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Enthalpies of formation of UGa_2 and UGa_3 by calorimetry

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Abstract

Enthalpies of formation of the intermetallic compounds, UGa_2 and UGa_3, at 298.15 K were determined by using high-temperature liquid gallium solution calorimetric measurements at 1427 K to be -40.4 ± 6.0 and -38.3 ± 4.4 kJ gatom^{-1}, respectively. The enthalpies of formation of UGa_2 at 1563 K and UGa_3 at 1038 K were determined to be -79.1 ± 2.5 and -40.6 ± 1.5 kJ gatom^{-1} by using the precipitation calorimetric method. The enthalpies of formation of UGa_3 at 298.15 and at 1038 K are found to be in agreement with each other, whereas that of UGa_2 at 1563 K is highly exothermic compared to that at 298.15 K.

Keywords: Thermodynamics; Calorimetry; Alloys; Enthalpy; U–Ga system

1. Introduction

Thermodynamic properties of U–Ga alloys are of interest in the pyrochemical processes for the extraction of uranium from molten salts by using liquid Ca–Ga alloys [1]. There are three intermetallic compounds, UGa_3, UGa_2 and U_2Ga_3 in the U–Ga system [2]. Palenzona and Cirafici [3] have measured the enthalpy of formation of UGa_3 by reaction calorimetry. The Gibbs free energies of formation of UGa_3 have been determined by Johnson and Feder [4] and Lebedev et al. [5] by molten salt galvanic cell measurements. Alcock et al. [6] have measured the vapour pressures of gallium over gallium metal as well as U–Ga alloys and derived the Gibbs free energies of formation of all the three intermetallic compounds. The phase diagram and the thermodynamic data of the system has been reviewed by Chiotti et al. [7]. Recently Gardie et al. [8] have measured the vapour pressures over uranium-rich U–Ga alloys. There exists large disagreement among the thermodynamic data for UGa_3 determined by vapour pressure measurements, reaction calorimetry and molten salt emf method. The only data available for UGa_2 is that of Alcock et al. [6]. In this study, we have adopted two different calorimetric methods to determine the enthalpies of formation of UGa_3 and UGa_2. The enthalpies of formation of these compounds at 298.15 K were determined by high-temperature gallium solution calorimetry. The enthalpy of formation of UGa_3 at 1038 K, and that of UGa_2 at 1563 K, were derived from the integral enthalpies of formation of U–Ga alloys at these temperature measured over the biphasic regions, $\{U\text{–}Ga\}+\langle UGa_3\rangle$ and $\{U\text{–}Ga\}+\langle UGa_2\rangle$, respectively. In this paper, these calorimetric results are discussed.

2. Experimental

2.1. Sample preparation and experimental procedure

The intermetallic compounds UGa_3 and UGa_2 were prepared by arc melting followed by annealing under argon atmosphere. The X-ray diffraction patterns of the annealed samples of UGa_3 confirmed the presence of single phase, whereas UGa_2 samples showed a very small amount of UGa_3 phase also to be present. Since standard X-ray diffraction patterns were not available for these compounds in JCPDS files, the lattice parameters reported by Buschow [9] and their crystal structures were used to generate them. The concentration of UGa_3 in the UGa_2 sample was determined to be only 4% by quantitative metallography.

The calorimetric measurements were carried out using a high-temperature differential calorimeter (Model HT-1500 of M/s., Setaram, France) described elsewhere [10]. The procedures adopted for the solution, as well as the precipitation calorimetric measurements, were similar to the ones used in our earlier studies on U–Al alloys described elsewhere [11], except that the calibration here was done by dropping $\alpha\text{-}Al_2O_3$ (SRM-720, NIST) samples after the

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Table 1
Experimental data for the measurement of thermal effects of dissolution of uranium in liquid gallium at 1408 K

Calibration			Measurement				
			$\langle U\rangle_{298.15} \rightarrow [U]_{\{Ga,1408\}}$				
No.	Wt. of α-Al_2O_3 (mg)	Peak area (counts)	No.	Wt. of U (mg)	Peak area (counts)	X_U (at.%)	Q^E_U (kJ gatom^{-1})
1	62.60	188.0	1	18.06	−7.0	0.23	−38.5
2	69.83	206.0	2	18.71	−6.0	0.48	−31.8
3	72.40	210.5	3	21.10	−9.0	0.75	−42.4
4	77.20	252.0	4	20.47	−8.0	1.01	−38.8
5	31.35	101.0	5	15.97	−6.0	1.21	−37.3
					$Q^{E,\infty}_U = -37.8$ kJ gatom^{-1}		

Amount of gallium in the calorimeter, 2.25460 g; $(H^O_T - H^O_{298.15})$ of α-Al_2O_3 at 1408 K, 130.2722 kJ mol^{-1}; calibration constant, 0.4172±0.0218 J count^{-1}; overall uncertainty in $Q^{E,\infty}_U$, ±4.3 kJ gatom^{-1}.

completion of the calorimetric measurements on U–Ga alloys.

