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Los Alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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ABSTRACT

Non-stationary emf techniques were used to ensure reversibility and singularity of electrode reactions in the emf cell $\text{Pu}(l)/\text{PuCl}_3, \text{LiCl-KCl}/\text{PuRu}_2 + \text{Ru}(s)$ at temperatures between 913 and 1078°K. The free energy of formation of PuRu_2 at 1000°K was found to be $\Delta G_{1000}^\circ = -8.08 + 0.0013 T$ kcal/mole. Thermodynamic properties were estimated at lower temperatures.

I. INTRODUCTION

The intermetallic compound PuRu_2 is isostructural with PuFe_2 for which thermodynamic properties were recently determined.¹ The difference in the atomic size of Ru and Fe is the principal parameter to be related to differences in the stabilities of the two compounds. The radius ratio of Pu to Fe in PuFe_2 is 1.249 and the radius ratio of Pu to Ru in PuRu_2 is 1.188.² The ideal size ratio for strain-free packing of Laves phase structures is 1.225. Deviation from the ideal size ratio produces packing strain.

The phase diagram of the PuRu system³ indicates that the compound of highest Ru content is PuRu_2 and that this compound is in equilibrium with hcp Ru up to temperatures of about 1650°K. Since the activity of Ru

in the PuRu_2 phase is necessarily the same as the activity of hcp Ru in the free state, an emf cell can be constructed which measures the free energy of formation of PuRu_2 directly.

II. EXPERIMENTAL

Non-stationary emf techniques were used to ensure reversibility and singularity of the electrode reactions in $\text{PuCl}_3, \text{LiCl-KCl}$ fused-salt electrolyte. These techniques have been described in previous reports.^{1, 4, 5}

The Pu-Ru electrodes were made by arc-melting and casting into 1/4-in.-diam rods, a plutonium and ruthenium mixture such that the rod contained 57.7 wt% Ru. X-ray powder diffraction analysis showed the sample to be a mixture of fcc PuRu_2 with lattice dimensions of

TABLE I

SPECTROCHEMICAL IMPURITY ANALYSIS
OF PuRu_2 + Ru ELECTRODE

Element	Concentration, (ppm)	Element	Concentration, (ppm)
Al	45	Mn	2
Ba	15	Mo	< 1
Be	< 0.2	Na	6
Ca	70	Ni	< 1
Cd	< 1	Pb	< 1
Co	< 1	Re	< 1
Cr	< 1	Rb	< 1
Cs	< 4	Sn	< 1
Cu	30	Sr	< 0.2
Hf	< 1	Tl	< 0.4
K	< 1	V	< 1
La	< 2	Y	< 0.2
Li	< 2	Zn	< 10
Mg	< 2	Zr	< 0.2

$7.4737 \pm 0.0007 \text{ \AA}$ and hcp Ru. The presence of other compounds was not evident. A spectrographic impurity analysis of the PuRu_2 electrode is given in Table I.

The PuRu_2 + Ru electrode was attached to the end of a 1/8-in.-diam tantalum rod by notching and fixing in a cylindrical tantalum screw clamp.

The mole fraction of PuCl_3 in the LiCl-KCl solution was 0.00560.

III. RESULTS AND DISCUSSION

The emf for the cell

from 913°K (melting point of Pu) to 1078°K is given by the equation

$$E = 0.1141 + 2.688 \times 10^{-4}(T - T_m) + 4.0259 \times 10^{-11} T^2 + 3.1331 \times 10^{-14} T^3 (\pm 0.0005) \text{ (V)}.$$

The emf measurements are given in Table II and Fig. 1.

Since the reaction for the cell is

the free energy of formation of PuRu_2 is expressed as

$$-\Delta G_f^\circ = 3 \text{ FE}.$$

As a consequence

TABLE II

EMF MEASUREMENTS ON THE CELL
 $\text{Pu}(s, l)/\text{PuCl}_3, \text{LiCl-KCl}/\text{PuRu}_2 + \text{Ru}(s)$

