THE CHEMICAL THERMODYNAMIC PROPERTIES OF PLUTONIUM COMPOUNDS[1]

FRANKLIN L. OETTING

The Dow Chemical Company, Rocky Flats Division, Golden, Colorado

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I. INTRODUCTION

The need for reliable thermodynamic information on nuclear materials is well recognized by both the engineer and the scientist. The first comprehensive review of the thermodynamic properties of plutonium compounds was undertaken during the Second World War by Brewer, Bromley, Gilles, and Lofgren and published in 1949 (19). Although experimental thermochemical data were deficient at that time, the review was indeed commendable considering the circumstances under which it was developed.

Considerable efforts have been made since 1949 on the experimental thermodynamics of plutonium and its compounds by many able scientists. Although experimental investigations on the plutonium system are by no means complete, sufficient additional information has become available to warrant a second comprehensive review of the chemical thermodynamics of plutonium compounds.

The format of this review, which is thermodynamically more complete than the original work, is divided into two parts. The first part is concerned with an evaluation of the published thermochemical data on plutonium compounds. The second part is a tabulation of the evaluated data.

The aim of the thermochemist is to provide data from which the position of any desired equilibrium, at any desired temperature, may be calculated. To do this, the heat of formation, the entropy at 298°K, and the variation of heat capacity with temperature through all phases of interest must be known. From these data the free energy of formation can be calculated, resulting in a direct correlation to the equilibrium status. The heat of formation is the most important part of the needed information for calculating the free energy of formation. Fortunately, most of the heat of formation values used in this compilation are based, either directly or indirectly, on experimental results. Although experimental data are deficient for absolute entropies and heat capacities above room temperature, this is not of serious consequence because reliable estimations are made by comparison with similar systems where the data are known. In this work, estimations made by others, as well as those made by the author, are used. Future reliable experimental data should certainly be incorporated into the tables when it becomes available.

The first part of this report is an evaluation of the thermodynamic data on plutonium compounds found in the literature through June 1966. Explanations of the method used for making estimations, where applicable, are included. The degree of uncertainty is also given; however, there is usually no definitive information available to define the accuracy of the estimation.

There appears to be reliable thermodynamic data on the element plutonium. The low-temperature data have given a good value for the absolute entropy at 298°K. The thermodynamic properties of the gas have been adequately calculated from the electronic spectra. Excellent vapor pressure data unite the gas and solid properties although there appears to be a wide discrepancy in the results of many investigations on the six transition temperatures and heats of transition. The heat capacity of plutonium metal from room temperature to the melting point as well as the heat capacity of plutonium liquid should be repeated as this appears to be the weak link in the thermodynamic structure of plutonium metal.

The thermodynamic properties of the hydride and deuteride are based entirely upon the decomposition pressure data which gives a fairly reliable value for the heat of formation; however, the remainder of the thermodynamic quantities are estimated.

The heat of formation of PuO_2 has been accurately measured, and the partial molar heats of solution of oxygen in the oxides between Pu_2O_3 and PuO_2 can be integrated to give reliable values for the heats of formation of α-Pu_2O_3 and β-Pu_2O_3. Entropy and heat-capacity data were again estimated.

The heats of formation of the three fluorides are all related by equilibrium data to the heat of formation of

PuF_3. This value was originally determined by measuring the heat of solution of PuF_3 in 6 *M* HCl assuming the fluoride precipitated out as an anhydrous salt. Since then it has been shown that the PuF_3 will precipitate as a hydrate which relates some uncertainty (±2.5 kcal/mole) to the heat of formation value. The thermodynamic properties of PuF_6 gas are well defined as calculated by statistical mechanics.

The heats of formation of $PuCl_3$ and PuOCl have been accurately measured. These serve as an accurate basis to estimate the heats of formation of the other halides and oxyhalides.

The available thermodynamic data on the plutonium carbides presents a great deal of uncertainty as to the validity of the respective thermodynamic tables. Preliminary values for the heat of formation of the monocarbide and sesquicarbide are very near 0 kcal/mole, yet equilibrium data between each of the four carbides combined with the decomposition data of PuC_2 indicate the free energy of formation of all carbides to be much more negative than the indication derived from the heat of formation data. This is partly overcome by assuming unusually large entropies for the plutonium carbides. This assumption is theoretically unsound; however, it does produce a reasonable set of internally consistent thermodynamic tables.

Electromotive force data combined with decomposition data on PuN serve to give a fairly reliable heat of formation for PuN.

The properties of the sulfides and sulfate of plutonium were estimated by comparison with analogous cesium and uranium compounds.

The second part of this review contains the thermodynamic tables for plutonium compounds. These tables were computed using the fundamental thermodynamic equations

$$H_T = H_{298} + \int_{298}^{T} C_p \mathrm{d}T$$

$$S_T = S_{298} + \int_{298}^{T} (C_p/T) \mathrm{d}T$$

$$G_T = H_T - TS_T$$

$$\Delta H_{fT} = \Delta H_{f298} + (H_T - H_{298})_{\text{compound}} - \Sigma(H_T - H_{298})_{\text{elements}}$$

$$\Delta G_{fT} = \Delta H_{f298} - T\{[(G^\circ_T - H^\circ_{298})/T]_{\text{compound}} - \Sigma[(G^\circ_T - H^\circ_{298})/T]_{\text{elements}}\}$$

where H_T, S_T, G_T, and C_p are the heat content, entropy, Gibb's free energy, and heat capacity per mole of a substance at the temperature T°K, and ΔH_{fT} and ΔG_{fT} are the heat of formation and the free energy of formation per mole of a substance at the temperature T°K.

Values for heat capacity (C_p°), entropy (S°), free-energy function $[-(G^\circ_T - H^\circ_{298})/T)]$, enthalpy ($H^\circ_T - H^\circ_{298}$), heat of formation ΔH_f°), free energy of formation (ΔG_f°), and log K_p are presented at 100° intervals from 298° to the temperature where reliable thermodynamic information is believed to exist. The computer has carried these values out to three decimal places, which is not justified from the standpoint of absolute accuracy. However, these numbers are retained for internal consistency. All standard states for the elements, except plutonium and deuterium, used in these calculations are taken from the "JANAF Thermochemical Tables (48)." The fundamental constants are those recommended by the National Academy of Sciences–National Research Council and adopted by the National Bureau of Standards, October 1963.

These tables represent a thorough survey of the open literature on the chemical thermodynamic properties of plutonium and its compounds. It is intended that this work assemble the available thermodynamic properties under one cover to be of service to the nuclear engineer as well as the nuclear scientist.

A. SYMBOLS

C_p	$(\partial H/\partial T)$ heat capacity at constant pressure in calories degree^{-1} mole^{-1}
c	crystalline state
E	= internal or intrinsic energy in calories mole^{-1}
G	$= E + PV - TS = H - TS$, free energy in calories mole^{-1}
g	gaseous state
H	$= E + PV$, enthalpy (or heat content) in calories mole^{-1}
K	equilibrium constant
liq	liquid state
ln	logarithm to the base e ($e = 2.718218$)
log	logarithm to the base 10
M	molecular weight in grams mole^{-1}
P	pressure in atmospheres
R	ideal gas constant in calories mole^{-1} degree^{-1}
S	entropy in calories mole^{-1} degree^{-1}
T	temperature in degrees Kelvin ($T^\circ = t^\circ + 273.15^\circ$)
t	temperature in degrees Celsius
V	volume in cubic centimeters

Subscripts

b	boiling point at 1 atm pressure
d	dissolution
e	equilibrium position
f	formation from elements in their standard state
m	melting
p	constant pressure
r	reaction
s	sublimation
t	transition
v	vaporization

B. TERMINOLOGY

Circular superscripts, °, indicate the thermodynamic standard state.

Numerical subscripts, as 298, denote the temperature in degrees Kelvin.

Δ indicates the increment in a given property for a given process or reaction, taken as the value for the final state (or sum of the products) less that for the initial state (or sum of the reactants).

ΔH, ΔG, ΔS, and ΔC_p equal the increment in enthalpy, free energy, entropy, and heat capacity, respectively, for a process or reaction.

$\Delta H_f°$ represents the standard heat of formation, which is the increment in enthalpy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\Delta H_r°_{298}$ represents the heat change in a given reaction at 298.15°K and constant pressure with all the reactants and products in their appropriate standard states. When the reaction or process evolves heat, the sign of the heat term is arbitrarily taken to be negative. Conversely, when the reaction or process absorbs heat, the sign of the heat term is positive.

$\Delta G_f°$ denotes the standard free energy of formation, which is the increment in free energy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

Log K_p stands for the logarithm (base 10) of the equilibrium constant of formation for the reaction of forming the given compound from its elements.

$(H°_T - H°_{298})$ indicates the enthalpy (or heat content) in the standard state at temperature T less the enthalpy in the standard state at 298.15°K.

$-(G°_T - H°_{298})/T$ denotes the free energy function in the standard state at temperature, T, and is defined as $S°_T - (H°_T - H°_{298})/T$.

$S°_T$ represents the absolute entropy of the thermodynamic standard state at the absolute temperature, T, and may be found by integrating the heat capacity by the natural logarithm of the temperature from absolute zero to the temperature indicated by T.

The standard state is taken as the state at 1 atm pressure and the temperature under consideration for the solid, liquid, and ideal gas.

Throughout the text and tables, the temperature, 298°K, will always refer to 298.15°K.

All gram atomic weights for the elements except plutonium are taken from the chemical scale based on carbon-12. The gram atomic weight for plutonium is taken from the physical scale based on carbon-12 as 239.052 which is the nuclidic mass for the ^{239}Pu isotope (37).

II. PLUTONIUM

A. PLUTONIUM CRYSTAL AND LIQUID

1. *Allotropy*

The transition temperatures and heats of transition of the six forms of plutonium (Pu) metal as determined by a high-temperature adiabatic calorimeter have been published by Kay and Loasby (52). These values were selected for the compilation of the plutonium crystal–liquid table of thermodynamic properties as these data appear to be more accurate than other published values. The data of Kay and Loasby of the transformations in plutonium metal follow.

Transition	Temp, °K	Latent heat, cal/mole
α–β	392	803 ± 10
β–γ	477	152 ± 15
γ–δ	584	125 ± 5
δ–δ'	731	20 ± 10
δ'–ϵ	753	444 ± 10
ϵ–liquid	911	693 ± 10

A Russian calorimetric investigation (56) on the temperatures of transition as well as the heats of transition are in agreement with the selected values although they do not claim the accuracy of Kay and Loasby. A calorimetric investigation at Mound Laboratory (32) gave high-temperature results which were in agreement with the heats of transition. The reported temperatures of transition were slightly higher, especially the α–β transition which was reported as 9° higher than the selected value of 392°K.

A thorough dilatometry and thermal analysis study on plutonium metal (49) reported results on the temperatures of transition which are in good agreement with the above selected values considering the sluggishness and hysteresis phenomena of the metal. The results from an early electrical resistivity study from Los Alamos Laboratory (102) were also in good agreement with the above transition temperatures except for the α–β transition (4° high) and the γ–δ transition (8° high). A value of 938 ± 10 cal/mole for the heat of the α–β transition was derived from these measurements which is considerably higher than the selected value of 693 ± 10 cal/mole. A more recent electrical resistivity study (11) on a high-purity specimen of plutonium reported the α–β transition temperature as 390.2 ± 0.5°K which is approximately 2° lower than the selected value. An extensive study (44) on the $\alpha \rightleftarrows \beta$ and $\beta \rightleftarrows \gamma$ transformation behavior of plutonium metal shows the corresponding temperatures of transition to be 385 ± 1 and 457 ± 2°K, respectively. These values are considerably lower than the temperatures reported by Kay and Loasby.

From this survey it is apparent that there is a considerable spread in the reported temperatures of transition and heats of transition. It is recognized that an accurate determination of the temperatures and heats of transition in plutonium metal is difficult to determine owing to the hysteresis of the metal between transition temperatures and the ever-present self-heating of plutonium metal. Further difficulties are encountered in possible differences in the structure and properties of each phase depending on how the phase was formed. There are apparently marked differences in some physical properties in the β phase as formed from the α phase as compared to the properties of the β phase when formed from the γ phase (79).

There are numerous reports in the literature on the kinetics of these transformations in plutonium although the transformation temperatures and heats are not discussed in detail. Perhaps the best review on the transformations of plutonium from a metallurgical standpoint is that of Lord (63). More recent investigations may be found elsewhere (91).

2. Entropy

Low-temperature heat-capacity measurements on plutonium metal, an isotopic mixture consisting primarily of ^{239}Pu, have been reported by several investigators (61, 100, 108). The early results of Sandenaw (100), in which he gives 12.30 ± 0.12 cal/mole °K as the absolute entropy of plutonium metal, were characterized by spurious peaks and irreproducibility from run to run. This characterization was probably due to the annealing-out process of the self-irradiation damage which is consequential when ^{239}Pu is held at low temperatures for any length of time. Taylor was able to circumvent the self-irradiation effect by quickly quenching the plutonium to the liquid-helium temperatures and immediately commencing with the heat-capacity measurements (108). The results were then a smooth sigmoid curve, indicating no effects from self-irradiation. This effect was later verified (109) by holding the plutonium at 10°K for 50 hr and then observing the effect of self-irradiation on the heat capacity up to room temperature. The entropy value derived from the results on the quenched specimen is 13.18 ± 0.04 cal/mole °K for plutonium metal at 298°K.

A magnetic effect between 40 and 60°K has been observed in α-plutonium from studies on the lattice parameters (59, 60) although the magnetic transition was not apparent from the low-temperature heat-capacity measurements (61, 109). Analysis of the plutonium α-phase data does show an anomaly in the electronic specific heat term. The specific heat measurements of Lee, Mendelssohn, and Sutcliffe (61) taken from 10 to 80°K are in good agreement with the results reported by Taylor (108). Since the magnetic transition does not adversely influence the heat-capacity value, it is also assumed that the magnetic transition has a negligible affect upon the entropy at 298°K, at least within experimental error. Accordingly, the absolute entropy of α-plutonium metal at 298°K was derived to be 13.18 ± 0.04 cal/mole °K from the heat capacity measurements of Taylor. The value for $(H°_{298} - H°_0)$ was found to be 1687 ± 50 cal/mole for α-plutonium.

3. High-Temperature Heat Capacity

Kay and Loasby (52) give high-temperature heat capacity data on plutonium metal to within ±5%. (Loasby later quoted an error band of ±10% due to unsuspected errors in the chemical and isotopic analyses used in the calculation of the self-heating coefficients (108).) They used an elegant adiabatic calorimeter and utilized the self-heating of the isotopic mixture of plutonium as the heat source in the determination of the heat-capacity values. Such a method has the advantage of ensuring uniform heating of the specimen; however, it has the disadvantage of errors arising from nonequilibrium conditions, in particular, the transformation regions. The main source of error in these heat-capacity measurements lies in an accurate value of each isotopic power output as well as accurate isotopic analysis of the metal specimen. Recent power-output values for the individual plutonium isotopes are in good agreement with the listed power-output values of Kay and Loasby except for the value for ^{241}Pu (80). This results in an error of approximately 2% in the total power value for the sample which is still within experimental error of ±10% quoted on the heat-capacity measurements.

The heat capacity for the α and β phase of plutonium metal have been verified by another laboratory (32). The high-temperature results do not agree with the low-temperature data from room temperature to the α–β transition (392°K) where the high-temperature results are about 0.6 cal/mole °K (~8%) high in this range.

This difference of the heat-capacity values near room temperature as given by the high- and low-temperature measurements has been attributed to the self-irradiation effects (52) which presumably influenced the low-temperature results of Sandenaw (100), but which did not affect the results of Taylor (108). Both low-temperature results nearly coincide at room temperature and above, indicating that the annealing process as observed by Sandenaw is complete. As both low-temperature data are low by approximately 0.6 cal/mole °K at room temperature when compared to the high-temperature data, the reason for the difference as given above is erroneous. The low-temperature results are given more weight for the selected heat-capacity values primarily because it is believed that they are more accurate.

Accordingly, the selected values were taken from the low-temperature data and extrapolated to the α–β transition temperature (392°K). The heat capacity data of Kay and Loasby were used to the melting point. The heat capacity of plutonium liquid has been estimated to be constant and equal to 8.5 cal/mole °K for all temperatures above the melting point.

4. Melting Point and Heat of Fusion

The melting point of plutonium metal has been reported to be in the range of 912 ± 2°K (29, 32, 49, 52, 86). The value of 911°K (52) was selected from this compilation as it is believed to be the most accurate. The heat of fusion of 693 ± 10 cal/mole was used (52) although this is not in agreement with other results of 655 ± 6 (32) and 938 ± 10 cal/mole (102).

B. PLUTONIUM IDEAL MONATOMIC GAS

1. Thermodynamic Properties

Feber and Herrick (33) have reported the thermodynamic properties of ^{239}Pu as an ideal gas. Their data are based on the preliminary classification of the 293 energy levels in the plutonium I spectrum (13, 41, 96). The thermodynamic functions, C_p, S, $H°_T - H°_{298}$, and $-(G°_T - H°_{298})/T$ were calculated from the compilation of all 293 energy levels.

2. Vapor Pressure

The vapor pressure of liquid plutonium has been determined by the Knudsen effusion technique in the temperature range of 1100–1800°K (71, 88). The equation relating the correlation of the vapor pressure to temperature is

$$\log P \text{ (atm)} = -17.420/T + 4.913$$

with a standard deviation of ± 0.045 in $\log P$. The heat of vaporization and entropy of vaporization are 79.71 kcal/mole and 22.48 cal/mole °K, respectively, in the temperature range of 1100–1800°K.

Using the thermodynamic functions for the plutonium condensed phase and for plutonium gas as given in Tables I and II, respectively, it is then possible to calculate $\Delta H_f°$, $\Delta G_f°$, and $\log K_p$ for plutonium gas throughout the temperature range of 298 to 3000°K. Using the second-law treatment, that is, the method of enthalpy increments, the heat of vaporization at 298°K is calculated to be 83.6 kcal/mole. This is in good agreement with the third-law treatment which gives a value of 82.8 kcal/mole for the heat of vaporization at 298°K. The same calculation has been reported by Mulford (71) as 82.14 kcal/mole by the second law and 82.28 kcal/mole by the third law using slightly different thermodynamic functions for the condensed states of plutonium. The small difference between these two calculations, which is due to the different interpretations of the thermodynamic properties, is within the experimental error of the vapor-pressure equation from which the heat of vaporization at 298°K was derived. Since the third-law calculation of the heat of vaporization is more valid for this type of analysis, the heat so derived as 82.8 kcal/mole was used in this compilation.

