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THE SOLUBILITY OF HYDROGEN IN PLUTONIUM
IN THE TEMPERATURE RANGE
475 to 825 DEGREES CENTIGRADE

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by

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This thesis for the Master of Science degree by

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has been approved for the

Department of Chemistry

by

Larry G. Anderson

John M. Haschke

Date _____

Allen , Thomas Howard (Master of Science, Chemistry)
The Solubility of Hydrogen in Plutonium in the
Temperature Range 475 to 825 Degrees Centigrade
Thesis Directed by Professor Larry G. Anderson

The solubility of hydrogen (H) in plutonium metal (Pu) was measured in the temperature range of 475 to 825 °C for unalloyed Pu (UA) and in the temperature range of 475 to 625 °C for Pu containing two-weight-percent gallium (TWP). For TWP metal, in the temperature range 475 to 600 °C, the saturated solution has a maximum hydrogen to plutonium ratio (H/Pu) of 0.00998 and the standard enthalpy of formation ($\Delta H_f^\circ(s)$) is (-0.128 ± 0.0123) kcal/mol. The standard entropy of formation ($\Delta S_f^\circ(s)$) is (-0.0915 ± 0.0150) cal/mol K. The phase boundary of the solid solution in equilibrium with plutonium dihydride (PuH_2) is temperature independent. In the temperature range 475 to 625 °C, UA metal has a maximum solubility at $\text{H/Pu} = 0.011$ with $\Delta H_f^\circ(s) = (-0.0209 \pm 0.00598)$ kcal/mol and $\Delta S_f^\circ(s) = 0$. The phase boundary between the solid solution region and the metal+ PuH_2 two-phase region is temperature dependant. The solubility of hydrogen in UA metal was also measured in the temperature

range 650 to 825 °C with $\Delta H_f^\circ(s) = (-0.104 \pm 0.0143)$ kcal/mol and $\Delta S_f^\circ(s) = 0$. The phase boundary is temperature dependent and the maximum hydrogen solubility has H/Pu = 0.0674 at 825 °C. The empirical temperature (T) - pressure (P) relationship for unalloyed metal in the two-phase region over the 773 to 1098 K range is

$$\ln P_{(H_2, atm)} = 14.583 - 17313.132 * [1/T (K)]$$

and is in poor agreement with literature values. The most probable cause of the difference is in the experimental procedures used to measure equilibrium H_2 pressures. The enthalpy of formation (ΔH_f°) for PuH_2 is (-35.18 ± 0.68) kcal/mole and the entropy of formation (ΔS_f°) is (-33.3 ± 1.03) cal/mole K. These results are in excellent agreement with the literature values. ΔH_f° for forming PuH_2 with TWP metal is (-34.44 ± 1.83) kcal/mole and $\Delta S_f^\circ = (-33.0 \pm 3.0)$ cal/mole K. ΔH_f° for TWP metal is in poor agreement with the literature values, but, ΔS_f° is in excellent agreement. Unexpected features are seen in the pressure - composition isotherms for both the TWP and UA metals and possible reasons for these features are presented.

The form and content of this abstract are approved. I recommend its publication.

Signed _____

Larry G. Anderson

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CHAPTER 1

INTRODUCTION

Metal hydrides have been studied extensively. Much attention has been focused on the transition metal and rare earth metal hydrides¹. For example, the iron-hydrogen² system has been studied extensively because of the property changes that the metal undergoes due to hydrogen embrittlement. Palladium³ is used as a catalyst for organic hydrogenation reactions and because the metal is easy to handle, its hydrogen absorbing properties have been thoroughly investigated. More recently, new materials such as the lanthanum-nickel-five⁴ inter-metallics (LaNi_5) have been used for H_2 storage and supply. The pressure - composition - temperature relationship of LaNi_5 can be tailored by the addition of other metals such as silver, copper, and iron. With the addition of these other metals, the formula unit becomes $\text{LaNi}_{5-x}\text{M}_x$ where M = the third metal in the alloy.

In general metal hydrides have several uses such as safe storage for large quantities of H_2 , supplying extremely pure H_2 , the production of pure metals, and as

chemical reducing agents. This study focuses on the solubility of hydrogen in plutonium (Pu). Although Pu hydride is not considered to be a reasonable candidate for some of the above applications, (due to its potential radiological and environmental hazards) this work does fill a vacancy in the knowledge and understanding of plutonium chemistry.

Specific interest in the Pu-H system stems from three areas. First, hydriding is used as a recovery method for Pu metal and to obtain finely divided metal powders. The second area of interest is somewhat more esoteric: the comparison of the H solubility in two different allotropic forms, delta (δ) and epsilon (ϵ) phases, in the same temperature range. The third area of interest is in accurately defining the solubility limit of hydrogen in the metal.

Prior to the initiation of this study only three other studies of the Pu-H system had been done, one by I. B. Johns⁵ and two by Mulford and Sturdy^[6,7]. The Johns work was carried out using unalloyed Pu in the composition range $H/Pu \geq 2.0$ in the temperature range between 25 and 500 °C. The first Mulford and Sturdy study⁶, also using unalloyed Pu, investigated the composition range between $H/Pu = 0.1$ and 2.0 in the temperature range between 575 and 800 °C. There is a

small amount of solubility data for the low composition region, though not enough to accurately determine the phase boundary for dissolution of hydrogen in the metal. The second report by Mulford and Sturdy⁷ covered the composition range $H/Pu \geq 2.0$ in the same temperature range as their first paper. A Pu-H phase diagram is presented which combines the results from both references 6 and 7, however, the boundaries indicated for hydrogen solubility in plutonium differ between the two papers by approximately a factor of 2 and implies that the phase equilibria and thermodynamic properties are uncertain. This suggests an error in calculation of the hydrogen concentration. Concurrent with this experimental work, an independent study of hydrogen solubility in the liquid metal was completed by Condit and others.⁸ The results of Condit's work are discussed in chapter 4.

THE PHYSICAL AND CHEMICAL PROPERTIES OF PLUTONIUM

Plutonium was the second transuranic element to be discovered. It was produced in 1940 by Seaborg, McMillan, Kennedy and Wahl by bombarding uranium with deuterons. Naturally occurring Pu has also been found in uranium ores. The primary use of Pu is in nuclear weapons although other uses, such as power sources for spacecraft and fuel for power reactors, have been noted.

The isotope used in nuclear weapons is ^{239}Pu while ^{238}Pu is used in spacecraft power sources.

Plutonium is produced in nuclear reactors by the reaction of a neutron (n) with ^{238}U fuel rods by the following sequence:⁹

The reactor product is then cooled (not thermally) to allow the decay of short lived radionuclides. At the end of the cooling period, the cladding is removed from the uranium fuel rods and the rods dissolved in acid. The U and Pu are separated from the solution by solvent extraction using tributyl phosphate in a kerosene-type solvent¹⁰. After reduction of the Pu^{+IV} to Pu^{+III} by ferro sulfamate, the Pu is removed from the U - Pu organic phase into an aqueous phase. This is followed by reduction of Pu^{+III} to metal.

Plutonium, atomic number 94, is a radioactive element. The atomic weight is 242 grams/mole*. The

* The atomic weight of Pu is listed as 242 g/mol in the *CRC Handbook of Chemistry and Physics*. The atomic weight is the average weight based on the isotopic distribution. The isotopic distribution is dependant on both the neutron energy and time spent in the reactor and

metal has a theoretical density of 19.8 g/ml (α phase), the melting point is 640 °C (913 K), and the boiling point is 3232 °C (3503 K). Fifteen isotopes of Pu are known (molecular weight 232 to 246). The metal exhibits six allotropic forms (Table 1-1) and 5 oxidation states (+III, +IV, +V, +VI, and +VII) with the +IV state being the most stable in the solid state. The stability of the +IV state is due to the lower ionization potential for the 5f electrons (e^-). Pu is fissionable (a neutron source) and small amounts of gamma radiation are emitted, but, the primary mode of decay is by alpha emission. Unalloyed Pu has a negative coefficient of thermal expansion prior to melting. Figure 1-1¹¹ shows the idealized thermal expansion of unalloyed Pu on heating. The phase transitions from $\delta \rightarrow \delta'$, $\delta' \rightarrow \epsilon$, and $\epsilon \rightarrow$ liquid are accompanied by contraction.

The ground state electronic configuration for Pu is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6 5f^6 7s^2$ which would be predicted by the actinide theory. Seaborg¹² suggested that actinium and latter elements should form a series similar to the lanthanide series. This theory was attractive because of the differences in chemistry between neptunium and rhenium and between plutonium and

is targeted to yield ^{239}Pu for weapons use. All future references to Pu and it's alloys will assume ^{239}Pu .

TABLE 1-1							
Phase	Symmetry	Temperature Range (°C)	Lattice Constants (Å)				X-Ray Density
			a_0	b_0	c_0	β	
α	mono ¹	<122	6.183	4.822	10.96	101.79	19.86
β	mono	122 - 207	9.284	10.46	7.859	92.13	17.70
γ	ort ²	207 - 315	3.159	5.768	10.16	-	17.40
δ	fcc	315 - 457	4.637	-	-	-	15.92
δ'	bct	457 - 479	3.34	-	-	-	16.0
ϵ	bcc	479 - 640	3.636	-	-	-	16.51

¹Monoclinic

²Orthorhombic

Figure 1-1. Idealized coefficient of thermal expansion for unalloyed plutonium.

osmium. The theory has been supported by the evidence. As with the lanthanide series, there is also an actinide contraction which is also due to the presence of the 5f electrons.

Pu reacts with several common gases at elevated temperatures including O_2 , NH_3 , N_2 , H_2 , CO , CO_2 and the halogens. H_2 and O_2 react with Pu at room temperature. The metal also reacts with water and water vapor. Pu dissolves in several acids including HCl , HBr , HF , dilute H_2SO_4 , $HClO_4$, H_3PO_4 , and sulfamic acid. HNO_3 , at any concentration, and concentrated H_2SO_4 do not react with Pu because of passivation.¹³

Numerous elements form binary compounds with Pu. Other elements are miscible or form phases of variable composition with Pu. Table 1-2¹⁴ is a partial list of elements and their expected reaction with Pu. One of the more studied binary systems is the Pu-Ga system. Figure 1-2-A¹⁵ shows the Pu-Ga phase diagram and figure 1-2-B is the Pu-Ga phase diagram up to two-weight-percent Ga.

