

## Standard molar Gibbs free energy of formation of URu<sub>3</sub>(s)

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### Abstract

$\Delta_f G_m^\circ(\text{URu}_3, s, T)$  has been determined by direct manometric measurement of the equilibrium N<sub>2</sub>(g) pressure over UN(s) + Ru(s) + URu<sub>3</sub>(s) in the temperature range 1245–1402 K, and CO(g) pressure over UO<sub>2</sub>(s) + C(s) + Ru(s) + URu<sub>3</sub>(s) in the temperature range 1562–1652 K.  $\Delta_f G_m^\circ$  values in the temperature ranges 1245–1402 K and 1562–1652 K can be expressed by the equations  $\Delta_f G_m^\circ(\text{URu}_3, s, T)$  (kJ mol<sup>-1</sup>)  $\pm 3.0 = -192.188 + 0.02647T(K)$  and  $\Delta_f G_m^\circ(\text{URu}_3, s, T)$  (kJ mol<sup>-1</sup>)  $\pm 2.0 = -175.435 + 0.01467T(K)$  respectively. The third-law enthalpies of formation  $\Delta_f H_m^\circ(\text{URu}_3, s, 298.15 \text{ K})$  obtained from the two sets of measurements are respectively  $(-160.60 \pm 3.00)$  kJ mol<sup>-1</sup> and  $(-159.45 \pm 2.00)$  kJ mol<sup>-1</sup>.

### 1. Introduction

The presence of intermetallics of the type (U,Pu) (Ru,Rh,Pd)<sub>3</sub> was first reported by Bramman *et al.* [1] in irradiated oxide fuel. Kleykamp [2] reported the presence of white inclusions in postirradiation studies of the mixed oxide fuel of fast reactors. The formation of these intermetallics indicates very high thermodynamic stability for these compounds since they must be formed by reduction of very stable oxides of uranium and plutonium. Thermodynamic properties of these intermetallics are of importance in analysing the phase behaviour in these systems. Three measurements have been reported for the free energy of formation of URu<sub>3</sub> [3–5]. The free energies of formation  $\Delta_f G_m^\circ$  measured by the galvanic cell method reported by Holleck and Kleykamp [3] and Wijbenga and Cordfunke [4] are in good agreement. However, the mass spectrometric measurements by Edwards *et al.* [5] gave an entirely different value for  $\Delta_f G_m^\circ(\text{URu}_3)$ . Also there are differences in the values of enthalpies and entropies of formation obtained in the two sets of measurements using galvanic cells. In the present study an attempt to resolve this has been made by measuring equilibrium constants for the following reactions:



and then calculating the free energy of formation of URu<sub>3</sub>(s) from known free energy values for UN(s), UO<sub>2</sub>(s) and CO(g).

## 2. Experimental details

The compound  $URu_3$  was prepared by arc melting uranium and ruthenium metals (purity, better than 99.9 mass%) in 1:3 atom ratios. The compound was annealed in a vacuum-sealed quartz capsule at 1000 K for 100 h before use. The X-ray diffraction pattern of the compound matched with the reported data [6]. Uranium nitride (UN) microspheres used in the present work were prepared by the sol-gel technique [7].

### 2.1. Equipment

An all-metal ultrahigh vacuum system was employed to measure the CO and  $N_2$  pressures. Various joints in the system were made with CF flanges and copper gaskets. An alumina reaction tube was coupled to this vacuum system through a CF flange fixed to the tube with an epoxy resin. All the valves employed in the system were metal bellow sealed Vakum Apparate Technik (VAT) valves with CF flanges and a leak rate less than  $10^{-9}$  mbar  $l\ s^{-1}$ . The composition of the gas after equilibration was measured with a Leybold Hereaus Quadruvac Q 200 quadrupole mass spectrometer coupled online with the system through a Varian leak valve as shown in Fig. 1. Differential pressures were measured manometrically using Apiezon B oil having a density of  $0.8656\ g\ cm^{-3}$  at 298 K. The complete system was baked for several hours at about 423 K before carrying out the measurements.

