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Mass Spectrometric Studies of Plutonium Compounds at High Temperatures: I. The Heats of Vaporization of Gold and Plutonium and the Heat of Decomposition of Plutonium Mononitride

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Mass Spectrometric Studies of Plutonium Compounds at HighTemperatures: I. The Heats of Vaporization of Gold and Plutonium and the Heat of Decomposition of Plutonium Mononitride

by

R. A. Kent
J. A. Leary

MASS SPECTROMETRIC STUDIES OF PLUTONIUM COMPOUNDS AT HIGH TEMPERATURES : I. THE HEATS OF VAPORIZATION OF GOLD AND PLUTONIUM AND THE HEAT OF DECOMPOSITION OF PLUTONIUM MONONITRIDE

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ABSTRACT

This report describes the mass spectrometer - Knudsen cell apparatus which has been constructed and employed to measure the enthalpy of vaporization of gold, the vapor pressure and enthalpy of vaporization of plutonium, and the partial pressures and enthalpies of formation of Pu(g) and N_2(g) above solid PuN.

In the temperature range 1426-1658°K, liquid plutonium vaporizes predominately to the monomer with the vapor pressure given by the least-squares equation

$$\log_{10} P(\mathrm{atm}) = (4.924 \pm 0.120) - \frac{17420 \pm 184}{T^{\circ}K} .$$

The standard enthalpy of vaporization is $\Delta H^{\circ}_{298} = 83.0 \pm 0.5$ kcal. mole^{-1}.

In the temperature range 1658-1976°K, PuN(s) decomposes invariantly according to the reaction

$$\mathrm{PuN(s)} = \mathrm{Pu(g)} + \frac{1}{2}\,\mathrm{N_2(g)}$$

with an enthlpy of reaction of $\Delta H^{\circ}_{298} = 156.1 \pm 2.5$ kcal. mole^{-1}. The partial pressure of Pu(g) above solid PuN is given by

$$\log_{10} P_{Pu}(\mathrm{atm}) = (6.436 \pm 0.055) - \frac{21958 \pm 98}{T^{\circ}K} .$$

The standard enthalpy of formation of solid PuN is calculated to be $\Delta H^{\circ}_{f298} =$ -73.1 ± 2.7 kcal. mole^{-1}.

1. Introduction and Description of the Apparatus

Among the parameters that are of interest in design of reactor fuel systems employing refractory materials are the thermodynamic properties of the individual constituents. A convenient method of determining the thermodynamic properties of materials at high temperatures is the measurement of vapor pressures and enthalpies of sublimation and/or vaporization by the well-established Knudsen technique. Vaporization processes at high temperatures, however, are often complex and a detailed knowledge of the identity and relative concentrations of the vapor species in equilibrium with the condensed phases is required if the vaporization process is to be characterized.

In order to determine both the vapor species present over condensed plutonium materials at high temperatures and the partial pressures of these vapor species, the high temperature mass spectrometer assembly shown in Fig. 1 has been constructed. The unit consists of two basic components, an oven assembly incorporating an electron bombardment-heated Knudsen cell, and an Ultek Corporation Model 200 quadrupole residual gas analyzer. These component parts are contained in a differentially pumped Type 304 stainless steel vacuum envelope. Vacuum of the order of 10^{-8} torr is achieved with the Knudsen cell at 1600°C by means of two ion pumps, one rated at 400 ℓ/sec, connected to the quadrupole region, the other, rated at 100 ℓ/sec, connected to the oven region.

The oven assembly closely resembles that described by Chupka and Inghram(1) and consists basically of a Knudsen cell heated by electron bombardment from a tungsten filament and surrounded by a series of six concentric tantalum radiation shields. The high voltage power supply is capable of heating the Knudsen cell to 2100°C, and in tests the Knudsen cell has been held at 1600 ± 4°C for as long as 12 hours.

The temperature of the Knudsen cell is measured by sighting with a microoptical pyrometer through calibrated windows in the glove box and the vacuum system into a blackbody hole in the base of the cell.

The molecular beam which effuses from the Knudsen cell passes through a collimating slit in a movable shutter plate and into the quadrupole region. The movable shutter plate allows one to close the slit to the molecular beam so as to distinguish sample vapors from background species.

The mass spectometer consists of three parts, an ionizer region, a quadrupole analyzer region, and a detector consisting of an electron multiplier with a gain of about 10^5. The electron multiplier is so designed that one can measure its gain, allowing one to normalize data taken on different samples and/or on different days. The ionizer assembly has been redesigned and rebuilt so as to provide better collimation of both the molecular beam and the ionizing electron beam. When molecules enter the ionizer region they pass through a beam of electrons of approximately known energy and positive ions are formed according to the reaction

$$M + e^- = M^+ + 2e^- \quad . \qquad (1)$$

The positive ion beam is focused and accelerated into the quadrupole analyzer region. The signal from the multiplier can be fed either to an oscilloscope or through an electrometer to a strip chart recorder.

2. Enthalpy of Vaporization of Gold

The vapor pressure of gold has been determined by a number of workers employing a variety of techniques. Most of the published data have been critically reviewed by Hultgren et al.,(2) who list recommended values for the vapor pressure as a function of temperature.

In order to test the apparatus for experiments involving high molecular weight species and to provide a standard for absolute pressure measurement, the enthalpy of vaporization of gold was determined in the usual manner by monitoring the ion current (I) of the gold peak ($^{197}Au^+$) as a function of temperature in the range 1370-1788°K. The sample consisted of melted gold wire of 99.98 percent purity contained in a graphite Knudsen cell held inside a tantalum shell.

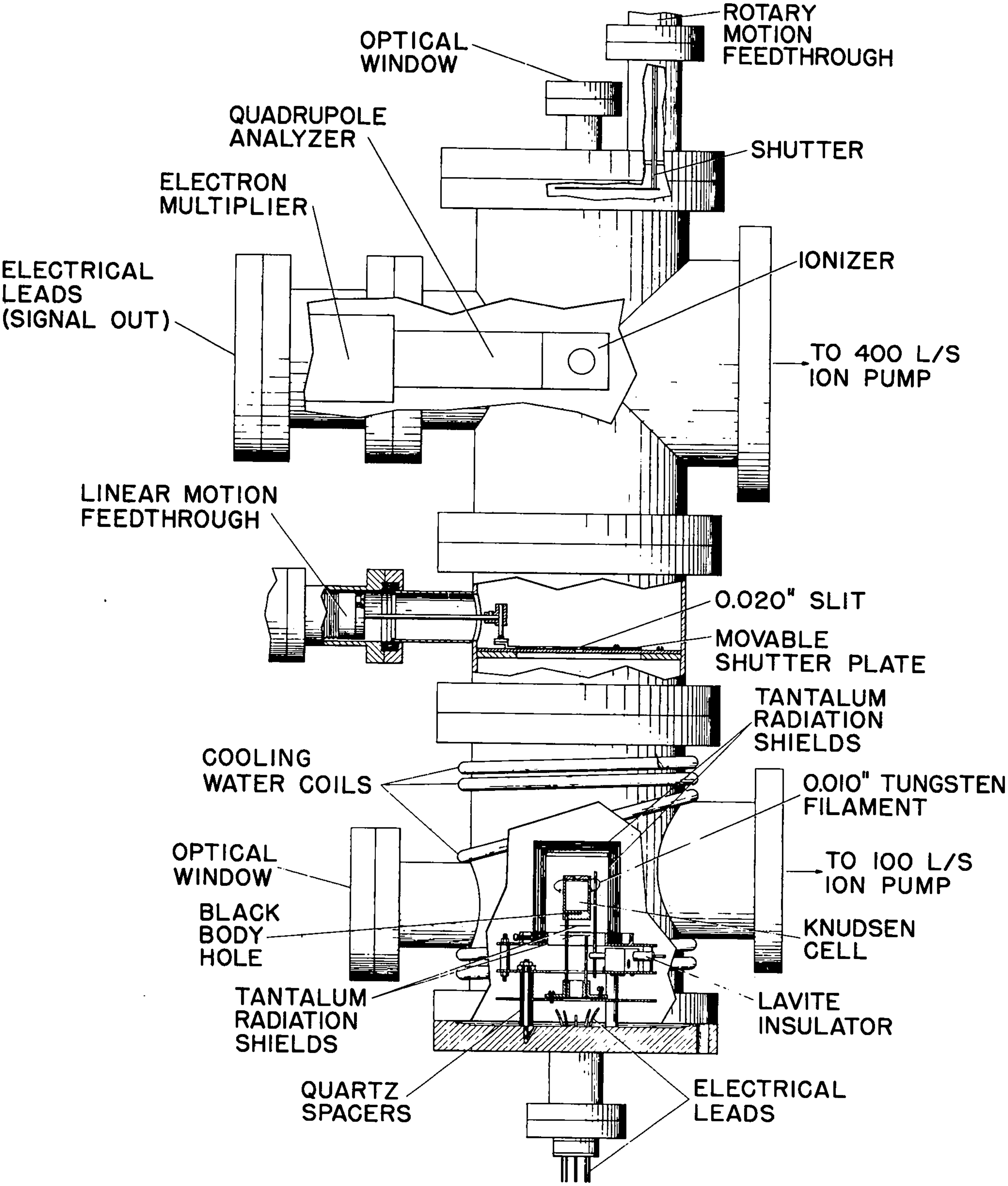

Fig. 1. High-temperature mass spectrometer assembly.

