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On the estimation of thermodynamic excess properties of binary solid solutions

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Abstract

An empirical estimation method for the heat of formation of solid solutions of binary mixtures of non-metallic chemically coherent substances from the lattice enthalpies of the pure substances is described. The method was tested on binary mixtures of the following groups of chemically coherent substances: alkali halides, alkaline earth oxides, *p*-dihalobenzenes and the cryogenic noble gases. Irrespective of the type of substance (ionic, molecular, atomic), the heat of formation of the solid solution as a function of composition could be estimated in good agreement with the experimental heat of formation data. An empirical estimation method for the characteristic temperature, the ratio of excess enthalpy and excess entropy, of binary solid solutions is described.

INTRODUCTION

Within a chemically coherent group of substances, for instance the alkali halides, the thermodynamic (and other) properties show regularities. Lattice enthalpies [1], enthalpies of dimerization [2] and other thermodynamic properties [3] can be correlated to the nearest neighbour cation–anion distances in the solid state, or in case of non-ionic substances to the nearest neighbour interatomic or intermolecular distances in the solid state, if all group members have the same crystal structure. The existance of these correlations offer the opportunity to test theories, to check experimental data for their consistency and to estimate physical properties of substances which have not yet been measured, or which are difficult to measure. These considerations also hold for the thermodynamic mixing properties of substances within a chemically coherent group. This has resulted in the uniform description of the thermodynamic excess properties of binary common-ion alkali halide mixtures [4–6], binary

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p-dihalobenzene mixtures [7] and binary alkaline earth oxide mixtures [8]. From these investigations it appeared that the ratio of excess enthalpy and excess entropy, which is called the characteristic temperature, is approximately constant within a chemically coherent group of binary mixtures. Moreover, there appears to be a trend in the characteristic temperatures of all kinds of binary solid solutions. Oonk et al. [9] described a double logarithmic correlation between the 'equal Gibbs energy temperatures' (the temperature at which the molar Gibbs energies of the solid and liquid state are equal at a given composition) at equimolar composition and the characteristic temperature of the mixed crystal. When the characteristic temperature of a binary mixture is known, then one value of the excess Gibbs energy at a specified temperature or the heat of mixing is sufficient to describe the excess Gibbs energy of the mixture as a function of temperature. Once the excess Gibbs energy as a function of temperature is known, it becomes possible to calculate a reliable phase equilibrium diagram of the mixture, which is of great importance in materials research. The first part of this paper pertains to the development of a method for the estimation of the heats of mixing of non-metallic binary mixtures of chemically coherent substances, which show a positive deviation from ideal mixing behaviour. The second part gives a simple empirical method for the estimation of the characteristic temperatures of binary solid solutions.

THE ESTIMATION OF EXCESS ENTHALPIES OF BINARY SOLID SOLUTIONS WITHIN NON-METALLIC CHEMICALLY COHERENT GROUPS OF SUBSTANCES

Binary common-ion alkali halide (BCIAH) mixtures

For the internal energy $U^{\mathrm{ss}}(x)$ of a BCIAH solid solution $[(1-x)\mathrm{MX}+x\mathrm{NX}](\mathrm{s})$ or $[(1-x)\mathrm{MX}+x\mathrm{MY}](\mathrm{s})$ we write the approximation

$$U^{\mathrm{ss}}(x)=(1-x)^2\frac{r_2}{r_1}U_{\mathrm{L1}}+x^2\frac{r_1}{r_2}U_{\mathrm{L2}}+2x(1-x)\sqrt{U_{\mathrm{L1}}U_{\mathrm{L2}}} \tag{1}$$

in which $(1-x)^2$, x^2 and $2x(1-x)$ represent the probabilities of $\mathrm{MX}\cdot\mathrm{MX}$, $\mathrm{NX}\cdot\mathrm{NX}$ and ($\mathrm{MX}\cdot\mathrm{NX}$ and $\mathrm{NX}\cdot\mathrm{MX}$) pairs respectively; U_{L1} and U_{L2} are the lattice energies of the pure substances MX and NX respectively; $\sqrt{U_{\mathrm{L1}}U_{\mathrm{L2}}}$ is the geometric mean of U_{L1} and U_{L2}, giving an estimation of the magnitude of a mixed interaction; and r_2 and r_1 are the nearest neighbour cation–anion distances in the lattice of NX and MX respectively.

