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Journal of Nuclear Materials 294 (2001) 112–118

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Thermodynamic studies on $ThGa_2$

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Abstract

The enthalpy of formation of $ThGa_2$ was determined by high temperature gallium solution calorimetry and precipitation calorimetry. The values thus obtained are $-(55.1 \pm 4.8)$ and $-(69.6 \pm 5.6)$ kJ g atom^{-1} with reference to α-thorium and solid gallium at 298.15 and 1100 K, respectively. These are the first calorimetric results for the enthalpy of formation of $ThGa_2$. The Gibbs energy of formation of $ThGa_2$ with reference to α-thorium and liquid gallium was determined by molten salt galvanic cell measurements to be $-75.1 + 0.024T$ kJ g atom^{-1} in the temperature range 682–891 K. The partial molar excess Gibbs energy of thorium in liquid gallium in the saturated solution at 787 K was determined to be $-(123.3 \pm 4.7)$ kJ g atom^{-1}. The partial molar enthalpy of solution of thorium in liquid gallium at infinite dilution at 1095 K was determined to be $-(178.6 \pm 6.8)$ kJ g atom^{-1} and partial molar enthalpy of thorium in liquid gallium in the saturated solution at 787 K to be $-(164.2 \pm 4.7)$ kJ g atom^{-1}.

1. Introduction

In the pyrochemical processes involving actinides, some actinide chlorides or oxides remain in the molten salt after the completion of the process which have to be recovered. Equilibrating the salt with Ca–Ga alloys [1] is one of the methods of recovery wherein calcium reduces the actinide halides or oxides to the respective metals. These actinide metals may react with gallium to form intermetallic compounds which provides additional driving force for the reduction reaction. Hence the thermodynamic properties of the intermetallic compounds of actinide–gallium systems are of importance. We have taken up systematic studies on the thermodynamic properties of actinide–gallium systems by calorimetry and molten salt galvanic cell measurements. Thermodynamic properties of the intermetallic compounds of U–Ga system have been determined earlier [2,3]. In this study, thermodynamic measurements on $ThGa_2$ have been carried out.

There exists no phase diagram for the Th–Ga system in the literature. Palenzona et al. [4] investigated the Th–Ga system by using crystallography and metallography. They reported the presence of four intermetallic compounds, $ThGa_2, ThGa, Th_3Ga_2$ and Th_2Ga. There are no experimental data on the enthalpy of formation of these intermetallic compounds. The solubility of thorium in gallium-rich alloys in the temperature range 765–1003 K and the partial molar Gibbs energies of thorium in the temperature range 648–1056 K in the two-phase region containing thorium in liquid gallium and the co-existing intermetallic compound were measured by Poyarkov et al. [5] by using molten salt emf measurements. Poyarkov et al. [5] have reported the Gibbs energy of formation of the intermetallic compound co-existing with liquid gallium without specifying the stoichiometry of the compound. In this study, we have adopted two different calorimetric methods to determine the enthalpy of formation of $ThGa_2$ and high temperature molten salt galvanic cell method to determine the Gibbs energy of formation of $ThGa_2$.

2. Experimental

2.1. Preparation of alloys and electrolyte salt

Thorium metal of nuclear grade purity from Bhabha Atomic Research Centre, Mumbai and gallium (99.99%)

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PII: S0022-3115(01)00467-6

metal from Nuclear Fuel Complex, Hyderabad, were used for the preparation of the $ThGa_2$ and Ga-8.5 at.% Th alloys by arc melting. The $ThGa_2$ sample was annealed at 873 K for 168 h under argon atmosphere at sub-ambient pressure. The X-ray diffraction pattern of the annealed sample was in agreement with that reported in the JCPDS file, confirming the presence of single-phase $ThGa_2$.

The salt mixture of LiCl–KCl of eutectic composition was purified by melting it under a stream of HCl gas at 673 K [6]. The salt thus purified was loaded with about 5 wt% $ThCl_4$ by equilibrating the salt containing $CdCl_2$ with thorium metal in an alumina crucible at 707 K under argon atmosphere inside an argon atmosphere glove box.