T ($^\circ\text{K}$)	Emf (V)	$-\Delta G$ (kcal/mole)
881.8	0.1007	6.97
901.7	0.1005	6.95
922.4	0.0986	6.82
936.7	0.0996	6.89
954.9	0.0988	6.81
955.6	0.0998	6.90
969.1	0.0982	6.79
1002.9	0.0976	6.75
994.0	0.0985	6.81
994.6	0.0987	6.83
1013.3	0.0978	6.77
1028.1	0.0979	6.77
1077.9	0.0970	6.71
1063.3	0.0974	6.74
1041.3	0.0980	6.78
1021.3	0.0982	6.79
1000.1	0.0983	6.80
983.9	0.0979	6.77
966.3	0.0989	6.84
949.4	0.0998	6.90
934.6	0.0999	6.91
913.5	0.1009	6.98
894.9	0.1009	6.98

$$\Delta G_f^\circ = -7696.4 - 0.18598(T - T_m) - 2.7851 \times 10^{-6} T^2 - 2.1675 \times 10^{-9} T^3 (\pm 38) \text{ cal/mole}$$

$$\Delta H_f^\circ = -7896.4 - 0.18598(T - T_m) - 2.7851 \times 10^{-6} T^2 - 2.1675 \times 10^{-9} T^2 (\pm 82) \text{ cal/mole}$$

Fig. 1. Emf measurements for the cell $\text{Pu}(s, l)/\text{PuCl}_3, \text{LiCl-KCl}/\text{PuRu}_2 + \text{Ru}(s)$.

$$\Delta S_f^0 = -0.18598 \ln T + 5.5702 \times 10^{-6} T + 6.5025 \times 10^{-9} T^2 (\pm 0.2) \text{ cal/deg/mole}$$

$$\Delta C_p / -0.18598 + 5.5702 \times 10^{-6} T + 1.3005 \times 10^{-8} T^2 (\pm 0.3) \text{ cal/deg/mole}$$

where ΔG_f^0 , ΔH_f^0 , ΔS_f^0 , and ΔC_p are the Gibbs free-energy change, enthalpy change, entropy change, and heat capacity change with formation, represented by the cell reaction. T represents any temperature between 913 and 1078°K.

The heat capacity in the temperature range of the measurements can be calculated by combining data for the pure elements⁶ with ΔC_p . Below this temperature, however, pure plutonium undergoes several phase changes which are not indicated for PuRu₂. To estimate thermal functions at lower temperatures, the heat capacity of PuRu₂ was set equal to

$$C_p(\text{PuRu}_2) = C_p(\text{PuC}_{0.86}) - C_p(0.86\text{C}) + C_p(2\text{Ru}) + \Delta C_p^*$$

ΔC_p^* was calculated at the temperature of the measurements and assumed to be constant at lower temperatures. The choice of $C_p(\text{PuC}_{0.86})$ ⁷ to be used in the approximation is predicated by the limited amount of experimental data available. Since ΔC_p for most intermetallic compounds is small, the error introduced by using this method of approximation should also be small. The standard deviations indicated in the equations are a measure of the precision of the data and do not necessarily correspond to its accuracy.

TABLE III

THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF PuRu₂

T (°K)	$-\Delta H_f^0$ (kcal/mole)	ΔS_f^0 (cal/deg/mole)	$-\Delta G_f^0$ (kcal/mole)
298.15	5.32	+ 3.5	6.35
400.0	6.06	+ 1.6	6.70
500.0	6.30	+ 1.1	6.83
600.0	6.62	+ 0.5	6.94
700.0	6.80	+ 0.2	6.96
800.0	7.37	- 0.5	6.93
900.0	7.38	- 0.6	6.88
1000.0	8.06	- 1.3	6.80
1100.0	8.09	- 1.3	6.67

The thermodynamic properties based on the results of this study and their extrapolation are given in Tables III and IV. These results are to take precedence over results reported previously⁸ in which the conventional techniques did not permit analysis of electrode reactions.

As in the case of PuFe₂, the calculated enthalpy of formation based on the change in coordination number of Pu is $-\Delta H_{f238.15}^0 = 11.86$. PuFe₂ with the nearly ideal atomic ratio was found to have $-\Delta H_{f238.15}^0 = 11.4$. The results for PuRu₂ as indicated in Table III show $-\Delta H_{f238.15}^0 = 5.3$. This follows the general trend found in other compounds involving Laves phases⁹ where deviation from the ideal size ratio has been correlated with the magnitude of the enthalpy of formation.

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TABLE IV

THERMAL FUNCTIONS FOR PuRu₂

T (°K)	C _p (cal/deg/mole)	$H_f^0 - H_{298.15}^0$ (kcal/mole)	S_f^0 (cal/deg/mole)	T (°K)
298.15	20.0	0.0	30.3	298.15
400.0	20.5	2.06	30.3	31.1
500.0	21.0	4.24	30.0	32.6
600.0	21.5	6.27	29.9	34.3
700.0	21.9	8.03	29.1	36.1
800.0	22.3	10.04	28.1	37.8
900.0	22.7	12.09	26.7	39.4
1000.0	23.1	15.10	26.1	40.9
1100.0	23.4	17.90	26.3	42.4

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