For the internal energies $U^{\mathrm{mm}}(x)$ of the mechanical mixture

$$U^{\mathrm{mm}}(x)=(1-x)U_{\mathrm{L1}}+xU_{\mathrm{L2}} \tag{2}$$

TABLE 1

Comparison of evaluated experimental enthalpies of mixing [6] and of calculated enthalpies of mixing from eqn (4) for some BCIAH mixtures

System	H_l(exp)/ kJ mol^{-1}	H_l(calc)/ kJ mol^{-1}	System	H_l(exp)/ kJ mol^{-1}	H_l(calc)/ kJ mol^{-1}
(Li,Na)Br	11.3	10.5	Na(Cl,Br)	5.0	5.1
(Na,K)Cl	18.2	18.2	K(Cl,Br)	3.7	3.2
(Na,K)Br	14.6	14.4	Rb(Cl,Br)	3.4	2.7
(Na,K)I	10.8	10.3	Na(Br,I)	9.8	9.5
(K,Rb)Cl	4.3	3.0	K(Br,I)	7.1	6.3
(K,Rb)Br	3.3	2.5	Rb(Br,I)	5.8	5.2
(K,Rb)I	2.5	1.8			

and the excess energy of a mixture is defined by

$$U^{\mathrm{E}}(x) = U^{\mathrm{ss}}(x) - U^{\mathrm{mm}}(x) \tag{3}$$

Combining eqns. (1)–(3) leads to the excess energy of a BCIAH solid solution

$$U^{\mathrm{E}}(x) = x(1-x)r_1 r_2\left[\sqrt{\frac{|U_{\mathrm{L1}}|}{r_1^2}} - \sqrt{\frac{|U_{\mathrm{L2}}|}{r_2^2}}\right]^2 \tag{4}$$

Table 1 and Fig. 1 compare the experimental and calculated values of

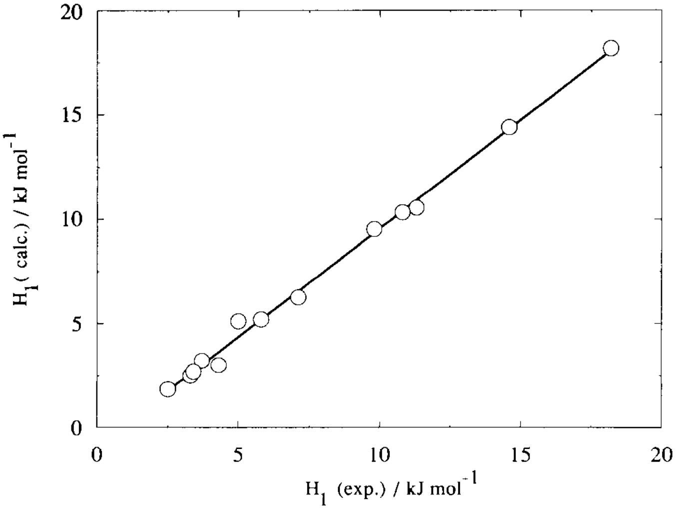

Fig. 1. Calculated excess enthalpies (eqn. (4)) for some binary common-ion alkali halide mixtures as a function of the evaluated experimental values [6]. The mean standard deviation of the calculated H_l values from the evaluated experimental values is 341 J mol^{-1}.

the first Redlich–Kister (R-K) coefficient of the heat of mixing. The calculated values were obtained by means of eqn. (4) in which, for reasons of convenience, the lattice energy was replaced by the lattice enthalpy. This approximation can be made without introducing a large error and we shall use it throughout this paper. Lattice enthalpies and nearest neighbour cation–anion distances were taken from Holbrook et al. [1].