It is evident from the above discussion that the chemistry of Pu is rich and complex. This is due in large measure to the energy spacing of the valance electrons which leads to varied hybridization.

TABLE 1-2

Metals Forming Binary Compounds With Pu							
Be	Mg	Al	Sc	Mn	Fe	Co	Ni
Cu	Zn	Ga	Ge	Zr	Ru	Rh	Pd
Ag	Cd	In	Sn	Sb	Hf	Re	Os
Ir	Pt	Au	Hg	Tl	Pb	Bi	

Nonmetals Forming Binary Compounds With Pu				
H ₂	B	C	N ₂	O ₂
F ₂	Si	P	S	Cl ₂
As	Se	Br ₂	Te	I ₂

Elements That Are Immiscible In Pu							
Li	Na	K	Rb	Cs	Ca	Sr	Ba

Transition Metals With Limited or No Miscibility In Pu					
V	Cr	Nb	Mo	Ta	W

Metals That Are Miscible And May Form Phases of Variable Composition With Pu				
Ti	Y	La	Ce	Pr
Nd	Sm	Eu	Gd	Tb
Dy	Ho	Er	Tm	Yb
Lu	U	Np	Am

Figure 1-2-A. Plutonium - gallium phase diagram.

Figure 1-2-B. Subsection of the plutonium - gallium phase diagram to two-weight-percent Ga. Temperature range 400 to 700 °C.

FOCUS OF THE STUDY

The specific interest of this study is in the solubility of H in the ϵ , δ , and liquid phases of Pu. As is seen in table 1-1 and figure 1-2-B, the ϵ phase is present in unalloyed metal in the temperature region between 475 and 640 °C. Epsilon phase metal is body centered cubic (bcc). Figure 1-3¹⁶ shows a projection of a bcc unit array. The unit cell yields 6 tetrahedral sites or 1.5 octahedral sites per metal atom. These sites are mutually exclusive because both cannot be simultaneously occupied by interstitial atoms.

Delta phase metal is face centered cubic (fcc). Figure 1-4¹⁷ shows a projection of the fcc unit cell with 2 tetrahedral sites and one octahedral site per metal atom. These sites can be occupied simultaneously by interstitials.

It has been clearly and repeatedly established that H, when dissolved in an electropositive metal, prefers tetrahedral sites¹. This being the case, and based on simple arithmetic, it can be argued that the ϵ phase metal should dissolve more H than δ phase metal. The Pu-H system provides a unique opportunity to test this hypothesis.

In order to directly compare the solubility of hydrogen in the δ and ϵ phases of plutonium at the same

Figure 1-3. Body-centered-cubic array. Open circles are metal atoms, solid circle is tetrahedral site, and solid diamond is octahedral site.

Figure 1-4. Face-Centered-Cubic Unit Cell. Large open circles are metal atoms. Solid circles are tetrahedral sites and solid diamonds are octahedral sites.

temperatures, the stability range of one of the phases must be altered. As shown by figure 1-2-B, the δ phase is stable up to 600 °C when two-weight-percent Ga is alloyed with the plutonium. Since the ϵ phase is formed by unalloyed Pu over the temperature range 479 - 640 °C, the relative solubilities of hydrogen in the two phases can be determined from equilibrium H_2 pressure measurements in the 479 - 600 °C range.

The value of equilibrium measurements extends far beyond this objective. The solubility limit of hydrogen in solid and liquid plutonium can be more accurately defined and the thermodynamic properties of the Pu-H system can be more adequately determined than is possible from earlier studies.

CHAPTER 2

THEORY

INTRODUCTION

The dissolution of hydrogen (H) in a metal is a multi-step process that includes: 1) adsorption of H_2 on the metal surface, 2) dissociation of the H_2 molecule, and 3) movement of hydrogen atoms into the bulk metal. Once in the metal, hydrogen occupies interstitial sites or defects in the metal, e.g., at grain boundaries. The amount of hydrogen dissolved depends on the size, geometries (tetrahedral or octahedral, etc.), concentration of interstitial vacancies, the defect concentration, and the chemical environment provided by the metal. Within the metal, hydrogen can move or exists as H^0 , H^+ , or H^- depending on the specific chemical environment.

The following sections will more fully expand the concepts of dissolution, the determination of the solubility limit, and the calculation of thermodynamic quantities based on the experimental data.

ADSORPTION AND DISSOLUTION

Adsorption can occur as described by two mechanistic models. The first mechanism involves a loosely bound, high energy state in which the molecule is held on the metal surface through Van der Waals forces. In this state the molecule can be easily removed from the metal with vacuum and moderate heating. The second mechanism of adsorption involves a strong gas to metal chemical interaction, called chemisorption. Chemisorption is a chemically bound state in which the adsorbed molecule shares, donates, or accepts electrons from the metal surface. The gas can remain on the surface as a chemisorbed species or continue to the next step, dissociation.

The second step in the dissolution process is the dissociation of the gas molecule. For this step to occur, one of the following two conditions must exist at the metal surface; 1. the surface must be catalytic or 2. the adsorbed molecule must have sufficient kinetic energy to dissociate. If the metal surface is catalytic and the adsorbate is H_2 , the energies and symmetries of occupied free orbitals of the metal overlap with the antibonding orbitals of the H_2 molecule and dissociation follows. The activation energy of this process is very low.

Figure 2-1 shows a potential energy diagram (PED) for a non-catalytic dissociation process. Curve 1 is the PED for the chemisorption of H_2 and curve 2 is the PED for the metal-H atom bond. In this case, in order for dissociation to occur, the hydrogen molecule must have sufficient total energy to traverse, right to left, along curve 1 until it intersects with curve 2. At the intersection of curve 1 and curve 2, the molecule can follow curve 2, dissociate, and the atom react with the metal surface. If the molecule does not have sufficient energy to overcome E_A (E_A is the intersection of curve 1 and curve 2), then it is adsorbed at point Q_C . Dissociation must precede dissolution.

According to Speiser¹⁸, the chemisorption bond between hydrogen and Pu is covalent. This is supported by recent theoretical calculations by Eriksson¹⁹ et al, using the film linear muffin-tin orbital method. By analogy with PuO_2 , Eriksson assumed the surface form to be PuH_2 . The results show that the density of states is dominated by the 6d orbitals for Pu and the 1s orbital for hydrogen. Little charge transfer between Pu and hydrogen is observed (this is also observed in the bulk hydride). This suggest that the H-Pu bond is covalent and is a hybridization of the H1s and the Pu6d orbital. The total energy is minimized when the H atom is 0.03Å

Figure 2-1. Potential energy diagram for a noncatalytic dissociation process. Curve 1 is the potential energy diagram for chemisorption of H_2 . Curve 2 is the potential energy diagram for the formation of a metal-hydrogen bond. The intersection of the two curves is the activation energy for bond formation.

from the surface plane. In addition, the H1s energy states are about 6 eV below the Fermi level, while the Pu 6d states are at or above the Fermi level.

Titanium (Ti) forms a cubic dihydride similar to that of Pu. In looking at the Ti-H system, Switendick²⁰ has shown that since the H1s orbitals lie below the Fermi level, the energy of the system is lowered when the hydrogen orbitals are filled.

Haschke et al²¹ suggest that hydrogen in bulk PuH₂ is hydridic (H⁻) and that Pu is in the +III oxidation state, with one electron from the metal donated to each of the H atoms and the third electron going to the conduction band. Recent XPS work by Larson and Motyl²², on clean metal surfaces show the Pu metal to be in the +III oxidation state even when exposed to hydrogen pressures as low 1×10^{-5} torr. The findings of Haschke and Switendick and the experimental evidence of Larson do not agree with the theory of Speiser and Eriksson, but no explanation is offered. This area requires additional investigation.

In the following discussions, it will be assumed that the hydrogen is H⁻. With this condition existing at the surface, movement of hydrogen into the bulk metal should be quite facile, as there would be no energy barrier between the electronic state of the hydrogen at

the metal surface and the electronic state of the hydrogen in the bulk metal. On the other hand, should the dissociated hydrogen at the surface be bound in other chemical states (e.g. covalent bonds), then some activation energy should be present relating to the conversion of the hydrogen surface state to the H^- needed in the bulk metal state.

The spatial orientation for the approach of the hydrogen molecule is critical to the type of surface interaction. There are two ways in which hydrogen can approach the metal surface: with the bond axis parallel to or perpendicular to the metal surface. The bulk of the electron density in hydrogen is between the two H atoms. Therefore, if H_2 approaches the metal surface in a parallel manner, then, based on coulombic arguments, one would expect a Van der Waals type of interaction. In a perpendicular attack, the H_2 presents an area of low e^- density to the metal. Since Pu is electro-positive, the donation of an e^- to hydrogen is more likely with hydrogen in the perpendicular orientation. The higher the probability of chemisorption, the higher the probability of dissociation and dissolution. Hoffmann²³ presents a case for H_2 attacking nickel perpendicularly.

Although no information was found on the parallel attack of hydrogen, it can be argued that this type of

attack would lead to a Van der Waals type of interaction. This is because the bulk of the electron density of hydrogen is between the two H atoms and the electron density of Pu at the surface is very diffuse. Electron-electron interactions would prevent interaction in the more positive regions of the hydrogen molecule.

DETERMINATION OF SOLUBILITY LIMIT

The Gibbs' phase rule (equation 2-1) leads to a method for determining the solubility limit. Specifically,

$$F = C - P + 2 \quad (2-1)$$

where, F is the number of degrees of freedom (variables), specifically, "...the number of variables to which values must be assigned, in order to specify completely the state of the system."²⁴; C is the number of components in the system, specifically, "... a chemical species whose concentration in a phase can be varied independently of the other species' concentrations."²⁵; and P is the number of phases in the system. A phase is considered to be any homogeneous part of the system.

