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Gibbs energy of formation of $UPd_3(s)$

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Abstract

Gibbs energy of formation of $UPd_3(s)$ has been determined by measuring the equilibrium CO(g) pressure over $\{UO_2(s) + C(s) + UPd_3(s) + UPd_4(s)\}$ and is given as

$$\Delta_f G^0_m(UPd_3, s, T)\ \text{kJ mol}^{-1} \pm 4.1 = -526.9 + 0.1259\ T\ (K), \quad (1175 \leqslant T\ (K) \leqslant 1333).$$

Using the required literature data, $\Delta_f H^0_m(UPd_3,\ s,\ 298.15\ K)$ has been calculated as $-(502.3 \pm 5.1)$ kJ mol^{-1}. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In continuation of our work on U–Pd system [1], the Gibbs energy of formation of $UPd_3(s)$ is reported in this paper. Earlier, reported data on $\Delta_f G^0_m(UPd_3,s)$ include mass spectrometric work by Lorenzelli and Marcon [2]: -259 kJ mol^{-1} at 1673 K, fluorine bomb calorimetry [3]: -527 kJ mol^{-1} at 1673 K and drop calorimetry [4]: -530 kJ mol^{-1} at 1200 K. Burriel et al. [4] have given $\Delta_f S^0_m(UPd_3,s)$ as 7.0 J K^{-1} mol^{-1} at 298.15 K which is quite small and thus $\Delta_f G^0_m(T)$ and $\Delta_f H^0_m(T)$ are quite close. However, the enthalpy of formation of $UPd_3(s)$ measured by direct reaction calorimetry is $-(295 \pm 3)$ kJ mol^{-1} at 298.15 K [5]. Most recently, Kleykamp and Kang [6] have reported $\Delta_f G^0_m(UPd_3,s)$ as $-(312 \pm 16)$ kJ mol^{-1} at 1323 K from their study on the U–Pd–Sn system. Thus, it seems that the Gibbs energy of formation of $UPd_3(s)$ has a large scatter, suggesting further work on this system. In the present work, equilibrium CO(g) pressures over $\{UO_2(s) + C(s) + UPd_3(s) + UPd_4(s)\}$ mixture have been used to calculate the Gibbs energy of formation of $UPd_3(s)$. The phase diagram on U–Pd system, as reported by Kleykamp and Kang [7], shows that $UPd_3(s)$ co-exists with $UPd_4(s)$. Increasing uranium content of $UPd_4(s)$ by reacting it with $\{UO_2(s) + C(s)\}$ mixture, will give rise to $UPd_3(s)$ and CO(g) making it a convenient method for the determination of $\Delta_f G^0_m(UPd_3,T)$ by measuring equilibrium CO(g) pressures.

2. Experimental

2.1. Preparations

$UPd_3(s)$ and $UPd_4(s)$ were prepared by arc melting of high purity (99.99 mass percent) uranium and palladium metals. $UPd_4(s)$ was made with 21.6 at.% U(s) while $UPd_3(s)$ was made stoichiometric. These compounds were annealed in vacuum-sealed quartz capsules at 1323 K for 100 h before use. The powdered X-ray diffraction (XRD) patterns were taken on a DIANO X-ray diffractometer using nickel filtered Cu K_α ($\lambda = 0.15418$ nm) radiation. The room temperature XRD pattern of powdered $UPd_3(s)$ is given in Fig. 1 and Table 1. The lattice parameters of $UPd_3(s)$ (hexagonal, $TiNi_3$ type) are computed to be: $a = 577.5$ pm and $c = 965.4$ pm and that for $UPd_4(s)$ (fcc structure, $AuCu_3$ type) is computed to be: $a = 404.7$ pm [1]. These cell constants match very well with those reported by Kleykamp and Kang [7].

2.2. CO(g) pressure over $\{UO_2(s) + C(s) + UPd_4(s) + UPd_3(s)\}$

An all-metal ultra-high vacuum system used in our earlier work [1], was employed in the present study.

