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The Thermodynamic Properties and Equilibria
at High Temperatures of the Compounds of
Plutonium.

by

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Paul W. Gilles and Norman L. Lofgren

CLASSIFICATION CANCELLED

For the Atomic Energy Commission

Charles A. Keller
Declassification Officer

February 1, 1949

(based exclusively on data available in the declassified literature).

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Abstract

Values of the thermodynamic data for plutonium compounds are given in four tables in Part I. Table 1 gives melting, vapor pressure, and boiling data. Table 2 gives the constants for the free energy of vaporization equation together with heat and entropy of vaporization at the boiling point. Table 3 gives values of the free energy function $\frac{\Delta F - \Delta H_{298}}{T}$ and ΔH_{298} , the heat of formation.

Table 4 gives the heat, free energy, and entropy of formation for the aqueous ions.

Part II contains the references and the discussion of the high temperature chemistry of the compounds considered. Part III presents five graphs to show the equilibrium concentrations of halogen or halide in plutonium and halogen systems at three different pressures, one atm., 10^{-3} atm., and 10^{-6} atm.

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THE THERMODYNAMIC PROPERTIES AND EQUILIBRIA AT HIGH
TEMPERATURES OF THE COMPOUNDS OF PLUTONIUM

By Leo Brewer, Leroy Bromley, Paul W. Gilles & Norman L. Lofgren

For research, development, or manufacturing work.

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Part I
Thermodynamic Tables

Introduction

The usefulness of thermodynamic data as an aid in predicting what reactions may occur in any system is well recognized. This tool is especially valuable at high temperatures where most reactions are rapid. It is not only necessary, however, to have thermodynamic data but, if time is to be saved, it is also necessary to know the important species that are likely to exist in the system under consideration. In this paper the thermodynamic data of plutonium compounds are presented and an attempt is made to indicate the species which are likely to be encountered in work with them at different conditions of pressure and temperature. A shorter but similar treatment of neptunium compounds is also available⁽⁷¹⁾.

This paper is rightly a part of a more comprehensive thermodynamic study of inorganic halides which is found in the authors' Halide Report⁽²⁶⁾, but because of the nature of the contents of the present report, it has been presented as a separate unit. The methods used in this report are the same as those used in the Halide Report and they are discussed in some detail in the latter. Further explanation of thermodynamic calculations can be found in another report by the authors⁽⁵⁸⁾.

This paper gives in Table 1 values of the melting point, heat and entropy of fusion, vapor pressures or boiling point, and heat and entropy of vaporization. In Table 2, constants for the free energy equation for vaporization are given. In Table 3, values of the free energy function $\frac{\Delta F - \Delta H_{298}}{T}$ at different temperatures and the heat of formation, ΔH_{298} , for the halides, oxides, carbides, nitrides, and silicides of plutonium are given. Contrary to what has been done in other papers(1, 26), values of the functions $-\frac{(F-H_{298})}{T}$, $H_T - H_{298}$, and $S_T - S_{298}$ are not included because the corresponding values for the metal were not available and it was therefore easier to estimate directly the values of $\frac{\Delta F - \Delta H_{298}}{T}$ than to estimate heat capacities and to calculate the functions(26). In Table 4 are given the values of the thermodynamic constants for formation of the ions.

In so far as was possible, all data of thermodynamic significance available in the declassified literature on Feb. 1, 1949 have been considered in obtaining the values given in these tables. Where data were not available or were considered to be too sketchy or inaccurate, estimates were made.

Such estimates were based largely upon data presented by the authors(1, 26) for compounds of uranium and the rare earth metals. It should therefore be noted that to maintain consistency, corresponding changes in plutonium values should be made if new data become available on the uranium system. Thus the present revision of this report is due to the April 1947 revision of the uranium report(1).

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All temperatures are expressed in degrees Kelvin. The references to the values in all the tables are given together under each compound.

STANDARD STATES ARE GASEOUS FLUORINE, CHLORINE, BROMINE AND IODINE, NITROGEN, $S_2(g)$, AND SOLID METALS, GRAPHITE, AND SILICON. The units, generally, are kilocalories per mole for the energy terms and calories per degree per mole for the entropy and heat capacity terms.

Description of Tables

Table 1 The melting and boiling data are self-explanatory. For all vapor pressure data in Table 1, experimental values, when available, were used to determine a free energy of vaporization equation using an estimated ΔC_p of vaporization. This allowed more accurate extrapolation of the data to the boiling point. The equations used are given in Table 2. The vapor pressures given are the partial pressures of the gaseous species of the same composition as the solid or liquid, and as such are a measure of the free energy of vaporization. In many cases the compound vaporizes at a lower temperature than that given in the table because of decomposition or disproportionation. By reference to the figures it can be seen which method of vaporization is important.

Table 2 This table gives the constants for the free energy of vaporization equations $\Delta F = \Delta H_0 - \Delta C_p T \ln T + IT$ and $\log p = \frac{-\Delta F}{4.575T}$. Constants are given for both the liquid and solid for most of the compounds. The heats and entropies of vapor-

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ization at the boiling point under one atmosphere pressure are also given. In every case, the free energy of vaporization refers to the simple vaporization from the solid or liquid standard state to the perfect gas standard state at one atmosphere pressure.

Table 3 It will be noted that $\frac{\Delta F - \Delta H_{298}}{T}$ at 298°K is in reality $-\Delta S$ for formation although the same relationship does not hold at other temperatures. The reason for tabulating this function is that its variance with temperature is small and this allows accurate interpolation. It will be noted that

$$\frac{\frac{\partial \Delta F - \Delta H_{298}}{\partial (T)}}{T} = \frac{\Delta H_{298} - \Delta H}{T^2}$$

and hence at 298°K, the rate of change of the function with temperature is zero; and as long as ΔH at other temperatures does not differ greatly from ΔH_{298} the function will change slowly with temperature. In the last column of the table are given the heats of formation, ΔH_{298} , which can be used with the function $\frac{\Delta F - \Delta H_{298}}{T}$, to obtain ΔF at any temperature. ALL

HEATS OF FORMATION AND OTHER DATA ARE FROM GASEOUS FLUORINE, CHLORINE, BROMINE, IODINE, OXYGEN, NITROGEN, DIATOMIC SULFUR, AND SOLID METALS, GRAPHITE, AND SILICON.

For the substances other than the halides and tetravalent oxide, no values for $\frac{\Delta F - \Delta H_{298}}{T}$ are given above 298°K. In such cases it is entirely satisfactory, for the most part, to assume that the ΔH of formation is constant and equal to ΔH_{298} ,

hence $\frac{\Delta F - \Delta H_{298}}{T}$ and also ΔS are the same at any temperature.

Since $\Delta F = \Delta H - T\Delta S$, ΔF is linear with temperature if ΔH is constant. Since the values of ΔH have been obtained from free energies derived from high temperature chemistry for a number of substances in this class, it should be pointed out that they do not necessarily represent accurate or even good values of heat and entropy of formation at 298°K but when combined together in the equation $\Delta F = \Delta H - T\Delta S$ do give in the temperature range which is of most interest a value of ΔF such that observed phenomena can be calculated.

