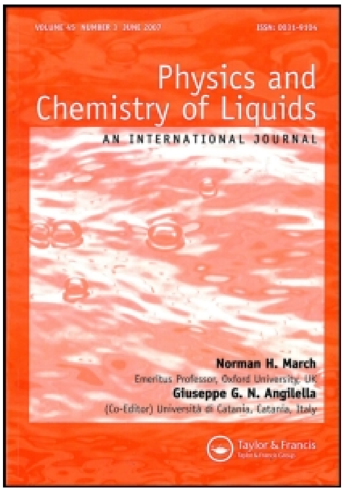

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Partial Enthalpies of Bi and Te in Bi-Te Melts and of in and Te in In-Te Melts

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PARTIAL ENTHALPIES OF Bi AND Te IN Bi-Te MELTS AND OF In AND Te IN In-Te MELTS

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Calorimetric measurements are reported which allow the enthalpic behaviour of Bi-Te melts to be established. Further work is required, however, to supplement results obtained for In-Te melts.

The partial enthalpies of bismuth and tellurium in the Bi-Te melts at 755 K and those of indium and tellurium in the In-Te melts at 1010 and 987 K were measured at high dilution by direct reaction calorimetry (drop method) with the help of a Tian-Calvet high-temperature calorimeter. The limiting partial enthalpies of the components were deduced by extrapolation at infinite dilution:

$\Delta h^{f,\infty}{}_{Bi}(755\,K)/kJ \cdot mol^{-1} = -34.0$ and $\Delta h^{f,\infty}{}_{Te}(755\,K)/kJ \cdot mol^{-1} = -24.1$ in the Bi-Te melts
$\Delta h^{f,\infty}{}_{In}(1010\,K)/kJ \cdot mol^{-1} = -75.9$ and $\Delta h^{f,\infty}{}_{Te}(1010\,K)/kJ \cdot mol^{-1} = -47.8$ in the In-Te melts.
$\Delta h^{f,\infty}{}_{In}(987\,K)/kJ \cdot mol^{-1} = -75.2$ and $\Delta h^{f,\infty}{}_{Te}(987\,K)/kJ \cdot mol^{-1} = -48.0$ in the In-Te melts

All above values are with reference to liquid metals.

Keywords: Calorimetry; partial enthalpy; Bi-Te; In-Te

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1. INTRODUCTION

The limiting partial enthalpy of tellurium, Δh^{f}_{Te}, in liquid bismuth has been measured by calorimetry by different authors: Robinson and Leach [1] at 623 K, Skeoch and Heyding [2] at 625 K, Howlett *et al.* [3] at 625 K, Morgant *et al.* [4] at six temperatures between 583 and 743 K and Laffitte *et al.* [5] at 737 K. We could also derive Δh^{f}_{Te} from the calorimetric determinations of the integral enthalpy of mixing of the Bi–Te melts in the concentrated range by Maekawa *et al.* [6] at 877 K. Blachnik and Enninga [7] also measured the integral enthalpy of mixing of this system at 873 K but they gave their results for only nine compositions and it was not possible to derive the limiting partial enthalpies with confidence. According to our knowledge, Δh^{f}_{Bi} was only measured by Laffitte *et al.*

There is no direct determination of the limiting partial enthalpies of In and Te in liquid In–Te alloys but Said and Castanet [8] at 987, 1123 and 1340 K, Maekawa *et al.* [9] at 998 K measured by direct reaction calorimetry the integral enthalpy of mixing of the melts in the whole range of concentration from which $\Delta h^{f,\infty}_{Te}$ and $\Delta h^{f,\infty}_{In}$ could be derived. Lee and Lee [10] determined the integral enthalpy of mixing on the In rich side and on the Te-rich side at 976 and 891 K respectively from which $\Delta h^{f,\infty}_{Te}$ and $\Delta h^{f,\infty}_{In}$ could be determined.

2. EXPERIMENTAL

The partial enthalpies of dissolution of Bi and Te in the Bi–Te melts at 755 K and of In and Te in the In–Te melts at 987 and 1010 K were deduced from the heat effects corresponding to successive additions of small quantities of solid Bi or Te into the same Bi–Te bath and to small quantities of solid In and Te into the same In–Te 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 [11]. 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 to the metallic bath (about five) of small quantities of Nat. Bur. Stand. (US) α-alumina at T_0, the enthalpy of which is well known [12]. The bath were placed in a graphite crucible at the bottom of the calorimetric cell at temperature T. Before the first addition of solute, the bath (about 10 g) was pure bismuth or pure tellurium in the case of Bi–Te or pure indium or pure tellurium in the case of In–Te. The pure components used for the measurements were purchased from Koch-Light with metallic impurities less than 10^{-5} mass%.