2.2. Equipment

Calorimetric measurements were carried out by using a high temperature differential calorimeter (Model HT-1500 of M/s. Setaram, France) described elsewhere [7]. The output of the thermopile calorimetric detector was directly measured, without any amplification, by using a digital multimeter (HP 34970A) whose output was fed to a personal computer. The peak areas were determined by using Microcal Origin 5 software.

2.3. Calorimetric measurements

The procedures adopted for the solution, as well as the precipitation calorimetric measurements were similar to the ones used for such measurements in our earlier studies [2,8]. Calibration was done by dropping a known amount of α-Al_2O_3 (SRM-720, NIST) samples from the ambient into the calorimeter at the experimental temperature, the corresponding enthalpy increments being taken from the work of NIST group [9].

2.3.1. Solution calorimetric measurements

About 2 g of gallium was taken in an alumina crucible which was loaded into the calorimeter and heated to the temperature of measurement. Thorium metal samples, each weighing about 15 mg and maintained at ambient temperature, were dropped successively into the liquid gallium. The amount of thorium and gallium were so chosen as to form dilute solutions of thorium in gallium. The calorimetric signals recorded corresponded to the thermal effects of dissolution of thorium in liquid gallium (Q^{E}_{Th}) at the temperature of measurements. The thermal effects of dissolution of $ThGa_2$, ($Q^{E}_{ThGa_2}$) samples, each weighing about 20–30 mg, were measured in a separate experiment by using a similar procedure.

2.3.2. Precipitation calorimetric measurements

About 0.5 g of gallium was initially placed in the alumina crucible of the calorimeter and heated to the experimental temperature. Samples of thorium metal maintained at ambient temperature, were dropped into liquid gallium and the calorimetric signals were recorded.

2.4. Galvanic cell emf measurements

The procedure used for assembling the cell was similar to the one followed for the U–Ga system described elsewhere [3]. Thorium metal was used as the reference electrode and Ga-8.5 at.% Th alloy as the alloy electrode in this concentration cell. In the temperature range of measurement, the alloy is a two-phase mixture containing liquid gallium saturated with thorium and the solid intermetallic compound, $ThGa_2$. The Gibbs energy of formation of $ThGa_2$ was determined from the emf measurements of the following cell

$$\langle \mathrm{Th}\rangle//\{\mathrm{ThCl_4\ in\ LiCl{-}KCl_{(eut)}}\}//\langle \mathrm{ThGa_2}\rangle+\{\mathrm{Th}_x\mathrm{Ga}_{1-x}\}$$

in the temperature range 682–891 K. Initial equilibrium was attained within 3–4 h at 682 K and for further changes in temperature, equilibrium was reached in about one hour.

3. Results

3.1. Enthalpy of formation of $ThGa_2$ at 298.15 K by solution calorimetry

The thermal effects of dissolution of (Q^{E}_{Th}) thorium in liquid gallium at 1095 K, measured by adding thorium maintained at 298.15 K into gallium at 1095 K are given in Table 1. The thermal effects of dissolution of $ThGa_2(Q^{E}_{ThGa_2})$ in liquid gallium are given in Table 2. As can be seen from Tables 1 and 2, the thermal effects of dissolution of Th as well as those of $ThGa_2$ are independent of the composition of the alloy in the crucible, within experimental uncertainty. Hence the mean of the Q^{E} values were taken as $Q^{E,\infty}$, the thermal effect of dissolution at infinite dilution. The overall uncertainties in the $Q^{E,\infty}$ values were computed by taking into account the uncertainties in the measurement as well as calibration, and are given in the respective tables.

From the thermal effects of dissolution at infinite dilution, the enthalpy of formation of $ThGa_2$ at 298.15 K (kJ g atom^{-1}) was computed by using the following equation:

$$\Delta_f H^0_{298.15}\langle \mathrm{Th}_{1/3}\mathrm{Ga}_{2/3}\rangle = 1/3Q^{E,\infty}_{Th} + 2/3Q^{E,\infty}_{Ga} - Q^{E,\infty}_{Th_{1/3}Ga_{2/3}}. \quad (1)$$

