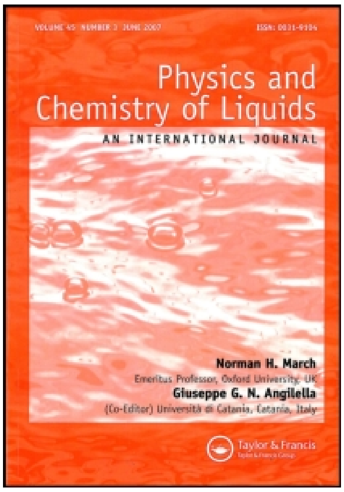

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PARTIAL ENTHALPIES OF SILICON, VANADIUM, ZIRCONIUM, NIOBIUM AND MOLYBDENUM IN LIQUID TIN AT HIGH DILUTION

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The partial enthalpies of silicon, vanadium, zirconium, niobium and molybdenum in liquid tin at 1173 K were measured at high dilution by direct reaction calorimetry (drop method) with the help of a Tian-Calvet high-temperature calorimeter. When referred to liquid metals we found $h_{Si}/\mathrm{kJ\cdot mol^{-1}} = 99.4 - 263.0\,x_{Si}$, $h_V/\mathrm{kJ\cdot mol^{-1}} = 102.8 - 14.8\,x_V$, $h_{Zr}/\mathrm{kJ\cdot mol^{-1}} = 124.2 - 18.1\,x_{Zr}$, $h_{Nb}/\mathrm{kJ\cdot mol^{-1}} = 81.7 + 72.5\,x_{Nb}$ and $h_{Mo}/\mathrm{kJ\cdot mol^{-1}} = 115.4 - 159.9\,x_{Mo}$. The limiting partial enthalpies were deduced by extrapolation at infinite dilution.

Keywords: Calorimetry; partial enthalpy; Si; V; Zr; Nb; Mo; Sn

1. INTRODUCTION

The most used and the most accurate method to measure the enthalpies of formation of intermetallic compounds in the solid state is undoubtedly the dissolution method. Such a method needs the knowledge of the enthalpy of dissolution of the compound at infinite dilution as well as those of their pure components into the same solvent. The most commonly solvent used for that is undoubtedly tin. Tin melts at relatively low temperature (505 K), it dissolves easily the

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*Corresponding author.

greatest number of pure metals and the enthalpies of dissolution are generally small enough to minimise the errors on the determination of the enthalpy of formation of the compounds. However, the enthalpies of dissolution at infinite dilution of some refractory metals were still unknown. Then, it is the purpose of this work to produce such data.

2. EXPERIMENTAL

The limiting partial enthalpies of silicon, vanadium, zirconium, niobium and molybdenum, Δh_i^∞, in liquid tin at 1173 K have been measured by dissolution calorimetry using a well-known high-temperature Tian-Calvet apparatus. The partial enthalpies of dissolution of i (i = Si, V, Zr, Nb and Mo) in tin *versus* composition were deduced from the heat effects corresponding to successive additions of small quantities of solid metal i into the same bath. The apparatus used for the measurements was a high-temperature Tian-Calvet calorimeter built in the laboratory. The method used (drop method) was already described [1]. The quantities of pure metals at T_0 (near 298 K) added to the baths were about 20–50 mg. The calibration of the calorimeter was performed from the heat effects due to some additions (about five) to the metallic bath of small quantities of Nat. Bur. Stand. (US) α-alumina at T_0, the enthalpy of which is well known [2]. The bath was placed in a graphite crucible at the bottom of the calorimetric cell at 1173 K. Before the first addition of solute, the bath (about 10 g) was pure tin. The pure components used for the measurements were purchased from Koch-Light with metallic impurities less than 10^{-5} mass%.

Then the thermal effects produced adding i to the i-Sn melt correspond to the following reaction:

$$ni(cr, T_0) + mi_x\mathrm{Sn}_{1-x}\,(1173\,\mathrm{K}) \rightarrow (n+m)i_{x+dx}\mathrm{Sn}_{1-x-dx}\,(1173\,\mathrm{K})$$

Each heat effect corresponding to successive additions of i leads to the partial enthalpy of solute in the binary alloy against composition with respect to pure liquid metal at 1173 K taking into account the enthalpy change of solid metal from T_0 to 1173 K deduced from Hultgren *et al.* [3] and its enthalpy of fusion also taken from [3] neglecting any temperature dependence.