The two independent reports on the vapor pressure of plutonium liquid are in excellent agreement. The early work of Phipps, Sears, Seifert, and Simpson (88) was held in reservation for many years because of the possible effect of reaction of the tantalum cell with the plutonium liquid. In the recent work of Mulford (71), there were no differences found in the vapor pressure of plutonium in contact with tantalum, tantalum carbide, magnesia, and plutonium sesquioxide. These results support the earlier work (88) and give a very accurate relation between the vapor pressure and temperature for plutonium liquid. Mulford also examined the effect of oxygen partial pressure on the plutonium vapor pressure and found no effect at reasonable low oxygen partial pressures. This is in direct contrast to the uranium system where it has been found that the vapor pressure of metallic uranium is lowered, which is apparently caused by oxygen picked up from the vacuum system (95). Although the cause of this effect in uranium is not completely understood (4, 31), it apparently does not exist in the plutonium system.

The absolute entropy of Pu(g) at 298°K was calculated to be 42.902 cal/mole °K from the entropy of vaporization and the absolute entropy of solid plutonium. This appears to be reasonable when compared to the absolute entropy of Pu(g), 42.316 cal/mole °K, as calculated from the plutonium spectrum.

III. PLUTONIUM HYDRIDE AND DEUTERIDE

Plutonium forms a dihydride with a fluorite structure similar to the rare earth hydrides (62). Mulford and Sturdy (76) observed that PuH_2 will dissolve hydrogen in the interstices of its lattice, changing from a cubic structure to a hexagonal structure when the H/Pu ratio reaches approximately 2.7. As the hydrogen content is increased, *i.e.*, when $PuH_{2.9}$ is present, only the hexagonal phase is observed. There appears to be no sharp demarcation in the transition between the two phases.

The plutonium–deuterium system appears to be comparable to the plutonium–hydrogen system (76). The dideuteride exists as a cubic phase transforming to the hexagonal phase when the D/Pu ratio reaches 2.7. When sufficient deuterium has been added to make $PuD_{2.85}$, the structure is completely hexagonal.

A. PLUTONIUM DIHYDRIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium dihydride (PuH_2) at 298°K was estimated to be 14.3 ± 1.0 cal/mole °K by comparison with the metal whose entropy value was measured to be 13.18 cal/mole °K (section II.A.1). The above entropy estimation is taken for this compilation over the value derived from the decomposition data of plutonium dihydride (75). Plutonium dihydride decomposes according to the following reaction. The plutonium metal in this equation will

$$PuH_2(c) \rightarrow Pu + H_2(g)$$

be saturated with hydrogen, and the PuH_2 will be saturated with plutonium within the temperature range of 400–800°. The effect of dissolved hydrogen on the melting point of plutonium is not known, and consequently it is not known whether the plutonium hydride is in equilibrium with the solid or liquid plutonium at the above temperatures. Since the melting point of plutonium falls well within the temperature span of the decomposition measurements, it seems that the heat of fusion of plutonium metal would have an effect on the slope of the decomposition pressure plot *vs.* temperature. Apparently the decomposition pressures were of insufficient accuracy to detect the effect. It will be consequently assumed that the plutonium in the above equation is the solid metal, and all calculations will be made accordingly.

The decomposition pressure varies with the temperature in the range 400–800° as

$$\log P\ (\text{mm}) = 10.01 \pm 0.32 - (8165 \pm 263)/T°\text{K}$$

The change in entropy associated with the decomposition of plutonium hydride is calculated to be −32.6 ± 1.5 cal/mole °K at 600°. From the known entropies of Pu(c) and $H_2(g)$ (48), the absolute entropy of PuH_2 at 298°K is calculated to be 19.9 ± 1.5 cal mole °K, which is considerably higher than the estimated entropy value of 14.3 ± 1.0 cal/mole °K. Since the absolute entropy of a specific hydride rarely exceeds the entropy of the parent metal by a significant magnitude, the estimated entropy of PuH_2 is more reasonable, indicating that a third-law analysis is not applicable to this decomposition data.

2. *Heat of Formation*

The heat of formation of PuH_2 has been determined from the decomposition pressure of plutonium hydride according to the following equation.

$$PuH_2(c) \rightarrow Pu + H_2(g)$$

As explained above, the state of plutonium is undefined as written but is assumed to be plutonium metal. The variation of decomposition pressure with respect to temperature is given as

$$\log P\ (\text{mm}) = 10.01 \pm 0.32 - (8165 \pm 263)/T°\text{K}$$

in the temperature range 400–800°. The heat of decomposition of PuH_2 may be found from the decomposition pressure equation by standard techniques. The reverse of the heat of decomposition is the heat of formation. The heat so obtained is

$$Pu + H_2(g) \rightarrow PuH_2(s) \qquad \Delta H = -37.4 \pm 1.2 \text{ kcal/mole}$$

which is valid in the temperature range of the decomposition pressure measurements, 400–800°. By making the corresponding enthalpy corrections for Pu(s), $H_2(g)$ (48), and $PuH_2(s)$ to 298°K from 873°K (600°C), one obtains a value of −33.3 ± 1.2 kcal/mole for the heat of formation of PuH_2 at 298°K.

3. *High-Temperature Heat Capacity*

The high-temperature heat capacity of PuH_2 was estimated by analogy with the known heat capacities of ZrH_2 (35) and YH_2 (36) in comparison with the corresponding metal. Unfortunately, there is no experimental data available in the literature to confirm the estimated values.

4. *Melting Point*

There is no published data on the melting point of plutonium hydride. If the decomposition data of plutonium hydride (75) is extrapolated above the experimental range, it is estimated that plutonium hydride will decompose to 1 atm of hydrogen gas at about 1000°K. In view of this, thermodynamic calculations were made to this temperature.

B. PLUTONIUM TRIHYDRIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium trihydride (PuH_3) was estimated to be 15.50 ± 1.0 cal/mole °K by comparison with plutonium dihydride. This is in favorable agreement with the entropy of UH_3 at 298°K of 15.20 cal/mole °K (94).

2. *Heat of Formation*

The heat of formation of plutonium trihydride has been estimated from the decomposition pressure data of PuH_2, $PuH_{2.60}$, and $PuH_{2.87}$ (50). According to this early work, which gives slightly different results from later PuH_2 decomposition data (section II.A.1), the constancy of pressure with changing mole ratio below 2 indicates that when the atomic ratio is below 2 the reaction is

$$Pu + H_2 \leftrightarrows PuH_2 \qquad \text{(I)}$$

the Pu and PuH_2 being separate phases. In the region from H/Pu = 2 to H/Pu = 3 the reaction is

$$PuH_2 + 0.5H_2 \leftrightarrows PuH_3 \qquad \text{(II)}$$

the PuH_2 and PuH_3 being in solid solution in one another. By plotting log P against ($1/T$°K) in the temperature range of 400 to 500°, the equations for the best straight line through the points are

$$\mathrm{H/Pu} = 1.97, \log P\ (\mathrm{mm}) = -7.13 \times 10^3/T + 8.77$$

$$\mathrm{H/Pu} = 2.60, \log P\ (\mathrm{mm}) = -4.17 \times 10^3/T + 9.9$$

$$\mathrm{H/Pu} = 2.87, \log P\ (\mathrm{mm}) = -2.7 \times 10^3/T + 8.8$$

From the slopes of these lines the heats of reaction (cal/mole) are found to be: for reaction I, $\Delta H = -32{,}500$; for reaction II, $\Delta H = -9550$ when H/Pu = 2.6 and $\Delta H = -6180$ when H/Pu = 2.87. Extrapolation to the mole ratio of H/Pu = 3 gives $\Delta H = -4500$ cal/mole. If this is added to reaction I, the total will be

$$\mathrm{Pu} + 1.5\mathrm{H_2} \rightarrow \mathrm{PuH_3} \qquad \Delta H = -37{,}000 \text{ cal/mole} \quad \text{(III)}$$

Although the decomposition data of PuH_2 (75) published in 1955 is probably more reliable, the above data on PuH_2 were used to maintain internal consistency.

Conversion of this heat of reaction for reaction III to 298°K by making the appropriate enthalpy correction results in an estimated heat of formation of PuH_3 of -33 ± 3.0 kcal/mole.

3. *High-Temperature Heat Capacity*

The high-temperature heat capacity of plutonium trihydride was estimated by comparison with the heat capacity of plutonium dihydride.

4. *Melting Point*

From the vapor-pressure data of Johns (50), plutonium trihydride apparently will decompose to the elements at about 600 °K. However, in preference to this, PuH_3 will decompose to PuH_2 and hydrogen involving an apparently complex equilibria of PuH_2 in solution with PuH_3.

C. PLUTONIUM DIDEUTERIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium dideuteride (PuD_2) at 298°K was estimated to be 16.3 ± 1.0 cal/(mole °K) by analogy with the comparable hydrogen-deuterium systems: PuH_2–PuD_2, ZrH_2–ZrD_2 (35), and YH_3–YD_3 (36). The absolute entropy of PuD_2 at 298°K may also be calculated from the decomposition data taken in the temperature range 600–800° (75) which corresponds to the following reaction

$$\mathrm{PuD_2(s)} \rightarrow \mathrm{Pu} + \mathrm{D_2(g)}$$

The plutonium metal in the above equation will be saturated with deuterium, and the PuD_2 will be saturated with plutonium within the specified temperature range. The effect of dissolved deuterium on the melting point of plutonium is not known, and consequently the state of the plutonium in the above equation cannot be specified. As pointed out earlier, the melting effect of plutonium is too small to be observed in the decomposition data and thus the magnitude of the entropy involved in the assumption is well within the magnitude of the entropy error derived from the decompostion data.

The variation of the decomposition pressure with temperature is given by

$$\log P\ (\mathrm{mm}) = 9.71 \pm 0.19 - (7761 \pm 151)/T$$

in the temperature range 600–800°. The change in entropy for this reaction is -31.2 ± 1.0 cal/mole °K. By making the appropriate entropy corrections for Pu(l) and $D_2(g)$, the entropy of plutonium dideuteride is calculated to be 23.3 ± 1.0 cal/mole °K at 298°K. This is not in good agreement with the entropy differences of other hydrogen–deuterium systems (35, 36) and indicates that a third-law analysis of this decomposition data is not applicable.

2. *Heat of Formation*

The heat of formation of plutonium dideuteride was calculated from the data of Mulford and Sturdy (75) who determined the decomposition pressure of PuD_2 in the temperature range 600–800° according to the following reaction

$$\mathrm{PuD_2(c)} \rightarrow \mathrm{Pu} + \mathrm{D_2(g)} \qquad \Delta H = +35.5 \pm 0.7 \text{ kcal/mole}$$

The heat of formation of PuD_2 at 298°K was calculated by reversing the above equation and making the appropriate enthalpy corrections from 700° for the respective components. The state for plutonium is the liquid even though this is not specified in the above equation. Although the decomposition data gave no evidence of melting, it is most probable that this is the phase present. The value obtained for the heat of formation by making the appropriate corrections is -32.2 ± 0.7 kcal/mole for plutonium dideuteride at 298°K.

3. *High-Temperature Heat Capacity*

The heat capacity of PuD_2 above room temperature was estimated by comparison with PuH_2 and the corresponding ZrH_2–ZrD_2 (35) and YH_3–YD_3 (36) systems.

4. *Melting Point*

There is no published data on the melting point of PuD_2. From the decomposition data of Mulford and Sturdy (75), plutonium dideuteride will decompose forming 1 atm of deuterium gas at about 950°. In view of this, thermodynamic calculations were made to only 1000°K.

IV. PLUTONIUM OXIDES

Plutonium, like uranium, forms nonstoichiometric oxides. Where uranium adds oxygen interstitially to form UO_{2+x} oxides, plutonium loses oxygen to form PuO_{2-x} oxides. Four stoichiometric oxides of plutonium have been reported: PuO, β-Pu_2O_3 (hexagonal), α-Pu_2O_3 (body-centered cubic), frequently referred to as $PuO_{1.61}$, and PuO_2 (face-centered cubic).

The existence of plutonium monoxide has not been proven conclusively although several reports have been published on its preparation (10, 27, 119), especially on the surface of plutonium metal. Apparently small concentrations of carbon tend to stabilize the plutonium monoxide. Although there is contradictory evidence for PuO in the bulk form, nevertheless, a temporary thermochemical table has been formulated.

β-Plutonium sesquioxide is not an allotrope of α-plutonium sesquioxide but has a hexagonal structure similar to the A modification of the rare earth sesquoxides such as La_2O_3 (26). The oxygen plutonium ratio in hexagonal plutonium sesquioxide has an upper limit of 1.510 (40), whereas the lower limit has not been completely defined by the phase diagram of the plutonium–oxygen system.

α-Plutonium sesquioxide has a body-centered cubic configuration showing a defect structure similar to the C modification of the rare earth sesquioxides and can contain more than 48 oxygen atoms as indicated by the composition formula. The lower limit of oxygen–plutonium ratio has been prescribed as 1.515 (40). Evidence has been reported indicating that there is an allotrope of α-Pu_2O_3 which is referred to as α′-Pu_2O_3 having a transition temperature somewhere below 900° (26) and above 800° (40). Because of the uncertainty of the transformation temperature as well as the heat associated with the transformation of the α to α′ form, no effort was made to include this in the table for α-plutonium sesquioxide. The α-plutonium sesquioxide will add oxygen until the oxygen–plutonium ratio is approximately 2.0, thereby forming the most stable oxide of the plutonium oxides.

Plutonium dioxide has a face-centered cubic structure. Unlike its uranium analog, plutonium dioxide does not as a rule incorporate excess oxygen in interstitial holes, and consequently PuO_{2+x} compositions are rarely prepared especially where x is of significant magnitude. There have been cases where the dioxide has a formula of $PuO_{2.09}$; however, the excess oxygen over the dioxide is probably incorporated in the crystal as adsorbed oxygen. The defect equilibria of PuO_{2-x} at higher temperatures has been actively investigated (12, 67).

A. PLUTONIUM MONOXIDE CRYSTAL

1. Entropy

The absolute entropy at 298°K of plutonium monoxide (PuO) has been estimated to be 16.9 ± 1.5 cal/mole °K of which 13.0 cal/mole °K is attributed to the lattice entropy and 3.9 cal/mole °K is attributed to the magnetic entropy (116). This estimated value appears to be reasonable when compared to the reported entropy values of ThO (15.0 cal/mole °K) and UO (16.2 cal/mole °K) (116).

2. Heat of Formation

The heat of formation of plutonium monoxide has been previously estimated to be between −130 and −140 kcal/mole (19). As this estimate appears to be reasonable, a value of −135 ± 5 kcal/mole for the heat of formation of PuO at 298°K was selected for these tables.

3. High-Temperature Heat Capacity

The high-temperature heat capacity of PuO was estimated by comparing the heat of capacities of the following oxide systems: PuO–PuO_2, PbO(yellow)–PbO(red)–PbO_2 (54), and MnO–MnO_2 (54).

4. Melting Point

The melting point of pure PuO has been estimated to be approximately 1900° (2173°K) (26) which is taken from a report on the plutonium–oxygen–carbon system (104) in which the melting point of PuO containing 0.5 wt % carbon was 1900°.

5. Free Energy of Formation

The free energy of formation of PuO gas has been reported (5) to be represented by

$$\Delta G_f^\circ = -20{,}600 - 18.4T \text{ cal/mole}$$

between 1773 and 1973°K. This is derived from the pressure–temperature equation

$$\log P \text{ (atm)} = 8.61 - 29{,}500/T$$

which is assumed to apply to the following reaction.

$$PuO_2(c) + 0.4Ta(c) \rightleftarrows PuO(g) + 0.2Ta_2O_5(c)$$

Although there is no conclusive evidence that this reaction takes place as written, it is known that tantalum will reduce PuO_2. Accordingly, some reservation must be taken concerning the free energy of formation equation for PuO(g). The above equation is slightly altered by using the free-energy function for PuO_2 as given in Table IX instead of the estimated values used in the original calculations. The resulting equation is

$$\Delta G_f^\circ = -17{,}500 + 19.275T \text{ cal/mole}$$

for the free energy of formation of PuO(g) in the temperature range 1773–1973°K.

B. β-PLUTONIUM SESQUIOXIDE CRYSTAL

1. Entropy

Thermodynamic data has been obtained for plutonium oxides with O/Pu ratios between 1.53 and 2.00

using a high-temperature galvanic cell containing solid electrolytes reversible to oxygen ions only (68). From this the partial molar heats and entropies have been calculated for several phase regions of the plutonium–oxygen system.

The partial molar heat and entropy values can be integrated for the whole region $(Pu_2O_3)_{hex}(\beta\text{-}Pu_2O_3)$ to PuO_2. Accordingly, Markin and Rand (68) find for the reaction

$$2\beta\text{-}Pu_2O_3(c) + O_2(g) \leftrightarrows 4PuO_2(c)$$

$\Delta H_{1150} = -196.9$ kcal; $\Delta S_{1150} = -43.0$ cal/mole °K. Since the absolute entropy of PuO_2 is fairly well established (section IV.D.1), it is then a simple matter to calculate the absolute entropy of $\beta\text{-}Pu_2O_3$ at 298°K using the thermodynamic tables of $\beta\text{-}Pu_2O_3$ (Table VII) and PuO_2 (Table IX). The absolute entropy for $\beta\text{-}Pu_2O_3$ so calculated is 33.2 ± 3.0 cal/mole °K compared to the value of 36.4 cal/mole °K (68) obtained by the use of slightly different values for the heat capacity of $\beta\text{-}Pu_2O_3$ and PuO_2 (actually ΔC_p) between 298 and 1150°K. To maintain internal consistency in the tables the value of 33.2 cal/mole °K was used for the absolute entropy of $\beta\text{-}Pu_2O_3$ at 298°K. The discrepancy between these values of the absolute entropy at 298°K arises from the choice of heat capacity values for the plutonium oxides. Even though emf data indicate slightly erratic ΔC_p behavior, it is preferable to use a more conservative and straight forward approach toward the estimation of the heat-capacity values. A plot of the C_p *vs.* T for all of the plutonium oxides shows that the PuO_2 heat-capacity curve gradually rises, being slightly higher than one-half of the $\alpha\text{-}Pu_2O_3$ curve which is in turn slightly higher than the $\beta\text{-}Pu_2O_3$ curve. Accurate high-temperature heat-capacity data on the oxides would certainly eliminate this discrepancy. This value of 33.2 cal/mole °K taken for the absolute entropy of $\beta\text{-}Pu_2O_3$ is not in good agreement with the estimate of 37.2 cal/mole °K made from an estimation of the lattice and magnetic contributions by comparison with rare earth sesquioxides (116).

