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A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 9
AUGUST - NOVEMBER 1969

E. A. AITKEN
S. K. EVANS

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NUCLEONICS LABORATORY
VALLECITOS NUCLEAR CENTER
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PLEASANTON, CALIFORNIA

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ABSTRACT

In the eighth quarterly report (GEAP-12032), the continuing scope of work related to vaporization of urania, oxygen redistribution in a temperature gradient, and sodium fuel interaction was presented. Work progress is presented on these tasks.

In addition, the scope of follow-on experiments to study mechanistic aspects of oxygen redistribution in a temperature is presented.

1. INTRODUCTION

This quarterly report is ninth in a series which describes experiments directed toward understanding plutonium segregation in urania-plutonia solid solutions used in fast reactor environments. In the eighth quarterly report (GEAP-12032) the progress of several experiments which have a bearing on plutonium segregation was described. In this report, continued progress in these areas is described. New experiments in the thermal gradient area which will provide additional information concerning the mechanisms involved in oxygen migration are discussed.

2. DETERMINATION OF COMPONENT ACTIVITIES

The determination of uranium activity in a UO_2-PuO_2 solid solution is being carried out with a transpiration apparatus with air and CO/CO_2 as the carrier gas. Preliminary runs with U_3O_8 in air to establish the optimum flow rate for the system have been completed. The results of these runs are shown in Figure 1. The data indicate that the carrier gas is saturated with UO_3 vapor between about 40 and 80 cc/min flow rate. The values obtained are about 30% lower than data reported by Alexander.[1] Differences may lie in temperature calibration.

Experiments are in progress to determine the UO_3 vapor pressure in equilibrium with 10 CO_2/CO and CO_2/10 CO gas mixtures. Following these experiments, the effect of plutonium on the uranium activity in the mixed oxide system will be determined.

3. OXYGEN MIGRATION IN UO_2—20% PuO_2 AND PuO_{2-x} SYSTEMS

Molybdenum capsules containing hypostoichiometric UO_2—20% PuO_2 pellets have been heated in a temperature gradient from 1200 to 1600°C for periods up to 1070 hours. Data from mixed oxide capsules heated for 4, 15, 300, and 1000 hours has been reported in the sixth and eighth quarterly reports (GEAP-5777 and GEAP-12032). Similar data for a capsule heated for 120 hours is presented here.

Following the described heat treatments, the capsules were cut open and the pellets were removed. Thermogravimetric oxygen-to-metal ratio determinations were carried out on each of the pellets.