The thermal effects produced by adding A to the $A-B$ melt correspond to the following reaction:

$$nA(\mathrm{cr}, T_0) + mA_xB_{1-x}(T) \rightarrow (n+m)A_{x+dx}B_{1-x-dx}(T)$$

Each heat effect corresponding to successive additions of A (or B) leads to the partial enthalpy of solute in the binary alloy against composition with respect to pure solid sample at T, taking into account the enthalpy change of A or B from T_0 to T deduced from Hultgren *et al.* [13]. The enthalpies of melting used to change the reference state from $A(\mathrm{cr}, T)$ to $A(\mathrm{l}, T)$ was also taken from [13] neglecting any temperature dependence.

3. RESULTS

3.1. Bi–Te System

The experimental data concerning the Bi–Te system at 775 K are given in Table I (Δh^f_{Bi}) and in Table II (Δh^f_{Te}) and shown in Figure 1 with respect to concentration. They can be fitted according to the following equations with reference to liquid components:

$$\Delta h^f_{\mathrm{Bi}}(775\,\mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = -34.0 - 22.1\,x_{\mathrm{Bi}}$$
$$\Delta h^f_{\mathrm{Te}}(775\,\mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = -24.1 + 24.2\,x_{\mathrm{Te}}$$

The values of the limiting partial enthalpies deduced from the literature and that obtained in this work are given in Table III with reference to pure liquid metals. They can be fitted with respect to temperature according to the following equation:

$$\Delta h^{f,\infty}_{\mathrm{Te}} = (-18.9 - 6.5\,10^{-3}\,T)\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$$

TABLE I Partial enthalpy of Bi at 755 K in the Bi–Te melts at high dilution with respect to mole fraction of Bi and referred to pure liquid metals

Series 1		Series 2	
x_{Bi}	Δh^f_{Bi} $(kJ \cdot mol^{-1})$	x_{Bi}	Δh^f_{Bi} $(kJ \cdot mol^{-1})$
0.0011	−34.23	0.0014	−34.07
0.0031	−34.07	0.0043	−34.23
0.0049	−34.05	0.0076	−33.67
0.0075	−34.38	0.0107	−34.23
0.0108	−34.21	0.0137	−34.46
0.0145	−34.43	0.0164	−34.35
0.0184	−34.76	0.0193	−34.20

TABLE II Partial enthalpy of Te at 755 K in the Bi–Te melts at high dilution with respect to mole fraction of Te and referred to pure liquid metals

Series 1		Series 2	
x_{Te}	Δh^f_{Te} $(kJ \cdot mol^{-1})$	x_{Te}	Δh^f_{Te} $(kJ \cdot mol^{-1})$
0.0010	−24.85	0.0011	−23.72
0.0039	−23.93	0.0033	−23.84
0.0073	−24.05	0.0054	−24.04
0.0108	−23.52	0.0077	−23.76
0.0152	−23.55	0.0101	−24.05
0.0198	−23.56	0.0121	−23.98
0.0247	−23.38	0.0144	−24.06
		0.0172	−23.71
		0.0200	−24.09

Our value of $\Delta h^{f,\infty}_{\mathrm{Te}}$ agree well with the literature data as shown on Figure 2. Our $\Delta h^{f,\infty}_{\mathrm{Bi}}$ value shows good agreement with that obtained by [5] at 737 K ($-34.1\,\mathrm{kJ \cdot mol^{-1}}$) but differs strongly from that we derived from the integral determinations of Maekawa *et al.* [6] at 877 K ($-19.81\,\mathrm{kJ \cdot mol^{-1}}$).