3. Results and discussion

The thermal effects of dissolution of U (Q^E_U) in liquid gallium at 1408 K measured by adding U maintained at 298.15 K into gallium at 1408 K are given in Table 1. Similar results for the intermetallic compounds UGa_3 and UGa_2 at 1427 K are given in Table 2 Table 3, respectively. As can be seen from Tables 1–3, the thermal effects of dissolution of U, UGa_3 and UGa_2 (Q^E values) are independent of the composition of the alloy in the crucible, within experimental error. 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 of U, as well as those of the compounds, the enthalpies of formation of the compounds at 298.15 K were computed by using the following equation.

Table 2
Experimental data for the measurement of thermal effects of dissolution of UGa_3 in liquid gallium at 1427 K

Calibration			Measurement				
			$\langle U_{1/4}Ga_{3/4}\rangle_{298.15} \rightarrow [1/4U + 3/4Ga]_{\{Ga,1427\}}$				
No.	Wt. of α-Al_2O_3 (mg)	Peak area (counts)	No.	Sample wt. (mg)	Peak area (counts)	$X_{U_{1/4}Ga_{3/4}}$ (at.%)	$Q^E_{U_{1/4}Ga_{3/4}}$ (kJ gatom^{-1})
1	92.33	273.3	1	15.96	19.0	0.44	55.9
2	82.76	244.5	2	12.23	14.0	1.02	53.7
3	96.76	325.5	3	11.30	12.5	1.50	51.9
4	78.30	252.0	4	14.81	18.0	2.06	57.0
5	71.56	218.5	5	14.12	18.0	2.65	59.8
					$Q^{E,\infty}_{U_{1/4}Ga_{3/4}} = 55.7$ kJ gatom^{-1}		

Amount of gallium in the calorimeter, 1.04778 g; $(H^O_T - H^O_{298.15})$ of α-Al_2O_3 at 1427 K, 132.7688 kJ mol^{-1}; calibration constant, 0.4198±0.0234 J count^{-1}; overall uncertainty in $Q^{E,\infty}_{U_{1/4}Ga_{3/4}}$, ±4.3 kJ gatom^{-1}.

Table 3
Experimental data for the measurement of thermal effects of dissolution of UGa_2 in liquid gallium at 1427 K

Calibration			Measurement				
			$\langle U_{1/3}Ga_{2/3}\rangle_{298.15} \rightarrow [1/3U + 2/3Ga]_{\{Ga,1427\}}$				
No.	Wt. of α-Al_2O_3 (mg)	Peak area (counts)	No.	Sample wt. (mg)	Peak area (counts)	$X_{U_{1/3}Ga_{2/3}}$ (at.%)	$Q^E_{U_{1/3}Ga_{2/3}}$ (kJ gatom^{-1})
1	83.80	231.5	1	36.10	36.0	0.69	54.4
2	76.01	226.0	2	22.28	20.0	1.53	48.9
3	77.81	233.5	3	17.32	18.5	2.11	58.2
4	90.93	298.0	4	23.57	19.75	2.74	45.7
5	70.91	217.0	5	38.77	36.0	3.70	50.6
					$Q^{E,\infty}_{U_{1/3}Ga_{2/3}} = 51.6$ kJ gatom^{-1}		

Amount of gallium in the calorimeter, 1.5299 g; $(H^O_T - H^O_{298.15})$ of α-Al_2O_3 at 1427 K, 132.7688 kJ mol^{-1}; calibration constant, 0.4332±0.0266 J count^{-1}; overall uncertainty in $Q^{E,\infty}_{U_{1/3}Ga_{2/3}}$, ±5.8 kJ gatom^{-1}.

$$\Delta_f\, \mathrm{H}^0_{298.15}\langle \mathrm{U}_x\mathrm{Ga}_{(1-x)}\rangle = x \cdot Q^{\mathrm{E},\infty}_{\mathrm{U}} + (1-x)Q^{\mathrm{E},\infty}_{\mathrm{Ga}} - Q^{\mathrm{E},\infty}_{\mathrm{U}_x\mathrm{Ga}_{(1-x)}} \qquad (1)$$

The $Q^{\mathrm{E},\infty}_{\mathrm{Ga}}$ term in the above equation corresponds to the enthalpy increment, $H^{\mathrm{O}}_{T} - H^{\mathrm{O}}_{298.15}$, of Ga at 1427 K which was taken from the literature (35.7484 kJ gatom^{-1}) [12]. The only assumption that has been made in these calculations is that the $Q^{\mathrm{E},\infty}_{\mathrm{U}}$ measured at 1408 K will be the same at 1427 K, which introduces an error of ~0.25–0.35 kJ gatom^{-1} in the enthalpies of formation, and this is within the experimental error.

