

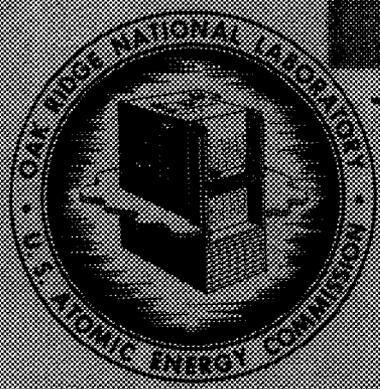
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THERMODYNAMIC PROPERTIES OF
THE URANIUM MERCURIDES
H. C. Farnberg

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Chemical Development Section B

THERMODYNAMIC PROPERTIES OF THE URANIUM MERCURIDES

H. C. Forsberg

This report was prepared as a thesis and submitted to the Faculty of the Graduate School of the University of Louisville in partial fulfillment of the degree of Doctor of Philosophy in the Department of Chemical Engineering.

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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. By means of vapor pressure measurements, using a dew point method, the mercury vapor pressure of the uranium-mercury system was determined as a function of both composition and temperature. The ΔF , ΔH , and ΔS of formation of three intermetallic compounds formed from uranium and mercury were calculated. The phase diagram for the system was re-evaluated and corrected. The relationships determined, which are applicable between the temperatures 175 and 375° C, are:

Vapor Pressures:

$$\text{For compositions between U and UHg}_2 \quad \log p = 7.29890 - 3134.83/T$$

$$\text{Between UHg}_2 \text{ and UHg}_3 \quad \log p = 7.55460 - 3226.21/T$$

$$\text{Between UHg}_3 \text{ and UHg}_4 \quad \log p = 7.88899 - 3351.89/T \text{ below } 300^\circ \text{ C}$$

$$\log p = 8.71063 - 3829.23/T \text{ above } 300^\circ \text{ C}$$

Between UHg₄ and Saturated solution of U in Hg

$$\log p = 7.78021 - 3132.74/T$$

Thermodynamic Equations of the Form $\Delta F_f = \Delta H_f - T \Delta S_f$

$$\text{For UHg}_2 \quad \Delta F_f = - 91.663 - 4.987T$$

$$\text{For UHg}_3 \quad \Delta F_f = - 555.467 - 6.312T$$

$$\text{For UHg}_4 \quad \Delta F_f = - 1594.130 - 6.106T \text{ below } 300^\circ \text{ C}$$

$$\Delta F_f = - 3777.484 - 2.348T \text{ above } 300^\circ \text{ C}$$

The corrected phase diagram is shown in Fig. 16.

CONTENTS

	<u>Page</u>
Introduction	1
Review of the Literature	3
Theoretical	12
Experimental	21
Data and Results	38
Discussion	50
Literature Cited	55

INTRODUCTION

The purpose of the work reported in this paper was to determine additional information about the phase relationships in the mercury-uranium system, and to determine some of the thermodynamic properties of the three known intermetallic compounds formed by the system. This information was needed as part of a large-scale study on methods of nuclear fuel reprocessing and decontamination. A brief background of this problem may be obtained most readily from the introductory paragraphs of an as yet unpublished paper by O. C. Dean, A. F. Messing, and this author:⁽¹⁾

Uranium, thorium, and plutonium form with mercury series of intermetallic compounds of low stability. Although these intermetallics are quite pyrophoric, they are wetted and protected from oxidative atmospheres by excess mercury. The uranium-mercury compound UHg_4 , which is stable at 1 atmosphere at temperatures below 365°C , is soluble in mercury up to 1.2 atom per cent uranium at 356°C . The plutonium compound is nearly as soluble, but PuHg_3 is about one order less soluble. Since the noble fission products, e.g., ruthenium and molybdenum, have mercury solubilities from two to five orders less than uranium, good separations may be obtained. The more soluble alkaline earths and rare earths are oxidized preferentially and their oxides are not wetted by mercury, so they can be filtered from the hot uranium solution.

Uranium and thorium are readily recovered from mercury. The mercurides crystallize and can be filtered from solution at 25°C . Vacuum distillation at 800°C removes the remaining mercury to 10 ppm. The uranium may be melted in the same retort, but thorium appears as a massive but porous sintered billet with a density 75% of theoretical.

The chlorides of uranium and thorium have been reduced to their respective mercurides by alkali metal amalgams. Impurities have been eliminated from the amalgams by washing and the massive metals have been recovered. Uranium hexafluoride has been reduced to UHg_4 with lithium amalgam and the uranium recovered with a yield of 80%.

The phase relationships in the mercury-uranium and mercury-thorium systems have been studied. A corrected phase diagram and the thermodynamic properties have been worked out for the uranium system (the

present paper). A tentative phase diagram is presented for the thorium-mercury system. Solubilities of ruthenium, palladium, molybdenum, and zirconium in mercury saturated with uranium have been determined. Solubilities of gadolinium, neodymium, samarium, uranium, and thorium in mercury have also been determined. Decontamination factors for uranium metal from major fission products on a 100-g scale ranged from 10 to 10^4 .

Acknowledgment. This report is based upon a thesis submitted to the University of Louisville in partial fulfillment of the requirements for the doctoral degree. The report describes research carried out in the Chemical Technology Division at the Oak Ridge National Laboratory.

The research was supported by the Oak Ridge Graduate Fellowship Program of the Oak Ridge Institute of Nuclear Studies and was directed by a committee appointed by Dean Greg Stevenson of the University of Louisville Graduate School which was composed of Dr. Gordon C. Williams and Dean R. C. Ernst at the University of Louisville and Dr. O. C. Dean and Dr. A. F. Messing of the Chemical Technology Division, and J. O. Betterton of the Metallurgy Division of the Oak Ridge National Laboratory.

REVIEW OF THE LITERATURE

The literature contained only two significant and widely quoted articles on the uranium-mercury system. These gave the composition, lattice parameters, and decomposition temperatures for three intermetallic compounds and an estimate of the mutual solubilities of mercury in uranium and intermetallic components. They presented techniques for the preparation and handling of uranium amalgams but no vapor pressure data nor thermodynamic data.

The first of these is a report by Ahmann, Baldwin, and Wilson⁽²⁾ reporting on work done with the uranium-mercury system at the Iowa State College AEC installation around 1945. The abstract of this report describes very well what was done:

The U-Hg system has been studied by thermal analysis, vapor pressure-temperature curves, and X-ray diffraction. Three compounds exist: UHg_4 which decomposes at 360°C to UHg_3 and Hg(v) , UHg_3 which goes to UHg_2 and Hg(v) at 390°C , and UHg_2 which breaks down into U and Hg(v) at 460°C . There appears to be some solubility of U in Hg and of Hg in U but no mutual solubility between the compounds. Because of the pyrophoric nature of the amalgams, all work was done under vacuum or an inert atmosphere.

This work produced, from the x-ray investigation, the characterization constants for the crystalline lattices of UHg_2 and UHg_3 but not for UHg_4 . The constants for UHg_4 are reported, however, by Rundle.⁽³⁾ A proposed⁽²⁾ complete phase diagram at 1 atmosphere total pressure has been reproduced widely in the later literature (Fig. 1).

On that project several facts important to the present work were made definite, and a number of experimental techniques were developed which this author has used also. The fact that there were three, and only three, intermetallics in the U-Hg system - UHg_2 , UHg_3 , and UHg_4 - with little or no mutual solubility was established. The order of magnitude of the solubility of uranium in mercury at elevated temperatures, close to the normal

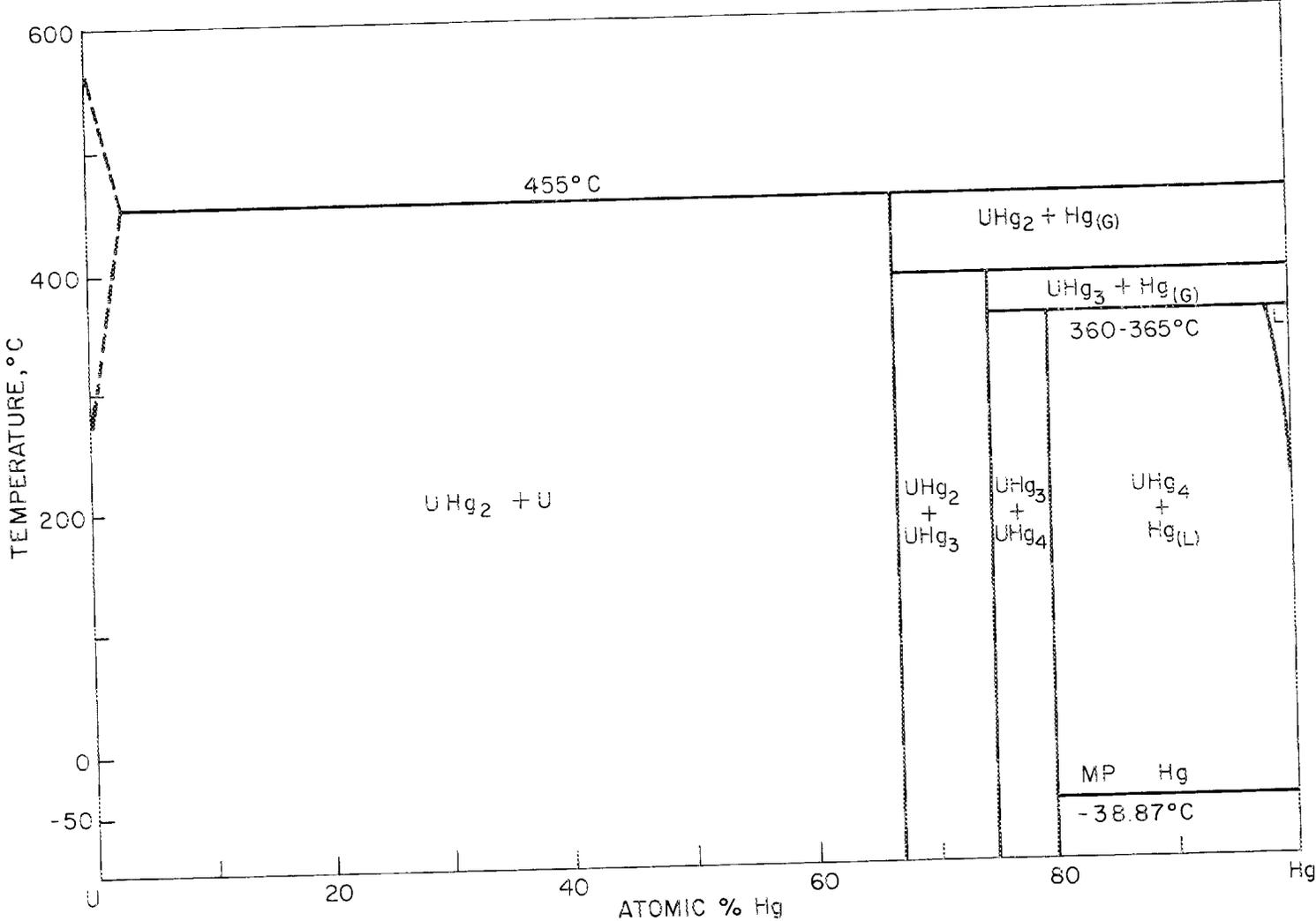


FIGURE 1. URANIUM-MERCURY DIAGRAM UNDER 1 ATMOSPHERE PRESSURE.
FROM WILSON⁽²⁾.

boiling point of mercury, was placed at about 1%, which agrees well with the much later work of Messing.⁽⁴⁾ An experimental technique was developed for the preparation of uranium amalgams by first preparing finely divided uranium through hydriding and dehydriding under vacuum.

Wilson's abstract states that vapor pressure--temperature curves were used. Because the present work consists mainly of the determination of such vapor pressure curves, it must be pointed out that their work consisted in observing vapor-pressure surges during distillation of a uranium-mercury mixture originally containing a high mercury content. The temperatures at which these surges occurred were used as reinforcing evidence to the thermal analysis determination of decomposition temperatures of the amalgam intermetallics.

In his report, Wilson states that practically no work had been done on the uranium-mercury system before 1941 and gives references to but a few other papers, published since 1941. These contained little except a single prediction of a possible intermetallic compound.

The second significant publication on the uranium-mercury system was an A.E.R.E. report⁽⁵⁾ by Frost on work done at Harwell in England about 1953. It essentially duplicated the previously described effort at Iowa, as indicated by the abstract:

The alloy system uranium-mercury has been examined by means of x-ray, thermal, and micrographic analysis. The high volatility of mercury necessitated the development of a hydriding process for the preparation of the alloys. At all except very dilute concentrations the alloys were pyrophoric and all operations were carried out in vacuo.

The solid solubilities of uranium in mercury and of mercury in uranium were both very small. Three compounds were identified to which the formulae UHg_2 , UHg_3 , and UHg_4 were assigned. The crystal structures of UHg_2 and UHg_3 were derived and are discussed in relation to their melting points.

Frost's work differed from the other mainly by the fact that the thermal analysis specimens were all sealed in constant volume vials. Pressures encountered at the higher temperatures reached high values of over 100 atmospheres. The phase diagram produced by Frost (Fig. 2) was similar to the one previously described, but here liquid mercury was in equilibrium with the uranium-mercury compounds and with uranium even at temperatures far above the normal boiling point of mercury. Thus the phases present at the higher temperatures were reported differently by Frost than by Wilson et al., but the decomposition (or transition) temperature agreed.

It is of interest that in Wilson's paper a single example is shown of an actual thermal analysis curve and corresponding vapor pressure surge curve. There is shown one definite change in slope in the thermal analysis curve which, although there is no corresponding vapor pressure surge, does show an agreement with the present work. This curve is reproduced in Fig. 3, and the point mentioned is discussed later in this paper.

Much work has been done on the determination of the electrochemical and thermochemical properties of amalgams of metals other than uranium. The objective of this work was for the most part the determination of basic data on solutions which might increase the realm of knowledge of solutions in general. The very nature of the amalgams, as stated in a report of Richards and Daniels⁽⁶⁾ in 1919, "renders them more susceptible to varied investigation than that of many other types of solutions." Papers previous to 1915 included vapor pressure measurements on zinc, silver, gold, and bismuth amalgams^(7, 8) and discussion of emf measurements on the amalgams of zinc, tin, lead, thallium, indium, and cadmium.⁽⁹⁾ A recent publication⁽¹⁰⁾ compiles much of this data as phase diagrams.