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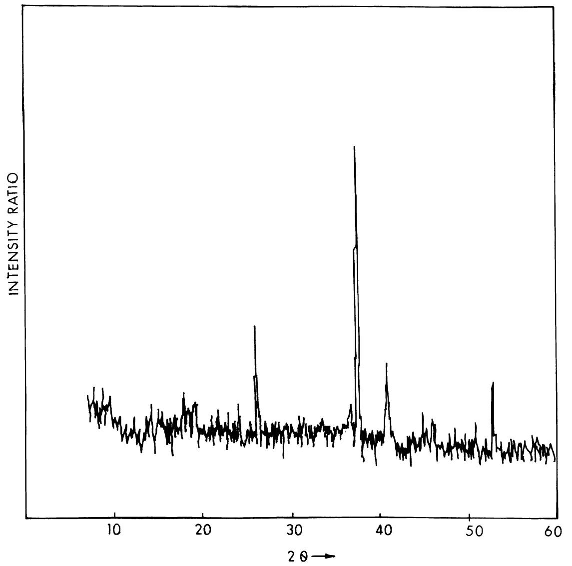

Fig. 1. X-ray diffraction pattern of $UPd_3(s)$. Intensity is plotted against 2Θ where Θ is the diffraction angle.

Table 1
X-ray dffraction patterns of $UPd_3(s)$

Observed *d* values in pm	Relative intensity	*h k l*
347.32	54	1 0 2
240.97	100	0 0 4
221.62	42	2 0 2
173.66	36	2 0 4

$UO_2(s)$, graphite, $UPd_4(s)$ and $UPd_3(s)$ all in powder form, were intimately mixed. $UPd_4(s)$ was taken in excess in order to maintain equilibrium phase field during the reaction. These pellets were loaded in to a quartz reaction tube and attached to the vacuum system for CO(g) pressure measurements. The assembly was evacuated and tested for leak tightness for several days before actual pressure measurements. The sample was heated by a Kanthal wire-wound furnace and the temperature of the sample was maintained to within ±1 K. The temperature of the sample was measured using a calibrated chromel-to-alumel thermocouple. A absolute pressure transducer supplied by Edwards, USA, measured the CO(g) pressures. The accuracy of the transducer is ±0.25% of the reading. An equilibrium time of 5–6 days was generally required for each measurement. Evacuating a small amount of CO(g) and allowing the equilibrium to be reestablished again checked the attainment of equilibrium. The measurements were carried out in the temperature range 1175–1333 K.

3. Results

The reaction for the formation of $UPd_3(s)$ and giving rise to CO(g) pressures is given by equation

$$UO_2(s) + 2C(s) + 3UPd_4(s) = 4UPd_3(s) + 2CO(g). \tag{1}$$

The Gibbs energy of reaction, $\Delta_r G^0_m(T)$, for the above reaction can be given by

$$\Delta_r G^0_m(T) = -RT \ln K = -2\,RT\ \ln p(\mathrm{CO}), \tag{2}$$

where K is the equilibrium constant of reaction (1). Also $\Delta_r G^0_m(T)$ can be written as

$$\begin{aligned}\Delta_r G^0_m(T) = {} & 4\Delta_f G^0_m(\mathrm{UPd_3, s}, T) + 2\,\Delta_f G^0_m(\mathrm{CO, g}, T) \\ & - \Delta_f G^0_m(\mathrm{UO_2, s}, T) - 3\,\Delta_f G^0_m(\mathrm{UPd_4})\end{aligned} \tag{3}$$

and thus, the Gibbs energy of formation of $UPd_3(s)$ can be obtained by

$$\begin{aligned}\Delta_f G^0_m(\mathrm{UPd_3, s}, T) = {} & 1/4[\Delta_r G^0_m(T) \\ & + \Delta_f G^0_m(\mathrm{UO_2, s}, T) \\ & + 3\,\Delta_f G^0_m(\mathrm{UPd_4, s}, T) \\ & - 2\,\Delta_f G^0_m(\mathrm{CO, g}, T)].\end{aligned} \tag{4}$$

The CO(g) pressures measured as a function of temperature are given in Table 2 and were least squares analyzed to get the expression

$$\ln p(\mathrm{CO})(\mathrm{kPa}) \pm 0.05 = 17.189 - 20064/T\ (\mathrm{K}). \tag{5}$$

Using Eq. (2) and converting to bar, the $\Delta_r G^0_m(T)$ for reaction (1) can be given by

$$\Delta_r G^0_m(T)(\mathrm{kJmol^{-1}}) \pm 1.2 = 333.6 - 0.2090\ T\ (\mathrm{K}). \tag{6}$$

