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THERMODYNAMIC PROPERTIES OF URANIUM-MERCURY SYSTEM

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Based on a M. S. thesis submitted to Iowa State University

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Thermodynamic properties of uranium-mercury system

by

Tsang-Sheau Lee

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The EMF values in the fused salt cells of the type $U(\alpha) | KCl-LiCl-BaCl_2$ eutectic, $UCl_3 | U-Hg$ alloy, for the different two-phase alloys in the uranium-mercury system have been measured and the thermodynamic properties of this system have been calculated. These calculated values are in good agreement with values based on mercury vapor pressure measurements made by previous investigators. The inconsistency of the thermodynamic properties with the phase diagram determined by Frost are also confirmed. A tentative phase diagram based on the thermodynamic properties measured in this work was constructed.

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I. INTRODUCTION

The phase diagram of the uranium-mercury system, Fig. 1, was established by Frost (1) and the existence of the three intermediate phases UHg_4 (22.88 wt % U), UHg_3 (28.35 wt % U), and UHg_2 (37.24 wt % U) had been well-established by Rundle and Wilson (2).

Uranium-mercury compound or uranium amalgam is an intermediate product of a nuclear fuel reprocessing method, known as Hermex process (3), in which mercury is used as solvent or extractant. The uranium metal is recovered by volatilizing the mercury in vacuum or inert gas stream, and melting the resulting sponge to massive metal. The thermodynamic properties of the compounds are important in developing and evaluating large-scale nuclear fuel reprocessing and decontamination.

The free energy of formation of the three compounds, based on mercury vapor pressure measurements by the dewpoint method, has been determined by Forsberg (4). The standard free energies of formation, in $\text{cal}\cdot\text{mol}^{-1}$, with liquid mercury and alpha uranium as standard states are given by Forsberg (4) as:

$$\Delta G_f^\circ(\text{UHg}_2) = -92 - 4.39T \quad (448-648\text{K}) \quad (1)$$

$$\Delta G_f^\circ(\text{UHg}_3) = -555 - 6.31T \quad (448-648\text{K}) \quad (2)$$

$$\Delta G_f^\circ(\text{UHg}_4) = -1594 - 6.11T \quad (448-573\text{K}) \quad (3)$$

$$\Delta G_f^\circ(\text{UHg}_4) = -3777 - 2.35T \quad (573-648\text{K}) \quad (4)$$

THE URANIUM-MERCURY SYSTEM AFTER FROST

Fig. 1. Phase diagram of uranium-mercury system from Ref. (1)

The entropies in these equations are positive and unrealistic. One would expect them to be negative. As pointed out by Johnson (5), Forsberg used an unconventional and apparently an improper correction procedure to account for low thermocouple readings of the dewpoint temperature. Forsberg's data were reevaluated by Chiotti et al. (6) and a correction of five degrees Celsius added to each dewpoint temperature. The corrected data yielded the following relations for the free energy of formation for the compounds. Two high temperature data points were discarded in arriving at Eq. 7.

$$\Delta G_f^\circ(\text{UHg}_2) = -4360 + 1.35T \quad (448-648\text{K}) \quad (5)$$

$$\Delta G_f^\circ(\text{UHg}_3) = -6520 + 2.56T \quad (448-648\text{K}) \quad (6)$$

$$\Delta G_f^\circ(\text{UHg}_4) = -8840 + 4.78T \quad (448-648\text{K}) \quad (7)$$

Jangg and Steppan (7) employed an "isoteniskop" to measure the vapor pressure of mercury and they report the free energies of formation, in $\text{cal}\cdot\text{mol}^{-1}$, as

$$\Delta G_f^\circ(\text{UHg}_2) = -13300 + 9.90T \quad (583-683\text{K}) \quad (8)$$

$$\Delta G_f^\circ(\text{UHg}_3) = -16000 + 12.2T \quad (553-683\text{K}) \quad (9)$$

$$\Delta G_f^\circ(\text{UHg}_4) = -19500 + 16.7T \quad (543-633\text{K}) \quad (10)$$

More recent measurements of the mercury vapor pressure by the dewpoint method by Mason and Chiotti (8) (unpublished data) yielded, in $\text{cal}\cdot\text{mol}^{-1}$, with alpha uranium and liquid mercury as reference states the following relations:

$$\Delta G_f^\circ(\text{UHg}_2) = -9422 + 4.83T \quad (727-853\text{K}) \quad (11)$$

$$\Delta G_f^\circ(\text{UHg}_3) = -11461 + 6.25T \quad (433-653\text{K}) \quad (12)$$

$$\Delta G_f^\circ(\text{UHg}_4) = -14460 + 10.39T \quad (397-634\text{K}) \quad (13)$$

All of these three works involved the measurements of the mercury vapor pressure. However, the results were not very consistent. The thermodynamic data as well as solubility data are not consistent with the phase diagram.

In Fig. 1, the mercury-rich liquidus curve up to 629K can be represented by the relation

$$\ln X_U = -4860T^{-1} + 5.615 \quad (293-629\text{K}) \quad (14)$$

At 629K, the solubility of uranium in mercury is 12 at.%. However, the solubility of uranium in mercury determined by Messing and Dean (9) can be represented by the relation

$$\ln X_U = -3251T^{-1} + 0.5728 \quad (293-629\text{K}) \quad (15)$$

This equation yields 1.0 at.% at 629K. The solubility determined by Jangg and Palman (10) can be represented by the relation

$$\ln X_U = -2804T^{-1} - 0.5721 \quad (293-523\text{K}) \quad (16)$$

which gives 0.65 at.% at 629K. Ahmann et al. (11) also found the solubility of uranium in mercury at 623K to be 0.89 at.%. However, their data cannot be fitted in a linear equation of the above type. As pointed out by Dean (12), Frost's data are in error. Therefore, the best relation for the solubility of uranium in mercury is taken to be the combined data of Eq. 15 and Eq. 16. The result is

$$\ln X_U = -3121T^{-1} + 0.2378 \quad (293-629K) \quad (17)$$

The solubility of uranium in mercury represented by Eq. 14, Eq. 15 and Eq. 16 and Ahmann et al. (11) data are shown in Fig. 2.

The purpose of this investigation is to determine the chemical potential of uranium in these alloys from EMF measurements in fused salt cells. From these measurements, the free energies of formation of the compounds can be obtained. An attempt will be made to resolve the discrepancy between the thermodynamic data and the phase diagram.

Fig. 2. Solubility data of uranium in mercury

II. EXPERIMENTAL PROCEDURE

A. Alloy Preparation

Three uranium-mercury alloys, 5 at.% U-Hg, 22 at.% U-Hg and 30 at.% U-Hg, were prepared for this investigation.

Uranium metal powder was prepared by the hydride method (13). Uranium shavings were used in this process and were cleaned with trichloro-ethane, then with 1:1 nitric acid and then washed with water and finally with acetone. The cleaned uranium shavings were heated at 230°C for half an hour under 1 atm. of hydrogen gas and then heated at 370°C for one hour under vacuum. The uranium powder was taken out in the glove box under helium gas atmosphere and identified by x-ray diffraction powder pattern.

The exact ratios of uranium powder and triply distilled mercury were sealed in 1/2" tantalum crucibles under a helium atmosphere. The sealed crucible was enclosed in a welded stainless steel jacket and heated in a rocking furnace. The 5 at.% U-Hg alloy was heated at 360°C for three weeks. The other two alloys were heated at 360°C, 400°C and 450°C for one week at each temperature.

