Thermochimica Acta, 92 (1985) 321-324
Elsevier Science Publishers B.V., Amsterdam

APPLICATION OF QUANTITATIVE DTA FOR DETERMINATION OF MIXING ENTHALPY IN MULTICOMPONENT SYSTEMS WITH VOLATILE AND CHEMICALLY ACTIVE COMPONENTS

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ABSTRACT

A technique was developed to determine mixing enthalpies in binary and multicomponent systems within 300-1300K by means of quantitative DTA method: 1) by direct mixing of liquid components; 2) by dissolving a solid component in a liquid one; 3) by dropping a solid volatile component, thermostated under standard conditions, into a melt of other components. We also investigated the influence of ratio of components masses, a form and sizes of DTA cell on reproducibility and reliability of the results obtained. Mixing enthalpies of tellurium with gallium, germanium, tin, lead, as well as mixing enthalpies in quasi-binary and ternary systems were obtained.

Mixing enthalpies are basic thermodynamic characteristics of melts, since their value is directly bound up with energies of interatomic interactions. A principle source to obtain reliable data is yet an experiment. But measurements of melts formation enthalpies by means of conventional thermodynamic methods is a difficult experimental problem requiring a lot of time and expensive materials. A quantitative DTA method allows to determine mixing enthalpies both in binary and multicomponent systems relatively simply and with little time expenditures.

We designed a quantitative DTA apparatus /1/ and developed a technique to determine mixing enthalpies in binary /2/ and ternary systems /3/. Here we took into consideration practical and theoretical propositions, described in papers of Dobovosek /4/, Ozawa /5/, Smajic /6/. In the developed quantitative DTA method in order to study thermodynamic properties of metal and semiconductor systems within 300-1300K transitions or reactions heats are determined by the equation /7/ $m\Delta H = K\cdot A$ where m is the sample mass, in which a transition takes place, ΔH is the enthalpy of this transition, A is DTA curve peak area, corresponding to the transition, and K is a proportionality constant. When working with metal samples we use quartz (or graphitized if necessary) sample and reference holders. In this case heat conductivity of the sample is considerably higher

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[x] Proceedings of ICTA 85, Bratislava

than that of the material of the sample holder and proportionality constant K may be considered as a function of the temperature only (if geometric parameters are not changed) /8/. Determination of K was done on melting heats of In, Sn, Bi, Pb, Te, Sb, Ge, Ag. When junctions of a differential thermocouple are located in the center of the sample and reference, K dependence is given by the equation, obtained by a least squares method for 300-1300K (J/cm^2):

$$K = -10.135 + 5.171 \cdot 10^{-2}T - 8.420 \cdot 10^{-5}T^2 + 4.142 \cdot 10^{-8}T^3 + 2.120 \cdot 10^{-11}T^4 - 2,348 \cdot 10^{-14}T^5$$

A sample mass for the apparatus calibration, determination of transition heats and melts formation enthalpies amounted to 0.3g. The speed of the recording instrument diagram band was 1800 mm/hr. The apparatus sensitivity was $0.1 cm^5/J$, if determined by the equation/5/:

$$J = \frac{A}{\rho_s \Delta H} = \frac{m \Delta H}{K \rho_s \Delta H} = \frac{V_s}{K}$$

where m in g, A in cm^2, ΔH in J/g, V_s is the sample volume, cm^3, ρ_s is the sample density, g/cm^3.

In order to determine melts formation enthalpies from liquid components by direct mixing we used a quartz cell /9/, which consisted of two parts connected by vacuum sections. The cell design allows to conduct experiments in vacuum or inert atmosphere (during mixing the cell is filled with argon after evacuation). A fusible component A was placed on the bottom of the cell and a more refractory element B was placed above the cell narrowing and was separated from component A by a quartz jacket of a thermocouple, functioning as a breechblock. The internal diameter of the cell narrowing equals to the diameter of the thermocouple jacket. Mixing of the components is done by lifting the thermocouple jacket. When determining mixing enthalpies in A-B-C ternary system we first measured mixing enthalpies of A and B components and then mixing enthalpies of this melt with C component. An error in determination mixing enthalpies by this method does not exceed ±3% for binary systems and ±5% for ternary ones. By direct mixing of the components we determined melts formation enthalpies of a number of binary (gallium-germanium, indium-gallium, selenium-tellurium, indium-tellurium, etc.) and ternary systems (germanium-gallium-antimony, germanium-lead-tellurium, etc.)/10/. The tables give experimental data on determination of mixing enthalpies in quasi-binary systems $GeTe-Ga_2Te_3$ and PbTe-SnTe.

