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Experimental determination of the partial enthalpies of mixing of tin and tellurium in Sn–Te melts

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Abstract

The partial molar enthalpies of Sn and Te at high dilution in Sn–Te melts have been measured by direct reaction calorimetry (drop method) with the help of a Tian–Calvet high temperature calorimeter, at 860, 1000 and 1100 K. They show only very weak temperature dependence. The values of the interaction parameters were also measured. The results obtained will be used to compare the different models available for strongly interacting liquid alloys.

Résumé

Les enthalpies molaires partielles de l'étain et du tellure dans les alliages liquides Sn–Te à 860, 1000 et 1100 K ont été mesurées en solutions diluées par calorimétrie de réaction directe à l'aide d'un calorimètre Tian–Calvet. Elles ne dépendent que faiblement de la température. Les valeurs des paramètres d'interaction ont également été mesurées. Les résultats expérimentaux ainsi obtenus seront utilisés pour comparer les différents modèles existants pour les alliages liquides à fortes interactions.

Keywords: Sn–Te; Liquid alloys; Partial enthalpy of mixing; Calorimetry

1. Introduction

A knowledge of the behaviour of dilute solutions is particularly useful for theoreticians to predict the thermodynamic properties of concentrated solutions. Indeed, the introduction of one A atom into a pure B matrix is purely an energetic problem, i.e. all the different configurations are equivalent. The statistical aspect playes a role only when more than one foreign atom is introduced into the matrix. Then, the different statistical models lead to the same value of the partial enthalpy at infinite dilution, and the differences affect only the enthalpic parameter, slope of the integral enthalpy of mixing at high dilution assuming a linear dependence vs. concentration.

We are mainly interested in binary alloys showing strong negative deviations from ideality. For such alloys it is possible to derive, from the experimental values of the limiting partial enthalpies of mixing with respect to temperature, corresponding for the associated solution model. We can then forecast the integral enthalpy of formation of the alloy in the whole range of concentration, as shown in a previous paper [1]. For the same purpose, the central atom model can also be applied [2].

We have therefore performed calorimetric determinations of the partial enthalpies of tin and tellurium in the Sn–Te melts at high dilution as a function of concentration and temperature in order to compare the availability of these models with strongly associated systems.

2. Calorimetric methods

The apparatus employed was a high-temperature ($T < 4000$ K) Tian–Calvet calorimeter. The drop method used (direct reaction calorimetry) has already been described [3]. The pure metals used were purchased from Koch-Light with metallic impurities less

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than 10^{-3} mass%. The calibration of the calorimeter was performed by adding some small pieces of α-alumina (U.S. National Bureau of Standards), the enthalpy of change from T_0 to T is well-known [4].

The partial enthalpies of dissolution of Sn and Te in the melts, $\Delta h_{\mathrm{Sn(Te)}}$, were deduced from the heat effects corresponding to successive additions of small quantities of Sn or Te (about 20 to 50 mg according to the concentration range) at T_0 (near 298 K) into the same bath placed in a graphite crucible at the bottom of the calorimetric cell at temperature T. Before the first addition of Sn or Te the melt was pure tellurium or pure tin (about 10 g) respectively.

The thermal effects of adding Sn to the Sn–Te melt correspond to the reaction

$$n\mathrm{Sn(cr}, T_0)$$
$$+ N\mathrm{Sn}_x\mathrm{Te}_y(\mathrm{l}, T) \longrightarrow (n+N)\mathrm{Sn}_{x+\mathrm{d}x}\mathrm{Te}_{y-\mathrm{d}y}(\mathrm{l}, T)$$

with $n << N$ and $y = 1 - x$.

Each heat effect corresponding to successive additions of Sn (or Te) yields 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 Sn or Te from T_0 to T, deduced from Ref. [5]. The enthalpies of melting used to change the reference state from Sn(cr, T) to Sn(l, T), and from Te(cr, T) to Te(l, T), were also taken from Ref. [5], neglecting any temperature dependence.

