_2 as the carrier gas. Non reproducibility of deposition rates reported in the last quarter was due in part to deposition of the UO_3 gas in the platinum tube section. Some of the gas was carried into the stainless steel tube which was not leached for uranium analysis. Checkout runs with U_3O_8 are continuing to establish the optimum flow rate for the system.

4. OXYGEN MIGRATION IN MIXED OXIDE SYSTEMS

Long-term heating tests of molybdenum capsules containing 20% PuO_{2-x} - 80% UO_2 and PuO_{2-x} pellets in a temperature gradient continued. Preliminary results indicated that oxygen transport in the range of 1200 to 1600° C requires time periods greater than 300 hours to achieve

a measurable gradient in the oxygen-to-metal ratio. These determinations will be completed and summarized in detail in the next report period.

5. PLUTONIUM-URANIUM SEGREGATION IN FAST REACTOR BY PREFERENTIAL VAPORIZATION

Fuel systems operated in a temperature gradient are subject to composition variation along the gradient. Variations in the oxygen-to-metal ratio have been observed and recently variations in plutonium-to-uranium ratio have been detected. To obtain a variation in the plutonium-to-uranium ratio, both cation species must be mobile (i.e., diffusion coefficient $>10^{-9}$ cm^2/sec or vapor pressure $>10^{-3}$ atm) so that segregation should be observed only at very high temperatures. Aside from the possibility of liquid-solid transformation, plutonium-to-uranium separation can occur by thermal diffusion, commonly known as Soret effect. This type of separation mechanism has been observed in C-Fe systems and H-Zr systems where one of the species is very mobile. To obtain steady-state separation caused by an imposed temperature gradient, there must be nonideal character in the solubility of the two mobile constituents or the heat flow caused by the temperature gradient must bias the jump frequency of the constituents so that movement of one of the constituents up the gradient is favored. At present, there is no evidence either for nonideal character of the solid solution of mixed oxides or for nonisothermal effect on the jump frequency so that predictions of pure Soret effect in mixed oxides are not possible. Numerical analysis of experimental data has resulted in no conclusive evidence for the validity of the Soret mechanism.

Another possible mechanism for separation which has not been proposed is preferential vaporization. There are several gaseous species which volatilize from plutonia and urania and their relative importance changes with temperature and oxygen-to-metal ratio. The relative importance of each species can be estimated from vaporization and other thermodynamic data and it is possible to determine approximately the degree of separation of the plutonium and the uranium by this mechanism. In the succeeding sections we will examine in detail the vaporization properties and determine separation tendencies by the preferential vaporization mechanism.

In this mechanism, it is assumed that vapor transport paths exist along the temperature gradient. Visual inspection of photomicrographs of the columnar grain growth region reveals numerous channels for gas flow so that movement of plutonium and uranium should occur more rapidly by gas diffusion rather than solid state diffusion. Detailed analysis of gas transport rates relative to solid state transport rates was presented recently.[2]

In the case of plutonia-urania transport, we may visualize the gas molecules in equilibrium with the solid at each point along the gradient. The total pressure of the urania and plutonia gases decreases with temperature producing a steady drift down the gradient. Initially the plutonium-to-uranium ratio of the solid is uniform so that if the plutonium-to-uranium ratio of the gas phase is different from that of the solid phase, then one constituent is removed preferentially. Eventually the solid phase composition is adjusted at each point along the gradient until there is a balance of flows between the urania and plutonia gases producing a stationary state.

The stationary state may depend on a particular condition or set of conditions depending on the dynamics of the flow of constituents due to gas diffusion and solid diffusion. If gas diffusion is the dominant transport mechanism and if the partial pressures are reasonably large ($>10^{-3}$ atm) then a possible condition at steady state is the absence of a gradient in plutonium-to-uranium ratio of the gas phase. This condition is similar to a constant CO-to-CO_2 ratio proposed by Markin and Rand[3] for establishing an oxygen-to-metal ratio of the fuel in a temperature gradient.

Before examining the consequences of gas diffusion mechanism, the vapor pressures of the important urania and plutonia species will be determined from thermodynamic data available in the literature. The data are not complete and reasonable extrapolations to higher temperatures are necessary. In spite of this limitation, useful trends appear from the vaporization data which aid in developing a transport mechanism. In all cases, the solid solution between urania and plutonia is assumed to be ideal so that the partial pressures of the plutonia and urania-bearing species for a given composition can be calculated from Raoult's Law.