Table 1. Mixing enthalpies of germanium telluride and gallium telluride melts at 1100K

Component masses GeTe	Ga_2Te_3	Composition at.% GeTe	A, cm^2	K, J/cm^2	ΔH^{mix} ±4% kJ/mol
0.0281	0.2718	21.2	2.0	0.59	1.8
0.0359	0.2700	25.7	2.0	0.77	2.2
0.0485	0.2508	33.5	5.6	0.59	4.5
0.0752	0.2250	46.5	6.9	0.77	6.6
0.0934	0.2063	54.1	9.4	0.59	6.4
0.0984	0.2019	56.0	8.8	0.59	5.9
0.1296	0.1705	66.5	3.8	1.34	5.1
0.1492	0.1511	72.0	3.3	1.34	4.3
0.1617	0.1385	75.3	2.4	1.34	3.0

Table 2. Mixing enthalpies of lead telluride and tin telluride melts at 1225K (K = 0.63 J/cm^2)

Component masses PbTe	SnTe	Composition at.% PbTe	A, cm^2	ΔH^{mix} ±4% J/mol
0.0401	0.2580	10.3	0.65	180
0.0928	0.2070	24.8	1.0	280
0.1641	0.1357	43.3	1.2	340
0.1678	0.1241	49.9	1.2	380
0.1897	0.1086	56.5	1.0	320
0.2160	0.0857	65.0	0.90	290
0.2390	0.0498	77.9	0.50	170

In a number of cases mixing of liquid components is difficult because of a high volatility of one of the components at mixing temperature. Here one faces with errors, which cannot be evaluated. They are due to indeterminacy of the volatile component mass. In order to avoid these difficulties we have developed two techniques:

1. Solution of a more refractory component at temperatures along the liquidus line. Here we use the same cell as in case of direct mixing of liquid components. Refractory component B is mixed with a liquid component A at the temperature of 20-30K which is higher the liquidus temperature for this compound. A liquid melt formation enthalpy is calculated by the following equation:

$$\Delta H^{mix}_{A-B} = \Delta H^{sol}_{B\ in\ A} - x\Delta H^{melt}_{B}$$

where x is a mol part of B component, ΔH^{melt}_{B} is B component melting heat at the solution temperature. An error in determination mixing enthalpies by this method does not exceed 5%. Mixing enthalpies of germanium-tellurium system /11/ determined by this technique agree with the data of Bergman and Castanet /12/.

2. Dropping technique. To determine mixing enthalpies by this technique we constructed a special cell /9/. Component B having a high vapour pressure at mixing temperature (which is usually more than 30K higher than the liquidus maximum temperature in this system) is thermostated at 298K in a branch pipe of the upper part of the cell, and when the mixing temperature is reached it is dropped into A component melt. When using this technique as well as during the apparatus calibration the total sample mass was 0.6g. Determination of constant K as a temperature function was carried out by dropping tin (or tungsten) thermostated at 298K into a melt of tin with the temperature from 510 to 1250K. We tried to find out whether constant K determined by this technique depended on the ratio of masses of thermostated and melted parts of the sample. It was stated that K did not depend on the ratio of these masses (the masses were changed from 0.0500 to 0.5000g respectively) within 2.5% error in its determination. By means of this technique we determined mixing enthalpies in gallium-tellurium, tin-tellurium systems/13/. The obtained results coincide with calorimetric data within 6% error/14/.

Thus, the developed method of quantitative differental thermal analysis allows to determine mixing enthalpies in multicomponent systems both with volatile and chemically active components.

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