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GEAP-12032
AEC RESEARCH AND
DEVELOPMENT REPORT
SEPTEMBER 1969

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A THERMODYNAMIC DATA PROGRAM INVOLVING PLUTONIA AND URANIA AT HIGH TEMPERATURES

QUARTERLY REPORT NO. 8

MAY 1 THROUGH AUGUST 1, 1969

E. A. AITKEN
S. K. EVANS

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

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E. A. Aitken
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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
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Springfield, Virginia
Price: $3.00 per copy

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3204-NL-12
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ABSTRACT

In the Seventh Quarterly Report (GEAP-12027), 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 on these tasks.

In addition, the scope of new experiments in progress to study interactions in the sodium-urania-plutonia system is presented.

1. INTRODUCTION

This quarterly report is eighth in a series which describes experiments directed toward understanding plutonium segregation in urania-plutonia solid solutions used in fast reactor environments. In the seventh quarterly report (GEAP-12027) the progress in several experimental areas bearing on plutonium segregation was described along with a new analysis of a preferential vaporization mechanism for plutonia-urania segregation.

In this report, progress in these areas is described. Also, introductory experiments to investigate interactions of urania-plutonia fuels with sodium are described.

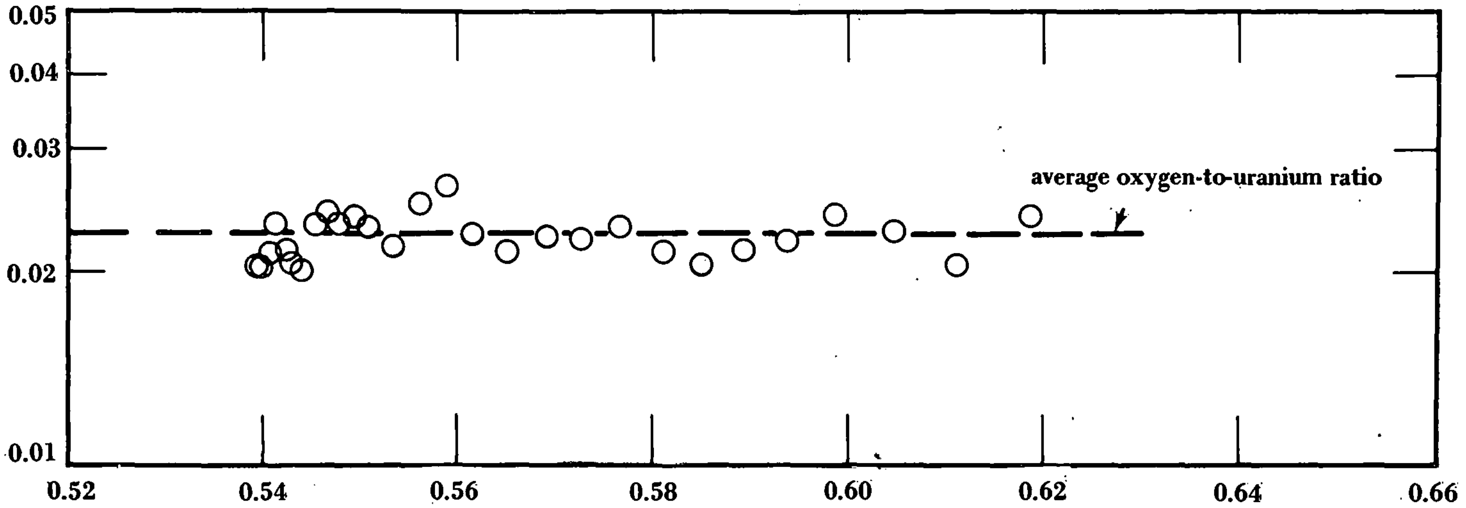
2. DETERMINATION OF COMPONENT ACTIVITIES

Transpiration experiments to determine uranium activity in urania-plutonia solid solutions are being carried out with air and CO/CO_2 as the carrier gas. Preliminary runs with U_3O_8 are continuing to establish the optimum flow rate for the system. Saturation of the carrier gas with uranium oxide vapors occurs for flow rates between 25 and 50 cc/min. At flow rates of 25 cc/min and below, diffusion of the vaporizing species into the platinum tube results in artifically high deposition rates. Under-saturation of the carrier gas by the vaporizing species at flow rates of 50 cc/min and above result in insufficient deposition. In continuing experiments, the size of the platinum tube orifice will be reduced to the limit diffusion of the uranium oxide vapor. Saturation of the carrier gas by the vapor will be extended to higher flow rates by use of larger amounts of U_3O_8 in the furnace hot zone.

