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Thermodynamic Properties of PuN
by Galvanostatic Potential Determination

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George M. Campbell

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ABSTRACT

The emf of the cell

has been determined over the temperature range 714 to 1032°K. By using a W microelectrode, the equilibrium potential of the Pu(s, ℓ) electrode was determined by a galvanostatic technique, avoiding the complications rising from reaction of N₂ with Pu. Over this temperature range, at 1 atm N₂ the emf is

$$E = 7.90071 - 2.31690 \times 10^{-2} T + 2.517855 \times 10^{-5} T^2 \\ - 9.1644 \times 10^{-9} T^3 (\pm 0.003) \text{ volts}$$

Above the melting point of Pu (913°K) the standard free energy of formation of PuN is

$$-\Delta G_T^\circ = 73.8 - 0.0225 T \text{ kcal/mole PuN}$$

From the condition $S_{298}^\circ(\text{PuN}) - S_{298}^\circ(\text{Pu}) = S_{298}^\circ(\text{UN}) - S_{298}^\circ(\text{U})$ the estimate $-\Delta H_{298}^\circ = 72.5 \text{ kcal/mole}$ is made.

INTRODUCTION

As the result of being a possible nuclear reactor fuel, PuN has been the object of several recent studies which were designed to produce information on its physical and thermodynamic properties. Emf measurements have previously been made in this laboratory by an indirect method.⁽¹⁾ Since the technique involved the use of a liquid junction and a solid Pu electrode, it was possible to make these measurements only over a very limited temperature range. More recently a technique has been developed which has made it possible to eliminate the liquid junction and otherwise minimize the technical difficulties which had existed. Rather than depend on a semipermanent reference electrode, this technique makes use of a W microelectrode upon which Pu³⁺ is

reduced to Pu by passing a constant current between the W microelectrode and third electrode. By reversing the current, the Pu is immediately reoxidized. The entire time for reduction and oxidation is completed in a few seconds. Since the concentration of Pu³⁺ at the microelectrode surface is a function of electrolysis time and current, the desired potential is obtained by making use of diffusion theory and monitoring the potential between the microelectrode and the PuN electrode. It is necessary, of course, to assume that the activity of Pu metal reduced onto the W electrode is the same as that of a semipermanent Pu electrode. This is not true at times near the beginning of the reduction process or the end of the oxidation process. Experiments

in which a semipermanent Pu electrode was used as a reference indicated, however, that this condition was met during the stripping process as the Pu^{+3} concentration gradient approached zero for stripping times of 1 sec or longer. The microelectrode used in these experiments was a W wire 0.04 cm diam dipping about 1 cm into the melt. The thermal emf of Ta vs W was determined by placing two electrodes in position and substituting Al metal (mp 659.7) for the electrolyte.

Spectroscopically pure N_2 gas at a carefully measured pressure was maintained in the cell at all times during the experiments. The temperature of the cells ranged from 714 to 1032°K. Although N_2 gas is known to react with Pu at these temperatures, it was possible to measure the extent of this reaction by stripping the PuN formed on the electrode after having stripped the Pu. Since the number of electrons per equivalent of Pu and of PuN is the same, the total Pu reduced was easily accounted for. The amount of PuN produced during the period of an average scan time was negligible at temperatures below about 1000°K. Above this temperature significant amounts of PuN was produced, as was indi-

versa, and (c) a reference electrode at equilibrium with the electrolyte and undisturbed by the passage of a current. While a direct current of constant magnitude is passed through the circuit formed by the current source, the microelectrode, and the counter electrode, the emf between the microelectrode and the reference electrode is measured as a function of time and recorded. The potential of the microelectrode is a function of the activities of the reduced and oxidized forms of the electroactive species at the electrode surface. As one of these forms is depleted to an activity approaching zero, a break is observed in the potential versus time trace.

The object here is to determine the emf of Pu metal in equilibrium with Pu^{+3} in solution at a time when the Pu^{+3} activity is equal to the Pu^{+3} activity in equilibrium with a semipermanent PuN electrode. In this case the semipermanent PuN electrode is made the reference electrode. First, Pu^{+3} is reduced onto the microelectrode by electrolysis with a current of constant magnitude. At a planar electrode the concentration of Pu^{+3} decreases during reduction, assuming no other reducible species present, and is given by⁽³⁾

$$C(x, t_1) = C^0 - \frac{2 i_1 t_1^{1/2}}{3FD^{1/2}\pi^{1/2}} \exp\left(-\frac{x^2}{4Dt_1}\right) + \frac{i_1 x}{3FD} \operatorname{erfc}\left(\frac{x}{2D^{1/2}t_1^{1/2}}\right) \quad (I)$$

cated by the chronopotentiometric trace.