VAPORIZATION FROM URANIA

The vaporization properties for urania were obtained from a combination of the data of Ackermann, Rauh, and Chandrasekharaiah[4] (ARC) at the U-UO_{2-x} boundary and the data of Tetenbaum and Hunt[5] (TH). The UO, UO_2, and UO_3 partial pressures were calculated along the phase boundary at several temperatures. By application of the Gibbs-Duhem relation to the variation in oxygen partial pressure as a function of composition one can obtain the UO, UO_2, and UO_3 partial pressures at other compositions. The oxygen partial pressure rises steeply with increasing oxygen content near stoichiometric UO_2 which in turn causes a steep increase in UO_3 partial pressure and steep decrease UO partial pressure. Figures 1 through 4, respectively, show the partial pressures of the urania-bearing gases and O gas at 2080, 2390, 2705 and 2900° K. The data for the last temperature were obtained by extrapolation. The other temperatures were selected from the data (TH). In Figure 3 the partial pressure of UO_3 was extended slightly to the hyperstoichiometric side to show how the UO_3 partial pressure becomes the dominant vapor species at high oxygen activity for a given temperature. A similar rise occurs at other temperatures. It has also been demonstrated in mass spectrometric studies[4] that for a given composition the UO_3 partial pressure increases with temperature at a faster rate than the UO_2 partial pressure. This phenomena will be important in demonstrating preferential vaporization.

VAPORIZATION FROM PLUTONIA

The most complete data on vaporization of plutonia are from Ackermann, Faircloth and Rand[6] (AFR). The vapor pressures of PuO, PuO_2, and O gas are shown in Figures 1 through 4 as a function of oxygen-to-plutonium ratio. It is seen that the PuO gas decreases with increasing oxygen and is nearly equal to the PuO_2 species over the composition range of interest.

VAPORIZATION FROM THE SOLID SOLUTION

Since both the plutonia and urania constituents in the solid solution are at equilibrium with the same oxygen activity, then the vapor pressures of the plutonia and urania gases are uniquely