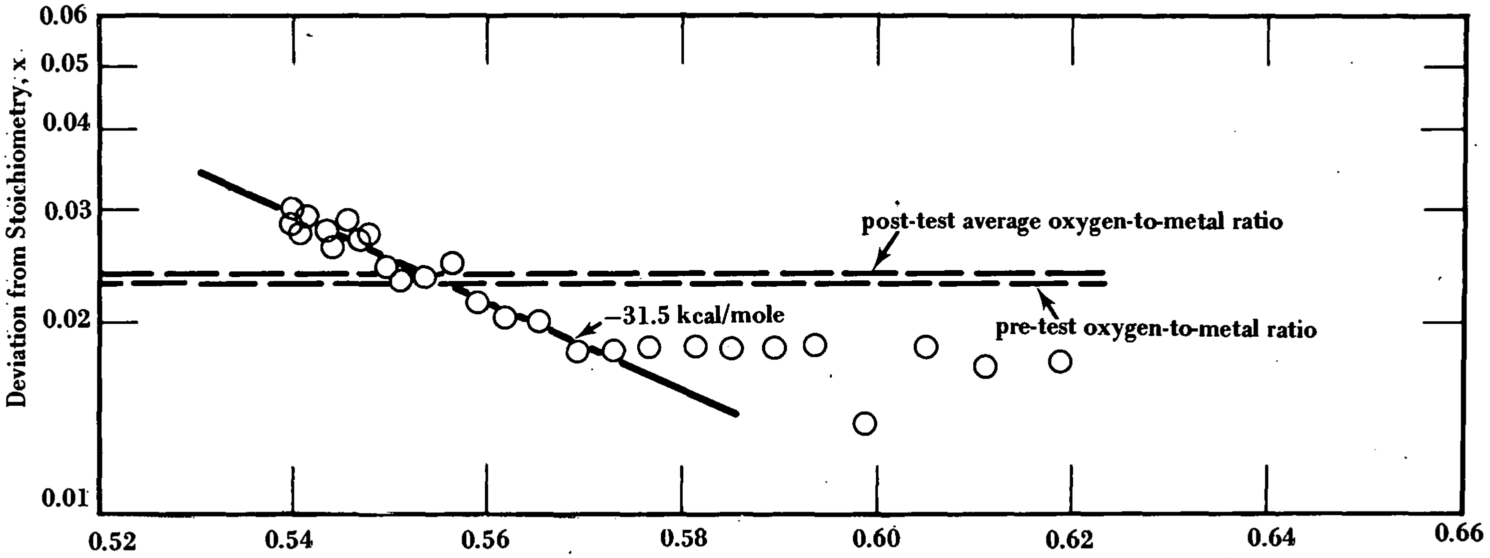
3. OXYGEN MIGRATION IN UO_2-20% PuO_2 AND PuO_{2-x} SYSTEMS

Molybdenum capsules containing hypostoichiometric UO_2 - 20% PuO_2 and PuO_{2-x} pellets have been heated in a temperature gradient from 1200 to 1600°C for periods up to 1070 hours. Results from mixed oxide capsules heated for 4 and 15 hours were presented in the sixth quarterly report (GEAP-5777). Similar data for mixed oxide capsules heated for 300 and 1000 hours and a PuO_{2-x} capsule heated for 1070 hours are presented here.