The integral enthalpies of formation of U–Ga alloys measured by precipitation calorimetry at 1038 and 1563 K are given in Table 4, and are plotted as a function of U concentration in Fig. 1 Fig. 2, respectively. At 1038 K, the measured values are over the two-phase alloys containing $\{\mathrm{U{-}Ga}\} + \langle \mathrm{UGa}_3\rangle$, which when extrapolated to 25 at.% uranium give the enthalpy of the following reaction at 1038 K

$$1/4\langle \mathrm{U}\rangle_\beta + 3/4\{\mathrm{Ga}\} \rightarrow \langle \mathrm{U}_{1/4}\mathrm{Ga}_{3/4}\rangle \qquad (2)$$

The value thus obtained was −45.5 kJ gatom^{-1}. The enthalpy of formation of $\mathrm{U}_{1/4}\mathrm{Ga}_{3/4}$ at 1038 K with reference to α-uranium and solid gallium was then computed to be −40.6±1.5 kJ gatom^{-1}. The thermodynamic data of gallium and uranium required for this computation were taken from Knacke et al. [12].

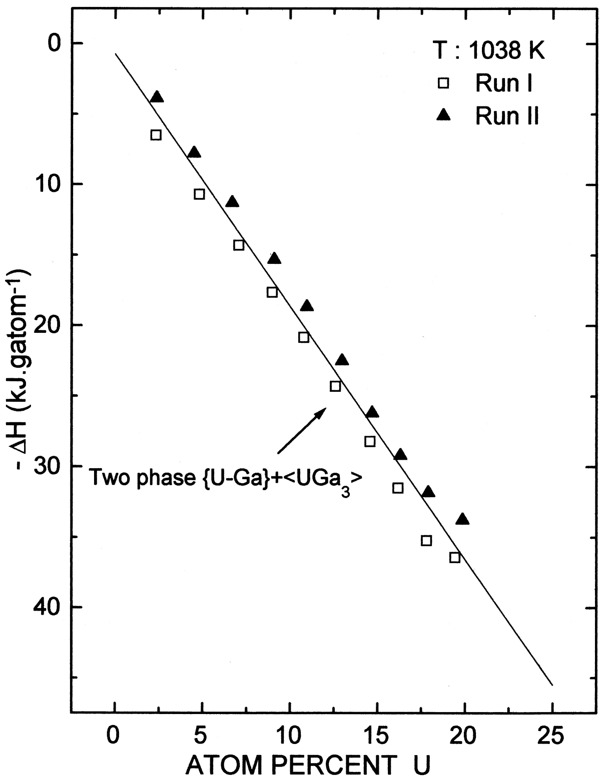

Fig. 1. Integral enthalpies of formation of U–Ga alloys at 1038 K.

The measurements of the integral enthalpies of formation at 1563 K initially covered the single-phase liquid alloy region up to about ~21.5 at.% U and then the two-phase region containing $\{\mathrm{U{-}Ga}\} + \langle \mathrm{UGa}_2\rangle$. The extrapolation of the integral enthalpy values in the two-phase region to 33.3 at.% uranium gives the enthalpy of the following reaction:

$$1/3\{\mathrm{U}\} + 2/3\{\mathrm{Ga}\} \rightarrow \langle \mathrm{U}_{1/3}\mathrm{Ga}_{2/3}\rangle \qquad (3)$$

The value thus obtained was −88.2 kJ gatom^{-1}. The enthalpy of formation of $\mathrm{U}_{1/3}\mathrm{Ga}_{2/3}$ with reference to α-uranium and solid gallium has been computed to be