A graph of the data in the form log (IT) vs reciprocal temperature (Fig. 2) yields the least-squares equation

$$\log_{10} (IT = (19.644 \pm 0.081) - \frac{17986 \pm 129}{T^{o}K} \qquad (2)$$

where I is the ion current, T the specimen temperature, and the uncertainties quoted are the standard deviations generated by the least-squares program. This equation leads to an enthalpy of vaporization of $\Delta H_{1602} = 82.3 \pm 0.6$ kcal. $mole^{-1}$ which is virtually the same as that listed by Hultgren at 1600°K, 82.06 kcal. $mole^{-1}$. When corrected to 298°K using the thermodynamic functions tabulated by Hultgren, the second law enthalpy of vaporization is calculated to be $\Delta H^{o}_{298} = 87.6 \pm 1.0$ kcal. $mole^{-1}$. In addition to the standard deviation, the uncertainty quoted takes into account possible errors in temperature measurement and in the thermodynamic functions employed.

3. Vaporization of Plutonium

3.1 Introduction

Although the vapor pressure of plutonium metal has been measured previously,(3,4) the vapor species in equilibrium with the liquid metal have never been positively identified. Phipps et al.(3) employed Ta Knudsen cells over the range 1392-1793°K and obtained an enthalpy of vaporization of $\Delta H_{V1593} = 80.47$ kcal. $mole^{-1}$. Mulford,(4) in his target collection-type experiments over the range 1133-1792°K, also employed Ta Knudsen cells and obtained $\Delta H_{V1479} = 79.71$ kcal. $mole^{-1}$. In addition, Mulford used internal cups of TaC, ThO_2, and MgO without finding any significant differences in vapor pressures.

In this work a series of experiments were performed in which liquid plutonium was effused from W Knudsen cells and from ThO_2 and ZrO_2 internal cups contained in W cells. The purposes of these experiments were to test the quadrupole unit for use with radioactive species and to test the unit's resolution in the range 200-300 amu, theoretically the range of poorest resolution for the Ultek machine. Also of interest was whether or not a significant amount of $Pu_2(g)$ dimer was present in the vapor in equilibrium with liquid

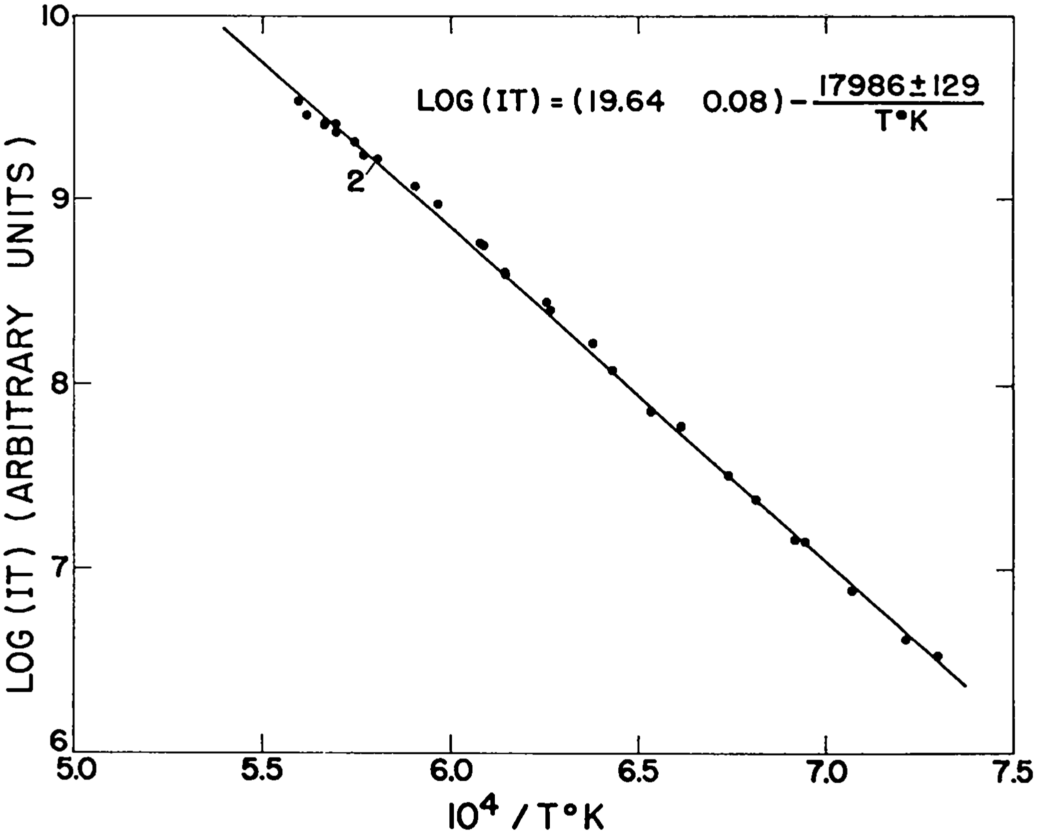

Fig. 2. Vaporization data for gold.

plutonium.

3.2 Sample Purity

The plutonium metal was in the form of 0.25-inch diameter rods of electrorefined metal.(5) A section was cut from the rod and filed under an argon atmosphere to give a bright shiny surface, and was stored and loaded in an argon atmosphere into a Knudsen cell which had been degassed in vacuum at 1800°C for 3 to 6 hours. Previous mass spectrometric analyses performed at Los Alamos had shown the isotopic composition to be 97.70 atom percent ^{239}Pu, 2.22 percent ^{240}Pu, 0.07 percent ^{241}Pu, and 0.01 percent ^{242}Pu. The results of the spectrochemical analysis are presented in Table I.

3.3 Experimental Results

Four experiments (A, B, C, and D) were performed in which liquid Pu was effused from W Knudsen cells over the range 1426-1658°K. When the mass spectrum was scanned, no $^{240}Pu^+$ and $^{241}Pu^+$ ions were observed, and the resolution of the quadrupole unit was such that it was impossible to separate to the base line the mass peaks $^{239}Pu^+$ and $^{240}Pu^+$, the $^{240}Pu^+$ signal occuring as a "shoulder" on the $^{239}Pu^+$ peak. No Pu_2(g) dimer was observed and, thus in the temperature range covered, would have constituted less than 2 percent of the vapor.

Table I

Spectroscopic and Chemical Analysis of Plutonium

Element	Concentration, ppm	Element	Concentration, ppm
Al	3	Mg	2
Am	< 10	Mn	< 0.5
B	< 0.001	Mo	< 1
Bi	< 1	N	3 ± 1
C	15 ± 5	Na	< 2
Ca	< 2	Ni	< 0.5
Cd	< 5	O	20 ± 10
Co	< 1	Pb	< 1
Cr	1	Pu	100.00 ± 0.06
Cu	< 0.05	Si	7
F	< 2	Sn	< 1
Fe	3	Ta	19
Ga	< 0.2	Th	< 15
H	10 ± 5	U	10
K	< 7.5	W	< 5
La	< 1	Zn	< 10
Li	< 0.005	Zr	< 10

In each of the four experiments the enthalpy of vaporization was determined in the usual manner by monitoring the ion current of the $^{239}Pu^+$ signal as a function of temperature.