The general procedure for the calculation of the heat and entropy of formation of a substance from high temperature chemistry is to estimate from whatever data are given for any particular reaction some quantity, such as a pressure, partial pressure, or equilibrium constant, which is a measure of the free energy of the reaction at the temperature under consideration. From the tables of $\frac{\Delta F - \Delta H_{298}}{T}$ and ΔH_{298} , free energies at this temperature may be calculated for the other substances involved in the reaction. Then from these free energies and the estimated free energy of reaction, the free energy of the compound under consideration may be calculated. This value together with an estimated entropy or $\frac{\Delta F - \Delta H_{298}}{T}$ will give a heat of formation according to the expression $\Delta H = \Delta F + T\Delta S$ or $\frac{\Delta H_{298}}{T} = \frac{\Delta F}{T} - \frac{\Delta F - \Delta H_{298}}{T}$. An inescapable result of this method is that all values in the tables are inextricably connected and consequently a self-consistent table will not be maintained if newer and even better values are indiscriminately substituted

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in the table without making corresponding changes in the related values.

Table 4 Values are given for the ions in 1M HCl and 1M HClO₄. The values for 1M HClO₄ may be used as infinitely dilute values with little error. The calculations of the values are described in the references. These values for the aqueous ions are consistent with the thermodynamic data given for the solid compounds. Throughout this paper, ΔH , ΔF , and ΔS values for ionic species are partial molal quantities. Concentrations are in moles per kg. water. The ΔF values are for all constituents at unit concentration, but with no corrections for activity coefficients, e.g., a formal potential.

It should be emphasized that neither the partial molal ΔF values nor the E values given in the text are standard values corresponding to unity activities of the various species, but they are "formal" values corresponding to unit concentrations of the various species. Thus for $\text{Pu}^{3+} + \text{H}^+ = \text{Pu}^{4+} + 1/2 \text{H}_2(\text{g})$, $E = E_{\text{obs.}} + 0.05914 \log m_{\text{Pu}^{4+}}/m_{\text{Pu}^{3+}} m_{\text{H}^+}$ where $E_{\text{obs.}}$ is the observed potential for the cell composed of a hydrogen electrode in solution of m_{H^+} hydrogen ion concentration against a Pu^{3+} -- Pu^{4+} electrode. m stands for concentration in moles per kilogram water and no activity coefficients corrections of any sort have been made to the observed potentials. This is emphasized since other papers in this volume have used a so called "formal" potential, which is erroneously used since corrections are made for activity coefficients of some species and not for others.

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Table I

Comp.	Melting Data			T _p = temperature at which partial pressure is 1 atm. Degrees Kelvin					
	T _m °K	ΔH _m Kcals.	ΔS _m e.u.	T _{10⁻⁶}	T _{10⁻⁵}	T _{10⁻⁴}	T _{10⁻³}	T _{10⁻²}	T ₁
PuF ₃	1580 ^{±20}	13.	7.75	1380	1450	1560	1690	1870	2460
PuCl ₃	1033 ^{±5}	15.2	14.7	1000	1090	1195	1315	1480	2040
PuBr ₃	954	13.4	14.0	920	1000	1085	1190	1335	1785
PuI ₃	(1050)	(12.0)	(11.4)	(865)	(930)	(1000)	(1090)	(1225)	(1650)
PuO ₂					(2200)				
PuO				(1850)					

Table II

Constants in Free Energy of Vaporization Equations

of the form $\Delta F = \Delta H_0 - 2.3 \Delta C_p T \log P + IT$

Comp.	Vaporization from solid			Vaporization from liquid			Heat and Entropy of Vaporization at Boiling pt.	
	ΔH_0 calories	ΔC_p e.u.	I e.u.	ΔH_0 calories	ΔC_p e.u.	I e.u.	ΔH kcal.	ΔS e.u.
PuF ₃	115,500	-14	-158.7	105,900	-16	-167.8	66.6	27.1
PuCl ₃	81,340	-10	-125.1	71,220	-12	-126.3	46.74	22.0
PuBr ₃	(82,100)	(-12)	(-142.8)	72,500	-16	-160.1	44.	24.9
PuI ₃	(69,400)	(-10)	(-120.3)	(59,500)	(-12)	(-124.2)	(39.7)	(24.)

Table III

	$\frac{\Delta F - \Delta H_{298}}{T}$					
	Calories per Degree					
	298°K	500°K	1000°K	1500°K	ΔH_{298}^* kilocalories	
PuF ₃	60	59	59	58	-374.	
PuCl ₃	54	54	53	50(1)	-229.3	
PuCl ₄	72	72	68(1)		-230.	
PuBr ₃	52	52	50(1)	48(1)	-199.0	
PuI ₃	52	52	49	48(1)	-155.	
PuO ₂	43	42	41	41	-251.	
PuO	21	The use of these values in the simple				
PuSi ₂	-10	$\Delta F = \Delta H - T\Delta S$				-211.
PuC	2	equation with $\Delta C_p = 0$				- 25.
PuN	17	will give correct ΔF				- 95.
PuOCl	38	values at high temperatures even though room				-222.6
PuOBr	33	temperature values may be off.				-210.
PuOI	32					-195.
Pu ₂ S ₃	72					-286.

*All values are based upon gaseous standard states for fluorine, chlorine, bromine, iodine, sulfur, (S₂), nitrogen, oxygen, and solid graphite, plutonium and silicon.

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Table IV

Thermodynamic Properties of the Aqueous Plutonium Ions

		$\Delta\bar{H}_{298}$	$\Delta\bar{S}_{298}$	$\Delta\bar{F}_{298}$	$\Delta\bar{H}_{298}$	$\Delta\bar{F}_{298}$
		in 1M HClO ₄			in 1M HCl	
Pu + 3H ⁺	= Pu ⁺³ + $\frac{3}{2}$ H ₂	-141.6 + 3		-142.7	-141.9	-142.7
Pu + 4H ⁺	= Pu ⁺⁴ + 2H ₂	-138.6 - 29		-120.1	-129.0	-120.6
Pu + H ⁺ + 2H ₂ O	= PuO ₂ ⁺ + $\frac{5}{2}$ H ₂	- 78. + 54		- 94.	- 78.	- 93.
Pu + 2H ⁺ + 2H ₂ O	= PuO ₂ ⁺⁺ + 3H ₂	-61.6 + 38		-72.8	- 62.2	-72.4

$\Delta\bar{H}$ and $\Delta\bar{F}$ values are in kilocalories per mole and $\Delta\bar{S}$ values are in calories per degree. All values are partial molal values. All concentrations are expressed in moles per kilogram water.

The $\Delta\bar{S}$ and $\Delta\bar{F}$ values are for the reacting species at unit concentration, but with no correction for activity coefficients. In other words, $\Delta\bar{F}$ corresponds to a formal potential rather than to a molal potential.

See page 11 for discussion of formal potentials.

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Part II

References and Discussion

Introduction

After each formula are given the references to the data in Part I as well as a critical discussion of the chemistry of the compound. In the cases of the halides these discussions supplement the figures in Part III of this paper while in the cases of the oxyhalides, oxides, nitrides, and carbides these discussions are substitutes for figures.

