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GEAP-12153  
AEC RESEARCH AND  
DEVELOPMENT REPORT  
DECEMBER 1970

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

QUARTERLY REPORT NO. 13  
AUGUST 1 TO OCTOBER 31, 1970

E. A. AITKEN  
S. K. EVANS

U.S. ATOMIC ENERGY COMMISSION  
CONTRACT AT(04-3)-189  
PROJECT AGREEMENT 53

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Prepared for the  
United States Atomic Energy Commission  
Contract No. AT(04-3)-189, Project Agreement 53

*Printed in U.S.A. Available from the  
Clearing House for Federal Scientific and Technical Information  
National Bureau of Standards, U.S. Department of Commerce  
Springfield, Virginia 22151*


*Price: \$3.00 per copy*

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## ABSTRACT

*In the twelfth quarterly report (GEAP-12133), the continuing scope of work related to vaporization of urania, oxygen activity at high temperatures, oxygen redistribution in a temperature gradient, and sodium fuel interactions was presented. Work progress is presented on these tasks.*

## 1. INTRODUCTION

This quarterly report is thirteenth in a series which describes experiments directed toward understanding plutonia segregation in urania-plutonia solid solutions and in fast reaction environments through a knowledge of its thermodynamic behavior. In the twelfth quarterly (GEAP-12133) the progress of several experiments which have a bearing on plutonium 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. THERMODYNAMIC BEHAVIOR OF SODIUM-FUEL REACTION PRODUCTS

### THERMAL GRADIENT EXPERIMENTS WITH EXCESS SODIUM

Sodium-bearing thermal gradient experiments analyzed and reported in the twelfth quarterly report gave indications of a reaction of sodium with the  $\text{UO}_2$ -20%  $\text{PuO}_2$  fuel at an oxygen-to-metal ratio of about 1.975 and a temperature of  $1000^\circ\text{C}$ . The results were independent of the quantity of sodium present in the capsules. These experiments serve as a base for investigating the properties of the sodium-fuel reaction in a temperature gradient.

Additional capsules are planned for use in the investigation of the effects of time, sodium temperature, stoichiometry, and plutonium content on the properties of the observed reactions. The time dependence of the sodium-fuel reaction properties will be investigated in two thermal gradient capsules containing  $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{1.965}$  containing 35 milligrams of sodium operated for 100 and 1000 hours in a temperature gradient from 1600 to  $900^\circ\text{C}$ . A third capsule will contain the same material as the first two, but the lowest temperature in the gradient will be raised to  $1100^\circ\text{C}$  and the duration of the test will be 300 hours. The purpose of this test will be to ascertain the effect of the gradient limits on the reaction behavior.

To determine the sodium-fuel reaction stoichiometry threshold, a capsule containing the same materials as those described above, except that the oxygen-to-metal ratio is decreased to 1.94, will be annealed for 300 hours in a 1600 to  $900^\circ\text{C}$  temperature gradient.

A capsule containing  $\text{PuO}_{1.8}$  previously subjected to a 1000-hour anneal in a 1600 to  $900^\circ\text{C}$  temperature gradient, but never examined, will be opened, have 35 mg sodium added, these undergo a 300-hour anneal in the same gradient.

The above capsules were being fabricated at the end of the quarter. Thermal gradient anneals will be made during the next quarter.

### ISOTHERMAL EXPERIMENTS IN EXCESS SODIUM

The sodium distillation apparatus described in the twelfth quarterly report was tested. The heater failed before the sodium reached a high enough temperature for significant distillation to occur. Redesign of the apparatus is in progress.

### 3. DETERMINATION OF COMPONENT ACTIVITIES

The determination of uranium activity in  $\text{UO}_2\text{-PuO}_2$  solid solutions is being studied by means of a transpiration technique with air and  $\text{CO/CO}_2$  as the carrier gases.

Installation of the transpiration equipment in an alpha enclosure was completed, and experiments were conducted with  $\text{UO}_2\text{-40% PuO}_2$  at 1390 and 1500°C with 10  $\text{CO}_2/\text{CO}$  as the carrier gas. The results of these experiments in comparison with previously reported  $\text{UO}_2$  data are shown in Figure 1.

The data are not yet conclusive, but the test at 1500°C indicates a reduction in the  $\text{UO}_3$  pressure of about 40% as a result of the presence of plutonium, which would be expected from ideal solution theory.