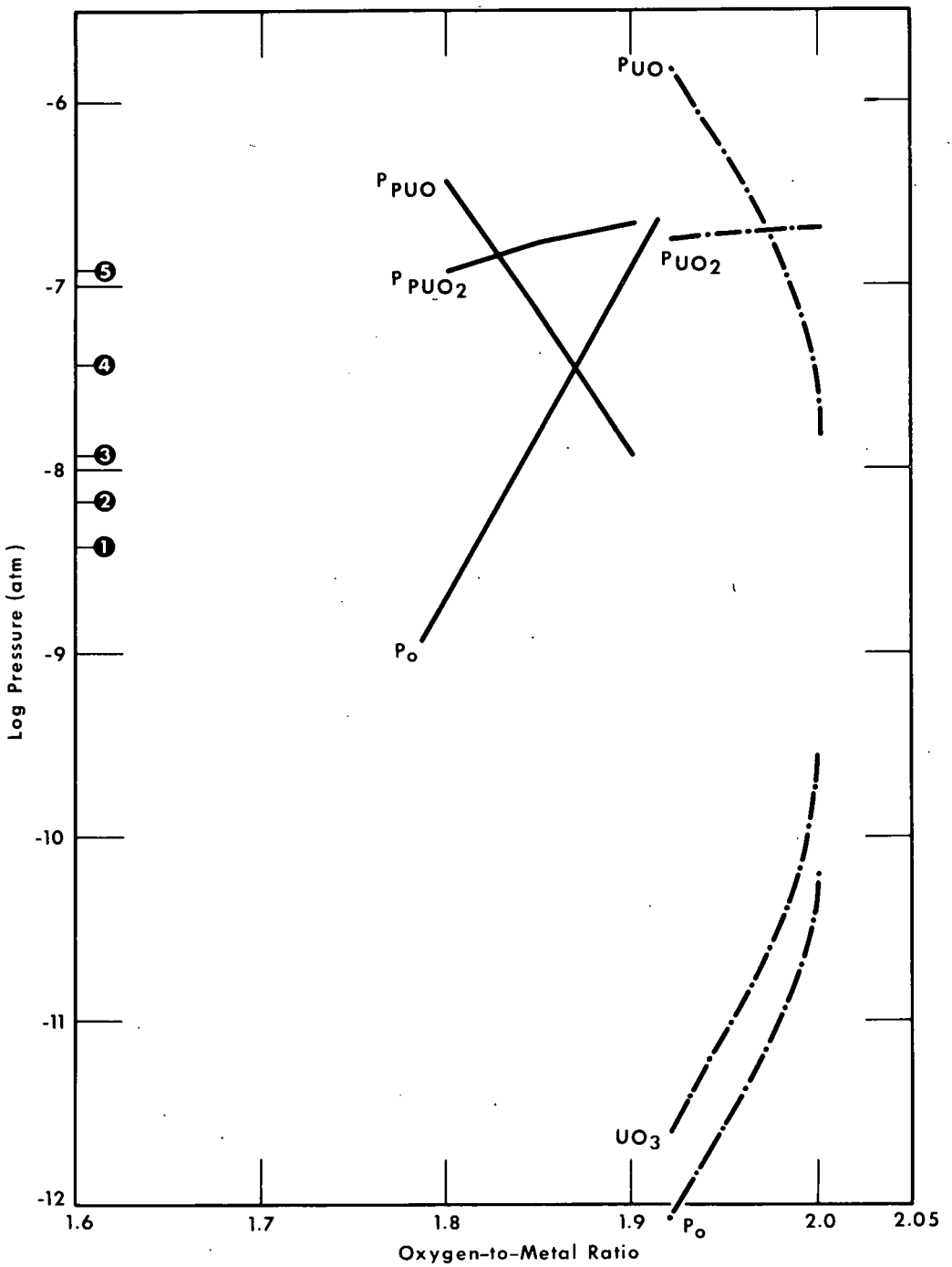

FIGURE 1. PARTIAL PRESSURES AT 2080°K OF GASEOUS CONSTITUENTS OVER PLUTONIA AND URANIA AS A FUNCTION OF OXYGEN-TO-METAL RATIO

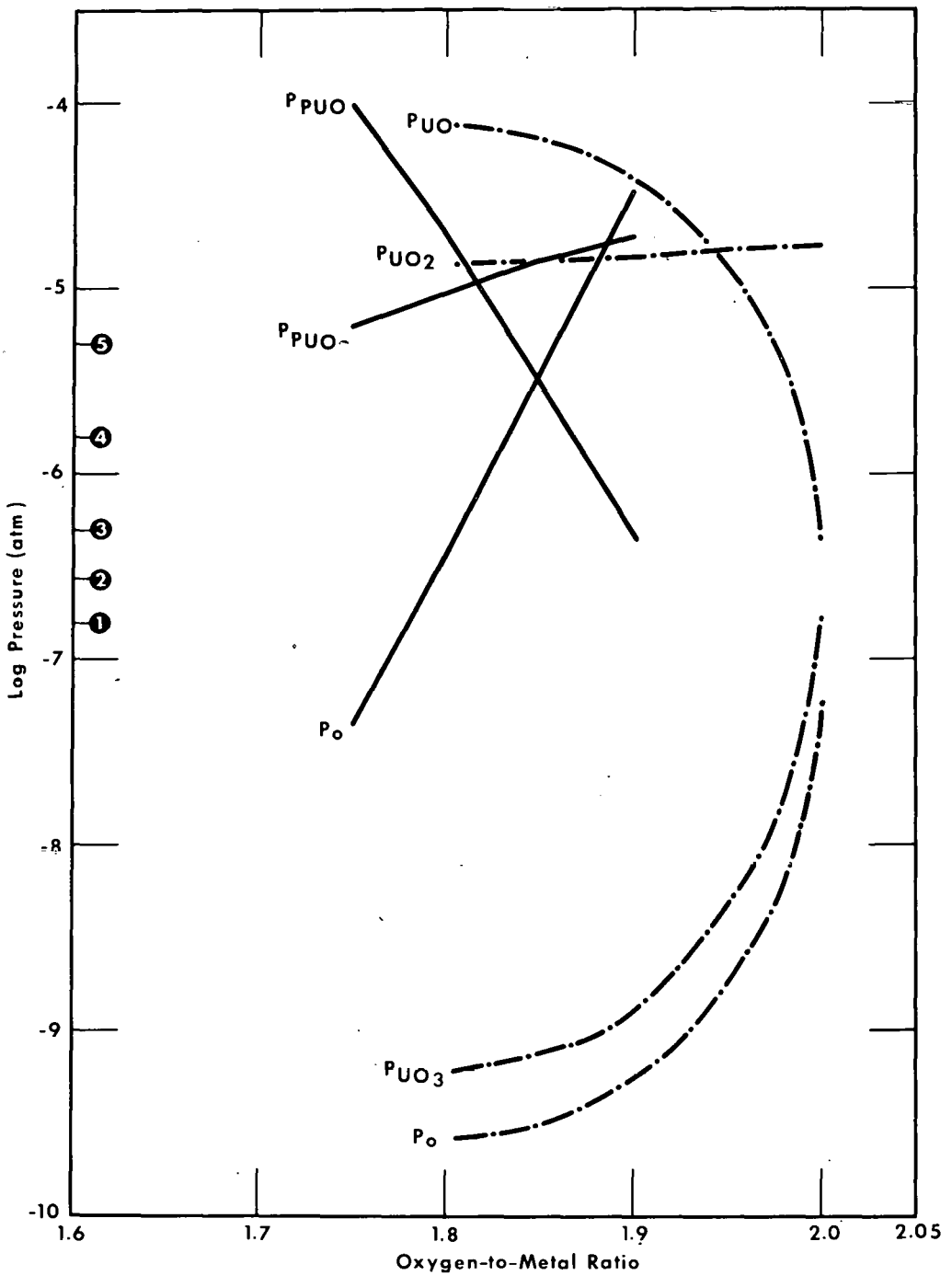

FIGURE 2. PARTIAL PRESSURES AT 2390°K OF GASEOUS CONSTITUENTS OVER PLUTONIA AND URANIA AS A FUNCTION OF OXYGEN-TO-METAL RATIO