3. Results

The results of the measurements of the enthalpy of dissolution of Sn(l, T) and Te(l, T) in the Sn–Te melts are listed in Table 1 and shown in figs. 1 and 2. No measurement could be performed above 1100 K owing to the high vapour pressure of Te ($P_{\mathrm{Te}} = 10.13$ kPa at 1100 K). The scattering of the data increases strongly at high temperature, as seen in the figures.

The data, smoothed assuming a linear dependence on concentration:

$$\Delta h_{\mathrm{i}}(\mathrm{kJ\ mol^{-1}}) = \Delta h_{\mathrm{i}}^{\infty} + \eta_{\mathrm{i}}^{\mathrm{i}} x_{\mathrm{i}}$$

lead to the limiting partial enthalpies of tin and tellurium, $\Delta h_{\mathrm{i}}^{\infty}$, and the interaction parameters, $\eta_{\mathrm{i}}^{\mathrm{i}}$ (i ≡ Sn or Te) listed in Table 2. In Table 3 we give the results of previous workers, obtained mainly from derivation of the integral enthalpy of mixing as a function of concentration (except those of Castanet et al. [6]).

Table 1
Partial molar enthalpies of Sn(l, T), Δh_{Sn} (kJ mol^{-1}), and Te(l, T), Δh_{Te} (kJ mol^{-1}), in the Sn–Te melts with respect to the molar fractions x_{Sn} of Sn and x_{Te} of Te

Series I		Series II		Series I		Series II		Series I		Series II	
x_{Sn}	Δh_{Sn}	x_{Sn}	Δh_{Sn}	x_{Sn}	Δh_{Sn}	x_{Sn}	Δh_{Sn}	x_{Sn}	Δh_{Sn}	x_{Sn}	Δh_{Sn}
T = 860 K				*T = 1000 K*				*T = 1100 K*			
0.00071	−55.92	0.00072	−55.09	0.00067	−59.46	0.0064	−50.00	0.0006	−51.22	0.0006	−44.27
0.0022	−58.05	0.0022	−53.10	0.0021	−59.37	0.0080	−58.18	0.0019	−53.40	0.0019	−51.81
0.0037	−51.68	0.0037	−55.10	0.0064	−52.60	0.0096	−54.77	0.0034	−57.10	0.0035	−54.42
0.0052	−51.72	0.0054	−56.55	0.0096	−59.98	0.0110	−55.10	0.0049	−49.71	0.0050	−54.08
0.0068	−53.67	0.0069	−47.76	0.0112	−49.98	0.0130	−54.69	0.0065	−51.67	0.0066	−60.43
0.0085	−51.26	0.0086	−54.11	0.0129	−52.17	—	—	0.0081	−48.69	0.0081	−54.76
0.0102	−62.39	0.0103	−49.59	0.0146	−50.65	—	—	0.0097	−49.07	0.0097	−49.18
0.0119	−53.99	0.0120	−56.44	—	—	—	—	0.0113	−55.96	0.0114	−54.73
0.0136	−55.42	0.0138	−52.56	—	—	—	—	0.0129	−56.41	0.0132	−53.59
0.0154	−57.76	0.0156	−45.39	—	—	—	—	0.0146	−49.44	0.0150	−51.40
Series I		Series II		Series I		Series II		Series I		Series II	
x_{Te}	Δh_{Te}	x_{Te}	Δh_{Te}	x_{Te}	Δh_{Te}	x_{Te}	Δh_{Te}	x_{Te}	Δh_{Te}	x_{Te}	Δh_{Te}
T = 860 K				*T = 1000 K*				*T = 1100 K*			
0.0006	−34.61	0.0006	−28.48	0.0005	−30.41	0.0005	−35.29	0.0005	−40.29	0.00061	−36.94
0.0017	−36.50	0.0018	−32.45	0.0015	−31.89	0.0016	−31.67	0.0016	−37.65	0.0018	−31.20
0.0029	−31.08	0.0030	−28.49	0.0026	−33.00	0.0028	−33.33	0.0028	−29.37	0.0031	−35.93
0.0042	−30.97	0.0043	−35.39	0.0038	−33.21	0.0039	−32.85	0.0041	−37.80	0.0043	−30.23
0.0055	−37.28	0.0056	−33.74	0.0050	−31.94	0.0051	−30.67	0.0053	−32.69	0.0056	−43.34
0.0068	−38.42	0.0069	−37.57	0.0062	−32.15	0.0063	−31.54	0.0066	−35.41	0.0068	−32.76
0.0082	−32.44	0.0082	−31.18	0.0074	−33.52	0.0076	−31.51	0.0079	−28.51	0.0082	−26.66
—	—	0.0096	−34.50	0.0086	−33.31	0.0088	−32.66	0.0093	−39.43	0.0095	−32.65
—	—	0.0109	−35.64	0.0099	−33.40	0.0100	−33.19	0.0107	−33.36	0.0110	−34.86
—	—	—	—	0.0114	−33.35	0.0117	−33.06	0.0121	−39.64	0.0125	−43.15