Since the gas mixture used in these experiments results in a slightly hyperstoichiometric fuel composition at the test temperature, it must be established whether any correction factors on the  $\text{UO}_3$  pressure are necessary to relate the data to the stoichiometric  $\text{UO}_2\text{-PuO}_2$  system. The approach of Aitken, Edwards, and Joseph<sup>1</sup> will be used as a format in the calculation of the necessary correction factors.

The solid solution  $\text{U}_y\text{Pu}_{1-y}\text{O}_{2+x}$  can be considered as made up of the three components  $\text{UO}_2$ ,  $\text{PuO}_2$ , and  $\text{O}_2$ . Following Aitken's format, the activity of  $\text{UO}_2$  in the hyperstoichiometric solid solution can be calculated from

$$a_{\text{UO}_2}(y,x) = \frac{P_{\text{UO}_3}(y,x)}{P_{\text{UO}_3}(1,0)} \left[ \frac{P_{\text{O}_2}(1,0)}{P_{\text{O}_2}(y,x)} \right]^{1/2} \quad (1)$$

(1,0) indicates pressure over  $\text{UO}_2$  at unit activity.

The values of  $P_{\text{O}_2}(y,x)$  and  $P_{\text{UO}_3}(1,0)$  can be calculated from known data.<sup>1</sup> The value of  $P_{\text{UO}_3}(y,x)$  is measured in the experiment.

The activity of  $\text{UO}_2$  in the solid solution  $\text{U}_y\text{Pu}_{1-y}\text{O}_{2+x}$  can be related to the activity of  $\text{UO}_2$  in the stoichiometric solid solution by the following equation derived by Wagner<sup>2</sup>

$$RT \ln \left( \frac{a_{\text{UO}_2}(y,x_0)}{a_{\text{UO}_2}(y,0)} \right) = \int_0^{x_0} \left[ \bar{G}_{\text{O}_2} + (1-y) \frac{\partial \bar{G}_{\text{O}_2}}{\partial y} \right]_y \frac{dx}{2} - \frac{x_0}{2} \bar{G}_{\text{O}_2}(\text{at } x_0) \quad (2)$$

Markin and McIver<sup>3</sup> have published data on partial molar free energy of oxygen in  $\text{U}_y\text{Pu}_{1-y}\text{O}_{2+x}$  up to 1100°C. They found that  $\bar{G}_{\text{O}_2}$  is insensitive to plutonium content in the hyperstoichiometric range. An empirical linear equation can be constructed from their data at 900°C as follows:

$$\bar{G}_{\text{O}_2} = 96x - 57 \quad (\text{kcal/mole}) \quad (3)$$

where  $x$  is the deviation from stoichiometry. From the data of Markin and McIver a correction factor of about 5 kcal/mole should be added to the intercept term in Equation (3) for each 100°C increase in temperature. However, this correction factor has no effect on the final result as will be seen below.