Although eqn. (4) gives very good results for the equimolar composition of the alkali halide mixtures, heat of mixing data appear to be asymmetrical, which is not taken into account in eqn. (4). By analogy with eqn. (4) and with the semi-empirical formula proposed recently by Königsberger and Schrunner [10], eqn. (5) is introduced for the calculation of the enthalpies of mixing of these mixtures

$$H^{E}(x) = 2x(1-x)\left[(1-x)\left(\frac{r_2 - r_1}{r_1}\right)^2 |H_{L,1}| + x\left(\frac{r_2 - r_1}{r_2}\right)^2 |H_{L,2}|\right] \qquad (5)$$

with a mean standard deviation of 80 J mol^{-1} at the equimolar composition for the thirteen investigated BCIAH mixtures. For a detailed discussion on the enthalpies of mixing and the lattice parameters of these mixtures, the reader is referred to Königsberger and Schrunner [10].

Binary mixtures of alkaline earth oxides

For three of the six binary alkaline earth oxide mixtures (with the NaCl structure), the heats of formation of solid solutions are known. For the systems (Ca,Sr)O and (Sr,Ba)O, these values have been determined by means of solution calorimetry by Flidlider et al. [11]. The experimental H_1 values for these systems are respectively 23.4 and 37.1 kJ mol^{-1}. For (Mg,Ca)O, the H_1 value has been calculated by several authors [12–14] from phase diagram data, leading to H_1 values in the range 85.4–101.5 kJ mol^{-1}. Table 2 gives a comparison of the evaluated [8] experimental excess enthalpies and those calculated by means of eqn. (4).

TABLE 2

Comparison of evaluated experimental [8] and calculated (eqn. (4)) excess enthalpies for some binary mixtures of alkaline earth oxides. Lattice enthalpies were taken from ref. 1

System	H_1(exp)/kJ mol^{-1}	H_1(calc)/kJ mol^{-1}
(Mg,Ca)O	93.0	113.65
(Ca,Sr)O	23.3	26.59
(Sr,Ba)O	29.1	31.43

A general approach to the estimation of excess enthalpies of non-metallic binary solid solutions

Equation (4) may be regarded as a modified form of the relation for the heats of mixing of binary liquid mixtures $H^E(x) = x(1-x)[\sqrt{H_{VA}} - \sqrt{H_{VB}}]^2$, published by Hildebrand and Wood [15], where H_{VA} and H_{VB} are the heats of vaporization of components A and B respectively.

As a first approximation, eqn. (4) can be used for the calculation of excess enthalpies of binary common-ion solid solutions, within one group of chemically coherent substances with a cubic lattice. However, it seems reasonable to assume that with some modification it will probably be applicable to other types of lattices and other types of solid solutions. The important point is that, within a chemically coherent group of substances, there is always an approximate relation between internal energy and bond distances. Hence we may write, as a first approximation, for the excess enthalpy of a binary mixture of chemically coherent substances in its symmetrical form

$$H^E(x) = x(1-x)\left[\left(\frac{r_2}{r_1}\right)^n |H_{L1}| + \left(\frac{r_1}{r_2}\right)^n |H_{L2}| - 2\sqrt{H_{L1}H_{L2}}\right] \tag{6}$$

In this equation the value of n is related to the dependence of the lattice energy of the pure substances within a family to the nearest neighbour bond distance r in the lattice. Within one group of chemically coherent substances, the difference in bond distance between the family member with the largest bond distance and the member with the smallest bond distance is only a few ångströms. For instance, for the alkali halides $2.013\ \text{Å} \leqslant r \leqslant 3.955\ \text{Å}$, and for the alkaline earth oxides $2.107\ \text{Å} \leqslant r \leqslant 2.771\ \text{Å}$. Therefore, the possible variation of $(r_2/r_1)^n$ and $(r_1/r_2)^n$ values is limited. This observation implies that it may be possible to write an approximation for the excess enthalpy of a binary mixture within a chemically coherent group of substances which holds for several chemically coherent groups of substances. Fitting the experimental data of the binary common-ion alkali halide mixtures and the alkaline earth oxide mixtures leads to

$$H^E(x) = [11.23 \pm 0.13]x(1-x)[\sqrt{|H_{L1}|} - \sqrt{|H_{L2}|}]^2 \tag{7}$$

In the next sections, this relation is tested on molecular and atomic solid solutions.