Aqueous Ions

Pu⁺³ Robinson and Westrum^(47,66) have determined the heat of solution of PuCl₃ in various concentration of HCl and have extrapolated their values to pure water and have obtained for the reaction: $\text{PuCl}_3(s) = \text{Pu}^{+3} + 3\text{Cl}^-$, $\Delta H_{298} = -31.9$ kcals. This value combined with the -39.943 kilocal from Rossini⁽³⁹⁾ for the heat

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of formation of Cl^- , and the heat of formation of $\text{PuCl}_3(\text{s})$, gives for the reaction at zero HCl concentration:

Applying the method used by Evans⁽⁴⁵⁾ we can calculate the entropy of Pu^{+3} from the entropy of $\text{Gd}^{+3} = -32.5^{(50)}$ by correcting for different ionic radii, different masses, and different amounts of magnetic entropy. From plots of ionic entropies for trivalent positive ions against radius of the ion, it was found that the entropy changes about 82 units per Angstrom. Zachariasen⁽⁴⁸⁾ gives 1.01 Å for the radius of Pu^{+3} and gives values for the radii Ce^{+3} , Pr^{+3} , Nd^{+3} , and Sm^{+3}

By comparison with the values given by Goldschmidt⁽⁴⁹⁾ for the same ions and for Gd^{+3}

we find that Pu^{+3} is larger than Gd^{+3} by 0.06 Angstroms and this difference should make a contribution of 4.9 e.u. to the difference between the entropies of Pu^{+3} and Gd^{+3} . The magnetic entropy of gadolinium, $R \ln 8 = 4.1 \text{ e.u.}$ should be subtracted while the mass correction, 1.2 should be added giving -30.9 without any contribution from the magnetic entropy of plutonium. Such a contribution would make the entropy less negative and so we have estimated -30 for the entropy of Pu^{+3} . Combining this with the entropy of hydrogen⁽⁵¹⁾ and an estimated entropy of plutonium of 13 e.u. we obtain ΔS_{298} and subsequently for the reaction at zero HCl concentration:

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This corresponds to an E° of 2.06 volts. These values may be used either for the infinitely dilute values or for the values in 1M HClO_4 since the difference will be less than the uncertainties of these values.

To obtain the values for Pu^{3+} in 1M HCl , one may use Robinson and Westrum's^(47, 66) partial molal $\Delta H_{298} = -31.76$ kilocal. for $\text{PuCl}_3(\text{s})$ dissolving in 0.1M HCl and -29.50 for $\text{PuCl}_3(\text{s})$ dissolving in 1.55 moles HCl per kilo water to calculate $\Delta H_{298} = -30.36$ kilocal. for $\text{PuCl}_3(\text{s})$ dissolving in 1M HCl . This together with a value of $L = 645$ calories for 1M HCl from Sturtevant⁽⁶⁰⁾ allows one to calculate for

$\text{Pu}(\text{s}) + 3\text{H}^+ = \text{Pu}^{3+} + 3/2 \text{H}_2(\text{g})$, $\Delta H_{298} = -141.9$ kilocal. in 1M HCl . As the best value which can be given for 1M HCl , $\Delta F_{298} = -142.7$ kilocal, the same as at infinite dilution will be taken.

Pu^{4+} Evans⁽⁴⁵⁾ ...

... has determined the heat of oxidation of Pu^{3+} to Pu^{4+} by Fe^{+++} and $\text{Cr}_2\text{O}_7^{=}$. Correcting her data to agree with recent determinations of the $\text{Fe}^{2+} - \text{Fe}^{3+}$ couple by Fontana⁽⁶¹⁾, one calculates $\Delta H_{298} = 11.6$ kilocalories for the $\text{Pu}^{3+} - \text{Pu}^{4+}$ couple in 0.5M HClO_4 . However Connick and McVey⁽⁶⁵⁾ have determined the potential of this couple in 1M HClO_4 over a range of temperatures and have obtained $\Delta H_{298} = 13.5$ kilocalories. The Connick and McVey value is considered more reliable. There should be no great difference between the value in 0.5M HClO_4 and 1M HClO_4 . For the reaction

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one accepts as the best value in 1M HClO₄, $\Delta H_{298} = 13 \pm 1$ kilocalories.

Connick and McVey⁽⁶⁵⁾ obtained -0.982 volts as the formal potential, or actually observed value with no corrections, for the Pu³⁺ - Pu⁴⁺ couple in 1M HClO₄ or $\Delta F_{298} = 22.6$ kilocalories. This value together with the ΔH of the couple yield $\Delta H_{298} = -128.6$ kilocal. and $\Delta F_{298} = -120.1$ kilocalories for the formation of Pu⁴⁺ in 1M HClO₄ from the metal.

The ΔF for the formation of Pu⁴⁺ in 1M HCl can be obtained from the Pu³⁺ value and the Pu³⁺ - Pu⁴⁺ potential measurements in 1M HCl by Howland, Kraus, and Hindman⁽⁶³⁾, Krauss,⁽⁴²⁾ and Hindman⁽⁵²⁾. Connick and McVey⁽⁶⁵⁾ have recalculated these measurements to obtain -0.959 volts for the formal potential in 1M HCl or the observed potential uncorrected for activity coefficients. This then corresponds to $\Delta F_{298} = 22.1 \pm 0.1$ kilocalories for $\text{Pu}^{3+} + \text{H}^+ = \text{Pu}^{4+} + 1/2 \text{H}_2(\text{g})$ and therefore $\Delta F_{298} = -120.6$ kilocalories for the formation of Pu⁴⁺ in 1M HCl from the metal according to the reaction $\text{Pu}(\text{s}) + 4\text{H}^+ = \text{Pu}^{4+} + 2\text{H}_2(\text{g})$. The ΔH value in 1M HCl can be obtained by assuming the same ΔS value for the Pu³⁺ - Pu⁴⁺ couple as for the corresponding uranium couple or by assuming the same change in ΔH in going from HClO₄ solutions to HCl solutions as given in the case of uranium by Brewer, Bromley, Gilles, and Lofgren⁽¹⁾. The two results agree closely. The average gives $\Delta H_{298} = -129.0$ kilocalories for the formation of Pu⁴⁺ in 1M HCl.

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PuO_2^{++} Correcting Evans⁽⁴⁵⁾ determinations to agree with Fontana⁽⁶¹⁾ as in the case of Pu^{4+} , one obtains for

$\Delta H_{298} = 80 \pm 2$ kilocalories in 0.5M HClO_4 , which will be also taken as the 1M HClO_4 value. Connick and McVey⁽⁶⁵⁾ have combined the Pu^{4+} - PuO_2^{++} potential measurements of Hindman⁽⁵²⁾ and Krauss⁽⁴²⁾ with the equilibrium determinations of Kasha and Sheline⁽⁶²⁾ to obtain -1.042 volts as the formal potential for the Pu^{4+} - PuO_2^{++} couple in 1M HCl . Connick and McVey⁽⁶⁵⁾ also give -1.023 volts for the couple in 1M HClO_4 . Thus we obtain $\Delta F_{298} = -72.4$ kilocalories for the formation of PuO_2^{++} from the metal in 1M HCl and $\Delta F_{298} = -72.8$ for the formation in 1M HClO_4 . One would expect the HCl value to be more negative. The Pu^{4+} - PuO_2^{++} potential in 1M HClO_4 is probably not negative enough, but the differences are within the experimental error of the measurements.