The x-ray diffraction powder patterns were taken of the three alloys. The powdered samples were sealed in 0.3 mm glass capillaries under a helium atmosphere. Only a few diffraction lines appeared in 5 at.% U-Hg sample pattern.

According to the phase diagram, it is supposed to contain

UHg₄ and free mercury. There is no x-ray file data for the UHg₄ compound, i.e., it is still an unknown crystal structure. For 22 at.% U-Hg alloy, 71 lines were measured in the powder pattern film. This alloy is supposed to contain UHg₄ and UHg₃. However, none of the lines is identical to any line of UHg₃ x-ray file data. Therefore, the lines were taken to be for the UHg₄ compound. The diffraction lines of this alloy are listed in Appendix A. The absence of UHg₃ in the 22 at.% U-Hg alloy can be explained on the assumption that the UHg₃ existed in the center of the particles with UHg₄ surrounding the UHg₃. Because both uranium and mercury are heavy metals, x-ray cannot penetrate to the center of the sample particles and little or no scattering of the UHg₃ is observed. However, some of the strong lines for UHg₃ could be accounted for by some of the weak lines observed and it is assumed that this alloy actually contained both phases, UHg₄ and UHg₃.

The 30 at.% U-Hg alloy contained both UHg₃ and UHg₂ which were identified by the x-ray diffraction patterns.

B. Cell Arrangement and Apparatus

The preparation of the electrodes and the assemblage of the fused-salt cells were all done in a controlled atmosphere glove box filled with helium. The helium was purified by circulating it through a molecular sieve to remove moisture and through zirconium chips and titanium sponge at 650°C to

remove oxygen. An atmosphere of helium was maintained in the glove box while the EMF was being measured.

A schematic diagram of the cell is shown in Fig. 3. The cell container is 1 1/2" in diameter and 3" in height and made from tantalum sheet. The uranium rod anode was cleaned with 1:1 nitric acid and acetone and fastened on the end of 1/8" tantalum tube. The uranium-mercury cathode was alloy powder contained in a 3/8" diameter tantalum crucible welded on to a 1/8" tantalum tube. A chromel-alumel thermocouple was located inside the tantalum tube of the cathode electrode. The ternary eutectic salt, K_2Cl_2 37.1 at.%, Li_2Cl_2 51.4 at.%, $BaCl_2$ 11.5 at.%, was used as electrolyte in the cell and 5 wt.% of UCl_3 was added.

The cell EMF was measured with a differential voltmeter, Model 1002 made by Precision Standards Corporation. The temperature of the cell was measured with a chromel-alumel thermocouple.

C. EMF Measurements Employed to Check the Apparatus

EMF measurements of a 9.0 wt.% U-Zn alloy vs. U were made to check the experimental apparatus. The EMF of this alloy vs. U is well-established and its EMF has been reviewed by Chiotti and Mason (14). The relation for the EMF, in volts, and the temperature, in degrees Kelvin, is

$$E = 0.76245 - 5.309 \times 10^{-4} T \quad (18)$$

Fig. 3. Apparatus used for EMF measurements

- A. Anode lead wire
- B. Cap of furnace tube
- C. Glove box bottom
- D. Cooling water inlet
- E. Stainless furnace tube
- F. Quartz sleeve for furnace tube
- G. Quartz sleeve for electrode
- H. Tantalum tube
- I. Tantalum cell container
- J. Uranium rod as an anode
- K. Quartz glass stand
- L. Fire brick
- M. Tantalum crucible
- N. Thermocouple junction
- O. Heating furnace
- P. Cooling water outlet
- Q. "O" ring seal
- R. Cathode lead wire
- S. Thermocouple lead wires
- T. "O" ring seal

for the temperature range from the melting point of zinc, 693°K, to 953°K. The alloy consists of UZn_{12} in equilibrium with dilute liquid zinc solution. The derived standard free energy of formation of UZn_{12} from alpha uranium and liquid zinc is

$$\Delta G_f^\circ = -52746 + 36.729T \quad (19)$$

For temperatures below 693°K, the standard free energy of formation of UZn_{12} can be obtained by summing the free energy change for the following reactions:

Therefore, the EMF of the above cell for temperatures below 693°K should vary with temperature according to the relation

$$E = 0.4563 - 8.877 \times 10^{-5} T \text{ (volt)} \quad (23)$$

The EMF of UZn_{12} vs. U were measured from 603°K to 813°K. The results are expressed by the following equations:

$$E = 0.4355 - 5.593 \times 10^{-5} T \text{ (volt)} \quad (603-693\text{K}) \quad (24)$$

$$E = 0.7645 - 5.312 \times 10^{-4} T \text{ (volt)} \quad (693-813\text{K}) \quad (25)$$

The EMF measurements are within ± 1 mv of the previous literature values, Eq. 18, for temperatures above 693°K and within ± 2 mv from Eq. 23 for temperatures below 693°K.

These results are within the uncertainty of the Eqs. 18

and 23. Consequently, it may be concluded that the experimental apparatus was functioning properly.

D. Relations between Cell EMF's and the Free Energy of Formation of Compounds UHg_4 , UHg_3 and UHg_2

For a UHg_4 -Hg alloy as a cathode electrode and uranium rod as an anode electrode the reactions of anode, cathode and overall cell are

and

$$\begin{aligned} \Delta G_{\text{RXN}} &= -nFE_{\text{cell}} = \Delta \bar{G}_{\text{U}(\alpha)} - \bar{G}_{\text{U}}^{\ell} - G_{\text{U}}^{\circ, \alpha} \\ &= \Delta G_{\text{f}}^{\circ}[\text{UHg}_4] - 4\Delta \bar{G}_{\text{Hg}} \end{aligned} \quad (29)$$

from which the free energy of formation of UHg_4 can be calculated by the relation,

$$\Delta G_{\text{f}}^{\circ}[\text{UHg}_4] = -nFE_{\text{cell}} + 4\Delta \bar{G}_{\text{Hg}} \quad (30)$$

where n , the number of electrons transferred is 3, F , Faraday's constant is 23060 cal/volt-equivalent, and E_{cell} is EMF of the cell in volts.

For UHg_3 - UHg_4 two-phase alloy as a cathode electrode and uranium rod as an anode electrode, the anode, cathode and overall reactions can be expressed as follows:

and

$$\begin{aligned} \Delta G_{\text{RXN}}^{\circ} &= -nFE_{\text{cell}} = \Delta \bar{G}_{\text{U}(\alpha)} - \bar{G}_{\text{U}}^{\circ} - G_{\text{U}}^{\circ, \alpha} \\ &= 4\Delta G_{\text{f}}^{\circ}[\text{UHg}_3] - 3\Delta G_{\text{f}}^{\circ}[\text{UHg}_4] \end{aligned} \quad (34)$$

from which the free energy of formation of the UHg_3 compound can be obtained by the relation,

$$\Delta G_{\text{f}}^{\circ}[\text{UHg}_3] = -1/4 nFE_{\text{cell}} + 3/4 \Delta G_{\text{f}}^{\circ}[\text{UHg}_4] \quad (35)$$

where $\Delta G_{\text{f}}^{\circ}[\text{UHg}_4]$ is obtained from Eq. 30.