In another experiment, E, the liquid Pu was effused over the range 1482-1579°K from a ThO_2 cup inside the W cell. In this temperature range the only sample vapor species observed was Pu(g). No PuO(g) was observed, although metallographic analyses showed the presence of an oxide layer, mostly hex Pu_2O_3, where the walls of the ThO_2 cup were in contact with the liquid Pu and a very thin skin of Pu_2O_3 was observed on the surface of the Pu metal residue. As before, the enthalpy of vaporization was determined by monitoring the $^{239}Pu^+$ signal as a function of temperature.

The sensitivity of the quadrupole unit is such that it was impossible to determine the gain of the multiplier for Pu in the pressure range of the experiments. However, one can measure the gain of the N_2 background peak and calculate the multiplier gain for Pu from

$$G_{Pu} = G_{N_2} \left(M_{N_2}/M_{Pu}\right)^{\frac{1}{2}} \tag{3}$$

where G is the multiplier gain for a given species and M is its molecular weight. This was done and the data for experiments A through E were normalized for multiplier gain changes and combined to yield the least-squares equation

$$\log_{10} (IT) = (20.03 \pm 0.12) - \frac{17420 \pm 184}{T\ {}^{o}K} \tag{4}$$

where I is the current of the $^{239}Pu^+$ signal, T the temperature in degrees Kelvin, and the quoted uncertainties are the standard deviations generated by the least-squares program.

3.4 Absolute Pressure Calibration

One may calculate the absolute Pu vapor pressure from the ion current data through the relationship

$$P = K\ (IT) \tag{5}$$

where K is the machine constant. From section 2 above, $\log_{10}$ (IT) = 7.950 for Au at 1538°K, and from Hultgren,

$\log_{10}$ P atm = -5.778 for Au at the same temperature. Hence, from Eq. (5), $K_{Au} = 1.87 \times 10^{-14}$ atm amp^{-1} deg K^{-1} at 1538°K. The machine constant for Pu is given by

$$K_{Pu} = K_{Au}\left[\left(G_{Au}/G_{Pu}\right)\cdot\left(\sigma_{Au}/\sigma_{Pu}\right)\cdot\left(\Delta E_{Au}/\Delta E_{Pu}\right)\right] \qquad (6)$$

where G is the multiplier gain for a given species, σ is its ionization cross section, and ΔE is the difference between the energy of the ionizing electron beam and the appearance potential for a given species. The multiplier gains were determined as described above, the cross sections of Au and Pu, 6.46 and 10.0, respectively, are from Mann,(6) and the ionization potential of Au was taken to be 9.2 eV.(7) The ionization potential of Pu, however, is unknown and, in practice, one cannot measure appearance potentials below about 8 eV with the Ultek quadrupole unit. For this work, the ionization potential of Pu was estimated to be 5.5 ± 0.5 eV, an average of two literature values; Dawton and Wilkenson(8) obtained 5.1 eV in a surface ionization experiment, and Bauche <u>et al.</u> (9) estimated the value to be 5.8 eV, based on a single level they identify as $^9F_1$ of a $5f^6$ 7s 8s configuration.

From Eq. (6), K_{Pu} is calculated to be 6.92×10^{-16} atm amp^{-1} deg K^{-1} at 1538°K. Combination of this value with the ion current data yielded the least-squares equation

$$\log_{10} P \text{ atm} = (4.924 \pm 0.120) - \frac{17420 \pm 184}{T^{\circ}K} \qquad (7)$$

where again the quoted uncertainties are the standard deviations generated by the least-squares program. This equation, which is the integrated form of the Clausius-Clapeyren equation, leads to an enthalpy of vaporization for Pu of

$$\Delta H_{1538} = 79.71 \pm 0.84 \text{ kcal. mole}^{-1},$$

and an entropy of $\Delta S^{o}_{1538} = 22.53 \pm 0.55$ eu.

In order to correct these values to 298°K one needs accurate heat capacity data for liquid and gaseous Pu. Feber and Herrick(10) have calculated the thermodynamic functions for Pu vapor as an ideal gas, based on 293 spectroscopic levels from the data of Bauche <u>et al.</u>,(9) Gerstenkorn, (11) and Richards and Ridgeley.(12) Unfortunately, accurate heat capacity data for condensed Pu at high temperatures do not exist. Rand(13) has reviewed the data appearing in the literature and lists recommended values for the heat capacity as a function of temperature. The thermodynamic functions employed for Pu(s, ℓ) from Rand, and for Pu(g) from Feber and Herrick are listed in Table II.

When the enthalpy of vaporization is corrected to 298°K, using the functions from Table II, the second law results become $\Delta H_{298} = 83.24$ kcal. mole^{-1} and $\Delta S_{298} = 29.42$ eu.

The Pu vapor pressure data are shown in Fig. 3.

3.5 <u>Third Law Enthalpy of Vaporization</u>

When the absolute values of the vapor pressure of Pu are combined with the free energy functions for liquid and gaseous Pu taken from Table II, the third law enthalpy of vaporization is calculated from the equation

$$\Delta H^{o}_{298} = -T\left[2.3\,R\log P - \Delta\left(\frac{F^{o}_{T} - H^{o}_{298}}{T}\right)\right] \qquad (8)$$

to be $\Delta H^{o}_{298} = 82.94 \pm 0.13$ kcal. mole^{-1}. The third law data are presented in Table III.

Table II

Thermodynamic Functions for Plutonium

Temp., °K	$\left(H^{o}_{T} - H^{o}_{298}\right)(s,\ell)$ cal. mole^{-1}	$\left(H^{o}_{T} - H^{o}_{298}\right)(g)$ cal. mole^{-1}	$-\left(\frac{F^{o}_{T} - H^{o}_{298}}{T}\right)(s,\ell)$ eu	$-\left(\frac{F^{o}_{T} - H^{o}_{298}}{T}\right)(g)$ eu
298	0	0	13.20	42.32
1000	8177	4330	19.14	45.10
1200	9877	5994	20.64	45.95
1400	11677	7842	21.91	46.76
1600	13277	9860	23.02	47.56
1800	14977	12020	24.00	48.30

Table III

Vaporization Data for Plutonium

Pt.[a]	Temp., °K	P Pu, atm × 10^7	$-\Delta\left(\frac{F^o_T - H^o_{298}}{T}\right)$ eu	ΔH^o_{298} kcal. $mole^{-1}$
A1	1566	6.62	24.59	82.98
A2	1597	9.96	24.54	83.06
A3	1589	9.14	24.55	82.91
A4	1600	10.2	24.53	83.10
A5	1608	12.7	24.52	82.81
A6	1629	16.8	24.50	82.95
A7	1654	24.9	24.47	82.88
B1	1658	27.3	24.47	82.78
B2	1648	24.0	24.47	82.71
B3	1647	23.6	24.48	82.73
B4	1623	14.9	24.51	83.07
B5	1628	16.9	24.50	82.90
B6	1611	13.1	24.52	82.89
B7	1594	10.4	24.54	82.76
B8	1548	4.78	24.61	82.86
C1	1521	2.89	24.66	83.02
C2	1513	2.64	24.67	82.88
C3	1508	2.42	24.68	82.88
C4	1488	1.71	24.71	82.84
C5	1489	1.66	24.71	83.00
C6	1488	1.63	24.71	82.99
C7	1505	2.32	24.68	82.84
C8	1507	2.32	24.68	82.95
C9	1518	2.90	24.67	82.87
C10	1557	5.88	24.60	82.69
C11	1564	6.49	24.59	82.75
C12	1530	3.68	24.72	82.86
C13	1507	2.37	24.68	82.88
D1	1426	0.501	24.81	83.01
D2	1426	0.501	24.81	83.01
D3	1460	0.982	24.67	82.97
D4	1461	1.02	24.75	82.91
D5	1461	1.02	24.75	82.91
D6	1475	1.38	24.73	82.79
D7	1475	1.36	24.73	82.82
D8	1492	1.73	24.70	83.01
D9	1489	1.66	24.71	83.00
D10	1496	1.60	24.73	82.83
E1	1595	9.47	24.54	83.12
E2	1579	7.42	24.57	83.09
E3	1578	6.95	24.56	83.22
E4	1554	4.80	24.61	83.19
E5	1546	4.24	24.62	83.14
E6	1533	3.38	24.64	83.17
E7	1511	2.36	24.67	83.10
E8	1482	1.41	24.71	83.08
E9	1511	2.44	24.67	83.00
E10	1488	1.63	24.71	82.99
			Av =	82.94 ± 0.13

[a] Runs A, B, C, and D in W crucibles, Run E in ThO_2 cup. All runs normalized for changes in multiplier gain.