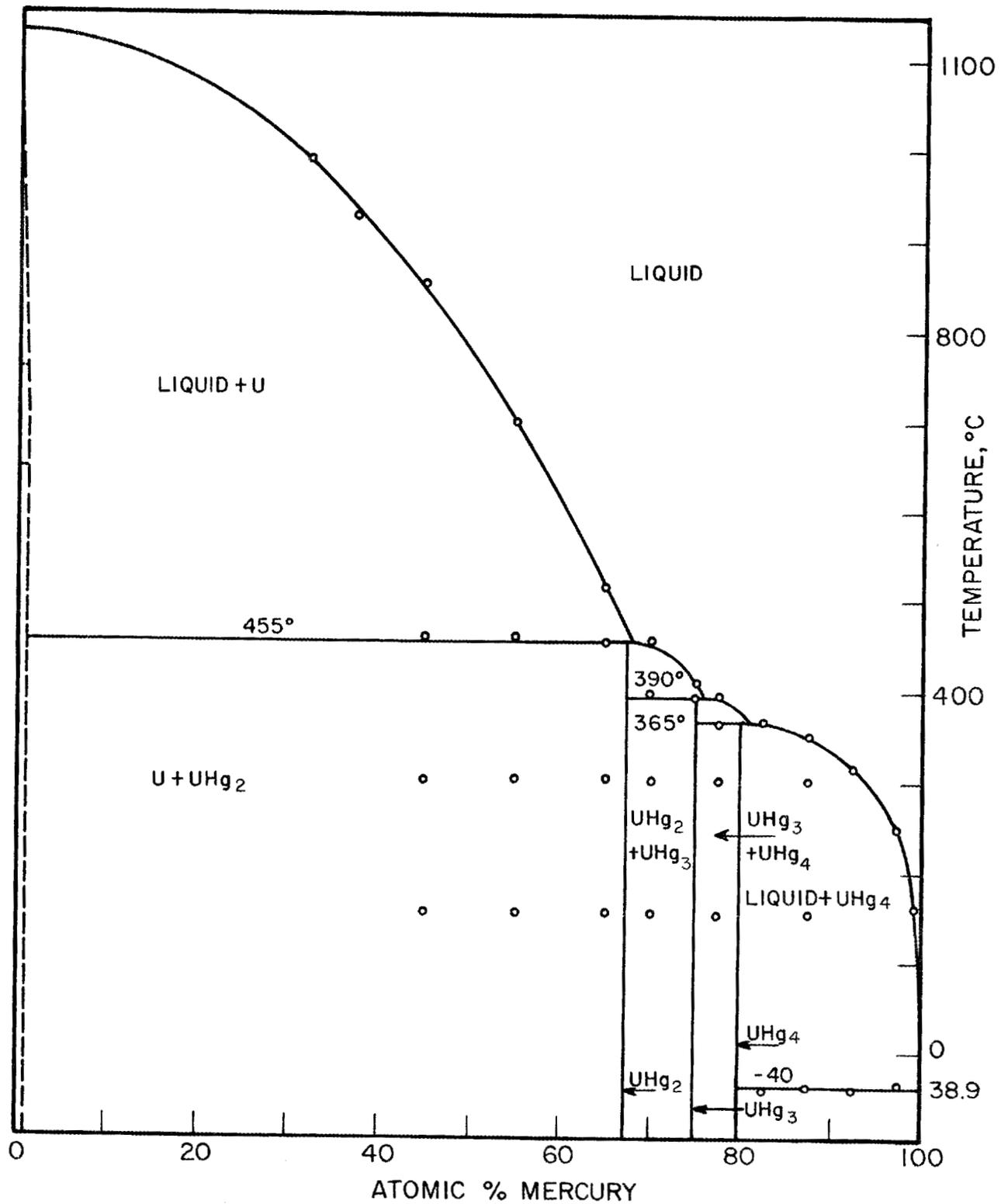


FIGURE 2. THE SYSTEM URANIUM-MERCURY SHOWING CRITICAL ALLOYS. FROM FROST⁽⁵⁾.

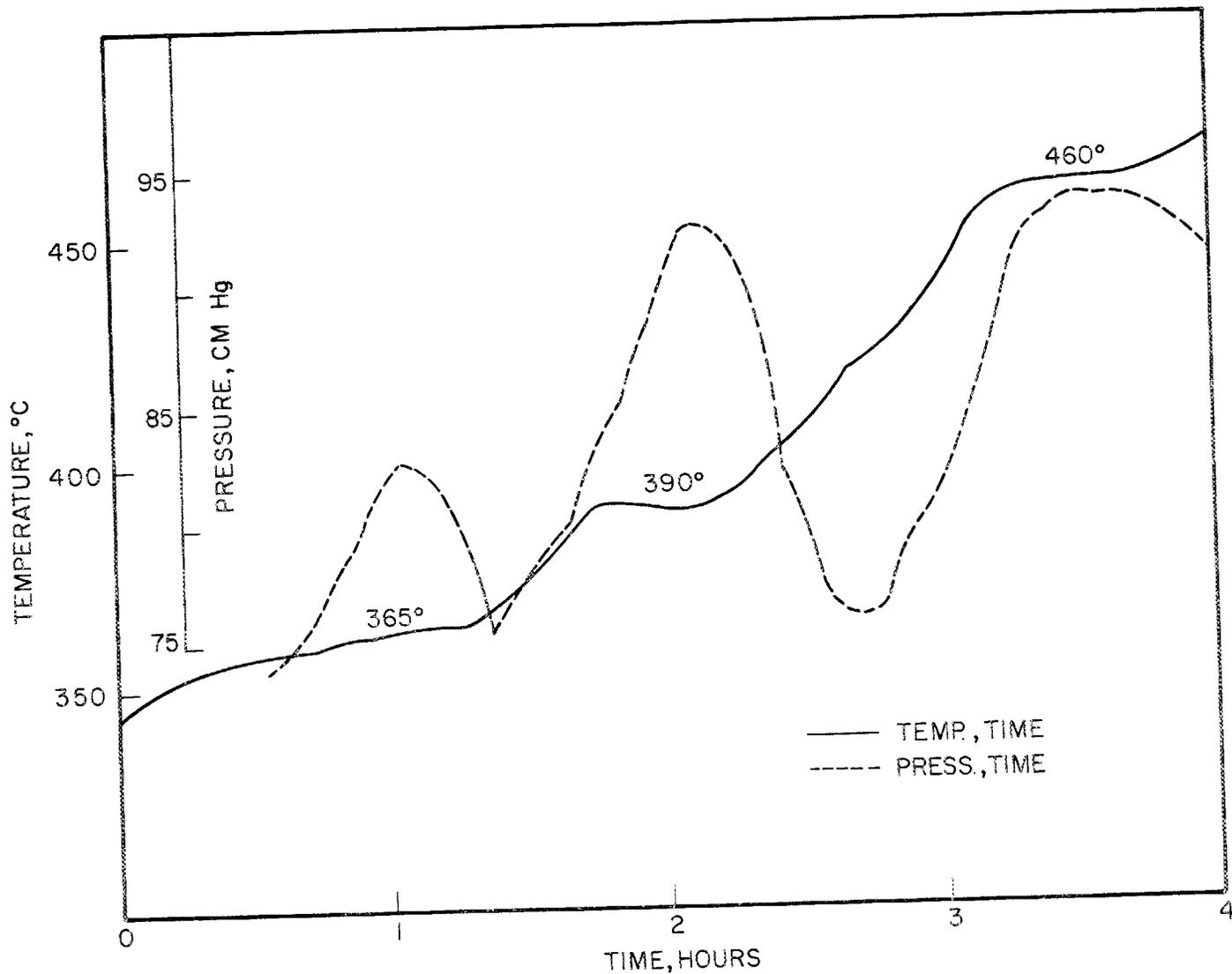


FIGURE 3. TEMPERATURE, PRESSURE, TIME CURVES FOR URANIUM-MERCURY SYSTEM. FROM WILSON⁽²⁾.

In 1915 Hildebrand and Eastman,⁽¹¹⁾ at the University of California, reported extensive work on the vapor pressure of thallium amalgams at approximately 318° C. They found the thallium amalgams to be of particular interest because of two rather special properties. In the thallium-mercury system only one compound, $TlHg_2$, existed in the solid state and this also existed in the solutions, and such amalgams were able to contain as high as 43% thallium at 20° C. Their vapor pressure measurements were made using a mercury manometer connected to a bulb containing the amalgam immersed in a molten salt thermostat. The system contained low-pressure hydrogen gas and was calibrated by means of a second identical system containing pure mercury in the bulb. This was the same equipment, described in a previous paper,⁽¹¹⁾ which had been used on bismuth amalgams. Measurements were made on compositions of from 22.1 down to 0.25 moles of mercury per mole of thallium. All data were for a single temperature, controlled between 323 and 329° C. These data were used to determine the deviation of this system from simple Raoult's law behavior and for the development of other vapor pressure equations and theories to explain the deviations. This information does not apply to the uranium-mercury system in the present investigation, but the interest of the workers and their laboratory methods opened the way to further efforts.

Practically every textbook on thermodynamics, when considering the subject of vapor pressure and emf data as a source of thermodynamic data, quotes or at least mentions the extremely detailed report of Richards and Daniels⁽⁶⁾ published in 1919: "Concentrated Thallium Amalgams: Their Electrochemical and Thermochemical Behavior, Densities and Freezing Points."

This paper is a masterpiece of completeness and detail and bespeaks of laboratory work in which no particular was slighted which might produce less than the very best results possible. The paper made a valuable contribution to this author's knowledge of equipment, methods, and fundamentals of calculation, specifically two other approaches to the problem that were presented. Both were considered in the early stages of this present work: emf measurements of amalgam concentration cells and a variety of calorimetric determinations.

In 1921 Lewis and Randall⁽¹²⁾ published a paper combining the works of Richards and Daniels⁽⁶⁾ and Hildebrand and Eastman⁽⁸⁾ entitled, "The Thermodynamic Treatment of Concentrated Solutions, and Application to Thallium Amalgams." Much of the theoretical treatment, covered in the later literature, stems originally from this work.

The literature contains a large number of papers covering electromotive force measurements of metal systems and the related thermodynamic determinations. Since this approach to the uranium-mercury system did not seem to afford too much hope of success because of the great chemical reactivity of uranium, these papers will not be discussed; however, it is felt they should be mentioned as a definite part of the general background of the problem and as a source of information for further work on this system or application to other systems not yet investigated.

Recent work reported using vapor pressure measurements is much less extensive than work using emf data. However, several papers were reviewed which described types of apparatus for such measurements.

Besides the rather crude method used by Eastman and Hildebrand⁽⁸⁾ work has been done on amalgams by a number of both static and dynamic methods.

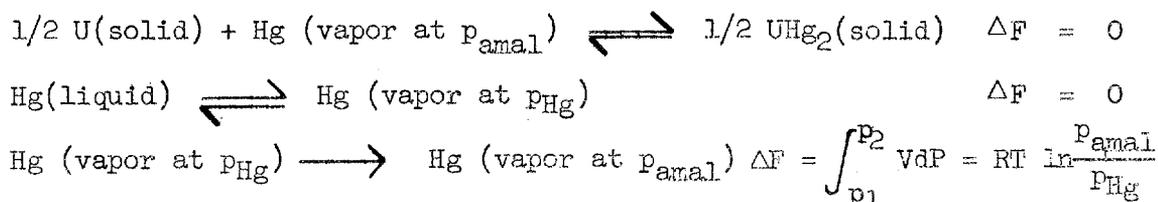
Most of these methods, including one similar to that used in the present work, are nicely described in the chapter on experimental methods in a recent book by Kubaschewski and Evans.⁽¹³⁾ Included among these are a method using the isoteniscope, several using manometers where either a known vapor pressure or an inert gas pressure is used as a standard, spectrographic measurement of metallic vapor concentrations, dew point methods, methods depending on diffusion of mercury from the amalgam to a body of pure mercury at a different temperature until equilibrium is reached, and effusion rates through an orifice. In addition an interesting method used by Buesman⁽¹⁴⁾ in determining vapor pressures of certain fused salt systems was the Rodebush-Dixon vapor pressure cell and was originally described in 1925.⁽¹⁵⁾

The experimental procedure used in the present work was originally proposed for liquids by Lescoeur in 1889,⁽¹³⁾ applied to metal systems by Hargreaves⁽¹⁶⁾ in 1939, and has been known under his name ever since. Variations of the dew point apparatus, fully described in the experimental section of this report, have been used recently on the uranium-zinc system by Chiotti⁽¹⁷⁾ and others at Iowa State and on the zirconium-cadmium system by Betterton⁽¹⁸⁾ and others at Oak Ridge National Laboratory. The results described in these two reports parallels the present work closely and is discussed in a later section.

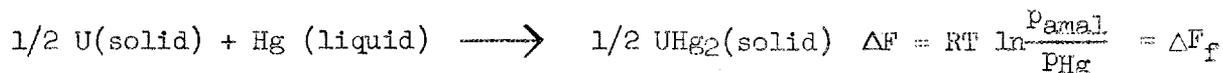
THEORETICAL

The uranium-mercury system forms three intermetallic compounds which are not mutually soluble.⁽¹⁹⁾ The only solubility found in the system is a maximum at 356° C of 1.2%⁽³⁾ uranium in mercury (by weight). The vapor phase in equilibrium with these compounds and solution at temperatures encountered in this work consisted of pure monatomic⁽²⁰⁾ mercury. On this basis the following thermodynamic calculations may be made.

For the determination of the standard free energy of formation, ΔF_f^0 , of the intermetallic compound UHg_2 three chemical equations must be considered:



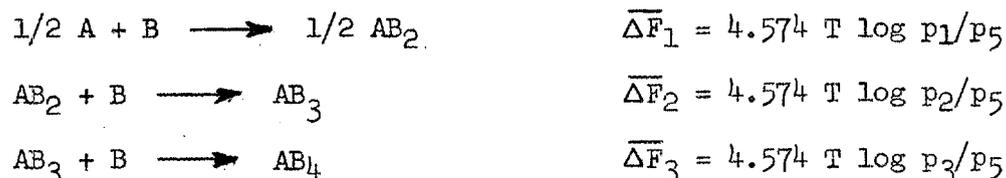
Addition of the three gives:



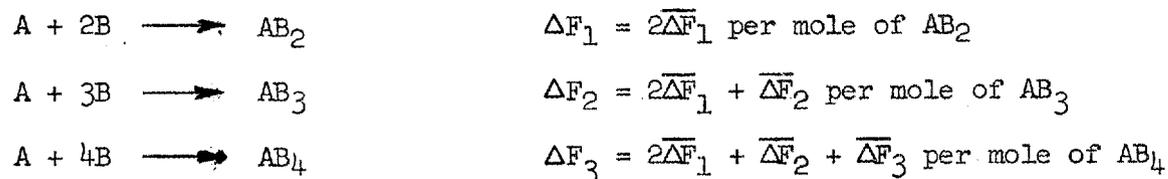
The first equation denotes a state of equilibrium between the two solids, and a gas phase consisting of pure mercury vapor, at a pressure which is the equilibrium decomposition pressure of the amalgam UHg_2 at the existing temperature. The second equation is for the isothermal vaporization of liquid mercury to mercury vapor at its equilibrium vapor pressure at the same temperature. By the very fact that both equations denote equilibrium, ΔF for each reaction is zero. The third equation denotes an isothermal expansion for which ΔF is expressed as a function of the pressure change. Any standard text such as the one by Klotz⁽²¹⁾ will show the fundamental developments used here, but it should be again pointed out that the assumption of ideal conditions has been made and is justified in this case.

For the final equation, considering standard state for solids and liquids as the usual state at the existing temperature, the ΔF can be seen to be actually the standard free energy of formation ΔF_f^0 . Likewise, since $\Delta F_f^0 = -RT \ln K_p$, then $K_p = p_{\text{Hg}}/p_{\text{amalg}}$. According to Kubaschewski and Evans⁽¹³⁾ the uranium-mercury system can be considered as one in which only the mercury is volatile, and UHg_2 , UHg_3 , UHg_4 , and a solution of UHg_4 in excess mercury are condensed phases. Schematically, letting A = uranium and B = mercury, an isothermal vapor pressure curve would appear as shown in Fig. 4 where p is the vapor pressure.