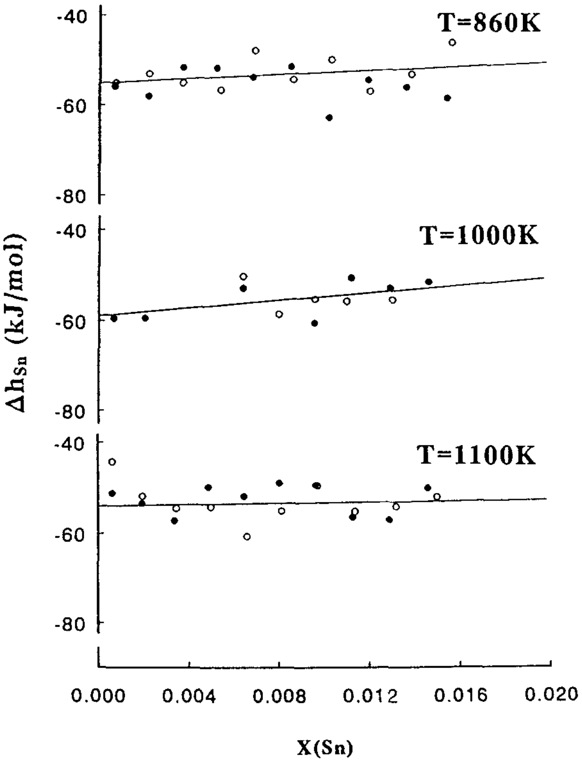

Fig. 1. Molar enthalpy of dissolution of Sn in Sn–Te melts at different temperatures T referred to 1 mol of Sn(l, T) as a function of the molar fraction of Sn. Each symbol corresponds to a separate run of measurements.

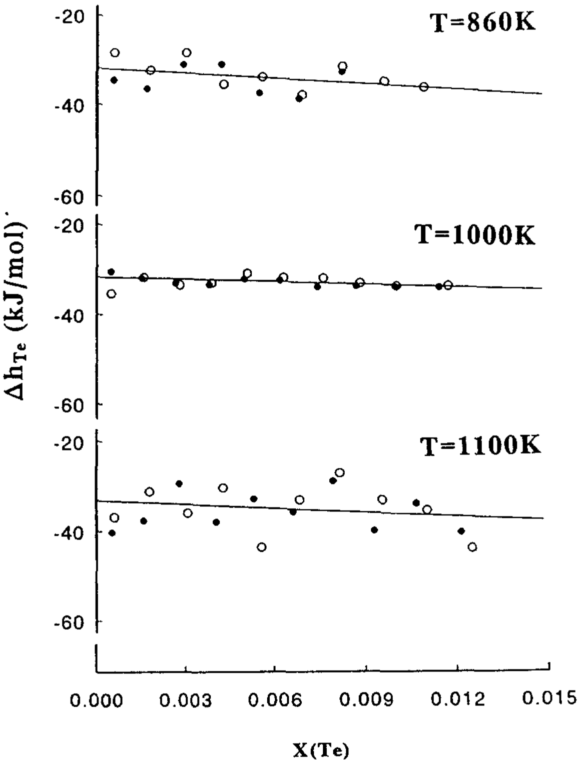

Fig. 2. Molar enthalpy of dissolution of Te in Sn–Te melts at different temperatures T referred to 1 mol of Te(l, T) as a function of the molar fraction of Te. Each symbol corresponds to a separate run of measurements.