2. Heat of Formation

The heat of formation of $\beta\text{-}Pu_2O_3$ has been indirectly measured by determining the partial molar heat for the entire phase region from $\beta\text{-}Pu_2O_3$ to PuO_2 (68). By integrating the partial molar heat for the following reaction

$$2\beta\text{-}Pu_2O_3(c) + O_2(g) \rightleftharpoons 4PuO_2(c)$$

the enthalpy change at 1150°K was found to be −196.9 kcal. Since the heat of formation of PuO_2 is well defined (section IV.D.2), a fairly accurate value for the heat of formation of $\beta\text{-}Pu_2O_3$ may be calculated from the heat of formation of PuO_2, the above enthalpy change for the written reaction, and the heat capacities of $\beta\text{-}Pu_2O_3$ and PuO_2 from the thermochemical Tables VII and IX, respectively. The value for the heat of formation of $\beta\text{-}Pu_2O_3$ at 298°K so calculated is approximately −410 ± 4 kcal/mole, which is in good agreement with the value of −407.2 kcal/mole given by Markin and Rand (68) using slightly different values for the difference in heat capacities.

The value of −410 kcal/mole for the heat of formation of $\beta\text{-}Pu_2O_3$ differs considerably from estimates of −387 (19) and −393 kcal/mole (97) based on comparison with similar rare earth oxide systems. Even though the value of −410 ± 4 kcal/mole for the heat of formation is not a direct measurement, but an indirect measurement, it is probably more reliable than the estimates given above.

3. High-Temperature Heat Capacity

The high-temperature heat capacity of $\beta\text{-}Pu_2O_3$ was estimated by comparing the heat capacities of the following series of compounds: PuO_2–$\beta\text{-}Pu_2O_3$, PbO_2–Pb_2O_3 (54), and MnO_2–Mn_2O_3 (54).

4. Melting Point

The melting point of $\beta\text{-}Pu_2O_3$ was taken as 2358°K from the phase diagram of the plutonium–oxygen system (26).

C. α-PLUTONIUM SESQUIOXIDE CRYSTAL

1. Entropy

The absolute entropy of $\alpha\text{-}Pu_2O_3$ has indirectly been measured by the determination of the change in entropy in the conversion of $\beta\text{-}Pu_2O_3$ to $\alpha\text{-}Pu_2O_3$ (68) by means of emf cell measurements on the plutonium–oxygen system. For the following reaction

$$\frac{1}{0.11}\beta\text{-}Pu_2O_3(c) + O_2(g) \rightleftharpoons \frac{2}{0.11}PuO_{1.61}(c)$$

where $PuO_{1.61}$ is also known as $\alpha\text{-}Pu_2O_3$, the cell measurements indicated a change in entropy of −21.7 cal/mole °K at 1150°K. Utilizing the entropy value of $\beta\text{-}Pu_2O_3$ (section IV.B.1), oxygen (48), and this above change in entropy, the calculation for the absolute entropy value at 1150°K is 44.2 cal/mole °K for $PuO_{1.61}$ or 88.4 cal/mole °K for $\alpha\text{-}Pu_2O_3$. Correction of this entropy value to 298°K using Tables VII and VIII, respectively, results in a value of 36.7 ± 3.0 cal/mole °K for the absolute entropy of $\alpha\text{-}Pu_2O_3$. This is in fair agreement with the value of Markin and Rand (68) who arrived at 38.4 cal/mole °K using slightly different C_p values. The value used here of 36.7 ± 3.0 cal/mole °K is also lower than the estimate of 39.0 cal/mole °K based on a lattice contribution of 32.0 cal/mole °K and a magnetic contribution of 7.0 cal/mole °K (116). Again as in the case of $\beta\text{-}Pu_2O_3$ the discrepancy between the cited values lies in the estimation of the heat capacities of the plutonium oxides between 298 and 1150°K.

2. Heat of Formation

The heat of formation of α-Pu_2O_3 has been measured indirectly in two ways. With the use of electrolytic cells, Markin and Rand (68) were able to establish that the heat of reaction for the following process

$$\frac{1}{0.11}\beta\text{-}Pu_2O_3(c) + O_2(g) \rightleftarrows \frac{2}{0.11}PuO_{1.61}(c)(0.5\alpha\text{-}Pu_2O_3)$$

is equal to -181.7 kcal at 1150°K. Utilizing the heat of formation of β-Pu_2O_3 (section IV.B.2) at 1150°K and the corresponding heat capacity values of β-Pu_2O_3 (Table VII) and α-Pu_2O_3 (Table VIII) between 298 and 1150°K, the heat of formation of α-Pu_2O_3 at 298°K is calculated to be approximately -430 ± 4 kcal/mole. This is in good agreement with the calculation of Markin and Rand (68) who arrived at -427.8 kcal/mole for the heat of formation of α-Pu_2O_3 using slightly different heat-capacity values.

The free energy of formation of α-Pu_2O_3 at 1400°K has been derived from equilibrium experiments on the reduction of PuO_2 by hydrogen (26). According to the following reaction

$$2PuO_2(c) + 0.76H_2(g) \rightleftarrows Pu_2O_{3.24}(c) + 0.76H_2O(g)$$

the value quoted for the free energy of formation of α-Pu_2O_3 is about -340 kcal/mole at 1400°K. If a third-law calculation is made using the values for the free-energy function of α-Pu_2O_3 as given in Table VIII, the heat of formation is -434 kcal/mole at 298°K for α-Pu_2O_3. This is in contrast to the value of -432 kcal/mole for the heat of formation as given by the authors of the equilibrium data who also estimated the free-energy function for α-Pu_2O_3.

The two independent methods of arriving at the heat of formation of α-Pu_2O_3 are in excellent agreement. From these data it appears as if the heat of formation of α-Pu_2O_3 is very near -430 ± 4 kcal/mole at 298°K.

3. High-Temperature Heat Capacity

The high-temperature heat capacity of α-Pu_2O_3 was estimated by comparing the heat capacities of the following series of compounds: PuO_2–α-Pu_2O_3, PbO_2–Pb_2O_3 (54), and MnO_2–Mn_2O_3 (54).

4. Melting Point

The melting point of α-Pu_2O_3 was taken as 2638°K from the phase diagram of the plutonium–oxygen system (26).

D. PLUTONIUM DIOXIDE CRYSTAL

1. Entropy

Sandenaw has measured the low-temperature heat capacity of PuO_2 (101). Although the measured heat capacity is somewhat irregular below 115°K, Sandenaw derived an absolute entropy value of 16.33 ± 0.16 cal/mole °K for plutonium dioxide at 298°K. This value is considerably lower than the estimation of 19.7 cal/mole °K proposed by Osborne and Westrum (82) by analogy with the measured entropies at 298°K of ThO_2, UO_2, and NpO_2. Since thorium dioxide is diamagnetic, the measured entropy is due entirely to lattice contributions. Uranium dioxide and neptunium dioxide have unpaired electrons which result in a magnetic contribution to the absolute entropy at 298°K. Osborne and Westrum have assumed that the lattice entropy of ThO_2 is identical with the lattice entropies of UO_2, NpO_2, and PuO_2 with the excess entropy of UO_2, NpO_2, and PuO_2 over ThO_2 being due entirely to magnetic contributions. They noted that in both UO_2 and NpO_2 the magnetic contribution to the entropy at 298°K exceeded the spin-only value by 0.86 cal/mole °K. By assuming that the difference between the magnetic entropy and the spin-only value is roughly constant for the isomorphous actinides, they estimate that the entropy of PuO_2 at 298°K is given approximately by the entropy of thorium dioxide at this temperature (*i.e.*, the lattice contribution) plus $R \ln (2S + 1)$ plus 0.85 cal/mole °K. Thus, Osborne and Westrum report 19.7 cal/mole °K for the entropy of PuO_2 at 298°K. As will be noted, this is not in agreement with the measured value of 16.33 cal/mole °K as determined by Sandenaw. Westrum and Grønvold (116) in a later paper attribute the low results of Sandenaw to either of the following: (a) the magnetic entropy contributions at lower temperatures have not yet been detected; or (b) "self-annealing" of radiation damage has provided an unmeasured energy source over broad ranges of temperature. An examination of Sandenaw's heat-capacity data shows an unusual depression in the C_p *vs.* T curve above 100°K. Sandenaw attributes this apparent dip in his heat capacity curve to annealing out of radiation damage which undoubtedly accounts for his supposedly low value for the entropy of PuO_2. It is difficult to evaluate the extent of the energy release from the annealing out process and thus arrive at the true entropy value which is most certainly higher than the value measured by Sandenaw. The estimation of the absolute entropy of Osborne and Westrum is valid as apparently the magnetic behavior of plutonium compounds is very similar to that of analogous rare earth compounds. The only case of this point rests with the electronic structure of plutonium carbide which is similar to the electronic structure of rare earth carbides (28). As a consequence the estimation of 19.7 ± 2.0 cal/mole °K was taken as the absolute entropy of PuO_2 at 298°K.

2. Heat of Formation

The heat of formation of plutonium dioxide has been measured by two independent groups of workers. The values so obtained are −252.87 ± 0.38 (46) and −252.4 ± 1.1 kcal/mole (90). As both values are in excellent agreement, the former value of −252.87 ± 0.38 kcal/mole was adopted as the heat of formation of PuO_2 at 298°K. It must be noted that this is one of the few instances where the heat of formation of a plutonium compound has been reliably determined. Since the heats of formation of β-Pu_2O_3 and α-Pu_2O_3 are derived from the heat of formation of PuO_2 (sections IV.B.2 and IV.C.2), it is fortunate that a reliable value for the heat of formation of PuO_2 is available.

3. High-Temperature Heat Capacity

The heat capacity of PuO_2 from 298°K to the melting point was estimated by comparison of the heat-capacity data of thorium dioxide (111) and uranium dioxide (94).

4. Melting Point

The melting point of PuO_2 has been reported as approximately 2675°K by workers at Harwell (99) with the oxygen pressure at 0.1–1.0 atm in equilibrium with PuO_2. Melting points of 2603 ± 10°K have frequently been observed in a pure argon atmosphere (99).

5. Vapor Pressure

The vapor pressure of plutonium dioxide has been measured by Phipps, Sears, and Simpson (89), Mulford and Lamar (74), and Pardue and Keller (84). The vapor-pressure measurements by Phipps, Sears, and Simpson were made utilizing a tantalum effusion cell. Evidence given by Mulford and Lamar (74) indicates that tantalum reduces PuO_2 according to the following reactions.

$$2PuO_2(c) + Ta(c) \rightarrow Pu_2O_3(c) + TaO(g)$$

$$Pu_2O_3(c) + Ta(c) \rightarrow 2PuO(g) + TaO(g)$$

Consequently, the vapor-pressure results of Phipps, Sears, and Simpson probably apply to a complex system of evaporation involving tantalum.

Mulford and Lamar (74) also used the Knudsen effusion-cell technique with a tungsten cell which they claimed did not react with PuO_2 although this claim has been challenged (84). They obtained

$$\log P \text{ (atm)} = \frac{-(29{,}240 \pm 530)}{T} + (8.072 \pm 0.239)$$

in the temperature range 2000–2400°K which applies to the reaction

$$PuO_{2-a}(c) \rightarrow (1 - a)PuO_2(g) + aPuO(g)$$

where a is of the order of 0.05. This reaction is based on the evidence that the crystal lattice parameter of the congruently vaporizing solid is larger than that of stoichiometric PuO_2. It has been shown that the increase in the lattice parameter is a result of oxygen deficiency in the PuO_2 crystal. From the above equation for the vapor pressure, a value of 133.8 ± 2.4 kcal/mole was calculated for the heat of vaporization, and 36.9 ± 1.1 cal/mole °K was calculated for the entropy of vaporization in the temperature range 2000–2400°K.

Pardue and Keller (84) have also determined the vapor pressure of plutonium dioxide. They have conducted their experiments in nonreducing atmospheres by the transpiration technique. They found that the vapor pressure of PuO_2 is highest in an argon atmosphere, lower in air, and still lower in an atmosphere of oxygen. Their vapor-pressure results under an argon atmosphere are in good agreement with the results reported by Mulford and Lamar (74). Pardue and Keller suggest that under an atmosphere of oxygen the vaporization process can be represented by the equation

$$PuO_2(c) \rightarrow PuO_2(g)$$

and the values obtained in oxygen would appear to more closely represent the vaporization process for stoichiometric PuO_2. Accordingly, they have calculated the free energy of formation of $PuO_2(g)$ to follow

$$\Delta G = -121{,}000 + 10.7T \pm 12{,}000 \text{ cal/mole}$$

in the temperature range 1500–2100°K. Their uncertainty connected with the above equation is associated with their estimation of the free energy of formation of $PuO_2(c)$ in the above temperature range. If one uses the free energies of formation for PuO_2 as given in the Table IX and the vapor-pressure data of Pardue and Keller at 1700 and 2000°K, respectively, the equation calculated for the free energy of formation of $PuO_2(g)$ is

$$\Delta G = -114{,}400 + 7.7T \text{ cal/mole}$$

in the temperature range 1700–2000°K.

V. PLUTONIUM HALIDES AND OXYHALIDES

A. PLUTONIUM TRIFLUORIDE CRYSTAL AND LIQUID

1. Entropy

The absolute entropy of plutonium trifluoride (PuF_3) at 298°K was first estimated to be 25.0 cal/mole °K (19), although others have suggested a value as high as 27.5 cal/mole °K (42). For comparison, uranium fluoride has an estimated entropy of 28.0 ± 2.0 cal/mole °K. Experimental evidence on the free energy of formation of PuF_3 (22) suggests that $\Delta G_f° = 93 \pm 1.5$ kcal/equiv at 1573°K. This is in good agreement with the tabulated value of the free energy of formation of PuF_3 obtained from the heat of formation value given in section V.A.2 and the absolute entropy value of 27.0 cal/mole °K. Even though the heat of formation of value has a certain degree of uncertainty, it would have to have considerable error before a significant change in the entropy value would be necessary. The value of 27.0 ± 2.0 cal/mole °K was thus adopted as the absolute entropy of PuF_3 at 298°K for this compilation.

2. Heat of Formation

The heat of formation of plutonium trifluoride has been determined by measuring the heat of precipitation of PuF_3 (115) accomplished experimentally by adding hydrofluoric acid to a solution of $PuCl_3$ in hydrochloric acid. With the use of the heat of precipitation value and other thermochemical data, the heat of formation of PuF_3 is calculated to be -374.6 kcal/mole. There are two corrections which must be made to this measured value, however. The first correction, although minor, involves the heat of formation of plutonium trichloride which was used in the calculation of heat of formation of PuF_3. This was previously determined to be -230.0 ± 0.3 kcal/mole (117). A recent value for the heat of formation of $PuCl_3$, -229.8 ± 0.5 kcal/mole (7), considered to be more reliable, should be used. The resulting calculation using this recent heat of formation of $PuCl_3$ gives the heat of formation of PuF_3 as -374.4 kcal/mole. Later studies on the precipitation of PuF_3 from hydrofluoric acid solution revealed the presence of occluded water in the precipitated PuF_3 (30) which means a slight correction to the heat of formation of PuF_3 as it was assumed in the precipitation measurements that the PuF_3 was anhydrous. It is difficult to make a correction for the occluded water as the precipitate is probably not a definite complex since it begins to lose weight as soon as the temperature is raised, and the amount of water it contains varies with the temperature of precipitation (30). Rand (92) has estimated the heat of hydration of PuF_3 to be -3.4 ± 2.5 kcal/mole by comparison with the heats of hydration of ThF_4 and UF_4 to their 0.4 hydrates (39) which have surprisingly different values of -1.2 and -6.1 kcal/mole. There is a significant degree of uncertainty in this estimation for the heat of hydration of PuF_3, but, lacking experimental data, it appears that the estimation of Rand is reliable. The heat of formation of PuF_3 consequently used for this compilation is -371.0 ± 3.0 kcal/mole.

3. High-Temperature Heat Capacity

The heat capacity of PuF_3 has been estimated to be represented by

$$C_p = 20.7 + 8.2T \text{ cal/mole °K}$$

in the temperature range from 298°K to the melting point (42). The heat capacity of the liquid has been estimated to be constant at 35.0 cal/mole °K.

4. Melting Point and Heat of Fusion

The melting point of PuF_3 has been determined to be 1699 ± 2°K (118). The estimated heat of fusion of 13 kcal/mole (19) was the value adopted for this compilation.

5. Vapor Pressure

The vapor pressure of plutonium trifluoride has been measured by an elaborate effusion technique (87). These data revealed a slight break in the vapor pressure *vs.* temperature curve at 1174.0° (1447.2°K) which was attributed to the melting process. The following equations were given representing the variation of vapor pressure with temperature assuming the vapor species to be monomeric PuF_3.

Solid PuF_3, $T = 1200–1440°K$

$$\log P \text{ (mm)} = (12.468 \pm 0.074) - (21.120 \pm 100)/T$$

Liquid PuF_3, $T = 1440–1770°K$

$$\log P \text{ (mm)} = (11.273 \pm 0.034) - (19.399 \pm 53)/T$$

Westrum and Wallmann (118) later determined the melting point of PuF_3 to be considerably higher (1699 ± 2°K) than the value interpreted from the vapor pressure measurements. They refitted the original vapor pressure to an equation of a different form given as

$$\log P \text{ (mm)} = -24{,}917/T - 7.5513 \log T + 38.920$$

which is valid from 1200 to 1660°K. The heat of sublimation has been calculated to be 89 kcal/mole at 1400°K. The vapor pressure of PuF_3 has also been measured by a less elegant apparatus than the original work; however, the vapor pressure results are in good agreement (24).

6. Free Energy of Formation

The free energy of formation of PuF_3 at 1573°K has been determined from an equilibrium study involving molten plutonium, molten irradiated uranium, and fused uranium tetrafluoride (22). Using the estimated free energy of formation of UF_4 as -443.5 kcal/mole (51), the free energy of formation of PuF_3 was calculated to be 93 ± 1.5 kcal/equiv at 1573°K. This value, also given in Table X, was used to establish the absolute entropy at 298°K.

B. PLUTONIUM TETRAFLUORIDE CRYSTAL AND LIQUID

1. Entropy

The absolute entropy of plutonium tetrafluoride (PuF_4) at 298°K can be determined from the equilibrium data of the reaction

$$PuF_4(c) + F_2(g) \rightleftarrows PuF_6(g)$$

Since the absolute entropies of $F_2(g)$ (48) and $PuF_6(g)$ (section V.D.1) are accurately known, the entropy value for $PuF_4(c)$ is entirely dependent upon the accuracy of the equilibrium measurements. Fortunately, reliable equilibrium results are available (110) on the above reaction which give a change of entropy for the reaction of −1.3 cal/mole °K at 550°K. With this value and the absolute entropies of $F_2(g)$ and $PuF_6(g)$, the absolute entropy of PuF_4 at 298°K is calculated to be 38.7 ± 0.5 cal/mole °K.

