Computer-Aided Determination of the Molar Excess Heat Capacity, \( \Delta C_p(T,X) \), from Calorimetric Data

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All traditional evaluation techniques for determining the temperature, \( T \), concentration, \( X \), dependences of the molar excess heat capacity, \( \Delta C_p(T,X) \), from calorimetric data involve the problem that the molar excess heat capacities, \( \Delta C_p(T,X) \), are determined from finite differences. In essence, a heat capacity value is then the quotient of the difference between two \( \Delta H \) values divided by the difference between the two corresponding temperature values. A new evaluation technique has been developed to overcome this problem. Considering the best-fit parameters as simultaneously dependent on the temperature, \( T \), and on the concentration, \( X \), an overall regression of all measured data of all investigated sample compositions, \( X \), and temperatures, \( T \), is possible. Application of the proposed evaluation technique is illustrated with data for liquid Cu-Sb, Mg-Pb, Bi-Te, In-Sb, and Au-Ga binary systems. The individual features of the systems as well as the advantage of an interactive evaluation are discussed in detail.

**Introduction**

The molar excess heat capacity, \( \Delta C_p \), is defined as the derivative of the molar enthalpy of mixing, \( \Delta H(T) \), with respect to the temperature, \( T \):

\[
\Delta C_p = \frac{\partial \Delta H(T)}{\partial T}
\]

(Eq 1)

It characterizes the deviations of the heat capacity of an alloy system from the Neumann-Kopp rule [69Fra]. However, determination of \( \Delta C_p \) from the calorimetrically investigated temperature dependence of the molar enthalpy of mixing, \( \Delta H(T) \), is often beset with considerable difficulty. (1) Even if calorimetric investigations on the temperature dependence are possible, they are limited to temperature ranges of \(-100 \) K above the melting area. (2) Usually the temperature dependence is small, often even smaller than the scatter of the measured points. (3) Traditional techniques have characterized the temperature dependence of the molar enthalpy of mixing, \( \Delta H(T) \), from graphical or tabular data. This last difficulty means the derivative in Eq 1 has been evaluated by forming the quotients of finite differences between the \( \Delta H(T) \) values at two measured points of the corresponding two different temperatures \( T_i \) and \( T_j \):

\[
\Delta C_p = \frac{\Delta H(T_i) - \Delta H(T_j)}{T_i - T_j}
\]

(Eq 2)

Necessarily, Eq 2 cannot yield \( \Delta C_p \) values free of inconsistencies. Additional difficulties arise by including the dependence of the molar excess heat capacity, \( \Delta C_p \), on the concentration \( X \). These problems may be overcome by applying computational evaluation techniques with all dependencies represented by means of algebraic functions.

The main thrust of the present study is the description of an evaluation technique that yields consistent values of the molar excess heat capacity, \( \Delta C_p \), over the whole calorimetrically investigated ranges of composition and temperature. The procedure requires computer assistance, but allows convenient, interactive evaluation of the experimental data.

**Temperature Dependence of the Enthalpy of Mixing, \( \Delta H(T) \)**

Recently it was shown [91Tom] that the temperature dependence of the molar enthalpy of mixing, \( \Delta H(T) \), can be expressed generally by:

\[
\Delta H(T) = b_1 - b_2[1 + \exp((T - b_3)/b_4)]
\]

(Eq 3)

where \( b_1 \) to \( b_4 \) are alloy specific parameters connected non-linearly. A best fit based upon Eq 3 represents, therefore, a non-linear regression problem that is not convenient for explicit computations. As already noted, the molar enthalpies of liquid mixing, \( \Delta H(T) \), are, with rare exception, determined only over small temperature ranges above melting; this excludes measurement on undercooled melts. The data from most experimental investigations are therefore most conveniently fit by replacing Eq 3 with a polynomial of the form \( \Delta H(T) = \Sigma c_i T^i \) where \( i \) refers to temperature-independent adjustable parameters and (\( i = 0, -1, ... \)):

\[
\Delta H(T) = c_0 + c_1 T^{-1} + ...
\]

(Eq 4a)

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Section I: Basic and Applied Research

The use of a polynomial as an approximation of the original function implies no uncertainties because the Weierstrass approximation theorem [66Mes] guarantees that such an approximation may be performed with arbitrary high accuracy, and the degree of the polynomial with an acceptable level of uncertainty must be decided on a case by case basis. An additional advantage of the polynomial approximation is that the definition of $\Delta C_p$ in Eq 1 allows a simple evaluation of the temperature derivative of Eq 4a to generate a polynomial description of the molar excess heat capacity with the same coefficients that appear in Eq 4a:

$$\Delta C_p = -c_{-1}T^{-2} + \ldots$$  \hspace{1cm} (Eq 4b)

Table 1  Cu-Sb Best-Fit Parameters

<table>
<thead>
<tr>
<th>$n$</th>
<th>$C_n$ $\cdot 10^3$</th>
<th>$C_{n-1}$ kJ/mol</th>
<th>Cn$\cdot 10^3$ kJ/mol</th>
</tr>
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<tr>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>-546.9</td>
<td>623.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
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<td>-1586</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-2279</td>
<td>1798</td>
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</tr>
<tr>
<td>5</td>
<td>980.6</td>
<td>-729.7</td>
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</tr>
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</table>

From [77Hay]. Eq 9: $N = 5, j = 0, -1$. $X$ is the mole fraction of the right component.

Table 2  Mg-Pb Best-Fit Parameters

<table>
<thead>
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<th>$n$</th>
<th>$C_n$ $\cdot 10^3$</th>
<th>$C_{n-1}$ kJ/mol</th>
<th>Cn$\cdot 10^3$ kJ/mol</th>
</tr>
</thead>
<tbody>
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<tr>
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</tr>
</tbody>
</table>

From [80Som]. Eq 9: $N = 5, j = 0, -1$. $X$ is the mole fraction of the right component.

Concentration Dependence of the Enthalpy of Mixing, $\Delta H(X)$

Real mixtures can show such a varied and complex dependence on concentration $X$ that no physical explanation has yet been found that is extensive enough to provide a general description [80Tom]. Therefore, a continuous representation of the concentration dependence of the molar enthalpy of mixing, $\Delta H(X)$, requires suitable approximation formulas. Among all formulas that have been suggested, polynomials in mole fraction $X$ (analogous to Eq 4a with $X$ substituted for $T$) have the same advantages for providing a complete description of the

Fig. 1  Molar enthalpy of mixing, $\Delta H(T, X)$, of Cu-Sb. 106 points at 11 temperatures from 843 to 1375 K. From [77Hay]. Best fit from Eq 9a using 5 parameters $C_n$ ($j = 0, -1$). See Table 1.

Fig. 2  Mg-Pb. 40 points at 943, 1033, and 1223 K. From [80Som]. Best fit from Eq 9a using 5 parameters $C_n$ ($j = 0, -1$). See Table 2.