Binary mixtures of p-dihalobenzenes

Recently, Calvet et al. [7] published a paper on binary p-dihalobenzene mixtures in which a correlation was made between the heat of mixing and

TABLE 3

Coefficients of crystalline isomorphism and first R-K coefficients of the excess heat of melting for the ten investigated binary *p*-dihalobenzene mixtures [7]

No.	System	ε_m	$-\Delta_s^l H_l$/kJ mol^{-1}
1	ClCl + ClBr	0.967	0.88
2	ClCl + BrBr	0.936	4.36
3	ClCl + ClI	0.879	8.92
4	ClCl + BrI	0.857	7.96
5	ClBr + BrBr	0.971	0.52
6	ClBr + ClI	0.915	3.92
7	ClBr + BrI	0.893	7.84
8	BrBr + ClI	0.946	3.04
9	BrBr + BrI	0.925	4.40
10	ClI + BrI	0.980	2.08

the coefficient of crystalline isomorphism (ε_m) [16] for these systems. Table 3 and Fig. 2 give a summary of the results reported by Calvet et al. [7]. The first R-K coefficients for the difference in excess enthalpy of the liquid and solid phase $\Delta_s^l H_l$ were obtained by means of DSC measurements. It was assumed that the liquid state of these mixtures shows ideal mixing behaviour, hence

$$H_l = -\Delta_s^l H_l \qquad (8)$$

For the system ClCl + BrBr, there is an additional value measured by

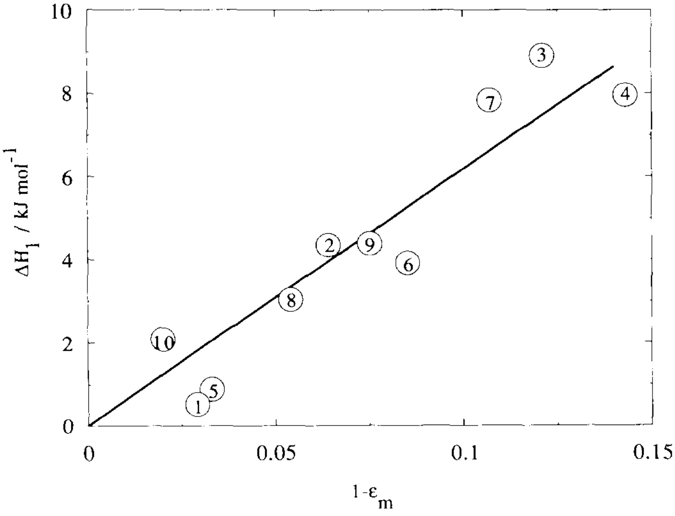

Fig. 2. $-\Delta_s^l H_l$ as a function of $1-\varepsilon_m$ for the ten investigated binary *p*-dihalobenzene mixtures [7]. The numbers in the figure correspond to the system numbers in Table 3.

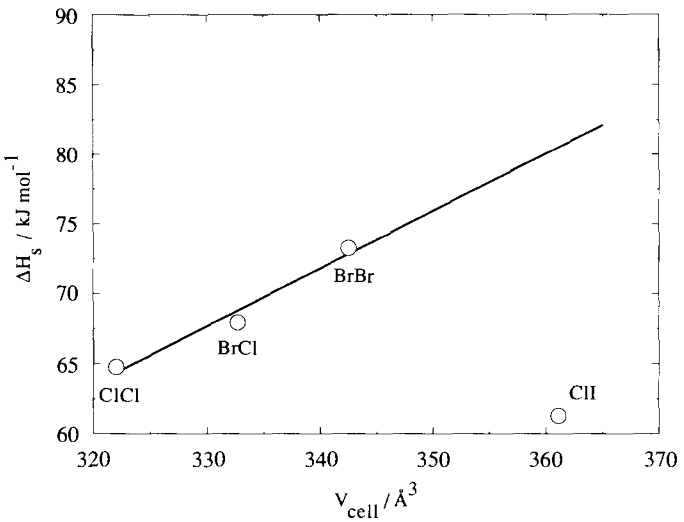

Fig. 3. Heats of sublimation [18] of the *p*-dihalobenzenes as a function of the cell volume [19, 20].