Galvanostatic Potential Determination

The electrochemical technique often referred to as chronopotentiometry or the galvanostatic technique has been used most frequently for the determination of diffusion coefficients of electroactive species in a liquid or in the determination of its concentration. Since the technique is described adequately in the literature,⁽²⁾ a complete explanation will not be given here. Three electrodes are involved when using the technique: (a) a microelectrode at which the electroactive species is reduced or oxidized, also called the working electrode, (b) a counter electrode through which the current is passed to complete the circuit with the microelectrode, serving as the anode when the microelectrode is the cathode and vice

For a definition of symbols see Appendix A.

An expression for the concentration after current reversal is arrived at by using Eq. (I) and the relation

$$D\left(\frac{\partial C}{\partial x}\right)_{x=0} = -\frac{i_2}{3F} \quad (II)$$

as boundary conditions for Ficks second law *

$$\frac{\partial C}{\partial t_2}(x, t_2) = D \frac{\partial^2 C}{\partial x^2}(x, t_2) \quad (III)$$

* See Appendix B for the development of Eq. (IV).

This results in the relation

$$C_{(0, t_2)} = C^0 - \frac{2}{3FD^{1/2}\pi^{1/2}} \left(i_1 t_1^{1/2} - i_1 t_2^{1/2} - i_2 t_2^{1/2} \right) \quad (IV)$$

The times of electrolysis of Pu^{+3} during reduction can be measured by observing the break in the potential time trace. To avoid the possibility of a difference in the current efficiency during the two processes, the relationship

$$i_1 t_1 = i_2 T_2 \quad (V)$$

is used. The only assumption necessary is that all the Pu^{+3} plated out is subsequently stripped from the electrode. Combining Eqs. (IV) and (V), the concentration during the stripping process is then

$$C_{(0, t_2)} = C^0 - \frac{2 i_2}{3FD^{1/2}\pi^{1/2}} \left(\frac{T_2}{t_1^{1/2}} - \frac{T_2 t_2^{1/2}}{t_1} - t_2^{1/2} \right) \quad (VI)$$

and

$$C_{(0, t_2)} = C^0$$

when

$$t_2^0 = t_1 \left(\frac{T_2}{t_1 + T_2} \right)^2 \quad (VII)$$

The foregoing equations are based on diffusion to a planar surface. The solution for the case of cylindrical diffusion has also been derived⁽⁴⁾ but is more complex and depends on a knowledge of the diffusion coefficient, D , which is a function of temperature. However, the two approaches give results in which significant differences are observed only when the volume containing the concentration gradient at the electrode surface becomes significantly different. In our case the currents used were sufficiently small (always considerably below the voltammetric diffusion limiting current) that the concentration gradient and therefore the volume containing them remained small. This was indicated by the relatively slow change of potential with time during the stripping process. The rate was usually of the order of 0.015 V/sec.

When the technique of chronopotentiometry is used

for determination of concentration, the solute concentration must approach zero at the transition time. Consequently, the volume containing the concentration gradient may be considerably different for the case of cylindrical as compared to that for planar electrodes. When the technique is used for emf determination at high temperatures, however, the solute concentration at the electrode surface need vary little from the bulk concentration. Consequently, the volume containing the concentration gradient is nearly the same for planar and for

cylindrical electrodes. This was verified experimentally by making galvanostatic determinations against a $Pu(l)$ reference electrode over the temperature range of these experiments. Agreement was always within ± 0.002 V. Stripping times used were between 1 and 2.3 sec. Electrodeposition times were between 3 and 7 sec.

EXPERIMENTAL

Equipment

1. Apparatus and Materials

The cell used for emf determinations is diagrammed in Fig. 1. The quartz container was surrounded by an electrically grounded nickel tube to provide shielding against stray electric fields. The quartz container, 18 in. deep and 1-7/8 in. in diam, was positioned so that the lower 9 in. were inside the tube furnace. A Cu cooling coil placed around the container above the furnace kept the cell top at a moderate temperature at all times.

The electrolyte was contained in a Ta cup 2.5 in. deep and 1.5 in. in diam.