The $Q^{E,\infty}_{Ga}$ term in the above equation corresponds to the enthalpy increment, $(H^0_T - H^0_{298.15})$ of gallium at 1095 K which was taken from literature (26.927 kJ g atom^{-1}) [10]. The enthalpy of formation of $ThGa_2$ at 298.15 K

Table 1
Experimental data for the thermal effects of dissolution of thorium in liquid gallium at 1095 K[a]

Calibration			Measurement $\langle Th\rangle_{298.15} \rightarrow [Th]_{\{Ga,1095\}}$				
No.	α-Al_2O_3 Wt. (mg)	Peak area (Counts)	No.	Wt. of Th (mg)	Peak area (Counts)	x_{Th} (at.%)	Q^E_{Th} (kJ g atom^{-1})
1.	67.60	1514.0	1.	16.65	−237.0	0.24	−136.8
2.	83.19	1830.0	2.	15.48	−216.0	0.49	−134.1
3.	59.42	1251.0	3.	15.47	−216.0	0.68	−134.1
4.	63.93	1346.0	4.	15.51	−229.0	0.90	−141.9
5.	48.68	979.0					

$Q^{E,\infty}_{Th} = -136.7$ kJ g atom^{-1}
Overall uncertainty = ±6.8 kJ g atom^{-1}

[a] Amount of gallium in the calorimeter = 2.09601 g. $(H^0_T - H^0_{298.15\ K})$ of α-Al_2O_3 at 1095 K = 89.900 kJ mol^{-1} [9]. Calibration constant = 0.0414 ± 0.0018 J Count^{-1}.

Table 2
Experimental data for the thermal effects of dissolution of $ThGa_2$ in liquid gallium at 1095 K[a]

Calibration			Measurement $\langle Th_{1/3}Ga_{2/3}\rangle_{298.15} \rightarrow [1/3Th + 2/3Ga]_{\{Ga,1095\}}$				
No.	α-Al_2O_3 Wt. (mg)	Peak area (Counts)	No.	Sample Wt. (mg)	Peak area (Counts)	$x_{Th_{1/3}Ga_{2/3}}$ (at.%)	$Q^E_{Th_{1/3}Ga_{2/3}}$ (kJ g atom^{-1})
1.	59.50	1304.0	1.	21.23	130.0	0.19	31.5
2.	67.78	1480.0	2.	19.22	109.0	0.37	29.2
3.	83.25	1798.0	3.	30.74	126.0	0.64	21.1
4.	86.22	1801.0	4.	30.34	175.0	0.91	29.7
5.	48.69	970.0	5.	28.97	147.0	1.16	26.1

$Q^{E,\infty}_{Th_{1/3}Ga_{2/3}} = 27.5$ kJ g atom^{-1}
Overall uncertainty = ±4.2 kJ g atom^{-1}

[a] Amount of gallium in the calorimeter = 2.04480 g. $(H^0_T - H^0_{298.15\ K})$ of α-Al_2O_3 at 1095 K = 89.900 kJ mol^{-1} [9]. Calibration constant = 0.0416 ± 0.00017 J Count^{-1}.

obtained is −(55.1 ± 4.8) kJ g atom^{-1}. The overall uncertainty on the enthalpy of formation was computed by using error propagation theory.

3.2. Enthalpy of formation of $ThGa_2$ at 1100 K by precipitation calorimetry

Enthalpy of formation of $ThGa_2$ at 1100 K was derived from the integral enthalpies of formation of two-phase Th–Ga alloys determined by precipitation calorimetry. The thermal effects were measured by dropping samples of thorium into liquid gallium until the concentration of thorium reached ∼20 at.% at 1100 K. The integral enthalpies of formation of Th–Ga alloys computed as a function of the composition of the alloys from the measured thermal effects at 1100 K (Run I and Run II) are given in Table 3. The method and procedure used for computation have been given elsewhere [8]. From the integral enthalpies of formation of the two-phase alloys, the enthalpy of formation of intermetallic compound $ThGa_2$ which coexists with the liquid alloy was derived.