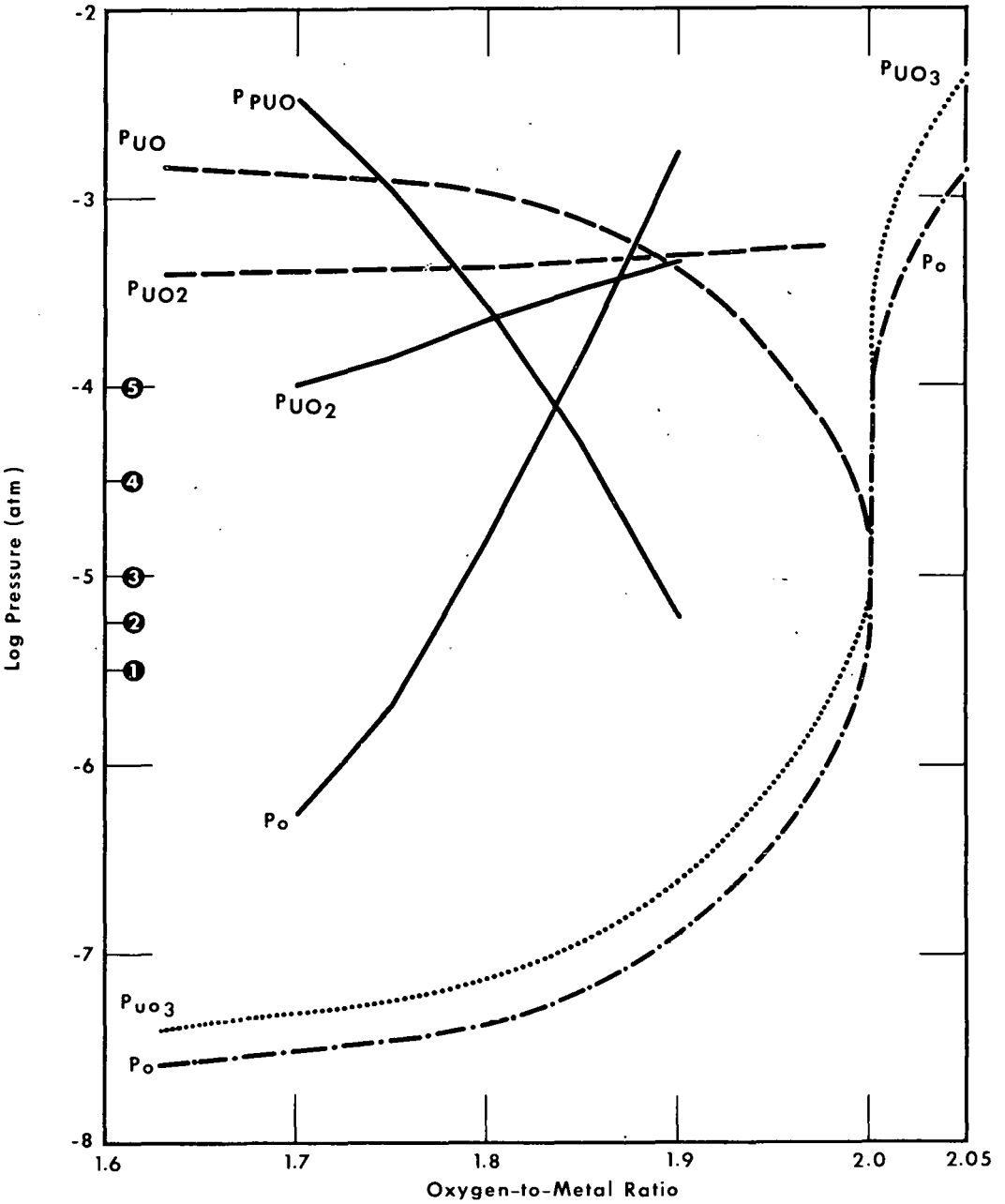

FIGURE 3. PARTIAL PRESSURES AT 2705°K OF GASEOUS COMPONENTS OVER PLUTONIA AND URANIA AS A FUNCTION OF OXYGEN-TO-METAL RATIO