3.2. In–Te System

The data concerning the In–Te binary at 1010 K and 987 K are given in Tables IV and V and are shown on Figures 3 and 4 with respect to concentration. They can be fitted according to the following equations with reference to liquid components:

$$\Delta h^f_{\mathrm{In}}(1010\,\mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = -76.5 - 107.5\,x_{\mathrm{In}}$$

$$\Delta h^f_{\mathrm{Te}}(1010\,\mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = -46.8 - 487.7\,x_{\mathrm{In}}$$

$$\Delta h^f_{\mathrm{In}}(987\,\mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = -75.2 + 289.5\,x_{\mathrm{In}}$$

$$\Delta h^f_{\mathrm{Te}}(987\,\mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = -48.0 - 153.5\,x_{\mathrm{In}}$$

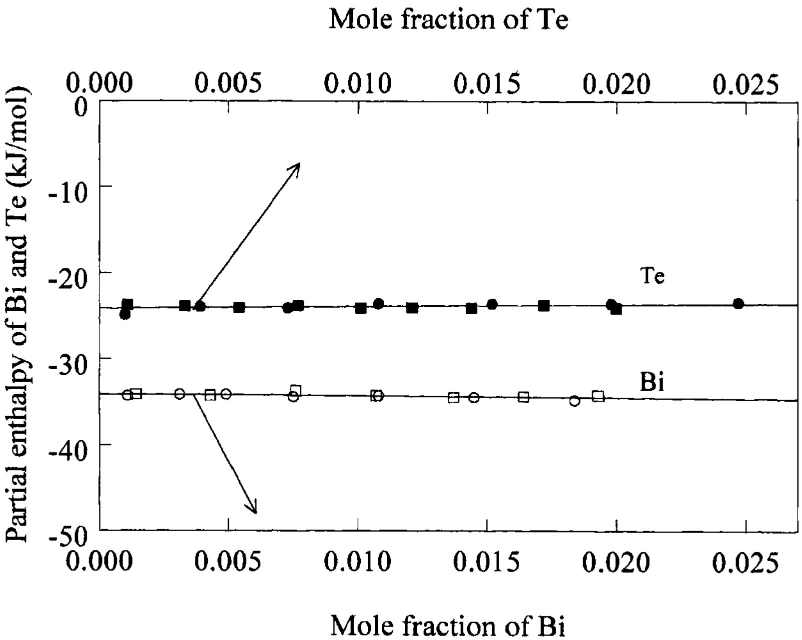

FIGURE 1 Partial enthalpies of Bi and Te at 755 K in the Bi–Te melts at high dilution with respect to mole fraction of Bi and Te and referred to pure liquid metals. Each symbol corresponds to a separate run of measurements.

TABLE III Limiting partial enthalpies of Te and Bi at 755 K in the Bi–Te melts according to the literature and this work and referred to pure liquid metals

Ref.	$T(K)$	$\Delta h_{Te}^{f,\infty}$ $(kJ \cdot mol^{-1})$
Robinson and Leach [1]	623	−22.22
Skeoch and Heyding [2]	625	−22.34
Howlett *et al.* [3]	625	−22.72
Morgant *et al.* [4]	583	−23.55
	614	−23.53
	653	−23.37
	688	−23.19
	713	−23.85
	743	−23.46
Laffitte *et al.* [5]	737	−22.80
Maekawa *et al.* [6]	877	−24.98
This work	755	−24.14
		$\Delta h_{\mathrm{Bi}}^{f,\infty}(\mathrm{kJ \cdot mol^{-1}})$
Maekawa *et al.* [6]	877	−19.81
Laffitte *et al.* [5]	737	−34.10
This work	755	−34.03

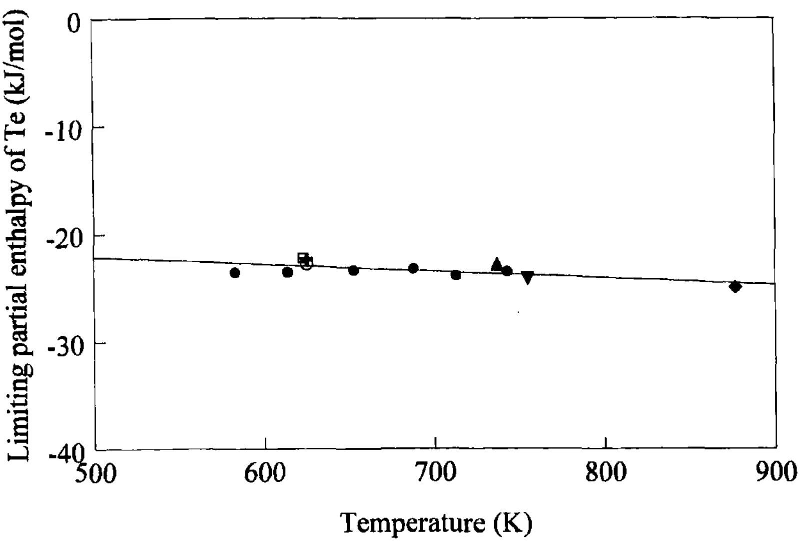

FIGURE 2 Limiting partial enthalpies of Te in the Bi–Te melts according to the literature with respect to temperature and referred to pure liquid metals. Ref. [1]: ■; Ref. [2]: ○; Ref. [3]: +; Ref. [4]: •; Ref. [5]: ▲; Ref. [6]: ◆; this work: ▼.