Table 4
Integral enthalpies of formation of U–Ga alloys

1038 K[a]				1563 K[b]			
Run-I		Run-II		Run-I		Run-II	
X_{U} (at.%)	$-\Delta H$ (kJ gatom^{-1})	X_{U} (at.%)	$-\Delta H$ (kJ gatom^{-1})	X_{U} (at.%)	$-\Delta H$ (kJ gatom^{-1})	X_{U} (at.%)	$-\Delta H$ (kJ gatom^{-1})
2.33	6.52	2.36	3.92	4.52	4.34	4.35	3.51
4.82	10.70	4.50	7.83	9.15	9.59	8.71	7.83
7.07	14.33	6.69	11.32	12.19	12.48	13.06	13.02
8.96	17.66	9.09	15.36	15.72	16.02	16.56	19.18
10.79	20.84	10.95	18.68	18.30	20.01	19.49	26.02
12.61	24.31	12.97	22.53	19.57	24.13	21.39	28.79
14.57	28.21	14.69	26.23	20.23	27.34	22.84	34.22
16.18	31.50	16.31	29.22	20.84	31.06	24.31	41.71
17.80	35.23	17.90	31.86	21.31	33.67	25.52	48.47
19.43	36.42	19.86	33.80	21.94	35.15	26.74	56.60
				22.37	36.98	27.71	62.63
				22.85	39.73	28.92	66.67
				23.18	42.07	29.93	73.61
				23.66	45.21		
				23.98	47.37		

[a] All measurements are over the two-phase region $\{\mathrm{U{-}Ga}\} + \langle \mathrm{UGa}_3\rangle$.

[b] Measurements up to 21.5 at.% U are in the {U–Ga} single-phase region and above 21.5 at.% U over $\{\mathrm{U{-}Ga}\} + \langle \mathrm{UGa}_2\rangle$ two-phase alloys.

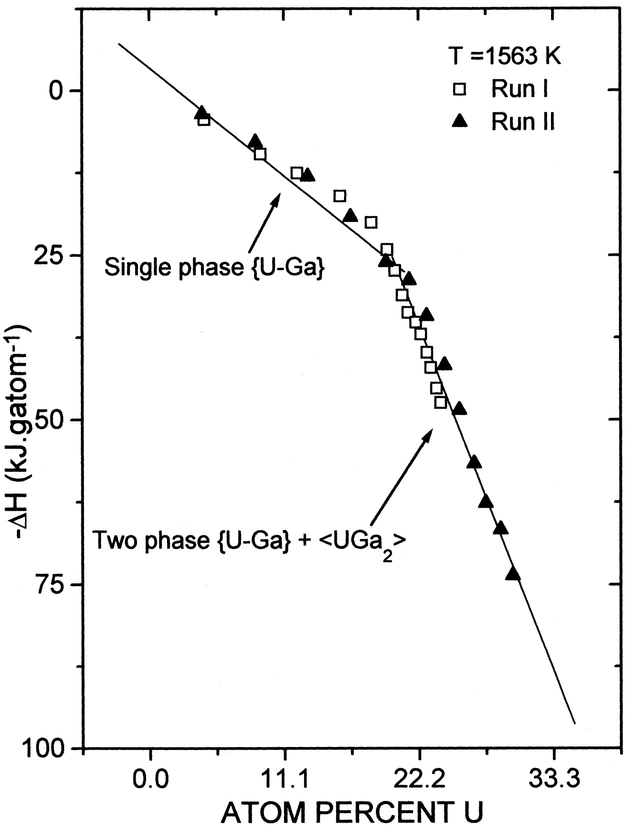

Fig. 2. Integral enthalpies of formation of U–Ga alloys at 1563 K.

-79.1 ± 2.5 kJ gatom^{-1}. The two lines for the integral enthalpies of formation of liquid and liquid+$\langle UGa_2\rangle$ alloys intersect at 20.1 at.% (Fig. 2), which is slightly lower than the liquid/liquid+$\langle UGa_2\rangle$ phase boundary value of 21.5 at.% as per the phase diagram [2].

The enthalpies of formation of UGa_3 and UGa_2 from the present study are compared with literature data in Table 5. As can be seen from the table, the enthalpy of formation of UGa_3 at 1038 K obtained by the precipitation calorimetric method is in agreement with our value at 298.15 K, obtained by solution calorimetry within the error limits. This shows that the ΔC_p for the formation reaction of UGa_3 is zero, which is in contradiction of the suggestion of Chiotti et al. [7] that the ΔC_p for UGa_3 might be large. The enthalpy of formation of UGa_3 at 433 K obtained by Palenzona and Cirafici [3] by reaction calorimetry, as well as that at 1250 K obtained by Alcock et al. [6] by vapour pressure measurements, are very much less exothermic than the present values. The errors in the vapour pressure measurements due to the possible but questionable presence of volatile gallium oxide species have been suggested as a possible contributing factor by Alcock et al. [6]. The present values agree fairly well with those at 828 and 890 K obtained by Johnson and Feder [4] and Lebedev et al. [5], respectively, by molten salt emf measurements. Chiotti et al. [7] recommended, in their review, the mean of the values of these two authors for the thermodynamic data of UGa_3. In fact, they had suggested that a room temperature calorimetric measurement should be made to resolve the large discrepancy between vapour pressure and emf values. Our measurements confirm the reliability of the values from emf cell measurements.