### 2.2. Nitrogen pressures over $UN(s) + Ru(s) + URu_3(s)$

Uranium nitride, ruthenium and  $URu_3$ , in powder form, were mixed thoroughly in a 1:4:0.1 mole ratio and pelletized. The pellet was contained in an alumina cup and loaded in the alumina reaction tube which had already been degassed at 1400 K and had a valve for isolation. All these operations were carried out inside an argon atmosphere box with less than 50 ppm

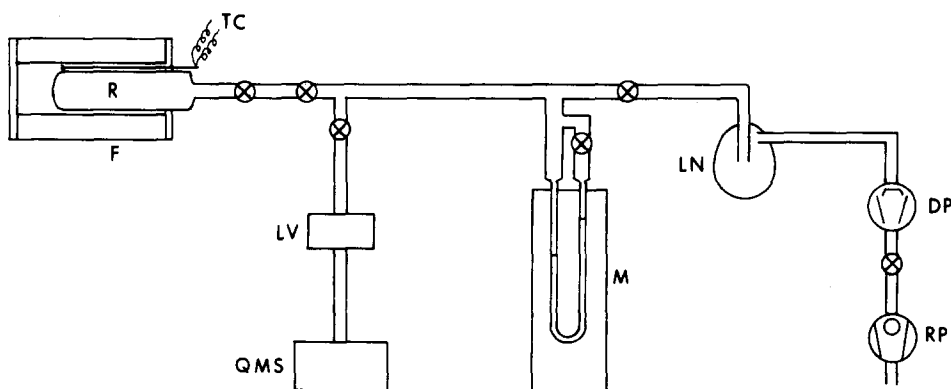


Fig. 1. Schematic of the equipment used: ⊗, bellows-sealed CF flange VAT valves; LV, Varian leak valve; QMS, quadrupole mass spectrometer; F, furnace; R, reaction tube; TC, thermocouple; M, oil manometer; LN, liquid nitrogen trap; DP, mercury diffusion pump; RP, rotary pump.

oxygen and 5 ppm moisture. A pot containing molten sodium near the handling area ensured purity of the argon atmosphere. The reaction tube after loading was taken out of the box and attached to the high vacuum assembly for the measurement of equilibrium nitrogen pressure. The assembly was evacuated and tested for leak tightness for several days before initiating the reaction by heating. No visible change was noticed in the differential manometer over this period. The sample was then heated with a Kanthal wire-wound furnace and the temperature was controlled within  $\pm 1$  K of the set point and measured with a precalibrated Pt/(Pt-13%Rh) thermocouple. An equilibrium time of 4–5 days was given prior to each measurement. The attainment of equilibrium was checked by evacuating some gas and allowing equilibrium to be attained again. After measuring the pressures the gas was analysed by an online quadrupole mass spectrometer [8] and found to be entirely nitrogen. The measurements were carried out in the temperature range 1245–1402 K.

### 2.3. CO pressure over $UO_2(s) + C(s) + Ru(s) + URu_3(s)$

Pellets of homogeneously mixed  $UO_2$ , carbon, ruthenium and  $URu_3$  powders in the mole ratio 1:2:4:0.1 were prepared in the argon atmosphere box and loaded in the reaction tube as described in Section 2.2. A silicon carbide furnace was used for heating the sample and the temperature was maintained constant within  $\pm 2$  K. Measurements were carried out in the temperature range 1562–1652 K. Equilibrium at each temperature was obtained within 2–4 days. The gas was analysed by quadrupole mass spectrometer [8] and found to be entirely CO, indicating no leakage in the system.