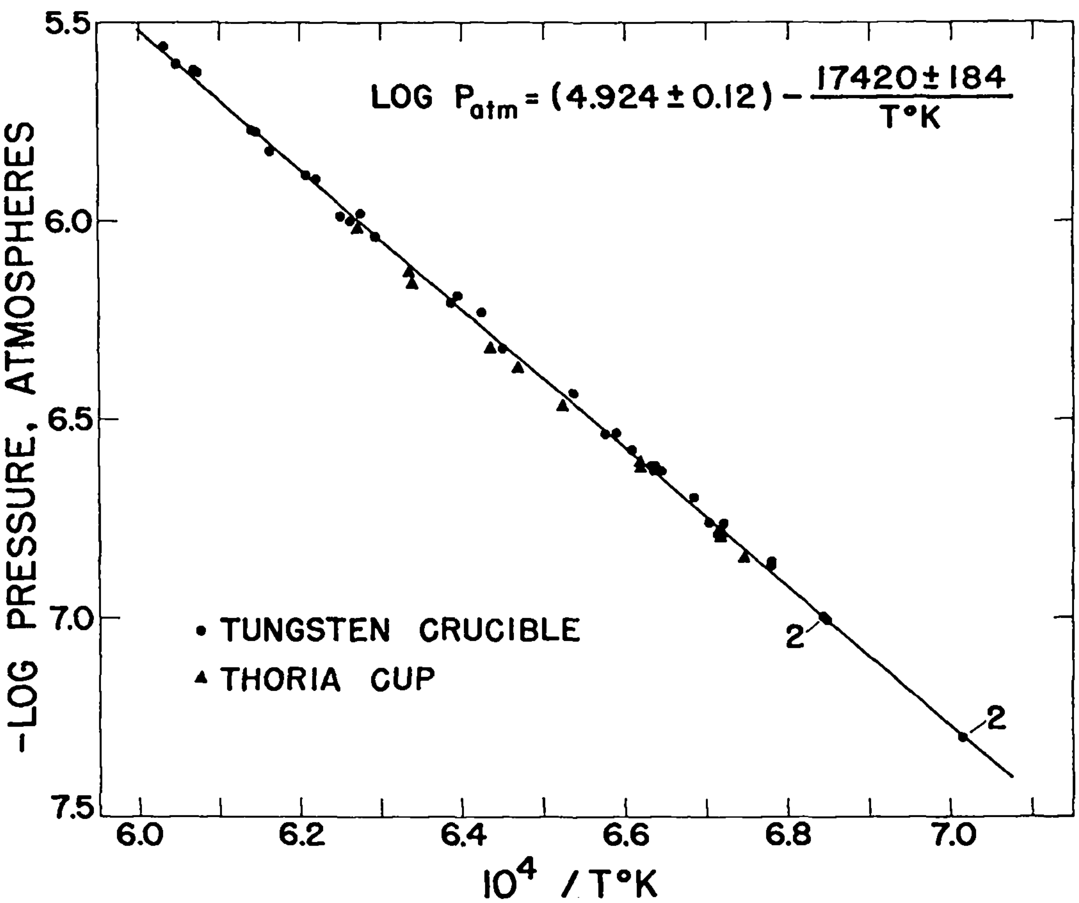

Fig. 3. Vapor pressure data for plutonium.

3.6 Discussion and Summary of Pu Vaporization Experiments

It may be noted in Fig. 3 and in Table III that when Pu was heated in the ThO_2 cup the vapor pressure was approximately 7 percent lower than that measured when W cells were employed. This slight difference in vapor pressure is in accord with the results reported by Mulford, who found no significant change in vapor pressure when Pu(ℓ) was contained in Ta cells and when it was contained in TaC, ThO_2, and MgO cups inside the Ta cells. Two possible causes of the lowering of the vapor pressure of Pu when contained in the ThO_2 cup may be stated. It was pointed out above that a thin oxide skin existed on the surface of the Pu metal residue. Also, the metallographic analysis indicated the residue to be δ-phase Pu, indicating the possible presence of a few percent Th metal dissolved in the Pu. This would likely result in a lowered Pu activity.

In summary, Knudsen effusion experiments performed with the mass spectrometer show that between 1400 and 1700^{0}K, Pu(ℓ) vaporizes predominately to the monomer. The vapor pressure and enthalpy values obtained in this work are in good agreement with those published previously, as indicated in Table IV, where the enthalpy values listed were obtained from a combination of the published vapor pressure data and the thermodynamic functions from Table II.

Table IV

Comparison of Vaporization Data for Pu

Source		Pu Pressure, atm at 1600^{0}K	Second Law ΔH^0_{298v}, kcal. mole^{-1}	Second Law ΔS^0_{298v}, eu	Third Law ΔH^0_{298v}, kcal. mole^{-1}
Phipps, et al.	(Ref 3)	1.05×10^{-6}	83.9	29.8	83.0
Mulford	(Ref 4)	1.06×10^{-6}	83.3	29.4	83.0
This Work		1.09×10^{-6}	83.2	29.4	82.9

The uncertainties quoted above in Eq. (7) and in the enthalpy and entropy values are the standard deviations generated by the least squares program. The actual error in these values may be expected to be larger owing to such factors as errors in temperature measurement and uncertainties in the heat capacity values estimated by Rand. However, the agreement between the results of this study and those obtained by Phipps and Mulford, and the fact that the third law results of this study show no temperature dependence when graphed vs temperature as shown in Fig. 4, indicate that the errors in these values are likely to be small. Accordingly, the enthalpy of vaporization of Pu is taken to be 83.0 ± 0.5 kcal. mole^{-1}.

3.7 Plutonium in ZrO_2

In an additional experiment, Pu metal was contained in a ZrO_2 cup inside the W Knudsen cell. In the temperature range covered above, no sample vapor species were observed. At higher temperatures, ca. 1900°K, the only vapor species observed was PuO(g). Equilibrium was not attained, however, and no quantitative measurements could be performed. X-ray diffraction and metallographic analyses showed the ZrO_2 cup to have been reduced and the sample residue to consist mostly of hex. Pu_2O_3 with trace amounts of PuO_2. These results are in accord with those of Ackermann *et al.*,(14) who report that the vapor above Pu_2O_3 consists of PuO(g), with the condensed phase slowly being oxidized to PuO_2.

4. Vaporization of PuN

4.1 Introduction

Relatively little is known about the vaporization of solid PuN under the conditions pertaining to Knudsen-type experiments. Olson and Mulford(15) have measured the decomposition pressure under a nitrogen atmosphere over the range 2290-2770°K. Rand(13) estimated the standard enthalpy of formation of PuN(s) to be -70 kcal. mole^{-1} and combined this value with an extrapolation of the data of Olson and Mulford to obtain the equation

$$-RT \ln P_{Pu} = 99{,}100 - 29.1\,T \qquad (9)$$

for the partial pressure of Pu above solid PuN in vacuum. Recent work performed in this Laboratory, however, indicates that the free energy of formation of PuN(s) is -60 kcal. mole^{-1} at 700°K.(16) This would indicate that the standard enthalpy of formation is more negative than -70 kcal. mole^{-1}. Anselin and Pascard(17) have reported that solid PuN vaporizes below 2650°K in nitrogen, presumably to PuN(g) which subsequently decomposes. Pardue *et al.* (18) have suggested that below 1800°C in vacuum PuN(s) vaporizes congruently with partial decomposition of the gaseous PuN. This is unlikely, as