Using Eq. (4) and $\Delta_r G^0_m(T)$ from Eq. (6), $\Delta_f G^0_m(\mathrm{UO_2, s}, T)$ from Cordfunke and Konings [8], $\Delta_f G^0_m(\mathrm{CO, g}, T)$ from JANAF tables [9] and $\Delta_f G^0_m(\mathrm{UPd_4, s}, T)$ from our earlier work [1]: $\Delta_f G^0_m(\mathrm{UPd_4, s}, T)$ (kJ $\mathrm{mol^{-1}}$) $\pm 4.5 = -528.1 + 0.1223\ T$ (K), the $\Delta_f G^0_m(\mathrm{UPd_3, s}, T)$ was calculated and can be given by

Table 2
Variation of CO(g) pressures p(CO) with temperature over $\{UO_2(s) + C(s) + UPd_3(s) + UPd_4(s)\}$ mixture

T (K)	*p*(CO) (kPa)
1175	1.067
1197	1.600
1220	2.266
1242	2.800
1254	3.200
1260	3.515
1271	3.733
1290	5.093
1296	5.893
1310	6.453
1333	8.533

$$\Delta_f G^0_m(\mathrm{UPd_3, s}, T)(\mathrm{kJ\ mol^{-1}}) \pm 4.1$$
$$= -526.9 + 0.1259\,T\ (\mathrm{K}). \qquad (7)$$

The intercept and slope of Eq. (7) give $\Delta_f H^0_m(T)$: −526.9 kJ $\mathrm{mol^{-1}}$ and $\Delta_f S^0_m(T)$: −125.9 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ of $\mathrm{UPd_3(s)}$ at average experimental temperature of 1254 K. The $\Delta_f H^0_m$ (298.15 K) was calculated using molar heat capacity data for $\mathrm{UPd_3(s)}$ from [4], for U(s) and Pd(s) from [8] and transition enthalpies for uranium from [8], the $\Delta_f H^0_m(\mathrm{UPd_3, s, 298.15\ K})$ thus obtained is −(502.3 ± 5.1) kJ $\mathrm{mol^{-1}}$. Similarly $S^0_m(\mathrm{UPd_3, s, 298.15\ K})$ is calculated as (66.0 ± 1.5) J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.

4. Discussion

Gibbs energy and enthalpy of formation data of this system along with the literature data are given in Table 3. Direct measurement of $\Delta_f G^0_m(\mathrm{UPd_3, s}, T)$ has been reported using mass spectrometry by Lorenzelli and Marcon [2] at only one temperature (1673 K). Most recently, Kleykamp and Kang [6] have calculated $\Delta_f G^0_m(\mathrm{UPd_3, s}, T)$ on the basis of phase field distribution in the U–Pd–Sn system. The other reported data are based on measurement of enthalpy of formation and heat capacities [3,4].

Our Gibbs energy value: −(360.3 ± 4.1) kJ $\mathrm{mol^{-1}}$ at 1323 K agrees within 48 kJ $\mathrm{mol^{-1}}$ with that calculated from the U–Pd–Sn phase diagram [6]: −(312 ± 16) kJ $\mathrm{mol^{-1}}$. Gibbs energy value: −(316.3 ± 4.1) kJ $\mathrm{mol^{-1}}$ at 1673 K from the present study agrees within 57 kJ $\mathrm{mol^{-1}}$ with that from [2]: −259 kJ $\mathrm{mol^{-1}}$. It can also be seen that the two $\Delta_f G^0_m(T)$ values from calorimetric data have excellent agreement with each other but are very much negative (around −200 kJ $\mathrm{mol^{-1}}$) compared to the experimental values of Refs. [2,6] and that of present data. All the directly determined values of $\Delta_f G^0_m(T)$ are about −300 kJ $\mathrm{mol^{-1}}$ which are much higher than values (−527 kJ $\mathrm{mol^{-1}}$ [3] and −530 kJ $\mathrm{mol^{-1}}$ [4]) calculated on the basis of $\Delta_f H^0_m(T)$ and $\Delta_f S^0_m(T)$.

Table 3
The comparision of $\Delta_f G^0_m(\mathrm{UPd_3, s}, T)$ and $\Delta_f H^0_m(\mathrm{UPd_3, s}, T)$ with the literature data

References	Method	Temperature (K)	$\Delta_f G^0_m$ (kJ $\mathrm{mol^{-1}}$)	$\Delta_f H^0_m$ (kJ $\mathrm{mol^{-1}}$)
[2]	Mass spectrometry	1673	−259 (−316.3[a])	–
[3]	Fluorine bomb calorimetry	298	–	524 ± 31
[3]	Fluorine bomb calorimetry and $C^0_{p,m}$	1673	−527	–
[4]	Fluorine bomb calorimetry and $C^0_{p,m}$	1200	−530	−546
[5]	direct reaction calorimetry	298	–	−295 ± 3
[6]	U–Pd–Sn phase diagram.	1323	−312 ± 16 (−360.3[a])	–
[10]	Miedema model	298	–	−244
Present study		1175–1333	−526.9 + 0.1259 T (K)	−(502.3 ± 5.1)[b]

[a] Extrapolated value calculated from the present study.
[b] Value at 298.15 K.

