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The Hg-Pu (Mercury-Plutonium) System

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Only the Hg-rich part of the Hg-Pu phase diagram is experimentally known. The diagram depicted in Fig. 1 consists of the following phases: (1) the liquid (L); (2) (Hg), probably with a low solid solubility of Pu; (3) (αPu); (βPu), (γPu), (δPu), (δ′Pu), and (εPu), likely with a small content of dissolved Hg with the exception of (εPu), for which several at.% Hg of solid solubility was predicted; and (4) two (or more) intermetallic phases, $Hg_{45}Pu_{11}$ and Hg_3Pu, formed in peritectic reactions. Various temperatures of $Hg_{45}Pu_{11}$ decomposition have been reported: 380 °C [1961Sch], 530 °C [1967Buc], and 550 °C [1968Ell]. The differences are probably related to different pressures (which were not specified). The decomposition temperature of Hg_3Pu has not been reported numerically, but the compound was marked on the Hg-Pu partial phase diagram as being stable up to 600 °C [1968Ell]. Hg melts at –38.8290 °C and boils at 356.623 °C, at 0.101325 MPa. Pu melts at 640 °C. The α ↔ β, β ↔ γ, γ ↔ δ, δ ↔ δ′, and δ′ ↔ ε transformations of Pu occur at 125, 215, 320, 463, and 483 °C, respectively [Massalski2].

The Pu amalgams may be prepared by direct melting of the metals [1955Whi, 1959Bow], by cementation of Pu(IV) in an acetic buffer solution with Na amalgam [1969Mal], and by electroreduction of Pu(IV) on a Hg electrode [1975Kob, 1984Mas]. The Pu amalgam obtained, after its decomposition at 700 to 1000 °C in an Ar atmosphere, is an appropriate starting material for the preparation of metallic Pu [1992Per].

The solubility of Pu in liquid Hg was investigated by [1955Whi], [1959Bow], [1961Bow], and [1959Fed]. The results are listed in Table 1. No details of the determination by [1959Fed] are reported. Because the data of [1959Fed] were obtained by W.J. Maraman in the same laboratory as those of [1959Bow] and [1961Bow], one may treat the results of [1959Fed] as preliminary solubility tests. [1955Whi], [1959Bow], and [1961Bow] prepared Pu amalgam by the direct contact of both metals in an inert atmosphere. After a proper equilibration at the selected temperature, the selected amalgam was filtered through a capillary [1955Whi] or a frit [1959Bow, 1961Bow]. The saturated liquid was decomposed with an HCl solution, and the radioactivity of the resulting solution was measured. The agreement of the results of [1955Whi], [1959Bow], and [1961Bow] is very good, and the temperature dependence of the solubility results may be expressed by:

$$\text{Log (solubility/at.\%Pu)} = 1.346 - 948/(T/K) \qquad \text{(Eq 1)}$$

[1967Ell] predicted a solid solubility of Hg in εPu of several at.% Hg; the solid solubilities in other allotropes of

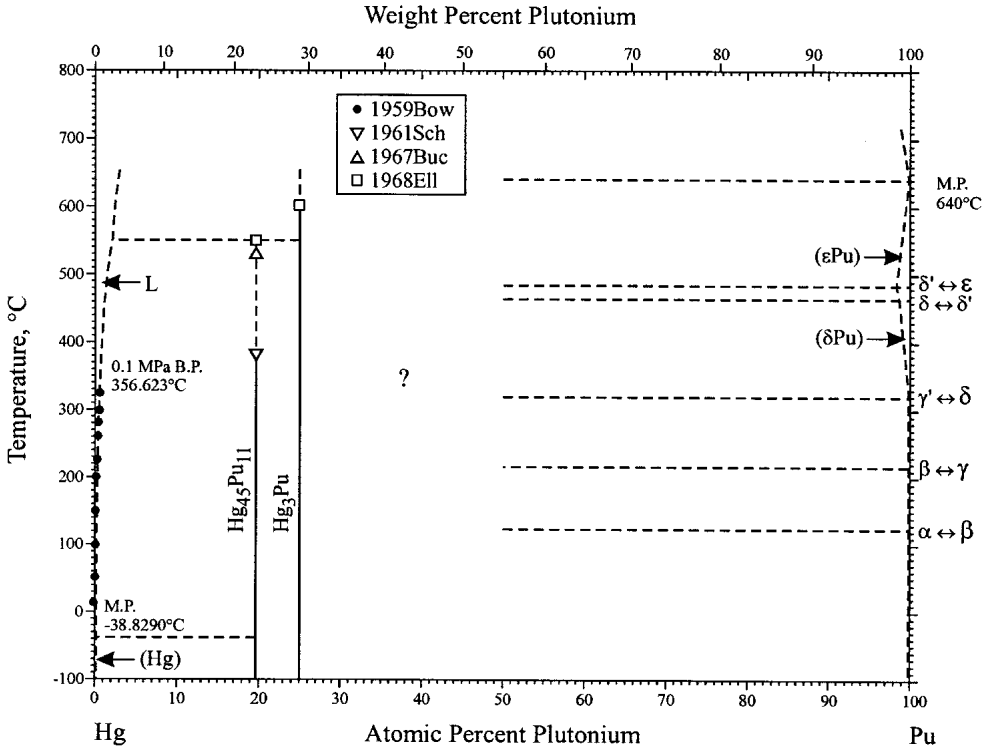

Fig. 1 Hg-Pu assessed phase diagram at a pressure sufficient to keep Hg as liquid