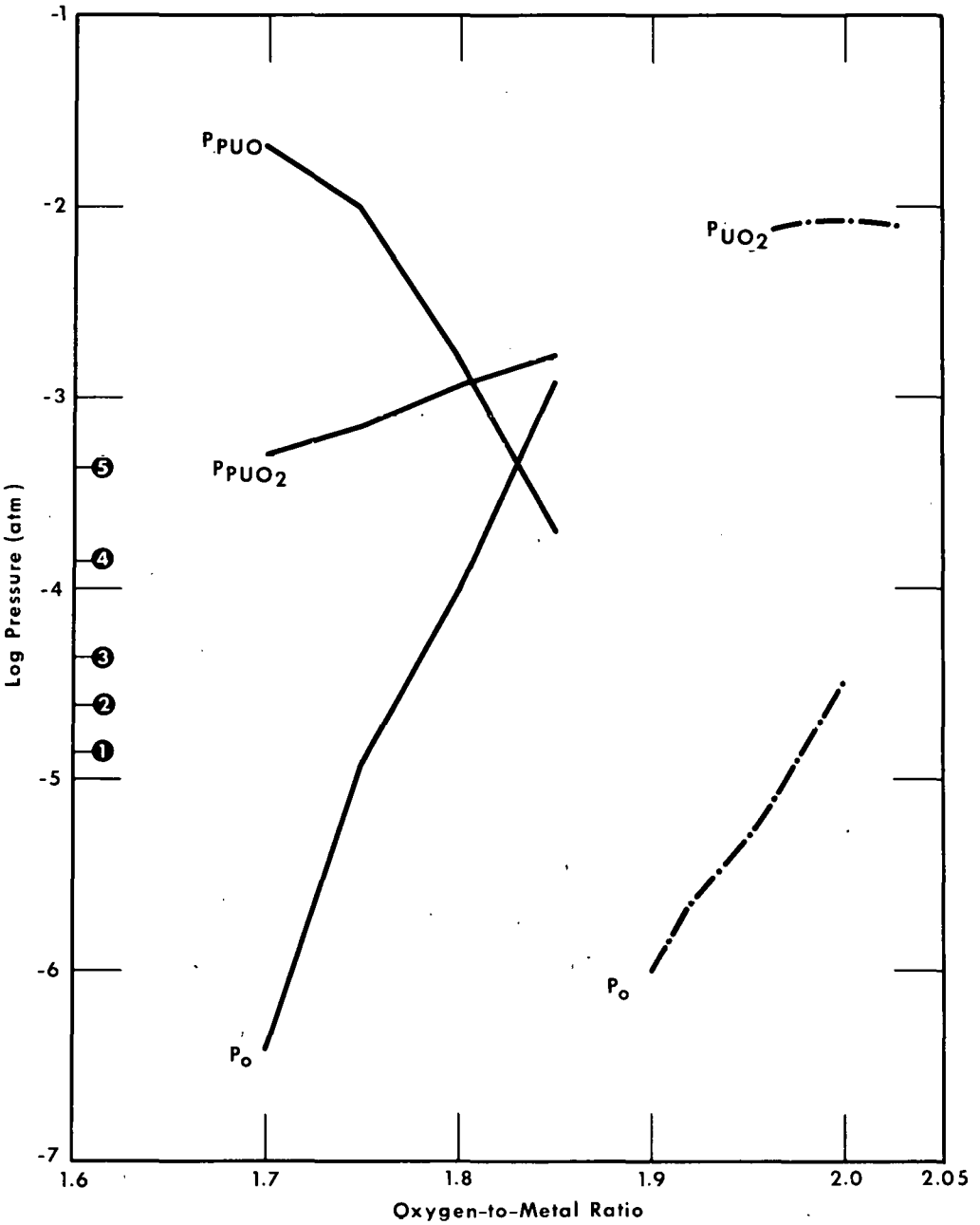

FIGURE 4. PARTIAL PRESSURES AT 2900°K OF GASEOUS CONSTITUENTS OVER PLUTONIA AND URANIA AS A FUNCTION OF OXYGEN-TO-METAL RATIO

determined at each temperature for a given oxygen activity. The oxygen activity in a sealed fuel rod can be controlled in two ways:

1. By equilibration with Cr/Cr_2O_3 in the stainless steel cladding;
2. By dissociation of the MO_2 fuel phase.

In the first case, the oxygen activity does not change during the irradiation period; in the last case, the oxygen activity is set initially by the starting oxygen-to-metal ratio of the fuel, but could change during irradiation due to the imposed thermal gradient and burnup.