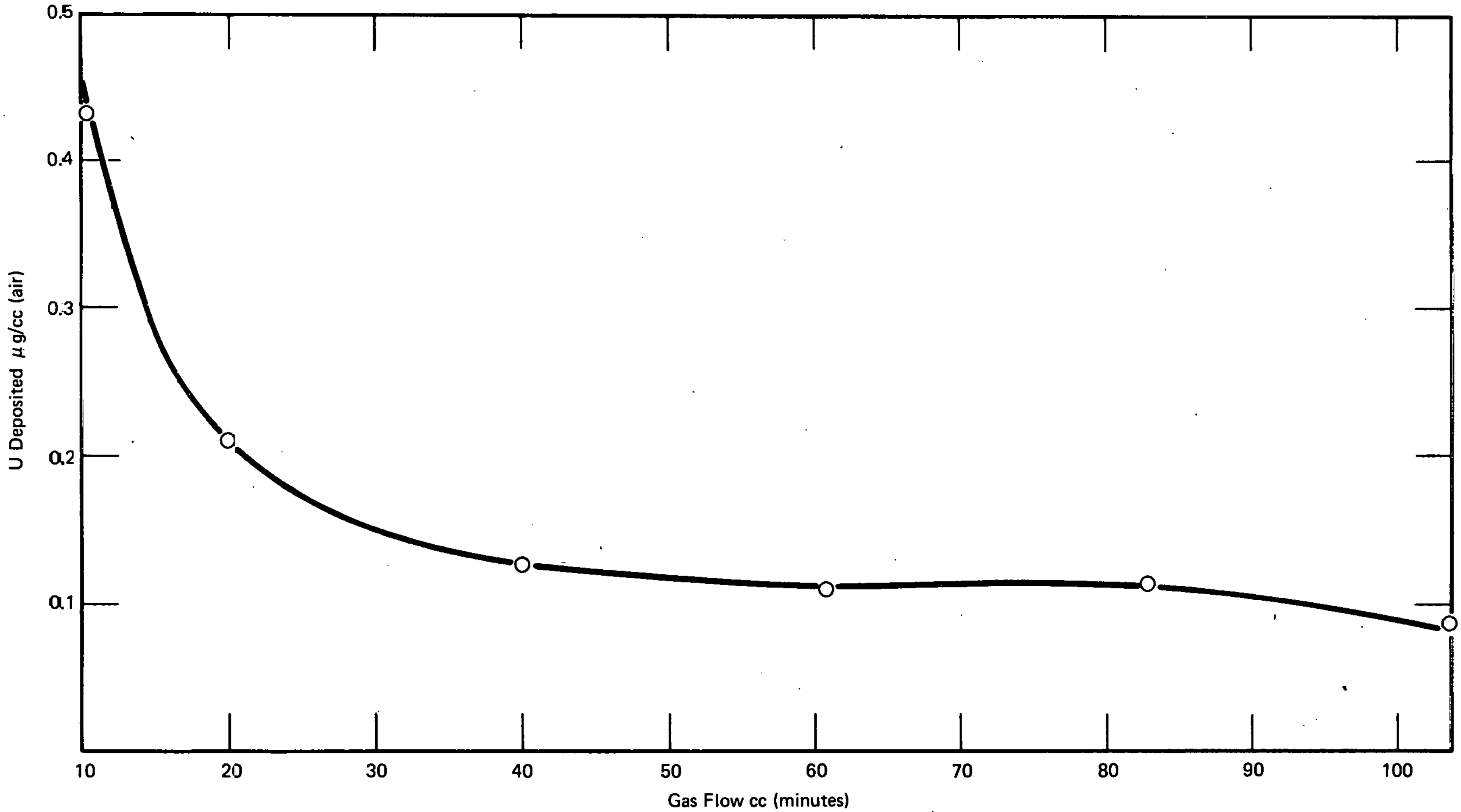

FIGURE 1. UO_3 TRANSPIRATION VERSUS GAS FLOW FOR AIR AT 1315°C

Figure 2 shows Arrhenius plots relating the deviation from stoichiometry, x, to the reciprocal temperature for 15-, 120-, 300-, and 1000-hour temperature gradient anneals of capsules containing $(U_{0.8}Pu_{0.2})O_{2-x}$.

The addition of the 120-hour data does not appreciably add to or modify the conclusions discussed in the eighth quarterly report. The end cap on this capsule was found to be pushed slightly out of the tube which resulted in an open system and increased the hydrogen over-pressure by orders of magnitude from what it was in the closed system. Therefore, the heat of transport measured cannot be correlated directly with those of the other tests in this series.

Initial experiments to determine oxygen migration behavior in PuO_{2-x} in a temperature gradient have been completed. These experiments are necessary to relate mixed oxide behavior to the end members of the binary system as discussed in the eighth quarterly report. Figure 3 represents Arrhenius plots relating the deviation from stoichiometry, x, to the reciprocal of temperature for PuO_{2-x} thermal gradient anneals of 15, 100, 300, and 1070 hours duration. The 3000-hour test originally scheduled was cancelled after the data from shorter time tests indicated that a steady state had been reached.

The behavior of oxygen migration in the PuO_{2-x} system significantly increased the understanding of transport processes in the UO_2—PuO_2 system also. The heats of transport measured for PuO_{2-x} increase monotonically from -15 kcal/mole at 15 hours to -4.1 kcal/mole at 1070 hours. Since the heat of transport measured during the 300-hour run was only slightly more negative than that measured during the 1070-hour run, it is assumed that a steady state has been reached at 1070 hours.

The post-test oxygen-to-metal ratios are significantly higher than the pre-test control specimen, with a random variation, a possible indication that the control value was in error or that the furnace gas H_2O-to-H_2 ratio was not constant and resulted in an uneven oxygen permeation ratio through the molybdenum tubes. In any event, the post-test oxygen-to-metal ratios are not significantly different.