There are three degrees of freedom in the Pu-H system; pressure (P), temperature (T), and composition (C) of the solid (liquid) phase²⁶. At the start of a Pu+H₂ equilibrium experiment, the temperature is set to a

specified value and there is no hydrogen in the metal. When a small amount of H_2 is added to a constant volume system, some of the hydrogen dissolves in the Pu metal (the dissolution process can be followed by the drop in H_2 pressure) and at equilibrium, the pressure is P_1 . If the above process is repeated at a higher starting pressure than P_1 , equilibrium is established at a new pressure P_2 , where $P_1 < P_2$. During this process the composition has changed from C_1 to C_2 . By adding a third charge of gas, it is observed that the process will repeat itself. Therefore, at each pressure, $P_1, P_2, \dots, P_n$, along an isotherm in a single-phase region, it is clear that either the P or the C must be defined in order to completely specify the state. This is characteristic of the Pu-H solid solution region. Therefore, there are two degrees of freedom in this region.

The same result can be seen by using equation 1. There are 2 components, hydrogen and plutonium ($C = 2$). There are 2 phases, gas and solid ($P = 2$). Inserting these values for C and P into equation 1, we see that $F = 2$, the expected result. Therefore, a plot of pressure vs composition yields a curve with a positive slope, which is characteristic of a solid solution region.

At sufficiently high H_2 pressures, plutonium forms a compound with H_2 , plutonium dihydride (PuH_2). If enough

H_2 is added to form PuH_2 , at equilibrium, the pressure is now P_3 , the dihydride decomposition pressure at the specified temperature. The system has crossed the solubility limit and a phase change has occurred. The system has now entered the two-phase region. The two-phase region is plutonium metal saturated with H (phase 1) in equilibrium with PuH_2 (phase 2).

If additional hydrogen is added to the system, the resultant equilibrium pressure (P_4) will be equal to P_3 . On the pressure vs composition plot, this region is seen as a flat line (slope = 0). Since $P_3 = P_4$; and if the process is repeated, $P_3 = P_4 = P_5$; it is seen that in the two phase region, only the temperature need be specified to completely define the state of the system. That is, the pressure and composition are a function only of temperature. Therefore, there is only one degree of freedom in this region.

This is also seen from the phase rule. The number of components $C = 2$ (number of species (S) = 3, number of relations (R) = 1, $C = S - R$)²⁷, and the number of phases = 3. Applying equation 2-1, the degrees of freedom = 1. The intersection of the region where $F=1$ and the region where $F=2$ is the solubility limit of the solid solution.

After all the Pu metal is converted to PuH_2 , the system enters another solid solution region. In this region H_2 dissolves in PuH_2 . As with the metal solid solution region, there are 2 degrees of freedom and the same arguments hold.

The solubility limit can also be determined by using Sievert's law¹⁸. The reaction for the dissolution of H_2 in a metal is

The equilibrium constant (K) for this reaction is

$$K = \frac{[\text{H}]_{(\text{in solution})}}{(\text{H}_{2(\text{gas})})^{1/2}} \approx \frac{N_H}{(P_{\text{H}_2})^{1/2}}$$

where $[\text{H}]_{(\text{in solution})}$ is the concentration of hydrogen in solution, $(\text{H}_{2(\text{gas})})^{1/2}$ is the quantity of hydrogen gas, N_H is the atom fraction of hydrogen in solution, and $(P_{\text{H}_2})^{1/2}$ is the square root of the hydrogen pressure, therefore,

$$N_H = K \cdot P^{1/2} \quad (2-2)$$

Equation 2-2 is Sievert's law, which states that the solubility of a diatomic gas in a metal is proportional to the square root of the gas pressure. Therefore, on a plot of concentration vs $P^{1/2}$, the inflection point (change in slope) is the solubility limit and the slope of the line is the equilibrium constant.

THERMODYNAMICS

At equilibrium the chemical potential (μ) of the hydrogen gas is equal to the chemical potential of the hydrogen dissolved in the metal.

$$\mu_{(H_{gas})} = \mu_{(H_{solution})} \quad (2-3)$$

Since μ is defined as $(\delta G / \delta n)_{T,P}$ (the change in free energy (G) with respect to a change in quantity (n) at constant temperature (T) and pressure (P)) and at equilibrium there is no net change in quantity ($\delta n = \text{constant}$);

$$\mu_{(equilibrium)} = G. \quad (2-4)$$

Therefore,

$$G = \mu_{(H_{gas})} = \mu_{(H_{solution})} \quad (2-5)$$

and

$$G = G^{\circ} + R \cdot T \cdot \ln P \quad (2-6)$$

After rearrangement equation 2-6 becomes

$$\Delta G = R \cdot T \cdot \ln P \quad (2-7)$$

The total ΔG for the process from $H/Pu = 0$ to $H/Pu > 0$, can be obtained by Gibbs-Duhem²⁸ integration. The Gibbs-Duhem equation can be written as

$$\sum n_j d\mu_j = 0 \quad (2-8)$$

or in this case,

$$\sum n_i G_i = 0. \quad (2-9)$$

Equations 2-8 and 9 state that at constant temperature and pressure, in a closed system, the total free energy is constant. Therefore, in a two component system, a change in the free energy of one component yields a corresponding, but opposite change in the other component. That is, the free energies of the two components cannot change independently²⁹. Therefore, the Gibbs-Duhem equation can be written as follows

$$dG = G_H dn_H + G_{Pu} dn_{Pu} \quad (2-10)$$

where dG is a constant.

In these experiments, the quantity of Pu does not change therefore, n_{Pu} does not change and $dn_{Pu} = 0$. Equation 2-10 becomes

$$dG = G_H dn_H \quad (2-11)$$

The total free energy to a specific composition can be calculated by integrating equation 2-11 over the composition range of interest.

$$\Delta G = \int_{H/Pu=0}^{H/Pu>0} G_H dn_H \quad (2-12)$$

The entropy (ΔS) and the enthalpy (ΔH) for the reaction can be calculated from the Gibbs equation

$$\Delta G = \Delta H - T\Delta S$$

(2-13)

by plotting ΔG vs temperature. The plot should yield a straight line with ΔH equal to the y-axis intercept and $(-\Delta S)$ equal to the slope of the line.

CHAPTER 3

EXPERIMENTAL

METHOD

The experimental technique chosen to measure the hydrogen (H) solubility in Pu metal was a pressure - volume - temperature (PVT) method. The experiments were performed isothermically, i.e., by varying gas pressure at a constant temperature. The experiments were performed in three groups; 1. unalloyed (UA) coupons, at 25 degree increments in the temperature range 475 to 625 °C, 2. two-weight-percent (TWP) coupons also in 25 degree increments in the above temperature range, and 3. UA coupons at 50 degree increments in the temperature range 650 to 825 °C. The general experimental method is described below. However, due to the high reactivity of molten Pu, special handling procedures were required at temperatures above the melting point of Pu. These special procedures will also be described below.

Using the PVT method, a 1 to 6 gram Pu coupon is first cleaned with a motorized stainless steel wire brush to remove all surface oxide. The coupon is considered clean when the metal surface has a shiny metallic luster.

The coupon is then weighed on a standard analytical balance to the nearest 0.1 mg and placed immediately in the reactor and the reactor sealed. The reactor is then connected to the pressure - vacuum system and evacuated to a pressure of about 140 millitorr (mtorr). The reactor and system are then flushed at least 3 times with 100 torr of high-purity helium. The system and reactor are then pumped overnight to achieve an ultimate pressure ≤ 10 mtorr.

Once the system is at a pressure ≤ 10 mtorr, it is leak checked. The leak check is accomplished by first valving out the vacuum pump. A mass spectrum of the residual gas is then taken using a quadrupole residual gas analyzer (RGA). The RGA is then valved out of the system and the system allowed to sit for at least one hour. During this time the pressure is monitored using a capacitance manometer calibrated for 1 torr full scale. The pressure is monitored as a qualitative indicator of the leak check. At the end of 1 hour, another mass spectrum is taken. The system is considered to be leak tight if the nitrogen 14 peak (^{14}N) is the same height as the ^{14}N peak in the first spectrum and is less than the height of the mass 15 peak. It is normal in this situation for the water peak ($^{18}\text{H}_2\text{O}$), CO_2 , and CO to rise as these species are out-gassed from the surface of the

reactor. If leaks are found, they are repaired before the test continues.

After the system has passed the leak check, a small amount of H_2 (approximately 0.1 to 0.5 torr) is added to the gas reservoir, the initial H_2 pressure recorded and the reservoir valved off. During this operation, the reactor is valved out of the system so that no H_2 can come in contact with the Pu coupon. The manifold is evacuated and the reactor is then opened to the vacuum pump and heated to the test temperature using a resistance furnace controlled by a PID temperature controller. During the heat-up, the reactor and coupon are both under dynamic vacuum.

Once the specified test temperature has been achieved, the vacuum pump is valved out of the system and the H_2 contained in the reservoir is released into the reactor and allowed to react with the Pu coupon. The progression of the reaction is followed using both a strip chart recorder and a digital data acquisition system. The reaction is considered complete when the H_2 pressure is steady. At this point: 1. the final system pressure, the reactor temperature, and the room temperature are recorded, and 2. the reactor is valved out of the system and another charge of H_2 is added to the gas reservoir. Each additional charge of H_2 is at a

higher pressure than the previous charge. The above process is continued until pressure in the system exceeds 760 torr or the experiment is terminated.

When working below 640 °C, the Pu coupon is in contact with the quartz reactor walls. Above 640° C, the molten Pu will react with the quartz reactor, therefore, a protective liner is used. The liner is a 304 stainless steel cup coated with erbium oxide (Er_2O_3) which is resistant to attack by molten Pu. However, the coating must be out-gassed prior to use in an experiment because some of the out-gassing constituents (H_2 , H_2O , CO_2 , and CO) from the coating will react with the Pu coupon.