A convenient way of specifying the oxygen activity is the H_2O-to-H_2 or CO-to-CO_2 ratio of the cover gas. Since these gases are likely to be abundant in a fuel rod, and their migration throughout the rod is relatively rapid, then it is reasonable to assume the H_2O-to-H_2 ratio is constant along the temperature gradient. This assumption is not necessary, but it will simplify an explanation of the trends in the Pu-to-U ratio of the vapor phase.

In Figure 5 the plutonium-to-uranium ratio of the vapor is shown as a function of temperature for an 80% UO_2 - 20% PuO_2 solid solution at various H_2O-to-H_2 ratios. The family of curves shows that the vapor becomes progressively more urania rich as the temperature increases above 2400° K. As the plutonium-to-uranium ratio of the vapor drops below 0.25, the solid solution will become richer in plutonia since more urania is leaving the solid than plutonia. It is apparent that plutonium enrichment of the solid requires progressively higher temperatures as the H_2O-to-H_2 ratio (oxygen activity) decreases.

This observation would also suggest that the degree of plutonium segregation in the fuel center may be somewhat less in hypostoichiometric fuels operated at the same actual temperature as stoichiometric fuels. Future analyses of the plutonium-uranium gradients in irradiated fuel should determine if this observation is correct.

Preferential migration of urania vapor will proceed until vapor flow stops (vapor channels become plugged) or until a steady-state condition is established. Post-irradiation examination of fuels usually reveals open channels in the columnar grain region so that vapor flow probably is present throughout the irradiation period. The existence of a steady state for a plutonium-uranium gradient has not been verified yet experimentally, but one may conceive such an occurrence similar to what has been demonstrated in the case of oxygen-to-metal gradients. Markin and Rand[3] proposed that the oxygen-to-metal gradient reached a steady state when the H_2O-to-H_2 or CO-to-CO_2 ratios were the same at each point along the temperature gradient (i.e., grad $P_{H_2O}/P_{H_2} = 0$) or (grad $P_{CO_2}/P_{CO} = 0$). This assumption was based on vapor transport being the dominant form of transport and that the partial pressures of the oxygen-bearing constituents were high enough to give mass flow in the vapor phase commensurate with the changes in oxygen-to-metal ratio.

A similar assumption could be made for the plutonium and uranium bearing constituents in the gas phase. The partial pressure of these constituents is high in the central fuel region where plutonia enrichment has been observed. If vapor transport is the dominant transport mechanism for plutonium and uranium separation, then a possible steady-state condition is grad $(Pu/U)_{vapor}=0$.

