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Note

DETERMINATION OF THE ENTHALPY OF FORMATION OF BINARY AND TERNARY ALLOYS CONTAINING A VOLATILE COMPONENT BY A QUANTITATIVE DTA METHOD

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We successfully used a quantitative DTA method for the determination of formation enthalpies of binary and multicomponent melts by means of direct mixing of liquid components heated in a DTA cell [1,2] separated by a 2 mm gap before mixing. However, there are certain difficulties in the determination of mixing enthalpies when using the above technique. They arise when one of the components is volatile and when high-melting point compounds (for example chalcogenides of II and IV group elements) are formed in the system. A mass change of a volatile component, when heated to a high temperature in a cell, introduces a non-correlated error into the measurements. Therefore, in order to determine the mixing enthalpies of tellurium with melts of *p*-elements of groups III, IV and V of the periodic system, we used a method of dropping solid tellurium into a melt of non-volatile components being heated in a DTA cell.

METHODS

The measurements were conducted on a quantitative DTA apparatus of original design [3]. In order to determine mixing enthalpies by means of dropping a solid component into a melt, a quartz cell was constructed. It allowed experiments to be conducted in vacuum or inert atmosphere and consisted of two parts connected by a vacuum section. The lower part of this cell is a test tube of 12 mm diameter with a conical end. The nonvolatile component and a quartz jacket for a differential thermocouple were placed at the bottom of the cone. The upper part of the cell has two branch pipes, one of which serves for evacuation and filling of an inert gas and the other for feeding the volatile component out of the thermostat. The experiments were conducted in argon atmosphere. The total sample mass was 0.6 g. Enthalpy calculation was done according to the equation $m\Delta H = KA$, where m is the sample mass, ΔH is the enthalpy change, K is a calibration

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TABLE 1

Calibration constant, *K*, determined by dropping tungsten into a tin melt

Tungsten mass (g)	Peak area (cm^2)	Tin melt temp. (K)	K ($J\ cm^{-2}$)
0.3790	19.2	525	0.401
0.3670	18.6	675	1.016
0.3605	18.1	825	1.544
0.3757	16.4	975	2.147
0.3674	13.0	1125	2.841
0.3632	14.2	1215	3.361

constant, and A is the DTA curve peak area. The volatile component was kept in a thermostat at 300 K and was dropped into the melt through the branch pipe in the upper part of the cell. For determination of the calibration constant, K, enthalpy increments of tungsten or tin, which were dropped into the tin melt at different temperatures, were used. The above calibrants were also placed in the thermostat at 300 K. The necessary data on tungsten and tin enthalpy increments were taken from ref. 4. The total mass of the substances during calibration also amounted to 0.6 g. DTA cell calibration results on tungsten dropping into tin heated up to different temperatures are given in Table 1.

The influence of thermostated and melted sample mass ratios on the calibration constant, K, was investigated. Within a relative error of ±4% and the assigned reliability being 0.95, K did not depend on variations of the mass of the solid tin being dropped in the range 0.05–0.55 g, while the total mass of the sample was 0.6 g. Since K considerably depends on cell size, which was not uniform, each cell was calibrated.

In order to check the reliability of the results of the formation enthalpies of melts by means of the dropping method we investigated the gallium–tellurium system for which reliable data on mixing enthalpy are available. Solid tellurium was dropped into a gallium melt at 1130 K. The necessary data on the fusion enthalpy and isobaric heat capacity of solid and liquid Te were taken from ref. 5. The experimental results of the enthalpies of formation of gallium–tellurium melts from liquid components at 1130 K are given in Table 2 ($K = 2.43\ J\ cm^{-2}$). Mixing enthalpy values in the gallium–tellurium system obtained by means of the above quantitative DTA method coincide with the results reported in ref. 6 within experimental error.

Mixing enthalpies in the tin–tellurium system at 1100 K were also determined by the present method. These data are given below (relative error was ±6%).

Te (atom%)	9.7	20.9	28.2	39.0	47.6	49.9	59.7	69.6	80.0
$-\Delta H^{liq}$ ($kJ\ mol^{-1}$)	3.0	7.8	11.2	16.9	22.9	24.9	23.2	17.7	13.9

TABLE 2

Enthalpies of formation of gallium–tellurium melts

Component masses (g)		Sample (Te) composition (atom%)	A (cm^2)	$-\Delta H^{\text{liq}}$ (±6%) (kJ mol^{-1})
Ga	Te			
0.5180	0.0821	8.0	2.7 [a]	2.6
0.4434	0.1569	16.2	4.2 [a]	5.7
0.3943	0.2053	22.2	2.7 [a]	8.6
0.3694	0.2300	25.4	2.0 [a]	10.2
0.3278	0.2730	31.3	1.5	13.9
0.2651	0.3342	40.8	7.6	20.4
0.2461	0.3535	44.0	17.5	25.6
0.2037	0.3920	51.3	21.3	30.5
0.1887	0.4095	54.3	28.1	34.8
0.1615	0.4380	59.7	28.5	37.7
0.1599	0.4400	60.0	31.3	39.0
0.1276	0.4739	67.0	8.0	33.0
0.1001	0.5001	73.2	9.6 [a]	27.1

[a] Areas corresponding to endothermial processes taking place while mixing solid tellurium with a gallium melt.

In the lead–tellurium system mixing enthalpies were determined by dropping solid tellurium into a lead melt at 1230 K. The following values of the enthalpies of formation of lead–tellurium melts from liquid components were obtained (relative error was ±6%).

Te (atom%)	9.6	10.9	20.5	31.8	41.8	47.7	49.4	60.3
$-\Delta H^{\text{liq}}$ (kJ mol^{-1})	4.4	5.0	9.3	15.8	22.6	25.0	26.3	24.2

Enthalpies of formation of melts in the In–Sn–Te system were determined at 1125 K by means of dropping solid tellurium into indium–tin melts. The mixing was carried out for five cuts with a constant indium-to-tin ratio: 4 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 4. Experimental data on mixing enthalpies of tellurium with indium–tin melts for the In : Sn = 1 : 1 cut (recalculated for liquid tellurium) are given below

Te (atom%)	10.0	17.0	33.0	48.0	55.0	61.0	65.0	76.0	85.0
$-\Delta H^{\text{mix}}_{\text{Te+InSn}}$ (kJ mol^{-1})	4.2	7.6	16.5	23.7	24.8	21.7	19.8	17.1	11.9

Mixing enthalpies of dropping solid tellurium into tin–lead melts with lead-to-tin ratios of 3 : 1, 1 : 1 and 1 : 3 were determined at 1225 K. The experimental data for the Pb : Sn = 1 : 1 cut recalculated for liquid tellurium are given below.

Te (atom%)	8.2	12.0	17.8	23.4	27.0	32.9	37.0	46.0	57.0	71.2
$-\Delta H^{\text{mix}}_{\text{Te+PbSn}}$ (kJ mol^{-1})	3.7	4.1	7.9	10.9	12.7	15.2	17.3	21.0	26.3	19.3

The relative error in the determination of mixing enthalpies of tellurium with binary melts by the dropping method does not exceed ±6%. On the basis of the experimental data of mixing tellurium with indium–tin and lead–tin melts, enthalpies of formation from liquid components in these ternary systems were calculated. The enthalpies of formation of melts are negative in the indium–tin–tellurium system, while their surface is a saddle with an axial line that goes approximately along the InTe–SnTe cut and decreases to the InTe side. The enthalpies of formation of melts in the tin–lead–tellurium system are of a sign-variable character and have a narrow region of positive values near the tin–lead binary system boundary (not exceeding 4 atom% Te).

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