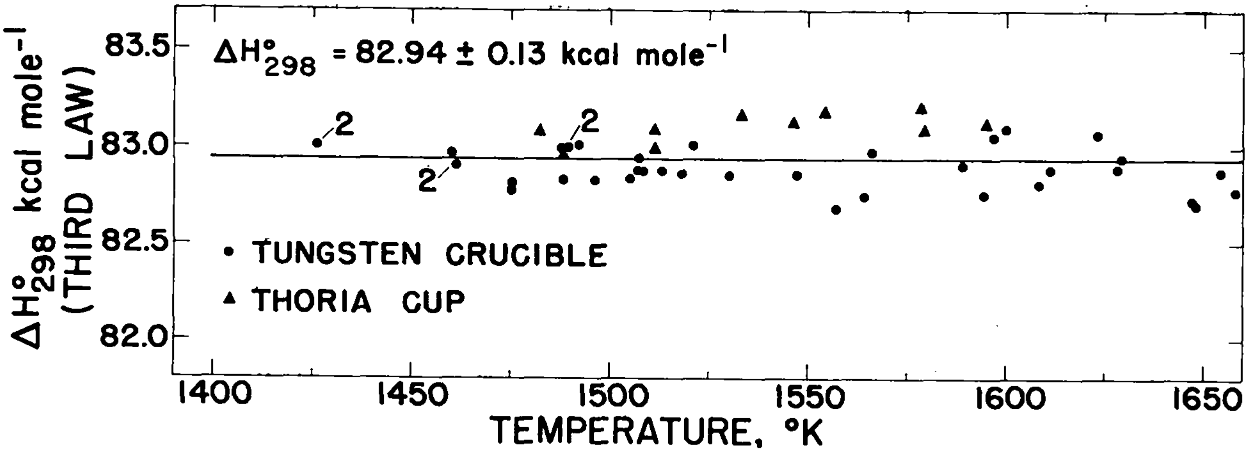

Fig. 4. Third law enthalpy of vaporization of plutonium vs temperature.

available literature data pertaining to the vaporization of refractory nitrides such as Be_3N_2,[19, 20] AlN,[20] TiN,[20] GaN,[21] and UN[22, 23] indicate that the vaporization mechanism is

$$M_xN_y(s) = xM(g) + y/2\ N_2(g) \quad . \qquad (10)$$

Gingerich,[24] however, has reported that at high temperatures UN(g) is a minor vapor species above solid UN. More recently, Pardue et al.[25] have reported some effusion data obtained in the range 1985-2300°K in which they assumed the vaporization process to yield gaseous Pu and N_2. Analysis of the residue, however, indicated a relatively large oxygen content in their sample.

In this work the vapor species above solid PuN in the range 1658-1976°K have been identified as gaseous Pu and N_2 and the enthalpy of the vaporization process has been determined. This value has been combined with the standard enthalpy of vaporization of Pu to yield the standard enthalpy of formation of solid PuN.

4.2 Sample Purity

The PuN(s) samples used in the vaporization experiments were prepared by pressing pellets at 30,000 psi from $PuN_{0.95}$ powder prepared by reacting N_2 gas with hydrided Pu.[26] The spectroscopic analysis of the PuN powder is listed in Table V. The pellets, each weighing approximately 2-2.5 g, were then heated at 1600°C for 15 hours in a W crucible under 0.5 atm nitrogen. The pellets were then stored under an argon atmosphere containing less than 10 ppm oxygen until loaded into W Knudsen cells which had been degassed at 2000°C in vacuum. Metallographic, chemical, and x-ray diffraction analyses of the pellets after they had been heated to high temperatures in nitrogen showed the pellet samples to be single phase with stoichiometries ranging from $PuN_{0.96}$ to $PuN_{0.99}$ with an average lattice parameter of 4.9055 ± 0.0003 Å. The metallographic results are typified by those shown in Fig. 5.

4.3 Experimental Results

When solid PuN was effused from W Knudsen cells over the range 1658-1976°K, in eight experiments, the

Table V

Spectrochemical and Chemical Analysis of PuN Starting Material

Element	Concentration, ppm
Al	7
B	0.5
Ba	0.5
Bi	< 1
Ca	< 2
Cd	< 1
Co	< 1
Cr	< 1
Cu	2
Fe	20
Hf	< 1
La	< 1
Mg	10
Mn	< 0.5
Mo	< 1
Na	2
Ni	0.5
O	410
Pb	< 1
Si	20
Sn	< 1
Ti	0.5
U	1
V	0.5
Zn	< 10
Zr	< 1

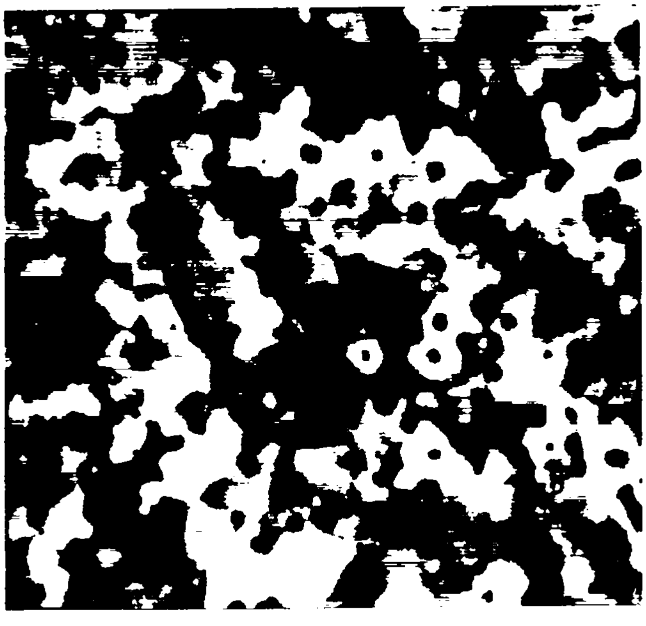

Fig. 5. PuN starting material.

only sample ions observed were Pu^+ and N_2^+. Thus any PuN^+ present would have constituted less than 2 percent of the sample signal.

In the usual manner, the ion current of the $^{239}Pu^+$ signal was monitored as a function of temperature to yield the least-squares equation

$$\log_{10} (IT) = (20.229 \pm 0.054) - \frac{21958 \pm 98}{T^{o}K} \qquad (11)$$

where the quoted uncertainties are the standard deviations generated by the least-squares program.

When the ion current data for Au and Pu and the vapor pressure data for Au at 1813°K were combined as described in section 3.4 above, the machine constant K_{Pu} was calculated to be 1.61×10^{-14} atm amp^{-1} deg K^{-1}. From a combination of Eqs. (5) and (11) one obtains for the partial pressure of Pu above solid PuN

$$\log_{10} P_{Pu} \text{ atm} = (6.436 \pm 0.055) - \frac{21958 \pm 98}{T^{o}K} \quad . \qquad (12)$$

This equation leads to an enthalpy of formation of Pu(g) above PuN(s) of $\Delta H_{1813} = 100.48 \pm 0.45$ kcal. $mole^{-1}$.

If PuN decomposes to the elements, then one would expect that approximately the same enthalpy of formation should be obtained for N_2(g) above solid PuN as was obtained for gaseous Pu. Because the N_2 background peak was large, it was difficult to obtain quantitative data for the N_2 partial pressure. However, 7 points were obtained by monitoring the ion current of the $^{28}N_2^+$ signal as a function of temperature. The enthalpy obtained was

$$\Delta H^{o}_{1848} = 99.5 \pm 3.9 \text{ kcal. mole}^{-1} \quad .$$

Metallographic, chemical, and x-ray diffraction analyses of the PuN residues indicated the residues to be single phase, with the stoichiometry $PuN_{0.96}$ to $PuN_{0.98}$ and an average lattice parameter of 4.9055 ± 0.0003 Å. Typical metallographic results as shown in Fig. 6 indicated that no free Pu or Pu oxide existed in the residue. As expected, the grain size of the PuN material increased during the vaporization process. The Pu partial pressure values obtained as a function of temperature were reproducible when points were repeatedly taken at successively increasing and decreasing temperatures. These observations, together with the measured enthalpies of formation of gaseous Pu and N_2 above solid PuN, lead one to conclude that in the temperature range of this investigation PuN decomposes invariantly according to the reaction

$$PuN(s) = Pu(g) + \tfrac{1}{2} N_2(g) \qquad (13)$$

with an enthalpy of reaction of $\Delta_{1813} = 150.7 \pm 0.6$ kcal. $mole^{-1}$.