The ΔH given above for the Pu^{3+} - PuO_2^{++} couple yields $\Delta H_{298} = -61.6$ kilocalories for the formation of PuO_2^{++} from the metal in 1M HClO_4 . To obtain the ΔH value in 1M HCl , the same procedure will be used as was used for Pu^{4+} in 1M HCl . Assuming the same ΔS as for the uranium system gives $\Delta H = -62.7$ kilocal. Assuming the same change from HClO_4 to HCl solutions as in the case of uranyl ion, one obtains $\Delta H = -61.7$. $\Delta H_{298} = -62.2$ kilocalories was taken as the partial heat of formation of PuO_2^{++} from the metal in 1M HCl .

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PuO_2^+ Kraus and Moore,⁽⁵³⁾ report -0.930 ± 0.015 volts for the formal potential of the $\text{PuO}_2^+ - \text{PuO}_2^{++}$ couple in about 0.1M ClO_4^- . We have taken this value as the 1M HClO_4 value. The difference in entropies of PuO_2^+ and PuO_2^{++} was estimated as 32 e.u. from plots of ionic radius against entropy for univalent and divalent ions. This gives then $\Delta F_{298} = +21.4 \pm 0.4$ kilocalories, $\Delta S_{298} = -16$ e.u., and $\Delta H_{298} = +16.6 \pm 2$ kilocalories for

Connick and McVey⁽⁶⁵⁾ give -0.912 volts for the $\text{PuO}_2^+ - \text{PuO}_2^{++}$ formal potential in 0.5M HCl . Using the uranium data to correct to 1M HCl , we obtain $\Delta F_{298} = 20.8$ kilocalories and using $\Delta S_{298} = -16$ e.u., $\Delta H_{298} = 16.0$ kilocalories is obtained for the above reaction in 1M HCl .

Summary of Heats and Free Energies of Ions

The following diagrams summarize the aqueous formal potentials in volts.

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The heats and free energies of formation of the ions from the metal are summarized in Table IV. The partial heats and free energies of formation of the ions from Pu^{3+} are given in kilocalories per mole as follows:

	<u>1M HClO₄</u>		<u>1M HCl</u>	
	ΔH_{298}	ΔF_{298}	ΔH_{298}	ΔF_{298}
$\text{Pu}^{3+} + \text{H}^+ = \text{Pu}^{4+} + 1/2 \text{H}_2(\text{g})$	13.0 $\pm$ 1	22.6 $\pm$ 0.1	12.9 $\pm$ 1	22.1 $\pm$ 0.1
$\text{Pu}^{3+} + 2\text{H}_2\text{O}(\text{l}) = \text{PuO}_2^+ + 2\text{H}^+ + \text{H}_2(\text{g})$	63 $\pm$ 3	48.5 $\pm$ 1	64 $\pm$ 3	49.5 $\pm$ 1
$\text{Pu}^{3+} + 2\text{H}_2\text{O}(\text{l}) = \text{PuO}_2^{++} + \text{H}^+ + 3/2 \text{H}_2(\text{g})$	80 $\pm$ 2	69.9 $\pm$ 1	80 $\pm$ 2	70.3 $\pm$ 1

The presentation of the data in this manner has some advantages over Table IV since these values do not depend upon the heat and free energy of solution of plutonium metal. Also the uncertainties of the data are better shown here. However either set of values will give the same results in calculations.

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Fluorides

PuF₃ The vapor pressure, boiling points, heat and entropy of fusion have been recalculated from vapor pressure measurements of

Phipps, Seifert, and Simpson⁽⁵⁹⁾. The latter group of workers have plotted the logarithms of their vapor pressures against reciprocal temperatures and through the points have drawn two lines to represent solid and liquid vaporization. The intersection of these lines is at 1447°K. They have taken this temperature to be the melting point and have calculated from the slopes the heat and entropy of fusion to be 7.88 kcals. and 5.47 e.u. An extrapolation of their equation gives a boiling point of 2310°K and a ΔS of vaporization of 38 e.u. The values so obtained of the melting point, heat, and entropy of fusion and entropy of vaporization do not seem to be reasonable when compared with the corresponding values for other fluorides.

For this reason we have examined their data and find that their points could better be considered to lie on a curve instead of on two straight lines. This is to be expected if the ΔC_p of vaporization is considered. A curve taking into account a ΔC_p of sublimation of -14 e.u. would represent their data over their entire temperature range extremely well and would not indicate a melting point. Thus we have used their data to calculate a free energy of sublimation equation of the form $\Delta F = \Delta H_0 - 2.3(-14) T \log T + IT$ from which the vapor pressures have been calculated up to 10^{-4} atm. In accord with

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other fluorides, a melting point of 1680°K and a heat of fusion of 13 kcaIs have been estimated. These have been used with the solid vaporization equation to obtain a similar one for the liquid using $\Delta C_p = -16$ from which the remaining vapor pressures and the heat and entropy of vaporization at the normal boiling point have been calculated. The resulting entropy of vaporization has the reasonable value of 27 e.u.

PuF_3 forms black or purple hexagonal crystals of the LaF_3 type with $a_1=4.087$, $a_3=7.240$, and a density of $9.32^{(21,69)} \text{ g/cc}$.

Values for $\frac{\Delta F - \Delta H_{298}}{T}$ have been estimated from the values for UF_3 calculated by the present authors⁽¹⁾. The heat of formation, ΔH_{298} , was determined by Westrum and Eyring⁽⁶⁷⁾ from the heat of precipitation of PuF_3 .

Calculations based upon the values given in the accompanying tables, indicate that PuF_3 vaporizes essentially undecomposed and that $\text{PuF}_3(\text{g})$ is stable to above 4000°K at one atmosphere. At lower pressures it decomposes to gaseous metal and F provided there are no important lower gaseous halides. At one atmosphere total pressure, at the boiling point of PuF_3 , ^{and} $\text{Pu}(\text{g})$ are barely noticeable due to slight disproportionation of the PuF_3 .

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PuCl₃ -- Chlorides Abraham, Brody, Davidson, Hagemann, Hyde, Katz, and Sheft⁽³⁴⁾ studied the preparation and properties of PuCl₃. The melting point has been determined by Robinson⁽⁹⁾. The vapor pressures and boiling points and heat and entropy of vaporization have been recalculated from the data of Erway, Gilpatrick, Jasaitis, Johnson, Phipps, Sears, Seifert, and Simpson⁽⁵⁹⁾ by taking into account a ΔC_p of vaporization of -12 and a ΔC_p of sublimation of -10 e.u. This procedure gave a more reasonable entropy of vaporization at the boiling point than did an extrapolation of their equation. Their equation and the one chosen

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agree over the experimental range. The heat of fusion has been determined by these same workers from their slopes of vapor pressure curve. The solid equation was obtained by using the heat of fusion and equating the vapor pressures of solid and liquid at the melting point. The vapor pressures used are somewhat lower than those of Weinstock⁽¹⁰⁾, and may be in error due to impurities. This is evidenced by a lower melting point being obtained from the vapor pressure curves than from a direct determination. PuCl_3 forms green hexagonal LaCl_3 type crystals with $a_1 = 7.380$, $a_3 = 4.238$ and a density of 5.70 g/cc. ⁽⁶⁹⁾

Values of the function $\frac{\Delta F - \Delta H_{298}}{T}$ have been estimated from those of the corresponding uranium compound⁽¹⁾. Westrum and Robinson^(68,47) have obtained from the heats of solution of the metal and the chloride $\Delta H = -229.3$ for the heat of formation of PuCl_3 in kilocalories per mole.