For UHg_3 - UHg_2 two-phase alloy as a cathode electrode and uranium rod as an anode, the anode, cathode and overall cell reactions are

and

$$\begin{aligned} \Delta G_{\text{RXN}}^{\circ} &= -nFE_{\text{cell}} = \Delta \bar{G}_{\text{U}(\alpha)} \\ &= 3 \Delta G_{\text{f}}^{\circ}[\text{UHg}_2] - 2 \Delta G_{\text{f}}^{\circ}[\text{UHg}_3] \end{aligned} \quad (39)$$

from which the free energy of formation of UHg_2 can be obtained by the relation

$$\Delta G_{\text{f}}^{\circ}[\text{UHg}_2] = -1/3 nFE_{\text{cell}} + 2/3 \Delta G_{\text{f}}^{\circ}[\text{UHg}_3] \quad (40)$$

where $\Delta G_{\text{f}}^{\circ}[\text{UHg}_3]$ is obtained from Eq. 35.

III. EXPERIMENTAL RESULTS AND CALCULATIONS

A. Results of EMF Measurements

The EMF values of the three two-phase alloys vs. temperature are shown graphically in Fig. 4. A least mean square linear equation of EMF, in volts, as a function of temperature, in degrees Kelvin, was determined for each of the alloys. For the 5 at.% U-Hg alloy which is in the Hg-UHg₄ two-phase region and EMF data were measured over the temperature range, 613 K to 627 K, the equation is

$$E = (0.2694 - 2.388 \times 10^{-4} T) \pm 0.00073 \text{ (volts)}. \quad (41)$$

For the 22 at.% U-Hg alloy which is in the UHg₄-UHg₃ two-phase region and EMF measured from 613 K to 648 K the equation is

$$E = (0.04607 + 7.178 \times 10^{-5} T) \pm 0.001 \text{ (volts)}. \quad (42)$$

For the 30 at.% U-Hg alloy which is in UHg₃-UHg₂ two-phase region and EMF measured from 613 K to 684 K the equation is

$$E = (0.08195 - 3.747 \times 10^{-5} T) \pm 0.00038 \text{ (volts)}. \quad (43)$$

The data were taken after the cell reaction attained equilibrium, i.e., the EMF reading was steady and reproducible. With the 5 at.% U-Hg and 22 at.% U-Hg alloys, it took one week to attain equilibrium and data were then taken for another week. With the 30 at.% U-Hg alloy, the cell reaction attained equilibrium after two weeks and EMF data were taken for another two weeks.

Fig. 4. Measured EMF versus temperature

The relative partial molal free energy of uranium in $\text{cal}\cdot\text{mol}^{-1}$, in the Hg-UHg_4 two-phase region is obtained directly from Eq. 41 by multiplication by -3×23060 to give

$$\Delta \bar{G}_{\text{U}(\alpha)} = -18639 + 16.52T. \quad (44)$$

If we accept Eq. 17 as the best solubility equation of uranium in mercury, then the molar fraction of mercury, X_{Hg} , at 625 K is 0.9914 and $\Delta \bar{G}_{\text{Hg}} = RT \ln X_{\text{Hg}} = -10.7 \text{ cal/mole}$ at 625 K. Therefore, $\Delta \bar{G}_{\text{Hg}}$ was assumed to be negligible and according to Eq. 30, the free energy of formation of UHg_4 is

$$\Delta G_f^\circ(\text{UHg}_4) = (-18639 + 16.52T) \pm 50 \quad (613-627 \text{ K}). \quad (45)$$

For UHg_3 and UHg_4 two-phase region, the partial molal free energy of uranium can be calculated from Eq. 34 and Eq. 42 and can be represented by the following equation in $\text{cal}\cdot\text{mol}^{-1}$,

$$\Delta \bar{G}_{\text{U}(\alpha)} = -3187 - 4.966T. \quad (46)$$

and, from Eq. 35, the free energy of formation of UHg_3 is

$$\Delta G_f^\circ(\text{UHg}_3) = (-14776 + 11.15T) \pm 70 \quad (613-648 \text{ K}) \quad (47)$$

For UHg_2 and UHg_3 two-phase region, the partial molal free energy of uranium which is calculated from the Eq. 39 and Eq. 43

$$\Delta \bar{G}_{\text{U}(\alpha)} = -5669 + 2.59T \quad (48)$$

and, from the Eq. 40, the free energy of formation of UHg_2 is

$$\Delta G_f^\circ(\text{UHg}_2) = (-11740 + 8.30T) \pm 30 \quad (613-684 \text{ K}). \quad (49)$$

Seven samples, 0.2, 0.3, 0.6, 1, 8, 15 and 18 at.% U-Hg alloys, which are all in Hg-UHg₄ two-phase region, were prepared by the addition of pure mercury to the 22 at.% U-Hg alloy. The EMF values of these seven samples relative to pure uranium were also measured. The results are summarized in Table 1. For these alloys, it took two or three days to attain equilibrium and data were taken for another three days to one week. Because of the high vapor pressure of mercury, the cell EMF could only be measured from the melting point of the ternary electrolyte salt, 339°C, to 356°C. In Table 1, the EMF data are listed for 350°C and 340°C only.

Table 1. EMF data of alloys in Hg-UHg₄ two-phase region

Sample	Composition	EMF, mv	
		at 340°C	at 350°C
A	18 at.% U-Hg	121.1	120.4
B	15 at.% U-Hg	121.1	120.1
C	8 at.% U-Hg	122.4	120.7
D	1 at.% U-Hg	121.1	120.4
E	0.6 at.% U-Hg	121.1	120.8
F	0.3 at.% U-Hg	140.4	142.4
G	0.2 at.% U-Hg	142.6	147.0

B. Solubility of Uranium in Mercury

According to the phase diagram, Fig. 1, the alloys A and B in Table 1 are in the same two-phase region up to 365°C and the alloys C, D, E, F and G are in the liquid phase region above 340°C. Therefore, the EMF values of alloys A and B should be the same and the emf values of alloys C, D, E, F and G should be higher. However, the EMF values of alloys A, B, C, D and E at 350°C and 340°C in Table 1 have the same value within the experimental error and the values for alloys F and G are higher. This means that the alloys A, B, C, D and E are in the same UHg_4 -Hg two-phase region and alloys F and G are in the liquid phase region above 340°C. Therefore, it may be concluded that the mercury-rich liquidus curve in Fig. 1 is wrong and Eq. 17 is accepted as the best representation for the solubility of uranium in mercury.

C. Comparison of Thermodynamic Data

Relations for the free energy of formation of the uranium compounds based on data obtained by various workers and in the present investigation are summarized in Table 2. The calculated free energies of formation at the peritectic temperatures are listed in Table 3. These values are in fair agreement except for Forsberg's (4) data.