As per the literature data for thorium solubility in gallium, at 1100 K the measurements are initially in the single phase region $\{Th_xGa_{1-x}\}$ until ∼1.6 at.% Th [5] and then over the two phase region, $\{Th_xGa_{1-x}\} + \langle ThGa_2\rangle$. The integral enthalpy values are plotted as a function of composition in the Fig. 1. The number of measurements in the single phase region are only two and hence, it is difficult to determine the phase boundary from the present data. The enthalpy increments, the enthalpy of fusion and enthalpy of transition of thorium from α to β form required for the computations were taken from literature [10]. The measured values at 1100 K over the two-phase alloys containing $\{Th_xGa_{1-x}\} + \langle ThGa_2\rangle$, when extrapolated to 33.33 at.% thorium give the enthalpy of the following reaction

$$1/3\langle Th\rangle_\alpha + 2/3\{Ga\} \rightarrow \langle Th_{1/3}Ga_{2/3}\rangle. \qquad (2)$$

The value thus obtained is −(73.3 ± 5.6) kJ g atom^{-1}. The enthalpy of formation of $Th_{1/3}Ga_{2/3}$ at 1100 K with reference to α-thorium and solid gallium was then computed by using the enthalpy of fusion of gallium from literature data [10]. The value thus obtained is −(69.6 ± 5.6) kJ g atom^{-1}.

Table 3
Integral enthalpies of formation of Th–Ga alloys at 1100 K[a]

Calibration			Measurement				
No.	α-Al_2O_3 Wt. (mg)	Peak area (Counts)	No.	Wt. of Th (mg)	Peak area (Counts)	x_{Th} (at.%)	$-\Delta H$ (kJ g atom^{-1})
Run I							
1.	83.01	1848.0	1.	11.70	−275.0	0.69	1.92
2.	76.83	1606.0	2.	11.33	−131.0	1.36	2.96
3.	86.15	1637.0	3.	12.32	−126.0	2.07	4.35
			4.	35.11	−175.0	4.04	8.96
			5.	45.46	−147.0	6.48	14.38
			6.	55.24	−1007.0	9.28	20.66
			7.	64.58	−1274.0	12.35	28.05
			8.	75.54	−1484.0	15.69	36.05
			9.	41.17	−824.0	17.40	40.23
			10.	75.90	−1497.0	20.38	47.41
Run II							
1.	76.82	1754.0	1.	12.67	−321.0	0.75	2.18
2.	83.29	1819.0	2.	13.62	−154.0	1.55	3.38
3.	86.11	1851.0	3.	25.99	−441.0	3.03	6.46
4.	79.21	1605.0	4.	46.83	−854.0	5.59	12.11
5.	77.80	1506.0	5.	56.94	−1100.0	8.53	18.93
			6.	67.88	−683.0	11.81	23.27
			7.	40.57	−1425.0	13.65	30.85
			8.	59.15	−1178.0	16.21	36.95
			9.	51.95	−1106.0	18.34	42.36
			10.	30.38	−293.0	19.53	43.73

[a] Measurements up to 1.55 at.% (second sample) are in the $\{Th_xGa_{1-x}\}$ phase region and above 1.55 at.% Th over $\{Th_xGa_{1-x}\} + \langle ThGa_2\rangle$ two phase region. Amount of gallium in the calorimeter in Run I & II $= 0.50269$ g; 0.50260 g. $(H^0_T - H^0_{298.15\ K})$ of α-Al_2O_3 at 1100 K $= 90.531$ kJ mol^{-1} [9]. Calibration constant for Runs I and II $= 0.0430 \pm 0.0035, 0.0421 \pm 0.0028$ J count^{-1}.

3.3. Partial molar enthalpy of dissolution of thorium in liquid gallium

The partial molar enthalpy of dissolution of thorium in liquid gallium at infinite dilution $\Delta\overline{H}^{\infty}_{Th}$ at 1095 K was calculated by using the following equation employed by Colinet et al. [11].

