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from EMF Measurements

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ABSTRACT

The free energy of formation of PuFe_2 was measured over the temperature range 792 to 1106°K by monitoring the emf of the cell

Transient potential methods were used to ensure reversibility and singularity of the electrode reactions. Sufficient precision was obtained to permit the calculation of thermodynamic and thermal functions at the temperature of the measurements and to make extrapolated estimates at lower temperatures.

INTRODUCTION

To utilize the great potential of the plutonium isotopes as energy sources, a knowledge of the physical properties of their compounds and alloys is essential. Many applications require containment at temperatures near 1000°K. The thermodynamic properties of a wide variety of plutonium compounds at the energy source and cladding temperatures is necessary in order to select the best materials for any particular application.

PuFe_2 is a possible source material as well as a cladding reaction component. The Pu/Fe atomic size ratio¹ is very close to the ideal ratio for its Laves-phase structure. Certain theoretical postulates,² which require further experimental verification, have been

made concerning the enthalpy of formation of such compounds.

The latest phase diagram³ of the Pu-Fe system (Fig. 1) indicates that α -Fe is in equilibrium with cubic (Strukturbericht Type C15) PuFe_2 up to 1033°K, which corresponds to the Curie temperature of α -Fe. Above this temperature, PuFe_2 has a hexagonal structure, transforming back to the cubic form at 1293°K. Solid solubility of iron in PuFe_2 is not indicated below 1140°K.

The most direct method for obtaining thermodynamic data in this temperature range is by the application of the emf method. This requires a procedure which ensures that the electrode reactions are well-defined and reversible.

Fig. 1. Plutonium-iron phase diagram.

Data obtained in this study using electrodes containing Pu-50 wt% Fe were precise enough to permit calculation of thermodynamic and thermal functions at the temperature of the measurements and extrapolation of estimates to lower temperatures. The lack of enthalpy measurements on PuFe_2 , which is reported to have a Curie temperature of 633°K ,⁴ increases the uncertainty of the extrapolated data. However, the enthalpy of formation at 298°K calculated from the emf measurements and that calculated using the sublimation energy of plutonium and its change in coordination number agree very well.

EXPERIMENTAL

The equipment and procedures for determining the potential of the anode reaction $\text{Pu} \rightarrow \text{Pu}^{3+} + 3\text{e}^-$ in fused salts which ensures reversibility and singularity of the reaction have been described previously.⁵ The singularity of the cathode reaction, $\text{Pu}^{3+} + 3\text{e}^- + \text{excess Fe} \rightarrow \text{PuFe}_2 + \text{excess Fe}$, was checked by following the potential time record after cathodic charging of the $\text{PuFe}_2 + \text{Fe}$ electrode. This technique involves shifting the potential of the cathode toward the anode by 100 to 150 mV to ensure completion of any electrochemical reactions caused by surface impurities while maintaining enough potential difference between anode and cathode to prevent a significant increase in plutonium activity. The potentiostatic charging period was terminated by switching to an open circuit after the cell current

$\text{Pu}(s, l)/\text{PuCl}_3, \text{LiCl} - \text{KCl}/\text{PuFe}_2 + \text{Fe}(s)$
at 800 to 1100°K is given by

The emf measurements are given in Table I and Fig. 2. A small, but apparently real, deviation from this line was measured as indicated at 980°K. The Curie temperature of iron is given as 1033°K.⁶ Owing to the anomalous enthalpy of iron at the Curie temperature, the free energies of formation deviate from a straight line. After calculating the free energy of formation from the relation $-\Delta G_F^0 = 3 \text{ FE}$, the other thermody-

TABLE I

EMF MEASUREMENTS ON THE CELL
 $\text{Pu}(s, \delta) / \text{PuCl}_3, \text{LiCl} - \text{KCl} / \text{PuFe}_2 + \text{Fe}(s)$

T (°K)	Emf (V)	-ΔG (kcal/mole)	T (°K)	Emf (V)	-ΔG (kcal/mole)
984.4	0.1492	10.32	833.0	0.1494	10.34
953.6	0.1489	10.30	825.4	0.1498	10.36
950.4	0.1473	10.19	850.8	0.1497	10.36
1024.7	0.1456	10.07	880.1	0.1492	10.32
1016.1	0.1460	10.06	822.8	0.1497	10.36
1039.8	0.1450	10.03	936.4	0.1483	10.26
1030.5	0.1460	10.10	954.6	0.1477	10.22
1064.1	0.1439	9.96	967.5	0.1488	10.16
1055.2	0.1450	10.03	967.8	0.1478	10.23
1070.2	0.1428	9.88	980.1	0.1507	10.43
1106.3	0.1401	9.69	972.7	0.1498	10.36
1097.3	0.1418	9.81	997.4	0.1471	10.18
1068.1	0.1436	9.83	1011.1	0.1459	10.09
925.4	0.1484	10.27	1035.4	0.1454	10.06
908.8	0.1482	10.25	1024.9	0.1481	10.11
892.3	0.1491	10.32	996.5	0.1488	10.16
876.0	0.1498	10.36	988.6	0.1472	10.18
859.9	0.1500	10.38	978.6	0.1508	10.43
845.1	0.1497	10.36	983.3	0.1501	10.38
824.2	0.1513	10.47	1033.3	0.1449	10.02
823.0	0.1517	10.50	1049.8	0.1448	10.02
792.9	0.1482	10.25	1062.0	0.1428	9.89
815.8	0.1507	10.43	1098.5	0.1420	9.82

