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SUBJECT: The Effects of Temperature and Composition on the Mercury
Vapor Pressure in the Uranium-Mercury System

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ABSTRACT

The use of mercury as a solvent in the recovery of uranium from spent fuels is of interest at Oak Ridge National Laboratory. The vapor pressure of mercury is lowered by increased concentration of uranium. By dew-point measurements, the vapor pressure at 175°C was found to vary between 2 and 8 mm of mercury, and at 375°C, between 300 and 1100 mm of mercury, depending upon composition as described below. Plots of the log of mercury vapor pressure vs the reciprocal of absolute temperature gave a family of straight lines. Each line corresponded to one of the compositions: UHg_2 , UHg_3 , UHg_4 , and a saturated solution of UHg_4 in Hg. No mutual solubility of the intermetallics was indicated.

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1.0 INTRODUCTION

The work reported is the determination of the mercury vapor pressure over the three known intermetallic compounds of uranium and mercury. These three compounds have been characterized by the formulas UHg_2 , UHg_3 , and UHg_4 , and phase diagrams have been presented in two reports by B.R.T. Frost¹ at Harwell in England and by Ahman, Baldwin and Wilson² at Iowa State College.

Interest in the uranium-mercury system stems mainly from development work done at Oak Ridge National Laboratory on uranium recovery processes. Mercury has shown promise as a solvent for uranium in extraction processes³ and also as a medium for the controlled reduction of uranium compounds by using amalgams of such reducing agents as lithium, sodium, and magnesium.⁴ The products of such reductions were the uranium amalgams.

Calculation of optimum reaction conditions and heat effects requires data on the thermodynamic properties of the uranium amalgams. These thermodynamic properties are to be derived from the vapor pressure data.

2.0 PROCEDURE

Vapor pressure data on the uranium amalgams was determined by using a dew-point method. The basic method was developed by Hargraves and is described in Kubaschewski and Evans.⁵ The amalgam was sealed into an evacuated pyrex tube (Fig. 1), connected through a sintered glass filter disk to another pyrex tube. This second tube was approximately 5 in. long, 1/2 inch in diameter and had plane glass windows in each end. The entire system was placed in a Marshall furnace with the amalgam situated near one end, and one observation window near the other end. The tapped winding in the furnace made it possible to control the temperature at any place within the furnace. The procedure then was to allow the furnace, containing the glass apparatus, to reach an equilibrium with the surroundings at some temperature, controlled by the current input to the windings. Then, holding the amalgam end at this temperature, the other end was allowed to cool by shunting a portion of the heating current through external resistors, (Fig. 2). A source of light directed through the plane glass observation windows allowed observation of the cooler window for the first droplet of condensed mercury indicating the attainment of the dew point. The temperatures of the amalgam and of the cooled observation window were continuously recorded on two modified Brown Elektronik recorders, calibrated against a Leeds and Northrup K-2 potentiometer. Thermocouples were individually calibrated 40 gauge copper-constantan. Thus the vapor pressure of the amalgam at its recorded temperature was equal to the vapor pressure of pure mercury, as taken from the accepted literature values, at the temperature indicated for the cooled window. This vapor pressure was corrected for thermal lag and supersaturation effects by referring to a similar vapor pressure curve run in the apparatus on a sample of pure mercury. The vapor pressure was measured over the temperature range of 175-375°C on two or three different compositions in each of the composition ranges: $\text{U} + \text{UHg}_2$, $\text{UHg}_2 + \text{UHg}_3$, $\text{UHg}_3 + \text{UHg}_4$, and $\text{UHg}_4 + \text{excess Hg}$.

Fig. 1. Vapor Pressure Sample Tube

Scale 3/4" = 1"

Fig. 2. Furnace Set Up and Control

Not to scale

All amalgam samples were prepared from purified, depleted uranium, and mercury which had been acid washed and doubly distilled. The uranium was reduced to a fine powder by hydriding and dehydriding. Sample preparation was done in the vapor pressure sample tube, under high vacuum ($0.5-2.0 \times 10^{-6}$ mm Hg) on a special apparatus which will be fully described in a final report.

3.0 RESULTS

The corrected vapor pressure curves are shown in Figure 3. Figure 4 shows several curves of isothermal vapor pressure vs composition of the type to be used in the calculation of the thermodynamic data. The portion of these curves between 99 and 100 atm % mercury were estimated from solubility data recorded by A. F. Messing.⁶

4.0 CONCLUSIONS

1. Correlation of the data by means of log of the vapor pressure vs the reciprocal of the absolute temperature plots shows a high degree of precision.
2. Variation of isothermal vapor pressure of several compositions within a given composition range, for example, between UHg_2 and UHg_3 , indicated no mutual solubility of the intermetallic compounds. This agrees with information in the literature.^{1,2,7}
3. Extrapolation of the curves to 760 mm Hg indicates the decomposition temperature for the intermetallic compounds at one atmosphere system pressure. Comparison of these temperatures with the decomposition temperatures as shown on the phase diagram of Ahman, Baldwin, and Wilson² is shown in Table 1. The phase diagram data was obtained by thermal analysis. Fair agreement is shown if it is noted that these investigators did not find a distinct temperature of decomposition for the saturated solution but only for the decomposition of the intermetallics. However their original thermal analysis curve indicated a definite change of slope at 425°C , which then supplies the missing point.

Table 1. Decomposition Temperatures of U-Hg Intermetallic Compounds at One Atmosphere Pressure

Compound	Decomposition Temperature - $^\circ\text{C}$		
	Present Work	From Phase Diagram of Wilson ² et al.	Modified from Wilson Data
Saturated solution of UHg_4 in Hg	368		365
UHg_4	383	365	390
UHg_3	412	390	425
UHg_2	431	460	460

Using the decomposition temperatures at one atmosphere total pressure which resulted from the present work, the phase diagram of Wilson² et al. was modified and is presented in Figure 5. Very similar results were obtained for the uranium-zinc system by Chiotti, Klepfer, and Gill⁸ at Iowa State in 1957.

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Fig. 4 Isothermal Vapor Pressure vs Composition Curves

Fig. 5 Uranium - Mercury Diagram Under 1 Atmosphere Pressure

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