$$\Delta\overline{H}^{\infty}_{Th} = Q^{E,\infty}_{Th} - \left(H^0_{1095} - H^0_{298.15}\right)_{Th} - \Delta_{trans}H^0(Th) - \Delta_{fus}H^0(Th), \qquad (3)$$

where $Q^{E,\infty}_{Th}$ is the thermal effect of dissolution of Th in Ga at infinite dilution. Since the $Q^{E,\infty}_{Th}$ value used in the above computation is obtained as a mean of the measured thermal effects, it includes the statistical errors as well as errors due to the interactions between thorium and gallium which are expected to be very small in these dilute solutions. The enthalpy increment, the enthalpy of fusion and the enthalpy of transition of Th from α to β ($T_{trans} = 1633$ K), which were taken from the literature [10] (24.515, 13.807 and 3.598 kJ g atom^{-1}), respectively, were used for the computation. The partial enthalpy of dissolution of thorium in liquid gallium at infinite dilution thus obtained is $-(178.6 \pm 6.8)$ kJ g atom^{-1}.

3.4. Gibbs energy of formation of $ThGa_2$ by galvanic cell measurements

The measured emf values of the galvanic cell are given in the Table 4. The emf of the cell is a measure of the difference between the chemical potential of thorium in pure solid and in the saturated solution in liquid gallium. The variation of the emf of the cell with temperature is shown in Fig. 2. The least-square regression analysis of the emf data of the cell yields

$$E/V = (0.584 \pm 0.009) - (0.189 \pm 0.011)10^{-3}\,T/K. \qquad (4)$$

The cell emf, E, and the standard Gibbs energy of formation of $ThGa_2, \Delta_f G^0_{ThGa_2}$ from solid thorium and liquid gallium are related by the equation

$$\Delta_f G^0_{ThGa_2} = -zFE + RT\ln a_{Th} + 2RT\ln a_{Ga}, \qquad (5)$$

where $z = 4$, is the number of electrons participating in the electrode reaction, F is the Faraday constant, a_{Th} is the activity of pure thorium and a_{Ga} is the activity of gallium in saturated solution. Since the activity of pure thorium is unity, the second term on the right hand side of the above equation vanishes. In the thorium-gallium system, the saturated solutions were sufficiently dilute

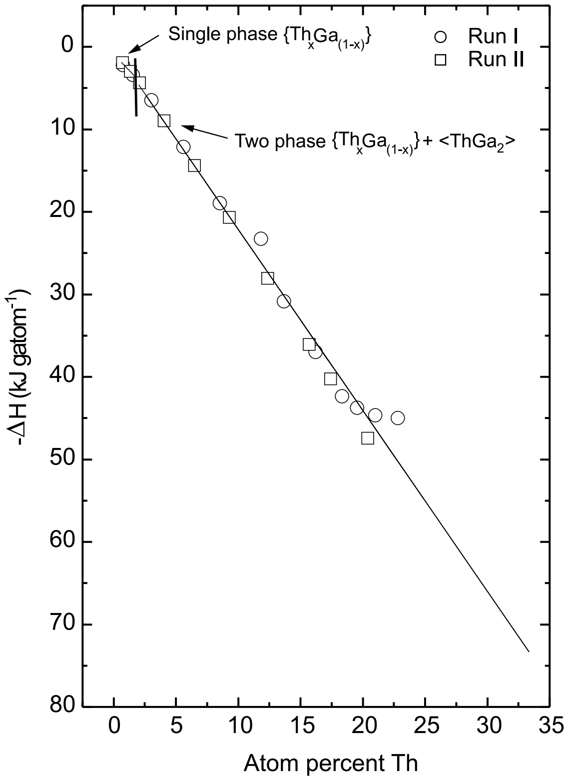

Fig. 1. Integral enthalpies of formation of Th–Ga alloys.