3. RESULTS

The experimental data concerning the investigated systems are given in Tables I to V and shown on Figures 1 to 5 with respect to concentration. They can be fitted according to the following equations with

TABLE I Partial enthalpy of Si at 1173 K in Si-Sn melts at high dilution with respect to mole fraction of Si referred to solid silicon at 298 K

Series 1		*Series* 2	
x_{Si}	$h_{Si}(kJ\cdot mol^{-1})$	x_{Si}	$h_{Si}(kJ\cdot mol^{-1})$
0.0048	98.42	0.0013	99.60
0.0073	97.76	0.0037	98.33
0.0093	96.01	0.0064	97.67
0.0112	93.88	0.0096	97.77
0.0133	95.38	0.0123	97.97
0.0150	95.55	0.0142	96.60
0.0169	95.13	0.0165	94.24
		0.0189	95.18

TABLE II Partial enthalpy of V at 1173 K in V-Sn melts at high dilution with respect to mole fraction of V referred to solid vanadium at 298 K

Series 1		*Series* 2	
x_V	$h_V(kJ\cdot mol^{-1})$	x_V	$h_V(kJ\cdot mol^{-1})$
0.0012	101.34	0.0010	104.53
0.0033	103.72	0.0030	101.56
0.0053	102.15	0.0048	101.61
0.0071	102.97	0.0069	104.48
0.0088	102.59	0.0089	102.58
0.0104	103.98	0.0108	101.14
0.0124	101.97	0.0136	101.38
0.0147	104.36	0.0163	102.19

TABLE III Partial enthalpy of Zr at 1173 K in Zr-Sn melts at high dilution with respect to mole fraction of Zr referred to solid zirconium at 298 K

x_{Zr}	$h_{Zr}(kJ\cdot mol^{-1})$	x_{Zr}	$h_{Zr}(kJ\cdot mol^{-1})$
0.0007	122.94	0.0020	124.33
0.0021	124.09	0.0033	124.30
0.0038	125.31	0.0045	124.35
0.0061	123.78	0.0058	124.69
0.0083	125.31	0.0072	124.30
0.0103	123.04	0.0088	124.25
0.0121	125.27	0.0105	121.43
		0.0121	124.25

TABLE IV Partial enthalpy of Nb at 1173 K in Nb-Sn melts at high dilution with respect to mole fraction of Nb referred to solid niobium at 298 K

x_{Nb}	$h_{Nb}(kJ \cdot mol^{-1})$	x_{Nb}	$h_{Nb}(kJ \cdot mol^{-1})$
0.0005	82.20	0.0008	81.61
0.0016	81.97	0.0021	80.89
0.0028	81.70	0.0032	82.58
0.0039	82.26	0.0041	82.29
0.0051	77.68	0.0050	81.44
0.0063	82.88	0.0058	83.31
0.0078	80.17	0.0069	81.47
0.0092	83.67	0.0081	82.80

TABLE V Partial enthalpy of Mo at 1173 K in Mo-Sn melts at high dilution with respect to mole fraction of Mo referred to solid molybdenum at 298 K

x_{Mo}	$h_{Mo}(kJ \cdot mol^{-1})$	x_{Mo}	$h_{Mo}(kJ \cdot mol^{-1})$
0.0010	115.77	0.0010	114.53
0.0030	113.87	0.0028	116.58
0.0051	112.63	0.0050	116.50
0.0070	110.84	0.0075	115.08
0.0091	116.38	0.0096	114.30
0.0112	113.07	0.0116	113.54
0.0132	111.35	0.0138	114.08
0.0155	112.82	0.0155	113.31

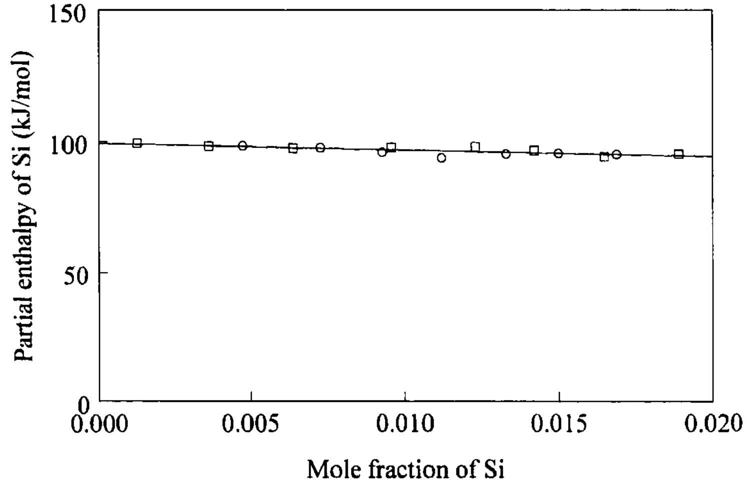

FIGURE 1 Partial enthalpies of Si at 1173 K in Si-Sn melts at high dilution with respect to mole fraction of Si referred to solid silicon at 298 K. Each symbol corresponds to a separate run of measurements.