The PuN reference electrode was made by clamping

Fig. 1. Emf cell.

a donut-shaped sintered pellet of PuN between W washers at the end of a Ta rod. Nitrogen content in the PuN was 0.99 atoms N to one atom Pu. X-ray powder diffraction analysis indicated that the material was single-phase PuN, with $a_0 = 4.9055 \text{ \AA}$. Spectroscopically pure N_2 was maintained at a carefully measured pressure in the cell.

The W microelectrode, or working electrode, was made by suspending a 0.04 cm diam W wire from a 3 mm i. d. quartz tube so that the wire was immersed to a depth of about 1 cm in the electrolyte. The quartz tube extended to within about 1 in. of the electrolyte and served as an electrical insulator from the other electrodes which were placed inside similar quartz tubes.

The auxiliary electrode was made by melting Pu metal into a 1/2 in. diam by 1/2 in. deep TaC-coated Ta cup attached to the end of a 1/8 in. Ta rod. In addition to serving to carry current, this electrode helped maintain the purity of the electrolyte.

A Chromel-Alumel thermocouple calibrated against the melting point of N. B. S. pure Zn and Al metal was used in all temperature measurements. The thermocouple was inserted into a 1/8 in. diam Ta tube which was closed at one end and immersed in the molten electrolyte.

Electric contacts for electrodes and thermocouples

were directed through Kovar seals at the top of the cell. This made it possible to evacuate the cell and flush it with N_2 to remove gaseous impurities.

2. Procedure

The preparation of the LiCl-KCl electrolyte has been described previously.⁽⁵⁾

All cell parts except the electrodes were assembled and outgassed overnight at 800°C . After cooling, the electrodes and electrolyte were added and the cell was repeatedly evacuated and flushed with N_2 as the temperature was slowly raised. The temperature was controlled with a Minneapolis Honeywell "Pyr-O-Vane" controller.

The emf between the PuN reference electrode and the Pu auxiliary electrode was monitored continuously on a Sargent model MR recorder. Chronopotentiograms were recorded periodically on a second Sargent model MR recorder. A constant current source of conventional design, built by the LASL instruments group, produced direct currents ranging from about 200 to $630 \mu\text{A}$ in magnitude. The current from this source was passed through a 10-ohm resistor before and after the potential vs time trace was recorded. The chart speed of the recorder during the electrolysis period was 1 in. per sec. After measuring the Pu plating and stripping periods, the time during stripping at which the Pu^{+3} concentration at the microelectrode surface was equal to the bulk concentration was calculated using Eq. VII. By bucking the recorder circuit with the potential from a Minneapolis Honeywell potentiometer until the recorder pen was located at the indicated chart position, the emf was read from the potentiometer. This made it possible to make each measurement using a standard calibrated Weston cell as a reference potential. At least three chronopotentiograms were recorded at each PuN equilibrium, with the current at a new setting each time. Regardless of the variation in plating and stripping times and in current, the measured emf usually varied less than 2 mV. In cases where the Pu plated on the microelectrode reacted to produce a significant amount of PuN, as indicated by a break in the potential time trace near the PuN reference potential, the stripping time for the PuN was added to the stripping time of Pu to arrive at the total stripping

time, T_2 .

After the emf was determined at one temperature setting, the temperature was raised or lowered by about 20° . At least 24 h was allowed for the PuN reference electrode to reach a new equilibrium.

Results

Since N_2 is known to react with Pu over the range of temperatures of these experiments, the cell reaction is properly written as

However, it is unlikely that the solubility of PuN in Pu is great enough to cause a significant difference in the emf at these temperatures. For this reason, the results will be treated as if the cell reaction were

and the schematic representation of the cell is

The results from the three cells are given in Table I. The correction for the thermal emf of Ta vs W was

$$E = -5.7240 \times 10^{-3} + 1.1966 \times 10^{-5} \times T + 2.9652 \times 10^{-9} T^2$$