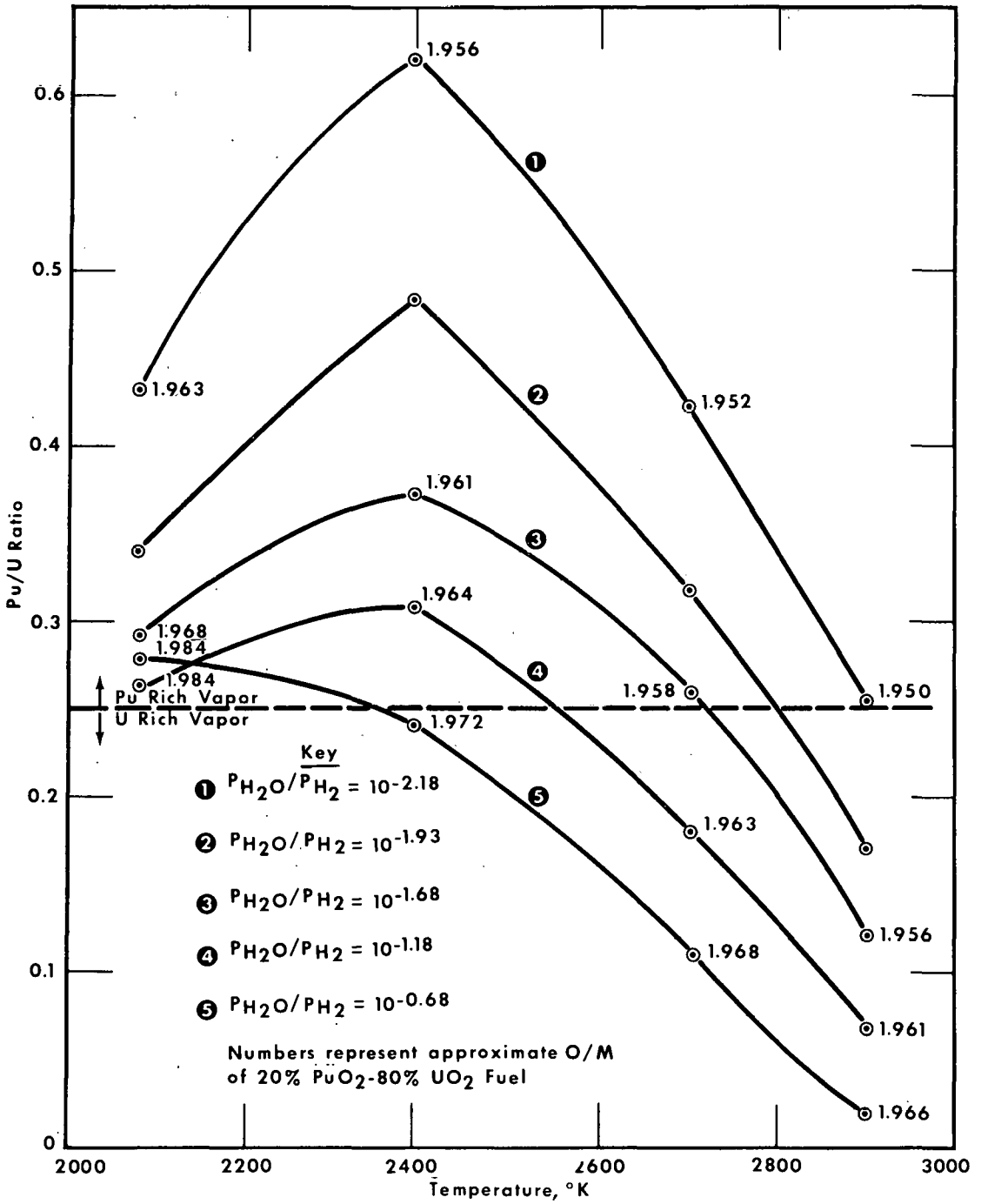

FIGURE 5. Pu/U RATIO OF GAS PHASE AS A FUNCTION OF TEMPERATURE AT VARIOUS WATER/HYDROGEN RATIOS

In the columnar grain growth region, the partial pressures of the uranium and plutonium constituents are of the order of millimeters which tends to support vapor transport as the dominant mechanism and suggests the not unlikely steady-state condition, grad $(Pu/U)_{vapor}=0$. With this condition we can estimate the $(Pu/U)_{solid}$ profile at steady state from the data shown in Figure 5 and the following relation:

$$y/(1-y) = z/(1-z) \left[(P^o_{Pu})/P^o_U)\right] \quad (1)$$

when y represents the mole fraction of plutonium vapor and 1-y represents the mole fraction of uranium vapor. Similarly, z represents the mole fraction of plutonium in the solid phase. Under the assumption of an ideal solid solution, the composition of the solid and vapor phases are connected by the ratio of the sum of partial pressures of plutonium vapor constitutents P^o_{Pu} and sum of pressures of uranium vapor constituents P^o_U.

The ratio of partial pressure sums is 4R where R is the ordinate of Figure 5. Thus

$$y/1-y = 4Rz/1-z \quad (2)$$

At steady state, grad y/1-y = 0 or y/1-y = constant.

To calculate z at steady state, we must specify the value for the constant (i.e., the plutonium-to-uranium ratio of the vapor phase at steady state). This ratio cannot be determined a priori; however, its value should be close to the composition of the fuel averaged over the temperature range where vapor transport can occur at a reasonable rate. The low temperature side of the gradient contains the larger fraction of fuel in a radial gradient of cylindrical geometry so that the average composition should be essentially the same as the starting composition or stated in another way the fuel in the low temperature side acts as a reservoir for plutonium and uranium vapor and fixes the plutonium-to-uranium ratio of the vapor phase. Inspection of Figure 5 shows that the plutonium-to-uranium ratio of the vapor phase approaches 0.25 for an 80% UO_2 - 20% PuO_2 solid solution at low temperature which suggests that $y/1-y \cong 0.25$ at steady state. Upon incorporation of this value for the constant in Equation (2) and by using values for R at various temperatures from Figure 5, a relationship between the solid phase composition z, and temperature was constructed as shown in Figure 6 for various H_2O-to-H_2 ratios. Again, the degree of plutonium enrichment at the highest fuel temperature depends on the H_2O-to-H_2 ratio or oxygen activity.

To compare these calculated results with observed plutonium-to-uranium gradients we have plotted the plutonia concentration profile obtained by Stalica[1] from microprobe examination of EBR II fuel containing 20% plutonia. The temperature profile was estimated from the center and surface fuel temperature given by Stalica and from an assumption of a uniform heat generation rate.

The observed concentration profile is similar to the calculated profile from the preferential vaporization concept at a H_2O-to-H_2 ratio of about $10^{-1.93}$. Agreement between the model and experiment at this stage of our understanding would be fortuitous until the calculations are substantiated by more observations. The prediction that could be confirmed most readily by observation is the effect of oxygen activity on the magnitude of the plutonium-to-uranium gradient.