2. Heat of Formation

The heat of formation of plutonium tetrafluoride at 298°K can be derived from the equilibrium data on the reaction

$$4PuF_3(c) + O_2(g) \rightleftarrows 3PuF_4(c) + PuO_2(c)$$

The equilibrium pressure of oxygen from this reaction has been given as 7.2 mm at 783°K and 7.5 cm at 1073°K (30). The free energy of formation of PuF_4 at these respective temperatures is then calculated from the free-energy change for the above reaction and the free energy of formation of the other components taken from Tables IX and X, respectively. Third-law treatments of the two $\Delta G_f°$ values so obtained for PuF_4 at the respective temperatures give a heat of formation of −413.1 and −415.7 kcal/mole at 298°K. The heat of formation value for PuF_4 used in this tabulation is −414.4 ± 4.0 kcal/mole at 298°K.

3. High-Temperature Heat Capacity

The heat capacity of plutonium tetrafluoride was estimated by comparison with the heat of capacity of plutonium trifluoride. The heat capacity of liquid PuF_4 was estimated to be constant at 41.0 cal/mole °K.

4. Melting Point and Heat of Fusion

The melting point and heat of fusion of plutonium tetrafluoride have been estimated to be the same as uranium tetrafluoride, 1310°K and 10.2 kcal/mole, respectively (20).

5. Vapor Pressure

The vapor pressure of plutonium tetrafluoride has been determined by two teams of investigators, both using the Knudsen effusion technique (18, 65). Mandleberg and Davies (65) found that between 700 and 1200° the vapor pressure varies with the temperature according to the equation

$$\log P \text{ (mm)} = 5.58 - 10{,}040/T$$

Above 1200°, where a more volatile species occurs, the vapor pressure is represented by

$$\log P \text{ (mm)} = 36.1 - 54{,}180/T$$

Above 1200° the residue is plutonium trifluoride, and they tentatively suggest that the species effusing above 1200° is the pentafluoride.

Berger and Gaumann (18) have suggested the disproportionation of PuF_4 may possibly begin to take place at a lower temperature, 1300°K (1027°C). From these Knudsen cell measurements they derive the vapor equation for PuF_4 to be

$$\log P \text{ (mm)} = 8.59 - 12{,}600/T$$

in the temperature range 1000–1300°K.

Apparently the exact nature of the vaporization process of PuF_4 is not completely understood as neither team of investigators was able to isolate PuF_5. The two reported equations for the change in vapor pressure with respect to temperature are not in good agreement over the overlapping temperature range, possibly indicating that the disproportionation of PuF_4 may be more complex than realized.

C. PLUTONIUM HEXAFLUORIDE CRYSTAL AND LIQUID

1. Entropy

The absolute entropy of PuF_6 crystal was derived from the entropy of PuF_6 gas, 88.29 cal/mole °K, and the entropy of sublimation, 35.1 cal/mole °K, at 298°K (113). The resulting calculation gives 53.2 ± 0.5 cal/mole °K as the absolute entropy of plutonium hexafluoride crystal at 298°K.

2. Heat of Formation

The heat of formation of crystalline plutonium hexafluoride was derived from the heat of formation of $PuF_6(g)$, −407.4 ± 4.0 kcal/mole at 298°K (section V.D.2), and the heat of sublimation, 11.6 kcal/mole, at 298°K (113). The resulting calculation indicates the heat of formation of crystal PuF_6 to be approximately −419.0 ± 4.0 kcal/mole at 298°K.

3. High-Temperature Heat Capacity

The high-temperature heat capacity of PuF_6 from 298 to 385.31°K was estimated to be identical with the heat capacity of UF_6 (94). The heat capacity of the liquid was estimated to be constant at 45.0 cal/mole °K.

4. Melting Point and Heat of Fusion

The melting point of crystalline PuF_6 has been reported as 54 ± 1° (66) and 50.7° (34), and the triple point as 51.59° at a pressure of 533.0 mm (112) with the heat and entropy of fusion for PuF_6 to be 4456 cal/mole and 13.72 cal/mole °K, respectively.

5. Vapor Pressure

Several investigators have reported the experimental determination of the vapor pressure of PuF_6 (34, 66, 113). The work of Weinstock, Weaver, and Malm (113) is preferred although there is general agreement among all investigators. Their vapor data are

Solid PuF_6 (0 to 51.59°)

$$\log P\,(\mathrm{mm}) = \frac{-2095.0}{T} + 3.4990 \log T + 0.39024$$

Liquid PuF_6 (51.59 to 77.17°)

$$\log P\,(\mathrm{mm}) = \frac{-1807.5}{T} - 1.5340 \log T + 12.14545$$

The normal boiling point for PuF_6 is calculated to be 62.16° from this data.

D. PLUTONIUM HEXAFLUORIDE IDEAL GAS

1. *Thermodynamic Properties*

The thermodynamic properties (heat capacity, heat content, free-energy function, and entropy) of plutonium hexafluoride (PuF_6) were computed from the fundamental vibrational frequencies (43, 64) listed below.

Designation	Symmetry species	Frequencies, cm^{-1}
ν_1	a_{1g}	628
ν_2	e_g	523
ν_3	f_{1u}	615
ν_4	f_{1u}	203
ν_5	f_{2g}	211
ν_6	f_{2g}	171

The product of the moment of inertia $I_A I_B I_C$ was calculated to be 5.07244×10^{-113} g^3 cm^6 assuming an O_h point group with the Pu–F distance equal to 1.972 A in all cases (78). The symmetry number was taken as 24. The thermodynamic properties of PuF_6 as a result of these calculations are given in Table XIII. The results so calculated are in agreement with previous calculated properties on PuF_6 (77, 107).

2. *Heat of Formation*

The heat of formation of plutonium hexafluoride gas was calculated from the equilibrium data reported on the following reaction.

$$PuF_4(c) + F_2(g) \rightleftarrows PuF_6(g)$$

Equilibrium data on this reaction have been reported by Trevorrow, Shinn, and Steunenberg from 150 to 400° (110), Weinstock and Malm at 220° (112), and Florin, Tannenbaum, and Lemons from 167 to 600° (34). The data of Trevorrow, Shinn, and Steunenberg were used for these calculations as the data of Florin, Tannenbaum, and Lemons appear to be high at the lower temperatures. The single datum point of Weinstock and Malm is slightly lower than the value selected at that temperature.

The data of Trevorrow, Shinn, and Steunenberg gave the equation

$$\log K = -\frac{1331}{T°\mathrm{K}} - 0.275$$

to represent the change in equilibrium constant with temperature for the above reaction. By calculating the free energy of formation of $PuF_6(g)$ from the equilibrium data, successive third-law calculations at 400, 500, 600, and 700°K, respectively, from Table XIII indicate the heat of formation of PuF_6 gas to be -407.4 ± 0.5 kcal/mole at 298°K. This value is in poor agreement with the previously estimated value of -453 kcal/mole (19) made by comparing the heats of formation of the UO_2^{2+} and PuO_2^{2+} ions, and the heat of formation of UF_6. As has been pointed out (110), this discrepancy between the third-law value and the estimated value leads to the conclusion that either the free-energy data used in the third law calculations are erroneous, which is highly doubtful, or that variations in the free energies of solution of uranium and plutonium tetrafluorides and hexafluorides, which are used to determine the estimated value of the heat of formation, are unexpectedly large.

E. PLUTONIUM TRICHLORIDE CRYSTAL AND LIQUID

1. *Entropy*

The absolute entropy of plutonium trichloride ($PuCl_3$) has been estimated to be 38.0 cal/mole °K at 298°K (19). This is in good agreement with the entropy value of 37.8 cal/mole °K as derived from electromotive force data (14) which give -53.3 cal/mole °K as the entropy of formation of $PuCl_3$ at 973°K. Later electromotive-force data (17) on the plutonium chloride–sodium chloride system as opposed to the plutonium chloride–potassium chloride system used in the earlier work from the same laboratory (14) give -51.6 cal/mole °K as the entropy of formation of plutonium trichloride at 973°K which results in a slightly lower entropy value at 298°K. As the two electromotive-force values are within experimental error, the estimated entropy value of 38.0 ± 3.0 cal/mole °K was adopted for $PuCl_3$ at 298°K.

2. *Heat of Formation*

The heat of formation of plutonium trichloride has been determined at 298°K by measuring the heat of solution of $PuCl_3$ in 6 *M* hydrochloric acid (117). The result so obtained by Westrum and Robinson is -230.0 ± 0.3 kcal/mole. One of the critical prerequisites in obtaining the heat of formation of $PuCl_3$ from the heat of solution data is knowing the heat of solution of plutonium metal in 6 *M* hydrochloric acid. Westrum and Robinson found this value to be -141.64 ± 0.2 kcal/mole in the initial paper (117). This was later confirmed by workers in the Soviet Union who reported -141.02 ± 0.19 (8) and 141.14 ± 0.14 kcal/mole (9). Recently Fuger and Cunningham at Berkeley redetermined the heat of solution of plutonium metal in 6 *M* hydrochloric acid and found the heat to be −138.90 ± 0.9 kcal/mole (38), which is in considerable disagreement with the three values reported previously. Fuger and Cunningham, referring only to the work of Westrum and Robinson, remarked that an error of approximately 2 kcal/mole was possible due to the failure to characterize the phase of the starting plutonium metal. This is quite conceivable since the early work of Westrum and Robinson was undertaken even before the six phases of plutonium metal were known, although the phase characteristics may have been withheld at that time because of security reasons. Fuger and Cunningham were unable to account for the remaining difference of approximately 1 kcal.

In a recent paper, Akhachinskii has reported the result of a recent determination of the heat of solution of α-phase plutonium metal in 6 *M* hydrochloric acid as −141.5 ± 0.4 kcal/mole (7). This value agrees well with the early Russian work and Westrum and Robinson, but not with the value measured by Fuger and Cunningham. Akhachinskii attributes the less negative results of Fuger and Cunningham to either oxide formation on the metal after analysis and before measurement or to a systematic error in the measurements. As Fuger and Cunningham checked the performance of their calorimeter by measuring the heat of solution of magnesium metal in 1 *M* HCl with good results, it is doubtful if the latter reason mentioned by Akhachinskii is the reason for the discrepancy in the heat of solution of plutonium metal. It is quite conceivable that the undetermined oxide formation on the plutonium metal used by Fuger and Cunningham was the cause for the discrepancy although there is no definite proof of this. It appears as if the last value as determined by Akhachinskii (7) of −141.5 ± 0.4 kcal/mole for the heat of solution of plutonium metal in 6 *M* HCl is the most reliable and has consequently been used in the calculation which gives the heat of formation of plutonium trichloride.

Using the value of −22.15 ± 0.1 kcal/mole for the heat of solution of $PuCl_3$ in 6 *M* HCl (117), the resulting heat of formation of $PuCl_3$ at 298°K is −229.8 ± 0.5 kcal/mole. The heat of solution of $PuCl_3$ in 6 *M* HCl appears to be reliable as Westrum and Robinson as well as Fuger and Cunningham have identical results on the heat of solution of $PuCl_3$ in less concentrated HCl solutions.

3. High-Temperature Heat Capacity

The heat capacity of plutonium trichloride was estimated by comparison with the heat capacity of uranium trichloride (94). The heat capacity of liquid $PuCl_3$ was estimated to be constant at 32.0 cal/mole °K.

4. Melting Point and Heat of Fusion

The melting point of plutonium trichloride was taken to be 1033 ± 5°K from a direct measurement (87). The reported heat of fusion and entropy of fusion as derived from the vapor pressure data are 15.2 ± 0.6 kcal/mole and 14.7 ± 0.7 cal/mole °K, respectively (87).

5. Vapor Pressure

The vapor pressure of plutonium trichloride has been determined by a modification of the Knudsen effusion method (87). The measurements were taken over a temperature range of 850 to 1250°K, and the variation of vapor pressure with respect to temperature may be represented by the equations

Solid $PuCl_3$ (850 to 1007°K)

$$\log P\ (\text{mm}) = (12.726 \pm 0.126) - (15{,}910 \pm 120)/T$$

Liquid $PuCl_3$ (1007 to 1250°K)

$$\log P\ (\text{mm}) = (9.428 \pm 0.075) - (12{,}587 \pm 82)/T$$

From these data, assuming that the vapor species is molecular $PuCl_3$, the heat of sublimation is calculated to be 72.8 ± 0.6 kcal/mole in the temperature range 850–1007°K and the heat of vaporization to be 57.6 ± 0.4 kcal/mole in the temperature range 1007–1250°K.

6. Free Energy of Formation

The free energy of formation of plutonium trichloride has been determined from electromotive force data on the $PuCl_3$–KCl system (14) and the $PuCl_3$–NaCl system (17). In both cases, the free energy of formation of $PuCl_3$(s) at 973°K is shown to be −170 kcal/mole. The free energy of formation of $PuCl_3$ at 973°K given in Table XIV as calculated from the heat of formation at 298°K, the heat capacity between 298 and 973°K, and the absolute entropy at 298°K, is nearer −177 kcal/mole. This discrepancy arises from the uncertainties in the estimation used in the $PuCl_3$ table calculations as well as an 8% uncertainty in the electromotive-force data.

F. PLUTONIUM TETRACHLORIDE IDEAL GAS

1. Free Energy of Formation

Experimental evidence (1) has shown that the preparation of pure crystalline $PuCl_4$ has been unsuccessful even though the Pu(IV) ion has been shown to exist in double chloride salts (16). Benz (15) has determined the equilibrium pressure for the reaction

$$PuCl_3(c) + 0.5Cl_2(g) \rightleftarrows PuCl_4(g) \rightleftarrows PuCl_4(g)$$

in the temperature range 674–1024°K, from which it is possible to deduce a free energy of formation of $PuCl_4$(g). The free-energy change for the above reaction may be represented by the following equation throughout the specific temperature range.

$$\Delta G = 37{,}700 - 28.3T \text{ kcal/mole}$$

The free energy of formation of $PuCl_4(g)$ may then be represented by

$$\Delta G_f^\circ = -191{,}222 \pm 25.38T \text{ kcal/mole}$$

using the free energy of formation values for $PuCl_3$ as given in Table XIV in the temperature range 674–1024°K. Data for the other thermodynamic quantities for $PuCl_4(g)$ are not given in tabular form because they are not available in the literature, and there is no reasonable method of estimation.

As the equilibrium data indicate, $PuCl_4(g)$ is unstable with respect to $PuCl_3(c)$ and $Cl_2(g)$ although, under high pressure of chlorine gas, the various phases of $PuCl_4$ would certainly form depending on the pressure of the gas. By comparison with thermodynamic data on $ThCl_4$, $NpCl_4$, and UCl_4, Benz (15) has estimated the following quantities for plutonium tetrachloride crystal and liquid: $\Delta H_m = 12{,}000$ cal/mole, $\Delta S_m = 14$ cal/mole °K, $\Delta H_v = 30{,}000$ cal/mole, $\Delta S_v = 27$ cal/mole °K, mp 857°K, and bp 1111°K.

G. PLUTONIUM TRIBROMIDE CRYSTAL AND LIQUID

1. Entropy

The absolute entropy of plutonium tribromide ($PuBr_3$) was estimated to be 46.10 ± 4.0 cal/mole °K at 298°K. This value was calculated from the additive entropy constants of Kelley (53) taking his value of the bromide ion, 10.5 cal/mole °K, and the entropy of the Pu(III) ion, 14.6 ± 0.6 cal/mole °K, as derived from the entropies of $PuCl_3$ and PuF_3 minus the entropy of the respective anion as given by Kelley.

2. Heat of Formation

The heat of formation of plutonium tribromide has been determined by Westrum (114) by measuring the heat of solution of plutonium tribromide and combining this in part with the heat of solution of plutonium metal in 6 *M* HCl. Recent data on the heat of solution of plutonium metal in 6 *M* HCl (section V.E.2) verifies his solution data. Accordingly, his value of −198.8 ± 0.5 kcal/mole is accepted as the heat of formation of $PuBr_3$ at 298°K.

3. High-Temperature Heat Capacity

The heat capacity of plutonium tribromide was estimated by comparison with the heat capacities of PuF_3, $PuCl_3$, and the corresponding uranium halides (94). The heat capacity of liquid $PuBr_3$ was estimated to be constant at 32.0 cal/mole °K.

4. Melting Point and Heat of Fusion

The melting point of plutonium tribromide has been directly determined to be 681 ± 5° (954 ± 5°K) (87). The reported heat and entropy of fusion as derived from the vapor-pressure data are 13.4 ± 0.3 kcal/mole and 14.0 ± 0.4 cal/mole °K, respectively (87).

5. Vapor Pressure

The vapor pressure of plutonium tribromide has been measured by a modified Knudsen effusion technique (87). The variation of vapor pressure with temperature over the temperature range of 800 to 1100°K is given by

Solid $PuBr_3$ (800 to 929°K)

$$\log P\,(\text{mm}) = (13.386 \pm 0.077) - (15{,}280 \pm 69)/T$$

Liquid $PuBr_3$ (929 to 1100°K)

$$\log P\,(\text{mm}) = (10.237 \pm 0.033) - (12{,}356)/T$$

Based on the assumption that the vapor consists of molecular $PuBr_3$, the following data have been derived from the vapor-pressure measurements: $\Delta H_s = 69.9 \pm 0.3$ kcal/mole, $\Delta H_m = 13.4 \pm 0.3$ kcal/mole, $\Delta H_v = 56.5 \pm 0.2$ kcal/mole, and $\Delta S_m = 14.0 \pm 0.4$ cal/mole °K.

H. PLUTONIUM TRIIODIDE CRYSTAL AND LIQUID

1. Entropy

The absolute entropy of plutonium triiodide (PuI_3) at 298°K was estimated to be 51.2 ± 5.0 cal/mole °K). This estimate was made by using an entropy value of 12.2 cal/mole °K for the iodide ion (53) and an entropy value of 14.6 ± 0.6 cal/mole °K for the Pu(III) ion as derived from the entropies of $PuCl_3$ and PuF_3 minus the entropy of the respective anion (53).

2. Heat of Formation

The heat of formation of plutonium triiodide at 298°K was estimated (19) to be −155 ± 5 kcal/mole by comparison with the heats of formation of UCl_3, UBr_3, and UI_3 with the heats of formation of $PuCl_3$, $PuBr_3$, and PuI_3. Recent values for the heats of formation of the unranium halides (94) are slightly different; however, the difference is not sufficient to cause a change in the estimated heat of formation value for PuI_3 at 298°K of −155 ± 5 kcal/mole.

3. High-Temperature Heat Capacity

The heat capacity of plutonium triiodide was estimated by comparison with the heat capacities of PuF_3, $PuCl_3$, and $PuBr_3$, and the heat capacities of the corresponding uranium halides (94). The heat capacity of the liquid PuI_3 was estimated to be constant at 34.0 cal/mole °K.

4. Melting Point and Heat of Fusion

The melting point of plutonium triiodide has been estimated to be 1050°K and the heat of fusion as 12.0 kcal/mole.