The basic differences between the mixed oxide and PuO_{2-x} data can be partially explained at this time in terms of Aitken's one-component cyclic model for oxygen migration.[2,3] According to this model an effective heat of transport may be defined as follows:

$$Q^*_{eff} = Q^*/[1+(L_s/L_g)] \qquad (1)$$

where Q^* is the heat of transport resulting from oxygen transfer in the gas phase only, L_s is related to the solid state oxygen diffusion coefficient, and L_g is related to gas phase diffusion of oxygen.

If it is assumed the 1000-hour UO_2—20% PuO_2 anneal has reached a steady-state, the heat of transport is 5.2 times greater in absolute magnitude than that of the PuO_{2-x} 1070-hour anneal. Since the mechanism for oxygen diffusion in the oxygen deficient fluorite lattice is probably oxygen vacancy transport, the oxygen diffusion coefficient should be proportional to the concentration of oxygen vacancies in the lattice. While the average oxygen-to-plutonium ratios of the 1000-hour mixed oxide and PuO_{2-x} anneal samples are similar (1.865 and 1.817, respectively) their oxygen-to-metal ratios and hence their oxygen vacancy concentrations are quite different. The 1.817 oxygen-to-metal ratio in the PuO_{2-x} system corresponds to a factor of 6.8 more oxygen vacancies than the 1.973 stoichiometry in the mixed oxide system. Prigogine[4] has shown that the coefficient L_s in the phenomenological equation for mass flow along a temperature gradient is directly proportional to the diffusion coefficient.

Interpretation of Aitken's[2] data indicates that the observed heat of transport in the 1000-hour anneal of the mixed oxide corresponds to $L_s/L_g = 2.23$.