Table 2
Partial molar enthalpies of Sn(l, T) and Te(l, T) at infinite dilution and interaction parameters $\eta_{\mathrm{Sn}}^{\mathrm{Sn}}$ and $\eta_{\mathrm{Te}}^{\mathrm{Te}}$ in Sn–Te melts as a function of temperature according to this work

T (K)	$\Delta h_{\mathrm{Sn}}^{\infty}$	$\eta_{\mathrm{Sn}}^{\mathrm{Sn}}$	$\Delta h_{\mathrm{Te}}^{\infty}$	$\eta_{\mathrm{Te}}^{\mathrm{Te}}$
860	−55.22	277.82	−31.98	−334.77
1000	−58.92	475.35	−31.62	−138.41
1100	−54.04	113.56	−33.27	−238.19

Table 3
Partial molar enthalpies of Sn(l, T) and Te(l, T) at infinite dilution in Sn–Te melts as a function of temperature according to the literature; all these results were obtained from derivation of their integral enthalpy of mixing, except those of Castanet et al. [6]

Reference	T (K)	$\Delta h_{\mathrm{Sn}}^{\infty}$	$\Delta h_{\mathrm{Te}}^{\infty}$	Technique
[7]	736	−55.7	−29.2	Cal.
[6]	737	−61.9	−33.4	Cal.
[8]	873	−67.50	−32.5	Cal.
[9]	≈ 900	−60.25	—	fem
[8]	1100	—	−35.46	fem
[10]	1100	−59.50	—	fem
[11]	1140	−54.10	−30.40	Cal.

4. Conclusion

The partial molar enthalpies of mixing of Sn and Te in the Sn–Te melts are shown in Fig. 3 with respect to temperature. The limiting partial enthalpies are strongly negative and exhibit a very weak temperature dependence, taking into account our data only. The results are very similar to those of the Pb–Te liquid alloys [12]. Such behaviour agrees well with the assumption that the Sn–Te melts are strongly associated. At this state any interpretation of the values of the interaction parameters is forbidden, since they correspond to complex interactions between three different species, i.e. SnTe associates and free Sn and

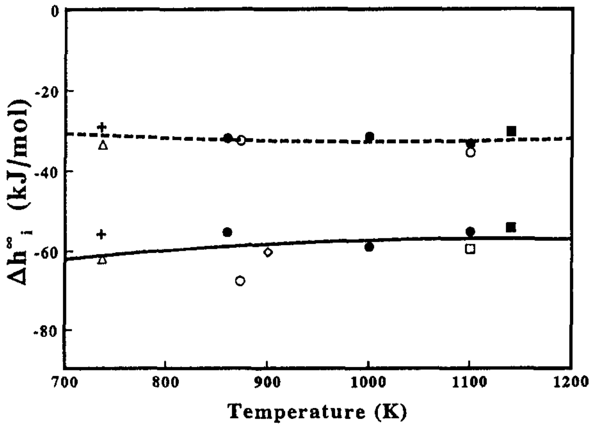

Fig. 3. Limiting molar enthalpies of dissolution of Sn and Te in Sn–Te melts at different temperatures T referred to 1 mol of Sn(l, T) or Te(l, T) as a function of temperature. i = Sn, ———; i = Te, --------. This work, ●; Ref. [6], △; Ref. [7], +; Ref. [8], ○; Ref. [9], ◇; Ref. [10], □; Ref. [11], ■.

Te atoms. We will report in a later paper the results of the application of the different models mentioned in the Introduction.

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