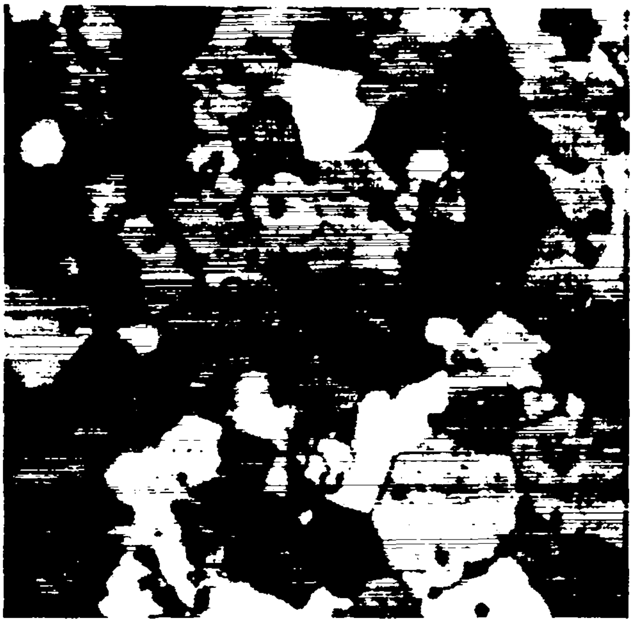

Fig. 6. PuN residue.

In order to correct this value to 298°K one needs reliable heat capacity values for Pu(g), N_2(g), and PuN(s). Unfortunately no such data exist for solid PuN. The heat capacity of PuN(s) was estimated to be 12.44 eu at 298°K from a combination of values of C^{o}_{p298} listed for UN(s),(27) U(s),(2) and Pu(s).(13) The value of C^{o}_{p298} obtained for PuN(s) was greater than that listed for UN(s)(27) by 8.8 percent. This ratio of $C_p(PuN)/C_p(UN)$ was assumed to hold over the temperature range of this study. The value of S^{o}_{298} for PuN(s) was estimated to be 16.3 ± 0.5 eu from a comparison of the values listed for UN(s),(28) U(s)(2) and Pu(s).(13) The thermodynamic functions employed in this work are listed in Table VI.

When the value of $(H^{o}_{T} - H^{o}_{298})$ for PuN from Table VI is combined with those for Pu(g)(10) and N_2(g),(29) the enthalpy of the decomposition reaction is calculated to

Table VI

Thermodynamic Functions for PuN

Temp., ^oK	C_P^o eu	$H_T^o - H_{298}^o$ cal. $mole^{-1}$	S_T^o eu	$-\left(F_T^o - H_{298}^o\right)/T$ eu
298	12.44	0	16.30	16.30
300	12.44	22	16.48	16.41
400	12.72	1257	19.93	16.79
500	13.05	2501	22.71	17.71
600	13.39	3778	25.03	18.73
700	13.77	5102	27.07	19.78
800	14.19	6474	28.91	20.82
900	14.62	7901	30.58	21.80
1000	15.09	9382	32.14	22.76
1100	15.56	10918	33.61	23.68
1200	16.08	12512	35.00	24.57
1300	16.61	14164	36.32	25.42
1400	17.17	15908	37.58	26.22
1500	17.73	17641	38.80	27.04
1600	18.33	19465	39.98	27.81
1700	18.94	21349	41.12	28.56
1800	19.56	23289	42.23	29.29
1900	20.22	25290	43.21	30.00
2000	20.88	27249	44.23	30.66
Estimated Error at				
298	3%	—	5%	5%
2000	30%	—	15%	15%

---

be $\Delta H_{298}^o = 156.19 \pm 0.81$ kcal. $mole^{-1}$.

The vapor pressure data are presented in Fig. 7.

4.4 Third Law Enthalpy of Decomposition

If the decomposition reaction is that indicated by Eq. (13), then the nitrogen partial pressure is given by

$$P_{N_2} = \frac{1}{2} P_{Pu}\left(M_{N_2}/M_{Pu}\right)^{\frac{1}{2}} \qquad (14)$$
$$= 0.171 \; P_{Pu}$$

where M is the molecular weight of a given gaseous species. The equilibrium constant for the decomposition reaction is then given by

$$K_{eq} = P_{Pu} \, P_{N_2}^{\;\;1/2} \qquad (15)$$
$$= 0.4135 \; P_{Pu}^{\;\;3/2} \quad .$$

When the values of K_{eq} are combined with the free energy functions for PuN from Table VI and those for $N_2(g)$(29) and Pu(g),(10) the third law enthalpy for the decomposition reaction is calculated to be $\Delta H_{298}^o = 156.13 \pm 0.25$ kcal. $mole^{-1}$. The third law data are presented in Table VII.

4.5 Weight Loss Measurement

In order to check the absolute pressure measurement involving calculated ionization cross section values and an estimated ionization potential for Pu, the vapor pressure was measured in the following manner. A PuN pellet was loaded into a degassed W Knudsen cell and degassed for 2 hours at 1700°C in vacuum. The cell and pellet were then weighed and inserted into the mass spectrometer. The cell was heated to a constant temperature and the ion current of the $^{239}Pu^+$ signal was monitored as a function of time. At the termination of the run,

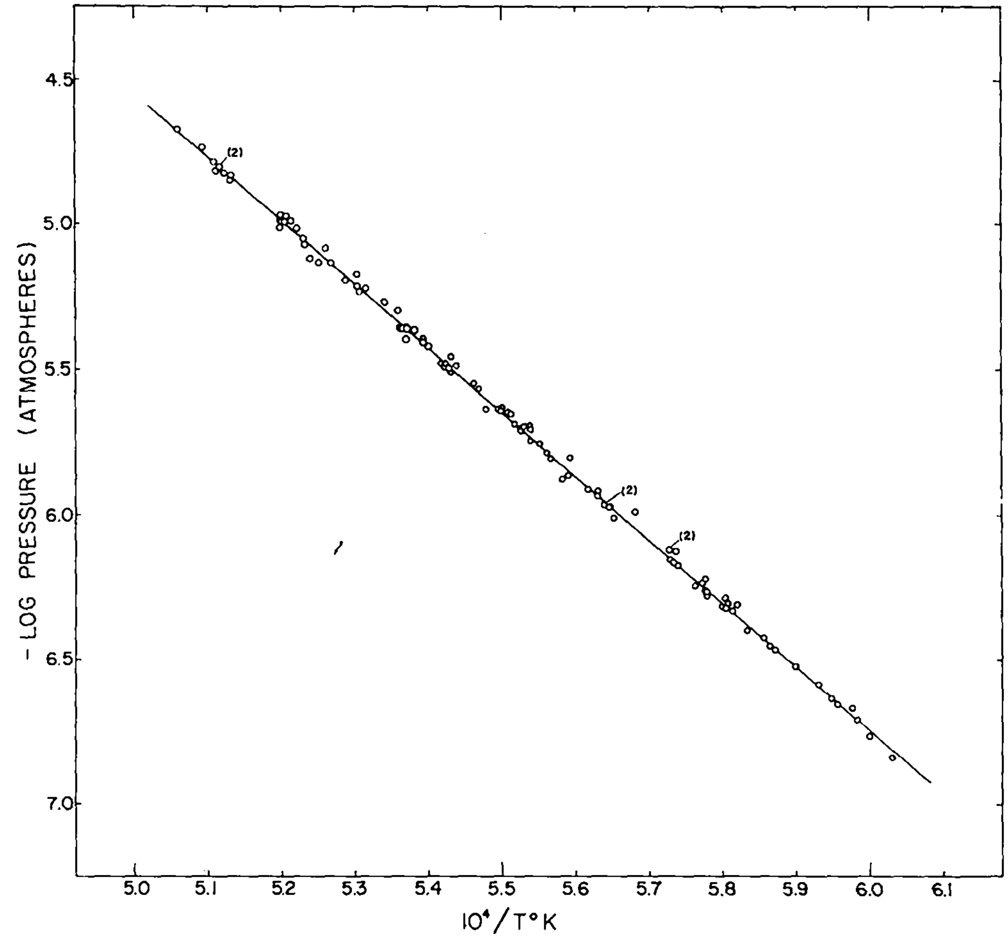

Fig. 7. Vapor pressure data for Pu(g) above solid PuN.