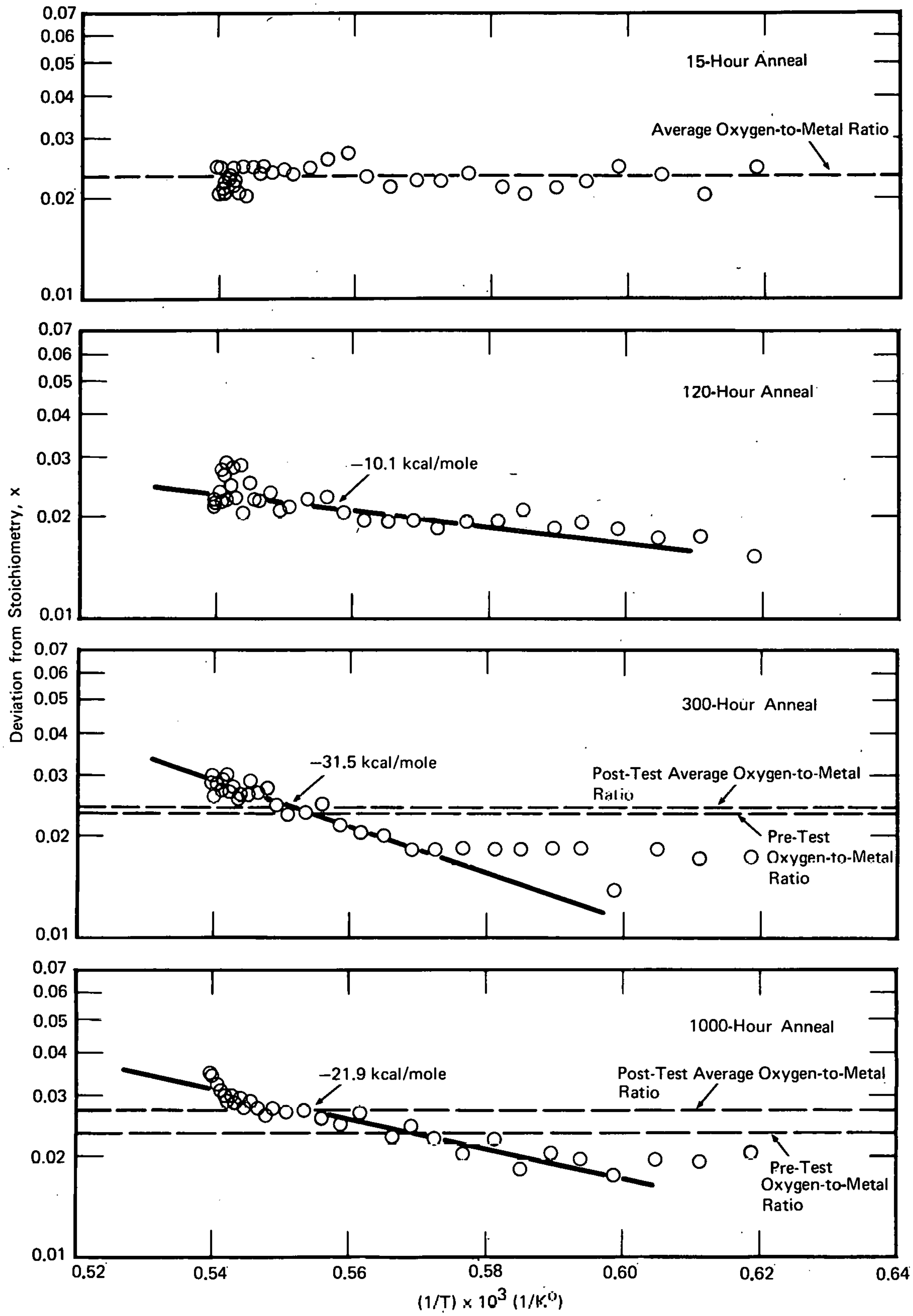

FIGURE 2. RESULTS OF $(U_{0.8}Pu_{0.2})\ O_{2-x}$ THERMAL GRADIENT EXPERIMENTS

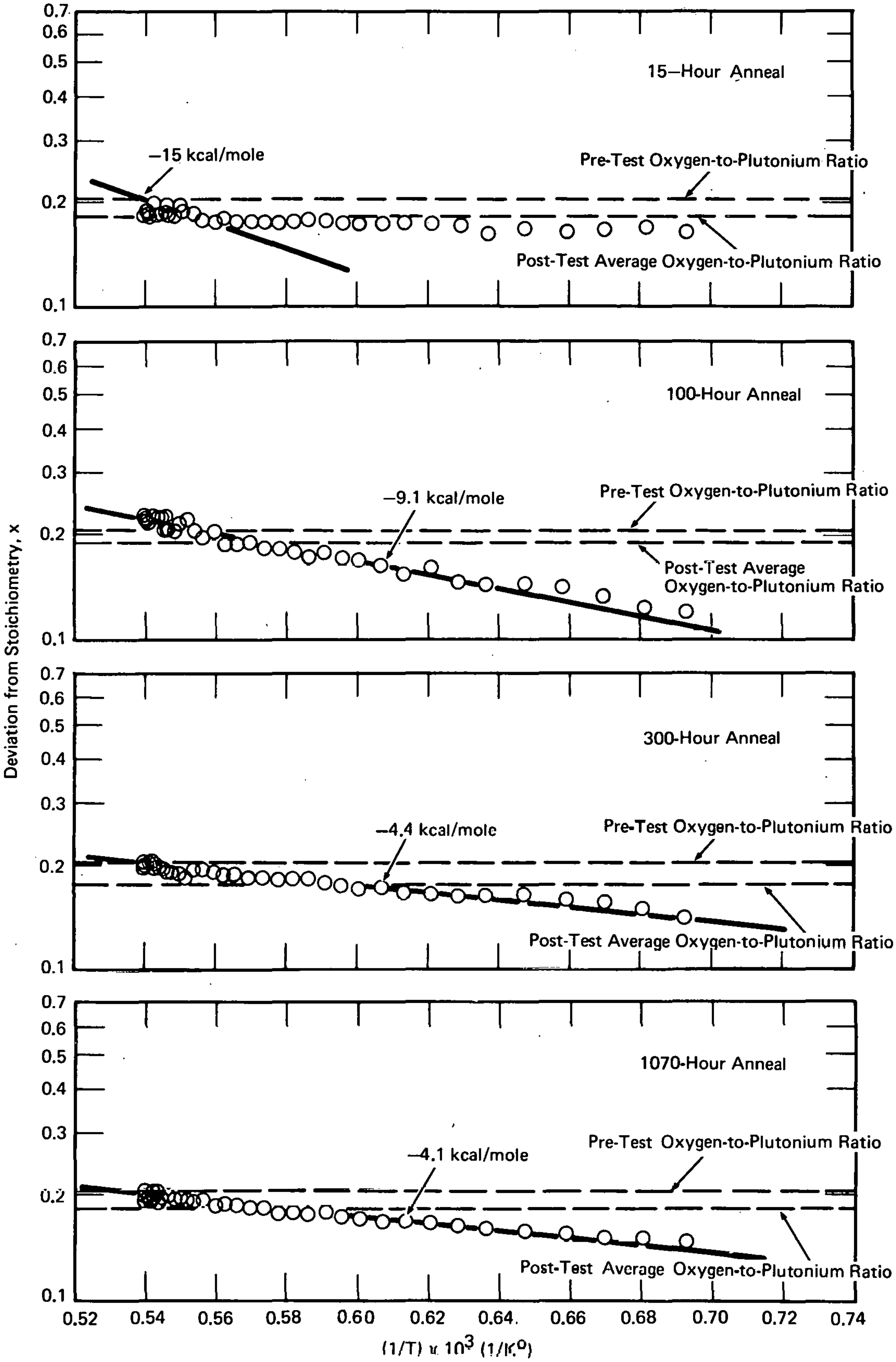

FIGURE 3. RESULTS OF PuO_{2-x} THERMAL GRADIENT EXPERIMENTS

From Equation (1),

$$Q^*_{eff_1}/Q^*_{eff_2} = \frac{1 + (L_{s_2}/L_g)}{1 + (L_{s_1}/L_g)}$$

For $L_{s_1}/L_g = 2.23$ and $L_{s_2} = 6.8\ L_{s_1}$, we have

$$Q^*_{eff_1}/Q_{eff_2} = 5.1$$

which is in excellent agreement with the difference observed.

In the one-component cyclic flow model proposed by Aitken,[2] the oxygen in the gas surrounding the pellets in the temperature gradient is in local equilibrium with the oxygen in the fuel. Since the mixed oxide and PuO_{2-x} 1000-hour anneal systems have similar oxygen activities, the oxygen activities in the gas phase would be similar and result in similar gas diffusion coefficients. Thus, the assumption of L_g remaining constant or nearly so between the mixed oxide and PuO_{2-x} of similar oxygen activity is not unreasonable.

The kinetic features of the approach to steady state are observable in the PuO_{2-x} data. The 15-hour anneal exhibits a larger negative value for the heat of transport than in longer time tests. The oxygen migration also demonstrates noticeable effect at the highest temperatures of the test. Longer time anneals exhibit oxygen migration throughout the pellet stack with less negative heats of transport observed as the annealing time is increased. The mixed oxide capsules show the same effect in the 300- and 1000-hour anneals, except that a possible interface reaction[5] in the mixed oxide capsules prevents extension of the oxygen-to-metal ratio gradient to the pellets at the lowest temperatures of the test. The interpretation of the kinetic phenomena is still under study.