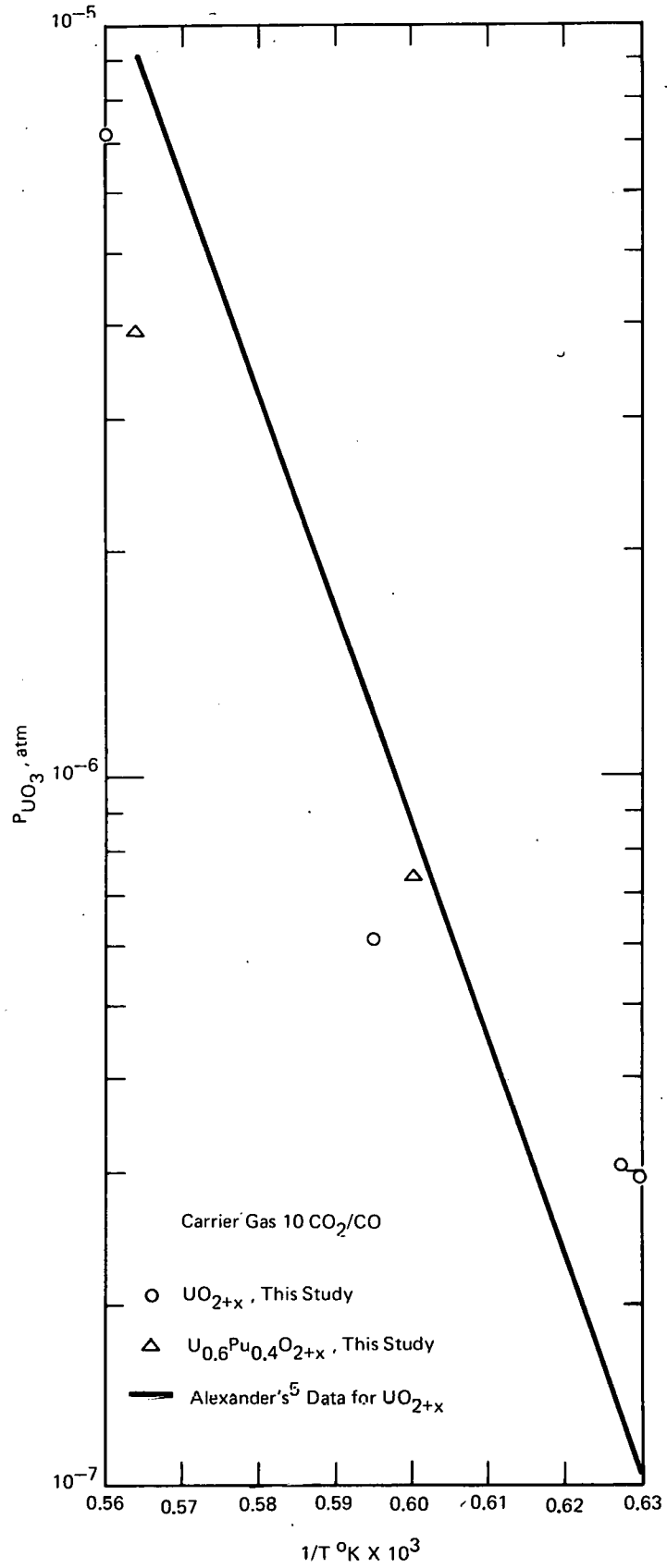


FIGURE 1. UO<sub>3</sub> PARTIAL PRESSURE VERSUS 1/T FOR UO<sub>2+x</sub> AND U<sub>0.6</sub>Pu<sub>0.4</sub>O<sub>2+x</sub>

Thus, at 1300°C

$$\bar{G}_{O_2} = 96x - 37 \text{ (kcal/mole)}$$

and at 1500°C

$$\bar{G}_{O_2} = 96x - 27 \text{ (kcal/mole)}$$

By using the extrapolated data of Rand and Markin,<sup>4</sup> the following stoichiometry information can be calculated for a 10 CO<sub>2</sub>/CO carrier gas mixture.

Temperature, °C	Oxygen-to-Metal Ratio
1300	2.015
1400	2.035
1500	2.06

With the above data available, Equation (2) can be implemented.

At 1300°C

$$RT \ln \left( \frac{a_{UO_2}(y, x_o)}{a_{UO_2}(y, o)} \right) = \int_o^{x_o} \left[ (96x - 37) + (1-y) \left( \frac{\partial \bar{G}_{O_2}}{\partial y} \right) \right] \frac{dx}{2} - \frac{x_o}{2} (96x_o - 37)$$

The term  $\frac{\partial \bar{G}_{O_2}}{\partial y}$  is zero since Markin and McIver show that  $\bar{G}_{O_2}$  is independent of  $y$ .

After simplifying the above equation, the result is

$$RT \ln \left( \frac{a_{UO_2}(y, x_o)}{a_{UO_2}(y, o)} \right) = \frac{96x_o^2}{4} - \frac{37x_o}{2} - \frac{96x_o^2}{2} + \frac{37x_o}{2} = -\frac{96x_o^2}{4}$$

The intercept term in the linear equation for  $\bar{G}_{O_2}$  disappears, therefore, this expression will be valid for higher temperatures as well

and

$$a_{UO_2}(y, o) = \exp \frac{24x_o^2}{RT} a_{UO_2}(y, x_o)$$

At 1300°C,  $x_o = 0.015$  and

$$a_{UO_2}(y, o)_{1300^\circ C} = 1.002 a_{UO_2}(y, 0.015)$$

At 1500°C,  $x_o = 0.06$  and

$$a_{UO_2}(y, o)_{1500^\circ C} = 1.025 a_{UO_2}(y, 0.06)$$

Thus, in the worst experimental case, the correction factor is only 1.025, which is less than experimental error and can be ignored.

Thus, in Equation (1),  $a_{\text{UO}_2}(y,x)$  can be replaced by  $a_{\text{UO}_2}(y,0)$  and the slightly hyperstoichiometric mixed oxide can be treated as being stoichiometric for this experiment.