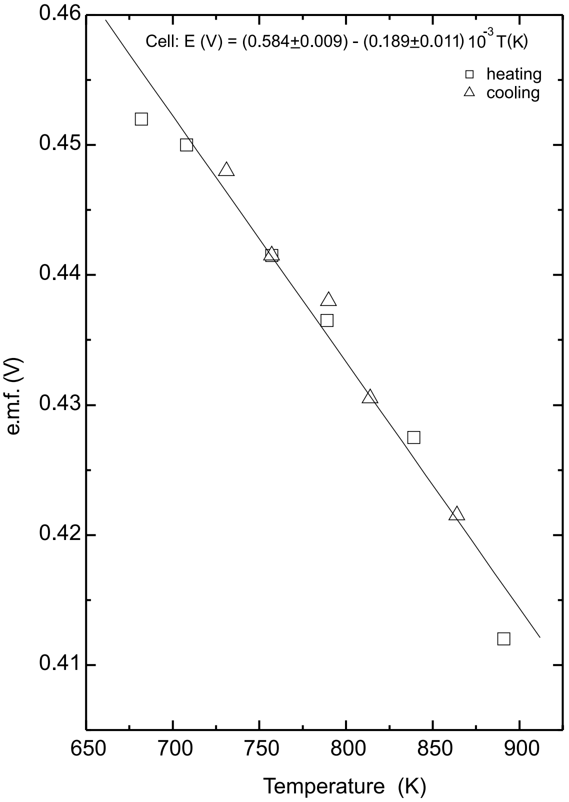

Fig. 2. Variation of emf of the cell ⟨Th⟩//{ThCl$_4$ in LiCl–KCl$_{(eut)}$}//⟨ThGa$_2$⟩ + {Th$_x$Ga$_{1-x}$} with temperature.

that the term $RT \ln a_{Ga}$ was estimated to the required accuracy by assuming that the solutions were ideal with respect to gallium. From the solubility data of thorium in liquid gallium from the literature [5], the gallium concentrations in the solutions in equilibrium with ThGa$_2$ in the temperature range 765–1103 K were computed and were fitted to an equation given by

$$\ln x_{Ga} = -0.05652 + 1.5177 \times 10^{-3} T - 1.0255 \times 10^{-7} T^2. \quad (6)$$

The standard Gibbs energy of formation of ThGa$_2$, $\Delta_f G^0_{ThGa_2}$, with reference to solid α-thorium and liquid gallium derived from the emf data is expressed as

$$\Delta_f G^0_{ThGa_2}/\text{kJ mol}^{-1} = -225.4 + 0.072\,T/\text{K}\ (\pm 4.7). \quad (7)$$

The enthalpy and entropy of formation of ThGa$_2$ are, thus, −225.4 kJ mol^{-1} and 72 J K^{-1} mol^{-1}, respectively. The uncertainty of the emf values has been estimated to be ±1 mV. The uncertainty on the Gibbs energy of formation has been computed by using this uncertainty.

The partial molar excess Gibbs energy of thorium in the liquid alloy in equilibrium with ThGa$_2$ was computed from the emf data of the cell and the solubility data of thorium from the literature [5] ($\ln x_{Th} = 2.524$–$7361.3/T\,\text{K}$) in the temperature range 765–1003 K. The partial molar excess Gibbs energy thus calculated is given below

$$\Delta\overline{G}^{xs}_{Th}/\text{kJ g atom}^{-1} = RT \ln \gamma_{Th} = -164.2 + 0.052\,T/\text{K}\ (\pm 4.7). \quad (8)$$

Table 4
Measured emf values of cell ⟨Th⟩//{ThCl$_4$ in LiCl–KCl$_{(eut)}$}//⟨ThGa$_2$⟩ + {Th$_x$Ga$_{1-x}$}[a]

Temperature (K)	emf (V)
682	0.4520^{h}
708	0.4500^{h}
731	0.4480^{c}
755	0.4430^{c}
757	0.4415^{h}
789	0.4365^{h}
790	0.4380^{c}
814	0.4305^{c}
839	0.4275^{h}
864	0.4215^{c}
891	0.4120^{h}

[a] c – cooling; h – heating.

The partial molar enthalpy and partial molar excess entropy of thorium in saturated solution in liquid gallium in the temperature range 682–891 K are −164.2 kJ g atom^{-1} and −52 J K^{-1} g atom^{-1}, respectively.