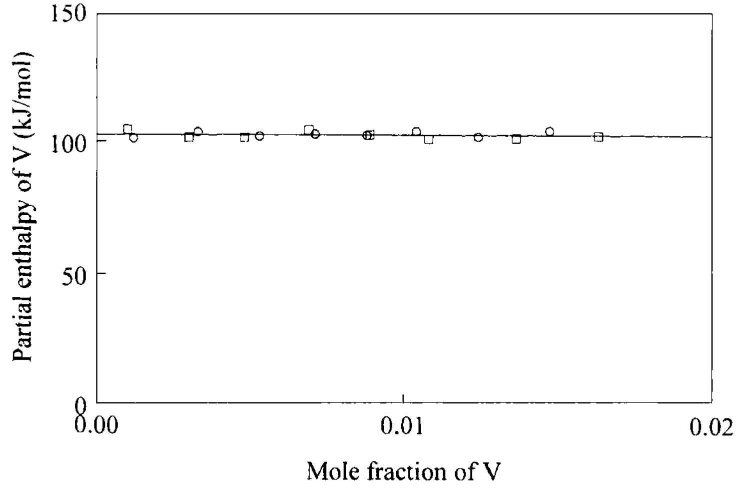

FIGURE 2 Partial enthalpies of V at 1173 K in V-Sn melts at high dilution with respect to mole fraction of V referred to solid vanadium at 298 K. Each symbol corresponds to a separate run of measurements.

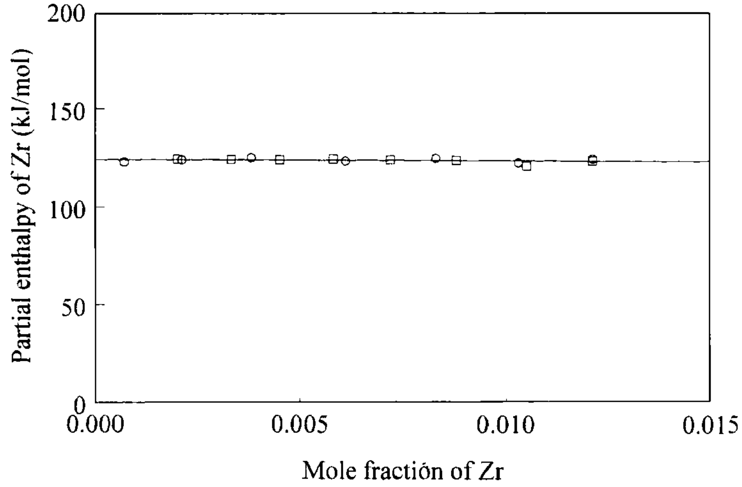

FIGURE 3 Partial enthalpies of Zr at 1173 K in Zr-Sn melts at high dilution with respect to mole fraction of Zr referred to solid zirconium at 298 K. Each symbol corresponds to a separate run of measurements.

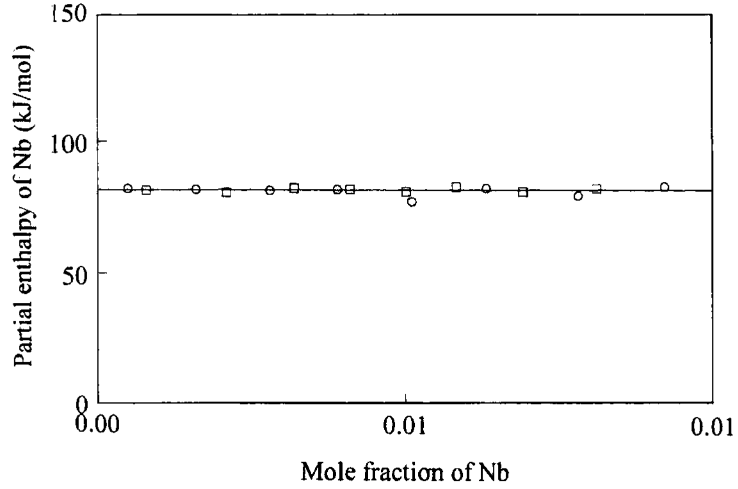

FIGURE 4 Partial enthalpies of Nb at 1173 K in Nb-Sn melts at high dilution with respect to mole fraction of Nb referred to solid niobium at 298 K. Each symbol corresponds to a separate run of measurements.