I. PLUTONIUM OXYFLUORIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium oxyfluoride (PuOF) at 298°K was estimated to be 21.9 ± 2.0 cal/mole °K (19) from the estimated entropy of formation of −40 cal/mole °K. From this entropy value along with the estimate of the entropy of the fluoride ion of 3.9 cal/mole °K (53), the entropy value for the PuO^+ ion is calculated to be approximately 18.0 cal/mole °K. This entropy value for the PuO^+ ion was used in estimation of the absolute entropies of the other oxyhalides.

2. *Heat of Formation*

The heat of formation of plutonium oxyfluoride was estimated by taking one-third of the heat of formation of PuF_3 and adding this to the estimation for the heat of formation of the PuO^+ ion. The heat of formation of the plutonyl ion was estimated as −146.1 kcal/mole by subtracting one-third of the heat of formation of $PuCl_3$ (section V.E.2) from the heat of formation of PuOCl (section V.J.2). The resulting calculation for the estimated value of the heat of formation of PuOF at 298°F is −269.8 ± 5.0 kcal/mole.

3. *High-Temperature Heat Capacity*

The high-temperature heat capacity of plutonium oxyfluoride was estimated to approximate the equation

$$C_p = 17.29 + 5.71 \times 10^{-3}T \text{ cal/mole °K}$$

from room temperature to the melting point. This estimated equation is in line with the estimated equation for the other plutonium oxyhalides.

4. *Melting Point*

No data on the melting point of PuOF could be found in the literature.

J. PLUTONIUM OXYCHLORIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium oxychloride (PuOCl) at 298°K was estimated by addition of the estimated entropy of the PuO^+ ion (section V.I.1) of 18.0 cal/mole °K and the entropy value of the chloride ion of 8.0 cal/mole °K (53). The total of 26.0 ± 2.0 cal/mole °K is in good agreement with the estimated value of 25.4 cal/mole °K for the absolute entropy of PuOCl at 298°K (19).

2. *Heat of Formation*

The heat of formation of plutonium oxychloride has been determined to be −222.8 kcal/mole by measuring the heat of solution of PuOCl in hydrochloric acid and combining this with the heat of solution of plutonium metal in hydrochloric acid to derive the heat of formation of PuOCl. Recent heat of solution measurements of plutonium metal in HCl (section V.E.2) alter the initial results slightly. As a consequence the slightly different value of −222.7 ± 0.5 kcal/mole was used as the heat of formation of PuOCl at 298°K (7).

3. *High-Temperature Heat Capacity*

The heat capacity of PuOCl above room temperature was estimated to approximate the equation

$$C_p = 18.29 + 5.71 \times 10^{-3}T \text{ cal/mole °K}$$

up to 1500°K. This equation is in proper alignment with the equations estimated for the heat capacities of the other plutonium oxyhalides.

4. *Melting Point*

No data on the melting point of PuOCl could be found in the literature.

5. *Free Energy of Formation*

The change in free energy for the reaction

$$PuOCl(c) + 2HCl(g) \rightleftarrows PuCl_3(c) + H_2O(g)$$

may be expressed by

$$\Delta G = -20.8 + 30.9 \times 10^{-3}T \text{ kcal/mole}$$

This expression was derived from the equilibrium pressure measurements taken between 814 and 969°K (103). By using the current free energy of formation values for $PuCl_3$, H_2O (48), and HCl (48), the free energy of formation of PuOCl at 900°K is calculated to be approximately −187 kcal/mole from the above equilibrium data. This is in good agreement with the free energy of formation value at 900°K given in the corresponding PuOCl table (Table XVIII). Equilibrium pressure measurements (2) of the reaction between 773 and 873°K

$$PuO_2(c) + 0.5H_2(g) + HCl(g) \rightleftarrows PuOCl(c) + H_2O(g)$$

indicate the free energy for this reaction to be

$$\Delta G = -8.5 + 9.5 \times 10^{-3}T \text{ kcal/mole}$$

Corrections made on this equation based on hydrogen diffusing through the quartz chamber (19) results in the following expression for the free-energy change

$$\Delta G = -7.9 + 9.5 \times 10^{-3}T \text{ kcal/mole}$$

for the same reaction. Using the current free energy of formation values at 800°K for PuO_2, PuOCl, H_2O (48), and HCl (48), the free-energy change calculated for the above reaction is +1.446 kcal/mole compared to the experimental value of +0.3 kcal/mole. This is in surprisingly good agreement considering the experimental difficulties mentioned in the equlibrium measurements (2) and the uncertainties associated with the PuO_2 and PuOCl thermodynamic tables (Tables IX and XVIII).

K. PLUTONIUM OXYBROMIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium oxybromide (PuOBr) at 298°K was estimated to be 28.50 ± 2.0 cal/mole °K by considering the entropy value for PuO^+ ion to be 18.0 cal/mole °K (section V.I.1) and the bromide ion to be 10.5 cal/mole °K (53).

2. *Heat of Formation*

The heat of formation of plutonium oxybromide was estimated by taking one-third of the heat of formation of $PuBr_3$ (section V.G.2) and adding this to the estimation of the heat of formation of the PuO^+ ion (section V.I.2). The resulting calculation for the estimated heat of formation of PuOBr at 298°K is -212.4 ± 5.0 kcal/mole.

3. *High-Temperature Heat Capacity*

The high-temperature heat capacity was estimated to approximate the equation

$$C_p = 19.28 + 5.71 \times 10^{-3}T \text{ cal/mole °K}$$

from room temperature up to 1500°K. This equation is in proper alignment with the equations estimated for the heat capacities of the other plutonium oxyhalides.

4. *Melting Point*

No data on the melting point of PuOBr could be found in the literature.

5. *Free Energy of Formation*

Equilibrium pressure measurements on the reaction

$$PuOBr(c) + 2HBr(g) \rightleftarrows PuBr_3(c) + H_2O(g)$$

from 813 to 918°K (103) indicate that the free-energy change for the above reaction may be expressed in the form

$$\Delta G = -22.8 + 33.2 \times 10^{-3}T \text{ kcal/mole}$$

The calculated free energy of formation of PuOBr from the above free-energy change of the reaction and the free energy of formation of the respective components results in the free energy of formation of approximately -186 kcal/mole for PuOBr at 900°K which is slightly different from the value of -182 kcal/mole as given in Table XIX although the difference is probably within the errors involved in experimental measurements as well as the possible errors involved in the calculation of the $PuBr_3$ and PuOBr thermodynamic tables (Tables XV and XIX).

L. PLUTONIUM OXYIODIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium oxyiodide (PuOI) at 298°K was estimated to be 30.2 ± 3.0 cal/mole °K by considering the entropy value for the PuO^+ ion to be 18.0 cal/mole °K (section V.I.1) and that of the iodide ion to be 12.2 cal/mole °K.

2. *Heat of Formation*

The heat of formation of plutonium oxyiodide was estimated by taking one-third of the heat of formation of PuI_3 (section V.H.2) and adding this to the estimation of the heat of formation of the PuO^+ ion (section V.I.2). The resulting calculation for the estimated heat of formation of PuOI at 298°K is -197.8 ± 5.0 kcal/mole.

3. *High-Temperature Heat Capacity*

The high-temperature heat capacity of PuOI was estimated to approximate the equation

$$C_p = 20.29 + 5.71 \times 10^{-3}T \text{ cal/mole °K}$$

up to 1500°K. This equation is in proper alignment with the equations estimated for the heat capacities of the other plutonium oxyhalides.

4. *Melting Point*

No data on the melting point of PuOI could be found in the literature.

VI. PLUTONIUM CARBIDES

The phase diagram on the plutonium–carbon system indicates there are four plutonium–carbide phases (72). Of the four plutonium–carbon compounds, the ζ phase, Pu_3C_2 ($PuC_{0.67}$), has the highest plutonium carbon ratio. Above 850°K $PuC_{0.67}$ disproportionates to $PuC_{0.85}$ and Pu(c).

The monocarbide is nonstoichiometric with an approximate composition of $PuC_{0.85}$. It has a NaCl-type structure with $a = 4.9582 \pm 0.0003$ A for carbon-poor PuC to $a = 4.9737 \pm 0.0003$ A for carbon-rich PuC (72).

Plutonium sesquicarbide (Pu_2C_3) is stable with respect to the monocarbide from 298 to 1927°K, the melting point of the monocarbide. However, hydrogen will reduce Pu_2C_3 to $PuC_{0.85}$ at about 1300°K with the reduced carbon probably present as CH_4 (46). Apparently plutonium will also reduce Pu_2C_3 to $PuC_{0.85}$ at about 1000°K. Plutonium sesquicarbide is not stable with respect to PuC_2 above 2000°K. Pu_2C_3 is closely stoichiometric having a body-centered cubic structure with $a = 8.1258 \pm 0.0003$ A.

Plutonium dicarbide, whose structure has not been determined accurately, is not stable with respect to Pu_2C_3 from 298 to about 2000°K. Above 2000°K the dicarbide is the stable plutonium–carbon compound.

There are a number of inconsistencies in the thermodynamic data of the plutonium carbides, especially in the resulting thermodynamic calculations from the vapor-pressure data on the monocarbide and the dicarbide. More emphasis has been placed on the known equilibrium situations regarding the individual carbides. In order to substantially maintain all stability conditions in the respective range of temperatures, considerable estimation is necessary which makes this section on the thermodynamics of plutonium carbides very tentative. Because of the preliminary nature of this section, there are no limits given on the estimated values. Further work is necessary on all aspects of the plutonium–carbon system.

A. PLUTONIUM CARBIDE (ζ PHASE) CRYSTAL

1. Entropy

The absolute entropy of the ζ phase of plutonium carbide, Pu_3C_2 ($PuC_{0.67}$), at 298°K has been estimated to be approximately 15.7 cal/mole °K (45). In accordance with the remaining absolute entropies of the plutonium carbides, the entropy value is probably higher. For this reason a value of 19.5 cal/mole °K is taken which appears to be better suited. Other authors (92) have stated that the absolute entropies of plutonium carbides are apparently unusually high.

2. Heat of Formation

The heat of formation of $PuC_{0.77}$ has been experimentally determined to be $+3.7 \pm 3.1$ kcal/mole (47). These results are tentative, however.

The ζ phase ($PuC_{0.67}$) is in equilibrium with the monocarbide phase ($PuC_{0.85}$) at 850°K and disproportionates to the monocarbide at higher temperatures. Accordingly, for the reaction

$$1.27PuC_{0.67} \xrightleftharpoons{850°K} PuC_{0.85} + 0.27Pu(e)$$

$\Delta G_{850°K} = 0$, $\Delta H_{850°K}$ is positive, and $\Delta S_{850°K}$ is positive. The free energy of formation of $PuC_{0.67}$ at 850°K is consequently -2.842 kcal/mole as calculated from the $PuC_{0.85}$ table (Table XXII) and the above equation. The heat of formation of $PuC_{0.67}$ as calculated from this free-energy relation by the third law is $+850$ cal/mole, which is within the tentative experimental value for the heat of formation of $PuC_{0.77}$ of 3.7 ± 3.1 kcal/mole.

3. High-Temperature Heat Capacity

The high-temperature heat capacity of $PuC_{0.67}$ has been estimated by comparison with the experimental heat-capacity results on PuC (58).

4. Melting Point

Before the melting point is reached, $PuC_{0.67}$ disproportionates to $PuC_{0.85}$ and Pu (ϵ phase) at 850°K. Because of this, the thermodynamic property table for $PuC_{0.67}$ extends only to 850°K.

B. PLUTONIUM MONOCARBIDE CRYSTAL

1. Entropy

The absolute entropy of plutonium monocarbide ($PuC_{0.85}$) at 298°K has been estimated to be approximately 17.0 cal/mole °K (45). Indications are, however, that the absolute entropies of the carbides are unusually high (92). In addition, to this supposition, (1) it is almost certain that the entropies of $PuC_{0.85}$ and PuC_2 are not very different, and (2) the sum of these two entropies should be very near the absolute entropy of Pu_2C_3. Since the absolute entropy of Pu_2C_3 was selected as 40.50 cal/mole, the absolute entropies of $PuC_{0.85}$ and PuC_2 are 20.00 and 20.50 cal/mole °K, respectively.

2. Heat of Formation

The heat of formation of $PuC_{0.77}$ has been experimentally determined to be $+3.7 \pm 3.1$ kcal/mole, although emphasis is made that this value is preliminary (47). It is also known that both hydrogen and plutonium metal will reduce Pu_2C_3 to the monocarbide at about 1300°K. Accordingly the free energy of formation of $PuC_{0.85}$ is about twice that of Pu_2C_3 at this temperature. Calculations from the thermodynamic property table of Pu_2C_3 (Table XXIII) show that the free energy of formation of $PuC_{0.85}$ at 1300°K is approximately -4.8 kcal/mole. By a third-law calculation from this value, the heat of formation of $PuC_{0.85}$ is found to be approximately $+0.250$ kcal/mole, which is in fair agreement with the tentative experimental value of 3.7 ± 3.1 kcal/mole for $PuC_{0.77}$.

3. High-Temperature Heat Capacity

The high-temperature heat capacity of plutonium monocarbide has been determined by a drop calorimeter from 400 to 1300°K on a sample having the composition of $PuC_{0.93}$ (58). The data were extrapolated below the experimental temperatures to 298°K and above to the melting point (1927°K).

4. Melting Point

The melting point of $PuC_{0.85}$ is given as 1927°K from the phase diagram of the plutonium–carbon system (72).

5. Vapor Pressure

The vapor pressure of plutonium monocarbide has been measured in the temperature range 1500–1565° and may be represented by the equation (83)

$$\log P \text{ (atm)} = 22.3 - (51{,}100)/T$$

The second-law heat of vaporization at 1806°K is calculated to be 235 ± 35 kcal/mole. It was assumed that the volatile species is PuC. Vapor-pressure measurements on PuC and (UPu)C, which are within experimental scatter (6), give the following relationship for the variation of vapor pressure with temperature in the temperature range 1700–2100°K.

$$\log P \text{ (atm)} = 5.47 - (23{,}000)/T$$

This gives a heat of vaporization of 105 kcal at 1900°K which is in serious disagreement with the value of 235 kcal/mole at 1535°K given previously. The latter case did report evidence of not only the monocarbide, but the sesquicarbide in the vapor phase which would then pertain to a very complex vaporization scheme. It is questionable whether the existing vaporization data can give any concrete support to the calculation of the thermodynamic quantities of plutonium monocarbide.

C. PLUTONIUM SESQUICARBIDE CRYSTAL

1. *Entropy*

The entropy of formation of plutonium sesquicarbide (Pu_2C_3) at 298°K has been estimated to be +9 (45) and +10 cal/mole °K (92). This leads to values of the absolute entropy of Pu_2C_3 of 39.5 and 40.5 cal/mole °K, respectively. The latter value was selected for this compilation even though it is considerably higher than the absolute entropy of isostructural U_2C_3 of 32.6 cal/mole °K.

2. *Heat of Formation*

A tentative value for the heat of formation of Pu_2C_3 at 298°K has been reported as −1.700 kcal/mole (47). The heat of formation of Pu_2C_3 was determined initially only as a correction to the heat of formation of $PuC_{0.77}$. As a consequence only two combustion runs were taken, and an extensive analytical investigation was not made on the combustion products. Therefore, the result given above is very tentative and should be taken as preliminary until further work is undertaken.

3. *High-Temperature Heat Capacity*

The heat capacity of Pu_2C_3 was estimated by considering the measured heat capacity of PuC (58) and the sum of the heat capacities of UC and UC_2 (70).

4. *Melting Point*

The melting point has been reported as 2323°K from the description of the plutonium–carbon system (72).

5. *Free Energy of Formation*

Several conclusions on the free energy of formation of the plutonium carbides have been made by Rand (92) which are based primarily on the vapor-pressure data of PuC and PuC_2. He indicates that the free energies of formation are considerably more negative than those surmised in this compilation. Rand has estimated ΔG_f(PuC) to be approximately −10 kcal/mole at 1800°K which means that $\Delta G_f(Pu_2C_3)$ is approximately −20 kcal/mole at 1800°K from the equilibrium data between PuC and Pu_2C_3. In order for $\Delta G_f(Pu_2C_3)$ to be in the range, the heat of formation of Pu_2C_3 would have to be considerably more negative than the experimental value of −1.700 kcal/mole without estimating an unreasonably large absolute entropy. This factor is resolved by ignoring the vapor-pressure data on PuC because of the uncertainty of the volatile species to derive any thermodynamic functions for PuC to correlate to Pu_2C_3 by equilibrium data. Relying entirely upon the experimental heat of formation and estimated entropy for Pu_2C_3, the calculated free energy of formation of Pu_2C_3 at 1800°K is approximately half of the estimated value by Rand. The free energy of formation correlation between Tables XXI, XXII, XXIII, and XVIV and the equilibrium processes still exists without demanding the extremely negative free energy of formation values as implied by the vaporization data.

D. PLUTONIUM DICARBIDE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium dicarbide (PuC_2) at 298°K has been estimated to be approximately 22.00 cal/mole °K (45). This value appears to be large when compared to the absolute entropy of 16.8 ± 2.0 cal/mole °K for uranium dicarbide (94). The value selected for this compilation is 20.50 cal/mole °K which is still slightly high; however, this is in accordance with the general conclusion that the absolute entropies of the plutonium carbide are unusually high. The internal consistency for the entropies of the carbides is maintained by selecting the sum of the entropy value for PuC and PuC_2 to be equal to the entropy value of Pu_2C_3.

2. *Heat of Formation*

The heat of formation of plutonium dicarbide was calculated from the vaporization data on PuC_2 (73). The equilibrium pressure assuming the reaction

$$PuC_2(c) \rightarrow Pu(g) + 2C(c)$$

in the temperature range 2000–2400°K may be represented by

$$\log P \text{ (atm)} = (-17{,}920 \pm 250)/T°K + (2.779 \pm 0.11)$$

The heat evolved in the above reaction is calculated to be 82.0 ± 1.1 kcal/mole. By a second-law calculation, the heat of formation of plutonium dicarbide at 298°K is found to be -0.273 ± 1.1 kcal/mole. It is also known that the following equilibrium exists at approximately 2000°K.

$$Pu_2C_3(c) + C(c) \rightleftarrows 2PuC_2(c)$$

Accordingly the free-energy change for this reaction is equivalent to zero at 2000°K, or the free energy of formation of PuC_2 is approximately one-half the free energy of formation of $Pu_2C_3(c)$ at 2000°K. The estimated free energy of formation of PuC_2 is approximately -5.7 kcal/mole at 2000°K from the equilibrium data and from the free energy of formation of Pu_2C_3. By a third-law calculation the heat of formation of $PuC_2(c)$ at 298°K is found to be -980 cal/mole or approximately -1.000 kcal/mole which is in good agreement with the second-law calculation from the vaporization data. As a consequence, a value of -1.000 kcal/mole was taken as the heat of formation of PuC_2 at 298°K.