4. Discussion

The enthalpy of formation of $ThGa_2$ obtained in the present study by solution calorimetry, precipitation calorimetry and molten salt emf methods are given in the Table 5 and compared with the values reported by Poyarkov et al. [5]. They have used molten salt galvanic cell emf measurements for the determination of the thermodynamic properties of the gallium rich compound co-existing with the saturated solution of thorium in liquid gallium at 1000 K. They have not defined the stoichiometry of the compound. XRD analysis of the sample obtained from our precipitation calorimetric measurements shows the presence of lines corresponding to $ThGa_2$ along with those of gallium. Similarly, the XRD pattern of the alloy sample used for emf measurements also shows the presence of $ThGa_2$ as the major phase. In a recent compilation, Colinet and Pasturel [12] have also reported the Gibbs energy values of Poyarkov et al. [5] to be those of $ThGa_2$. Hence we have concluded that the gallium rich compound in the system is $ThGa_2$ and have compared our values with those of Poyarkov et al. [5] by considering those also to be for $ThGa_2$.

The enthalpy of formation of $ThGa_2$ at 298.15 K from our solution calorimetric measurements is slightly less exothermic than that obtained at 1100 K by precipitation calorimetry. The value obtained by precipitation calorimetry is in very good agreement with that from emf measurements which in turn is in agreement with that of Poyarkov et al. [5]. Hence we consider the value obtained by precipitation calorimetry to be more reliable.

The Gibbs energy formation of $ThGa_2$ with reference to α-thorium and liquid gallium, derived from our emf measurements is $\Delta_f G^0_{ThGa_2} = -75.1 + 0.024\,T$ (K) (±1.6) kJ g atom^{-1}. It is in agreement with the Gibbs energy formation of $ThGa_2$ obtained from the emf measurements of Poyarkov et al. [5] which is given by $-76.0 + 0.021\,T$ (K) kJ g atom^{-1}.

The present partial molar enthalpy and partial molar excess Gibbs energy values are compared in Table 6 with literature data. They are in good agreement with that obtained by Poyarkov et al. [5]. The partial molar enthalpy of thorium in liquid gallium at infinite dilution at 1095 K derived from solution calorimetry is $\Delta\overline{H}^{\infty}_{Th} = -(178.6 \pm 6.8)$ kJ g atom^{-1}. The partial molar enthalpy of thorium at infinite dilution is only slightly more exothermic than the value obtained from emf measurements which is for the saturated solution. This shows that activity coefficient of thorium is only weakly dependent on concentration, as it varies only slightly on going from dilute solution to saturated one.

The Gibbs energies of formation of the intermetallic compounds of U–Ga systems reported elsewhere [3] ($\Delta_f G^0 UGa_3$ and UGa_2 at 850 K and U_2Ga_3 at 1250 K are −30.5, −31.6 and −24.3 kJ g atom^{-1}, respectively) are much higher than that of $ThGa_2$ and the partial molar excess Gibbs energy of uranium in liquid gallium is more than that of thorium in liquid gallium. Hence the Th–Ga system shows a more negative deviation from ideality than the U–Ga system. The enthalpy of formation of $ThGa_2$ derived from our calorimetric measurements is more exothermic than those of the compounds of the U–Ga system [13] which is in line with the above observation.

Table 5
Enthalpy of formation of intermetallic compound $ThGa_2$ with reference to α-thorium and solid Ga

Compound	$-\Delta_f H^0$ (kJ g atom^{-1})	T (K)	Method	Reference
$ThGa_2$	55.1 ± 4.8	298.15	Solution calorimetry	This study
	69.6 ± 5.6	1100	Precipitation calorimetry	This study
	71.4 ± 1.6	682–891	emf technique	This study
	72.3	648–1056	emf technique	Poyarkov et al. [5]

Table 6
Partial molar excess Gibbs energy and partial molar enthalpy of Th in the thorium saturated Th_xGa_{1-x} solution

$-\Delta\overline{G}^{xs}_{Th}$ (kJ g atom^{-1})	$-\Delta\overline{H}_{Th}$ (kJ g atom^{-1})	T (K)	Method	Reference
–	178.6 ± 6.8[a]	1095	Calorimetry	This study
123.3 ± 4.7	164.2 ± 4.7	787	emf technique	This study
123.0	166.4	852	emf technique	Poyarkov et al. [5]

[a] At infinite dilution.

5. Conclusion

This study provides the only calorimetric data for the enthalpy of formation of $ThGa_2$.

Acknowledgements

The authors are grateful to Shri I. Kaliappan for the help rendered in preparation of the intermetallic compound and to Dr K.V.G. Kutty for the characterization of the sample.

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