The free energy changes of each reaction step may be expressed as follows, noting that $2.303 R = 4.574$, giving ΔF in calories per mole of B:



where $\overline{\Delta F}$ indicates a partial quantity. Then the integral free energies in calories per mole of compound are given by:



Thus from the vapor pressure determinations the standard free energies of formation for the intermetallic compounds UHg_2 , UHg_3 , and UHg_4 can be determined.

Owing to the fact that the system under consideration is a metallic system, it was felt that the method of determination of the thermodynamic properties should also be developed by the methods of metallurgical thermodynamics. Thus, following the presentation of Wagner,⁽²²⁾ an extensive

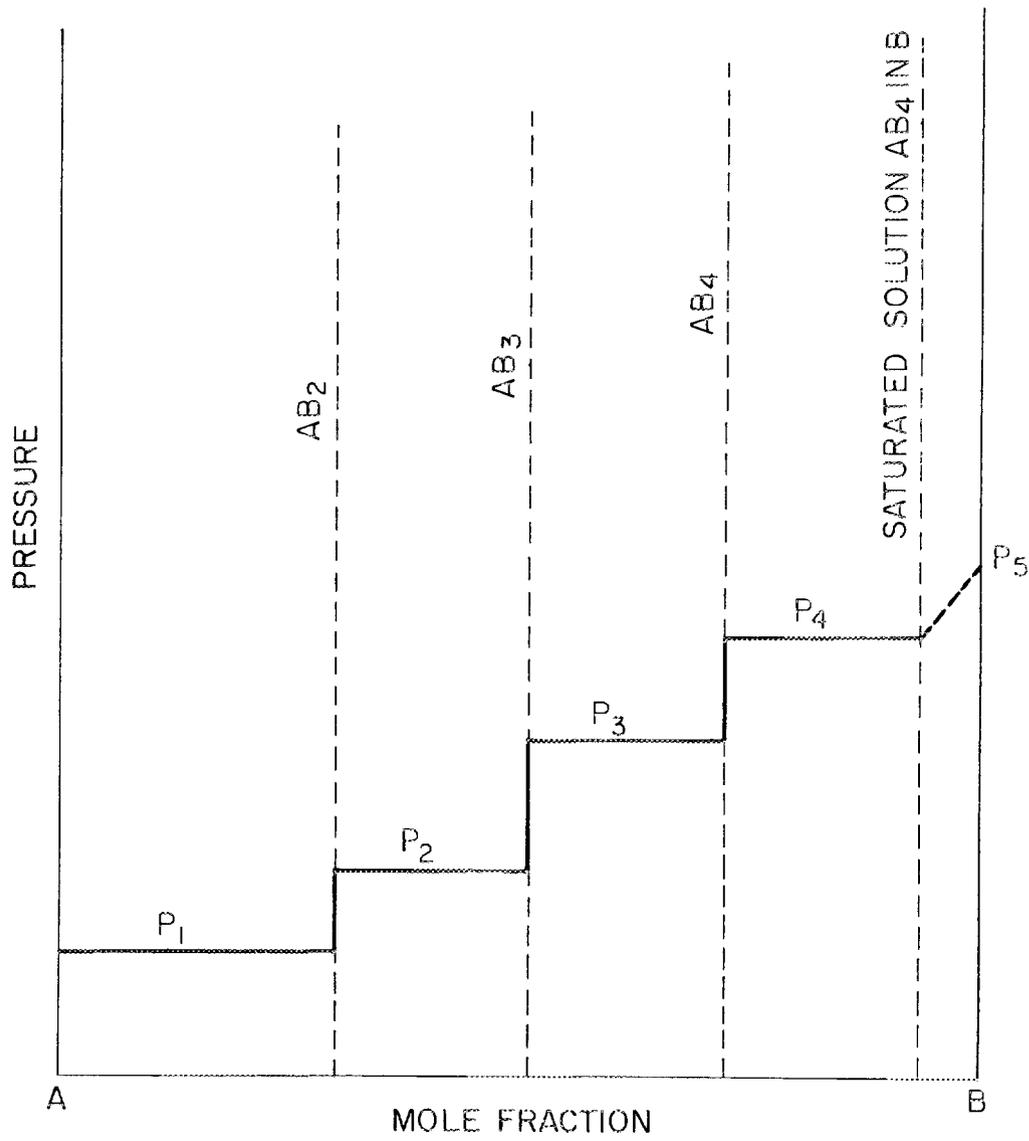
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FIGURE 4. ISOTHERMAL VAPOR PRESSURE.

thermodynamic property, which might be called G , is a homogeneous function of degree 1. At fixed temperature T and pressure P , such a function may be written $G = f(n_1, n_2)$ for a two-component system containing n_1 moles of component 1 and n_2 moles of component 2. To such a function Euler's theorem is applicable, giving:

$$n_1 \left(\frac{\partial G}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{\partial G}{\partial n_2} \right)_{n_1} = G \quad (1)$$

Defining the two partial derivatives as partial molar quantities:

$$\frac{\partial G}{\partial n_1} = \bar{G}_1 \text{ and } \frac{\partial G}{\partial n_2} = \bar{G}_2 \quad (2)$$

we can then write:

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2 \quad (3)$$

If this is divided by the total moles, $n_1 + n_2$, the quantity on the left-hand side of the equation becomes a molar quantity G_m , and the products of the mole fractions x_1 and partial molar quantities \bar{G} appear on the right:

$$G_m = x_1 \bar{G}_1 + x_2 \bar{G}_2 \quad (4)$$

Taking the total differential of equation (3):

$$dG = n_1 d\bar{G}_1 + \bar{G}_1 dn_1 + n_2 d\bar{G}_2 + \bar{G}_2 dn_2 \quad (5)$$

However from the definition of the partial molar quantities it follows that a property change dG caused by changing the number of moles by dn_1 and dn_2 equals:

$$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 \quad (6)$$

Comparison of equations (5) and (6) shows that:

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 = 0 \text{ or } x_1 d\bar{G}_1 + x_2 d\bar{G}_2 = 0 \quad (7)$$

noting that the relationship is valid only at constant T and P .

In equation (7) the differentials $d\bar{G}_1$ and $d\bar{G}_2$ are the changes in the partial molar quantities due to changes in composition, P and T being held constant. In a binary system the mole fraction x_2 is the only independent variable required for defining the composition. Thus equation (7) may be written:

$$x_1 (\partial \bar{G}_1 / \partial x_2)_{P,T} + x_2 (\partial \bar{G}_2 / \partial x_2)_{P,T} = 0 \quad (8)$$

In order to introduce a reference state necessary for complete definition of the functions of energy and entropy, a new quantity is defined, the relative partial molar quantity. $\Delta \bar{G}_i = \bar{G}_i - \bar{G}_i^{\circ}$ where \bar{G}_i° represents the partial molar quantity of component i, when it exists as a pure material.

At this point the general thermodynamic property G will be replaced by the free energy function F. Thus the relative partial molar free energy is the change in total free energy upon mixing 1 mole of pure substance i with an infinite quantity of a solution of given composition, at fixed T and P:

$$\Delta \bar{F}_i = \bar{F}_i - \bar{F}_i^{\circ} \quad (9)$$

As suggested by Wagner one experimental method for producing the process of reversible and isothermal mixing is by means of isothermal distillation. In the case of ideal behavior of the gas phase, the following expression results:

$$\Delta \bar{F}_i = RT \ln p_i / p_i^{\circ} \quad (10)$$

In this expression, R is the universal gas constant, p_i° is the partial vapor pressure of the pure metal, and p_i is the partial vapor pressure of the metal over the solution.

The Gibbs-Duhem relationship for free energy analogous to equation (8) is:

$$x_1 (\partial \Delta \bar{F}_1 / \partial x_2)_{P,T} + x_2 (\partial \Delta \bar{F}_2 / \partial x_2)_{P,T} = 0 \quad (11)$$

Now if the relative partial molar free energy of component 2 is measured as a function of x_2 , then the relative partial molar free energy of component 1 can be computed:

$$\Delta\bar{F}_1(x_2) = - \int_0^{x_2} \frac{x_2}{1-x_2} \left(\frac{\partial\bar{F}_2}{\partial x_2} \right) dx_2 \quad (12)$$

The lower integration limit is determined by the condition $\Delta\bar{F}_1 = 0$ for the pure substance 1, i.e., $x_2 = 0$. If equation (12) is integrated by parts:

$$\Delta\bar{F}_1(x_2) = \int_0^{x_2} \frac{\Delta\bar{F}_2}{(1-x_2)^2} dx_2 - \frac{x_2\Delta\bar{F}_2}{1-x_2} \quad (13)$$

Similar to the relative partial molar quantities for individual components, relative integral molar quantities can also be defined, and thus, by analogy with equation(4):

$$\Delta F_m = x_1 \Delta\bar{F}_1 + x_2 \Delta\bar{F}_2 \quad (14)$$

This is the change in free energy for the reversible and isothermal formation of 1 mole of alloy from x_1 mole of component 1 and x_2 mole of component 2.

If it is desirable to compute the concentration dependence of the relative integral molar free energy from measured values of the relative partial molar free energy of one component, this can be done by substituting equation (13) into (14):

$$\Delta F_m = (1-x_2) \int_0^{x_2} \frac{\Delta\bar{F}_2}{(1-x_2)^2} dx_2 \quad (15)$$

The above relations describe the behavior of a single phase. In heterogeneous systems the sum of the extensive thermodynamic functions for the individual phases equals the corresponding function for the entire system. Hence, if the molar quantities or the relative integral molar quantities are considered as functions of x_2 , linear functions in a heterogeneous region are obtained.

In the uranium-mercury system intermediate compounds are formed which are not mutually soluble to any extent and which decompose to give a vapor phase of monatomic mercury. Application of the Gibbs phase rule to a heterogeneous region of this system of three phases—two solid, one vapor—and with two components shows one degree of freedom, or $P = f(T)$, with the composition of the phases remaining constant. Also, a criterion for equilibrium is that each component have the same chemical potential, partial molar free energy, or activity in each phase. Thus the determination of these extensive thermodynamic functions for one phase defines them for the entire system.

Likewise, since our system will contain regions of heterogeneity where phase compositions remain constant, the partial molar quantities will remain constant over this whole region. If the relative partial molar free energy $\overline{\Delta F}_2$ of one constituent is known as a function of x_2 , then the $\overline{\Delta F}_1$ of the other constituent, and the integral molar free energy ΔF_m , can be computed from equations (13) and (15).

Assuming $\overline{\Delta F}_{Hg}$ is known for the compositions UHg_2 , UHg_3 , UHg_4 , it is required to calculate the ΔF_m for the three compounds by the application of equation (15). (Note that in this treatment 1 mole of UHg_n is equivalent to $(n+1)$ moles of solution.) Over the range of mercury content from $x = 0$ to $x = 2/3$, where $x =$ mole fraction of mercury:

$$\Delta F_m = (1-2/3) \int_0^{2/3} \frac{\overline{\Delta F}_2}{(1-x)^2} dx$$

However, $\overline{\Delta F}_2$ is constant over this range; therefore

$$\begin{aligned} \Delta F_m &= \frac{\overline{\Delta F}_2}{3} \int_0^{2/3} \frac{dx}{(1-x)^2} = \frac{\overline{\Delta F}_2}{3} \left[\frac{1}{1-x} \right]_0^{2/3} \\ &= \overline{\Delta F}_2 \cdot \frac{1}{3}(3-1) = \frac{2}{3} \overline{\Delta F}_2 \text{ per mole of solution} \end{aligned}$$

Since 1 mole of $\text{UHg}_2 = 3$ moles of solution, for UHg_2 :

$$\Delta F_m = 3 \times \frac{2}{3} \overline{\Delta F}_2 = 2 \overline{\Delta F}_2 \text{ per mole of } \text{UHg}_2$$

Likewise, between $x = 2/3$ and $x = 3/4$, $\overline{\Delta F}_3$ is constant and 1 mole of compound $\text{UHg}_3 = 4$ moles of solution; for UHg_3 :

$$\begin{aligned} \Delta F_m &= 3(1-x) \int_0^{2/3} \frac{\overline{\Delta F}_2}{(1-x)^2} dx + 4(1-x) \int_{2/3}^{3/4} \frac{\overline{\Delta F}_3}{(1-x)^2} dx \\ &= 3 \left(\frac{2}{3} \overline{\Delta F}_2 \right) + 4 \left\{ \frac{1}{4} \overline{\Delta F}_3 \left[\frac{1}{1-x} \right]_{2/3}^{3/4} \right\} \end{aligned}$$

$$\Delta F_m = 2\overline{\Delta F}_2 + \overline{\Delta F}_3 \text{ per mole of } \text{UHg}_3$$

For $x = 3/4$ to $x = 4/5$, $\overline{\Delta F}_4$ is constant and 1 mole of compound = 5 moles of solution; for UHg_4 :

$$\Delta F_m = 2\overline{\Delta F}_2 + \overline{\Delta F}_3 + 5(1-4/5) \left[\frac{1}{1-x} \right]_{3/4}^{4/5} \overline{\Delta F}_4$$

$$\Delta F_m = 2\overline{\Delta F}_2 + \overline{\Delta F}_3 + \overline{\Delta F}_4 \text{ per mole of } \text{UHg}_4$$

This agrees exactly with the other derivation.

The temperature dependence of these quantities was also determined over a temperature range 175° to 375° C. According to Zemanski, (23) since

$$\Delta F^\circ = -RT \ln K_p$$

from Van't Hoff's isobar

$$\frac{d}{dt} (\ln K) = \frac{\Delta H}{RT^2}$$

or

$$\Delta H = -2.303 R \frac{d \log K}{d 1/T} = \frac{d(\Delta F/T)}{d(1/T)}$$

ΔH may be determined for each compound and also ΔH as a function of temperature.

Since $\Delta F = \Delta H - T\Delta S$, ΔS may be determined. Also, since $d(\Delta H)/dT = \Delta C_p = C_{p\text{amalg}} - C_{pU} - nC_{p\text{Hg}}$, C_p of the amalgams may be computed. However, over the rather narrow range of temperature investigated, $\log p = A + B/T$, a straight line on semilog paper, and ΔH and ΔS may be evaluated more simply by:

$$\begin{aligned}\Delta F &= -RT(\ln p_{\text{amalg}} - \ln p_{\text{Hg}}) \\ &= -RT \left[(A_1 + B_1/T) - (A_2 + B_2/T) \right] \\ &= -RT (A_3 + B_3/T) \\ &= -R (B_3 + A_3T) = B_4 + A_4T\end{aligned}$$

Since $\Delta F = \Delta H - T\Delta S$, then $\Delta H = B_4$ and $\Delta S = -A_4$. Also since ΔH is therefore a constant, C_p is seen to be the sum of the heat capacities of the components.

EXPERIMENTAL

The objective of the experimental work was to prepare samples of pure uranium-mercury mixtures over a wide range of compositions in such a physical form that the intermetallics UHg_2 , UHg_3 , and UHg_4 would form. After the components reached an equilibrium state with reference to the phases present, the three intermetallics, excess uranium, or excess mercury, the mercury vapor pressure over the solid or liquid phases was to be measured as a function of both composition and temperature.

