



Standard enthalpy of formation of Cu_3As and heats of mixing in the liquid systems Cu–As and Fe–As by direct combination high temperature drop calorimetry

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Abstract

The standard enthalpy of formation of the congruent melting compound Cu_3As (m.p. 1000 K) was determined by high temperature direct synthesis drop calorimetry in fused silica capsules at 1113 K. We found ΔH_f° (298 K) = -14.6 ± 3.8 kJ mol⁻¹.

Using our measured values of the heats of reaction of the process $a\text{As}(s) + b\text{Cu}(s) \rightarrow c\text{Cu}_{1-x}\text{As}_x(l)$ at 1113 K, we calculated the liquid–liquid enthalpies of mixing for three alloy compositions in $\text{Cu}_{1-x}\text{As}_x$: $x = 0.235$, 0.26 and 0.375. We carried out similar measurements at 1123 K for the eutectic alloy $\text{Fe}_{1-x}\text{As}_x(l)$ at $x = 0.24$.

The calorimetric results for the solid and liquid alloys are compared with predicted values from Miedema's semiempirical model.

Keywords: Liquid systems; High temperature drop calorimetry; Fused silica capsules

1. Introduction

During recent years the laboratory of the senior author has pursued a programme of research on the heats of formation of intermetallic phases and related compounds. Among the "related compounds" we have studied, among others, binary compounds of Fe, Ni, Pd, Cu and Ag with non-metals from groups Vb and VIb in the periodic table. Most recently these studies have involved determinations by Boone and Kleppa [1–3] of the standard enthalpies of formation of phosphides of nickel [1], palladium [2] and copper [3] using high temperature direct synthesis drop calorimetry.

In the present paper these calorimetric studies are extended to alloys of copper and iron with arsenic. Previously reported thermodynamic data on these systems are limited to information obtained by the e.m.f. method [4] and vapour pressure measurements [5–8]. These earlier experiments yield information on the activities of the components in the solutions, which can in turn be used to derive information on the Gibbs

energies of mixing. However, we have found no earlier information on the enthalpies of mixing in these systems.

In the course of the present study we have used the technique of Boone and Kleppa to determine the standard enthalpy of formation of Cu_3As and to obtain some new heat-of-mixing data for the liquid alloys of Cu–As and Fe–As.

2. Experimental details

The experiments were carried out in a Calvet-type twin microcalorimeter developed at the James Franck Institute of the University of Chicago. The principles involved in the design of this calorimeter were described in an early publication by Kleppa [9]. However, in the newer unit actually used in our experiments, the aluminium jacket of the early calorimeter was replaced by a jacket machined from Inconel. This allows the calorimeter to be operated at temperatures up to 1000–1100 °C.

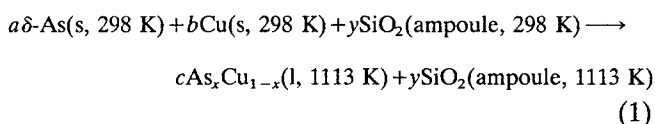
During our experiments only one of the two calorimeters in the twin system is involved in the actual

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measurements; the other calorimeter serves as a “dummy”. Each sample was dropped into a receiving vessel maintained inside a fused silica “liner”; this can easily be removed from or inserted into the calorimeter. The receiving vessel was a cylindrical gold crucible about 16 mm in diameter and 80 mm long, with a 0.5 mm wall. The calorimeter was calibrated by dropping weighed pieces of pure silica glass tubing from room temperature into the calorimeter and relating the resulting thermal effects to the known enthalpy increments of silica glass [10]. The calibrations were reproducible within $\pm 1\%$.

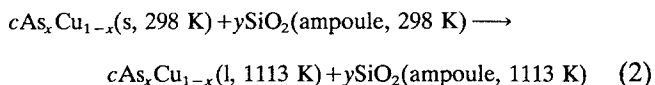
The samples were prepared from copper powder (99.95% purity) purchased from Johnson–Matthey and arsenic (99.9% purity) from Alfa Products. Prior to the reaction experiments the copper powder was reduced under hydrogen at about 873 K, while the arsenic was distilled in an evacuated silica ampoule under a temperature gradient. The powders of the two components were weighed, mixed together and then pressed into cylindrical pellets 4 mm in diameter. The pellets were sealed into silica glass capsules under vacuum. The weighed capsules were then dropped into the calorimeter.

The first drop of each sample capsule was used to measure the enthalpy change $\Delta H(1)$ associated with the process



Here a is the number of moles of δ -As, b is the number of moles of Cu, y is the number of moles of SiO_2 and c is the number of moles of the alloy formed. The silica in the capsule does not participate in the chemical reaction and the value of y , which is arbitrary, does not change during the experiments.