Specimens irradiated under the same conditions but at different oxygen-to-metal ratios should show different plutonium-to-uranium gradients by the preferential vaporization mechanism. Other parameters, such as plutonia content and temperature, should be investigated also. Close control of temperature during irradiation would be essential however to give meaningful results about the effect of temperature.

If the plutonia becomes concentrated near the fuel center, then an incremental increase in temperature would result from the non-uniform heat generation and, in turn, could lead to further plutonia enrichment in the center. It is interesting to note that plutonia enrichment under certain conditions could bring about melting because of the decreasing solidus temperature with increasing plutonia concentration. The solidus line is shown in Figure 6 and represents the upper limit for plutonia enrichment by preferential vaporization.

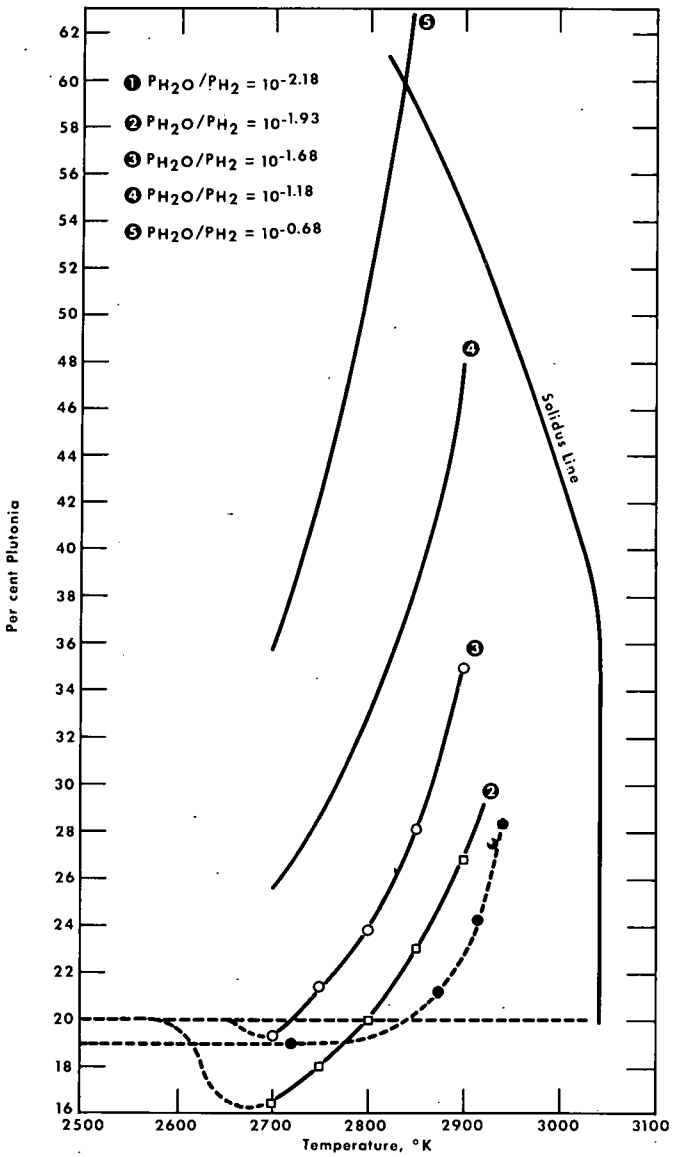

FIGURE 6. ESTIMATED PLUTONIA CONCENTRATION AS A FUNCTION OF TEMPERATURE UNDER STEADY-STATE CONDITIONS AND AT VARIOUS WATER TO HYDROGEN RATIOS

REFERENCES

1. Stalica, N. R., Seils, C. A., and Cronthanel, C. E., Argonne National Laboratory, "Electron Microprobe Analysis of Irradiated Oxide Fuel," presented at Symposium on Ceramic Nuclear Fuels, May 3-8, 1969, Washington, D.C. Also: ANL-7550, Chemical Engineering Division, Research Highlights, May 1968-December 1968.
2. Aitken, E. A., "Thermal Diffusion in Closed Oxide Fuel Systems," J. Nucl. Matl., 30, 62-73 (1969).
3. Markin, T. L. and Rand, M. H., UKAEA Report, AERE-R5560 (1967).
4. Ackermann, R. J., Rauh, E. G., and Chandrasekharaiah, M. S., "A Thermodynamic Study of the Uranium-Urania System," ANL-7048, July 1965.
5. Tetenbaum, M. and Hunt, P. D., "High Temperature Thermodynamic Properties of Oxygen-Deficient Urania," J. Chem. Phys., 49, 11, 4739-4744 (December 1968).
6. Ackermann, R. J., Faircloth, R. L., and Rand, M. H., J. Phys., 70, 3698 (1966).

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