Figure 3 indicates that PuCl_3 vaporizes undecomposed but that at higher temperatures and lower pressures, it decomposes to gaseous monatomic elements if there are no stable intermediate uni- or di-valent chlorides.

PuCl_4 There are no data which prove the existence of solid PuCl_4 and much data to indicate that it does not exist. Values of melting point, heat and entropy of fusion, vapor pressure, boiling points, and heat and entropy of vaporization can be taken the same as for uranium⁽¹⁾. Values of the function

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$\frac{\Delta F - \Delta H_{298}}{T}$ have been estimated from the same source.

Calculations based upon these values indicate that the dissociation pressure of Cl_2 over solid PuCl_4 at room temperature is about 10^7 atmospheres which accounts for the fact that PuCl_4 has not been found. Despite the non-existence of solid PuCl_4 there will be some PuCl_4 in the gaseous phase. The maximum concentration of $\text{PuCl}_4(\text{g})$ in a system of total composition PuCl_3 , which will occur in the neighborhood of the boiling point of the trichloride, is about 10^{-5} atm when the total pressure is one atm and the temperature is 2040°K . Much higher concentrations of $\text{PuCl}_4(\text{g})$ can of course be obtained by increasing the halogen pressure as by passing Cl_2 over heated PuCl_3 . For example, at 2000°K where the vapor pressure of PuCl_3 is about 0.1 atm, if the pressure of Cl_2 , which equals approximately the pressure of Cl , is about 0.5 atm, the pressure of PuCl_4 will be about 2×10^{-2} atm.

PuCl_5 and PuCl_6 There is no evidence for the existence of these substances in either the condensed or gaseous phase.

They would be expected to be even more unstable than PuCl_4 and to be of no importance under any conditions.

Bromides

PuBr_3 Davidson, Hagemann, Hyde, Katz, and Sheft⁽³⁶⁾ studied the methods of preparation and properties of PuBr_3 . The melting point has been determined by Robinson⁽⁹⁾. The heat of fusion has been determined by

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Phipps, Seifert, and Simpson⁽⁵⁹⁾ by the difference in slopes of vapor pressure curves for liquid and solid. The vapor pressures, boiling point, heat and entropy of vaporization have been recalculated from the data of these workers by taking into account a ΔC_p of vaporization of -16 and of sublimation of -12 e.u. The entropy of vaporization at the boiling point as determined by an extrapolation of their equation is far too large and is replaced by a more reasonable value when the extrapolation is made with the aid of an equation involving ΔC_p . Zachariassen⁽⁶⁹⁾

reports that PuBr_3 forms green orthorhombic NdBr_3 type crystals with a density of 6.65-6.69 g/cc.

Values of the function $\frac{\Delta F - \Delta H_{298}}{T}$ have been estimated from corresponding values for uranium⁽¹⁾. The heat of formation was obtained from the heats of solution of the metal and the salt in 6M (moles/liter) HCl, $\Delta H = -30.9$, obtained by Westrum^(47, 43). Westrum⁽⁶⁸⁾ has recently recalculated his results to obtain $\Delta H_{298} = -199.2$ kilocalories for the heat of formation of PuBr_3 .

Figure (4) indicates that PuBr_3 vaporizes undecomposed but that at higher temperatures and lower pressures decomposes to monatomic gaseous elements.

PuBr_4 There are no indications that PuBr_4 is stable in either a condensed or gaseous phase. Values of melting point, heat and entropy of fusion, vapor pressures, boiling points, and heat and entropy of vaporization have been taken the same as for the uranium system⁽¹⁾. Values of the function

$\frac{\Delta F - \Delta H_{298}}{T}$ have been estimated.

The calculated equilibrium decomposition pressure of PuBr_4 over solid PuBr_4 at room temperature is 10^{18} atmospheres. The PuBr_4 stability and concentration even in the gaseous phase is expected to be quite small, although in the presence of halogen and solid trivalent halide in the neighborhood of its boiling point, appreciable quantities of gaseous tetravalent halide probably exist.

PuBr_5 These are expected to be even less stable than PuBr_4
and
 PuBr_6 and to be of no importance.

PuI_3 -- Iodides Hagemann, Abraham, Davidson, Katz, and Sheft²⁴ have studied the preparation and properties of PuI_3 . The melting point, heat and entropy of fusion, vapor pressure, boiling points, heat and entropy of vaporization and values of the free energy function $\frac{\Delta F - \Delta H_{298}}{T}$ have been estimated from the values given for UI_3 ⁽¹⁾ and from the values for some of the rare earth iodides⁽²⁶⁾. The heat of formation was estimated by taking the same difference between the heats of formation for PuBr_3 and PuI_3 as existed between the heats of formation for UBr_3 and UI_3 . This procedure is not completely reliable but can be expected to give fairly good values in this case. As an indication of the closeness of this approximation we point to the difference of 32.4 ± 2 kcal between the heats of formation of UCl_3 and UBr_3 ⁽¹⁾ determined by the same worker and the difference of 30.3 between PuCl_3 and PuBr_3 . PuI_3 forms a bright green orthorhombic NdBr_3 type crystal with a density of 6.9 g/cc.

6.9 g/cc.
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PuI₄ See the discussion of PuBr₄. The calculated decomposition pressure of I₂ at room temperature is 10^{30} atm. It would be expected that the maximum concentration of PuI₄(g) would be much less than that of PuBr₄(g).

PuI₅
and
PuI₆ These compounds would be expected to be much less stable than the corresponding bromide compounds.

Oxides

PuO₃ Estimated heats predict no oxide above PuO₂ should be expected.

PuO₂ Phipps, Seifert, and Simpson⁽⁵⁹⁾ have measured the quantity of plutonium which vaporizes in a vacuum from a sample originally PuO₂. They found that the pressure increases with the time until some sort of a steady state is obtained. They have attributed this change to a decomposition of PuO₂. Thus from their data it is possible to give only a maximum vapor pressure of PuO₂. By comparing their results with the value for the vapor pressure of UO₂⁽¹⁾ we have chosen a pressure of 10^{-2} atm. for PuO₂(g)

in equilibrium with $\text{PuO}_2(\text{s})$ at 1800°K . From the free energy corresponding to this vapor pressure and an estimated entropy of vaporization of 30 e.u. the temperature at which the vapor pressure is equal to 10^{-5} atmospheres is calculated as 2200°K .

These workers also find in their curves a slight break about 2000°K which could be accounted for by a melting but this cannot be given unambiguously as the melting point of PuO_2 since the solid species was probably not pure PuO_2 . PuO_2 forms yellow cubic CaF_2 type crystals with $a = 5.386$ and a density of 11.44 g/cc. as reported by Mooney and Zachariasen⁽⁵⁷⁾.

Values of the function $\frac{\Delta F - \Delta H_{298}}{T}$ were estimated from the corresponding values in the uranium system⁽¹⁾.