dynamic and thermal functions given in Tables II and III were calculated using standard thermodynamic equations. The good precision and temperature reversibility of each cell were believed to justify extrapolated estimates to lower temperatures. In making these estimates, it was assumed that the anomalous enthalpy per atom of iron near to Curie temperature would be similar near the Curie temperature of PuFe_2 . The thermal properties of pure plutonium and iron given by Hultgren et al.⁶ and Rand⁷ were used in calculating the thermal properties of PuFe_2 .

Fig. 2. Emf for the cell $\text{Pu}(s, \delta) / \text{PuCl}_3, \text{LiCl} - \text{KCl} / \text{PuFe}_2 + \text{Fe}(s)$.

TABLE II

THERMODYNAMIC FUNCTIONS FOR
 THE FORMATION OF PuFe_2

T (°K)	$-\Delta H_f^\circ$ (kcal/mole)	$-\Delta S_f^\circ$ (cal/deg/mole)	$-\Delta G_f^\circ$ (kcal/mole)
298.15	11.4	0.68	11.2
400.00	12.3	2.77	11.1
500.00	12.2	2.71	10.9
600.00	11.9	2.09	10.7
620.00	11.7	1.76	10.6
633.00	11.6	1.45	10.6
640.00	11.5	1.29	10.6
660.00	11.3	0.91	10.7
680.00	11.3	0.78	10.7
700.00	11.3	0.77	10.7
800.00	11.6	1.56	10.4
900.00	11.9	1.79	10.3
1000.00	13.3	3.14	10.1
1100.00	14.0	3.83	9.79

Dehlinger and Schulze⁸ and, more recently, Kubaschewski⁹ suggested that the enthalpies of formation of the Laves phases might be estimated from the sublimation energies of the pure components and the increase in the coordination number. That this gives at least the right order of magnitude has been demonstrated for several compounds.² Using a coordination number of 14 for pure plutonium¹⁰ at 298.15°K and of 16 for plutonium in PuFe_2 , the heat of formation per mole of PuFe_2 becomes 1/7 of the sublimation energy of plutonium because there is no change in the coordination number of iron. At 298.15 the sublimation energy of plutonium is

TABLE III

THERMAL FUNCTIONS FOR PuFe_2

T (°K)	C_p (cal/deg/mole)	$H_T^\circ - H_{298.15}^\circ$ (cal/mole)	S_T° (cal/deg/mole)	$-(G_T^\circ - H_{298.15}^\circ)/T$ (cal/deg/mole)
298.15	20.5	0.0	25.5	25.6
400.00	23.3	2234.0	32.0	26.4
500.00	27.0	4747.0	37.6	28.1
600.0	34.0	7748.0	43.2	30.2
620.0	38.1	8520.0	44.3	30.8
633.0	42.7	9045.0	45.2	30.9
640.0	40.4	9336.0	45.6	31.0
660.0	33.9	10010.0	46.8	31.7
680.0	29.5	10597.0	47.8	32.2
700.0	28.1	11156.0	48.6	32.7
800.0	27.4	13838.0	52.2	34.8
900.0	28.6	16641.0	55.4	36.8
1000.0	29.8	19554.0	58.6	39.0
1100.0	30.6	22566.0	61.4	40.8

83.00 kcal/mole.¹¹ This results in $-\Delta H_{F298}^{\circ} = 11.86$ kcal/mole for the heat of formation of PuFe_2 . This agrees well with the value of $-\Delta H_{F298}^{\circ} = 11.4$ estimated from the emf data, but differs considerably from the only other experimentally determined value of $-\Delta H_{F298}^{\circ} = 6.5$ reported by Akachinski et al.¹² Owing to the complex nature of the plutonium crystal, choosing a coordination number smaller than 14 could be justified. This would result in predicting a higher change in enthalpy of formation, deviating further from both experimental values. Selecting a value of 12, for instance, leads to $-\Delta H_f^{\circ} = 27.7$ kcal/mole. Most other considerations including electronegativity and change in bond length would also seem to favor the larger enthalpy change.

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