The coating is prepared by a bake-out procedure under dynamic vacuum at the experimental temperature. Periodically during the bake-out, the system is flushed with high-purity He. After completion of this step, the cup is again baked-out at the test temperature with 5 to 10 g of Pu to reduce the oxide coating to a slightly substoichiometric oxide ($\text{Er}_2\text{O}_{3-\delta}$). At the completion of this process, the cup is ready for use. During loading and unloading of the Pu coupon, exposure of the coating to air is minimized.

SYSTEM

Figure 3-1 is a diagram of the system. The parts of the system opened to the reactor during the test are the 1 liter stainless steel gas reservoir; three MKS Baratron capacitance manometers in the pressure ranges 0 to 1 torr, 0 to 100 torr, and 0 to 1000 torr; and the interconnecting manifolds. The RGA is connected to the manifold through a high pressure (HP) valve and valved in or out of the system as needed. The volume of the system has been calibrated with a standard volume traceable to the National Institute Of Standards And Technology through the Rocky Flats Standards Laboratory.

The manifolds are made of $\frac{1}{4}$ inch outer-diameter (o.d.) HP 304 stainless steel tubing and Autoclave Engineering $\frac{1}{4}$ inch HP fittings and regulating valves. The reactor (figure 3-2) is a quartz-Kovar tube that is 6 inches long, $\frac{3}{4}$ inches in diameter, and sealed at one end. The Kovar end is welded to a $2\frac{3}{4}$ inch Varian[®] vacuum flange. The mating vacuum flange contains a $\frac{1}{2}$ inch HP nipple for connection to the vacuum system and a HIP[™] high pressure thermocouple pass-through. A 1/16 inch o.d. type K chromel-alumel thermocouple is used to measure the reactor temperature.

Surrounding the quartz tube is a 304 stainless steel outer tube with a $\frac{1}{4}$ inch HP nipple welded in the side.

Figure 3-1. Diagram of experimental solubility system.

LEGEND FOR
SOLUBILITY SYSTEM

1. 100 torr MKS Bartron pressure transducer
2. 1000 torr MKS Bartron pressure transducer
3. 1 torr MKS Bartron pressure transducer
4. Granville-Phillips thermocouple gauge tube
5. 50 torr bourdon tube pressure gauge
6. 1000 PSI bourdon tube pressure gauge
7. 100 PSI pressure gauge
8. 1/4" Autoclave Engineers high pressure regulating valve
9. 9/16" Autoclave Engineers high pressure regulating valve
10. 1/4" high pressure tubing
11. 9/16" high pressure tubing
12. 10 micron Autoclave Engineers particle filter
13. 600 PSI Autoclave Engineers rupture disk assembly
14. To glovebox exhaust

8

To
Vacuum
System
↓

e b o x

REACTOR

Figure 3-2. Diagram of the solubility reactor.

Thermocouple Passthrough
304 Stainless Steel
High-pressure Tube
To P/V System

TING
ANGE

The outer tube is welded to the vacuum flange and protects the quartz tube from mechanical damage and provides containment for the hydrogen gas in an inert atmosphere should the quartz tube break during an experiment. Prior to the beginning of each test, after the reactor has reached the test temperature, the volume between the quartz tube and the outer tube is evacuated and back-filled with He to a pressure $\approx$ 640 torr.

The RGA is a Balzers QMG 112 quadrupole mass spectrometer with a mass range of 1 to 200 atomic mass units (amu) and a Faraday cup detector. The RGA is differentially pumped with a Balzers TSH 040 50 liter/minute turbo-molecular pump. The RGA is used, as described above, for leak testing both before and after a gas charge, periodically during the test, and for verifying the purity of the H_2 . The test gas is introduced into the analyzing chamber via a Balzers EVN 010 needle valve. The pressure in the analyzing chamber is maintained in the 10^{-6} torr range during analysis.

The PID process controller is a Micricon™ Multi-loop Controller with two independent PID loops. The two independent loops can be linked to allow furnace control from the internal thermocouple. This feature of the controller was used on the isotherms at or below 625 °C.

At temperatures of 650 °C and above, the furnace was controlled from the outside thermocouple.

MATERIALS

The Pu metal was from the Rocky Flats foundry and, with the exception of the Ga content in the TWP metal, contained ppm impurity levels of Al, Fe, Ni, and Si. Chemical analysis of the TWP metal showed the average Ga content to be 1.802 weight percent.

The helium gas was high-purity and the supplier's analysis was accepted. The typical helium gas analysis was $N_2 = 0.1$ ppm, $CH_4 = 0.9$ ppm, and $H_2O = 1.2$ ppm. The hydrogen gas was also high-purity and again the manufacture's analysis was accepted without further testing. Typical analysis of a H_2 cylinder was O_2 and $N_2 < 2$ ppm; CO , CO_2 , Ar , and $H_2O < 1$ ppm; and $CH_4 < 0.5$ ppm.

DATA CALCULATIONS

The quantity of H_2 dissolved in each charge is calculated from pressure change data using the ideal gas equation of state;

$$PV = nRT \quad (3-1)$$

Where P = pressure in atmospheres (ATM), V = volume in liters (L), n = number of moles (mol), R = the ideal gas constant ($0.0821 \text{ L*ATM / mol*K}$), and T = temperature in

Kelvin (K). The composition, expressed as the molar ratio of H/Pu, was then calculated. The $\log_e$ (ln) of the equilibrium pressure is then plotted versus composition. The free energy (ΔG), is calculated from the equilibrium pressure at the test temperature using equation 2-7 and also plotted as a function of composition. The thermodynamic parameters free energy, enthalpy, and entropy, are then calculated as explained in chapter 2.

CHAPTER 4

RESULTS AND DISCUSSION

THE SOLID PHASE 475° to 625 °C

The primary objective of this study was to measure the solubility of H in Pu at compositions below $H/Pu = 0.1$. However, some of the isotherms were carried out to the high composition region, $H/Pu > 0.1$. Figure 4-1 is an idealized isotherm showing all of the features observed in this study. It is presented as a guide to the following discussion.

Two Weight Percent Pu

Figure 4-2 is a typical TWP low composition isotherm for temperatures ≤ 600 °C. Regions 1 & 2 together make up the solid solution region. This region is characterized by increasing pressure with increasing composition (2 degrees of freedom). At the termination of this region, inflection point 2, the metal is saturated with hydrogen. Region 3 is the two-phase region (one degree of freedom). This represents the region consisting of a mixture of plutonium dihydride (PuH_2) and hydrogen saturated Pu metal. This region is

Figure 4-1. Idealized isotherm showing all of the features observed in this study.

Figure 4-2. Upper plate is a typical low composition isotherm for two-weight-percent alloy. Figure 4-3. Lower plate is an example of the high composition isotherm for two-weight-percent alloy.

characterized by constant pressure with changing composition. Region 1 is unexpected and its significance will be discussed below.

Figure 4-3 is an example of the high composition region for TWP metal. Theory states that the slope of the pressure-composition curve between IP2 and IP3 should be 0, however, a statistically significant slope is observed on all isotherms. Region 4 is also unexpected and suggests that filling of octahedral sites in the substoichiometric dihydride begins before all of the tetrahedral sites in the fcc metal lattice are occupied. The temperature dependence of region 4 is not known, since only one isotherm was taken to the higher H/Pu values.

Region 5, is the second solid solution region. In region 5, hydrogen is being dissolved in the dihydride phase by continuing to occupy octahedral sites. At sufficiently high hydrogen pressures PuH_3 is formed.

Two forms of trihydride are known, cubic and hexagonal³⁰. The cubic trihydride is formed at moderate temperatures and high H_2 pressures. In this phase hydrogen fills all tetrahedral and octahedral sites in the fcc metal lattice. When sufficient thermal energy and H_2 pressure is provided, the cubic trihydride transforms into the hexagonal trihydride. The two forms

of trihydride have different properties, with the cubic form burning spontaneously in air, while the hexagonal form is stable in air.

Figure 4-4 shows the experimental data for the TWP isotherms at temperatures ≤ 600 °C in regions 1, 2, and three. Linear regression analysis of inflection points 1 and 2 versus temperature, shows that neither has a statistically significant temperature dependence.

The isotherms in region 1 (figure 4-4) are closely spaced and in fact the 575 and 600 °C isotherms cross in this region. Based on theory, the isotherms cannot cross and should be vertically spaced similarly to the corresponding segments in the two-phase region. In region 2, the vertical spacing of the isotherms expands somewhat so that it is closer to the spacing in the two-phase region. The reason for the change in vertical spacing is unknown. The most probable reason for line crossing is error in the PVT measurements.

To deconvolute the lines in region 1, each line was given a common slope, which is the average of all the slopes in the region. The X value was chosen as the average of inflection point one for the 6 isotherms. The Y value was then calculated from a plot of $\ln P$ vs temperature. The Y axis intercept was then calculated from the equation for a straight line using the average

Figure 4-4. Low composition isotherms for two-weight-percent alloy. Temperature range 475 to 600 °C.

slope and the X and Y coordinates determined above. Similar calculations were also performed on the lines in region two. Figure 4-5 shows the results with the inflection points and the Y-axis intercepts corrected for the observed temperature relationships and the theoretical constraints.

Figure 4-6 shows the addition of the 625 °C isotherm. As is seen, inflection point 2 moved significantly to the right and inflection point 1 was lost. The line defining the solid solution region undercuts the 550, 575, and 600 °C isotherms. The predicted plateau pressure, based on a plot of plateau pressures vs $1/T$ for temperatures between 475 and 600 °C, shows the measured pressure (7.7 torr) to be significantly less than the calculated pressure (12.6 torr). These results are inconsistent with anticipated behavior.

Unalloyed Plutonium

Figure 4-7 shows a typical low composition isotherm for unalloyed plutonium. In a comparison with figure 4-2, it is observed that the UA metal has a lower hydrogen solubility and that inflection point one is missing. A comparison of the plateau pressures in the two-phase region shows that the UA plateau pressure at each temperature is lower by about one $\log_e$ unit when compared

Figure 4-5. Deconvoluted low composition isotherms for two-weight-percent alloy. Temperature range 475 to 600 °C.