Several new experiments are being planned to explore the validity of the ideas presented in this report. Thermal gradient experiments involving UO_2—20% PuO_2 pellets of 1.93 and 1.99 oxygen-to-metal ratios are planned to investigate effects of average stoichiometry on the oxygen migration. An experiment involving UO_2—40% PuO_2 pellets of about 1.82 oxygen-to-plutonium ratio is planned to investigate effects of plutonium content on the oxygen migration phenomena. These three experiments will provide information regarding the nature of the oxygen migration mechanisms by varying both the oxygen vacancy concentrations in the fuel and the average oxygen activity in the fuel.

Another experiment is planned to investigate the relative roles of solid state and gas phase oxygen transport at interfaces between adjacent pellets in the thermal gradient. To prevent the possibility of solid state diffusion PuO_{2-x} will be placed in a molybdenum capsule separated by molybdenum spacers. The effect of this blockage of solid state oxygen transfer on the heat of transport will be studied.

4. SODIUM-FUEL INTERACTIONS

The first set of nickel capsules containing sodium, sodium oxide, and urania-plutonia fuel was annealed at 850°C in an evacuated container. Eight hours after the heat treatment was begun, loss of vacuum occurred in the chamber, indicative of a rupture of one or more ot the capsule experiments. The experiment was terminated and the capsules removed. Weld defects were found in each capsule and resulted in some loss of sodium. Even though the test was terminated prematurely, oxygen analyses will be made on the residual sodium; the fuel residue will be analyzed as though the experiment had undergone a full 4-day anneal.

A new set of nickel capsules with the same characteristics as the first set is being fabricated with modifications to prevent recurrence of the weld defect problem. The capsules will be annealed at 600°C for 7 days. Following the anneal, the sodium and fuel will be characterized as described in the eighth quarterly report.

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