The heat of formation has been obtained by combining the values of $\frac{\Delta F - \Delta H_{298}}{T}$ with the data of Abraham and Davidson⁽²²⁾

on the reaction $\text{PuO}_2 + \text{HCl} + 1/2 \text{H}_2 = \text{PuOCl} + \text{H}_2\text{O}$. These workers have measured the free energy change for this reaction over the temperature range $723-915^\circ\text{K}$ and have expressed their results in an equation of the form $\Delta F = -8.5 + 9.5 T/1000$ kilocalories. Although they estimated corrections which should be applied to their values to account for the amount of hydrogen diffusing out through their quartz chamber, they have not used these corrections in summarizing their data. We have used their estimated corrections for this effect and have obtained a free energy equation $\Delta F = -7.9 + 9.5 T/1000$ instead of their $\Delta F = -8.5 + 9.5 T/1000$ kilocalories. The values of the free energies of PuOCl from this report and of water and HCl from Brewer⁽³⁰⁾ were combined with this equa-

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tion to calculate the free energy of PuO_2 at high temperatures. The heat of formation was then obtained from the free energy and the $\frac{\Delta F - \Delta H_{298}}{T}$ tables. $\Delta H_{298} = -251$ kilocalories was obtained which is in excellent agreement with the U^{4+} and Pu^{4+} heats and the heat of formation of UO_2 .

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Pu₂O₃ There are no data on the melting or vaporization. A constant entropy of formation of -63 e.u. has been assumed in accord with the entropies of formation of other metallic oxides as presented by Brewer⁽¹⁴⁾. A value of -387 kilocalories for the heat of formation of Pu₂O₃ was obtained from a consideration of the difference in the heats of formation of 1/2 La₂O₃ and LaCl₃ and the heat of formation of PuCl₃. The heats of formation used for 1/2 La₂O₃ was -223 kilocalories from Bichowsky and Rossini⁽²⁸⁾ and for LaCl₃ was -264 kilocalories from the Halide Report by the authors of this paper⁽²⁶⁾.

The value so obtained indicates that if PuO is very stable, as is indicated by the measurements of :

... Phipps, . Seifert, and Simpson⁽⁵⁹⁾, then Pu₂O₃ will disproportionate to PuO and PuO₂. However it appears that PuO₂ may be reduced to a solid solution of PuO₂ and Pu₂O₃. Mooney and Zachariasen⁽⁵⁷⁾ report a solid solution range around Pu₄O₇. Westrum⁽¹⁶⁾ present results on the reduction of PuO₂ at high temperatures by K, Na, C, Ba, CH₄, Ta, Li, and Ca but these are not too readily used for the calculation of thermodynamic quantities.

PuO There are no data for the melting of this compound. It forms black cubic NaCl type crystals with a = 4.948 and a density of 13.95 g/cc.⁽⁵⁷⁾ The entropy of formation has been

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assumed constant and has been estimated in comparison with other metallic oxides which are summarized by Brewer⁽¹⁴⁾.

The species volatilizing from the samples used by

Phipps, Seifert, and Simpson⁽⁵⁹⁾ may be PuO(g) but their results have not as yet been interpreted completely.

From the data given by these workers, a very rough phase diagram has been sketched which indicates that probably in their experiments with oxidized metal, both PuO and Pu are vaporizing; while in the experiments with material originally PuO_2 , both O_2 and PuO are vaporizing. If such were the case, the composition would not change much and so the vapor pressure should approach a constant value at any temperature. This may be the explanation of their "steady-state". From this diagram and also from a consideration of the vapor pressure of $\text{UO}^{(1)}$, a value for the vapor pressure of PuO was estimated.

There are no data from which a good heat of formation may be calculated; however, one may by considering some chemical evidence make an estimate. From the fact that PuO is known to exist and Pu_2O_3 is believed to disproportionate, the heat of formation must be more negative per equivalent than PuO_2 and Pu_2O_3 in order to prevent disproportionation of the PuO .

From considering these data, we estimate that the heat of formation of PuO lies between -130 and -140 kcal/mole. If PuO is actually as stable as this, we would predict that it might be possible to prepare the divalent hal-

ides by heating the trivalent halides with the metal.

Carbide

PuC The value of the entropy of formation was estimated from corresponding values of other diatomic carbides which are considered by Brewer⁽¹⁴⁾ and was assumed constant with temperature. The heat of formation has not been measured and so only estimates can be made. PuC is reported by Zachariasen^(46,49) to have the NaCl crystal structure with $a = 4.910$ and a density of 13.99 g/cc . Considering the heat of formation of $\text{UC}^{(1)}$ we have estimated that the heat of formation of PuC is -25 kcal/mole .

Nitride

PuN The value for the entropy of formation was estimated from corresponding values for other metallic nitrides as summarized by Brewer⁽¹⁴⁾ and was assumed constant with temperature. PuN is brown and has the cubic NaCl type crystal structure with $a = 4.895$ and a density of 14.22 g/cc . as reported by Zachariasen^(46,69).

There has been no determination of the heat of formation; nor has there been much chemistry reported from which the heat can be calculated. Abraham, Davidson, and Westrum⁽²⁰⁾ report qualitative results on the reaction $\text{PuCl}_3 + 1/2 \text{ N}_2 + 3/2 \text{ H}_2 = \text{PuN} + 3\text{HCl}$. Estimates based upon their work indicate that the free energy of this reaction must be less than 73 kcal .

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This, when combined with the free energies of the other substances and the entropy of PuN gives a heat of formation more negative than -49 kcals. The value of -95 kcals chosen from a consideration of the heats of formation of the other metallic nitrides and especially of UN⁽¹⁾ is consistent with the calculated value.

Oxyhalides

PuOF There is insufficient evidence for the calculation or estimation of thermodynamic constants. It has been found by Robinson⁽⁵⁾ in some melting experiments and has been identified by Zachariasen^(21,60). It is black metallic in color and has the cubic CuF₂ type crystal structure with $a = 5.70$ and a density of 9.76 g/cc. Estimates based upon the heats and entropies of formation of PuOCl, PuCl₃, and PuF₃ indicate very roughly that the heat of formation of PuOF should be somewhat less negative than -270 kcals per mole and that the entropy of formation should be about -40 e.u.

PuOCl Abraham, Brody, Davidson, Hagemann, Hyde, Katz and Sheft⁽³⁴⁾ have studied the preparation and properties of PuOCl. There are no data on the melting point, heat and entropy of fusion, vapor pressures, boiling points, heat and entropy of vaporization. PuOCl is green or blue-green and has the tetragonal PbFCl type crystal structure with $a_1 = 4.004$, $a_3 = 6.779$, and a density of 8.81 g/cc.⁽⁶⁰⁾ The data of Sheft and Davidson⁽⁴⁰⁾ were used to obtain the values of the free energy equation for the formation of PuOCl. These workers have measured the equilibrium pressures of the reaction $\text{PuOCl} + 2\text{HCl} = \text{PuCl}_3 + \text{H}_2\text{O}$ between the temperatures 814°K and 969°K and have expressed their results in a free energy equation $\Delta F = -20.8 + 30.9 \frac{T}{1000}$ kilocal. This equation, when combined with the ΔH_{298}

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and $(\Delta F_{1000} - \Delta H_{298})/T$ values for PuCl_3 from this report and of HCl and H_2O from Section I of the Halide Report by Brewer⁽³⁰⁾, gave $\Delta F = -222.7 + 37.9 T/1000$ kilocal. for the formation of PuOCl around 1000°K . This is in excellent agreement with $\Delta H_{298} = -222.8$ kilocalories determined by Westrum and Robinson^(41,47) for PuOCl from its heat of solution.