## 3. Results

Nitrogen is generated by the reaction of ruthenium with UN as given in eqn. (1). The equilibrium constant for reaction (1) can be written as

$$K = \frac{a[URu_3(s)]p^{1/2}[N_2(g)]}{a[UN(s)]a^3[Ru(s)]} \quad (3)$$

Assuming no mutual solubility between UN(s), Ru(s) and  $URu_3(s)$ , the activity of the solid phases can be taken as unity and the standard free energy change for reaction (1) can be given by

$$\Delta_r G_T^\circ = -\frac{1}{2}RT \ln\{p[N_2(g)]\} \quad (4)$$

The standard molar Gibbs free energy of formation of  $URu_3(s)$  can now be calculated using the  $\Delta_r G_T^\circ$  value obtained from measured nitrogen pressures and  $\Delta_f G_m^\circ$  values for UN(s) from Potter and Spear [9]. The nitrogen pressures obtained are given in Table 1 and the data can be represented by the equation

$$\frac{\log\{p[N_2(g)]\}}{k} \pm 0.014 = -\frac{10986}{T(K)} + 8.257 \quad (5)$$

TABLE 1

N <sub>2</sub> (g) pressures over UN(s) + Ru(s) + URu <sub>3</sub> (s)		and CO(g) pressures over UO <sub>2</sub> (s) + C(s) + Ru(s) + URu <sub>3</sub> (s)	
T (K)	N <sub>2</sub> (g) pressure (kPa)	T (K)	CO(g) pressure (kPa)
1245	0.2645	1562	0.1706
1284	0.5118	1570	0.1962
1321	0.8786	1585	0.2388
1339	1.1430	1610	0.3753
1366	1.6374	1610	0.3583 <sup>a</sup>
1383	1.9444	1652	0.7080
1383	1.9277 <sup>a</sup>	1652	0.6995 <sup>a</sup>
1394	2.4997		
1402	2.5757 <sup>a</sup>		
1402	2.5845		

<sup>a</sup>Readings after disturbing the equilibrium.

with  $p$  in pascals.  $\Delta_r G_T^\circ$  of reaction (1) can thus be given by

$$\Delta_r G_T^\circ(\text{J}) = 105169 - 59.8407T(\text{K}) \quad (6)$$

Using  $\Delta_r G_T^\circ$  from the present study and  $\Delta_r G_m^\circ$  of UN(s) as reported by Potter and Spear [9],  $\Delta_r G_m^\circ(\text{URu}_{3,\text{s}}, T)$  has been calculated and can be represented by

$$\Delta_r G_m^\circ(\text{URu}_{3,\text{s}}, T) (\text{kJ mol}^{-1}) \pm 3.0 = -192.188 + 0.02647T(\text{K}) \quad (7)$$

The values of enthalpy of formation at 298.15 K,  $\Delta_r H_m^\circ(\text{URu}_{3,\text{s}}, 298.15 \text{ K})$ , were calculated using second- and third-law methods by first calculating  $\Delta_r H_{298.15 \text{ K}}^\circ$  for reaction (1) and then adding to this the value of  $\Delta_r H_m^\circ(\text{UN}, \text{s}, 298.15 \text{ K})$  ( $-290.79 \pm 2.50 \text{ kJ mol}^{-1}$ ) from the literature [10]. For the second-law calculations heat capacity values for ruthenium and URu<sub>3</sub> were taken from Cordfunke and Konninge [11], for UN from Prins *et al.* [10] and for N<sub>2</sub>(g) from Barin and Knacke [12]. For the third-law calculations the free energy functions for Ru(s) and URu<sub>3</sub>(s) were obtained from Cordfunke and Konninge [11], for N<sub>2</sub>(g) from Hultgren *et al.* [13] and for UN(s) from Prins *et al.* [10]. The second- and third-law values of  $\Delta_r H_m^\circ$  (298.15 K) were calculated to be  $(-176.14 \pm 3.00) \text{ kJ mol}^{-1}$  and  $(-160.64 \pm 2.00) \text{ kJ mol}^{-1}$  respectively.