Table I
Data From Pu vs PuN Emf Cells

Cell No.	Emf meas. (volts)	Temp. (°K)	Pressure (atm)	Emf cor. for thermal emf and to N_2 pressure of 1 atm
1	0.7425	950	0.720	0.7553
1	0.7450	950	0.716	0.7578
1	0.7380	968.5	0.749	0.7507
1	0.7488	968.1	0.734	0.7577
1	0.7375	987.2	0.751	0.7505
1	0.7415	986.2	0.751	0.7545
1	0.7310	1007.1	0.755	0.7444
1	0.7210	1025.9	0.755	0.7348
1	0.7295	1011.9	0.755	0.7430
1	0.7180	1031.6	0.755	0.7319
2	0.7382	954.2	0.728	0.7509
2	0.7424	944.4	0.714	0.7552
2	0.7494	929.3	0.707	0.7620
3	0.7596	846.0	0.774	0.7692
3	0.7688	827.2	0.746	0.7785
3	0.7795	810.3	0.742	0.7889
3	0.7885	792.4	0.739	0.7975
3	0.7925	775.5	0.742	0.8012
3	0.8046	753.5	0.741	0.8128
3	0.8259	734.5	0.752	0.8336
3	0.8508	713.8	0.737	0.8583
3	0.8733	698.4	0.739	0.8804
3	0.7648	830.1	0.786	0.7739
3	0.7524	865.3	0.786	0.7622

Table II
PuCl₃ Concentration

Cell #	Concentration (mole %)
1	0.338
2	0.166
3	0.112

where E is in volts and T is in $^\circ\text{K}$. Since Ta was the negative pole, the thermal emf was added to the measured galvanic emf. After correcting the N_2 pressure to one atom by using the equation

$$E_{(1 \text{ atm})} = E_{(\text{meas.})} - \frac{2.3 RT}{3F} \log p^{1/2} (\text{meas.}), \quad (\text{XI})$$

the emf is plotted vs temperature in Fig. 2. The least-squares line is represented by the equation

$$E = 7.90071 - 2.31690 \times 10^{-2} T + 2.517855 \times 10^{-5} T^2 - 9.1644 \times 10^{-9} T^3 (\pm 0.003) V \quad (\text{XII})$$

with T in $^\circ\text{K}$.

The results of previous experiments by an indirect method gave $0.8745 (\pm 0.005) V$ for the emf at 700°K . From the present experiments, the emf at this temperature is $0.8765 (\pm 0.003) V$, which is in good agreement.

The greatest phase change of Pu in this temperature range is the solid to liquid at 913°K . Since this involves only about 1 eu no change in the emf plot is detectible.

In the region of ϵ Pu ($749-913^\circ\text{K}$), a least squares analysis of the data gives

$$E = 1.1644 - 4.663 \times 10^{-4} T (\pm 0.019) V \quad (\text{XIII})$$

Fig. 2. Emf vs temperature, Eq. XII.

Fig. 3. Emf vs temperature, Eq. XIV

Above the melting point of Pu (913°K), the least-squares line from the two cells is (Fig. 3)

$$E = 1.0672 - 3.258 \times 10^{-4} T (\pm 0.003) V \quad (\text{XIV})$$

The decrease in emf with increasing temperature below the melting point of Pu is larger than can be accounted for by consideration of the known thermodynamic properties of the constituents. It seems likely that in the lower temperature range the emf includes a component that is not related to the free energy change in the Pu-N₂ reaction. This probably results because the surface of the PuN pellet is not in equilibrium with the center of the pellet.

Using the data above the melting point of Pu as

shown plotted in Fig. 2,

$$-\Delta G_T^0 = 73.8 - 0.0225 T \text{ kcal/mole} \quad (\text{XV})$$

for reaction (IX).

By combustion calorimetry, Lapage⁽⁶⁾ found $-\Delta H = 70.2 \pm 1.5$ kcal/mole at 298°K for reaction (IX). Using the UN data of Godfrey,⁽⁷⁾ the U data of Hultgren,⁽⁸⁾ the Pu data of Rand,⁽⁹⁾ and the relation

$$C_p(\text{PuN}) = C_p(\text{UN}) - C_p(\text{U}) + C_p(\text{Pu}),$$

$$(H_{1000} - H_{298}) \text{ PuN} = 8.5887 \text{ kcal/mole}$$

and

$$(S_{1000} - S_{298}) \text{ PuN} = 14.9 \text{ eu}$$

This gives $-\Delta H_{1000} = 72.35$ and is within experimental error of the intercept of Eq. XV. Eq. (XV) then leads to

$$-\Delta G_{298}^0 = 71.6 - 0.0185 T \text{ kcal/mole}$$

and $S_{298}^0(\text{PuN}) = 17.6$ eu. This compares with $S_{298}^0(\text{UN}) = 14.97$ eu. If the condition that

$$S_{298}^0(\text{PuN}) - S_{298}^0(\text{Pu}) = S_{298}^0(\text{UN}) - S_{298}^0(\text{U})$$

is used, $S_{298}^0(\text{PuN}) = 16.17$ eu and from the emf data $-\Delta H_{298}^0 = 72.5$ kcal/mole, which is within the experimental error of the determinations in this work and those in the work of Lapage.