3. *High-Temperature Heat Capacity*

The heat capacity of PuC_2 has been estimated by comparison of the heat capacity of the two systems, PuC_2–PuC and UC_2–UC. Experimental heat-capacity results have been reported on PuC (58) and UC and UC_2 (70).

4. *Melting Point*

The melting point of PuC_2 has been reported as 2525°K from the phase diagram on the plutonium–carbon system (72).

5. *Free Energy of Formation*

The vapor-pressure measurements on plutonium dicarbide have been made assuming the following decomposition process (73)

$$PuC_2(c) \rightleftarrows Pu(g) + 2C(c)$$

from 2000 to 2400°K. The variation of plutonium gas pressure with temperature as a function of temperature may be represented by

$$\log P\ (\text{atm}) = (-17{,}920 \pm 250)/T + (2.779 \pm 0.11)$$

The free-energy change for the above reaction at 2200°K is calculated to be approximately 54 kcal/mole. By changing the above reaction to read

$$Pu(liq)_{2200°K} + 2C(c)_{2200°K} \rightleftarrows PuC_2(c)_{2200°K}$$

and incorporating the free energy of vaporization for plutonium liquid, the free-energy change is then calculated to be -22.522 kcal/mole. A subsequent third-law calculation gives the heat of formation of PuC_2 at 298°K as -17.662 kcal/mole. This is not in agreement with the adopted heat of formation of -1.000 kcal/mole described earlier. Since the phase diagram for the plutonium–carbon system (72) shows that PuC_2 is not stable at room temperature, the free energy of formation for PuC_2 should be such that the disproportionation at 298°K is favored. The choice of -1.000 kcal/mole as the heat of formation meets this requirement.

Some reservations must be attached to the vapor-pressure measurements of PuC_2 so that, in reality, the chosen thermodynamic functions may be in error. Two assumptions were made in the vapor-pressure measurements: (a) the solid carbide species coexisting with graphite in the temperature range observed is PuC_2 as shown by the plutonium–carbon phase diagram, and (b) the vapor species is atomic plutonium. Either of these assumptions, if not valid, could lead to erroneous analysis of the data.

VII. PLUTONIUM NITRIDE

Unlike the corresponding uranium–nitrogen compounds (UN, U_2N_3, and $UN_{1.75}$), plutonium forms only the mononitride (3, 21, 85). This compound is closely stoichiometric; however, some variation in the composition has been observed depending upon the temperature at which the PuN was prepared (106).

A. PLUTONIUM MONONITRIDE CRYSTAL

1. *Entropy*

Apparently the absolute entropies of the metallic nitrides having the NaCl-type structure are not very different from the absolute entropy of the parent metal (93). Accordingly, the estimated entropy of plutonium nitride (PuN) exceeds the absolute entropy of Pu(c) at 298°K by 1 ± 1 cal/mole °K (81). The absolute entropy for PuN(c) at 290°K is therefore approximately 14.2 ± 1 cal/mole °K.

2. *Heat of Formation*

The heat of formation of plutonium mononitride may be estimated from the decomposition pressure data of PuN (81) in the temperature range 2560–3040°K. If the following decomposition reaction is assumed

$$PuN(c) \rightleftarrows Pu(\text{liq satd with N}) + 0.5N_2(g)$$

with the liquid plutonium saturated with nitrogen having unit activity, the decomposition data will serve as a method to derive the heat of formation of plutonium nitride. This may indeed be proper, especially in the low-temperature range where it is more likely that the assumption of unit activity is closely approximated. Successive third-law calculations for the heat of formation through the measured decomposition data temperature range show a large drift in the heat of formation values at 298°K, indicating some deviation from unit activity for the liquid plutonium. At the lower temperature, 2600°K, the third-law calculation gives the heat of formation as -63 kcal/mole which is compared to the result of Olson and Mulford (81) who calculated −64 kcal/mole using slightly different thermodynamic functions for Pu and PuN from 298 to 2600°K. Olson and Mulford feel, however, that the heat of formation of PuN at 298°K is perhaps more negative, in comparison with the heat of formation of uranium mononitride (−70 kcal/mole), and should have a value of approximately −70 kcal/mole.

Very recent thermodynamic properties of plutonium mononitride from electromotive-force measurements (23) indicate that the free energy of formation of PuN(c) at 700°K is −60 kcal/mole. A third-law calculation from these data reveals that the heat of formation of PuN at 298°K is −75.7 kcal/mole, which was the value adopted for this compilation. This is in agreement with the heat of formation value derived from the decomposition pressure data when it is realized that the plutonium liquid saturated with nitrogen is obviously not at unit activity.

3. High-Temperature Heat Capacity

The heat capacity of plutonium mononitride was estimated by comparison with the heat capacity of uranium mononitride (105). The heat-capacity curve for PuN is slightly higher but follows the curvature of the measured value of UN from 298 to 1400°K. The C_p values of PuN above 1400°K are extrapolated to the melting point.

4. Melting Point

Olson and Mulford (81) have determined the melting point of PuN as 2584 ± 30° under 1 atm of nitrogen pressure. Carroll (25) has determined the melting point to be 2556 ± 15°. Neither investigator was able to observe the congruent melting point of PuN since it apparently requires a rather high nitrogen pressure. The average of the two values, 2570 ± 30° (2843 ± 30°K), was taken as the melting point of PuN in 1 atm of nitrogen.

5. Vapor Pressure

The decomposition pressure of PuN according to the reaction

$$\mathrm{PuN(c)} \rightarrow \mathrm{Pu(l)} + 0.5\mathrm{N_2(g)}$$

has been measured in the temperature range 2290–2770°K (81). The variation of the decomposition pressure with temperature follows the equation

$$\log P\,(\mathrm{atm}) = 8.193 - 29.54 \times 10^{-3}T + 11.28 + 10^{18}T^5$$

in the above temperature range. The *A* and *B* coefficients in the above equation represent the standard entropy and enthalpy changes at the temperature, respectively, while the CT^5 represents the deviation from the standard states of the liquid plutonium and solid plutonium nitride. Olson and Mulford used the same *A* and *B* coefficients of the uranium nitride decomposition equation in the plutonium nitride equation, thus assuming the standard heat of formation and entropy of formation to be the same for both UN and PuN. They propose the difference in the two decomposition pressure equations is then represented by the difference in the *C* coefficient. By using a value for *C* of 11.28 for PuN, the above equation is a good representation of the experimental points. Even though this equation represents the experimental data, it must be realized that recent electromotive-force data indicate that the heat of formation of PuN is more negative than UN by approximately 5 kcal/mole which implies that the *A* coefficient in the two vapor pressure equations should not be equivalent.

VIII. PLUTONIUM SULFIDES AND SULFATE

A. PLUTONIUM MONOSULFIDE CRYSTAL

1. Entropy

The absolute entropy of plutonium monosulfide (PuS) has been estimated as 18.7 ± 1.0 cal/mole °K by comparison with the CeS (18.7 ± 0.2 cal/mole °K (55)) and US (18.6 ± 0.1 cal/mole °K (94)).

2. Heat of Formation

The heat of formation of plutonium monosulfide at 298°K was estimated by considering the difference between the heats of formation of US and U_2S_3 (94) and the estimated heat of formation of Pu_2S_3. The estimated value so obtained is −105.0 ± 5.0 kcal/mole for the heat of formation of PuS at 298°K.

3. High-Temperature Heat Capacity

The heat capacity of plutonium monosulfide has been estimated by comparison with the uranium–sulfur system. The heat capacity of uranium monosulfide at 298°K has been reported as 12.1 cal/mole °K (94). The heat capacity of plutonium monosulfide at 298°K was estimated to be 13.0 ± 1.0 cal/mole °K. The heat-capacity values to the melting point were estimated from the value at 298°K.

4. Melting Point

The melting point of plutonium monosulfide has been measured as 2623 ± 30°K (57).

B. PLUTONIUM SESQUISULFIDE CRYSTAL

1. Entropy

The absolute entropy of plutonium sesquisulfide (Pu_2S_3) at 298°K has been estimated as 46.0 ± 4 cal/mole °K by comparison with Ce_2S_3 (43.1 ± 0.4 cal/mole °K (55)) and U_2S_3 (45 ± 4 cal/mole °K (94)).

2. *Heat of Formation*

The heat of formation of plutonium sesquisulfide was estimated by comparison with the heat of formation of the analogous compounds of uranium (94), cerium (98), lanthanum (98), and neodymium (98). In each case it was assumed that the difference between the heat of formation of MCl_3 and $0.5M_2S_3$ is equal to the difference between the heat of formation of $PuCl_3$ and $0.5Pu_2S_3$. Accordingly, the following results for ΔH_f(Pu_2S_3) (in kcal/mole) were obtained: with uranium, −256.6; with lanthanum, 238.8; with cerium, −237.8; and with neodymium, −232.8. Since the uranium calculation is significantly different from the others, the heat of formation of Pu_2S_3 was estimated by averaging the values excluding uranium. This value was −236.5 ± 4.0 kcal/mole at 298°K.

3. *High-Temperature Heat Capacity*

The heat capacity of Pu_2S_3 above room temperature was estimated by comparison with the heat capacity of U_2S_3 which was in turn estimated from the known heat capacities of US and US_2 (94).

4. *Melting Point*

No data on the melting point of Pu_2S_3 were found in the literature.

C. PLUTONIUM SULFATE CRYSTAL

1. *Entropy*

The absolute entropy of plutonium sulfate ($Pu(SO_4)_2$) at 298°K was estimated to be 39.0 ± 2.0 cal/mole °K by comparison with the entropies of thorium sulfate (35.4 cal/mole °K (69)) and uranium sulfate (38.5 ± 2.0 cal/mole °K (94)).

2. *Heat of Formation*

The heat of formation of plutonium sulfate was estimated by comparison with thorium (98) and uranium systems (94). The difference between the heat formation of $M(SO_4)_2$ and twice the heat of formation of MO_2 was assumed to be identical in the thorium, uranium, and plutonium systems. Accordingly, for $Pu(SO_4)_2$, from the thorium analogy, $\Delta H_f = -524$ kcal/mole, and from the uranium analogy, $\Delta H_f = -526$ kcal/mole. The heat of formation at 298°K of $Pu(SO_4)_2$ selected for this compilation is −526 ± 5.0 kcal/mole.

3. *High-Temperature Heat Capacity*

The high-temperature heat capacity of plutonium sulfate was estimated from the heat capacity of thorium sulfate which was measured from 623 to 897°K (69). The heat-capacity results on thorium sulfate follow the equation

$$C_p = 25.0 + 55.2 \times 10^{-3}T \text{ cal/mole °K}$$

in the above temperature range. The heat capacity of plutonium sulfate was estimated to be slightly higher than the thorium analogy in the above temperature range, and extrapolation was then made below to 298°K and above to 1500°K.

4. *Melting Point*

No data on the melting point of $Pu(SO_4)_2$ were found in the literature.

IX. THERMODYNAMIC DATA IN TABULAR FORM

TABLE I

PLUTONIUM (Pu) (MOL WT 239.052) CRYSTAL AND LIQUID

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
α Crystal Phase							
298	7.670	13.180	13.180	0.000	0.000	0.000	0.000
300	7.680	13.227	13.180	0.014	0.000	0.000	0.000
392	8.670	15.402	13.448	0.766	0.000	0.000	0.000
β Phase							
392	8.150	17.450	13.448	1.569	0.000	0.000	0.000
400	8.170	17.600	13.532	1.627	0.000	0.000	0.000
477	8.550	19.069	14.308	2.271	0.000	0.000	0.000
γ Phase							
477	8.540	19.388	14.308	2.423	0.000	0.000	0.000
500	8.580	19.788	14.553	2.618	0.000	0.000	0.000
584	9.090	21.156	15.403	3.360	0.000	0.000	0.000
δ Phase							
584	9.000	21.370	15.403	3.485	0.000	0.000	0.000
600	9.000	21.609	15.567	3.625	0.000	0.000	0.000
700	9.000	22.996	16.532	4.525	0.000	0.000	0.000
731	9.000	23.386	16.814	4.804	0.000	0.000	0.000
δ' Phase							
731	11.200	23.413	16.814	4.824	0.000	0.000	0.000
753	11.200	23.744	17.011	5.070	0.000	0.000	0.000

TABLE I (*Continued*)

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
			ϵ Phase				
753	8.400	24.334	17.011	5.514	0.000	0.000	0.000
800	8.400	24.844	17.457	5.909	0.000	0.000	0.000
900	8.400	25.833	18.334	6.749	0.000	0.000	0.000
911	8.400	25.935	18.426	6.841	0.000	0.000	0.000
			Liquid				
911	8.500	26.696	18.426	7.534	0.000	0.000	0.000
1000	8.500	27.488	19.197	8.291	0.000	0.000	0.000
1100	8.500	28.298	19.988	9.141	0.000	0.000	0.000
1200	8.500	29.038	20.712	9.991	0.000	0.000	0.000
1300	8.500	29.718	21.379	10.841	0.000	0.000	0.000
1400	8.500	30.348	21.998	11.691	0.000	0.000	0.000
1500	8.500	30.935	22.574	12.541	0.000	0.000	0.000
1600	8.500	31.483	23.114	13.391	0.000	0.000	0.000
1700	8.500	31.998	23.622	14.241	0.000	0.000	0.000
1800	8.500	32.484	24.101	15.091	0.000	0.000	0.000
1900	8.500	32.944	24.554	15.941	0.000	0.000	0.000
2000	8.500	33.380	24.984	16.791	0.000	0.000	0.000
2100	8.500	33.795	25.394	17.641	0.000	0.000	0.000
2200	8.500	34.190	25.785	18.491	0.000	0.000	0.000
2300	8.500	34.568	26.159	19.341	0.000	0.000	0.000
2400	8.500	34.930	26.517	20.191	0.000	0.000	0.000
2500	8.500	35.277	26.860	21.041	0.000	0.000	0.000
2600	8.500	35.610	27.190	21.891	0.000	0.000	0.000
2700	8.500	35.931	27.508	22.741	0.000	0.000	0.000
2800	8.500	36.240	27.815	23.591	0.000	0.000	0.000
2900	8.500	36.538	28.110	24.441	0.000	0.000	0.000
3000	8.500	36.826	28.396	25.291	0.000	0.000	0.000

TABLE II: PLUTONIUM (Pu) (MOL WT 239.052) IDEAL GAS

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	4.984	42.316	42.316	0.000	82.800	74.113	−54.326
300	4.985	42.347	42.317	0.009	82.795	74.059	−53.952
400	5.103	43.794	42.513	0.512	81.685	71.208	−38.906
500	5.392	44.961	42.889	1.036	81.218	68.631	−29.999
600	5.822	45.980	43.321	1.596	80.771	66.148	−24.094
700	6.318	46.914	43.768	2.202	80.477	63.735	−19.899
800	6.817	47.791	44.217	2.859	79.750	61.393	−16.772
900	7.281	48.621	44.661	3.564	79.615	59.106	−14.353
1000	7.697	49.410	45.096	4.314	78.823	56.901	−12.436
1100	8.061	50.161	45.523	5.102	78.761	54.712	−10.870
1200	8.378	50.877	45.939	5.924	78.733	52.527	−9.566
1300	8.652	51.558	46.346	6.776	78.735	50.343	−8.463
1400	8.888	52.208	46.741	7.654	78.763	48.159	−7.518
1500	9.090	52.829	47.127	8.553	78.812	45.971	−6.698
1600	9.259	53.421	47.502	9.470	78.879	43.779	−5.980
1700	9.396	53.986	47.867	10.403	78.962	41.583	−5.346
1800	9.503	54.527	48.222	11.349	79.058	39.380	−4.781
1900	9.581	55.043	48.567	12.303	79.162	37.174	−4.276
2000	9.631	55.535	48.903	13.264	79.273	34.963	−3.821
2100	9.654	56.006	49.231	14.228	79.387	32.744	−3.408
2200	9.655	56.455	49.549	15.194	79.503	30.520	−3.032
2300	9.634	56.884	49.858	16.159	79.618	28.291	−2.688
2400	9.595	57.293	50.160	17.120	79.729	26.058	−2.373
2500	9.542	57.684	50.453	18.077	79.836	23.819	−2.082
2600	9.477	58.057	50.738	19.028	79.937	21.575	−1.814
2700	9.403	58.413	51.016	19.972	80.031	19.330	−1.565
2800	9.322	58.754	51.286	20.909	80.118	17.078	−1.333
2900	9.237	59.079	51.550	21.837	80.196	14.827	−1.117
3000	9.150	59.391	51.806	22.756	80.265	12.570	−0.916

TABLE III

PLUTONIUM DIHYDRIDE (PuH_2) (MOL WT 241.076) CRYSTAL

Temp,	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
°K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	9.330	14.300	14.300	0.000	−33.300	−24.329	17.834
300	9.350	14.358	14.300	0.017	−33.310	−24.274	17.683
400	10.240	17.174	14.678	0.998	−34.636	−21.166	11.565
500	10.930	19.535	15.420	2.058	−35.266	−17.737	7.753
600	11.530	21.582	16.280	3.181	−35.850	−14.184	5.167
700	12.050	23.399	17.169	4.361	−36.272	−10.539	3.290
800	12.500	25.039	18.052	5.589	−37.134	−6.804	1.859
900	12.880	26.533	18.913	6.859	−37.416	−2.995	0.727
1000	13.200	27.908	19.745	8.163	−38.372	0.910	−0.199

TABLE IV

PLUTONIUM TRIHYDRIDE (PuH_3) (MOL WT 242.084) CRYSTAL

Temp,	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
°K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	10.330	15.500	15.500	0.000	−33.000	−19.741	14.477
300	10.350	15.564	15.500	0.019	−33.014	−19.652	14.316
400	11.240	18.668	15.917	1.100	−34.587	−15.066	8.231
500	11.930	21.254	16.733	2.260	−35.467	−10.099	4.414

TABLE V

PLUTONIUM DIDEUTERIDE (PuD_2) (MOL WT 243.088) CRYSTAL

Temp,	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
°K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	11.320	16.300	16.300	0.000	−32.200	−22.812	16.729
300	11.330	16.370	16.300	0.021	−32.206	−22.748	16.571
400	12.270	19.762	16.756	1.202	−33.336	−19.530	10.670
500	13.060	22.588	17.648	2.470	−33.759	−16.039	7.010
600	13.680	25.025	18.679	3.808	−34.133	−12.468	4.541
700	14.220	27.175	19.742	5.204	−34.350	−8.840	2.760
800	14.670	29.104	20.794	6.648	−35.013	−5.151	1.407
900	15.070	30.855	21.816	8.136	−35.100	−1.412	0.343
1000	15.450	32.463	22.801	9.662	−35.866	+2.456	−0.537