The uranium metal used was of the highest chemical purity available. It was in the form of cast rod produced from the depleted product of a gaseous diffusion plant. Chemical analysis of the sample showed:

Carbon	200-300 ppm
Oxygen	13 ppm
Iron	40 ppm
Ni, Al, Si	Each less than 50 ppm

The rods were machined into lathe turnings and then broken up manually into thin chips approximately $1/4$ in. long by $1/16$ in. wide. The careful manual work was necessary because of the tendency for the fresh surfaces produced to ignite spontaneously. The mercury used was purified by the usual methods of filtering, washing with HNO_3 , and was doubly distilled under vacuum.

Immediately before use, the approximate amount of chips necessary for a sample was cleaned by washing in concentrated nitric acid which dissolved all surface oxide. Repeated washing with distilled water to remove the acid was followed by rinsing with acetone. The chips were dried under vacuum at room temperature or only slightly above to prevent reoxidation.

The combination sample preparation tube and vapor pressure cell (Figs. 5 and 6) was prepared for use, after manufacture in the glass shop, by careful cleaning with fresh cleaning solution (sulfuric + chromic acid), rinsing with distilled water until free of chromate, rinsing with acetone, and drying overnight in an oven at 110° C. The uranium chips were weighed on an analytical balance and placed in section D of the tube, and the purified mercury was weighed and placed in section E. The tube was then sealed, glass to glass, to the sample preparation apparatus (Fig. 7) close to point A, and sidearm C was drawn off and sealed. The system was immediately evacuated. Figure 8 shows the sample preparation apparatus with the tube in place.

The hydrogen was supplied from a tank of electrolytic hydrogen, drawn off through a catalytic deoxygenation chamber and drying tube. This supply was first used to purge that portion of the sample preparation system, including the gauge and second roughing pump. As soon as the main system including the sample preparation tube became evacuated to about 5×10^{-7} mm Hg total pressure, with the uranium chips heated to 100° C, the three-way valve was adjusted to allow hydrogen gas to enter the sample preparation tube to an absolute pressure of 1 atmosphere. The mercury was cooled with an ice bath and the uranium was heated to 250° C. As the uranium absorbed hydrogen, as indicated by falling hydrogen pressure, the hydrogen was replenished to raise the pressure back to 1 atmosphere. In a period of about an hour, depending on the size of the uranium sample, the hydrogen pressure no longer fell and hydriding was complete. Usually there was an initial induction period, before the uranium began to absorb the hydrogen, which varied from a few minutes to an hour. This may have been a function of the completeness of degassing of the uranium surface but did not appear to affect the final results.

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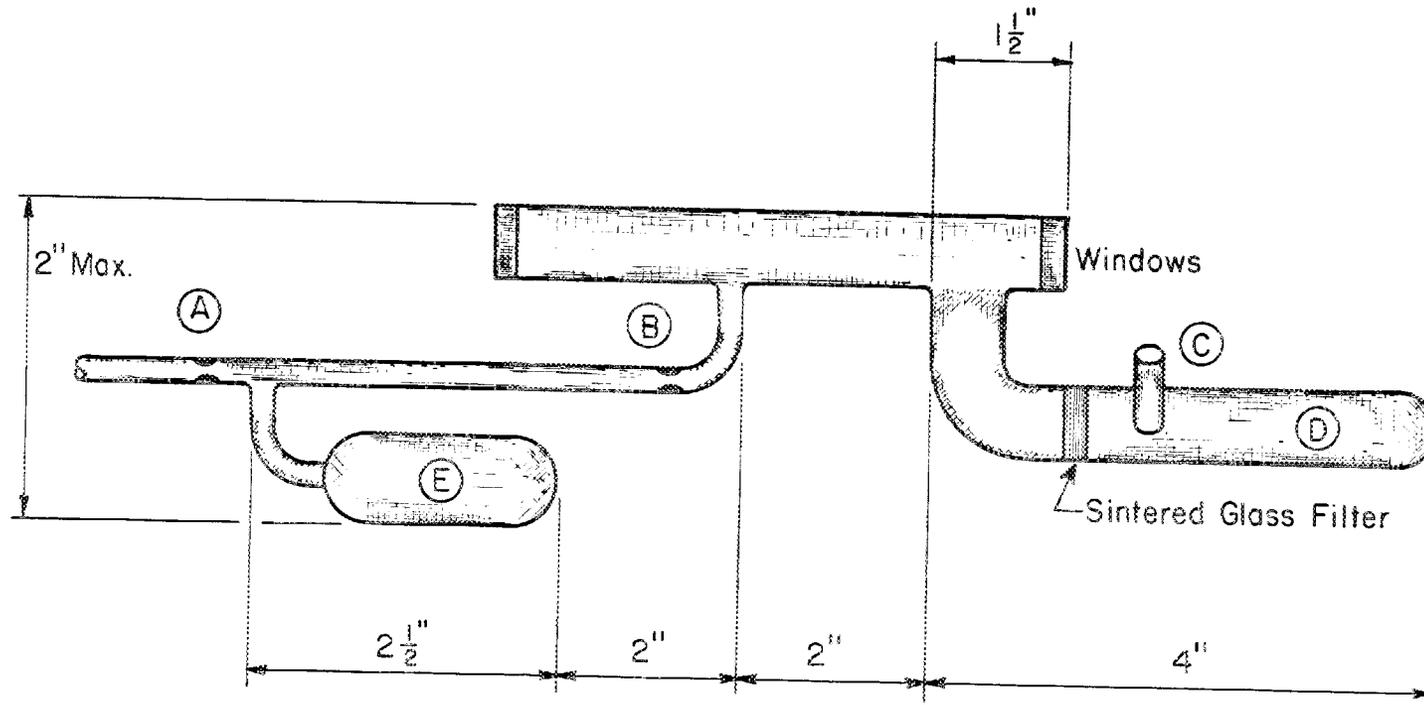


FIGURE 5. COMBINATION SAMPLE PREPARATION TUBE AND VAPOR PRESSURE CELL.

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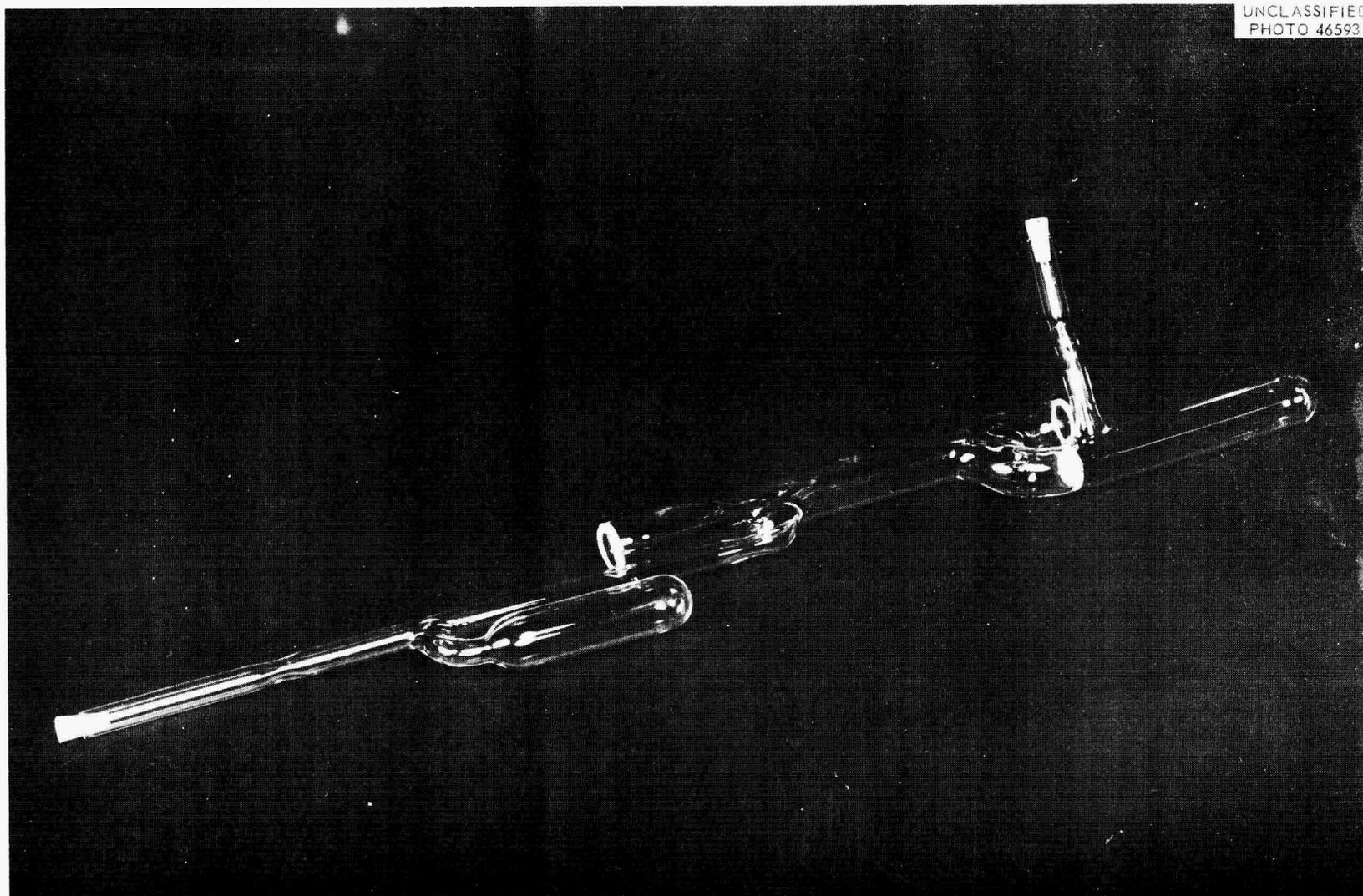


FIGURE 6. SAMPLE PREPARATION TUBE: VAPOR PRESSURE CELL.

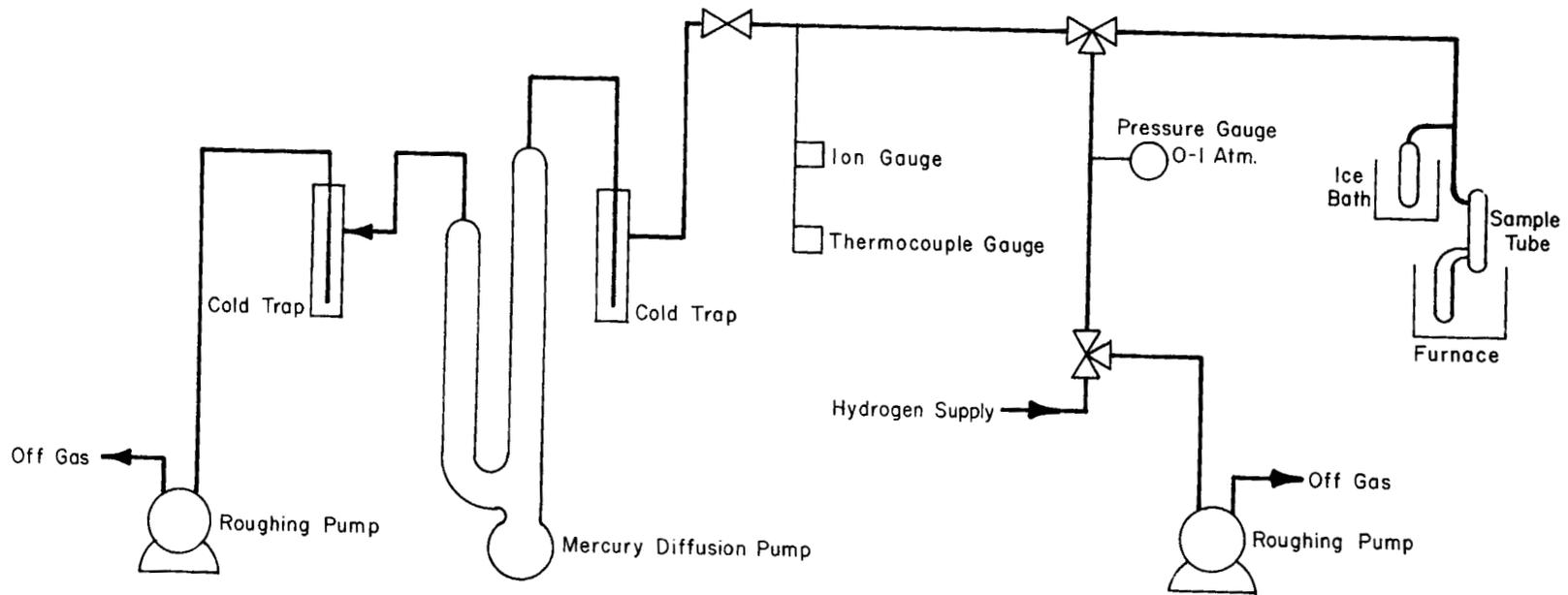


FIGURE 7. SAMPLE PREPARATION APPARATUS.