Subsequent drops of the same sample capsule provide the enthalpy change $\Delta H(2)$ of the process



Consequently, the standard enthalpy of formation of $\text{As}_x\text{Cu}_{1-x}$, $\Delta H_f^\circ(298\text{ K})$ (kJ g-atom^{-1}), is obtained from the measured heat effects of reactions (1) and (2):

$$\Delta H_f^\circ(298\text{ K}) = \frac{\Delta H(1) - \Delta H(2)}{c} \quad (3)$$

Similarly, the enthalpy of mixing of the liquid alloy $\text{As}_x\text{Cu}_{1-x}$ at 1113 K can be calculated from $\Delta H(1)$ if the number of moles of the silica ampoule, y , and the enthalpy changes for the two pure components and for silica glass between 298 and 1113 K are known. After subtracting the term y (heat content of SiO_2 glass)

from $\Delta H(1)$, one can derive the following expression for the enthalpy of mixing of the liquid alloy $\text{As}_x\text{Cu}_{1-x}$:

$$\Delta H_{\text{mix}}^m = \frac{\Delta H(1) - y(H_T^\circ - H_{298}^\circ)_{\text{SiO}_2(s)}}{c} - x(H_T^\circ - H_{298}^\circ)_{\text{As}(l)} - (1-x)(H_T^\circ - H_{298}^\circ)_{\text{Cu}(l)} \quad (4)$$

The adopted values of the heat contents of the pure substances used in evaluating the calorimetric experiments are based on Refs. [10–12]; they are summarized in Table 1. The results of the calorimetric experiments are presented in Table 2 and the calculated values of ΔH_{mix}^m are plotted in Fig. 1 as a function of alloy composition.

3. Discussion

The enthalpies of mixing of binary liquid alloys may be described by the equation

$$\Delta H_{\text{mix}}^m = \lambda x(1-x) \quad (5)$$

where x is the mole fraction of one of the components and the interaction parameter λ in general will be a function of composition, $\lambda = \lambda(x)$. In our experiments we have considered x to be the mole fraction of arsenic; unfortunately, we have not been able to carry out experiments over a large enough range of compositions to allow us to determine the concentration dependence of λ . For this reason we will assume that this parameter is constant for the Cu–As system; this is equivalent to assuming a regular solution model. On this basis we have calculated ΔH_{mix}^m for the whole range of compositions. The curve drawn for Cu–As in Fig. 1 is based on this assumption; we adopted an average value of $\lambda = -51.5\text{ kJ mol}^{-1}$ calculated from our measurements. The actual enthalpy-of-mixing curve can perhaps be approximated by combining our own enthalpy data for

Table 1
Adopted heat contents

Substance	Heat content (kJ mol^{-1})		Ref.
	1111 K	1123 K	
SiO_2 (glass, solid)	51.52	52.23	[10]
As (liquid)	45.06	45.35	[12]
Cu (liquid)	34.73 ^a	–	[11]
Fe (liquid)	–	40.86 ^a	[11]

^aIn calculating these values, it has been assumed that the heat capacity of the undercooled liquid is independent of temperature and is the same as the heat capacity of the liquid at the melting point. For Cu(l) at 1113 K, i.e. 243 K below the melting point, this should not introduce a significant error. However, for Fe(l) at 1123 K, i.e. 686 K below the normal melting point, this assumption may introduce a larger uncertainty.

Table 2
Experimental results obtained for binary Cu–As and Fe–As solutions

Sample	<i>a</i> (mmol As)	<i>b</i> (mmol Cu)	<i>c</i> (mmol As _{<i>x</i>} Cu _{1–<i>x</i>})	<i>x</i>	<i>y</i> (mmol SiO ₂)	$\Delta H(1)$ (J)	$\Delta H(2)$ (J)	ΔH_{1-1}^M (kJ mol ⁻¹)	$\Delta H_f^{\circ}{}_{298}$ (kJ g-atom ⁻¹)
1	0.4538	1.4792	1.9330	0.235	10.1514	578.6		–8.4	
2	0.4939	1.6051	2.0991	0.235	11.1000	631.8		–8.6	
3	0.5072	1.6523	2.1595	0.235	10.5092	597.6		–11.2	
4	1.1038	3.1521	4.2556	0.260	16.0393	943.5	965.3	–9.6	–5.1
5	1.0972	3.0985	4.1970	0.260	14.6031	869.5	884.2	–9.5	–3.5
6	1.1052	3.1599	4.2647	0.260	13.9025	835.2	849.3	–9.5	–3.3
7	1.1506	3.2795	4.4301	0.260	14.9626	889.8	904.9	–10.6	–3.4
8	1.0785	3.0875	4.1654	0.260	16.0509	943.8	956.0	–9.4	–2.9
9	1.1225	3.1945	4.3173	0.260	15.4502	918.9	930.7	–9.0	–2.7
						Av. value (4–9)		–9.6±0.6	–3.5±0.9
10	0.6140	1.0229	1.6369	0.375	10.8670	600.0		–14.1	
11	0.7074	1.1803	1.8876	0.375	11.1666	625.4		–12.1	
12	0.7608	1.2747	2.0351	0.374	11.2498	634.3		–11.7	
		<i>b</i> (mmol Fe)	<i>c</i> (mmol As _{<i>x</i>} Fe _{1–<i>x</i>})						
13	1.0278	3.2193	4.2495	0.240	14.4334	859.7		–17.0	
14	1.0451	3.2838	4.3306	0.240	14.6397	870.9		–18.4	
15	0.9290	2.9597	3.8871	0.240	15.4335	903.6		–18.1	