PuOBr Davidson, Hagemann, Hyde, Katz, and Sheft⁽³⁶⁾ have studied the preparation and properties of PuOBr . There are no data on the melting point, heat and entropy of fusion, vapor pressures, boiling points, heat and entropy of vaporization. PuOBr is deep green and has the tetragonal PbFCl crystal structure with $a_1 = 4.014$, $a_3 = 7.556$, and a density of 9.07 g/cc . Sheft and Davidson⁽¹²⁾ have measured the equilibrium constants for the reaction $\text{PuOBr} + 2\text{HBr} = \text{PuBr}_3 + \text{H}_2\text{O}$ and have expressed their results as $\Delta F = -22.8 + 33.2 T/1000$ kilocal. Their equation is used together with the ΔH_{298} and $(\Delta F_{1000} - \Delta H_{298})/T$ values of PuBr_3 from this report and of HBr and H_2O from Section I of the Halide Report by Brewer⁽³⁰⁾ to obtain $\Delta F = -210 + 33 T/1000$ kilocal. for the formation of PuOBr around 1000°K . By comparison with PuCl_3 and PuOCl one would estimate a ΔH_{298} value more negative by about 8-10 kilocalories and a $\frac{\Delta F_{1000} - \Delta H_{298}}{T}$ value some what more positive, but the values given in Table III should give ΔF values of the right order of magnitude around 1000°K .

PuOI This compound has been prepared in the attempted preparations of PuI_3 and found to have a green color and the tetragonal PbFCl crystal structure with $a_1 = 4.034$, $a_3 = 9.151$, and a density of 8.46 g/cc .⁽⁶⁹⁾ but it has never been extensively studied and so there are insufficient thermodynamic data to evaluate

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the heat and entropy of formation. However, estimates may be made based upon slight chemical evidence and the values of PuOBr and PuOCl . The entropy of formation of -32 e.u. is estimated for PuOI . From the report on study of preparation and properties of PuOI by Hagemann, (24) Abraham, Davidson, Katz, and Sheft free energy estimates have been made and combined with the above entropy to give a heat of formation more negative than -182 ($\text{PuO}_2 = -254$) kcal/mole. On the basis of different experiments of theirs a value more negative than -167 ($\text{PuO}_2 = -254$) was estimated. On the basis of the heats of formation for PuOBr , PuOCl , PuCl_3 , PuBr_3 and PuI_3 , one can estimate a heat of formation for PuOI more negative than -195 kcal/mole, which is taken as a very rough value for ΔH_{298} .

Silicide

PuSi_2 The work of Westrum (25) who found that the silicide reaction $\text{PuF}_3 + 1.1 \text{ CaSi}_2 = \text{PuSi}_2 + 1.1 \text{ CaF}_2 + 0.2 \text{ SiF}_4$ did not occur at 1573°K but did go at 1823°K was used to calculate the free energy of the reaction which was then used with the free energies of formation of the other substances to obtain a free energy of formation of PuSi_2 . The free energy and entropy of CaF_2 were obtained from the Halide Report by the present authors (26). For SiF_4 , the entropy of formation was calculated from the entropy of the compound as given by Kelley (27) and the entropies of the elements as given by Brewer (3) while the heat of formation was obtained from Bichowski and Rossini (28). For CaSi_2 the entropy of formation was estimated from a consideration of

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the entropies of other compounds of calcium as tabulated by Brewer⁽¹⁴⁾ while the heat of formation is from Bichowsky and Rossini⁽²⁸⁾. The entropy of PuSi_2 was estimated to be the same as CaSi_2 . The calculated free energy of PuSi_2 in the neighborhood of 1700°K is -228 kcals per mole and this combined with the estimated entropy gives -211 kcals/mole as the very approximate heat of formation. PuSi_2 has a silvery metallic color and the tetragonal ThSi_2 crystal structure with $a_1 = 3.97$, $a_3 = 13.55$ and $d = 9.12$ g/cc. as reported by Zachariasen⁽⁶⁴⁾.

Sulfides

There is insufficient evidence to enable the calculation of the thermodynamic values for any of the plutonium sulfides. Abraham, Davidson, and Westrum⁽³¹⁾ report the following observations. They have heated PuF_3 and Ca in a BaS crucible which was prepared by the present authors⁽³²⁾ and has obtained a phase which has been thought to be PuS . It was golden bronze and was believed to have the cubic NaCl crystal structure. Using an apparatus similar to that used by the present authors at Berkeley⁽³³⁾, they passed H_2S over PuO_2 and obtained $\text{Pu}_2\text{O}_2\text{S}$ and $\text{Pu}_{3-x}\text{S}_4$ both identified by Zachariasen⁽³⁵⁾. $\text{Pu}_2\text{O}_2\text{S}$ was slate-black and had the hexagonal La_2O_3 crystal structure with $a_1 = 3.919$, $a_3 = 6.755$ and a density of 9.95 g/cc. Pu_2S_3 was black with a purplish tinge and had the cubic Ce_3S_4 crystal structure with $a = 8.437$ and a density of 8.41 g/cc. In addition they obtained a product which analyzed nearly Pu_2S_3 but which is not isomorphous with the $\text{Ce}_{3-x}\text{S}_4$ prepared in the graphite- H_2S system. This system seems to be

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Part III

Graphs of Gaseous Halide Equilibria

Introduction

The [REDACTED] figures presented here are for the purpose of indicating the important plutonium halide species for a given circumstance so that the thermodynamic constants given in Part I of this paper can be correctly used to calculate gaseous equilibria in plutonium systems.

Each figure gives the percentages of each gaseous species in a system in which the total composition is fixed. For example, the PuI_3 figure applies to a system in which the ratio of total I to Pu is always three. The pressure is fixed at the value given and the percentage of the total pressure due to any gaseous species is shown as a function of the temperature. Solid or liquid phases are not indicated, but are usually evident from examination of Table 1 and the gaseous composition indicated in the figure.

If one is interested in compositions intermediate between those given one can usually estimate the distribution of species from the figures nearest to the desired composition. If one is passing a large excess of halogen through the system, one can usually estimate the species distribution from an examination of the graph for the highest oxidation state.

Since no accurate data are available on the extent of

40a³⁹

solid or liquid solution formation, solid and liquid solution formation was neglected in the calculations of these figures from the data of Tables 1 to 4. That is, all solids and liquids were assumed to be immiscible. In cases where the laws of solution are known, they may be used to calculate more precisely the system; and in cases where solution is known to occur but where the law of solution is not known, Raoult's Law may be assumed as a first approximation. In any event it is expected that the graphs would not be changed appreciably by more rigorous treatment. Certainly the form of the curves will remain unchanged. And, of course, since a large portion of each graph covers a range where everything is gaseous, condensed solution laws are not significant. In the event that solid solutions do occur, then the thermodynamic calculations should be not based upon stoichiometric compounds but rather upon the ends of the solid solution range which is nearest the overall composition, if the latter is outside the solid solution limits. If the overall composition is inside the solid solution limits, the midpoint of the range may be used for the calculations with sufficient accuracy.

Since the entropies are not known for any plutonium compounds, the ^{entropies} /estimated in Table III may be in error by as much as 5 e.u. which means that most thermodynamic calculations may be in error by as much as a factor of ten. However, the entropies have in most cases been chosen to agree with experimental equilibrium data and therefore will accurately reproduce the experimental results.