The enthalpy of formation of UGa_2 at 298.15 K from our solution calorimetric measurement is more highly exothermic than the value at 1250 K reported by Alcock et al. [6] from vapour pressure measurements. We believe the presence of a small amount of UGa_3 will not affect our results to a great extent. Further, the value of Alcock et al. [6] is likely to be in error as in the case of UGa_3. Chiotti et al. [7] combined the gallium pressure data of Alcock et al. [6] for the difference in the Gibbs free energies of formation of UGa_2 and UGa_3, with the mean of Gibbs free energies of formation of UGa_3 of Johnson et al. [4] and Lebedev et al. [5], to derive the value for UGa_2 As can be seen, the present data is in good agreement with the value recommended by Chiotti et al. [7]. Hence our value is considered more reliable than that of Alcock et al. [6]. The enthalpy of formation of UGa_2 computed using Miedema's

Table 5
Standard enthalpies of formation of U–Ga compounds with reference to α-uranium and Ga (s)

Compound	$-\Delta H^0_{f,298.15}$ (kJ gatom^{-1})				
	Present data		Literature data	Temp. range (K)	Reference
	Solution calorimetry	Precipitation calorimetry			
UGa_3	38.3 ± 4.4	40.6 ± 1.5[a]	25.5	433	[3]
			38.5	643–1013	[4]
			37.9	696–1084	[5]
			24.0	1250	[6]
			38.2[c]	298–942	[7]
			35.9	Miedema model	Miedema model
UGa_2	40.4 ± 6.0	79.1 ± 2.5[b]	24.3	1250	[6]
			43.2[c]	298–942	[7]
			46.0	Miedema model	Miedema model

[a] 1038 K.
[b] 1563 K.
[c] Assessment.

model [13] (-46.0 kJ gatom^{-1}) is slightly more exothermic than our value at 298.15 K, whereas that of UGa_3 (-35.9 kJ gatom^{-1}) is less exothermic than our value. The enthalpy of formation of UGa_2 at 1563 K obtained by precipitation calorimetry is more highly exothermic than the value at 298.15 K which is very unusual, but we have no satisfactory explanation for this at present.

References

[1] B. Mishra, J.J. Moore, Metall. Trans. 25B (1994) 151.
[2] H. Okamoto, J. Phase Equilibria 14 (1993) 125.
[3] A. Palenzona, S. Cirafici, Thermochim. Acta 13 (1975) 357.
[4] I. Johnson, H.M. Feder, in: Thermodynamics of Nuclear Materials, Proc. Symp., Vienna, IAEA, Vienna, 1962, p. 319.
[5] V.A. Lebedev, V.N. Seregin, A.M. Poyarkov, I.F. Nichkov, S.P. Raspopin, Russ. J. Phys. Chem. 47 (1973) 402.
[6] C.B. Alcock, J.B. Cornish, P. Grieveson, in: Thermodynamics, Proc. Symp., Vienna, vol. 1, IAEA, Vienna, 1966, p. 211.
[7] P. Chiotti, V.V. Akhachinskij, I. Ansara, M.H. Rand, in: The Chemical Thermodynamics of Actinide Elements and Compounds, Part 5, The Actinide Binary Alloys, IAEA, Vienna, 1981, p. 120.
[8] P. Gardie, G. Bordier, J.J. Poupeau, J. Le Ny, J. Nucl. Mater. 189 (1992) 85.
[9] K.H.J. Buschow, J. Less-Common Metals 31 (1973) 165.
[10] K. Nagarajan, Rita Saha, R. Babu, C.K. Mathews, Thermochim. Acta 90 (1985) 279.
[11] K. Nagarajan, R. Babu, C.K. Mathews, J. Nucl. Mater. 201 (1993) 142.
[12] O. Knacke, O. Kubaschewski, K. Hesselmann, in: Thermochemical Properties of Inorganic Substances, 2nd ed., Springer-Verlag, Berlin, 1991.
[13] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen (Eds.), Cohesion in Metals, North-Holland, Amsterdam, 1988.