Figure 4-6. Two-weight-percent low composition isotherms with the addition of the 625 °C isotherm.

Figure 4-7. Upper plate is a typical isotherm for unalloyed metal at low composition (same temperature as figure 4-2). Figure 4-8. Lower plate is a typical isotherm for unalloyed metal at high composition (same temperature as figure 4-3).

to the TWP plateau pressure. Figure 4-8 is a typical UA metal high composition isotherm. Inflection point 3 is not observed in UA metal, i.e. region 4 is missing.

Figure 4-9 shows the UA family of isotherms. Comparison of figure 4-9 to figures 4-5 and 4-6 shows that in general, the solubility of hydrogen is lower in UA than in TWP and the plateau pressures over the two-phase region are lower in UA metal than in TWP metal. Exceptions to this generality are for the 475 and 625 °C isotherms in which the plateau pressures for TWP and UA are comparable. In the 475 °C isotherms, the solubilities are also similar but in the 625 °C isotherm the limiting solubility (inflection point 2) differs significantly. Inflection point 1 is absent from all UA isotherms. As in the TWP isotherms, the lines in the solid solution region are closely spaced and there is significant crossing. The vertical spacing between the 475 and 500 °C isotherms in the two-phase region is much less than would be expected based on the higher temperature isotherms. The pressure - composition curves in the two-phase region have statistically significant slopes and the UA metal phase boundary (inflection point 2) is temperature dependant.

Five areas of interest come out of these results:

1. the unexpected inflection points (1 and 3) in the TWP

Figure 4-9. Unalloyed low composition isotherms. Temperature range 475 to 625 °C.

solid solution and two-phase regions, 2. the marked increase in the TWP hydrogen solubility and the lower plateau pressure at 625 °C, 3. the closely spaced isotherms in the solid solution region of both UA and TWP, 4. the overall higher hydrogen solubility in TWP, and 5. the slope of the pressure-composition curve in the two-phase region. Each of these areas will be discussed in the following sections.

TWP Inflection Points

There are three possible explanations for inflection point 1 observed in the TWP solid solution region: 1. geometrical and electronic considerations, 2. ordering of hydrogen in the Pu metal lattice, or 3. the existence of numerous stoichiometric phases across regions one and two. The presence of inflection point 1 for TWP metal and its absence for unalloyed metal suggest that its existence is related to the presence of gallium.

Geometrical and Electronic Considerations. Hydrogen solubility is determined by three factors: 1. the geometry of the interstitial site, 2. the size of the interstitial site, and 3. the electronic (or chemical) environment (the difference in electronegativity between H and Pu). The geometry of the interstitial site is determined by the spacial relationship of the metal atoms

(the packing of metal atoms, bcc, fcc, etc.) and the size of the site is a function of the distance between the metal atoms. Ellinger³¹ et al have shown that the average Pu lattice parameter decreases with increasing Ga content. This suggests that an attractive force is operating, and this conclusion is supported by the difference in electronegativity between Ga (1.81)³² and Pu (1.28)³². These values imply that the electrons shared between Ga and Pu spend more time around Ga than Pu.

A comparison of the atomic radii of Pu (1.62 Å)³³ and Ga (1.81 Å)³² shows that Ga is moderately larger than Pu. It can be argued that the tetrahedral sites surrounding Ga would be moderately larger when compared to the tetrahedral sites surrounding Pu. The hydrogen in Pu is in the form of H⁻, therefore, this large atom would tend to move to the larger sites. In the large sites surrounding Ga, electron transfer to hydrogen is less energetic because of the smaller difference in electronegativity between hydrogen (2.20)³² and Ga (1.81). Therefore the slope of the line on the ln P vs composition curve is quite steep.

When the large sites are filled, hydrogen must go into the smaller sites. The difference in electronegativity between hydrogen and Pu is larger than

between Ga and hydrogen, therefore, the electron transfer to hydrogen is more energetic. The result is a decrease in the slope in region 2 and the accommodation of hydrogen in the smaller site. The point at which this begins to occur is inflection point one.

This is seen in the $\ln$ pressure vs composition curves. At inflection point 1, the slope of the line decreases indicating a larger free energy and suggests that the size of the site has a smaller effect than the chemical environment.

Two additional possibilities may be placed under this heading. The first is the expansion of the Pu lattice as hydrogen is added. Anisotropic lattice expansion has been noted in the rare earth hydrides³⁶. The second is simply filling of octahedral sites.

Hydrogen Ordering. Inflection point 1 may also be caused by ordering of the hydrogen atoms within the Pu lattice. Numerous researchers have noted hydrogen pairing and hydrogen-pair chains in rare earth hydrides^[35-40]. In general, ordering is observed at room temperatures and below and, when compared to Pu, at much higher hydrogen concentrations ($H/Metal \approx 0.03$ to 0.18). In the H-Pu system, the solid solution region is at a much lower hydrogen concentration ($H/Pu \approx 0.01$) and at higher temperatures. Ordering is anticipated based on

the fact that the hydride ions seek to minimize their coulombic interactions, but the data do not support pairing under these test conditions.

Hydrogen pairs were first proposed for rare earth hydride solutions after neutron diffraction studies were performed at low temperatures. These studies were prompted by the discovery of a low temperature resistivity anomaly³⁴ in the rare earth hydrides. On the basis of data from neutron scattering experiments, Blaschko et al³⁵ proposed the existence of chains of hydrogen pairs in these hydrides. The hydrogen atoms are located on next nearest neighbor tetrahedral sites with a metal atom in between the two hydrogen atoms. The chains are 3 to 4 pairs long³⁶ and the pairs are staggered along the c axis of the hcp cell³⁷. The hydrogen-pair chains have been shown to interact with each other. A theoretical basis^{38,39} has also been established showing the existence of hydrogen pairs.

The ordering is both temperature and concentration dependent. Blaschko³⁷ et al show that the diffraction features associated with pairing decrease in intensity with increasing temperature. At 300 K, about 30% of the hydrogen is paired and dissociation occurs by breaking of the hydrogen chain before the pairs dissociate. The pair mechanism is not changed by the hydrogen

concentration, but, pair formation becomes diffusion controlled.

Anderson et al⁴⁰ have also studied the temperature and concentration dependence of pair formation. Anderson's data leads to different conclusions. At high hydrogen concentrations, Anderson shows a significant temperature dependence on the diffraction features associated with hydrogen pairing. At 240 K, only minimal evidence for pairing is observed. Anderson also shows that no pairing is observed at concentrations as high as $H/M = 0.06$.

Both Anderson and Blaschko agree that the driving force behind pair formation is a lowering of the metal lattice distortion. However, Anderson believes that at low concentrations an occupied isolated tetrahedral site is more stable, which leads to a significant concentration dependence.

The basic fact that allows the formation of H-pairs is the existence of a low temperature (≈ 300 K) hydrogen solid solution region in the rare earths. The reason given for the extended solid solution region is the lack of sufficient thermal energy to transform from the metal hcp lattice to the hydride cubic lattice. This situation is not observed in Pu, possibly due to the large enthalpy of formation for PuH_2 .

Although the rare earth hydrides are, in most cases, comparable to Pu hydride, the analogy seems invalid in this case. If the driving force for pair formation is relief of metal lattice strain, it can be argued that there is sufficient thermal energy to allow metal rearrangement to relieve distortion at 475 °C and above. Furthermore, at the highest hydrogen solubility in Pu, the concentration of hydrogen is only 1/3 of that at which the rare earths show decreased or no indication of pair formation. A conservative interpretation of the data shows that a temperature change of 130 K (170 to 300 K) yields a significant decrease in pairing. Therefore doubling that temperature (to 648 K) should further reduce pairing. It is therefore doubtful that inflection point 1 is due to this type of hydrogen ordering.

Stoichiometric Phases. The existence of solid solutions (phases with variable compositions) has been questioned. Anderson⁴¹ has suggested that continuous changes in the free energy - composition curve, as observed in figure 4-4, may result from the presence of a series of closely spaced line phases. A line phase is a compound "of ordered structure and definite composition". The focus, to this point has been on the most simple unit cell and the stoichiometry that it represents. However, there is the possibility of a "super structure" in which

the structure for a given composition is defined by an enlarged unit cell that frequently has lower symmetry than the simple cell.

There are two possibilities for explaining the line structure in the $\ln P$ versus composition plots. The first deals with the temperature dependence of the line phase. In free energy - composition - temperature (G, C, T) space, the line phase is a surface and will be seen (in 2 dimensions, G and X space) as an extremely narrow parabola. As the temperature is increased, the surface begins to expand in G and X space finally ending in a broad surface representing non-stoichiometry. Simply stated, above a certain temperature, the most stable form is the non-stoichiometric form while below that temperature the stoichiometric form is most stable.

The second possibility for explaining the solid solution is the formation of numerous stoichiometric phases. In this case, the line phases appear on the free energy plot as a continuous change, because data were not taken at a frequency high enough to show the actual phases. The phases may coexist with each other. Eyring⁴² has shown the existence of closely spaced phases in the praseodymium-oxygen and terbium-oxygen systems. Each of the $\text{Pr}_n\text{O}_{2n-2}$ and $\text{Tb}_n\text{O}_{2n-2}$ oxides (where $n = 7$ to 12) are line phases. The various phases can be

shown to be derivations of the same basic crystal structure. Simply by taking out (putting in) oxygen, the new phase and its structure are formed. The key factor is that several phases can coexist because they are all easily derived from and related to the starting crystal structure and have similar free energies. It should be noted that this situation can also have the above temperature dependence superimposed on it.

Inflection Point Three - Region 4. Since the majority of the metal is consumed at the start of inflection point 3, the effect of the metal phase on the system should be minimal. With the exception of the Ga content, the hydride product of both UA and TWP metals should be the same, that is, cubic hydride. However, the UA isotherms do not show inflection point three. This now focuses attention on the Ga and how the Ga is accommodated in the hydride.