Figure 1-- Gaseous Equilibrium

Overall Composition, PuF_3

③ - PuF_3

F - Monatomic Fluorine

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Figure 3 - Gaseous Equilibrium

Overall Composition, PuCl_3 (Cl) - Monatomic Chlorine, (3) PuCl_3 .

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Figure 4 - Gaseous Equilibrium

Overall Composition, PuBr₃(Br) - Monatomic Bromine, and (3) - PuBr₃.48a³⁹

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Figure 5 - Gaseous Equilibrium

Overall Composition, PuI_3

(I) - Monatomic Iodine,

and (3) - PuI_3 .49a³⁹

1. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "The Thermodynamic Properties and Equilibria at High Temperatures of Uranium Halides, Oxides, Nitrides, and Carbides", Paper MDDC-1543, April 1, 1947.
3. L. Brewer, "The Properties of the Elements", Paper MDDC-438-C, July 23, 1945.
6. S. Fried and N. R. Davidson, Paper MDDC-1250, June 30, 1947 and Paper 6.1 of Vol. 14B of P.P.R.(1947).
9. H. P. Robinson, Vol. 14B of P. P. R., Paper 6.150 (1947).
10. B. Weinstock, MDDC-1345, August 16, 1944.
12. I. Sheft and N. R. Davidson, Paper MDDC-1712 and Paper 6.24 of Vol. 14B of P.P.R.(1947).
13. B.M. Abraham and N. R. Davidson, Paper 6.12 of Vol. 14B of P.P.R. (1947).
14. L. Brewer, Paper UCRL-104, July 1948 and Paper MDDC-438-D, October 1945.
16. E. F. Westrum, Paper 6.57 of Vol. 14B of P.P.R.(1948), AEC D-2528.
20. B.M. Abraham, N. R. Davidson, and E. F. Westrum, Paper 6.60 of Vol. 14B of P.P.R.(1938) and Paper MDDC-1640 (Jan. 16, 1948).

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BC-88

21. W. H. Zachariasen, Paper MDDC-1396, Oct. 18, 1947 and Paper 20.5 of Vol. 14B of P.P.R.(1947), and Paper MDDC-1151, June 11, 1947.
22. B. M. Abraham and N. R. Davidson, Paper MDDC-1359, Oct. 13, 1947 and Paper 6.10 of Vol. 14B of P.P.R.(1947).
23. E. F. Westrum, Paper 6.4 of Vol. 14B of P.P.R.(1948).
24. F. Hagemann, B. M. Abraham, N. R. Davidson, J. J. Katz, and I. Sheft, Paper MDDC-1371 and Paper 6.170 of Vol. 14B of P.P.R. (1947),
25. E. F. Westrum, Paper MDDC-1393 and Paper 6.5 of Vol. 14B of P.P.R. (1948).
26. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "The Thermodynamic Properties of the Halides", Paper MDDC-438-F, October 15, 1945.
27. K. K. Kelley, U. S. Bureau of Mines Bulletin 434 (1941).
28. F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances" Reinhold Publishing Corp. New York, 1936.
30. L. Brewer, Paper MDDC-438-E, July 13, 1945.
31. B. M. Abraham, N. R. Davidson, and E. F. Westrum, Paper 6.18 of Vol. 14B of P.P.R., and paper MDDC-1788.
32. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, Paper MB-LB-18-6, declassified Sept. 7, 1948.
33. L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Paper MB-LB-18-5, declassified Aug. 25, 1948.
34. B. M. Abraham, B. B. Brody, N. R. Davidson, F. Hagemann, E. K. Hyde, J. J. Katz and I. Sheft, Paper 6.7 of Vol. 14B of P.P.R.
35. W. H. Zachariasen, Paper 20.4 of Vol. 14B of P.P.R., and Paper MDDC-1537.
36. N. R. Davidson, F. Hagemann, E. K. Hyde, J. J. Katz and I. Sheft, Paper 6.8 of Vol. 14B of P.P.R.

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38. E. F. Westrum and H. P. Robinson, Paper 6.51 of Vol. 14B of P.P.R. (1948).
39. F. D. Rossini, J. Research NBS 9, 679, (1932), RP 499.
40. I. Sheft and N. R. Davidson, Paper MDDC-1713 and Paper 6.25 of Vol. 14B of P.P.R.(1947).
41. E. F. Westrum and H. P. Robinson, Paper 6.56 of Vol. 14B of P.P.R. (1948), AECD-2527.
42. K. A. Krauss, Paper MDDC-814, March 19, 1947.
43. E. F. Westrum, Paper 6.55 of Vol. 14B of P.P.R.(1948), AECD-2525.
45. M. W. Evans, Paper MDDC-1206, August 27, 1947.
46. W. H. Zachariasen, AECD-2195, Aug. 2, 1948 and Paper 20.2 of Vol. 14B of P.P.R.
47. E. F. Westrum, Paper AECD-1903, March 1948.
48. W. H. Zachariasen, Paper MDDC-1572, November 17, 1947.
49. Goldschmidt, Ber., 60, 1263 (1927).
50. Coulter and W. M. Latimer, J.A.C.S. 62, 2557 (1940).
51. W. M. Latimer, "Oxidation Potentials", Prentice-Hall 1938.
52. J. C. Hindman, Paper AECD-1893, March 1938.
53. K. A. Kraus and G. E. Moore, Paper MDDC-906, April 16, 1947 and Paper 4.19 of Vol. 14B of P.P.R.
56. M. W. Evans, MDDC-438-I, Aug. 13, 1945.
57. R. C. L. Mooney and W. H. Zachariasen, Paper MDDC-1787, July 1946.
58. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "The Use of the Halide Report and the Thermodynamic Properties of Molybdenum and Tungsten Halides", Paper MDDC-438H, September 1, 1945.
59. Erway, Gilpatrick, Jasaitis, Johnson, Phipps, Sears, Seifert, and Simpson, CN-3223, September 26, 1945.
60. Sturtevant, J.A.C.S., 62, 3265 (1940); 64, 762 (1942).

61. B. J. Fontana, Declassified AEC Papers BC-66, April 1, 1947; MDDC-542, October 18, 1946; MDDC-1452, August 19, 1947.
62. M. Kasha and G. E. Shel'ine, MDDC-392, August 30, 1946.
63. J. J. Howland, J. C. Hindman, K. A. Kraus, Paper MDDC-1260, September 9, 1947.
64. W. H. Zachariasen, Paper 20.3 of Vol. 14B of P.P.R. and Paper MDDC-1394.
65. R. E. Connick and W. H. McVey, Paper UCRL-70, March 1948, Declassified January 25, 1949. See also M. Kasha, MDDC-904, August 30, 1946 and L. Brewer, AECD-1899 and AECD-1911, Feb. 1948.
66. H. P. Robinson and E. F. Westrum, Paper 6.54 of Vol. 14B of PPR(1948).
67. E. F. Westrum and L. Eyring, Paper 6.52 of Vol. 14B of P.P.R. 1948, AECD-2529.
68. E. F. Westrum and H. P. Robinson, PPR Vol. 14B, Paper 6.53, AECD-2526.
69. W. H. Zachariasen, Chapter XX, Vol. 14A, PPR, Paper 20.6 of Vol. 14B, PPR and MDDC-1442.
71. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, The Halides of Neptunium, Paper MDDC-1417, Sept. 19, 1947.