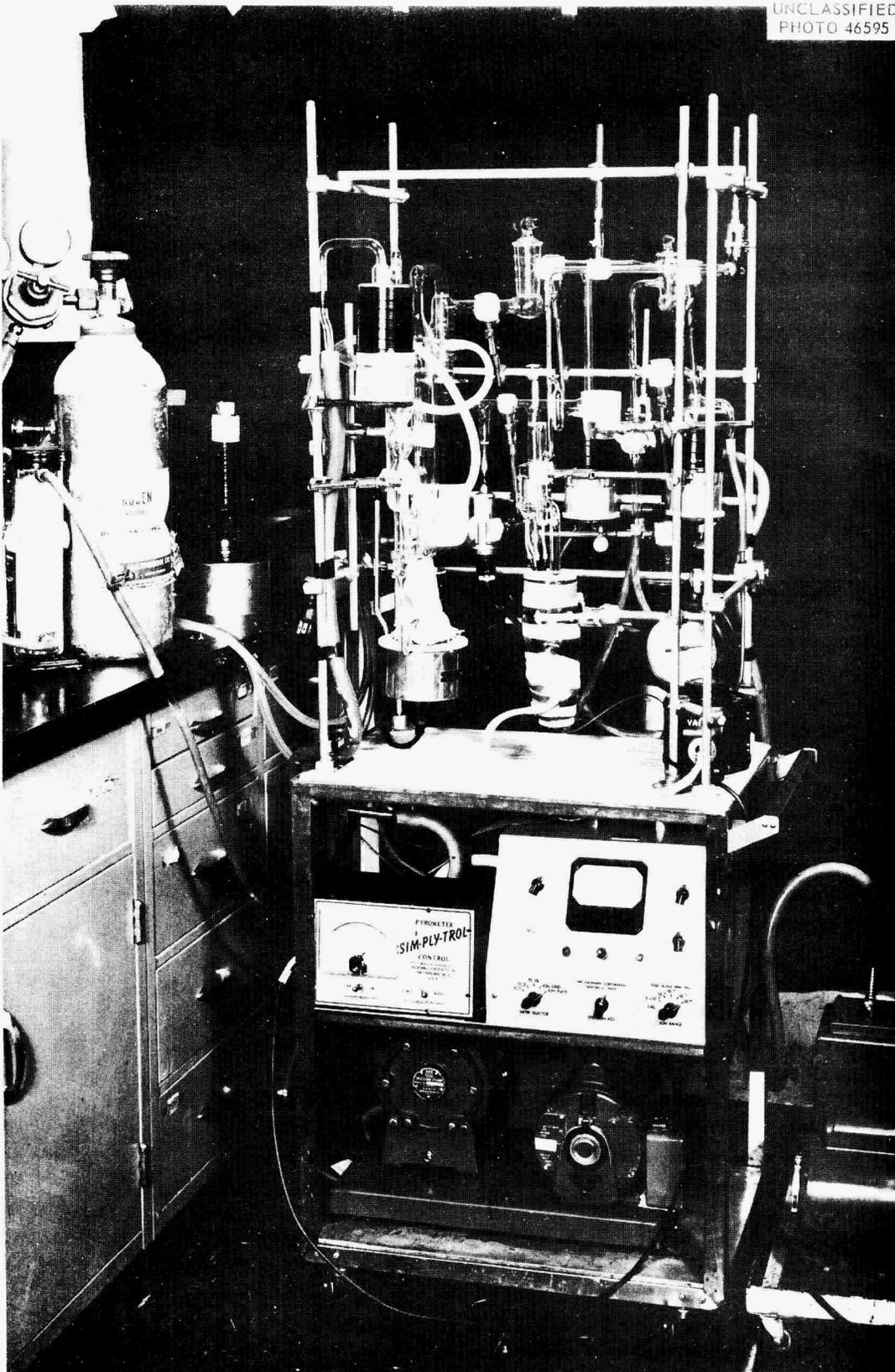


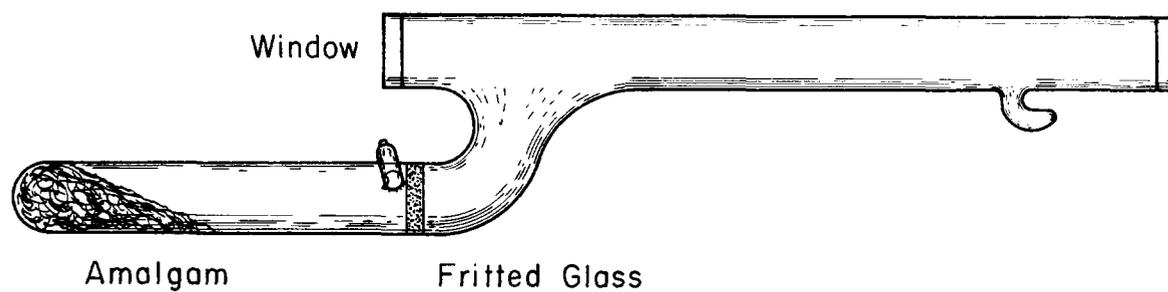
FIGURE 8. SAMPLE PREPARATION APPARATUS.

When the hydriding step was completed, the second roughing pump was used to remove the hydrogen and the furnace temperature was raised to 300° C. At the end of about an hour, when evolution of hydrogen from the sample had slowed as shown by the pressure gauge after the system had been isolated from the pump, the hot sample tube was again opened into the high-vacuum part of the system where the pressure could be continuously monitored by the thermocouple gauge and later the ion gauge. During several hours' continued pumping the total pressure was finally decreased to 1 to 2 x 10⁻⁶ mm Hg, measured with the uranium still at 300° C. The sample tube was then carefully sealed off at the constriction A (Fig. 5) and removed from the system. After this treatment the uranium was a finely divided powder, sometimes lightly sintered but very porous.

In order to eliminate any possibility of contamination of the amalgam with oxides of mercury, the evacuated and sealed sample tube was next gently heated by placing the end containing the mercury inside a tube furnace, causing the mercury to vaporize out of container E (Fig. 5) and condense in D, where it combined with the uranium. After all mercury had been transferred out of E, constriction B was sealed off. The vapor pressure tube then appeared as shown in Fig. 9.

The vapor pressure was measured by the dew point method with the equipment shown in Figs. 10 and 11. The furnace was a stock model made by Marshall Products Company of Columbus, Ohio, 13 in. long with a 2.5-in.-i.d. ceramic tube. The windings were tapped along its length at 10 points, and the temperature was controlled by varying the input current, generally in the range of 3 to 6 amp at a voltage of about 20-50 volts. Variable sliding-

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Scale $3/4'' = 1''$

FIGURE 9. VAPOR PRESSURE SAMPLE.

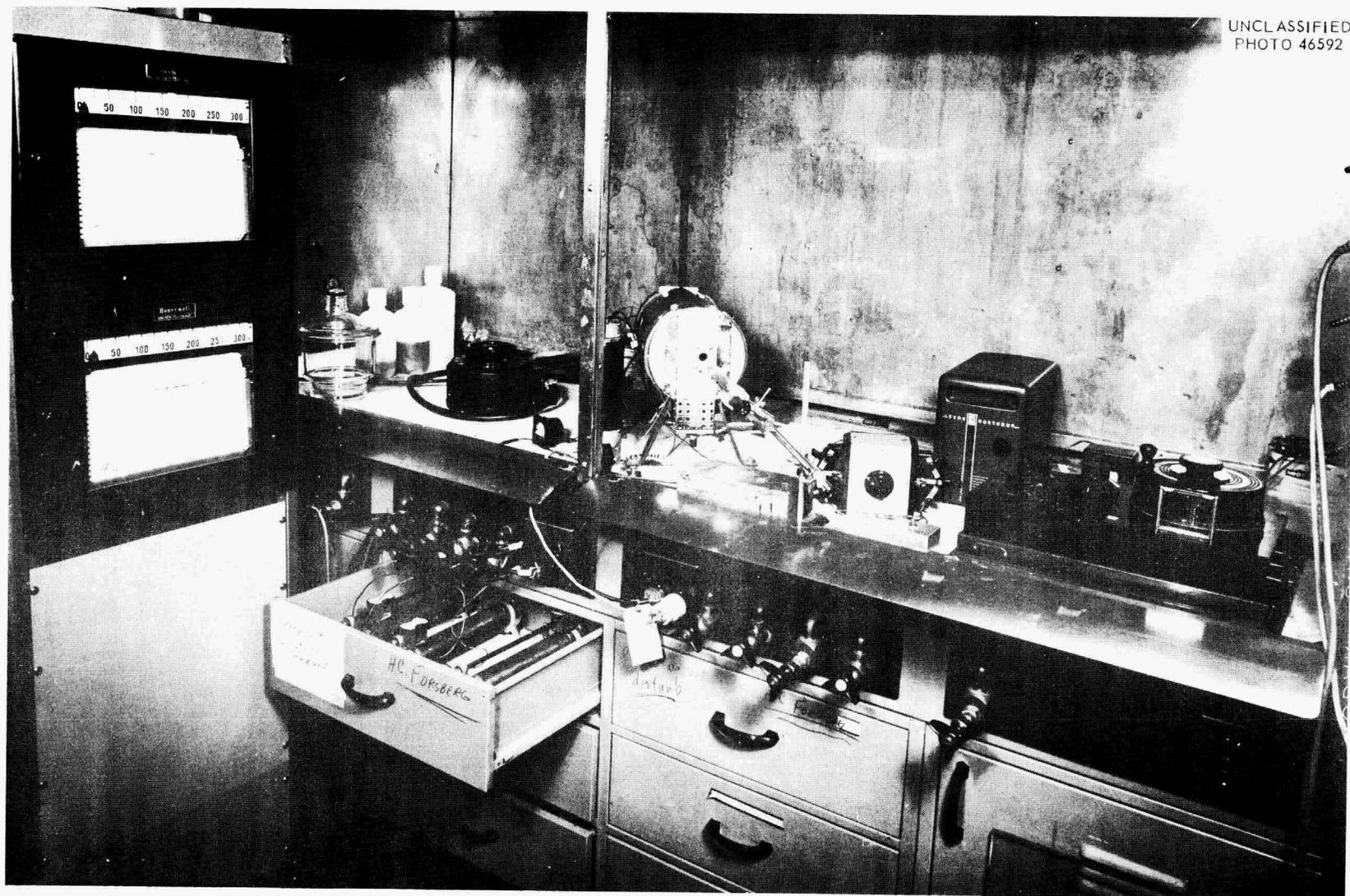


FIGURE 10. VAPOR PRESSURE MEASURING EQUIPMENT.

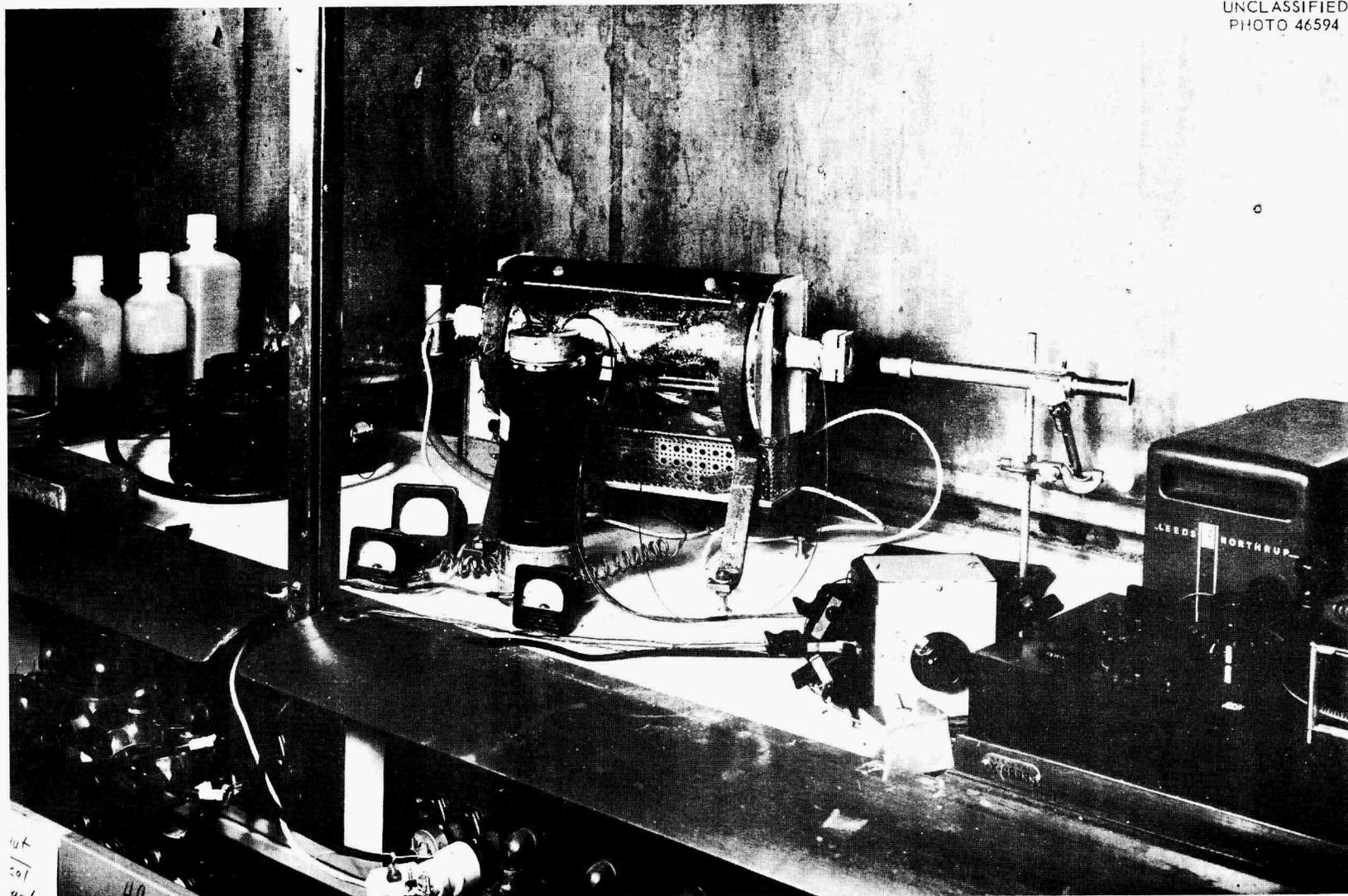


FIGURE 11. VAPOR PRESSURE MEASURING EQUIPMENT.

contact resistors of 0-24 ohms were shunted across the windings at each end (Fig. 12) to vary the end temperatures as required.

The vapor pressure tube was clamped into the holder with the two observation windows lined up with the collimating tubes (Figs. 12 and 13). The thermocouples were fastened in place with fine copper wire or with asbestos tape and glass fiber adhesive tape. Aluminum foil radiation shields were placed both around the tube containing the amalgam and around the main tube extending out over the cooled observation window. The unit was installed in the Marshall furnace, and the ends of the furnace were closed by means of asbestos sheet. A safety thermocouple, connected to a controller in the main furnace power supply, was placed in the furnace tube. The furnace power was turned on and the shunt resistors were adjusted to give an approximately uniform temperature over the entire furnace length. Control of the total furnace power input, by means of a Variac, fixed the temperature of the furnace after reaching thermal equilibrium with the surroundings. Using an on-off controller was not practical as it produced too great a temperature fluctuation during a run. With a new amalgam sample it was necessary to allow several days at temperature for chemical equilibrium, whereas thermal equilibrium was generally obtained in a matter of hours.

The temperature measuring equipment is shown in Fig 14. After thermal and chemical equilibrium had been reached, the temperatures of the amalgam and of the observation window were determined by using the K-2 potentiometer. The two Brown recorders were then adjusted to read the correct temperature range by setting the switches so that an emf from the K-2 was fed into the input of the Brown recorders. These two recorders had been modified

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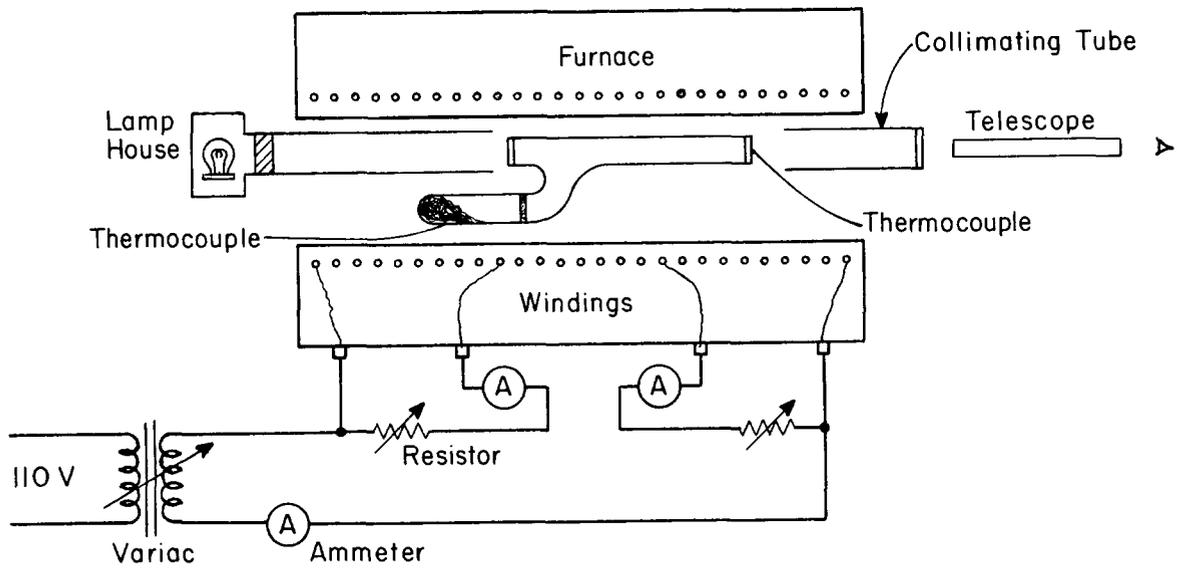


FIGURE 12. FURNACE AND CONTROLS.