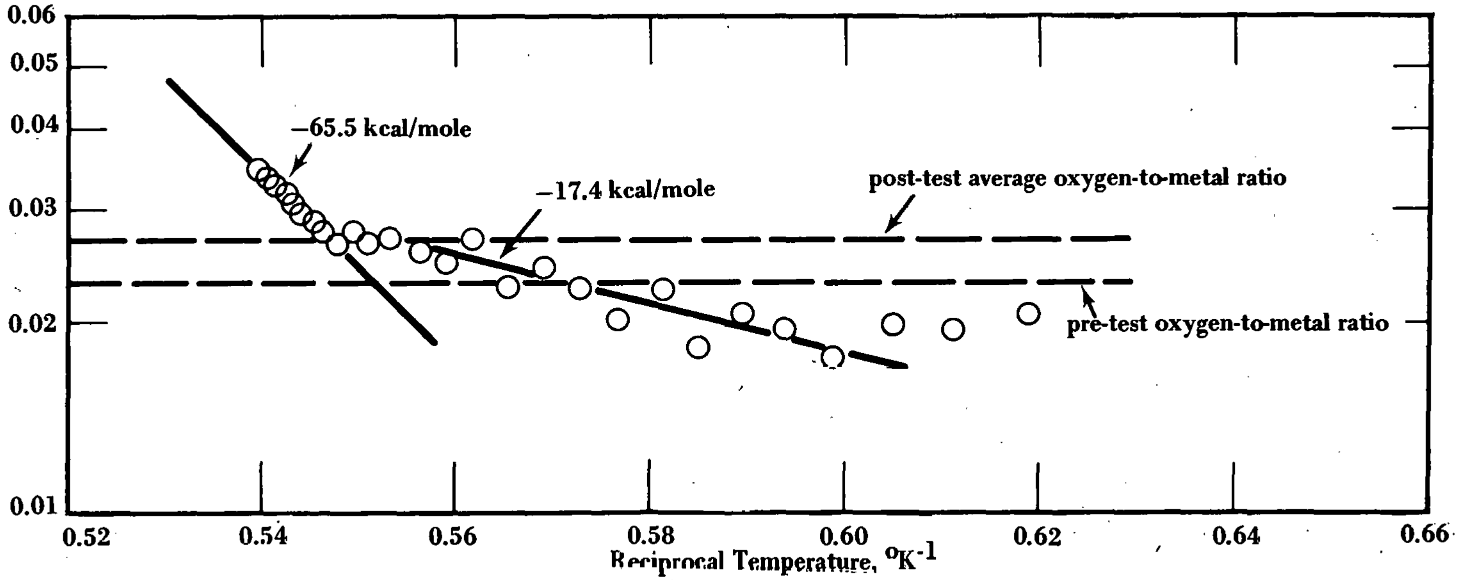
Following the described heat treatments, each capsule was cut open and the pellets removed. Thermogravimetric oxygen-to-metal ratio determinations were carried out on each of the pellets. Figure 1 shows Arrhenius plots relating the de-



$(U_{0.8}Pu_{0.2})\ O_{2-x}$ 15-Hour Anneal



$(U_{0.8}Pu_{0.2})\ O_{2-x}$ 300-Hour Anneal



$(U_{0.8}Pu_{0.2})\ O_{2-x}$ 1000-Hour Anneal

FIGURE 1. RESULTS OF $(U_{0.8}Pu_{0.2})\ O_{2-x}$ THERMAL GRADIENT EXPERIMENTS

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

The data indicate that the approach to a steady state in the thermal gradient is very slow and is not yet complete after 1000 hours. The observed heats of transport, therefore, are not representative of steady state and must be evaluated in terms of slowly varying behavior. The 15-hour capsule exhibits no observable oxygen migration at all which indicates only that more time is needed for the transport mechanisms to produce noticeable change.

At 300 hours, oxygen migration is evident, but the low temperature regions of the capsule show no gradient in the oxygen activity. The observed heat of transport for the high temperature portion of the capsule is -31.5 kcal/mole, which is a factor of 3 more negative than heats of transport reported for similar composition at higher temperatures.(1) It is difficult, however, to make meaningful comparisons since the current data are not at steady-state conditions. During the high temperature study, it was noted that where steady-state was not reached, those pellets not participating in the oxygen migration remained essentially at the average initial oxygen-to-metal ratio. In the current study, the low temperature pellets contain more oxygen than the initial average, at the highest oxygen-to-metal ratio in the capsule.