The relative partial molal free energies of mercury and uranium in various two-phase regions of uranium-mercury system are listed in Table 4 and Table 5 respectively. It is

Table 2. Parameters A and B for equations for the standard free energy of formation of uranium compounds

$$\Delta G_f^\circ = A + BT$$

Compound	ΔG_f° in cal/mole		Temp. span °K	Reference
	A	B		
UHg ₂	-4360	1.35	448-648	Forsberg (4)
	-9422	4.83	727-853	Mason & Chiotti (8)
	-13300	9.90	583-683	Jangg & Steppan (7)
	-11740	8.30	613-684	This work
UHg ₃	-6520	2.56	448-648	Forsberg (4)
	-11461	6.25	433-653	Mason & Chiotti (8)
	-16000	12.20	553-683	Jangg & Steppan (7)
	-14776	11.15	613-648	This work
UHg ₄	-8840	4.78	448-648	Forsberg (4)
	-14460	10.39	397-634	Mason & Chiotti (8)
	-19500	16.8	543-633	Jangg & Steppan (7)
	-18639	16.52	613-627	This work

Table 3. Calculated free energy of formation of uranium compounds at peritectic temperatures based on various investigators, this investigation and phase diagram

$\Delta G_f^\circ(\text{UHg}_2)$ at 728K	$\Delta G_f^\circ(\text{UHg}_3)$ at 663K	$\Delta G_f^\circ(\text{UHg}_4)$ at 638K	Reference
-3377	-4823	-5790	(4)
-5905	-7317	-7831	(8)
-6092	-7911	-8782	(7)
-5698	-7384	-8099	this work
-732	-1002	-1214	from U-rich liquidus ^a
-1920	-3491	-4335	from Hg-rich liquidus ^b

^aThe data are obtained from the uranium-rich liquidus shown in the following section IV A-1.

^bThe data are obtained from the mercury-rich liquidus shown in the following Section IV A-2.

Table 4. Relative partial molal free energy of uranium,
 $\Delta \bar{G}_U = (\bar{G}_U - \bar{G}_U(\alpha))$, for various two-phase regions
of the U-Hg system

Equilibrium phases	Temp. K; cal·mol ⁻¹			Ref.
	400	600	800	
UHg ₂ -UHg ₃				
$\Delta\bar{G}_U = -40 - 1.07T$	-468	-682	-896	(4)
$\Delta\bar{G}_U = -5344 + 1.99T$	-4548	-4150	-3752	(8)
$\Delta\bar{G}_U = -7900 + 5.30T$	-5780	-4720	-3660	(7)
$\Delta\bar{G}_U = -5669 + 2.59T$	-4633	-4115	-3597	this work
UHg ₃ -UHg ₄				
$\Delta\bar{G}_U = 440 - 4.1T$	-1200	-2060	-2840	(4)
$\Delta\bar{G}_U = -2464 - 6.17T$	-4932	-6166	-7400	(8)
$\Delta\bar{G}_U = -5500 - 1.60T$	-6140	-6460	-6780	(7)
$\Delta\bar{G}_U = -3187 - 4.966T$	-5173	-6166	-7159	this work
UHg ₄ -Hg				
$\Delta\bar{G}_U = -8840 + 4.78T$	-6928	-5972	-5016	(4)
$\Delta\bar{G}_U = -14460+10.39T$	-10304	-8226	-6148	(8)
$\Delta\bar{G}_U = -19500+16.80T$	-12780	-9420	-6060	(7)
$\Delta\bar{G}_U = -18639+16.527$	-12032	-8727	-5423	this work

Table 5. Relative partial molal free energy of mercury,
 $\Delta\bar{G}_{\text{Hg}} = (\bar{G}_{\text{Hg}} - \bar{G}_{\text{Hg}(\text{l})})$, for various two-phase regions
of the U-Hg system

Equilibrium phases	Temp. K; cal·mol ⁻¹			Reference
	400	600	800	
UHg ₂ -U				
$\Delta\bar{G}_{\text{Hg}} = -2180 + 0.675T$	-1910	-1775	-1640	(4)
$\Delta\bar{G}_{\text{Hg}} = -4711 + 2.42T$	-3743	-3759	-2775	(8)
$\Delta\bar{G}_{\text{Hg}} = -6650 + 4.95T$	-4670	-3680	-2690	(7)
$\Delta\bar{G}_{\text{Hg}} = -5870 + 4.15T$	-4210	-3380	-2550	this work
UHg ₂ -UHg ₃				
$\Delta\bar{G}_{\text{Hg}} = -2160 + 1.21T$	-1676	-1434	-1192	(4)
$\Delta\bar{G}_{\text{Hg}} = -2039 + 1.42T$	-1471	-1187	-903	(8)
$\Delta\bar{G}_{\text{Hg}} = -2700 + 2.30T$	-1780	-1320	-860	(7)
$\Delta\bar{G}_{\text{Hg}} = -3036 + 2.85T$	-1896	-1326	-756	this work
UHg ₃ -UHg ₄				
$\Delta\bar{G}_{\text{Hg}} = -2320 + 2.22T$	-1432	-988	-544	(4)
$\Delta\bar{G}_{\text{Hg}} = -2999 + 4.14T$	-1343	-515	+313	(8)
$\Delta\bar{G}_{\text{Hg}} = -3500 + 4.60T$	-1660	-740	+180	(7)
$\Delta\bar{G}_{\text{Hg}} = -3863 + 5.37T$	-1715	-641	+433	this work

seen that $\Delta\bar{G}_U$ and $\Delta\bar{G}_{Hg}$ for the various two-phase regions are all in fair agreement except for some of Forsberg's (4) data. It should be noted that Forsberg's (4) data for $\Delta\bar{G}_{Hg}$, Table 5, are in good agreement except for the data for the UHg_2 -U two-phase alloys. It appears that his vapor pressure data for this region is in error. This error is propagated in the calculation of the thermodynamic properties of the compounds and in some of the calculated quantities given in Table 4. The $\Delta\bar{G}_U$ vs. temperature and $\Delta\bar{G}_{Hg}$ vs. temperature of Jangg and Steppan (7), Mason and Chiotti (8) and this work are shown in Fig. 5 and Fig. 6, respectively. The relative partial molal free energies of mercury, $\Delta\bar{G}_{Hg}$, are all observed data except for this work. The relative partial molal free energies of uranium, $\Delta\bar{G}_U$, are all calculated from the free energies of formation of uranium-mercury compounds except for this work wherein $\Delta\bar{G}_U$ was obtained directly from the EMF measurements.

D. Relative Partial Molal Excess Free Energy of Uranium at Infinite Dilution in Liquid Mercury

The data obtained permit a calculation of the relative partial molal excess free energy at infinite dilution relative to pure liquid uranium, $\Delta\bar{G}_{U(l)}^{XS,\infty}$. In the EMF measurements, pure solid α -uranium was the reference electrode. It is necessary to correct to pure uranium liquid as reference state. If we accept the Equation 44 for the partial molal free energy of uranium in the mercury-rich region and use Eq. 74 (which is

Fig. 5. The relative partial molal free energy of uranium in various two-phase regions

Fig. 6. The relative partial molal free energy of mercury in various two-phase regions

derived in the following section) as the free energy of fusion of uranium for the temperatures below 938 K, then

$$U(\alpha) \rightarrow U(l_s) \quad \Delta \bar{G}_{U(\alpha)} \quad (50)$$

$$U(l) \rightarrow U(\alpha) \quad -\Delta G_U^{\circ, \alpha \rightarrow l} \quad (51)$$

$$U(l) \rightarrow U(l_s) \quad \Delta \bar{G}_{U(l)} \quad (52)$$

$$\begin{aligned} \Delta \bar{G}_{U(l)} &= \Delta \bar{G}_{U(\alpha)} - \Delta G_U^{\circ, \alpha \rightarrow l} \\ &= -21146 + 17.456T \end{aligned} \quad (53)$$

and with Eq. 17 for the solubility of uranium in mercury, leads to

$$\begin{aligned} \Delta \bar{G}_{U(l)}^{xs, \infty} &= \Delta \bar{G}_{U(l)} - RT \ln X_U \\ &= -21146 + 17.456T - (-6201 + 0.472T) \\ &= -15130 + 16.98T \quad (293-629K) \end{aligned} \quad (54)$$