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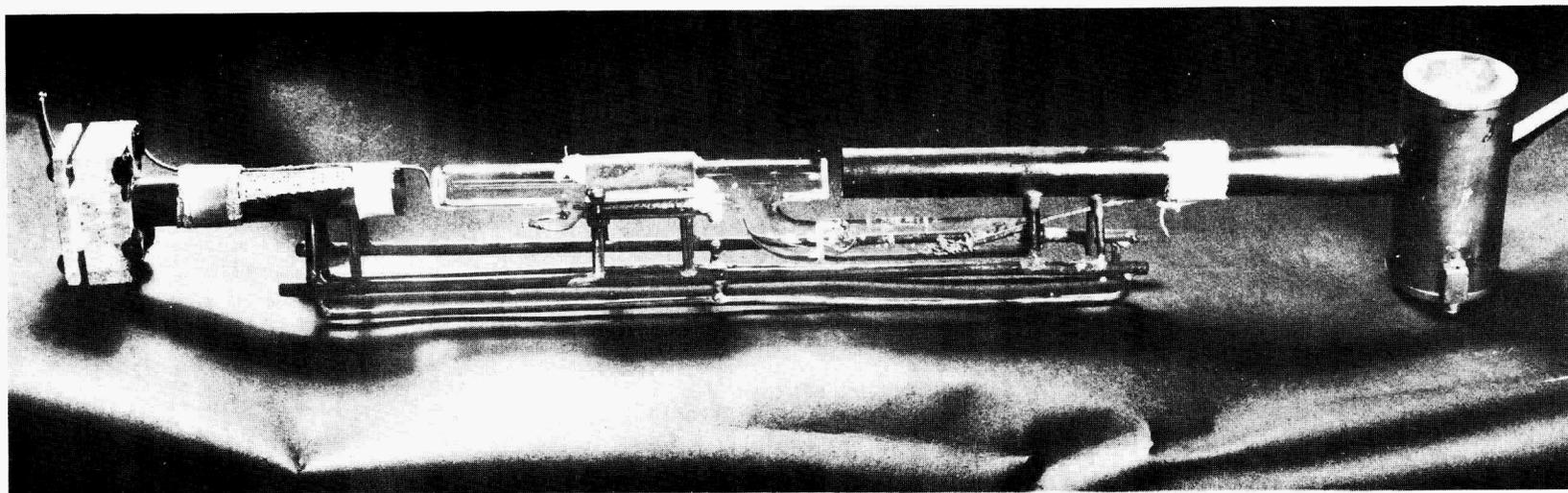


FIGURE I3. VAPOR PRESSURE CELL AND HOLDER.

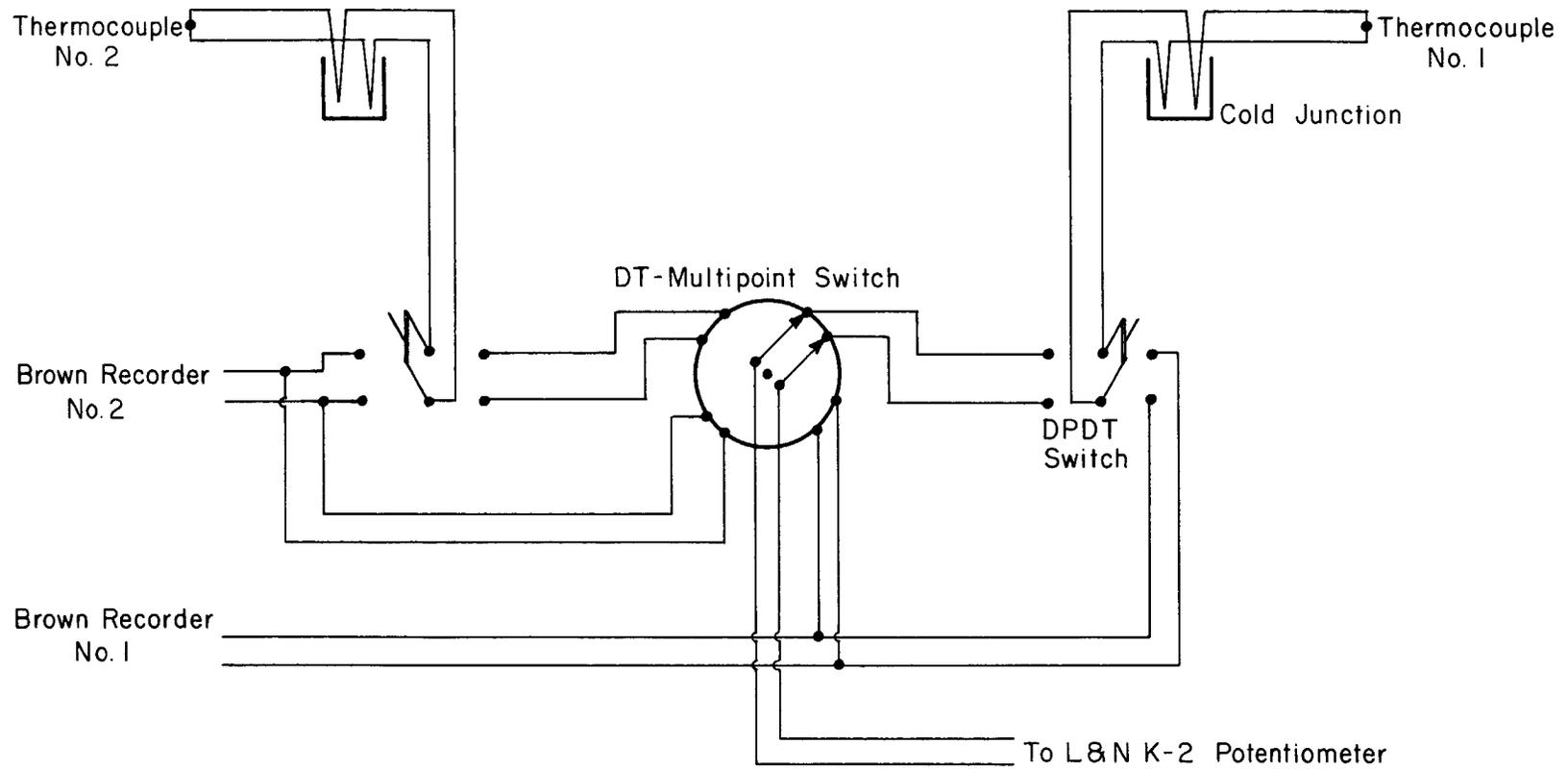


FIGURE 14. THERMOCOUPLE WIRING.

to have a 3-mv full-scale span, with an adjustment (30 mv suppression) for changing the range anywhere within the range of 0-30 mv. After each recorder had been adjusted to the correct portion of the scale and calibrated, they were switched to the thermocouples for direct, continuous monitoring of the two temperatures. The 40 in./hr. chart drive was turned on only during an actual run.

While the total current input to the furnace was held constant with the Variac, the shunt resistor connected to the end of the furnace to be cooled was changed to a lower resistance, which allowed about 65% of the heating current to bypass that part of the furnace element. As the temperature of this end slowly dropped, all controls were varied as needed to keep one end cooling and hold the other end at as constant a temperature as possible. The center portion of the furnace was the only portion to continue to carry the full heating current and therefore tended to remain close to, or even slightly higher than, the amalgam end. The cooling rate varied somewhat from run to run depending on the starting temperature, but experimentally this did not seem to affect the results. An average cooling rate was 1.5 to 2^o C per minute.

The cooled window was observed through a small telescope. As soon as the first droplet of condensed mercury appeared, a switch was momentarily closed which shorted the input to the two recorders simultaneously, marking both charts at the temperatures of the end point. Immediately a calibration was run on each chart at a known point near the end point, by again feeding a signal from the K-2 potentiometer. Any drift of the recorders during the run was thus corrected. From the recorder charts, the temperature of the dew point and of the amalgam was read to the nearest 0.01 mv.

The vapor pressure of the amalgam at its recorded temperature was then assumed as equal to the vapor pressure of pure mercury, taken from hand-book⁽²⁴⁾ values, at the temperature of the cooled window. This reading was corrected for temperature lag across the glass barrier by comparing it with the value obtained in a run in which only mercury was used in the vapor pressure cell.

Subsequent runs at different temperatures on the same sample were made only after a 2- to 4-hr period to allow chemical and thermal equilibrium to again be reached. With practice the furnace controls could be adjusted to give a desired temperature and to allow equilibrium to be reached with a temperature differential between the two ends of the furnace so that cooling would not have to cover such a wide temperature range. This made it much easier to keep the amalgam temperature constant during a run.

During the course of the experimental work several variations were tried and abandoned. These should be mentioned for their possible value to future workers in this field. In order to get more exact temperature measurements on the amalgam, the first vapor pressure cell was designed with a thermocouple well extending into the amalgam. Glass thermocouple wells broke as the solid amalgams formed, causing stress on the wells. A stainless steel well attached by a Kovar-to-glass seal was abandoned as it appeared to have some affinity for the mercury. Both a platinum and a tungsten wire sealed through the glass to act as a thermal conductance probe caused leaks and were difficult to make good contact with the thermocouple. The method finally used was to place the thermocouple against the glass, shielding it with an aluminum foil against radiation from the furnace walls, and calibrating the

system for heat lag etc. by checking against a sample tube containing only pure mercury.

Another technique that was varied was the method of detecting the dew point. When a photoelectric cell was used, the condensate on the cooled observation window decreased the amount of transmitted light but the method lacked sensitivity. Also, variations in line current resulted in false responses. Another method was the use of a 16-mm movie camera set to photograph the observation window every 15 sec. This method worked well, but delayed the availability of the data until the film was developed.

DATA AND RESULTS

In order to compensate for temperature lag across the glass barriers, etc., runs X-1 to X-7 were made with a sample of pure mercury (Table I). These data were fitted to an equation of the form $\log p = a + b/T$ where p is the vapor pressure in millimeters of mercury, T is the temperature in degrees Kelvin, and a and b are constants. The fit was made using the standard statistical method of least squares, ^(25, 26) minimizing the residuals in $\log p$, by using the Oracle (the digital computer at the X-10 site of Oak Ridge National Laboratory). The result was:

$$\log P_{\text{corrected}} = 7.95371 - 3211.91/T$$

TABLE I. CORRECTION CURVE, VAPOR PRESSURE

Run No.	Measured Hg Temperature, °C	Dew Point Temperature, °C	True Vapor Pressure of Hg at Dew Point, mm Hg
X-1	164.0	158.0	3.87
X-2	202.4	196.5	15.40
X-3	279.0	274.0	136.0
X-4	282.0	277.2	146.8
X-5	349.7	345.2	615.0
X-6	207.0	203.8	19.50
X-7	195.5	191.0	12.85

A standard deviation in $\log p$ was estimated, by the machine, to be 0.0268835.

This corresponds to a deviation in p of about 4%.

This correction equation was next used to calculate a corrected pressure at every amalgam temperature in the other runs. Likewise, the vapor pressure of pure mercury, as given in the International Critical Tables, was determined at this same temperature. Since the correction curve pressure was lower in all cases than the vapor pressure of pure mercury, the difference between the two pressures was added as a correction to the amalgam vapor pressure determined for each run (Table II). Figure 15 shows the corrected vapor pressure data plotted as $\log p$ versus the reciprocal of the absolute temperature.

By the method of least squares, an equation was fitted to the corrected vapor pressure values on the digital computer. These equations and the estimated standard error of fit are:

For UHg_2 , or composition between U and UHg_2 ,

$$\log p = 7.29890 - 3134.83/T, \quad \sigma_{\text{fit}} = 0.0279806$$

For UHg_3 ,

$$\log p = 7.55460 - 3226.21/T, \quad \sigma_{\text{fit}} = 0.0196916$$

For UHg_4 ,

$$\log p = 7.88899 - 3351.89/T \text{ below } 300^\circ \text{ C}, \quad \sigma_{\text{fit}} = 0.0248472$$

$$\log p = 8.71063 - 3829.23/T \text{ above } 300^\circ \text{ C}, \quad \sigma_{\text{fit}} = 0.00871414$$

For saturated solution of UHg_4 in Hg,

$$\log p = 7.78021 - 3132.74/T, \quad \sigma_{\text{fit}} = 0.0125523$$

The ΔF 's of formation of each of the three compounds UHg_2 , UHg_3 , and UHg_4 were calculated from the equations derived in a previous section, in two forms. The first was the calculation of ΔF values at nine temperatures covering the range of the investigation (Tables III and IV, Fig. 16).