the cell and pellet were weighed and the value of the effective vapor pressure, P_E, was calculated from the Knudsen equation

$$P_E(\text{atm}) = \frac{0.022557\, w}{S_o\ t\ W_o}\left(T/M\right)^{\frac{1}{2}} . \qquad (16)$$

In Eq. (16), w is the amount of material in grams of molecular weight M, which effuses through an orifice of area S_o and Clausing factor W_o in a time t at a temperature T. For this run, 1.59×10^{-2} g effused through an orifice of area 8.1×10^{-3} cm^2, with a Clausing factor of 0.9956, in 12.9×10^3 sec at a temperature of 1911°K. Assuming the vapor to be PuN, M is 253 and from Eq. (16) one calculates P_E to be 9.76×10^{-6} atm. The Pu partial pressure may be calculated from the value of P_E through the relationship

$$P_E = P_{Pu}\left(M_{PuN}/M_{Pu}\right)^{\frac{1}{2}} . \qquad (17)$$
$$= 1.029\ P_{Pu}$$

The partial pressure of Pu was found to be 9.49×10^{-6} atm at 1911°K, in good agreement with the value 8.83×10^{-6} atm calculated from Eq. (12) for the same temperature. The Pu partial obtained in this run leads to a third law value of $\Delta H^o_{298} = 155.9$ kcal. mole^{-1} for the decomposition reaction, in excellent agreement with the value listed in Table VII. The intensity of the $^{239}Pu^+$ signal remained constant throughout the duration of the run, indicating the vaporization process to be an

Table VII

Vaporization Data for PuN

Pt.	Temp., ^oK	P_{Pu}, atm × 10^6	P_{N_2}, atm × 10^7	ΔF_T kcal. mole^{-1}	$-\Delta\left(F^o_T - H^o_{298}\right)/T$ eu	ΔH^o_{298} kcal. mole^{-1}
I - A1[a]	1742	0.676	1.16	76.84	45.52	156.1
I - A2	1731	0.608	1.04	76.89	45.53	155.7
I - A3	1723	0.516	0.882	77.38	45.55	155.9
I - Ar	1718	0.490	0.838	77.43	45.56	155.7
I - A5	1725	0.481	0.823	77.83	45.55	156.4
I - A6	1705	0.354	0.605	78.50	45.58	156.2
I - A7	1819	2.31	3.95	73.56	45.39	156.1
I - A8	1814	2.20	3.76	73.61	45.40	156.0
I - A9	1812	2.07	3.54	73.86	45.39	156.1
I - A10	1794	1.57	2.68	74.61	45.43	156.1
I - A11	1796	1.56	2.67	74.75	45.43	156.3
I - A12	1776	1.17	2.00	75.44	45.46	156.2
I - A13	1745	0.703	1.20	76.76	45.52	156.2
I - A14	1730	0.540	0.923	77.45	45.54	156.2
I - A15	1843	3.32	5.68	72.54	45.35	156.1
I - A16	1851	3.78	6.46	72.13	45.34	156.1
I - A17	1805	2.00	3.42	73.77	45.41	155.7
I - A18	1801	1.77	3.03	74.26	45.41	156.0
I - A19	1771	1.07	1,83	75.69	45.46	156.2
I - A20	1732	0.584	0.999	77.16	45.54	156.0
I - B1	1789	1.37	2.34	75.14	45.44	156.4
I - B2	1780	1.22	2.09	75.37	45.46	156.3
I - B3	1854	3,92	6.70	72.06	45.34	156.1
I - B4	1885	6.07	10.4	69.52	45.28	156.2
I - B5	1863	4.35	7.44	71.82	45.31	156.2
I - B6	1891	6.38	10.9	70.74	45.34	156.5
I - B7	1911	8.41	14.4	69.92	45.25	156.6
I - B8	1915	9.57	16.4	69.34	45.24	156.2
I - B9	1952	15.0	25.6	68.07	45.20	156.3
I - B10	1869	5.00	8.55	71.28	45.31	156.0
I - B11	1918	10.2	17.4	69.09	45.23	155.8
I - B12	1920	10.6	18.1	68.93	45.23	155.8
I - B13	1956	15.2	26.0	68.13	45.19	156.5
I - B14	1900	8.23	14.1	69.65	45.26	155.6
I - B15	1854	3.97	6.79	71.99	45.34	156.0
I - B16	1815	2.24	3.83	73.56	45.40	156.0
I - C1	1885	6.69	11.4	70.27	45.28	155.6
I - C2	1923	10.7	18.3	68.98	45.23	156.0
I - C3	1954	15.7	26.8	67.86	45.18	156.1
I - C4	1963	18.3	31.3	67.27	45.18	156.0
I - C5	1954	15.7	26.8	67.86	45.18	156.1
I - C6	1921	10.2	17.4	69.21	45.24	156.1
I - C7	1976	21.4	36.6	66.81	45.16	156.0
I - C8	1840	3.30	5.64	72.46	45.36	155.9
I - C9	1841	3.48	5.95	72.20	45.35	155.7
I - C10	1858	4.29	7.34	71.72	45.32	155.9
I - C11	1884	5.90	10.1	70.93	45.28	156.2

Table VII continued

Pt.	Temp., ^oK	P_{Pu}, atm × 10^6	P_{N_2}, atm × 10^7	ΔF_T kcal. $mole^{-1}$	$-\Delta\left(F^o_T - H^o_{298}\right)/T$ eu	ΔH^o_{298} kcal. $mole^{-1}$
II - A1	1723	0.479	0.819	77.78	45.55	156.3
II - A2	1708	0.378	0.646	78.29	45.58	156.2
II - A3	1686	0.262	0.448	79.12	45.63	156.1
II - A4	1671	0.197	0.337	79.84	45.67	156.2
II - A5	1673	0.216	0.369	79.47	45.66	155.9
II - A6	1703	0.343	0.587	78.56	45.59	156.2
II - A7	1722	0.489	0.836	77.61	45.55	156.0
II - A8	1746	0.764	1.31	76.37	45.51	155.8
II - A9	1746	0.764	1.31	76.37	45.51	155.8
II - A10	1720	0.469	0.802	77.74	45.55	156.1
II - B1	1791	1.33	2.27	75.38	45.44	156.8
II - B2	1773	1.01	1.73	75.71	45.47	156.3
II - B3	1743	0.750	1.28	76.32	45.52	155.7
II - B4	1730	0.530	0.906	77.56	45.54	156.3
II - B5	1768	0.975	1.67	76.04	45.47	156.4
II - B6	1825	2.32	3.97	73.77	45.38	156.6
II - B7	1830	2.83	4.84	72.91	45.37	155.9
II - B8	1845	3.27	5.59	72.69	45.35	156.4
II - B9	1828	2.74	4.69	73.01	45.37	156.0
II - B10	1805	1.80	3.08	74.35	45.41	156.3
II - B11	1744	0.687	1.17	76.84	45.51	156.2
II - B12	1841	3.10	5.30	72.85	45.35	156.3
II - B13	1860	4.32	7.39	71.74	45.32	156.0
II - B14	1861	4.38	7.49	71.70	45.33	156.1
II - B15	1844	3.21	5.49	72.76	45.35	156.4
II - B16	1798	1.63	2.79	74.58	45.42	156.2
II - B17	1771	1.01	1.73	75.69	45.46	156.2
II - B18	1735	0.572	0.978	77.38	45.53	156.4
II - B19	1714	0.398	0.681	78.30	45.55	156.4
II - B20	1681	0.232	0.397	79.51	45.64	156.2
II - B21	1679	0.221	0.378	79.63	45.65	156.3
II - B22	1664	0.172	0.294	80.19	45.68	156.2
II - B23	1658	0.145	0.248	80.74	45.70	156.5
II - C1	1760	1.00	1.71	75.45	45.48	155.5
II - C2	1805	1.98	3.39	73.82	45.41	155.8
II - C3	1808	2.03	3.47	73.82	45.40	155.9
II - C4	1843	3.52	6.02	72.21	45.35	155.8
II - C5	1903	7.35	12.6	70.39	45.26	156.5
II - C6	1898	7.35	12.6	70.21	45.26	156.1
II - D1	1861	3.99	6.82	72.23	45.33	156.6
II - D2	1924	10.3	17.6	69.26	45.23	156.3
II - D3	1923	9.66	16.5	69.57	45.23	156.6
II - D4	1908	7.57	12.9	70.41	45.25	156.7
II - D5	1864	4.44	7.59	71.88	45.33	156.4
II - D6	1809	1.98	3.39	73.99	45.41	156.1
II - D7	1773	1.01	1.73	75.67	45.47	156.3
II - D8	1727	0.540	0.923	77.34	45.54	156.0
II - D9	1693	0.289	0.494	78.98	45.61	156.2
II - E1	1817	2.28	3.90	73.57	45.39	156.0
II - E2	1872	5.37	9.18	70.99	45.31	155.8
II - E3	1921	10.0	17.1	69.21	45.24	156.1