TABLE VI

PLUTONIUM MONOXIDE (PuO) (MOL WT 255.059) CRYSTAL

Temp,	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
°K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	12.250	16.900	16.900	0.000	−135.000	−128.804	94.416
300	12.270	16.976	16.900	0.023	−134.998	−128.765	93.806
400	12.890	20.593	17.389	1.282	−135.707	−126.686	69.218
500	13.410	23.527	18.332	2.597	−135.748	−124.437	54.391
600	13.840	26.010	19.410	3.960	−135.770	−122.181	44.504
700	14.250	28.175	20.511	5.365	−135.654	−119.925	37.442
800	14.600	30.101	21.591	6.808	−135.994	−117.656	32.142
900	14.930	31.840	22.635	8.285	−135.764	−115.377	28.017
1000	15.210	33.428	23.636	9.792	−136.213	−113.057	24.709
1100	15.480	34.890	24.594	11.326	−135.948	−110.754	22.005
1200	15.720	36.248	25.509	12.887	−135.661	−108.476	19.756
1300	15.940	37.515	26.384	14.470	−135.357	−106.223	17.858
1400	16.140	38.704	27.222	16.074	−135.034	−103.994	16.234
1500	16.300	39.823	28.025	17.696	−134.698	−101.788	14.830
1600	16.460	40.880	28.796	19.334	−134.348	−99.606	13.606
1700	16.600	41.882	29.537	20.987	−133.986	−97.446	12.527
1800	16.720	42.834	30.249	22.653	−133.615	−95.306	11.572
1900	16.830	43.741	30.936	24.331	−133.235	−93.187	10.719
2000	16.950	44.608	31.598	26.020	−132.845	−91.091	9.954
2100	17.010	45.436	32.237	27.718	−132.450	−89.011	9.263
2173	17.050	46.018	32.690	28.961	−132.150	−87.509	8.801

TABLE VII

β-PLUTONIUM SESQUIOXIDE (β-Pu_2O_3) (MOL WT 526.118) CRYSTAL

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	31.300	33.200	33.200	0.000	−410.000	−390.124	285.968
300	31.500	33.394	33.201	0.058	−409.989	−390.000	284.115
400	35.000	42.972	34.483	3.396	−410.944	−383.398	209.479
500	36.960	51.004	37.006	6.999	−410.420	−376.592	164.608
600	38.320	57.867	39.925	10.765	−409.800	−369.901	134.736
700	39.400	63.858	42.925	14.653	−408.879	−363.323	113.435
800	40.260	69.176	45.880	18.637	−408.860	−356.818	97.478
900	41.060	73.965	48.739	22.703	−407.695	−350.382	85.084
1000	41.800	78.330	51.483	26.846	−407.876	−343.942	75.168
1100	42.500	82.347	54.109	31.063	−406.618	−337.609	67.077
1200	43.060	86.070	56.619	35.341	−405.312	−331.393	60.355
1300	43.600	89.538	59.019	39.675	−403.964	−325.287	54.686
1400	44.020	92.785	61.316	44.056	−402.579	−319.288	49.843
1500	44.440	95.837	63.517	48.479	−401.162	−313.386	45.660
1600	44.800	98.716	65.628	52.941	−399.715	−307.582	42.014
1700	45.140	101.448	67.655	57.439	−398.241	−301.870	38.808
1800	45.440	104.031	69.605	61.968	−396.745	−296.243	35.969
1900	45.720	106.496	71.482	66.526	−395.229	−290.700	33.438
2000	45.960	108.847	73.929	71.110	−393.695	−285.239	31.169
2100	46.200	111.095	75.039	75.719	−392.144	−279.851	29.124
2200	46.400	113.249	76.727	80.349	−390.582	−274.543	27.273
2300	46.580	115.316	78.360	84.998	−389.007	−269.305	25.590
2358	46.68	116.463	79.270	87.702	−388.088	−266.304	24.681

TABLE VIII

α-PLUTONIUM SESQUIOXIDE (α-Pu_2O_3) (MOL WT 526.118) CRYSTAL

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	31.800	36.700	36.700	0.000	−430.000	−411.167	301.393
300	32.000	36.897	36.701	0.059	−429.988	−411.050	299.450
400	35.500	46.619	38.002	3.447	−430.893	−404.806	221.176
500	37.460	54.763	40.563	7.100	−430.319	−398.371	174.128
600	38.820	61.717	43.523	10.916	−429.649	−392.060	142.808
700	39.900	67.785	46.565	14.854	−428.678	−385.871	120.474
800	40.760	73.170	49.560	18.888	−428.609	−379.762	103.746
900	41.560	78.017	52.457	23.004	−427.394	−373.728	90.753
1000	42.300	82.435	55.237	27.197	−427.525	−367.696	80.360
1100	43.000	86.500	57.897	31.464	−426.217	−361.777	71.878
1200	43.560	90.266	60.439	35.792	−424.861	−355.977	64.832
1300	44.100	93.775	62.870	40.176	−423.463	−350.294	58.890
1400	44.520	97.058	65.196	44.607	−422.028	−344.719	53.813
1500	44.940	100.144	67.424	49.080	−420.561	−339.246	49.428
1600	45.300	103.056	69.561	53.592	−419.064	−333.875	45.605
1700	45.640	105.813	71.613	58.140	−417.540	−328.598	42.244
1800	45.940	108.430	73.587	62.719	−415.994	−323.410	39.267
1900	46.220	110.922	75.487	67.327	−414.428	−318.308	36.614
2000	46.460	113.299	77.318	71.961	−412.844	−313.292	34.235
2100	46.700	115.572	79.086	76.620	−411.243	−308.352	32.091
2200	46.880	117.748	80.794	81.299	−409.632	−303.491	30.149
2300	47.080	119.837	82.447	85.997	−408.008	−298.704	28.383
2400	47.260	121.844	84.047	90.714	−406.374	−293.982	26.771
2500	47.440	123.777	85.597	95.449	−404.731	−289.336	25.294
2600	47.620	125.641	87.102	100.202	−403.076	−284.753	23.936
2638	47.690	126.332	87.622	102.123	−402.444	−283.036	23.445

TABLE IX
PLUTONIUM DIOXIDE (PuO_2) (MOL WT 271.058) CRYSTAL

	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
Temp, °K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	16.400	19.700	19.700	0.000	−252.870	−240.203	176.074
300	16.500	19.802	19.700	0.030	−252.867	−240.125	174.931
400	18.250	24.807	20.371	1.774	−253.447	−235.893	128.886
500	19.230	28.990	21.688	3.651	−253.292	−231.532	101.203
600	19.910	32.558	23.210	5.609	−253.096	−227.207	82.760
700	20.450	35.669	24.772	7.628	−252.755	−222.918	69.598
800	20.880	38.428	26.310	9.695	−252.870	−218.649	59.732
900	21.280	40.911	27.797	11.803	−252.416	−214.398	52.063
1000	21.650	43.172	29.223	13.950	−252.638	−210.130	45.924
1100	22.000	45.253	30.587	16.133	−252.144	−205.905	40.909
1200	22.280	47.179	31.890	18.347	−251.628	−201.723	36.739
1300	22.550	48.974	33.136	20.589	−251.093	−197.587	33.217
1400	22.760	50.652	34.328	22.854	−250.542	−193.490	30.205
1500	22.970	52.230	35.469	25.141	−249.976	−189.434	27.601
1600	23.150	53.718	36.564	27.447	−249.397	−185.418	25.327
1700	23.320	55.127	37.615	29.771	−248.805	−181.438	23.325
1800	23.470	56.464	38.625	32.110	−248.205	−177.492	21.550
1900	23.610	57.737	39.598	34.465	−247.595	−173.579	19.966
2000	23.730	58.951	40.535	36.832	−246.978	−169.700	18.544
2100	23.850	60.112	41.440	39.211	−246.354	−165.851	17.260
2200	23.940	61.223	42.314	41.600	−245.727	−162.032	16.096
2300	24.040	62.290	43.160	43.999	−245.094	−158.243	15.037
2400	24.130	63.315	43.978	46.408	−244.457	−154.479	14.067
2500	24.220	64.302	44.772	48.825	−243.818	−150.745	13.178
2675	24.380	65.945	46.105	53.078	−242.688	−144.270	11.786

TABLE X
PLUTONIUM TRIFLUORIDE (PuF_3) (MOL WT 296.055) CRYSTAL AND LIQUID

	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
Temp, °K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
				Crystal			
298	23.140	27.000	27.000	0.000	−371.000	−353.454	259.088
300	23.160	27.143	27.000	0.043	−370.992	−353.345	257.412
400	23.980	33.918	27.919	2.400	−371.403	−347.506	189.868
500	24.800	39.357	29.680	4.839	−371.166	−341.571	149.301
600	25.620	43.951	31.685	7.360	−370.900	−335.685	122.273
700	26.440	47.962	33.730	9.963	−370.473	−329.849	102.983
800	27.260	51.546	35.737	12.648	−370.471	−324.046	88.525
900	28.080	54.804	37.677	15.415	−369.858	−318.279	77.289
1000	28.900	57.805	39.542	18.264	−369.879	−312.516	68.300
1100	29.720	60.598	41.330	21.195	−369.136	−306.816	60.959
1200	30.540	63.219	43.046	24.208	−368.318	−301.184	54.853
1300	31.360	65.696	44.694	27.303	−367.428	−295.625	49.699
1400	32.180	68.050	46.279	30.480	−366.461	−290.138	45.293
1500	33.000	70.299	47.806	33.739	−365.419	−284.722	41.484
1600	33.820	72.455	49.280	37.080	−364.300	−279.380	38.162
1699	34.600	74.448	50.630	40.467	−363.192	−274.092	35.256
				Liquid			
1699	35.000	82.099	50.630	53.467	−350.192	−274.092	35.256
1700	35.000	82.181	50.709	53.503	−350.104	−274.115	35.240
1800	35.000	84.182	52.513	57.003	−348.837	−269.685	32.744
1900	35.000	86.074	54.230	60.503	−347.573	−265.319	30.519
2000	35.000	87.869	55.868	64.003	−346.313	−261.020	28.523

Table XI
Plutonium Tetrafluoride (PuF_4) (mol wt 315.054) Crystal and Liquid

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
				Crystal			
298	28.880	38.700	38.700	0.000	−414.400	−393.120	288.164
300	28.900	38.879	38.701	0.053	−414.389	−392.988	286.292
400	29.600	47.289	39.842	2.978	−414.617	−385.927	210.860
500	30.300	53.969	42.022	5.973	−414.227	−378.812	165.579
600	31.000	59.555	44.491	9.038	−413.833	−371.774	135.418
700	31.700	64.386	46.996	12.173	−413.300	−364.805	113.897
800	32.400	68.665	49.442	15.378	−413.211	−357.885	97.770
900	33.100	72.522	51.795	18.653	−412.528	−351.010	85.237
1000	33.800	76.046	54.047	21.999	−412.494	−344.146	75.213
1100	34.400	79.295	56.196	25.408	−411.719	−337.349	67.025
1200	35.100	82.318	58.249	28.883	−410.888	−330.622	60.214
1300	35.800	85.155	60.210	32.428	−409.999	−323.969	54.464
1310	35.870	85.430	60.402	32.787	−409.910	−323.304	53.935
				Liquid			
1310	41.000	93.216	60.402	42.987	−399.710	−323.304	53 935
1400	41.000	95.940	62.600	46.677	−398.414	−318.102	49.658
1500	41.000	98.769	64.918	50.777	−396.986	−312.413	45.519

Table XII
Plutonium Hexafluoride (PuF_6) (mol wt 353.054) Crystal and Liquid

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
				Crystal			
298	40.000	53.200	53.200	0.000	−419.000	−387.614	284.258
300	40.020	53.447	53.201	0.074	−418.982	−387.419	282.231
324.74[a]	42.494	56.688	53.343	1.086	−418.734	−384.694	258.886
				Liquid			
324.74[a]	45.000	70.410	53.343	5.542	−414.278	−384.694	258.886
335.31[b]	45.000	71.851	53.904	6.018	−414.132	−383.697	250.076

[a] Triple point 324.74°K (533.0 mm). [b] Boiling point 335.31°K.

Table XIII
Plutonium Hexafluoride (PuF_6) (mol wt 353.054) Ideal Gas

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	30.933	88.294	88.294	0.000	−407.400	−386.462	283.284
300	30.994	88.485	88.295	0.057	−407.399	−386.332	281.443
400	33.444	97.773	89.544	3.292	−408.087	−379.308	207.244
500	34.816	105.397	91.976	6.711	−408.080	−372.127	162.657
600	35.640	111.824	94.762	10.237	−408.057	−364.947	132.932
700	36.167	117.360	97.604	13.829	−407.918	−357.771	111.701
800	36.521	122.214	100.383	17.465	−408.264	−350.587	95.776
900	36.771	126.531	103.053	21.130	−408.067	−343.389	83.386
1000	36.952	130.415	105.598	24.816	−408.578	−336.146	73.465
1100	37.088	133.943	108.017	28.519	−408.401	−328.911	65.349
1200	37.192	137.175	110.314	32.233	−408.228	−321.690	58.588
1300	37.274	140.155	112.497	35.956	−408.064	−314.484	52.870
1400	37.340	142.920	114.572	39.687	−407.904	−307.293	47.971
1500	37.392	145.498	116.549	43.424	−407.750	−300.109	43.726
1600	37.436	147.913	118.435	47.165	−407.604	−292.941	40.014
1700	37.472	150.184	120.236	50.911	−407.462	−285.778	36.739
1800	37.502	152.326	121.960	54.660	−407.329	−278.628	33.830
1900	37.528	154.355	123.612	58.411	−407.200	−271.479	31.227
2000	37.550	156.280	125.198	62.165	−407.077	−264.335	28.885
2100	37.569	158.113	126.722	65.921	−406.961	−257.206	26.768
2200	37.586	159.861	128.189	69.679	−406.852	−250.078	24.843

TABLE XIII (*Continued*)

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			Log K_p
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	
2300	37.600	161.532	129.602	73.438	−406.748	−242.951	23.086
2400	37.613	163.133	130.966	77.199	−406.651	−235.833	21.476
2500	37.624	164.668	132.284	80.961	−406.562	−228.717	19.994
2600	37.634	166.144	133.558	84.724	−406.478	−221.605	18.628
2700	37.643	167.565	134.791	88.488	−406.399	−214.494	17.362
2800	37.651	168.934	135.986	92.252	−406.326	−207.391	16.188
2900	37.658	170.255	137.145	96.018	−406.260	−200.282	15.094
3000	37.664	171.532	138.271	99.784	−406.203	−193.191	14.074

TABLE XIV

PLUTONIUM TRICHLORIDE ($PuCl_3$) (MOL WT 345.419) CRYSTAL AND LIQUID

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			Log K_p
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	
				Crystal			
298	24.580	38.000	38.000	0.000	−229.800	−213.368	156.403
300	24.600	38.152	38.000	0.045	−229.791	−213.266	155.364
400	25.200	45.311	38.973	2.535	−230.159	−207.809	113.542
500	25.800	50.999	40.828	5.085	−229.880	−202.264	88.409
600	26.400	55.756	42.930	7.695	−229.580	−196.777	71.676
700	27.000	59.869	45.063	10.365	−229.128	−191.346	59.741
800	27.700	63.521	47.146	13.100	−229.105	−185.950	50.799
900	28.300	66.818	49.151	15.900	−228.481	−180.593	43.854
1000	29.000	69.841	51.071	18.770	−228.484	−175.241	38.299
1033	29.230	70.786	51.686	19.731	−228.499	−173.475	36.700
				Liquid			
1033	32.000	85.486	51.686	34.931	−213.299	−173.475	36.700
1100	32.000	87.510	53.807	37.072	−212.387	−170.943	33.963
1200	32.000	90.294	56.734	40.272	−211.387	−167.219	30.455
1300	32.000	92.855	59.415	43.472	−210.390	−163.578	27.500
1400	32.000	95.227	61.889	46.672	−209.396	−160.015	24.980
1500	32.000	97.434	64.186	49.872	−208.405	−156.521	22.805

TABLE XV

PLUTONIUM TRIBROMIDE ($PuBr_3$) (MOL WT 478.787) CRYSTAL AND LIQUID

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			Log K_p
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	
				Crystal			
298	25.780	46.100	46.100	0.000	−198.800	−192.343	140.991
300	25.790	46.259	46.100	0.048	−198.816	−192.302	140.092
400	26.290	53.747	47.118	2.652	−210.185	−187.922	102.676
500	26.790	59.667	49.056	5.306	−209.846	−182.407	79.730
600	27.290	64.596	51.247	8.010	−209.481	−176.962	64.458
700	27.790	68.840	53.464	10.764	−208.967	−171.582	53.570
800	28.300	72.584	55.624	13.568	−208.890	−166.247	45.416
900	28.800	75.947	57.699	16.423	−208.222	−160.957	39.086
954	29.070	77.632	58.780	17.985	−207.861	−158.101	36.217
				Liquid			
954	33.000	91.632	58.780	31.852	−194.461	−158.101	36.217
1000	33.000	93.233	60.329	32.904	−194.634	−156.324	34.165
1100	33.000	96.378	63.465	36.204	−193.537	−152.547	30.308
1200	33.000	99.249	66.330	39.504	−192.441	−148.868	27.112
1300	33.000	101.891	68.965	42.804	−191.349	−145.281	24.424
1400	33.000	104.336	71.405	46.104	−190.258	−141.778	22.133
1500	33.000	106.613	73.677	49.404	−189.170	−138.354	20.158

TABLE XVI

PLUTONIUM TRIIODIDE (PuI_3) (MOL WT 619.773) CRYSTAL AND LIQUID

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			Log K_p
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	
				Crystal			
298	26.730	51.200	51.200	0.000	−155.000	−153.922	112.828
300	26.740	51.365	51.201	0.049	−155.001	−153.914	112.127
400	27.230	59.125	52.255	2.748	−161.673	−153.322	83.771
500	27.720	65.254	54.263	5.495	−177.201	−149.776	65.467
600	28.210	70.351	56.531	8.292	−176.757	−144.342	52.577
700	28.700	74.736	58.826	11.137	−176.160	−138.986	43.393
800	29.200	78.602	61.061	14.032	−176.001	−133.686	36.521
900	29.690	82.069	63.206	16.977	−175.252	−128.442	31.190
1000	30.180	85.223	65.252	19.970	−175.158	−123.215	26.929
1050	30.420	86.701	66.239	21.485	−175.111	−120.602	25.101
				Liquid			
1050	34.000	98.129	66.239	33.485	−163.111	−120.602	25.101
1100	34.000	99.711	67.724	35.186	−162.153	−118.636	23.571
1200	34.000	102.670	70.515	38.586	−160.967	−114.732	20.896
1300	34.000	105.391	73.095	41.986	−159.780	−110.926	18.648
1400	34.000	107.911	75.493	45.386	−158.598	−107.213	16.737
1500	34.000	110.257	77.733	48.786	−157.418	−103.585	15.092