The circumstances are similar with the capsule containing $(U_{0.8}Pu_{0.2})O_{2-x}$ heated for 1000 hours in a temperature gradient, except that the oxygen composition gradient extends to about 1420°C compared to 1480°C for the 300-hour capsule. Presumably with tests of a longer duration, the composition gradient region would extend to lower temperatures.

Two discernible heats of transport are evident in the 1000-hour mixed oxide anneal. The high temperature slope of -65.5 kcal/mole was reported in the sixth quarterly report (GEAP-5777). The intermediate slope exhibits a heat of transport of -17.4 kcal/mole. It is difficult to say whether or not the high temperature heat of transport represents a truly different mechanism or is an experimental artifact since the 95/95 confidence limits on the stoichiometry determination are $\pm$ 0.003. In any event, the lower temperature heat of transport for the 1000-hour anneal is significantly less negative than that for the 300-hour anneal. This difference may indicate that, as steady-state is approached, the heat of transport reaches a less negative value. A possible contributing factor in a trend to a larger (arithmetically) value for the heat of transport in the 1000-hour case is that loss of oxygen through the molybdenum cladding has significantly lowered the average oxygen-to-metal ratio in the 1000-hour capsule. In higher temperature thermal gradient experiments, the heats of transport become less negative as the average oxygen-to-metal ratio was lowered, therefore, the same effect may be taking place in this study.

The heats of transport measured in this work are generally more negative than for higher temperature studies. According to Aitken's one component cyclic model for oxygen migration,(2,3) an effective heat of transport may be defined as follows:

$$Q^*_{eff} = \frac{Q^*}{[1 + (Ls/Lg)]}$$

where Q^* is the heat of transport resulting from oxygen transport 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 oxygen migration in the gas phase becomes relatively more important than solid state oxygen diffusion as the temperature is decreased, then numerically larger values for the heat of transport will result at lower temperatures. It may be that interfaces between pellets in the stack become more important at low temperatures and decrease the relative importance of solid state diffusion.

None of the mechanisms described so far explain the gradient-free uptake of oxygen at the lowest temperatures of the experiments. A possible explanation for this phenomenon may be that an oxygen exchange mechanism at the solid-gas interface controls the reaction at low temperatures. If this is the case, the low-temperature pellets in the capsule would pick up oxygen at a rate prescribed by this mechanism. Then as the experiment progressed, the lowest temperature pellets would gradually assume higher oxygen-to-metal ratio. The junction between the gradient part and the constant composition part of the Arrhenius plot would gradually move to lower temperatures and higher oxygen-to-metal ratios until the composition gradient extended throughout the system.

Thermal gradient experiments are in progress to determine oxygen migration behavior in PuO_{2-x} in a temperature gradient. These experiments are necessary to relate mixed oxide behavior to the end members of the binary system. Markin and McIver(4) have shown that oxygen activity in the hypostoichiometric (U,Pu) O_2 mixed oxide system is a function of oxygen-plutonium ratio for compositions ranging from 10 to 30% Pu. Thus, knowledge of the PuO_{2-x} system is of greatest importance in interpretation of behavior in the solid solution with uranium. Figure 2 represents an Arrhenius plot relating the deviation from stoichiometry, x, to the reciprocal temperature for the 1070 hour anneal of a PuO_{2-x} capsule in the same temperature gradient used for the mixed oxide capsules. The similar plot for the 1000-hour mixed oxide capsule is reproduced for comparison. The heat of transport measured from the PuO_{2-x} data is -4.1 kcal/mole. Besides the numerically smaller heat of transport measured for the PuO_{2-x} capsule, a significant difference between it and the corresponding mixed oxide capsule is the absence of a gradient-free composition region at the low temperature end of the capsule. If we accept the basis of an interface reaction controlling the oxygen migration at low temperatures, then such a reaction is more rapid in PuO_{2-x} than in the mixed oxide. Oxygen permeation through the cladding has resulted in an increase in oxygen-plutonium ratio during the test from 1.797 to 1.817. This increase in oxygen content of the pin (although in the opposite direction from the decrease in oxygen noted in the mixed oxide pins) is consistent with the expected oxygen activity of the furnace atmosphere surrounding the pins during the anneals.