There is no information in the literature on how Ga is accommodated in Pu hydride. It is known, however, that Ga does not react with hydrogen on an elemental basis to form a hydride.⁴³ No metallographic or chemical distribution data were obtained on the TWP hydride during the course of these experiments. However, using similar arguments as in the above section, the Ga in the hydride may make filling of the octahedral sites

energetically favorable.

TWP 625 °C Isotherm

The isotherm for TWP alloy at 625 °C shows a marked increase in hydrogen solubility and an unexpectedly low plateau pressure. An examination of the Pu-Ga phase diagram (figure 1-2-B) shows that the 625 °C isotherm lies in the $\delta+\epsilon$ region. The transition from a single phase region to a mixed phase region causes a change in the defect structure of the metal. Defects can also hold H. Since the metal defects are also an energetically favorable holding site for hydrogen, additional hydrogen can be accommodated above that dissolved in the interstitial lattice sites. The result is an increase in the observed H/Pu ratio and a lowering of the plateau pressure.

Vertical Spacing Of Isotherms

It was noted that in the solid solution regions of both TWP and UA metals, that the vertical spacing of the isotherms changed when going from the solid solution region to the two-phase region. Such behavior seems to be a unique feature of the Pu-H system as no model hydride system was found to be similar. Although no explanation can be offered at this point, the results imply that unlike the hydriding reaction in the two-phase region,

the dissolution process has a low temperature dependence.

Hydrogen Solubility In TWP and UA Metals

One of the original hypothesis of this work was that UA metal should dissolve more hydrogen than TWP metal. This hypothesis was based on the fact that in the temperature range, 500 to 600 °C, UA metal is in the ϵ phase. The ϵ phase, as stated earlier, is body-centered-cubic (bcc) and the interstitial sites are tetrahedral (6 tetrahedral sites per metal atom) or octahedral (1.5 sites per atom). In the same temperature range TWP is in the δ phase and has 2 tetrahedral sites and one octahedral site per metal atom. Since H prefers tetrahedral sites, with more tetrahedral sites, UA metal should dissolve more hydrogen.

The data in figure 4-4 and 4-9 show that TWP metal has the higher hydrogen solubility. The occurrence of a Ga-H₂ reaction has already been ruled out, but another possible explanation is H-H repulsive interactions, provided that hydrogen in Pu is hydridic (H⁻). The fcc unit cell in two-weight-percent Ga (δ phase) has a lattice parameter of 4.59 Å. In bcc ϵ phase metal the unit cell has a lattice parameter of 3.64 Å. Lundin et al⁴⁴ has shown a correlation between tetrahedral hole size and the stability of hydrides: the larger the hole the more stable the hydride. An estimate of the hole

radius for δ and ϵ phases, based on a regular tetrahedron, is 0.66 and 0.64 Å respectively. In the solid solution region, TWP has the more negative ΔG_f° which is consistent with this argument.

Slope Of Two Phase Region

As stated above, the plateau should be flat in the two-phase region. However, in both TWP and UA metals, the plateau has a statistically significant slope. In general, the slopes are larger for TWP metal (average value = 0.674) than for UA metal (average value = 0.329). The Ga in the metal, here considered as a contaminate, may contribute to the higher slope. Although there is no Ga added to the UA metal, there are a known amount of contaminants in the metal (see chapter 3 for chemical analysis of the metal). Other metals such as palladium also show a larger plateau slope with increasing contaminate concentration.⁴⁵

THE LIQUID PHASE 650 to 825 °C

Figure 4-10 shows the family of isotherms between 650 and 825 °C. These isotherms were measured for UA metal only. In the liquid solution region (region 1), all of the isotherms (figure 4-11), with the exception of the 750 °C isotherm (figure 4-12), have a low composition inflection point (IP1). In a manner consistent with the

Figure 4-10. Unalloyed liquid phase low composition isotherms. Temperature range 650 to 825 °C.

Figure 4-11. Upper plate is a typical high temperature isotherm showing low composition inflection point and a solubility wall. Figure 4-12. Lower plate is the 750 °C isotherm which shows no low composition inflection point.

lower temperature UA isotherms, there is significant crossing of the lines in regions one and two. The 825 °C isotherm undercut both the 700 and 750 °C isotherms and the 750 °C isotherm undercut the 700 °C isotherm. At the measured solubility limit (IP2), there is a discontinuity in the pressure. The pressure goes up, without change in composition, until it reaches the dihydride decomposition (plateau) pressure for that temperature. This behavior is also observed in the 625 °C and to some extent the 600 °C isotherm (figure 4-9). At that point, the system moves into the two-phase region. The two-phase region, at these temperatures, is solid PuH_2^{**} and liquid metal saturated with hydrogen.

The 650, 700, and 750 °C plateaus all have slopes of similar value to the lower temperature plateaus. The slope of the 825 °C plateau is larger and there is an unexpected increase in the hydrogen solubility based on the earlier data. Both of these observations are probably due to iron (Fe) contamination of the Pu melt. The Fe is present because the Er_2O_3 coating on the stainless steel containment vessel failed during the

^{**}The melting point (MP) of PuH_2 has not been measured due to the extremely high H_2 pressures required to keep it from decomposing. However, the MP is expected to be in the same range as TiO_2 and the iso-structural compound CaF_2 whose melting points are 1550 and 1360 °C respectively.

experiment. Plutonium readily forms a low melting Pu-Fe alloy, $\text{Pu}_6\text{Fe}^{46}$. The Er_2O_3 coating on the 750 °C isotherm also failed, but the only change observed was the loss of the low composition inflection point (IP1). The difference in the two runs may be the amount of Fe that reacted. There were no diagnostic tests run to determine the amount of Fe in either melt and there was no indication in the PVT data taken during the experiment that any change had occurred.

Condit et al⁴⁷ has also studied the solubility of H in Pu in this same temperature range, but by a different technique. Condit introduced a known quantity of H_2 into a gas tight chamber containing a measured mass of Pu. The H_2 reacted with the Pu at room temperature and then the temperature of the system was varied. The equilibrium pressure was measured as a function of temperature and the composition of the solubility limit was calculated from PVT measurements for the temperatures at which the pressure dependence changed. Figure 4-13 shows Condit's data superimposed on the current data. The two data sets are in fair agreement and Condit's data confirms the shape of the phase boundary. It should be noted that at the same temperatures, in all cases, Condit has measured a higher plateau pressure. The H/Pu ratios at inflection point 2 (and 2A) vary from excellent

Figure 4-13. Family of isotherms for unalloyed liquid phase metal at low composition with Condit's data (open circles) superimposed on these data. Temperature range 650 to 825 °C.

agreement at 650 and 825 °C to fair agreement at 700 °C and off by a factor of 2 at 750 °C.

It was proposed above that the increased hydrogen solubility at 825 °C is due to Fe contamination of the Pu. However, Condit's data suggest that Fe has no effect on the solubility of hydrogen, but changes only the slope of the plateau in region 3.

Three areas of interest come out of these data: 1. super-saturation of the gas phase near the solubility limit, 2. the crossing of isotherms in the liquid solution region, and 3. appearance of an inflection point in the liquid solution region.

As was stated earlier, it is clear that isotherms in the solid and liquid solution regions are closely spaced and that the crossing is due to errors in the PVT measurements. Undercutting of the isotherms in the higher temperature ranges is also promoted by their unusual shape. That is, since the lower temperature isotherm reaches it's solubility limit at a lower pressure than the dihydride decomposition pressure, the only way for the phase boundary to maintain it's shape is by undercutting the previous isotherms.

The shape of the 650 to 825 °C isotherms suggests inhomogeneity in the molten phase. Wittenberg⁴⁸ has suggested that "liquid like clusters" exist in the bcc

solid phase at temperatures around 600 °C which creates an inhomogeneous system. A similar isotherm shape was also observed in the 600 and 625 °C runs, which supports this hypothesis. If this hypothesis is accepted, then, both the supersaturation and the inflection point can be explained.

The explanation is as follows. Hydrogen first dissolves in the residual ϵ phase metal. This is supported by the fact that there is a correlation between IP1 in the liquid phase and IP2 in the solid phase. Once the solid phase is saturated, hydrogen then dissolves in the liquid phase. The point at which the solid is saturated and the liquid begins to dissolve hydrogen is the observed inflection point. Because the metal contracts on melting, (which implies an attractive force and ordering in the liquid phase) the hydrogen solubility is limited. When both the solid and molten metal phases are saturated with hydrogen, no more hydrogen can dissolve, but the hydrogen pressure has not reached the dihydride decomposition pressure. Therefore, the composition cannot change, but the pressure must go up until the plateau pressure is reached. When the plateau pressure is reached, the system moves into the two-phase region.

The isotherms for the unalloyed solid and liquid form a consistent data set (exclusive of the 475 °C isotherm). Figure 4-14 is a graphical representation of the data and table 4-1 is a table of the solubility limits. It is evident that the phase boundary is temperature dependant. A plot of $\ln(H/Pu)$ vs $1/T$ yields the following equation,

$$\ln \frac{H}{Pu} = (3.31 \pm 0.57) - \frac{(6968.66 \pm 500.)}{T}$$

The functionality of the phase boundary is therefore

$$\frac{H}{Pu} = B e^{-\frac{A}{T}}$$

where $B = 27.2$ and $A = 6968.66$. Based on the above results, H/Pu at 300 K is $(2.22 \times 10^{-9} \pm 1.23)$. Assuming a 5 gram Pu sample, 2.3×10^{-11} moles of H_2 are dissolved in the metal at room temperature. The same analysis was done for Condit's data and the results show that at 300 K the calculated H/Pu ratio is $(4.38 \times 10^{-12} \pm 1.16)$. Assuming a 5 gram metal sample, 4.58×10^{-14} moles of H_2 are dissolved in the metal.

The pressure - temperature relationship (figure 4-15) in the saturated metal + hydride two-phase region of the unalloyed system is defined by the following equation,

Figure 4-14. Complete data set of isotherms for unalloyed metal (exclusive of the 475 °C isotherm).