IV. CONSISTENCY OF THE PHASE DIAGRAM DATA WITH MEASURED THERMODYNAMIC PROPERTIES

A. Calculations of the Thermodynamic Properties of Liquid Alloys

1. Calculations based on uranium-rich liquidus

Some of the thermodynamic properties for the liquid alloys can be calculated from the phase diagram, Fig. 1. However, these calculations are valid only if the phase diagram is correct. According to the phase diagram, the liquid phase is in equilibrium with nearly pure solid uranium at temperature above 728°K. Therefore, the partial molal free energy of uranium relative to pure liquid uranium can be expressed as follows:

$$\Delta \bar{G}_{U(l)} = - \Delta G^{\circ}(\text{fusion } \gamma\text{-U}) \quad (1408\text{-}1049\text{K}) \quad (55)$$

$$\Delta \bar{G}_{U(l)} = - \Delta G^{\circ}(\text{fusion } \gamma\text{-U}) - \Delta G_U^{\circ}(\beta \rightarrow \gamma) \quad (1049\text{-}942\text{K}) \quad (56)$$

$$\Delta \bar{G}_{U(l)} = - \Delta G^{\circ}(\text{fusion } \gamma\text{-U}) - \Delta G_U^{\circ}(\beta \rightarrow \gamma) - \Delta G_U^{\circ}(\alpha \rightarrow \beta) \quad (942\text{-}728\text{K}) \quad (57)$$

Therefore, accepting the liquidus curve above 728 K in Fig. 1, $\Delta \bar{G}_U$ relative to pure liquid uranium can be calculated from the liquidus data and the known enthalpy of fusion and transformation of uranium, and the heat capacity of liquid, α , β and γ phases. Alpha (α) uranium is stable up to 942 K, β uranium to 1049 K and γ uranium to 1408 K. These data were obtained from reference (15) and were used in the calcula-

tions. The results are

$$\Delta \bar{G}_{U(l)} = 1307 - 18.907T + 2.48T \ln T \quad (1408-1049^\circ\text{K}) \quad (58)$$

$$\Delta \bar{G}_{U(l)} = -994 - 8.992T + 1.37T \ln T \quad (1049-942^\circ\text{K}) \quad (59)$$

$$\Delta \bar{G}_{U(l)} = 1390 - 59.342T - 4.65 \times 10^{-3} T^2 + 8.994T \ln T \quad (942-298^\circ\text{K}) \quad (60)$$

At temperatures of 1173, 1073, 1049, 973, 873, 773 and 728 K. the mole fractions of uranium in the liquid are 0.606, 0.519, 0.500, 0.452, 0.394, 0.346 and 0.327, respectively. The excess relative partial molal free energy of uranium at these temperatures can be obtained by the following equation

$$\Delta \bar{G}_U^{xs} = \Delta \bar{G}_{U(l)} - RT \ln X_U \quad (61)$$

and the results are listed in Table 6. These data were fitted to a relation of the type

$$\Delta \bar{G}_U^{xs} / (1 - X_U)^2 = (\alpha + \beta T) + (\alpha' + \beta' T) X_U^n \quad (62)$$

where α , β , α' , β' and n are constants. The Gibbs-Duhem equation leads to

$$\Delta \bar{G}_{Hg}^{xs} / (1 - X_{Hg})^2 = (\alpha + \beta T) + (\alpha' + \beta' T) X_U^{n-1} \left(X_U - \frac{n}{n+1} \right) \quad (63)$$

A computer was employed to obtain the five parameters which best fit the liquidus data. Constants were found to be $\alpha = -2993$, $\beta = 6.364$, $\alpha' = -8908$, $\beta' = 9.209$ and $n = 1.2$. The comparison of $\Delta \bar{G}_U^{xs}$ values from Eq. 61 and Eq. 62 are listed in Table 6. Further details on the use of equations of this type have been presented elsewhere (16).

Table 6. The comparison of $\Delta\bar{G}^{xs}$ values from Eq. 61 and Eq. 62

Temp. °K	X_U	$\Delta\bar{G}_U^{xs^a}$	$\Delta\bar{G}_U^{xs^b}$	$\Delta\bar{G}_U^{xs^b}$	- $\Delta\bar{G}_U^{xs^a}$
		cal/mole			
1173	0.606	855	855		0
1073	0.519	987	990		3
1049	0.500	1013	1002		-11
973	0.452	963	966		3
873	0.394	828	837		9
773	0.346	606	609		3
728	0.327	492	482		-10

$^a\Delta\bar{G}_U^{xs}$ is calculated from Eq. 61.

$^b\Delta\bar{G}_U^{xs}$ is obtained from Eq. 62 and the five obtained parameters.

The free energies of formation of the three compounds at the peritectic temperatures can be calculated from the phase diagram data and data for the liquid alloys. At 728 K, we have the equilibrium

and

$$\Delta G_f^\circ(\text{UHg}_2) = 2\Delta \bar{G}_{\text{Hg}} = 2(\Delta \bar{G}_{\text{Hg}}^{\text{xs}} + RT \ln X_{\text{Hg}}) \quad (65)$$

where ls represents liquid solution with $X_{\text{U}} = 0.327$, according to Frost's phase diagram, Fig. 1. The above parameters and Eq. 63 yield $\Delta G^\circ(\text{UHg}_2) = -732$ cal/mole. Similarly at the 663°K peritectic, we have the equilibrium

with $X_{\text{U}} = 0.236$. The above equation can be obtained by the summation of the following equations:

Therefore

$$\Delta G_f^\circ(\text{UHg}_3) = 3\Delta \bar{G}_{\text{Hg}} + \Delta G_{\text{U}}^{\circ, \alpha \rightarrow \text{l}} + \Delta \bar{G}_{\text{U}(\text{l})} \quad (72)$$

where $\Delta G_{\text{U}}^{\circ, \alpha \rightarrow \text{l}}$ is the standard free energy of fusion of -U.

According to Eq. 60

$$\Delta G_{\text{U}}^{\circ, \alpha \rightarrow \text{l}} = -\Delta \bar{G}_{\text{U}(\text{l})} = -1390 + 59.342T + 4.65 \times 10^{-3}T^2 - 8.99T \ln T \quad (73)$$

for temperatures from 942°K to 298°K. This equation was linearized to $a+bT$ to simplify subsequent calculation with minor loss in accuracy, the result is

$$\Delta G_U^{\circ, \alpha \rightarrow \ell} = 2507 - 1.936T \quad (942-298K) \quad (74)$$

The free energy of formation of UHg_3 follows from the relations

$$\bar{\Delta G}_{Hg} = \bar{\Delta G}_{Hg}^{XS} + RT \ln X_{Hg} \quad (75)$$

$$\bar{\Delta G}_U = \bar{\Delta G}_U^{XS} + RT \ln X_U \quad (76)$$

$$\Delta G_f^{\circ}(UHg_3) = -1002 \text{ cal/mole} \quad (663K) \quad (77)$$

At 663 K, we also have the equilibrium

and

$$\Delta G_{RXN} = -\bar{\Delta G}_{Hg} = \Delta G_f^{\circ}(UHg_2) - \Delta G_f^{\circ}(UHg_3) \quad (82)$$