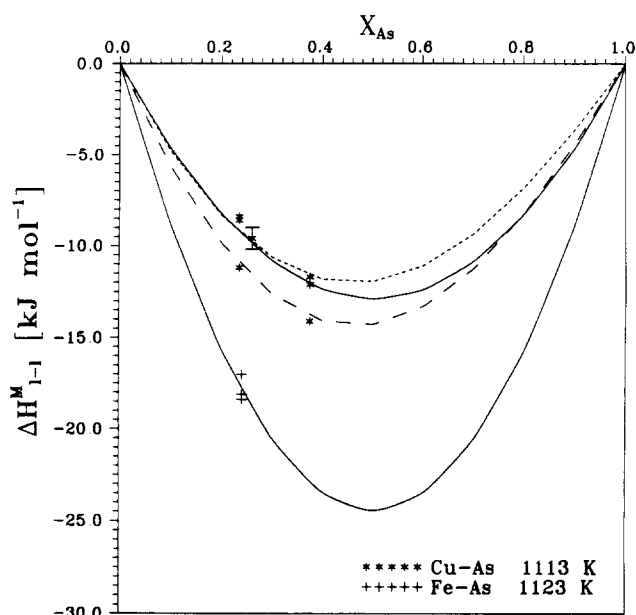


Fig. 1. Heats of mixing for Cu–As and Fe–As liquid solutions. Solid curves are based on the regular solution model: $\lambda(\text{Cu–As}) = -51.5$ kJ mol⁻¹; $\lambda(\text{Fe–As}) = -97.8$ kJ mol⁻¹. Broken curves are obtained from the Miedema model: ----, Cu–As; --, Fe–As.

values of *x* up to 0.375 with estimated values for larger values of *x* from the activity data for arsenic obtained from the vapour pressure and e.m.f. measurements quoted in Section 1.

For comparison with our results on liquid Cu–As alloys at 1113 K, we carried out a few experiments on liquid Fe–As alloys at 1123 K at the eutectic composition

$x_{\text{As}} = 0.24$. The results of these experiments are reported in Table 2 and plotted in Fig. 1. The calculated value of the regular solution parameter λ for this system is -97.8 kJ mol⁻¹ i.e. significantly more exothermic than for the Cu–As system.

The enthalpies of mixing of liquid alloys can be predicted from the semiempirical theory of Miedema [13]. The predicted values from this theory are plotted as broken lines along with our experimental data and calculated heat-of-mixing curves in Fig. 1. This comparison shows that there is good agreement between theory and experiments for the Cu–As system. However, there is a wide discrepancy for the Fe–As system, which has much larger exothermic values than predicted by Miedema.

Our experimental runs for the composition $x = 0.26$ in the Cu–As system (samples 4–9 in Table 2) allow us to determine the standard enthalpy of formation of the compound Cu₃As(s) and also its average heat content at 1113 K. We find the value -3.5 ± 0.9 kJ g-atom⁻¹ (-14.6 kJ mol⁻¹) for ΔH_f° and 31.3 ± 0.8 kJ g-atom⁻¹ for the heat content. The value of $\Delta H_f^{\circ}(298 \text{ K})$ is negative, but much less negative than that given by Savelsberg [14] and quoted by Weibke and Kubaschewski [15], -26.8 kJ g-atom⁻¹.

However, it seems that the experiments of Savelsberg, who investigated the reaction between copper and arsenic trioxide at high temperature, were not precise enough to provide a reliable value for the heat of formation of Cu₃As. There is probably more interest in comparing our new enthalpy-of-formation value for

Cu_3As (-3.5 ± 0.9 kJ g-atom $^{-1}$) with the early value for Cu_3Sb , for which Kleppa [16] reported 0.6 kJ g-atom $^{-1}$ at 450 °C, with the value of Boone and Kleppa [3] for Cu_3P , -8.7 ± 0.9 kJ g-atom $^{-1}$, and with the recent value for Cu_3Ge , for which Meschel and Kleppa [17] give a standard enthalpy of formation of -4.05 ± 0.6 kJ g-atom $^{-1}$. It is apparent that the quoted enthalpy values are all in the same ballpark. On the other hand, the standard enthalpy of formation of Cu_3As calculated from the semiempirical theory of Miedema [13] is -18 kJ g-atom $^{-1}$, a much too exothermic value.

The small exothermic heat of formation of Cu_3As seems entirely consistent with the binary phase diagram of Cu–As [18]. This diagram shows a single, non-stoichiometric, congruent melting compound with about 26.25 at.% As. This compound has a relatively low melting point (1100 K) compared with the melting point of pure copper (1358 K).

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