Table VII continued

Pt.	Temp.,	P_{Pu}, atm × 10^6	P_{N_2}, atm × 10^7	ΔF_T kcal. mole^{-1}	$-\Delta\left(F^o_T - H^o_{298}\right)/T$ eu	ΔH^o_{298} kcal. mole^{-1}
II - E4	1949	14.7	25.1	68.06	45.20	156.2
II - E5	1957	16.3	27.9	67.73	45.19	156.2
II - E6	1947	14.1	24.1	68.26	45.20	156.3
II - E7	1912	8.91	15.2	69.62	45.24	156.1
II - E8	1881	5.93	10.1	70.78	45.29	156.0
II - E9	1838	3.28	5.61	72.42	45.36	155.8
II - E10	1818	2.31	3.95	73.52	45.39	156.0
II - E11	1776	1.02	1.74	75.25	45.46	156.0
					Av =	156.13±0.25

[a] Points for all runs normalized for changes in multiplier gain.

invariant one.

4.6 Solubility of Pu in PuN

In two experiments a mixture of Pu metal and PuN (10 weight percent Pu metal) was heated in a W Knudsen cell, and the ion current of the $^{239}Pu^+$ species was monitored as a function of temperature in the usual manner. In the temperature range 1544 - 1635°K, the second and third law enthalpies of formation of Pu(g) obtained were $\Delta H^o_{298} = 82.6 \pm 1.4$ kcal. mole^{-1} and $\Delta H^o_{298} = 83.2$ kcal. mole^{-1}, respectively, in excellent agreement with the value $\Delta H^o_{298} = 83.0 \pm 0.5$ kcal. mole^{-1} listed in section 3.6 for the vaporization of Pu metal. From this one concludes that, in the temperature range covered, the solubility of N or PuN in Pu(ℓ) is negligible.

4.7 Discussion of Results

From the evidence presented above we conclude that PuN decomposes invariantly to the gaseous elements in the temperature range 1600-2000°K. Within the limits imposed by the accuracy of the chemical analyses we conclude that the decomposition process is congruent within this temperature range. Evidence from other studies, however, indicates that, at higher temperatures, there is a tendency to form Pu(ℓ) rather than gaseous Pu. Olson and Mulford(15) report that in a nitrogen atmosphere, the change over in mechanism occurs at 2650°K. Leary et al. (30) report that when PuN is heated to above 2400°K, they find free Pu at the specimen surface, at grain boundaries, and uniformly throughout the grain interiors, indicative of precipitation during cooling. Thus, it is likely that, at temperatures above 2200°K, there is a considerable solubility of Pu in PuN and that this solubility increases with increasing temperature.

The second and third law enthalpies obtained above for the decomposition reaction are in excellent agreement and the uncertainties generated by the least-squares program are small. The true error in the enthalpy, however, may be much larger owing to uncertainties in the temperature measurement, the estimated ionization potential of Pu, the ionization cross sections employed, and most of all in the estimated thermodynamic functions for PuN. The lack of a significant temperature dependent trend when the third law enthalpy is graphed vs temperature as in Fig. 8 indicated, however, that the estimated thermodynamic functions for PuN are less inaccurate than might be expected.

The standard enthalpy for the decomposition of PuN is taken to be $\Delta H^o_{298} = 156.1 \pm 2.5$ kcal. mole^{-1}.

4.8 The Standard Enthalpy of Formation of PuN

When the enthalpy of the decomposition reaction, $\Delta H^o_{298} = 156.1 \pm 2.5$ kcal. mole^{-1}, is combined with the standard enthalpy of vaporization of Pu, $\Delta H^o_{298} = 83.0 \pm 0.5$ kcal. mole^{-1}, one obtains the standard enthalpy of formation of solid PuN, $\Delta H^o_{f298} = -73.1 \pm 3.0$ kcal. mole^{-1}.

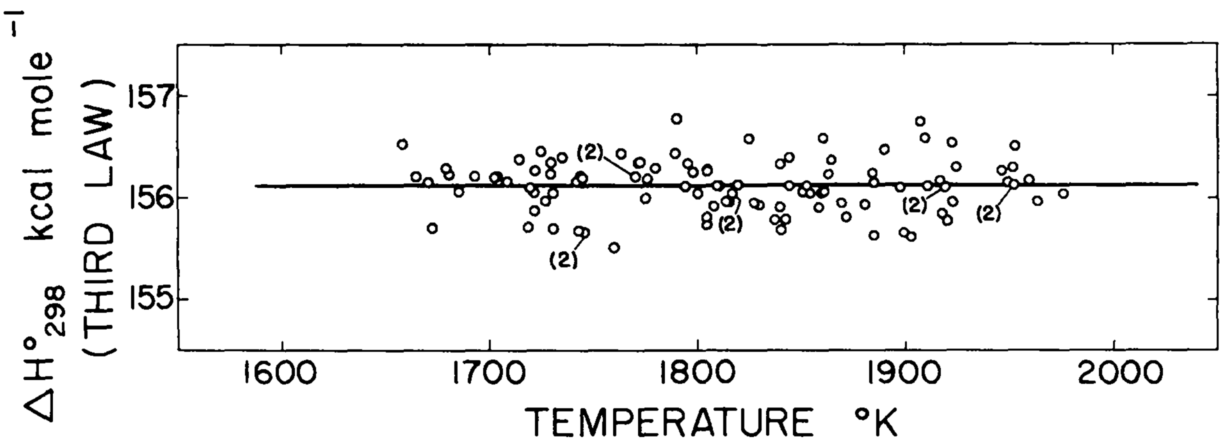

Fig. 8. The third law enthalpy vs temperature for the reaction $PuN(s) = Pu(g) + 0.5\ N_2(g)$.

4.9 An Approximation of the Partial Pressure of Gaseous PuN

Although no gaseous PuN was observed in the temperature range of this study, one may calculate an approximate value for its partial pressure. Gingerich(24) has determined that for UN(g) the dissociation energy is $D_0^0 = 126.0 \pm 5.0$ kcal. mole^{-1} and from this has estimated, based on the method of Colin and Goldfinger, (31) $D_0^0 = 112 \pm 15$ kcal. mole^{-1} for gaseous PuN. From this we calculate $D_{298}^0\ (PuN) = D_0^0 + (3R/2)(298) \approx 113$ kcal. mole^{-1}. When this value is combined with the enthalpy of vaporization of Pu and the dissociation energy of $N_2(g)$,(29) we obtain 82 ± 20 kcal. mole^{-1} for the enthalpy of formation of PuN(g) at 298°K. This value when combined with the enthalpy of formation of PuN(s) yields an enthalpy of sublimation at 298°K of 155 ± 25 kcal. mole^{-1}.

An approximate value for the free energy function for PuN(g) at 2000°K may be obtained by combining the functions at 2000°K for gaseous ZrN,(29) Zr(29) and Pu.(10) The value so obtained, -64.9 eu when combined with the free energy function of PuN(s) from Table VI, yields a Δ fef at 2000°K of -34 eu for the reaction

$$PuN(s) = PuN(g) \tag{18}$$

From a combination of the free energy functions for PuN(s) and PuN(g) and the enthalpy of sublimation of PuN, one calculates that the partial pressure of PuN(g) above PuN(s) at 2000°K is 2×10^{-10} atm (± 100%). From Eq. (12), the partial pressure of Pu above PuN is 2.86×10^{-5} atm at the same temperature. Thus, at 2000°K, the ratio of the partial pressure of PuN(g) to that of Pu(g) is of the order of 7×10^{-6}. From this, we conclude that at any temperature below 2000°K the partial pressure of PuN(g) will contribute a negligible amount of the total pressure of the system.

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