Therefore

$$\begin{aligned} \Delta G_f^{\circ}(UHg_2) &= \Delta G_f^{\circ}(UHg_3) - \bar{\Delta G}_{Hg} \\ &= -1002 + 250 \\ &= -752 \text{ cal/mole} \end{aligned} \quad (83)$$

At the 638 K peritectic temperature we have the equilibrium

with $X_U = 0.174$. This equation can be obtained by the summation of the following relations:

Therefore

$$\Delta G_f^\circ(UHg_4) = 4\Delta \bar{G}_{Hg} + \Delta G_U^{\circ, \alpha \rightarrow \ell} + \Delta \bar{G}_U(\ell) \quad (90)$$

and

$$\Delta G_f^\circ(UHg_4) = -1214 \text{ cal/mole} \quad (638 \text{ K}). \quad (91)$$

At 638 K, there also exists the equilibrium

and

From Eq. 95

$$\Delta G_{RXN} = -\Delta \bar{G}_{Hg} = \Delta G_f^\circ(UHg_3) - \Delta G_f^\circ(UHg_4) \quad (96)$$

and

$$\begin{aligned} \Delta G_f^\circ(UHg_3) &= \Delta G_f^\circ(UHg_4) - \Delta \bar{G}_{Hg} \\ &= -1214 + 186 \\ &= -1028 \text{ cal/mole} \end{aligned} \quad (97)$$

These values are summarized in Table 3 and it is seen that all are lower in magnitude than the other values.

2. Calculations based on mercury-rich liquidus and uranium-rich liquidus

The two parameters, α and β , of Eq. 62 are directly related to $\Delta G_{U(l)}^{XS,\infty}$, the excess partial molal free energy of uranium in liquid mercury at infinite dilution. At infinite dilution ($X_U \rightarrow 0$), $\Delta G_{U(l)}^{XS,\infty}$ is given by Eq. 54. Therefore, $\alpha = -15130$ and $\beta = 16.98$, values for α' and β' with $n = 1$ were calculated from the data for the uranium-rich liquidus as described in the preceding section. It was found that $\alpha' = 28430$ and $\beta' = -24.20$. With these two parameters in Eq. 62, the free energy of formation of UHg_2 at 728 K can be obtained by substitution in Eq. 65 to obtain

$$\Delta G_f^\circ(UHg_2) = -1920 \text{ cal/mole} \quad (98)$$

Similarly, at 663 K Eqs. 72 and 82 were used and the free energy of formation of UHg_3 and UHg_2 are -3491 cal/mole and -2738 cal/mole respectively. At 638 K, Eqs. 90 and 96 were applied to obtain $\Delta G_f^\circ(UHg_4) = -4335$ cal/mole and $\Delta G_f^\circ(UHg_3) = -3835$ cal/mole, respectively. These values are still lower in magnitude than the values listed in Table 3.

Although the Eqs. 62 and 63 may not be exact functional relations for the temperature and composition dependence of the excess thermodynamic properties of the liquid alloys, they should be reasonably good approximations. The results summarized in Table 4 indicate the phase diagram is not consistent with the measured thermodynamic data.

B. Construction of a Tentative Phase Diagram

The above calculations indicate the phase diagram, Fig. 1, is inconsistent with the thermodynamic data and the mercury-rich liquidus of Fig. 1 is not consistent with solubility data obtained by other investigators. A tentative phase diagram based on the free energies of formation of U-Hg compounds obtained from this work and the solubility of uranium in mercury reported by Dean (12) was constructed and shown in Fig. 7. In the derivation of the phase diagram the parameters α , β , α' , β' and n were reevaluated as described below.

According to Dean (12), the solubility of uranium in mercury exceeds 19 at.% at 600°C. It was assumed that the solubility of uranium in mercury is 20 at.% at 600°C. The liquidus curve was extrapolated from 600°C to 350°C to meet data for Eq. 17 to obtain the values listed in Table 7.

In the following calculations, the assumption is made that the equilibrium phases are liquid and UHg_2 above 390°C in the mercury-rich region. Therefore, from the temperature 390°C up to 600°C, we have the equilibrium reaction

and this reaction can be obtained by the summation of the following reactions

Therefore

$$\Delta \bar{G}_{\text{U}(\ell)} = \Delta G_f^\circ(\text{UHg}_2) - \Delta G_U^{\circ, \alpha \rightarrow \ell} - 2\Delta \bar{G}_{\text{Hg}} \quad (105)$$

and

$$\Delta \bar{G}_{\text{U}(\ell)}^{\text{xs}} = \Delta G_f^\circ(\text{UHg}_2) - \Delta G_U^{\circ, \alpha \rightarrow \ell} - 2\Delta \bar{G}_{\text{Hg}} - RT \ln X_{\text{U}} \quad (106)$$

The equilibrium reaction between 365°C and 390°C leads to the Eq. 66. According to the Eq. 72 the excess molal free energy of uranium is

$$\Delta \bar{G}_{\text{U}(\ell)}^{\text{xs}} = \Delta G_f^\circ(\text{UHg}_3) - \Delta G_U^{\circ, \alpha \rightarrow \ell} - 3\Delta \bar{G}_{\text{Hg}} - RT \ln X_{\text{U}} \quad (107)$$

and the equilibrium reaction below 365°C is the same as the Eq. 84 and the excess molal free energy of uranium in this region is expressed as

$$\Delta \bar{G}_{\text{U}(\ell)}^{\text{xs}} = \Delta G_f^\circ(\text{UHg}_4) - \Delta G_U^{\circ, \alpha \rightarrow \ell} - 4\Delta \bar{G}_{\text{Hg}} - RT \ln X_{\text{U}} \quad (108)$$

which is derived from Eq. 90.

The excess molal free energies of uranium up to 600°C were calculated from these equations and the equations of the standard free energies of formation of the U-Hg compounds of this work listed in Table 2. The results are listed in Table 7.

If we assume the values of $\Delta \bar{G}_{\text{U}}^{\text{xs}}/(1-X_{\text{U}})^2$ below 455°C can

be represented by a relation of $\alpha + \beta T$ type, then the best values for α and β are -12671 and 13.41, respectively. With these two constants, solubility data and the $\Delta\bar{G}_{U(l)}^{xs}$ data of columns 2 and 3 in Table 7, for temperatures above 455°C, values of $\Delta\bar{G}_{U(l)}^{xs}/(1-X_U)^2$ were calculated. The best values of α' and β' obtained by a least mean square method are 17130 and -30.27, respectively, and n is equal to one. Substituting these parameters into Eq. 62 and Eq. 63 yields

$$\Delta\bar{G}_{U(l)}^{xs} = [(-12671+13.41T)+(17130-30.27) X_U](1-X_U)^2 \quad (109)$$

and

$$\Delta\bar{G}_{Hg}^{xs}=[(-12671) +13.41T)+(17130-30.27)(X_U-0.5)]X_U^2 \quad (110)$$

The $\Delta\bar{G}_{U(l)}^{xs}$ values calculated from Eq. 109 and from Eqs. 106, 107 and 108 are listed in Table 7, column 4 and 3, respectively, for comparison.