TABLE 4-1		
TEMPERATURE DEGREES C	H/Pu RATIO at INFLECTION POINT ONE	H/Pu RATIO at INFLECTION POINT TWO
475		0.00267
500		0.00327
525		0.00402
550		0.00746
575		0.00718
600		0.0107
625		0.00819
650	0.00265	0.0156
700	0.00505	0.0178
750		0.0254
825	0.0162	0.0674

Figure 4-15. Pressure - temperature relationship for unalloyed plutonium.

$$\ln P = A_1 + \frac{A_2}{T} \quad (4-1)$$

where P is the pressure at the phase boundary in atmospheres, T is the temperature in kelvin, $A_1 = (14.583 \pm 0.355)$, and $A_2 = (-17313.132 \pm 315)$. Table 4-2⁴⁹ lists the results of other researchers. As is seen in table 4-3, when compared to the present results, the pressures defined by the results of Mulford and Sturdy are generally higher at a given temperature. The $\ln P$ vs $1/T$ curves cross near 535 °C and the situation is reversed at low temperatures. Comparison of equilibrium pressures for this work with those in table 4-3 from the work of Condit shows that the present values are substantially lower.

A common factor between the work by Mulford and Sturdy and that by Condit is in the experimental method. In both studies (and in that by Johns), the plutonium was hydrided at room temperature, and then pressure measurements were made as the temperature of the closed system was increased. The differences in the data suggests that the plateau pressure may be sensitive to the temperature at which the hydride is formed or to the heating procedure. Differences in plateau pressure are commonly associated with the so-called hysteresis effects in which the plateau observed during hydride formation

TABLE 4-2		
RESEARCHER	A_1	A_2
I. B. Johns (673 to 773) ³	18.10	-19894
Mulford and Sturdy (727 to 1073)	16.42	-18800
Haschke and Stakebake (600 to 769)	16.25	-19150
Current results for comparison (773 to 1098)	14.58	-17313

³Numbers in parenthesis are the temperature range of the work in Kelvin.

TABLE 4-3			
TEMPERATURE Degrees C	PRESSURE Atmospheres (Mallory & Sturdy)	PRESSURE Atmospheres (Allen)	PRESSURE Atmospheres (Condit)
475		0.000310	
500	0.000366	0.000371	
525		0.000791	
550	0.00161	0.00164	
575		0.00293	
600	0.00610	0.00576	
625		0.0106	
650	0.0196	0.0153	0.0292
700	0.0551	0.0432	0.0740
750	0.141	0.107	0.188
800	0.335	0.267 (825 °C)	0.449

(progressive addition of hydrogen along an isotherm) is higher than that encountered during hydride decomposition (progressive removal of hydrogen along the isotherm).³ The higher formation pressure is apparently necessary to compensate for strain energy expended in expanding the metal lattice during hydriding. In the procedure used by Mulford and Sturdy and by Condit, hydride decomposed as the temperature increased. Although a lower pressure is expected than for the formation procedure used in this study, the reverse pressure relationship is observed. However, the heating method simultaneously induces large changes in temperature, pressure, and composition of the system within a few hours. In contrast, the isothermal formation procedure used in the present study induces small changes in pressure and composition over a period of weeks. The isothermal method promotes annealing and attainment of a minimum-energy configuration in the system; the non-isothermal method tends to produce a non-equilibrium system with a high hydrogen pressure.

THERMODYNAMIC RESULTS

The reaction for the dissolution of H in Pu metal can be represented by the following equation,

where subscript S indicates H in solution. ΔS_f° for the reaction can be estimated using equation 4-2,

$$\Delta S_{f(298)}^\circ = S_{\text{PuH}_2}^\circ - S_{\text{Metal}}^\circ - S_{\text{Pu}}^\circ \quad (4-2)$$

and correcting the calculated value to the median temperature of 836 K. At 298 K, $S_{\text{H}_2}^\circ = 31.211^{50}$, $S_{\text{Metal}}^\circ = 13.18^{51}$, and $S_{\text{PuH}_2}^\circ = 14.3^{51}$, cal/mol K. The entropy values for the metal and the dihydride are approximately equal, opposite in sign, and therefore, contribute little to the overall entropy. Therefore, $\Delta S_{f(298)}^\circ$ is (-31.211) cal/mol K. Assuming ΔC_p° for the formation of dihydride is independent of temperature, the calculated entropy value is (-32.15) cal/mol K at the median temperature of 836 K.

Figure 4-16 shows a linear regression analysis of $\Delta G_{f(s)}^\circ$ vs T for the solid solution region of UA metal in the temperature range 500 to 625 °C integrated between H/Pu = 0 and 0.0028. The slope of the line is somewhat positive and it can be seen that the positive slope is due to the points at 575 and 600 °C. Statistical analysis of the data shows that the first order coefficient is not significant, which suggest that the entropy of formation for the solid solution is 0, therefore, $\Delta G_{f(s)}^\circ = \Delta H_{f(s)}^\circ$. Based on the above analysis, $\Delta G_{f(s)}^\circ = \Delta H_{f(s)}^\circ = (-0.0209 \pm 0.00578)$ kcal/mol at the median temperature of 836 K.

Figure 4-16. Free energy of formation versus temperature for unalloyed plutonium in the solid solution region. Temperature range 475 to 625 °C.

Comparison of the calculated entropy value with the measured value shows that the two are in poor agreement. $\Delta S_{f(s)}^{\circ} \approx 0$ suggests that $\Delta G_{f(s)}^{\circ}$, in this region, is independent of temperature and that the order in the solid phase is approximately the same as in the gas phase. The disorder is possibly due to the high mobility of H in plutonium.

Figure 4-17 shows a linear regression analysis of $\Delta G_{f(s)}^{\circ}$ vs T for H dissolution in UA metal in the temperature range 650 to 825 °C integrated between H/Pu = 0 and 0.0082. As in the solid phase, statistical analysis of the data shows the first order coefficient to be insignificant. Since the Y intercept from this analysis is positive and the reaction is obviously spontaneous, the average value of $\Delta G_{f(s)}^{\circ}$ is used. Therefore, $\Delta G_{f(s)}^{\circ} = \Delta H_{f(s)}^{\circ} = (-0.104 \pm 0.0143)$ kcal/mol.

Figure 4-18 shows a linear regression analysis of $\Delta G_{f(s)}^{\circ}$ vs T for H dissolution in the TWP alloy. The calculated value for $\Delta H_{f(s)}^{\circ}$ is (-0.128 ± 0.0122) kcal/mol and the value for $\Delta S_{f(s)}^{\circ}$ is (-0.0915 ± 0.0150) cal/mol K at the median temperature of 811 K integrated between H/Pu = 0 and 0.0088. These data are consistent with anticipated results for the solid solution region.

Figure 4-19 shows a linear regression analysis of $\Delta G_{f(s)}^{\circ}$ vs T for UA metal in the temperature range 525 to 750

Figure 4-17. Free energy of formation versus temperature for unalloyed plutonium in the liquid solution region. Temperature range 650 to 825 °C.

Figure 4-18. Free energy of formation versus temperature for two-weight-percent alloy plutonium in the solid solution region. Temperature range 475 to 600 °C.

Figure 4-19. Plot of free energy of formation (ΔG_f°) versus temperature (in Kelvin) for the reaction of unalloyed plutonium with hydrogen to form PuH_3 .

°C for the dihydride. The data include only isotherms for which measurements were made in region five.

Analysis of the data shows that ΔH_f° for UA metal is (-35.18 ± 0.68) kcal/mol and ΔS_f° for UA metal is (-30.19 ± 0.749) cal/mol at the median temperature of 911 K. As seen in table 4-4⁵², the ΔH_f° value is approximately 3 kcal/mol more positive than those of other workers.

Figure 4-20 shows a linear regression analysis of ΔG_f° vs T for TWP metal in the temperature range 475 to 600 °C. The analysis assumes the terminal point to be H/Pu = 1.69^{***}. ΔH_f° is (-34.44 ± 1.83) kcal/mol and ΔS_f° is $(-33.0 \pm 3.)$ cal/mol K. The entropy value is in excellent agreement with the values shown in table 4-4. However, the calculated enthalpy value is significantly lower than the values in table 4-4. The lower enthalpy value would be expected since the TWP plateaus are at higher pressures than those for UA metal.

In addition to the above integral method for the calculation of ΔH_f° and ΔS_f° , these thermodynamic properties can be calculated from second law principles. Equation 4-3,

***The terminal point was chosen as 1.69 because the shape of the isotherm would not allow for extrapolation beyond that point and the temperature dependence of region 4 is not known.

TABLE 4-4		
RESEARCHER	ΔH_f (Kcal/Mole)	$-\Delta S_f$ (cal/Mole K)
I. B. Johns	-39.5 ± 2.3	35.9 ± 2.8
Mulford and Sturdy	-37.12 ± 1.2	$32.6 \pm 1.$
Haschke and Stakebake	-38.1 ± 1.7	32.3 ± 1.7
J. W. Ward median temp 550 K	-37.2 ± 2.6	33.1 ± 2.6
Below are current results for comparison.		
TWP	-34.4 ± 1.83	$33.0 \pm 3.$
UA	-35.2 ± 0.68	30.2 ± 0.75

Figure 4-20. Plot of free energy of formation (ΔG_f°) versus temperature (in Kelvin) for the reaction of two-weight-percent plutonium with hydrogen to form PuH_2 .

$$\ln P = \frac{\Delta S_f^\circ}{R} - \frac{\Delta H_f^\circ}{R \cdot T} \quad (4-3)$$

can be derived from equations 2-7 and 2-13, where $R = 1.987$ cal/mol K, $T =$ temperature in Kelvin, and $P =$ pressure in atmospheres. As can be seen from the above equation, a plot of $\ln P$ vs $1/T$ yields a straight line where $\Delta S_f^\circ/R$ is the Y intercept and $\Delta H_f^\circ/R$ is the slope of the line. This is exactly the form of equation 4-1. Substitution of the values for A_1 and A_2 from equation 4-1 into equation 4-3 yields the following results: $\Delta S_f^\circ = (-28.976 \pm 0.705)$ cal/mol K and $\Delta H_f^\circ = (-34.40 \pm 0.626)$ kcal/mol at the median temperature of 911 K for UA metal. This analysis assumes that the substoichiometric two-phase region is entered into immediately and does not take into account the contribution to the total free energy from the solid solution region.