Table 4
Thermodynamic functions for $\mathrm{UPd_3(s)}$

T (K)	$C^0_{p,m}$ (T) (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	S^0_m (T) (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	$-\{G^0(T) - H^0$ (298.15 K)$\}/T$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)	$H^0(T) - H^0$ (298.15 K) (J $\mathrm{mol^{-1}}$)	$\Delta_f H^0_m$ (T) (kJ $\mathrm{mol^{-1}}$)	$\Delta_f G^0_m$ (T) (kJ $\mathrm{mol^{-1}}$)
298.15	102.1	66.0	66.0	0	−524.0	−489.4
300	102.1	66.6	66.0	189	−524.0	−489.1
400	103.3	96.2	70.0	10 458	−524.5	−476.5
500	104.4	119.3	77.7	20 840	−525.4	−464.0
600	105.5	138.5	86.2	31 336	−526.5	−451.4
700	106.7	154.8	94.9	41 947	−528.1	−438.8
800	107.8	169.1	103.3	52 671	−530.0	−426.2
900	109.0	181.9	111.3	63 510	−532.5	−413.6
1000	110.1	193.4	119.0	74 463	−537.8	−401.0
1100	111.2	204.0	126.2	85 530	−544.8	−388.4
1200	112.4	213.7	133.1	96 710	−546.8	−375.8
1300	113.5	222.8	139.7	108 006	−548.8	−363.2
1400	114.7	231.2	145.9	119 415	−551.0	−350.6
1500	115.8	239.2	151.9	130 939	−563.2	−338.1

Our $\Delta_f H_m^0$(1254 K): -526.9 kJ mol^{-1} and $\Delta_f H_m^0$ (298.15 K): -502.3 kJ mol^{-1} agree reasonably well with experimental calorimetric values of -546 kJ mol^{-1} at 1200 K [4] and $-(524 \pm 31)$ kJ mol^{-1} at 298.15 K [3], respectively, indicating the reliability of our enthalpy of formation values. $\Delta_f H_m^0$(298.15 K) calculated using Miedema model [10] is very low (-244 kJ mol^{-1}) compared to all other literature values. This low value could be improved by changing the parameters in the semi-empirical equation of Miedema model [10] for the U–Pd system which is discussed in our previous paper [1].

Cordfunke and Konnings [8] have reviewed the experimental measurements by Burriel et al. [4] and obtained S_m^0(298.15 K) as: 176.4 J K^{-1} mol^{-1} which is 110.4 J K^{-1} mol^{-1} more positive than our value: 66.0 J K^{-1} mol^{-1}. Other experimental measurements are not available. However, Johnson [11] has reported a method for calculation of the standard entropies of formation of uranium intermetallic compounds based on the experimental data. Using Johnson's method [11], $S_m^0(\mathrm{UPd_3, s, 298.15\ K})$ is calculated as: 75.1 J K^{-1} mol^{-1}. This value is very close to S_m^0(298.15 K) value: 66.0 J K^{-1} mol^{-1} derived from the present study. Thus, there seems to be some error in the $\Delta_f S_m^0$(298.15 K): 7.0 J K^{-1} mol^{-1} value reported by Cordfunke and Konings based on data of Burriel et al. [4]. The present $S_m^0(\mathrm{UPd_3, s, 298.15\ K})$: 66.0 J K^{-1} mol^{-1} value is selected.

The present study is the first to give the Gibbs energies as a function of temperature. Table 4 gives the thermodynamic potentials for UPd_3(s) at temperature intervals of 100 K. It is generated using available experimental data in the literature. Where more than one data reported, directly experimentally determined data have been taken. $\Delta_f H_m^0$(298.15 K), $C_{p,m}^0$(298.15 K) from [8] and S_m^0(298.15 K), $\Delta_f G_m^0(T)$ from the present measurements have been selected for the generation of the Table 4.

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