Table 1 Solubility of Pu in liquid Hg

Reference	Temperature, °C	Composition, at.% Pu
[1955Whi]	18-20	0.0136
[1959Fed]	20	0.0011
	100	0.011
	150	0.030
	200	0.067
	250	0.126
	300	0.22
	350	0.32
[1959Bow]	21	0.0131
	24	0.0161(a)
	50	0.0255
	100	0.0625
	150	0.126(a)
	190	0.182
	200	0.190
	225	0.275
	260	0.380
	280	0.421
	300	0.496
	325	0.561(a)

(a) Also reported in [1961Bow]

Pu at lower temperatures seem to be significantly lower. If one assumes that the Hg-Pu system is of the eutectic type in the Hg-rich region, then one should not expect a solid solubility of Pu in Hg higher than the calculated liquid solubility of Pu in Hg at the melting temperature of Hg (2×10^{-3} at.% Pu).

Powdered Hg-Pu alloys were investigated by x-ray diffraction (XRD) analysis [1955Cof, 1966Ber]. The formula for $Hg_{45}Pu_{11}$ was initially reported as Hg_4Pu [1955Cof] and was later changed to $Hg_{21}Pu_5$ [1966Ber] due to a more precise crystallographic investigation. The formula $Hg_{45}Pu_{11}$ was postulated by [1979Mer] by analogy to the isostructural compounds of U and lanthanides. The XRD identification of Hg_3Pu is not very certain, but undoubtedly a hexagonal structure ought to be ascribed to its crystal symmetry [1955Cof]. Similar to the thorium and uranium alloys made with Hg, a Ni_3Sn type structure is postulated for Hg_3Pu. The Hg-Pu crystal structures and lattice parameter data of the known phases are collected in Tables 2 and 3. [1992Koz] reported the formation of an Hg_2Pu phase in the Hg-Pu system, very likely by comparison to the |Cd-Pu| and Pu-Zn systems [Massalski2]. However, no proper background for this information was given. The formation of Pu-rich compounds, by similarity to the Cd-Pu and Pu-Zn systems, seems improbable.

Table 2 Hg-Pu crystal structures

Phase	Composition, at.% Pu	Pearson symbol	Space group	Strukturbericht designation	Prototype
Hg	0	*hR*1	$R\bar{3}m$	*A*10	αHg
$Hg_{45}Pu_{11}$	19.7	*cF*448	$F\bar{4}3m$	…	$Cd_{45}Sm_{11}$(a)
Hg_3Pu	25	*hP*8(b)	$P6_3/mmc$	…	Ni_3Sn(b)
αPu	100	*mP*16	$P2_1/m$	…	αPu
βPu	100	*mC*34	*C*2/*m*	…	βPu
γPu	100	*oF*8	*Fddd*	…	γPu
δPu	100	*cF*4	$Fm\bar{3}m$	*A*1	Cu
δ′Pu	100	*tI*2	*I*4/*mmm*	*A*6	In
εPu	100	*cI*2	$Im\bar{3}m$	*A*2	W

(a) Predicted by this compiler by analogy to $Hg_{45}U_{11}$. According to [1966Ber], the formula is $Hg_{21}Pu_5$, $D8_{1\text{-}3}$ Strukturbericht designation, and γ-brass prototype. According to [Pearson4], the Pearson symbol is *cF*416 and $Cu_{41}Sn_{11}$ prototype. (b) Predicted by the evaluator

Table 3 Hg-Pu lattice parameter data

Phase	Composition, at.% Pu	Lattice parameters, nm				Temperature, °C	Reference
		a	*b*	*c*	α or β, °		
Hg	0	0.3005	…	…	70.53	−48	[Massalski2]
$Hg_{45}Pu_{11}$	19.7	0.361(a)	…	…	…	RT	[1956Cof]
		2.178(b)	…	…	…	RT	[1966Ber]
αPu	100	0.6183	0.4822	1.0963	101.97	25	[Massalski2]
βPu	100	0.9284	1.0463	0.7859	92.13	>125	[Massalski2]
γPu	100	0.31587	0.57682	1.0162	…	>215	[Massalski2]
δPu	100	0.46371	…	…	…	>320	[Massalski2]
δ′Pu	100	0.33261	…	0.44630	…	>463	[Massalski2]
εPu	100	0.36343	…	…	…	>483	[Massalski2]

(a) For Hg_4Pu formula assumed. (b) For $Hg_{21}Pu_5$ formula assumed. RT, room temperature

[1975Mie] predicted the enthalpies of formation of $Hg_{45}Pu_{11}$ and Hg_3Pu to be −20 and −24 kJ/mol atoms, respectively. This is indicative of strong interactions between Hg and Pu. It is assumed that Hg was liquid in the standard state. [1983Nie], using the same cellular model, predicted partial enthalpies of solution at infinite dilution for $Hg_{(L)}$ in $Pu_{(L)}$, conversely at −80 and −69 kJ/mol metal, respectively.

Some explanation should be given here about the so-called "*red mercury*" producing sensations over years. This name was given to the reddish powder of a Pu amalgam [2001Lad]. Because Hg captures neutrons, any transportation or transformation of the alloy is easier than that for pure Pu. Pure Pu simply may be extracted from the red Hg by Hg evaporation at high temperatures [2001Orl].

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# Indicates presence of the phase diagram.

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