Equations 109 and 110 were employed to calculate the free energy of formation of UHg_4 , UHg_3 and UHg_2 at 365°C, 390°C and 455°C, to obtain

$$\Delta G_f^\circ(UHg_4) = -8158 \text{ cal/mole at } 365^\circ\text{C} \quad (111)$$

$$\Delta G_f^\circ(UHg_3) = -7096 \text{ cal/mole at } 390^\circ\text{C} \quad (112)$$

$$\text{and } \Delta G_f^\circ(HUg_2) = -5965 \text{ cal/mole at } 455^\circ\text{C} \quad (113)$$

These values compare favorably to the values of the free energy of formation of U-Hg compounds of this work listed in Table 3.

The free energy of fusion of UHg_2 can be obtained by the

Table 7. The comparison of $\Delta\bar{G}_U^{xs}$ values calculated from Eq. 109 and from Eqs. 106, 107 and 108 and $\Delta\bar{G}_{Hg}^{xs}$ values calculated from Eq. 110 at different temperatures in the tentative phase diagram

Temp. °K	X_U	$\Delta\bar{G}_{U(l)}^{xs}$ ^a	$\Delta\bar{G}_{U(l)}^{xs}$ ^b	$\Delta\bar{G}_{Hg}^{xs}$
		cal/mole		
873	0.200	-1745	-1807	73
858	0.176	-1843	-1848	53
838	0.150	-1969	-1928	33
823	0.134	-2065	-2008	21
773	0.090	-2346	-2376	3
728	0.057	-2482	-2835	-2
663	0.030	-3868	-3640	-2
638	0.015	-3970	-4025	-1
573	0.0055	-4672	-4934	0
473	0.0017	-6417	-6302	0

^aThe $\Delta\bar{G}_{U(l)}^{xs}$ values are calculated from Eqs. 106, 107 and 108 at the different temperatures.

^bThe $\Delta\bar{G}_{U(l)}^{xs}$ values are obtained from Eq. 109.

following cycle

$$\Delta G_{UHg_2}^{fus} = -\Delta G_f^\circ(UHg_2) + 3\Delta G_m + \Delta G_U^{\circ, \alpha \rightarrow \ell} \quad (116)$$

where ΔG_m is the molal free energy of mixing

$$\Delta G_m = X_U \bar{\Delta G}_U + X_{Hg} \bar{\Delta G}_{Hg} \quad (117)$$

where X_U is equal to 0.333 and X_{Hg} is 0.667. The Eq. 113 for $\Delta G_f^\circ(UHg_2)$ and Eq. 74 for $\Delta G_U^{\circ, \alpha \rightarrow \ell}$ are applied in Eq. 116 and the result is

$$\Delta G_{UHg_2}^{fus} = 7704 - 8.439T \quad (118)$$

From this equation, the melting point of UHg_2 is 913 K or 640°C.

The liquidus curves on either side of UHg_2 compound also can be determined by the above cycle. The liquidus curve with the solid uranium as an equilibrium phase is determined by the relation

$$\bar{\Delta G}_{U(\ell)} = RT \ln X_U + \bar{\Delta G}_{U(\ell)}^{xs} \quad (119)$$

The Eqs. 58, 59 and 60 were used for $\bar{\Delta G}_{U(\ell)}$ for the α , β and γ phases, respectively, and Eq. 109 was applied for $\bar{\Delta G}_{U(\ell)}^{xs}$. A eutectic point was found at 375°C and $X_U = 0.65$. The calculated phase diagram is shown in Fig. 7.

Fig. 7. Tentative phase diagram of U-Hg system

V. CONCLUSIONS

(1) The temperature spans of the EMF measurements in this investigation are narrow, especially in UHg₄-Hg two-phase region, but the precision is better than that obtained by the other investigators. The results of this work are in fair agreement with the other works.

(2) The best values of the free energies of formation of UHg₂, UHg₃ and UHg₄ compounds at temperatures 728 K, 663 K and 638 K, respectively, obtained by taking the mean value of the data of Mason and Chiotti (8), Jangg and Steppan (7) and this work as listed in Table 3, are

$$\Delta G_f^\circ(\text{UHg}_2) = -5906 \text{ cal/mole at } 728 \text{ K}$$

$$\Delta G_f^\circ(\text{UHg}_3) = -7550 \text{ cal/mole at } 663 \text{ K}$$

$$\Delta G_f^\circ(\text{UHg}_4) = -8254 \text{ cal/mole at } 638 \text{ K}$$

(3) The solubility of uranium in mercury does not exceed 1 at.% at 350°C as indicated by Jangg and Palman (10), Ahman et al. (11), Messing and Dean (9) and the EMF measurements of this work. Therefore, we may conclude that the liquidus in the mercury-rich region of Frost's (1) phase diagram, Fig. 1, is wrong. The equation which best represents the solubility of uranium in mercury is Eq. 17

$$\ln X_U = -3121T^{-1} + 0.2378 \quad (293-623\text{K}) \quad (17)$$

(4) The thermodynamic data imply that the UHg₂ compound should not decompose peritectically at 455°C (728 K) and

exist in equilibrium with α -uranium and mercury-rich liquidus.

(5) The tentative phase diagram, Fig. 7, may not be realistic. The assumption is made in the construction of the phase diagram that the equilibrium phases at 455°C are liquid and UHg_2 instead of liquid, α -uranium and UHg_2 . The result is the formation of a eutectic point at 375°C and $X_{\text{U}} = 0.65$, however, no such phenomenon has been reported to date. The α' , β' , α and β parameters in Eqs. 109 and 110 may need modification to yield a more realistic phase diagram.

(6) It should be noted that the U-Hg alloys need a long time to reach equilibrium. When the alloys are heated above the peritectic temperatures and cooled down, the reverse reaction requires more than two weeks at the temperatures just below the peritectic temperatures to attain equilibrium. Consequently time did not permit a detailed thermal analysis of the U-Hg alloys.

VI. REFERENCES

1. Frost, B. R. T. "The system uranium-mercury," J. Inst. Metals, 82, 456-462 (1954).
2. Rundle, R. E. and Wilson, A. S. "The structures of some metal compounds of uranium," Acta Cryst., 3, 148-150 (1949).
3. Morrison, B. H. and Blanco, R. E. "The Hermex Process for metal decontamination by mercury processing," USAEC Report ORNL-CF-56-1-151, 1956.
4. Forsberg, H. C. "Thermodynamic properties of the uranium mercurides," USAEC Report ORNL-2885, 1960.
5. Johnson, I. "Thermodynamics of plutonium, thorium, and uranium metallic systems," in "Compounds of interest in nuclear reactor technology," Nuclear Metallurgy Vol. X, Met. Soc. AIME, Ann Arbor, Mich., 1964, pp. 171-192.
6. Chiotti, P., Akhachinskiy, V. V., Ansara, I., and Rand, M. H. "The chemical thermodynamics of actinide elements and compounds, Part VIII - The actinide alloys," International Atomic Energy Agency, Vienna, to be published.
7. Jangg, G. and Steppan, F. "Dampfdruckmessungen an binären Amalgamen," Z. Metallk., 56, 172-178 (1965).
8. Mason, J. T. and Chiotti, P., Ames Laboratory, Ames, Iowa, Private communication, 1977.
9. Messing, A. F. and Dean, O. C. "Solubilities of selected metals in mercury," USAEC Report ORNL-2871, 1960.
10. Jangg, G. and Palman, H. "Die Löslichkeit verschiedener Metalle in Quecksilber," Z. Metallk., 54, 364-369 (1963).
11. Ahmann, D. H., Baldwin, R. R. and Wilson, A. S., "The uranium-mercury system," Ames Laboratory Report CT-2960, 1945.
12. Dean, O. C. "Mercury processing of uranium and its alloys," in "Progress in nuclear energy series," Process Chemistry Vol. 2. Pergamon Press Ltd., London, 1958, pp. 412-419.