TABLE II. VAPOR PRESSURES OF THE URANIUM AMALGAMS

Run No.	Amalgam Temp., °C	Amalgam $\frac{1}{T^{\circ}K} \times 10^5$	Amalgam Measured Vapor Pressure, mm Hg	Calculated log p_{cor}	p_{cor} , mm Hg	Vapor Pressure of Pure Hg, mm Hg	Corrected Amalgam Vapor Pressure, mm Hg	Log Corrected Amalgam Vapor Pressure
M*-1	275.0	182.5	23.4	2.09197	123.59	139.34	39.15	1.59273
2	305.0	173.0	51.8	2.39711	249.52	275.02	77.30	1.88818
3	337.3	163.9	108.6	2.68939	489.10	529.85	149.35	2.17421
4	378.5	153.5	251.2	3.02343	1055.4	1110.20	306.00	2.48572
5	212.5	206.0	3.46	1.33718	21.736	25.626	7.350	0.86629
6	217.4	203.9	4.09	1.40463	25.388	29.734	8.436	0.92614
E*-4	383	152.4	306.0	3.05876	1144.9	1196.6	357.70	2.55352
5	346.5	161.4	137.8	2.76969	588.42	630.51	179.89	2.25501
6	176	222.7	0.68	0.80079	6.3211	7.626	1.985	0.29776
7	172	224.7	0.70	0.73655	5.4519	6.596	1.842	0.26529
8	220	202.8	4.03	1.43996	27.540	32.133	8.623	0.93566
9	270	184.2	18.75	2.03737	108.99	123.47	33.23	1.52153
10	295	176.1	37.2	2.29754	198.40	221.04	59.84	1.77699
11	320	168.6	70.2	2.55770	361.16	376.33	85.37	1.93131
12	353	159.7	152.2	2.82429	667.25	710.68	195.63	2.29144
13	268	184.3	16.7	2.01810	104.26	117.57	30.01	1.47727
H*-3	308.8	171.8	69.8	2.43565	272.68	298.18	95.30	1.97909
4	285.5	179.0	37.4	2.20439	160.10	182.43	59.73	1.77619
5	240.2	194.9	10.7	1.69370	49.397	57.164	18.467	1.26640
6	373	154.7	309.0	2.98489	965.81	1011.5	354.69	2.54985
7	200	211.4	2.78	1.16373	14.579	17.287	5.488	0.73941

TABLE II (continued)

Run No.	Amalgam Temp., °C	Amalgam $\frac{1}{T^{\circ}\text{K}} \times 10^5$	Amalgam Measured Vapor Pressure, mm Hg	Calculated Log P _{cor}	P _{cor} , mm Hg	Vapor Pressure of Pure Hg, mm Hg	Corrected Amalgam Vapor Pressure, mm Hg	Log Corrected Amalgam Vapor Pressure
C*								
-4	292	177.0	47.4	2.26863	185.62	206.70	68.48	1.83556
5	357	158.7	228.5	2.85641	718.47	764.08	274.11	2.43792
8	263	186.6	19.8	1.96029	91.262	103.85	32.388	1.51038
9	358	158.5	236.0	2.86283	729.17	777.92	284.75	2.45446
J*								
1	312	170.9	81.5	2.46456	291.45	319.02	109.07	2.03771
2	268	184.8	28.4	2.01810	104.26	117.57	41.71	1.62024
3	278.6	181.3	31.4	2.13052	135.06	151.79	48.13	1.68242
4	225	200.8	7.1	1.50419	31.929	37.222	12.393	1.09318
5	351	160.3	215.0	2.80502	638.29	685.17	261.88	2.41810
6	312	170.9	84.4	2.46456	291.45	319.02	111.97	2.04910
D*								
-5	277.5	181.7	46.8	2.11767	131.12	147.89	63.57	1.80325
6	201	211.0	4.28	1.17658	15.017	17.854	7.117	0.85230
7	283	179.9	55.6	2.17548	149.79	168.26	74.07	1.86964
9	304.7	173.1	92.7	2.39389	247.68	273.27	118.29	2.07295
F*								
-2	303	173.6	94.0	2.37783	238.69	263.42	118.73	2.07456
3	238	195.7	12.8	1.66800	46.559	53.812	20.053	1.30218
4	368.5	155.9	505	2.94634	883.77	936.15	557.38	2.74615
5	334	164.7	217	2.66369	460.99	497.12	253.13	2.40334
6	185	218.3	1.94	0.94211	8.7521	10.472	3.660	0.56348
7	218	203.7	6.60	1.41105	25.766	30.271	11.105	1.04552
9	349.2	160.7	311.2	2.79217	619.68	662.86	354.38	2.54947
10	382.5	152.6	679	3.05234	1128.1	1186.8	737.7	2.86788

TABLE II (continued)

Run No.	Amalgam Temp., °C	Amalgam $\frac{1}{T^{\circ}K} \times 10^5$	Amalgam Measured Vapor Pressure, mm Hg	Calculated log P _{cor}	P _{cor} , mm Hg	Vapor Pressure of Pure Hg, mm Hg	Corrected Amalgam Vapor Pressure, mm Hg	Log Corrected Amalgam Vapor Pressure
G* -1	221	202.4	22.15	1.45280	28.366	33.100	26.884	1.42949
2	250.5	191.0	54.7	1.81896	65.911	75.366	64.155	1.80723
3	290.3	177.5	145	2.25257	178.88	198.93	165.05	2.21762
4	358	158.5	579	2.86283	729.17	777.92	627.75	2.79779
5	189.2	216.4	7.68	1.00314	10.073	12.092	9.699	0.98673
L* -1	298.5	175.0	174.8	2.33287	215.21	238.84	198.43	2.29761
2	367.2	156.2	737	2.93671	864.39	915.21	787.82	2.89643
3	270.8	183.9	92.0	2.04701	111.43	125.90	106.47	2.02723
6	204.8	209.3	14.2	1.23118	17.029	20.158	17.329	1.23877

* Composition M - 49.0 atom % Hg, U + UHg₂
 E - 60.2 atom % Hg, U + UHg₂
 H - 69.0 atom % Hg, UHg₂ + UHg₃
 C - 71.5 atom % Hg, UHg₂ + UHg₃
 J - 73.5 atom % Hg, UHg₂ + UHg₃
 D - 76.6 atom % Hg, UHg₃ + UHg₄
 F - 78.2 atom % Hg, UHg₃ + UHg₄
 G - 84.9 atom % Hg, UHg₄ + Hg
 L - 95.0 atom % Hg, UHg₄ + Hg

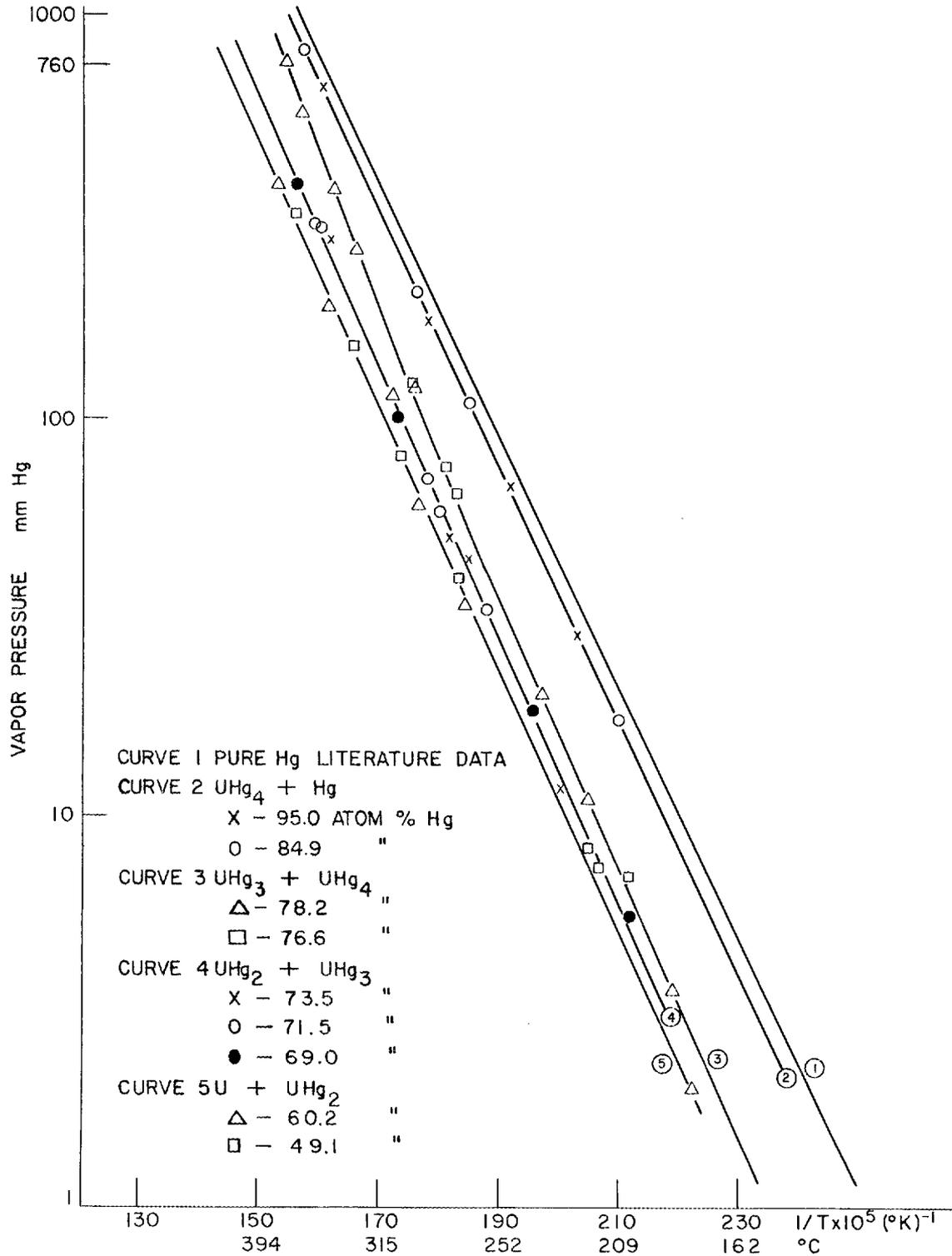


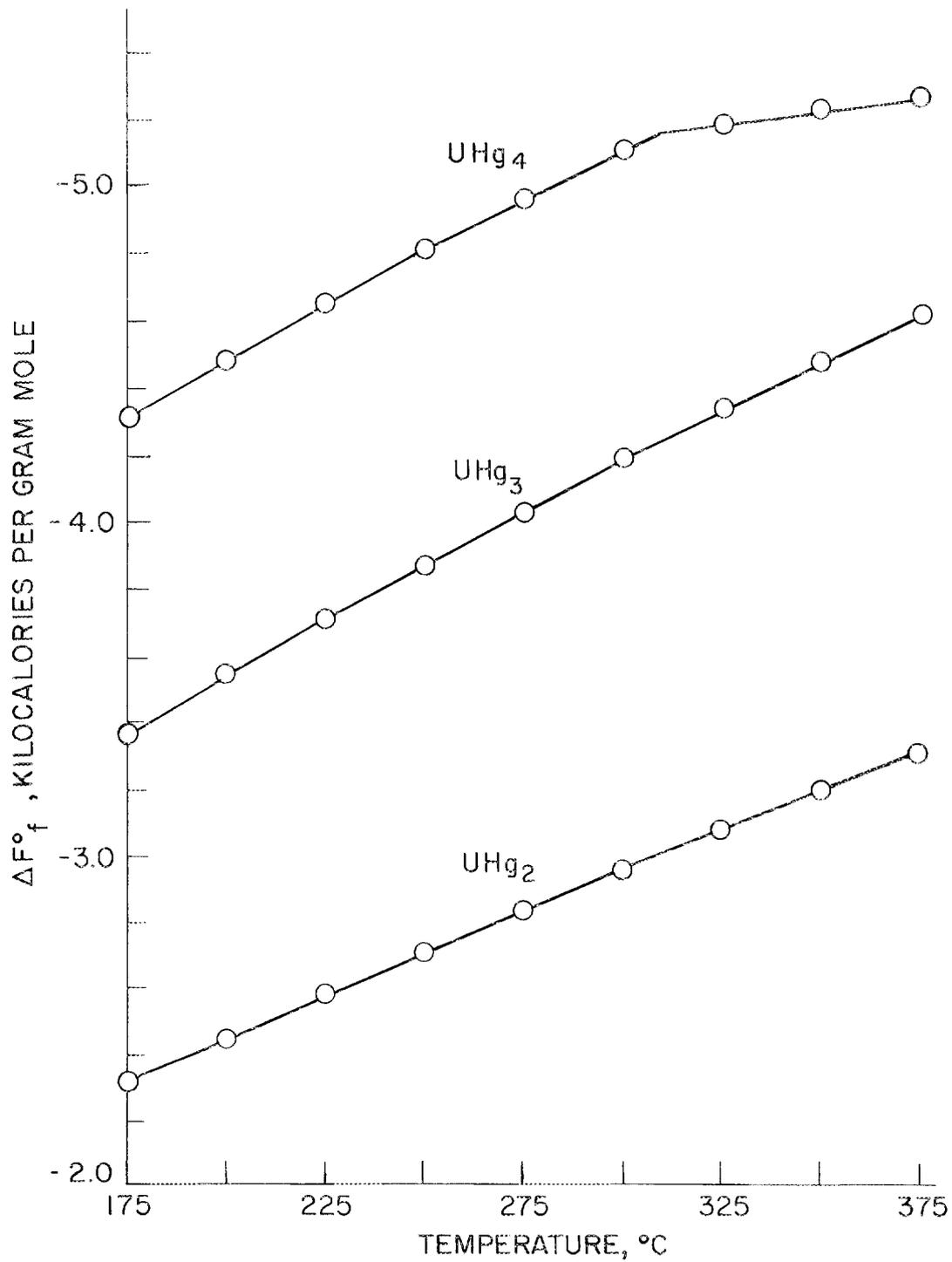
FIGURE 15. VAPOR PRESSURE OF URANIUM AMALGAM.

TABLE III. CALCULATION OF $\overline{\Delta F}_f$

Temp., °C	(A) 4.574T	log p _{amal}	log p _{Hg}	(B)	A x B = $\overline{\Delta F}_f$ kcal/mole
				log $\frac{p_{amal}}{p_{Hg}}$	
For UHg ₂					
448	2049.152	0.301517	0.86664	-0.56512	-1.15802
473	2163.502	0.671364	1.23772	-0.56636	-1.22532
498	2277.852	1.00406	1.57080	-0.56674	-1.29095
523	2392.202	1.30494	1.87143	-0.56649	-1.35516
548	2506.552	1.57840	2.14408	-0.56568	-1.41791
573	2620.902	1.82799	2.39235	-0.56436	-1.47913
598	2735.252	2.05671	2.61942	-0.56271	-1.53915
623	2849.602	2.26706	2.82781	-0.56075	-1.59791
648	2963.952	2.46120	3.01974	-0.55854	-1.65549
For UHg ₃					
448	2049.152	0.353234	0.86664	-0.51341	-1.05206
473	2163.502	0.733862	1.23772	-0.50386	-1.09010
498	2277.852	1.07626	1.57080	-0.49454	-1.12649
523	2392.202	1.38591	1.87143	-0.48552	-1.16146
548	2506.552	1.66734	2.14408	-0.47674	-1.19497
573	2620.902	1.92421	2.39235	-0.46814	-1.22695
598	2735.252	2.15959	2.61942	-0.45983	-1.25775
623	2849.602	2.37607	2.82781	-0.45174	-1.28728
648	2963.952	2.57587	3.01974	-0.44387	-1.31561
For UHg ₄ up to 300°C					
448	2049.152	0.407098	0.86664	-0.45954	-0.941667
473	2163.502	0.802554	1.23772	-0.43517	-0.941491
498	2277.852	1.15829	1.57080	-0.41251	-0.939637
523	2392.202	1.48001	1.87143	-0.39142	-0.936356
548	2506.552	1.77239	2.14408	-0.37167	-0.931660
573	2620.902	2.03927	2.39235	-0.35308	-0.925388
For UHg ₄ above 300°C					
598	2735.252	2.30724	2.61942	-0.31218	-0.853891
623	2849.602	2.56418	2.82781	-0.26363	-0.751241
648	2963.952	2.80132	3.01974	-0.21842	-0.647386

TABLE IV. INTEGRAL ΔF_f

Temp., °C	$\overline{\Delta F}_1$	$2\overline{\Delta F}_1 = \Delta F_1$ for UHg ₂ , kcal/mole	$\overline{\Delta F}_2$	$\Delta F_1 + \overline{\Delta F}_2 = \Delta F_2$ for UHg ₃ , kcal/mole	$\overline{\Delta F}_3$	$\Delta F_2 + \overline{\Delta F}_3 = \Delta F_3$ for UHg ₄ , kcal/mole
175	-1.15802	-2.31604	-1.05206	-3.36810	-0.94167	-4.30977
200	-1.22532	-2.45064	-1.09010	-3.54074	-0.94149	-4.48223
225	-1.29095	-2.58190	-1.12649	-3.70839	-0.93964	-4.64803
250	-1.35516	-2.71032	-1.16146	-3.87178	-0.93636	-4.80814
275	-1.41791	-2.83582	-1.19497	-4.03079	-0.93166	-4.96245
300	-1.47913	-2.95826	-1.22695	-4.18521	-0.92539	-5.11060
325	-1.53915	-3.07830	-1.25775	-4.33605	-0.85389	-5.18994
350	-1.59791	-3.19582	-1.28728	-4.48310	-0.75124	-5.23434
375	-1.65549	-3.31098	-1.31561	-4.62659	-0.64739	-5.27398

UNCLASSIFIED
ORNL-LR-DWG 40199FIGURE 16. ΔF°_f OF URANIUM MERCURIDES.