4. SODIUM-FUEL INTERACTIONS

The use of liquid sodium as a coolant for fast reactors and the inevitable juxtaposition of sodium with urania-plutonia fuel through either sodium bonding or fuel pin failure renders a study of sodium interactions with fuel to be of utmost importance. Aitken(5) has reviewed the thermodynamic behavior of the sodium-oxygen system and its probable effects on urania-plutonia fuels. Several points are evident from his study. The reducing power of sodium is insufficient to remove oxygen from stoichiometric mixed oxides unless the oxygen impurity in the sodium is less than 100 ppm. Sodium monouranate is formed when hyperstoichiometric urania is in the presence of excess sodium oxide. If sodium is not saturated with sodium oxide in contact with UO_{2+x} some of the excess oxygen in the urania is consumed to produce Na_2O, but some Na_2UO_4 is also formed. In the case of UO_2 - 20% PuO_2, comparable sodium-fuel compounds may be formed for oxygen-to-metal ratios as low as 1.95.

For UO_2 in the presence of excess sodium, Pepper, Stubble, and Tottle(6) have shown that Na_3UO_4 is formed rather than Na_2UO_4. They indicate that the pentavalent uranium compound is more stable than the hexavalent compound in a sodium environment. With excess sodium and the presence of Na_3UO_4 phase, the oxygen content of sodium was invariant at 850°C in the range $+ 2.0 <$ oxygen-to-uranium < 3.0. The oxygen content was approximately 175 ppm which represents a measure of the oxygen activity threshold for formation of the sodium-fuel compound.

Keller, Koch, and Walter(7) have observed the formation of Na_3PuO_4 by direct reaction of Na_2O and PuO_2 in air at 600°C. Formation of sodium-fuel compounds were observed by Aitken and Evans(8) during an isothermal anneal of hyperstoichiometric UO_2 - 20% PuO_2 in a sodium environment at 750°C for 1000 hours. The reaction caused swelling to the extent of significant cladding deformation.

The presence of such compounds and their attendant volume expansion necessitates a study of the conditions for their formation and the thermodynamic properties to understand their role in fuel behavior. Such a study is now in progress to investigate the formation of these compounds and determine some of their properties.

Since no work is available on characterization of sodium-uranium-plutonium-oxygen compounds in a sodium environment, such as might be expected with sodium bonding or fuel pin failure. Experiments will be carried out by encapsulating the fuel materials and sodium in nickel capsule assemblies containing two small capsules separated by 1/8 in. nickel tubing. The fuel will be placed in one side only. The capsules will then be welded shut and heated to 850°C for 4 days. Following the heat treatment, the tubing separating the capsule sides will be pinched off and the sodium from the nonfuel side will be analyzed for oxygen content. The sodium from the fuel side will be mercury extracted and analyzed for oxygen also. The fuel compound will be pressed into a pellet and hopefully sintered into a dense mass; metallography