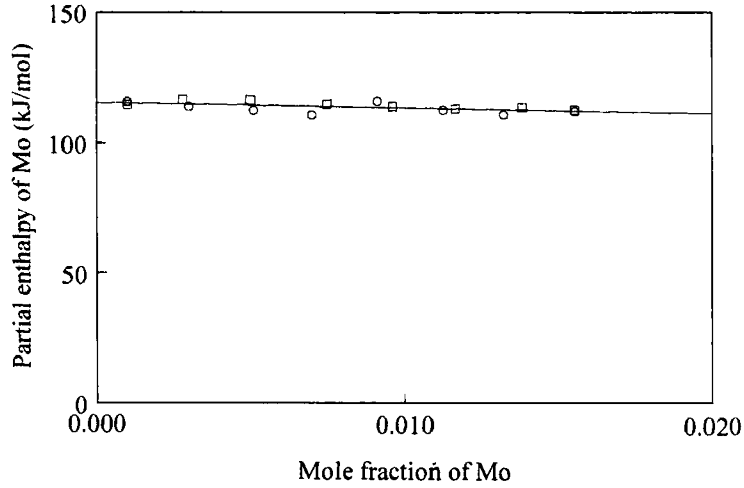

FIGURE 5 Partial enthalpies of Mo at 1173 K in Mo-Sn melts at high dilution with respect to mole fraction of Mo referred to solid molybdenum at 298 K. Each symbol corresponds to a separate run of measurements.

TABLE VI Limiting partial enthalpies of metal i at 1173 K in pure tin referred to i(solid, 298 K) (column 2), referred to i(liquid, 1173 K) (column 5). All the data are expressed in $\mathrm{kJ \cdot mol^{-1}}$. ΔH is the variation of the heat content of i from 298 K to 1173 K and h^{fus} is the enthalpy of melting of i, both taken from Ref. [3]

Solute i	h_s^{∞}	Δh	h^{fus}	h_l^{∞}
Si	99.45	21.72	50.21	27.52
V	102.78	24.95	21.50	56.33
Zr	124.23	30.53	21.00	72.70
Nb	81.67	23.58	30.00	28.09
Mo	115.36	23.59	37.48	54.29

reference to solid components at 298 K:

$$h_{\mathrm{Si}}/\mathrm{kJ \cdot mol^{-1}} = 99.4 - 263.0\,x_{\mathrm{Si}}$$

$$h_{\mathrm{V}}/\mathrm{kJ \cdot mol^{-1}} = 102.8 - 14.8\,x_{\mathrm{V}}$$

$$h_{\mathrm{Zr}}/\mathrm{kJ \cdot mol^{-1}} = 124.2 - 18.1\,x_{\mathrm{Zr}}$$

$$h_{\mathrm{Nb}}/\mathrm{kJ \cdot mol^{-1}} = 81.7 + 72.5\,x_{\mathrm{Nb}}$$

$$h_{\mathrm{Mo}}/\mathrm{kJ \cdot mol^{-1}} = 115.4 - 159.9\,x_{\mathrm{Mo}}$$

The values of the limiting partial enthalpies obtained in this work are given in Table VI with reference to liquid metals at 1173 K.

4. CONCLUSION

All the limiting partial enthalpies of the investigated pure liquid metals in liquid tin at 1173 K are positive. To our knowledge, there is no data in the literature for Si, Zr and Nb. Darby and Jugle [4] found a value of $52.3\,\mathrm{kJ \cdot mol^{-1}}$ for vanadium which is not so far from ours ($56.3\ \mathrm{kJ \cdot mol^{-1}}$). The value of [4] was calculated from the equilibrium solubility limits in the temperature range from 827 to 1211 K. Bowersox [5] used these solubility data to calculate again the limiting partial enthalpy of vanadium. He obtained according to three different ways the following values: $50.5\,\mathrm{kJ \cdot mol^{-1}}$ (called empirical method which is that of Darby and Jugle), $31.6\,\mathrm{kJ \cdot mol^{-1}}$ (called differential method) and $41.3\,\mathrm{kJ \cdot mol^{-1}}$ (called physical method). The two last values, obtained by indirect methods, are not in agreement with ours. Finally, Allen [6] obtained for the limiting partial enthalpy of molybdenum in liquid tin at 2473 K from solubility data a value of 59.17 kJ · mol^{-1} not so far from ours (54.3 kJ · mol^{-1}).

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