CO is generated by the reaction of Ru(s) with UO<sub>2</sub>(s) in the presence of graphite as shown in eqn. (2). Some other possible reactions which can lead to the production of CO(g) are



The equilibrium CO(g) pressures for the reactions given by eqns. (8), (9) and (10) at 1600 K were calculated from the data reported by Potter [14] and are 0.1 kPa, 0.08 kPa and  $5 \times 10^{-8}$  kPa respectively. Since in the present work a UO<sub>2</sub>:C mole ratio of 1:2 was used, reaction (10) is expected to be the likely additional source of CO(g). As pressures of CO(g) for this reaction are quite small as compared with the pressures observed in the present study, reaction (2) can be considered to be solely responsible for the generation of CO(g). Thus from eqn. (2) we get

$$\Delta_f G_m^\circ \text{URu}_3(\text{s}) = \Delta_f G_m^\circ \text{UO}_2(\text{s}) - 2\Delta_f G_m^\circ (\text{CO}) - 2RT \ln p_{\text{CO}} \quad (11)$$

Thus from the equilibrium CO(g) pressure over UO<sub>2</sub> + C + Ru + URu<sub>3</sub>, and the free energies of formation for UO<sub>2</sub>(s) and CO(g), we can calculate the free energy of formation of URu<sub>3</sub>(s). The CO(g) pressures measured at various temperatures are given in Table 1 and can be represented by the expression

$$\log[p(\text{CO})(\text{kPa})] \pm 0.0106 = -\frac{17807}{T(\text{K})} + 10.629 \quad (12)$$

$\Delta_f G_T^\circ$  for reaction (2) can be given by

$$\Delta_f G_T^\circ (\text{kJ}) = 681.866 - 0.330T(\text{K}) \quad (13)$$

The free energies of formation of URu<sub>3</sub>(s) were calculated using  $\Delta_f G_m^\circ$  data for UO<sub>2</sub>(s) and CO(g) from Srivastava *et al.* [15] and can be given by

$$\Delta_f G_m^\circ (\text{URu}_{3,\text{s}}, T) (\text{kJ mol}^{-1}) \pm 2.0 = -175.435 + 0.0146T(\text{K}) \quad (14)$$

The second- and third-law enthalpies of formation of URu<sub>3</sub>(s) were calculated by first finding  $\Delta_f H_m^\circ(\text{s}, 298.15 \text{ K})$  for reaction (7) by the second and third laws and then adding  $\Delta_f H_m^\circ(\text{s}, 298.15 \text{ K})$  values for UO<sub>2</sub>(s) and CO(g) from the literature [11, 16]. For the second-law calculations heat capacity values for carbon and CO were taken from JANAF tables [16], for UO<sub>2</sub>(c) from Kubaschewski and Alcock [17] and for ruthenium and URu<sub>3</sub> from Cordfunke and Konninge [11]. For the third-law calculations free energy function data values for C(s) and CO(g) were taken from JANAF tables [16], and for Ru(s) and URu<sub>3</sub>(s) from Cordfunke and Konninge [11]. Free energy functions for UO<sub>2</sub>(c) were calculated using  $C_p$  values from Kubaschewski and Alcock [17] and the  $S_{298}^\circ$  value from Cordfunke and Konninge [11]. The second- and third-law values obtained are  $(-188.59 \pm 2.00) \text{ kJ mol}^{-1}$  and  $(-159.45 \pm 2.00) \text{ kJ mol}^{-1}$  respectively.

#### 4. Discussion

The  $\Delta_f G_m^\circ (\text{URu}_{3,\text{s}}, T)$  values obtained from the present work are compared with the reported data in Table 2. It can be seen that the present data on free energy of formation, from N<sub>2</sub>(g) pressure measurements, are in good agreement with those of Wijbenga and Cordfunke [4] and of Holleck and Kleykamp [3]. The free energies of formation obtained from CO(g) pressure

TABLE 2

Standard molar Gibbs free energy of URu<sub>3</sub>  $\Delta_r G_m^\circ(\text{URu}_{3,s}, T) = A + BT(\text{K})$ 

Ref.	Temperature range (K)	Technique	-A	B	$-\Delta_r G_m^\circ$ (kJ mol <sup>-1</sup> )				
					1200 <sup>a</sup>	1300	1500	1600	
[3]	1000–1140	E.m.f.	199160	35.98	156.0	152.4	–	–	
[4]	1090–1180	E.m.f.	178540	16.29	159.0	157.4	–	–	
Present study									
	N <sub>2</sub> pressure	1245–1402	Manometry	192184	26.35	160.6	157.9	–	–
	CO pressure	1562–1652	Manometry	175435	14.56	–	–	153.6	152.1

<sup>a</sup>Temperature *T* (K).