TABLE IV Partial enthalpy of In and Te in the In–Te melts at 1010 K and at high dilution with respect to mole fraction of In and Te and referred to pure liquid metals

x_{In}	Δh^f_{In} $(kJ \cdot mol^{-1})$	x_{Te}	Δh^f_{Te} $(kJ \cdot mol^{-1})$
0.0006_3	−79.73	0.0004_8	−39.22
0.0019	−78.62	0.0014	−50.86
0.0032	−77.13	0.0024	−46.99
0.0045	−76.35	0.0034	−48.97
0.0059	−76.91	0.0044	−49.64
0.0073	−81.35	0.0055	−46.43
0.0087	−79.21	0.0066	−52.20
0.0105	−78.12	0.0077	−50.16
0.0117	−78.72	0.0089	−50.41
0.0132	−77.24	0.0100	−46.58
0.0006_2	−73.52	0.0005_2	−45.33
0.0018	−76.04	0.0016	−48.09
0.0031	−73.95	0.0026	−48.71
0.0044	−76.05	0.0037	−50.19
0.0086	−79.76	0.0071	−49.53
0.0102	−75.71	0.0082	−50.77
0.0115	−78.46	0.0094	−50.02
0.0131	−75.29	0.0106	−52.86

TABLE V Partial enthalpy of In and Te at 987 K in the In-Te melts at high dilution with respect to mole fraction of In and Te and referred to pure liquid metals

x_{In}	Δh^f_{In} $(kJ \cdot mol^{-1})$	x_{Te}	Δh^f_{Te} $(kJ \cdot mol^{-1})$
0.0006_2	−84.24	0.0004_2	−42.56
0.0018	−68.21	0.0013	−50.47
0.0031	−72.56	0.0023	−49.39
0.0044	−73.49	0.0033	−48.54
0.0056	−73.59	0.0045	−47.41
0.0069	−72.28	0.0057	−52.29
0.0083	−65.78	0.0069	−47.28
0.0096	−72.09	0.0081	−45.79
0.0111	−70.37	0.0094	−54.48
0.0126	−73.72	0.0107	−52.87
0.0006_4	−79.05	0.0004_8	−51.47
0.0019	−71.01	0.0015	−46.81
0.0032	−72.48	0.0025	−46.52
0.0045	−76.15	0.0037	−54.25
0.0058	−78.19	0.0048	−50.85
0.0071	−64.05	0.0060	−46.12
0.0085	−79.78	0.0072	−44.58
0.0099	−70.39	0.0084	−50.07
0.0113	−73.16	0.0096	−44.74
0.0128	−75.63	0.0109	−50.04