If stoichiometric  $\text{UO}_2\text{-PuO}_2$  solid solutions exhibit ideal solution behavior, then

$$a_{\text{UO}_2}(y,0) = y a_{\text{UO}_2}(1,0)$$

and, for this experiment

$$a_{\text{UO}_2}(y,x) = y a_{\text{UO}_2}(1,x)$$

The data taken so far, while not conclusive, indicates that ideal solution behavior in the  $\text{UO}_2\text{-PuO}_2$  system is not unreasonable.

#### 4. OXYGEN MIGRATION IN (U,Pu) $\text{O}_2$ SYSTEMS

The twelfth quarterly report contained a description of the results of a series of thermal gradient experiments designed to investigate mechanisms of oxygen migration in  $\text{UO}_2\text{-PuO}_2$  solid solutions in the presence of a temperature gradient. The results of these experiments indicated that more studies were necessary to determine the kinetic behavior of the oxygen migration in capsules containing mixed oxide with an average oxygen-to-metal ratio of 1.98 or lower. Several additional tests are planned to investigate the kinetic aspects of the oxygen migration behavior. The 1.94 oxygen-to-metal ratio experiment is to be repeated at 100 and 300 hours in a 1600 to 900°C temperature gradient to investigate shorter term kinetic behavior for the low stoichiometry case. It is hoped that these short-term experiments will give a clue to the rate of approach to steady state in this material.

Three experiments are planned to investigate the approach to steady state behavior in the 1.965 to 1.97 oxygen-to-metal ratio material. Thermal gradient experiments on  $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{1.97}$  with and without molybdenum spacers between the pellets will be extended to 2000 hours. In addition, a 2000-hour experiment will be conducted on the same material when the pellets are replaced by 3-inch-long rods of mixed oxide to investigate the effect of changes in the solid-state and gas diffusion paths for oxygen.

A special die set has been fabricated for making the 3-inch rods. Initial testing of the die set is in progress. Fabrication of the other rods mentioned was in progress at the end of the quarter.

#### 5. A THEORETICAL STUDY OF PLUTONIUM-URANIUM SEGREGATION IN FCR MIXED OXIDE FUELS

A detailed theoretical analysis of possible mechanisms for plutonium-uranium segregation within mixed (U,Pu) oxide fuels has been started. The possibility of Pu-U segregation across high radial temperature gradients occurring by preferential vaporization  $\rightleftharpoons$  condensation was considered in the seventh quarterly report. In addition to this mechanism, other sources of Pu-U segregation, such as single-phase, solid-state thermal diffusion (Soret Effect) and two-phase equilibration (liquid-solid and solid-solid) need to be examined.

The vapor-phase evaporation  $\rightleftharpoons$  condensation mechanism, which can occur either along channels (i) or by the migration of gas bubbles up columnar grains (ii) within an operating fuel, is being reanalyzed by using the best available thermodynamic data and comparisons with results from the most recent vapor pressure measurements,<sup>6</sup> as a first approximation it has been assumed that  $\text{UO}_2\text{-PuO}_{2-x}$  solid solutions are ideal, however, later calculations will be made more realistic by incorporation of a regular solution model. Because the same steady-state conditions are

expected to hold for both gas phase mechanisms, *i.e.*,  $\text{grad} (\Sigma\text{Pu}/\Sigma\text{U})_{\text{vap}} = 0$  and  $(\Sigma\text{Pu}/\Sigma\text{U})_{\text{vap}} = \text{constant} \cong (\text{Pu}/\text{U})_{\text{over all}}$ , essentially the same radial composition gradient will result in each case. It is hoped to obtain some knowledge of the time-dependence of Pu-U segregation in gas phase mechanism (ii) by treating the plastic columnar grain growth region as a type of distillation column and utilizing typical bubble densities and bubble migration rates. The relative effectiveness of each gas phase mechanism will be related to the fuel restructuring which takes place during the early stages of irradiation.

The validity of the so-called Soret Effect mechanism is being assessed by using an irreversible thermodynamic treatment of solid-state thermal diffusion in conjunction with existing transport (*i.e.*, cationic diffusion rates) and thermochemical data for  $\text{UO}_2\text{-PuO}_2$  solid solutions. Considerations of this type indicate that it is unlikely a significant Soret Effect will occur in this system. Consequently, attention will be focussed on what are considered to be the most likely mechanisms: preferential evaporation  $\rightleftharpoons$  condensation and, when there has been center melting, liquid-solid segregation.

Ultimately, it is intended to develop a general model incorporating all likely segregation mechanisms which will be capable of predicting both radial and axial U/Pu variations for any fuel composition (oxygen-to-metal ratio and Pu/U+Pu specified) and linear power rating.

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