Alternately, the equations for $\log p$ as a function of $1/T$ were used to produce an expression for each ΔF as a function of temperature.

First an expression was obtained which fitted the International Critical Tables data on vapor pressure of pure mercury over the temperature range 175-375° C:

$$\log P_{\text{Hg}} = 7.84409 - 3124.81/T$$

From this equation and the ones previously presented, the expressions for ΔF were found and checked against the point-by-point calculations made earlier. These expressions gave directly the values for ΔH and ΔS :

For UHg_2 ,

$$\log P_{\text{amalg}} = 7.29890 - 3134.83/T$$

$$\log P_{\text{Hg}} = 7.84409 - 3124.81/T$$

$$\begin{aligned} \overline{\Delta F} &= 4.574T \log P_{\text{amalg}}/P_{\text{Hg}} \\ &= 4.54T \left(7.29890 - \frac{3134.83}{T} - 7.84409 + \frac{3124.81}{T} \right) \\ &= 4.574T \left(-0.545190 - \frac{10.02}{T} \right) \\ &= - (45.83148 + 2.49370T) \end{aligned}$$

Check:

T	$\overline{\Delta F}$	$\overline{\Delta F}$ (from Table IV)
448	-1163.009	-1158.02
548	-1412.379	-1417.91
648	-1661.749	-1655.49

$$\Delta F_{\text{UHg}_2} = 2\overline{\Delta F}_{\text{UHg}_2} = - (91.66296 + 4.98740T)$$

$$\Delta H = -91.6629 \text{ cal/mole}$$

$$\Delta S = 4.9874 \text{ eu}$$

For UHg₃

$$\log P_{\text{amal}} = 7.554460 - 3226.21/T$$

$$\log P_{\text{Hg}} = 7.84409 - 3124.81/T$$

$$\begin{aligned} \overline{\Delta F} &= -4.574T \left(.28949 + \frac{101.40}{T} \right) \\ &= - (463.8036 + 1.3241T) \end{aligned}$$

Check:

T	$\overline{\Delta F}$	$\overline{\Delta F}$ (from Table IV)
448	- 1057.0057	- 1052.06
548	- 1189.4177	- 1194.97
648	- 1321.8297	- 1315.61

$$\begin{aligned} \Delta F_{\text{UHg}_3} &= \Delta F_{\text{UHg}_2} + \overline{\Delta F}_{\text{UHg}_3} \\ &= - (91.66296 + 4.98740T + 463.8036 + 1.32412726T) \\ &= - (555.46656 + 6.31152726T) \end{aligned}$$

$$\Delta H = -555.46 \text{ cal/mole}$$

$$\Delta S = 6.3115 \text{ eu}$$

For UHg₄ up to 300° C,

$$\log P_{\text{amal}} = 7.88899 - \frac{3351.89}{T}$$

$$\log P_{\text{Hg}} = 7.84409 - \frac{3124.81}{T}$$

$$\begin{aligned} \overline{\Delta F} &= 4.574T \left(0.04490 - \frac{227.08}{T} \right) \\ &= - (1038.66392 - 0.2053726T) \end{aligned}$$

Check:

T	$\overline{\Delta F}$	$\overline{\Delta F}$ (from Table IV)
548	-926.120	-931.660

$$\begin{aligned}
\Delta F_{\text{UHgl}_4} &= \Delta F_{\text{UHg}_3} + \overline{\Delta F}_{\text{UHgl}_4} \text{ up to } 300^\circ \text{ C} \\
&= - (555.46656 + 6.31152726T + 1038.66392 - .2053726T) \\
&= - (1594.13048 + 6.106154590T) \\
\Delta H &= - 1594.13 \text{ cal/mole} \\
\Delta S &= 6.10615 \text{ eu}
\end{aligned}$$

For UHgl_4 above 300° C

$$\begin{aligned}
\log P_{\text{amal}} &= 8.71063 - \frac{3829.23}{T} \\
\log P_{\text{Hg}} &= 7.84409 - \frac{3124.81}{T} \\
\overline{\Delta F} &= 4.574T \left(0.86654 - \frac{704.42}{T} \right) \\
&= - (3222.01708 - 3.96355396T)
\end{aligned}$$

Check:

T	$\overline{\Delta F}$	$\overline{\Delta F}$ (from Table IV)
648	- 653.63	- 647.386

$$\begin{aligned}
\Delta F_{\text{UHgl}_4} &= \Delta F_{\text{UHg}_3} + \overline{\Delta F}_{\text{UHgl}_4} \text{ over } 300^\circ \text{ C} \\
&= - (555.46656 + 6.31152726T + 3222.01708 - 3.96355396T) \\
&= - (3777.48364 + 2.34797330T) \\
\Delta H &= - 3777.4836 \text{ cal/mole} \\
\Delta S &= 2.34797 \text{ eu}
\end{aligned}$$

DISCUSSION

The first conflict with previous data came when it was found that compositions between UHg_4 and pure Hg produced a $\log p$ vs. $1/T$ line distinct from the pure mercury line (note Fig. 15). This was not expected on the basis of a previously published phase diagram (Fig. 1). However, Wilson's diagram indicated that at one point four phases existed: UHg_3 , UHg_4 , Hg(gas), and Hg(liquid). With the components uranium and mercury and the temperature, pressure, and composition fixed, substitution in Gibbs' phase rule for the system indicated that this was an impossible situation. This same diagram corrected to agree with the data of the present work is shown in Fig. 17. Note that the decomposition temperatures, at 1 atmosphere pressure, agree reasonably well except that, since the present work added a distinct isotherm for the equilibrium vaporization of mercury from a saturated solution of uranium in mercury, which is not present in Wilson's diagram, a somewhat different interpretation must be given to the various thermal holds with which Wilson fixed his temperatures. Figure 3 indicates a slight thermal hold at about 420°C , which appears to supply the missing temperature.

TABLE V. DECOMPOSITION TEMPERATURES OF URANIUM-MERCURY INTERMETALLIC COMPOUNDS AT 1 ATMOSPHERE

Compound	Temperature, $^\circ\text{C}$		
	Present Experimental	From Wilson Article	Modified from Wilson Data
Saturated soln.	366		365
UHg_4	383	365	390
UHg_3	417	390	420
UHg_2	436	460	460

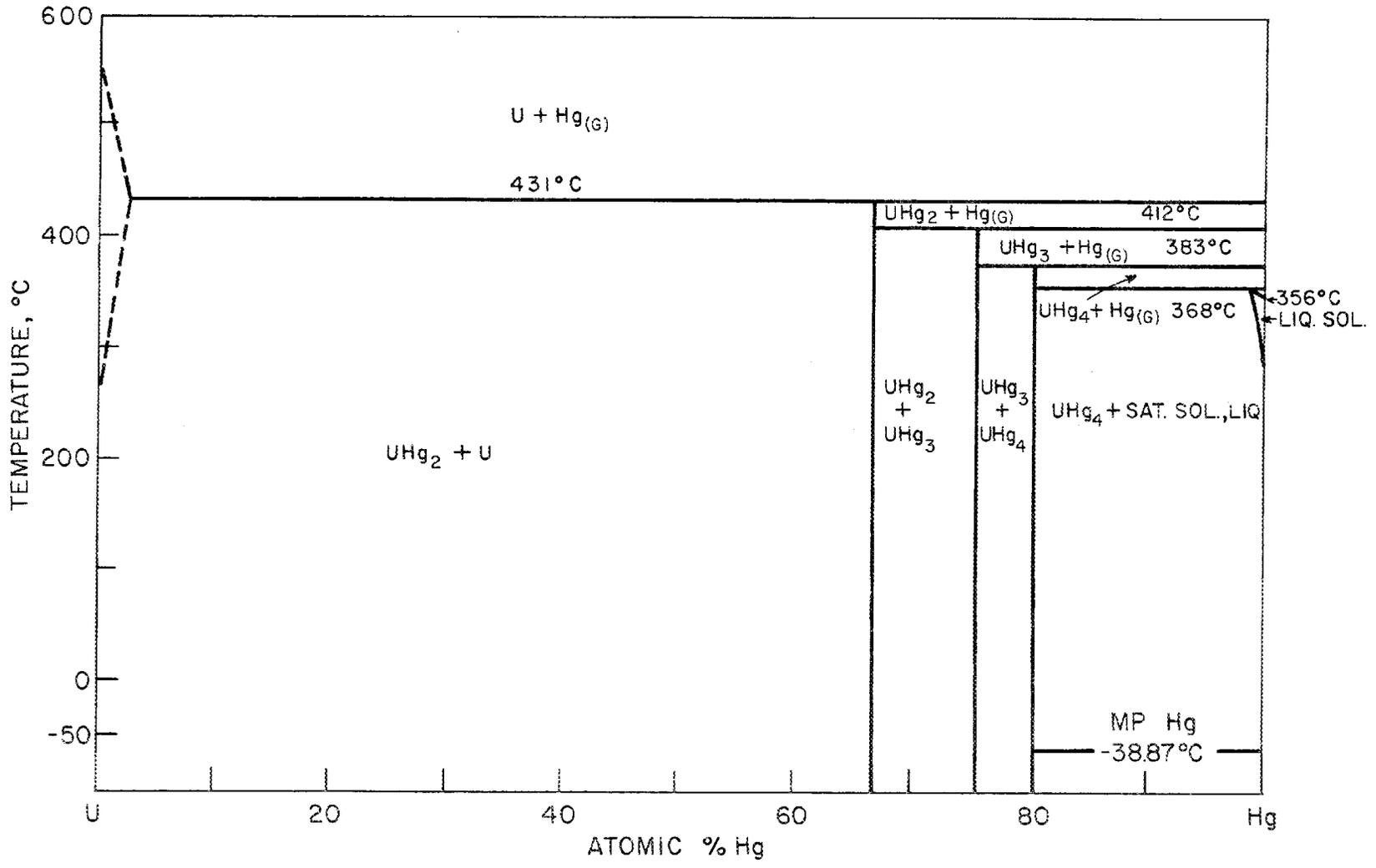


FIGURE 17. URANIUM-MERCURY DIAGRAM UNDER 1 ATMOSPHERE PRESSURE.

As further evidence of the possible distinct isobar for a saturated solution in this system reference can be made to a recent publication by Chiotti, Klepfer, and Gill⁽¹⁷⁾ covering work at Iowa State College on the uranium-zinc system. This investigation was carried out by vapor pressure measurements very similar to the present work, and a distinct vapor pressure isobar was found for the saturated solution. The phase diagram likewise showed an area similar to that shown here in Fig. 17.

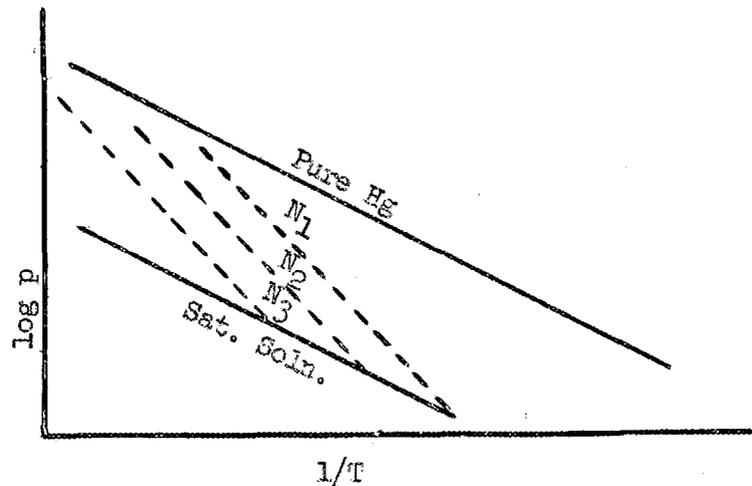
The slight but rather sharp change in slope of the vapor pressure curve for UHg_4 indicates some sort of crystallographic transformation. No known transformation exists for either uranium or the compound at this temperature. Also, no method of further investigation was available. Such behavior is not unique to this case but shows up in other systems occasionally, and it was not deemed of sufficient importance to the present objectives to pursue.

From the work of Messing⁽⁴⁾ it is possible to calculate an integral ΔH of solution. Glasstone⁽²⁷⁾ develops the equation

$$\Delta H_{\text{sol}} = - \frac{R \ln N_2/N_1}{1/T_2 - 1/T_1}$$

where N is the mole fraction and T the absolute temperature. By this means Messing has calculated the heat of solution to be about -6.67 kcal per mole of uranium over the temperature range investigated in the present work, 175 - 375° C. At first it was hoped that the information determined in this work concerning the vapor pressure of the saturated solution of uranium in mercury would enable a comparison or check calculation between the two independent laboratory studies. However this was not found to be possible.

In the case of the solubility data the heat effect of change of mole fraction with temperature, at constant pressure, $(\partial N/\partial T)_p$, was determined. In the present work the change of pressure with temperature was measured, but not at constant mole fraction. The concentration also changed with temperature since there was always excess uranium present. Graphically, what was measured in the present work was seen to be a series of terminal points, at saturation, of a family of $(\partial P/\partial T)_N$ curves:



As shown here the dotted lines are at constant mole fraction with $N_1 < N_2 < N_3$, etc. The vapor pressure of these unsaturated solutions would have to be investigated further before thermodynamic calculations could be made for the solutions by the methods used in the present work. This is not recommended because of the very narrow range of solubility, only up to 1.3% by weight of uranium in mercury at its boiling point.

The choice of a function of the type $A + B/T$ to fit both the experimentally determined data on the amalgams and the vapor pressure of pure mercury might be considered open to question. It cannot be denied,

however, that such a choice simplifies the curve fitting and other calculations. Assumption of the usual form of equation for heat capacity, $C_p = A + BT$, and conversion of this assumption to ΔH , ΔF , and $\log p$ equations produces for the latter case:

$$\log p = A + B/T + C \log T$$

Some data published in 1955 by Spedding and Dye⁽²⁸⁾ on the vapor pressure of pure mercury were given in this form. However, the simpler form was chosen for the present work since the temperature range covered was so narrow. The calculated σ_{fit} given in this report for the resulting equations justifies the choice. It is of interest also to note that the data of Spedding and Dye, as well as other data they quoted, agreed within 0.2% with the International Critical Tables values.

Finally, it is the opinion of the author that the present investigation has resulted in significant new information necessary and applicable to the problems at hand in nuclear fuel reprocessing. Further efforts, using different laboratory methods, might extend these data into other ranges of temperature. Likewise, it is possible that measurements on unsaturated solutions would be of value. The technical difficulties of this latter work would be great and some other approach would probably be better.

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