13. Chiotti, P. and Rogers, B. A. "The production of uranium and thorium in the powder form," USAEC Ames Laboratory Report ISC-31, 1959.
14. Chiotti, P. and Mason, J. T. "Phase diagram and thermodynamic properties of the uranium-zinc system," J. Less-Common Metals, 40, 39-55 (1975).
15. Oetting, F. L., Rand, M. H., and Ackermann, R. J. "The chemical thermodynamics of actinide elements and compounds, Part I - The actinide elements," International Atomic Energy Agency, Vienna, 1976, p. 40.
16. Chiotti, P., Simmons, M. F. and Kateley, J. A. "Calculation of thermodynamic properties from phase diagrams," in "Symposium on reprocessing of nuclear fuels," Nuclear Metallurgy Vol. 15, USAEC Report CONF-69081, 1969, pp. 659-688.

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VIII. APPENDIX A. X-RAY DATA OF 22 at.% U-Hg ALLOY

Camera: 114.2 cm diameter Debye-Scherrer camera

X-ray target: copper

Filter: nickel

Exposure time: 12 hours

Table A1. X-ray data of the 22 at.% U-Hg alloy

Line no.	Wavelength	Intensity	Angle ^a	Sin θ	Spacings d, Å
1	AA ^b	W ^c	15.96	0.27499	2.80339
2	AA	W	17.00	0.29234	2.63700
3	AA	VVS ^d	17.60	0.30243	2.54896
4	AA	W	18.10	0.31067	2.48137
5	AA	VVW ^e	19.63	0.33590	2.29501
6	AA	VVW	19.95	0.34124	2.25906
7	AA	VVVW ^f	20.54	0.35084	2.19728
8	AA	W	20.89	0.35656	2.16201
9	AA	VW ^g	21.38	0.36447	2.11510
10	AA	VVVW	23.44	0.39784	1.93767
11	AA	W	25.35	0.42817	1.80043
12	AA	W	29.11	0.48645	1.58472
13	AA	W	29.57	0.49354	1.56196
14	AA	W	30.18	0.50279	1.53324
15	AA	VSh ^h	31.55	0.52327	1.47322
16	AA	VVW	32.58	0.53853	1.43148
17	AA	VW	33.75	0.55557	1.38756
18	AA	VVVW	34.34	0.56405	1.36671
19	AA	VW	35.31	0.57804	1.33363
20	AA	VW	36.17	0.59017	1.30621
21	AA	Si ⁱ	37.10	0.60322	1.27796
22	AA	VVVW	38.09	0.61693	1.24956
23	AA	S	42.37	0.67397	1.14380

^aThe angles have been corrected by the film shrinkage factor.

^bAA = average wavelength, 1.54178Å.

^cW = weak.

^dVVW = very very strong.

^eVVW = very very weak.

^fVVVW = line intensity is hard to distinguish.

^gVW = very weak.

^hVSh = very strong.

ⁱS = strong.

Table A1. (Continued)

Line no.	Wavelength	Intensity	Angle	Sin θ	Spacings d, Å
24	AA	VVVW	43.28	0.68551	1.12455
25	AA	VVVW	43.91	0.69355	1.11151
26	AA	W	44.72	0.70368	1.09551
27	AA	VVW	45.53	0.71367	1.08017
28	AA	VVVW	47.69	0.73949	1.04246
29	AA	W	48.88	0.75328	1.02338
30	AA	W	49.37	0.75894	1.01575
31	AA	VVVW	50.23	0.76864	1.00292
32	AA	VVVW	50.54	0.77210	0.99843
33	AA	VVVW	51.06	0.77784	0.99106
34	AA	VVVW	51.76	0.78548	0.98143
35	AA	W	52.88	0.79739	0.96677
36	AA	VVVW	53.63	0.80523	0.95735
37	AA	VVW	54.27	0.81177	0.94965
38	AA	VVVW	54.84	0.81760	0.94287
39	AA	VVW	55.30	0.82215	0.93765
40	AA	VVVW	57.36	0.84211	0.91542
41	AA	VVVW	58.64	0.85392	0.90276
42	AA	W	60.28	0.86845	0.88766
43	A1 ^j	W	60.57	0.87099	0.88434
44	A2 ^k	VVW	61.25	0.87669	0.88078
45	A1	VVW	61.63	0.87986	0.87543
46	A1	VVW	62.00	0.88296	0.87236
47	A1	VW	64.06	0.89929	0.85651
48	A1	VW	64.40	0.90184	0.85410
49	A2	VVW	64.75	0.90446	0.85373
50	A1	VVVW	65.65	0.91106	0.84545
51	A1	VVVW	66.05	0.91389	0.84283
52	A2	VVW	67.13	0.92142	0.83801
53	A1	W	67.98	0.92706	0.83086
54	A1	VVW	69.26	0.93522	0.82361
55	A2	VVW	69.62	0.93743	0.82167
56	A1	VVW	70.54	0.94288	0.81692
57	A1	VW	71.05	0.94581	0.81439
58	A2	VW	71.42	0.94786	0.81464
59	A1	VVVW	72.42	0.95332	0.80798
60	A1	S	73.02	0.95643	0.80534

^jA1 = K alpha one wavelength, 1.54051Å.

^kA2 = K alpha two wavelength, 1.54433Å.

Table A1. (Continued)

Line no.	Wavelength	Intensity	Angle	Sin θ	Spacings d, Å
61	A2	S	73.43	0.95847	0.80562
62	A1	W	74.06	0.96156	0.80105
63	A2	W	74.61	0.96413	0.80089
64	A1	S	75.20	0.96682	0.79669
65	A2	S	75.74	0.96918	0.79672
66	A1	S	77.01	0.97439	0.79050
67	A1	VW	77.66	0.97690	0.78847
68	A2	VW	78.29	0.97920	0.78857
69	A1	W	79.15	0.98212	0.78428
70	A2	W	79.90	0.98449	0.78433
71	A1	S	80.87	0.98732	0.78014
72	A2	S	81.80	0.98977	0.78014

IX. APPENDIX B. EXPERIMENTAL EMF DATA

Table B1. EMF data of U-Hg alloys.

Composition	Temp., °K	EMF, mv
30 at.% U-Hg	683	56.3
	678	56.6
	666	57.1
		57.5
	655	57.3
	646	57.5
		57.4
	645	57.9
		58.2
	643	56.8
	638	57.5
	636	58.2
		57.9
		58.4
	635	58.5
	634	58.1
	628	58.6
	624	58.6
	623	58.1
	622	59.0
	619	59.2
22 at.% U-Hg		58.9
	648	92.8
	645	93.6
	642	90.5
		91.6
	638	92.0
	634	92.6
	631	91.0
		90.2
	629	91.8
	627	92.4
	624	90.2
	618	89.8
5 at.% U-Hg		90.9
	627	119.0
	626	119.7
		120.7
	625	119.9
		121.0
	623	120.5
	622	120.7

Table B1. (Continued)

Composition	Temp., °K	EMF, mv
5 at.% U-Hg	621	121.2
	620	120.9
	618	122.5
		122.9
		121.6
		122.1
	617	120.6
	616	122.6