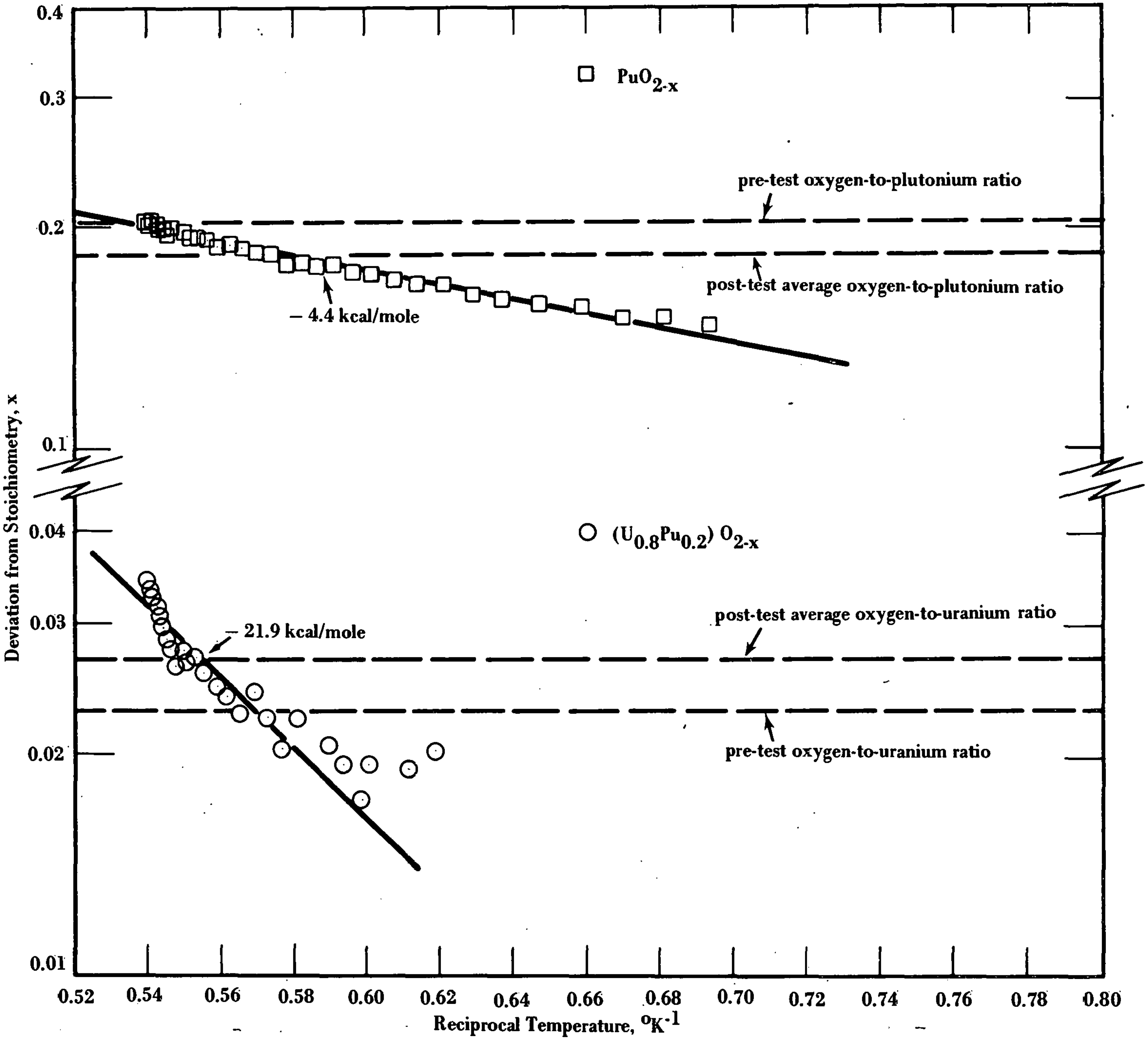


FIGURE 2. RESULTS OF THERMAL GRADIENT EXPERIMENTS – PuO_{2-x} 1070-HOUR ANNEAL AND UO_2 - 20% PuO_2 1000-HOUR ANNEAL

and x-ray analysis will then be performed on the pellet. A sample of the residue will be leached in water, then analyzed for sodium-to-heavy metal ratio.

The first experiment essentially will duplicate the work of Pepper, et al., by adding an excess of sodium to a predetermined amount of UO_2 and Na_2O. The second experiment will duplicate experiment 1 except that coprecipitated UO_2 - 20% PuO_2 powder will be used instead of UO_2. In the third experiment, physically blended UO_2 - 20% PuO_2 will be used to determine whether preferential reaction of the sodium with uranium or plutonium occurs. The fourth experiment will contain sodium only and will furnish a blank to be used in the oxygen analysis.

Nickel capsules have been fabricated for the four experiments. Fuel will be added and the capsules heat treated and examined during the next report period.

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