TABLE XVII

PLUTONIUM OXYFLUORIDE (PuOF) (MOL WT 274.050) CRYSTAL

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			Log K_p
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	
298	18.990	21.900	21.900	0.000	−269.800	−257.872	189.025
300	19.000	22.017	21.900	0.035	−269.792	−257.798	187.806
400	19.570	27.562	22.652	1.964	−270.217	−253.843	138.693
500	20.140	31.989	24.091	3.949	−269.992	−249.786	109.181
600	20.720	35.713	25.726	5.992	−269.749	−245.776	89.524
700	21.290	38.950	27.389	8.093	−269.363	−241.810	75.497
800	21.860	41.833	29.017	10.253	−269.419	−237.871	64.983
900	22.130	44.418	30.587	12.447	−268.910	−233.958	56.813
1000	23.000	46.797	32.091	14.706	−269.049	−230.035	50.274
1100	23.570	49.016	33.530	17.035	−268.436	−226.164	44.935
1200	24.140	51.091	34.908	19.420	−267.773	−222.349	40.495
1300	24.710	53.046	36.228	21.863	−267.060	−218.592	36.749
1400	25.280	54.898	37.496	24.362	−266.296	−214.893	33.546
1500	25.860	56.662	38.716	26.919	−265.481	−211.248	30.779

TABLE XVIII

PLUTONIUM OXYCHLORIDE (PuOCl) (MOL WT 290.512) CRYSTAL

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			Log K_p
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	
298	19.990	26.000	26.000	0.000	−222.700	−211.273	154.867
300	20.000	26.124	26.000	0.037	−222.691	−211.202	153.861
400	20.570	31.955	26.792	2.065	−223.046	−207.425	113.332
500	21.140	36.606	28.305	4.151	−222.744	−203.565	88.978
600	21.720	40.512	30.022	6.294	−222.420	−199.768	72.766
700	22.290	43.903	31.768	8.494	−221.947	−196.030	61.203
800	22.860	46.917	33.477	10.752	−221.916	−192.331	52.542
900	23.430	49.642	35.124	13.066	−221.293	−188.669	45.815
1000	24.000	52.140	36.702	15.438	−221.324	−185.012	40.434
1100	24.570	54.454	38.212	17.866	−220.614	−181.414	36.044
1200	25.140	56.617	39.657	20.352	−219.852	−177.884	32.397
1300	25.710	58.652	41.040	22.894	−219.039	−174.420	29.323
1400	26.280	60.578	42.368	25.494	−218.174	−171.020	26.697
1500	26.860	62.411	43.643	28.151	−217.255	−167.683	24.431

Table XIX: Plutonium Oxybromide (PuOBr) (mol wt 334.968) Crystal

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	20.990	28.500	28.500	0.000	−212.400	−204.238	149.711
300	21.000	28.630	28.500	0.039	−212.398	−204.188	148.751
400	21.570	34.749	29.331	2.167	−216.358	−200.759	109.690
500	22.140	39.624	30.918	4.353	−215.971	−196.915	86.072
600	22.720	43.712	32.718	6.596	−215.556	−193.151	70.355
700	23.290	47.257	34.548	8.896	−214.991	−189.461	59.153
800	23.860	50.404	36.336	11.254	−214.865	−185.823	50.764
900	24.430	53.247	38.060	13.668	−214.146	−182.235	44.253
1000	25.000	55.850	39.711	16.140	−214.080	−178.661	39.046
1100	25.570	58.260	41.289	18.668	−213.272	−175.159	34.801
1200	26.140	60.509	42.798	21.254	−212.412	−171.731	31.276
1300	26.710	62.624	44.242	23.896	−211.501	−168.378	28.307
1400	27.280	64.624	45.627	26.596	−210.536	−165.096	25.773
1500	27.850	66.526	46.958	29.352	−209.519	−161.886	23.587

Table XX: Plutonium Oxyiodide (PuOI) (mol wt 381.964) Crystal

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	21.990	30.200	30.200	0.000	−197.800	−191.431	140.323
300	22.000	30.336	30.200	0.041	−197.792	−191.392	139.429
400	22.570	36.743	31.070	2.269	−200.118	−189.236	103.394
500	23.140	41.841	32.731	4.555	−204.950	−186.077	81.334
600	23.720	46.111	34.615	6.898	−204.440	−182.359	66.424
700	24.290	49.810	36.527	9.298	−203.778	−178.730	55.802
800	24.860	53.091	38.396	11.756	−203.554	−175.167	47.853
900	25.430	56.052	40.196	14.270	−202.739	−171.668	41.687
1000	26.000	58.761	41.919	16.842	−202.575	−168.193	36.758
1100	26.570	61.265	43.565	19.470	−201.670	−164.798	32.742
1200	27.140	63.602	45.139	22.156	−200.713	−161.488	29.411
1300	27.710	65.797	46.644	24.898	−199.703	−158.260	26.606
1400	28.280	67.871	48.087	27.698	−198.642	−155.111	24.214
1500	28.850	69.842	49.472	30.554	−197.527	−152.041	22.152

Table XXI: Plutonium Carbide (ζ Phase) ($PuC_{0.67}$) (mol wt 247.107) Crystal

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	9.500	19.500	19.500	0.000	0.850	−0.763	0.559
300	9.520	19.559	19.500	0.018	0.851	−0.773	0.563
400	11.050	22.523	19.894	1.052	0.107	−1.306	0.714
500	11.930	25.088	20.682	2.203	0.054	−1.664	0.727
600	12.530	27.320	21.607	3.428	0.018	−2.013	0.733
700	12.910	29.281	22.566	4.700	0.106	−2.358	0.736
800	13.200	31.024	23.516	6.007	−0.279	−2.683	0.733
850	13.300	31.827	23.981	6.669	−0.197	−2.839	0.730

Table XXII: Plutonium Monocarbide ($PuC_{0.85}$) (mol wt 249.269) Crystal

Temp, °K	Cal mole⁻¹ deg⁻¹			kcal mole⁻¹			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	9.785	20.000	20.000	0.000	0.250	−1.439	1.055
300	9.880	20.061	20.000	0.018	0.251	−1.450	1.056
400	11.520	23.147	20.410	1.095	−0.495	−2.008	1.097
500	12.360	25.814	21.231	2.292	−0.560	−2.390	1.045
600	12.870	28.115	22.191	3.554	−0.626	−2.759	1.005
700	13.220	30.126	23.184	4.860	−0.582	−3.118	0.973
800	13.490	31.910	24.165	6.196	−1.020	−3.450	0.943
900	13.710	33.511	25.116	7.556	−0.914	−3.761	0.913
1000	13.900	34.966	26.029	8.936	−1.505	−4.016	0.878
1100	14.070	36.299	26.903	10.335	−1.401	−4.272	0.849
1200	14.230	37.530	27.738	11.750	−1.291	−4.537	0.826
1300	14.380	38.675	28.536	13.181	−1.178	−4.813	0.809
1400	14.520	39.746	29.299	14.626	−1.055	−5.096	0.795

TABLE XXII (*Continued*)

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
1500	14.660	40.752	30.029	16.085	−0.925	−5.387	0.785
1600	14.790	41.703	30.729	17.557	−0.787	−5.692	0.778
1700	14.920	42.603	31.402	19.043	−0.640	−6.003	0.772
1800	15.040	43.459	32.048	20.541	−0.484	−6.322	0.768
1900	15.160	44.276	32.670	22.051	−0.319	−6.651	0.765
1927	15.190	44.490	32.834	22.461	−0.272	−6.742	0.765

TABLE XXIII: PLUTONIUM SESQUICARBIDE (Pu_2C_3) (MOL WT 514.153) CRYSTAL

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	22.930	40.500	40.500	0.000	−1.700	−4.700	3.445
300	23.050	40.642	40.500	0.043	−1.697	−4.719	3.438
400	26.400	41.763	41.448	2.526	−3.178	−5.713	3.122
500	28.460	53.889	43.339	5.275	−3.368	−6.349	2.775
600	29.790	59.199	45.550	8.189	−3.602	−6.943	2.529
700	30.900	63.877	47.840	11.226	−3.640	−7.495	2.340
800	31.770	68.061	50.111	14.360	−4.651	−7.976	2.179
900	32.560	71.846	52.319	17.574	−4.578	−8.400	2.040
1000	33.620	75.339	54.449	20.891	−5.863	−8.694	1.900
1100	33.790	78.549	56.496	24.258	−5.765	−8.985	1.785
1200	34.310	81.512	58.458	27.665	−5.666	−9.277	1.690
1300	34.630	84.270	60.339	31.111	−5.567	−9.584	1.611
1400	35.080	86.854	62.142	34.597	−5.449	−9.894	1.545
1500	35.480	89.287	63.871	38.124	−5.314	−10.215	1.488
1600	35.970	91.593	65.532	41.698	−5.150	−10.552	1.441
1700	36.270	93.783	67.130	45.310	−4.960	−10.896	1.401
1800	36.560	95.865	68.669	48.952	−4.755	−11.252	1.366
1900	36.830	97.849	70.153	52.621	−4.532	−11.615	1.336
2000	37.080	99.744	71.586	56.317	−4.291	−11.993	1.311
2100	37.320	101.559	72.970	60.037	−4.032	−12.379	1.288
2200	37.550	103.301	74.309	63.781	−3.761	−12.792	1.271
2300	37.770	104.975	75.607	67.547	−3.471	−13.203	1.255
2323	37.820	105.351	75.900	68.416	−3.402	−13.104	1.233

TABLE XXIV: PLUTONIUM DICARBIDE (PuC_2) (MOL WT 263.082) CRYSTAL

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	13.150	20.500	20.500	0.000	−1.000	−2.372	1.739
300	13.170	20.581	20.500	0.024	−0.998	−2.381	1.734
400	14.880	24.616	21.039	1.431	−1.696	−2.842	1.553
500	16.100	28.075	22.108	2.983	−1.773	−3.132	1.369
600	16.920	31.084	23.359	4.635	−1.884	−3.404	1.240
700	17.680	33.751	24.657	6.366	−1.903	−3.655	1.141
800	18.280	36.151	25.946	8.164	−2.407	−3.870	1.057
900	18.850	38.338	27.203	10.022	−2.363	−4.058	0.985
1000	19.320	40.349	28.419	11.931	−3.008	−4.181	0.914
1100	19.720	42.210	29.589	13.883	−2.952	−4.303	0.855
1200	20.080	43.941	30.714	15.873	−2.884	−4.426	0.806
1300	20.400	45.561	31.794	17.898	−2.807	−4.559	0.766
1400	20.700	47.084	32.832	19.953	−2.714	−4.694	0.733
1500	20.960	48.522	33.831	22.036	−2.609	−4.839	0.705
1600	21.180	49.882	34.792	24.144	−2.491	−4.995	0.682
1700	21.350	51.171	35.718	26.270	−2.363	−5.156	0.663
1800	21.520	52.396	36.611	28.414	−2.227	−5.323	0.646
1900	21.670	53.564	37.472	30.574	−2.081	−5.498	0.632
2000	21.780	54.678	38.305	32.746	−1.929	−5.681	0.621
2100	21.880	55.743	39.110	34.929	−1.770	−5.869	0.611
2200	21.980	56.763	39.890	37.122	−1.609	−6.073	0.603
2300	22.080	57.743	40.645	39.325	−1.440	−6.276	0.596
2400	22.160	58.684	41.377	41.537	−1.268	−6.490	0.591
2500	22.240	59.590	42.087	43.758	−1.089	−6.712	0.587
2525	22.180	59.810	42.270	44.312	−1.044	−6.769	0.586

TABLE XXV
PLUTONIUM MONONITRIDE (PuN) (MOL WT 253.067) CRYSTAL

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	12.750	14.200	14.200	0.000	−75.700	−69.184	50.736
300	12.780	14.279	14.200	0.024	−75.697	−69.140	50.366
400	13.600	18.074	14.712	1.345	−76.337	−66.963	36.585
500	14.160	21.173	15.704	2.734	−76.290	−64.632	28.249
600	14.520	23.788	16.839	4.169	−76.218	−62.418	22.735
700	14.790	26.047	17.997	5.635	−76.016	−60.019	18.738
800	15.000	28.036	19.130	7.125	−76.282	−57.717	15.767
900	15.180	29.813	20.220	8.634	−75.993	−55.414	13.456
1000	15.360	31.422	21.261	10.161	−76.394	−53.075	11.599
1100	15.520	32.893	22.252	11.705	−76.094	−50.702	10.073
1200	15.670	34.250	23.196	13.256	−75.785	−48.467	8.827
1300	15.810	35.510	24.096	14.839	−75.467	−46.204	7.767
1400	15.940	36.687	24.953	16.426	−75.040	−43.963	6.863
1500	16.070	37.791	25.773	18.027	−74.804	−41.751	6.083
1600	16.200	38.832	26.557	19.640	−74.458	−39.558	5.403
1700	16.320	39.818	27.308	21.266	−74.104	−37.385	4.806
1800	16.440	40.754	28.029	22.904	−73.740	−35.236	4.278
1900	16.560	41.646	28.723	24.555	−73.366	−33.108	3.808
2000	16.670	42.498	29.390	26.216	−72.984	−31.010	3.505
2100	16.770	43.314	30.034	27.888	−72.593	−28.910	3.009
2200	16.870	44.097	30.656	29.570	−72.194	−26.840	2.666
2300	16.970	44.849	31.256	31.262	−71.786	−24.785	2.355
2400	17.070	45.578	31.833	32.964	−71.370	−22.751	2.072
2500	17.160	46.270	32.401	34.672	−70.950	−20.732	1.812
2600	17.250	46.958	32.948	36.425	−70.485	−18.734	1.575
2700	17.330	47.618	33.479	38.175	−70.024	−16.754	1.356
2800	17.410	48.250	33.996	39.912	−69.578	−14.789	1.154
2843	17.440	48.515	34.213	40.661	−69.383	−13.944	1.072

TABLE XXVI
PLUTONIUM MONOSULFIDE (PuS) (MOL WT 271.116) CRYSTAL

Temp, °K	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta H_f°$	$\Delta G_f°$	Log K_p
298	12.900	18.700	18.700	0.000	−105.000	−104.371	76.506
300	13.000	18.780	18.700	0.024	−105.000	−104.366	76.031
400	13.920	22.648	19.221	1.371	−106.365	−104.115	56.886
500	14.770	25.846	20.235	2.806	−106.859	−103.504	45.242
600	15.550	28.610	21.406	4.322	−107.207	−102.807	37.448
700	16.240	31.060	22.613	5.913	−107.316	−102.041	31.858
800	16.850	33.269	23.809	7.568	−120.870	−102.520	28.007
900	17.390	35.285	24.974	9.280	−120.436	−100.252	24.344
1000	17.920	37.145	26.099	11.046	−120.653	−97.966	21.411
1100	18.410	38.876	27.183	12.862	−120.130	−95.724	19.019
1200	18.880	40.498	28.225	14.727	−119.559	−93.529	17.034
1300	19.310	42.026	29.229	16.637	−118.944	−91.383	15.363
1400	19.700	43.472	30.195	18.588	−118.290	−89.288	13.938
1500	20.050	44.843	31.126	20.576	−117.600	−87.240	12.711
1600	20.340	46.147	32.025	22.596	−116.878	−85.240	11.643
1700	20.590	47.388	32.892	24.642	−116.131	−83.287	10.707
1800	20.800	48.571	33.731	26.712	−115.361	−81.377	9.880
1900	20.970	49.700	34.542	28.801	−114.572	−79.508	9.145
2000	21.110	50.779	35.327	30.905	−113.769	−77.683	8.489
2100	21.230	51.812	36.087	33.022	−112.954	−75.899	7.899
2200	21.340	52.802	36.825	35.151	−112.127	−74.153	7.366
2300	21.440	53.753	37.540	37.290	−111.291	−72.446	6.884
2400	21.530	54.668	38.235	39.438	−110.446	−70.776	6.445
2500	21.620	55.548	38.910	41.596	−109.591	−69.139	6.044
2600	21.700	56.398	39.566	43.762	−108.729	−67.540	5.677
2623	21.720	56.589	39.715	44.261	−108.529	−67.179	5.597

TABLE XXVII
PLUTONIUM SESQUISULFIDE (Pu_2S_3) (MOL WT 574.312) CRYSTAL

	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
Temp, °K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log K_p
298	30.990	46.000	46.000	0.000	−236.500	−235.530	172.648
300	31.000	46.192	46.001	0.057	−236.501	−235.524	171.579
400	31.800	55.219	47.226	3.197	−239.884	−235.082	128.443
500	32.600	62.401	49.567	6.417	−241.460	−233.720	102.159
600	33.400	68.416	52.220	9.717	−242.745	−232.064	84.529
700	34.200	73.624	54.914	13.097	−243.565	−230.145	71.854
800	35.000	78.243	57.547	16.557	−284.348	−231.920	63.358
900	35.800	82.412	60.082	20.097	−283.802	−225.400	54.735
1000	36.600	86.225	62.508	23.717	−284.589	−218.806	47.820
1100	37.400	89.751	64.826	27.417	−283.918	−212.264	42.173
1200	38.200	93.040	67.042	31.197	−283.170	−205.779	37.478
1300	39.000	96.129	69.162	35.057	−282.345	−199.360	33.516
1400	39.800	99.048	71.193	38.997	−281.446	−193.010	30.130
1500	40.600	101.822	73.143	43.017	−280.470	−186.732	27.207

TABLE XXVIII
PLUTONIUM SULFATE ($Pu(SO_4)_2$) (MOL WT 431.183) CRYSTAL

	Cal mole^{-1} deg^{-1}			kcal mole^{-1}			
Temp, °K	$C_p°$	$S°_T$	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log K_p
298	43.490	39.000	39.000	0.000	−526.000	−470.706	345.036
300	43.560	39.269	39.001	0.081	−526.005	−470.363	342.659
400	49.080	52.557	40.775	4.713	−528.028	−451.726	246.812
500	54.600	64.102	44.308	9.897	−528.635	−432.580	189.081
600	60.120	74.544	48.490	15.633	−528.640	−413.367	150.569
700	65.640	84.235	52.912	21.926	−527.959	−394.153	123.060
800	70.500	93.319	57.401	28.735	−553.376	−377.620	103.161
900	75.150	101.894	61.872	36.019	−551.064	−355.784	86.396
1000	79.550	110.040	66.285	43.755	−549.060	−334.156	73.030
1100	83.860	117.826	70.619	51.927	−545.980	−312.818	62.151
1200	88.020	125.306	74.867	60.527	−542.510	−291.768	53.138
1300	91.480	132.490	79.025	69.505	−538.700	−271.023	45.563
1400	94.600	139.385	83.092	78.810	−534.595	−250.587	39.118
1500	97.550	146.013	87.067	88.419	−530.216	−230.453	33.577

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