APPENDIX A

Some definitions of symbols used in the text.

C	Concentration in moles/cm ³ .	i ₂	Current density at the electrode surface during the stripping process in amp/cm ² .
C _(x, t)	Concentration at a distance, x, from the electrode at time, t.	t ₁	Total time of electrodeposition of Pu on the microelectrode measured from the inflection in the potential time curve to the time of current reversal (sec).
C ⁰	Concentration in the bulk of the electrolyte.	t ₂	Electrode stripping time measured from the time of current reversal (sec).
D	Diffusion coefficient of depolarizing agent in cm ² /sec.	T ₂	Total electrode stripping time measured from time of current reversal until the inflection in the time vs potential plot (sec).
erfc(y)	Complement of the error function, (1-erf(y)).	t ₂ ⁰	Time at which the concentration of Pu ³⁺ at the electrode surface is equal to the concentration in the bulk of the solution.
erf(y)	$2/\pi \int_0^y \exp(-z^2) dz$		
F	Faraday's constant (96492 coulombs/equivalent).		
i ₁	Current density at the electrode surface during the reduction process in amp/cm ² .		

APPENDIX B

Eq.(IV) was derived in the following manner. The Laplace transform of Eq.(III) is⁽¹⁰⁾

$$-U(x, 0) + s\bar{U}(x, s) = D \frac{d^2 \bar{U}(x, s)}{dx^2} \quad (1)$$

By defining

$$U(x, t_2) = C(x, t_2) - C^0 + F(C, x, t_1) \quad (2)$$

where from Eq. (1)

$$F(C, x, t_1) = \frac{2i_1 t_1^{1/2}}{3FD^{1/2}\pi^{1/2}} \exp\left(-\frac{x^2}{4Dt_1}\right) - \frac{i_1 x}{3FD} \operatorname{erfc}\left(\frac{x}{2D^{1/2}t_1^{1/2}}\right) \quad (3)$$

we have for $t_2 = 0$, $U(x, 0) = 0$. Eq. 1 then has a solution of the form

$$\bar{U}(x, s) = \alpha \exp\left(-\frac{s^{1/2}x}{D^{1/2}}\right) \quad (4)$$

From Eq.(2) we have

$$\frac{\partial U(x, t_2)}{\partial x} = \frac{\partial C(x, t_2)}{\partial x} + \frac{\partial F(C, x, t_1)}{\partial x} \quad (5)$$

but

$$\left(\frac{\partial C(x, t_2)}{\partial x}\right)_{x=0} = -\frac{i_2}{nFD}$$

and the transform of (5) is

$$\left(\frac{\partial \bar{U}(x, s)}{\partial x}\right)_{x=0} = -\frac{i_1}{nFDs} - \frac{i_2}{nFDs}$$

From Eq. (4)

$$\left(\frac{\partial \bar{U}(x, s)}{\partial x}\right)_{x=0} = -\frac{s^{1/2}}{D^{1/2}} \alpha \quad (7)$$

so

$$\alpha = \frac{i_1}{nFD^{1/2}s^{3/2}} + \frac{i_2}{nFD^{1/2}s^{3/2}} \quad (8)$$

$$\bar{U}(x, s) = \left(\frac{i_1}{nFD^{1/2}s^{3/2}} + \frac{i_2}{nFD^{1/2}s^{3/2}}\right) \exp\left(-\frac{xs^{1/2}}{D^{1/2}}\right) \quad (9)$$

$$\bar{U}(0, s) = \frac{i_1}{nFD^{1/2}s^{3/2}} + \frac{i_2}{nFD^{1/2}s^{3/2}} \quad (10)$$

The transform of Eq. (10) is

$$U(0, t_2) = \frac{2i_1 t_2^{1/2}}{nFD^{1/2}\pi^{1/2}} + \frac{2i_2 t_2^{1/2}}{nFD^{1/2}\pi^{1/2}} \quad (11)$$

From Eq.(2)

$$C(0, t_2) = C^0 - \frac{2i_1 t_1^{1/2}}{nFD^{1/2}\pi^{1/2}} + \frac{2i_1 t_2^{1/2}}{nFD^{1/2}\pi^{1/2}} + \frac{2i_2 t_2^{1/2}}{nFD^{1/2}\pi^{1/2}} \quad (12)$$

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