Comparison of the thermodynamic values to $H/Pu = 2.0$ calculated by both second law and integral methods provides internal verification of the data. If the values of the two methods agree, then the possibility of systematic errors can be ruled out. It is clear from table 4-5 that the values for ΔH_f° and ΔG_f° from the two methods are, within experimental error, in excellent agreement. This data shows that the contribution to the

TABLE 4-5		
	Integral	Second Law
ΔH_f° (kcal/mol)	-35.18 ± 0.68	-34.40 ± 0.626
ΔS_f° (cal/mol K)	-30.19 ± 0.749	-28.976 ± 0.705

total free energy from the solid solution region is minimal.

The question remains as to the 3 kcal/mol difference in the ΔH_f° values between these data and the data of Haschke⁴⁹ (table 4-4). The Haschke value was calculated using integral methods based on the data of Mulford & Sturdy⁶. The terminal composition of the solid solution region was taken as H/Pu = 0.01. The isotherms were extrapolated to H/Pu = 0 and their temperature dependence was assumed to be similar to the two-phase region. The $\Delta H_{f(s)}^\circ$ was calculated to be (-2.1 ± 0.21) kcal/mol.

The Haschke value and this value are in poor agreement. Two reasons are seen for this. One is the limits of integration; Haschke estimated the solubility limit to be at H/Pu = 0.01. These data were calculated based on a solubility limit of H/Pu = 0.0027. The second reason is the temperature dependence of the isotherms in the solid solution region. This data shows there to be no temperature dependence and Haschke assumed the temperature dependence to be similar to that in the two-phase region.

The integral method for calculation of ΔH_f° takes into account the contribution of $\Delta H_{f(s)}^\circ$. If the region corresponding to $\Delta H_{f(s)}^\circ$ is over estimated than ΔH_f° will be more negative. It is clear from these data that the

average H solubility in UA metal ($H/Pu = 0.006$) is much less than $H/Pu = 0.01$ and that the temperature dependence of ΔG_f° is, at best, minimal. Therefore, when Haschke's data are corrected for the above factors, the values of ΔH_f° calculated from the integral, second law, and Haschke's data are in excellent agreement (tables 4-5 and 4-6).

Figure 4-21 shows the Pu-H phase diagram derived from data for UA metal. The phases are labeled on the diagram. The general shape of the diagram is similar to that for the rare earth hydrides. The miscibility gap closes at the top of the diagram but the shape and temperature of closure is not known. However, there will clearly be some equilibrium condition between the dihydride on the right and hydrogen saturated liquid on the left. Although the general shape of the substoichiometric dihydride - dihydride phase boundary is confirmed by the data, some question is raised by the out-lying points at low temperature. There is no explanation for these points at this time. These boundary compositions are derived from data with a large potential for cumulative error and should be used with appropriate caution.

TABLE 4-6		
	UA METAL ^a	TWP METAL ^b
$\Delta H_f^\circ(s)$ 500 - 625 °C ^a 475 - 600 °C ^b	-0.0209 ± 0.00578 kcal/mole	-0.128 ± 0.0122 kcal/mol
$\Delta S_f^\circ(s)$ 500 - 625 °C ^a 475 - 600 °C ^b	0.0	-0.0915 ± 0.0150 cal/mol
$\Delta H_f^\circ(s)$ 650 - 825 °C ^a	-0.1042 ± 0.0143 kcal/mole	
$\Delta S_f^\circ(s)$ 650 - 825 °C ^a	0.0	
ΔH_f° 500 - 825 °C ^a 475 - 600 °C ^b	-35.18 ± 0.68 kcal/mol	-34.44 ± 1.83 kcal/mol
ΔS_f° 500 - 825 °C ^a 475 - 600 °C ^b	-30.19 ± 0.749 cal/mol	-33.0 ± 3.0 cal/mol
$\Delta H_f^\circ(s)$ Haschke	-2.1 ± 0.1 kcal/mol	
ΔH_f° Haschke (Corrected)	-36.02 kcal/mol

Figure 4-21. Unalloyed plutonium - hydrogen phase diagram.

TABLE 5-1		
TEMPERATURE (Degrees C)	H/Pu	
	Unalloyed	Two-Weight-Percent
475	0.00265	0.00575
500	0.00328	0.00777
525	0.00404	0.00983
550	0.00745	0.00998
575	0.00718	0.00899
600	0.0107	0.00938
625	0.00815	0.0180

hydrogen composition at pressures well below the two-phase plateau pressure (figure 4-11).

All of the isotherms show a small slope in the metal + dihydride two-phase region. The slope is attributed to contaminants in the metal. Evidence supporting this can be seen by comparing the average values of the slopes for the TWP (0.674), and UA (0.329) metals.

The TWP isotherms showed unexpected inflection points in both the solid solution and two-phase regions. The reason for the solid solution inflection point is not known. However, 3 possible explanations were presented; 1) geometrical and electronic considerations, 2) hydrogen ordering, or 3) the existence of stoichiometric line phases. A definitive explanation would require further experimental work.

The inflection point in the two-phase region should be independent of metal phase because at this point approximately 80% of the metal has been converted to dihydride. Assuming that the Ga is not segregated during hydriding, one can expect to find it in the hydride. The Ga is not easily accommodated in the hydride phase, and its presence may promote the formation of tetrahedral vacancies in the dihydride lattice.

Both sets of isotherms (UA and TWP) are quite sensitive to metal phase changes. The UA metal phase

transition from δ' to ϵ coincides with the decreased spacing between the 475 and 500 °C isotherms (figure 4-7). The phase transition from ϵ to liquid can be seen in the spacing change between the 625 and 650 °C isotherms (figure 4-17). This suggests that the enthalpy of liquefaction is negligible since no change of slope is suggested in figure 4-15. In TWP metal the phase transition between δ and $\delta+\epsilon$ can be seen in the spacing change between the 600 and 625 °C isotherms (figure 4-5). These features were not observed by Mulford and Sturdy.

When comparing the measured plateau pressures from these data with the data of Mulford and Sturdy and those of Condit, it is obvious that these pressures are lower in all cases. The Condit data are highest with Mulford and Sturdy's values in the middle. The difference is that Condit, and Mulford and Sturdy heated hydride that was formed at room temperature while the hydride in this study was formed at the test temperature. It has long been observed that there is a difference in the hydride depending on the temperature at which it was formed. These data strongly suggest that the hydride formed at high temperature is more stable. The reason for this is unknown. This also raises a question as to the accuracy of the Mulford and Sturdy method, as they did not see indications of the metal phase changes.

The calculated value for enthalpy of formation for UA metal is in excellent agreement with the corrected literature value (table 5-2). Also the calculated entropy value for TWP hydride is in excellent agreement with literature values. But, the calculated enthalpy value for TWP is lower. At first glance this appears to be a contradiction, TWP has the higher solubility but the lower enthalpy? The explanation is that the solid solution region contributes little to the overall ΔG_f° , therefore, the dominating region is the two-phase region and the measured plateau pressures in this region were consistently higher.

The empirical equation obtained for the pressure - temperature dependence in the UA metal + hydride region is in poor agreement with literature values (table 4-1).

$$\ln P_{(H_2, atm)} = 14.583 - \frac{17313.132}{T(K)}$$

The reason is found in the vertical spacing of the isotherms with respect to temperature. It was shown in table 4-4 that the higher temperature isotherms are more closely spaced in the Mulford and Sturdy data. As shown by equation 4-3 the empirical relationship provides an internal verification of consistency i.e., if the second and third law thermodynamic values are consistent then

TABLE 5-2		
	ΔH_f° (kcal/mole)	$-\Delta S_f^\circ$ (cal/mole K)
Literature Values	-37.12 to -39.5	32.3 to 35.9
UA Values	-35.18	30.19
TWP Values	-34.44	33.0
Corrected Literature Value	-36.02	

systematic errors can be ruled out. Table 4-5 shows that within experimental error, second and third law values agree.

THE UNANSWERED QUESTIONS

Several areas need further work. The most intriguing area is understanding the TWP low composition inflection point. One method of probing this region is with neutron diffraction. Neutron diffraction will allow the determination of the relative positions of the atoms. Transmission electron microscopy may also be of some use, however, the hydrogen atoms probably would not deflect the electrons sufficiently to reveal their location. All such measurements must be made at high temperatures because the samples will tend to loose hydrogen on cooling to room temperature.

Three other important areas of interest are; 1) how Ga is accommodated in the hydride, 2) how the formation temperature of the hydride affects the measured decomposition pressure, and 3) complete reevaluation of thermodynamic data for the Pu-H system. This thermodynamic reevaluation is a large undertaking that lies beyond the scope of the present study, but is necessary for adequately defining the properties of the plutonium hydrogen system.

CHAPTER 5

CONCLUSIONS

The primary objective of this study was to define the Pu-H phase diagram at low composition. Two allotropes of Pu were studied, ϵ phase (unalloyed metal) and δ phase (two-weight-percent) in the same temperature range. The data show that hydrogen is moderately soluble in both phases of Pu with the δ phase having the higher solubility at temperatures up to 625 °C (table 5-1). One reason for this is that, in δ phase metal the interstitial sites are larger and separated by the presence of the octahedral sites. This apparently lowers the coulombic repulsion between H^- ions and allows greater solubility.

Both allotropes showed some unusual features in the pressure-composition isotherms. In the solid solution region the isotherms are all closely spaced with respect to hydrogen pressure. This was especially true for the ϵ phase formed by UA metal. There is significant crossing of these isotherms, but this inconsistency is attributed to errors in the PVT measurements. Above the melting point, isotherms for UA metal show anomalies that are interpreted as inhomogeneity, reaching an invariant

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