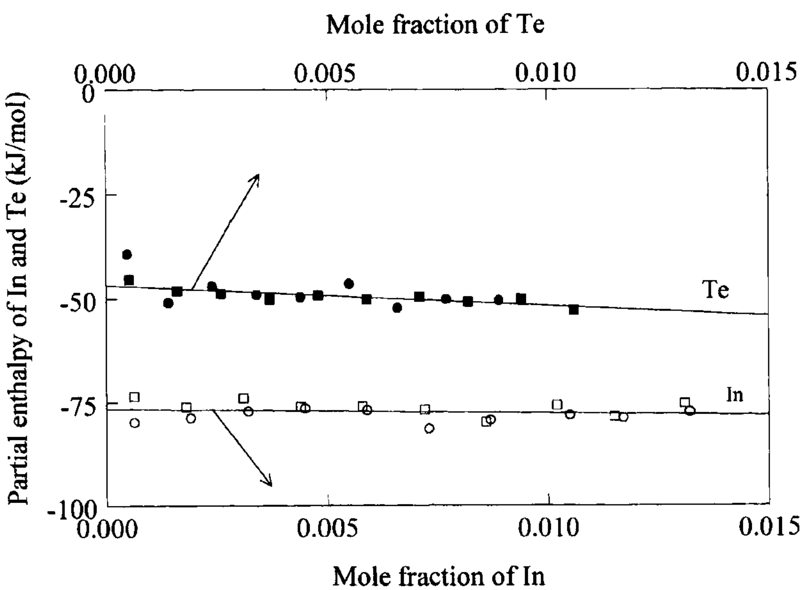

FIGURE 3 Partial enthalpies of In and Te at 1010 K in the In-Te melts at high dilution with respect to mole fraction of In and Te and referred to pure liquid metals. Each symbol corresponds to a separate run of measurements.

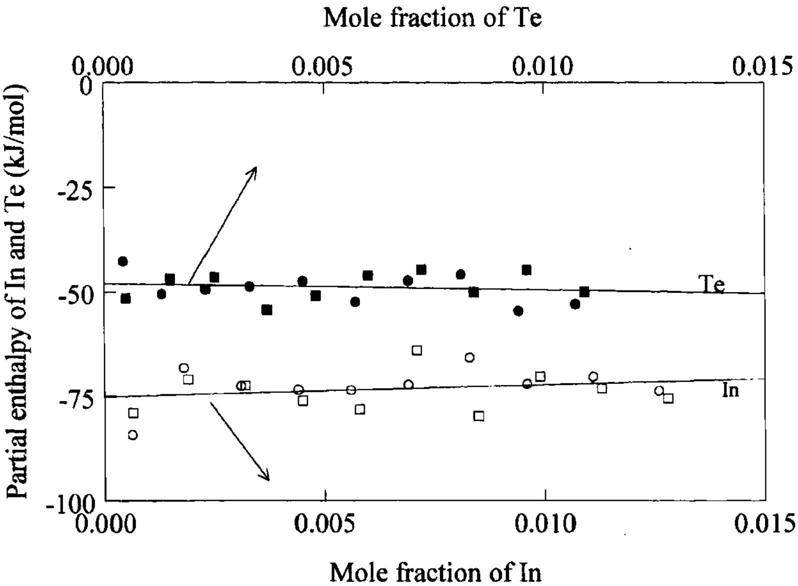

FIGURE 4 Partial enthalpies of In and Te at 987 K in the In – Te melts at high dilution with respect to mole fraction of In and Te and referred to pure liquid metals. Each symbol corresponds to a separate run of measurements.

The data at 987 K are more scattered especially for $\Delta h_{\mathrm{In}}^{f,\infty}$. It is well known that the errors on the values of the interaction parameters, η_i^i, (slopes of the previous equations) determined in such a way are, generally speaking, very large. Then the change of sign of $\eta_{\mathrm{In}}^{\mathrm{In}}$ from 1010 to 987 K has probably no significance. As shown in Table VI, the values of $\Delta h_{\mathrm{Te}}^{f,\infty}$ and $\Delta h_{\mathrm{In}}^{f,\infty}$ deduced from the literature agree well with

TABLE VI Limiting partial enthalpies of Te and In in the In – Te melts according to the literature and this work referred to pure liquid metals

Ref.	*T/K*	$\Delta h_{Te}^{f,\infty}$ $(kJ \cdot mol^{-1})$	$\Delta h_{In}^{f,\infty}$ $(kJ \cdot mol^{-1})$
Said and Castanet [8]	987	−47.4	
	1123	−47.4	
	1340	−47.4	
Lee and Lee [10]	976	−47.6	
	891		−81.3
Maekawa *et al.* [9]	877	−60.1	−91.0
This work	987	−48.0	−75.2
	1010	−47.8	−75.9

ours except those of Maekawa *et al.*, which are more negative. Then, no temperature dependence can be pointed out.

4. CONCLUSION

The enthalpic behaviour of the Bi – Te melts at high dilution appears now well known. Both limiting partial enthalpies of the components are negative but the interaction parameters show with out any doubt opposite signs. However, the temperature dependence of $\Delta h^{f,\infty}_{\mathrm{Te}}$ has to be still clarified.

Concerning the In – Te binary, the situation is not so evident due to the lack of measurements with respect to temperature. The limiting partial enthalpy are also negative and very close to each other at the two investigated temperatures suggesting no temperature dependence. Because of the change of sign with temperature of the In interaction parameter, new enthalpic determinations at different temperatures have to be performed.

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