TABLE 3

Standard molar enthalpy of formation of URu<sub>3</sub>  $\Delta_r H_m^\circ(\text{URu}_{3,s}, 298.15 \text{ K})$  from second-law and third-law methods

Ref.	$-\Delta_r H_m^\circ$ (kJ)		
	Second law	Direct calorimetry	Third law
[3]	Not reported		153.2 ± 0.2
[4]	Not reported		156
[5]	Not reported		49 ± 22
[18]		–124.0 ± 4.8	
Present study			
	N <sub>2</sub> pressure	176.14 ± 3.0	160.64 ± 3.00
	CO pressure	188.59 ± 2.0	159.45 ± 2.00

measurements relate to temperatures above the melting point of uranium and hence are not compared with the rest of the data.

The  $\Delta_r H_m^\circ(\text{URu}_{3,s}, 298.15 \text{ K})$  values obtained by second- and third-law methods from N<sub>2</sub>(g) and CO(g) pressure measurements are compared with literature values in Table 3. It can be seen from Table 3 that the second-law values of  $\Delta_r H_m^\circ$  from both sets of measurements are more negative than the third-law values. However, the third-law values from the two sets have excellent agreement and should be considered more reliable. The third-law values are also compared with the data in the literature and show fair agreement. The enthalpy of formation of URu<sub>3</sub> has been measured calorimetrically by Jung and Kleppa [18] and reported as  $(-124.0 \pm 4.8) \text{ kJ mol}^{-1}$ . The difference of about 36 kJ mol<sup>-1</sup> from our measurements cannot be explained.

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## References

- 1 J. I. Bramman, R. M. Sharpe, D. Thom and G. Yates, *J. Nucl. Mater.*, 25 (1968) 201.
- 2 H. J. Kleykamp, *J. Nucl. Mater.*, 131 (1985) 221.
- 3 H. Holleck and H. Kleykamp, *Z. Metallkde.*, 66 (1975) 298.
- 4 G. Wijbenga and E. H. P. Cordfunke, *J. Chem. Thermodyn.*, 14 (1982) 409.
- 5 J. G. Edwards, J. S. Starzynski and D. E. Peterson, *J. Chem. Phys.*, 73 (1980) 908.
- 6 T. J. Heal and G. I. Williams, *Acta Crystallogr.*, 8 (1955) 494.
- 7 S. K. Mukherjee, J. V. Dehadraya, V. N. Vaidya and D. D. Sood, *J. Nucl. Mater.*, 185 (1991) 39.
- 8 Y. S. Sayi, J. Radhakrishna, C. S. Yadav, P. S. Shankaran and G. C. Chhapru, *Anal. Lett.*, 23 (1990) 2049.
- 9 P. E. Potter and K. E. Spear, in *Proc. IAEA Conf. on Thermodynamics of Nuclear Materials, 1979*, E. R. A. Beck (ed.), Vol. II, International Atomic Energy Agency, Vienna, 1980, p. 195.
- 10 G. Prins, E. H. P. Cordfunke and R. Depaus, *J. Nucl. Mater.*, 89 (1980) 221.
- 11 E. H. P. Cordfunke and R. J. M. Konninge (eds.), *Thermochemical Data for Reactor Materials and Fission Products*, North-Holland, Amsterdam, 1990.
- 12 I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer, Berlin, 1973.
- 13 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, American Society for Metals, Metals Park, OH, 1973.
- 14 P. E. Potter, *Rep. AERE-R 6438*, Atomic Energy Research Establishment, Harwell, 1970.
- 15 D. Srivastava, S. P. Garg and G. L. Goswami, *J. Nucl. Mater.*, 161 (1989) 44.
- 16 *JANAF Thermochemical Tables*, NBRDS, National Bureau Reference Data Series, US Department of Commerce, Dow Chemical Company, Midland, MI, 1971.
- 17 O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th edn., Pergamon, New York, NY, 1979.
- 18 W. G. Jung and O. J. Kleppa, *J. Chem. Thermodyn.*, 23 (1991) 147.