adiabatic calorimetry ($H_\mathrm{l} = 2.8$ kJ mol^{-1}) by van der Linde [17] which is probably more accurate than the DSC value of 4.4 kJ mol^{-1} obtained for this system. The heats of sublimation [18] are tabulated for only four of the five pure *p*-dihalobenzenes. In order to overcome this problem and to rule out coincidental experimental errors, a correlation is made between the heats of sublimation and the cell volumes.

In Fig. 3, the heats of sublimation are plotted versus the cell volumes [19, 20]. It is to be expected that the heat of sublimation rises with increasing cell volume (and molecular mass). The heat of sublimation of *p*-chloroiodobenzene is suspect and is not taken into account; hence, for the group behaviour of the heats of sublimation, the values were calculated from the fit through the remaining three data points which yields the approximation

$$\Delta_s^g H/\mathrm{kJ\ mol^{-1}} = -68.37 + 0.41(V_\mathrm{cell}/\mathrm{Å}^3) \qquad (9)$$

For each substance, the heat of sublimation was calculated by means of eqn. (9) and for each mixture, the parameter $[\sqrt{\Delta_s^g H_1} - \sqrt{\Delta_s^g H_2}]^2$ was calculated. Figure 4 shows a plot of the experimental H_l values, as listed in Table 3, versus the $[\sqrt{\Delta_s^g H_1} - \sqrt{\Delta_s^g H_2}]^2$ parameter. A least-squares fit, through zero, of the data plotted in Fig. 4 leads to

$$H^\mathrm{E}(x) = [10.1 \pm 0.7]x(1 - x)[\sqrt{\Delta_s^g H_1} - \sqrt{\Delta_s^g H_2}]^2 \qquad (10)$$

which is indeed close to the result obtained in eqn. (7) for the binary common-ion alkali halide and alkaline earth oxide mixtures.

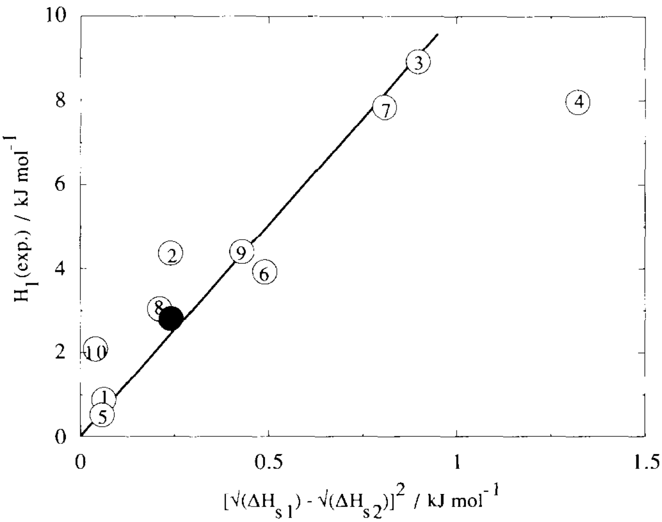

Fig. 4. Experimental first R-K coefficients of the heats of mixing [7] for the ten investigated *p*-dihalobenzene binary mixtures as a function of $[\sqrt{\Delta_s^g H_1} - \sqrt{\Delta_s^g H_2}]^2$. The largest (deviant) value, for the system ClCl + BrI, was not taken into account for the fit. The black dot represents the value obtained by means of adiabatic calorimetry.

Binary cryogenic noble gas mixtures

Figure 5 gives the enthalpy of sublimation [21] for the noble gases as a function of the nearest neighbour interatomic distance [21] in the lattice. The calculated first R-K coefficients of the enthalpies of mixing (fit Fig. 5 and eqn. (7)) for the systems Ar + Kr and Kr + Xe are 2.1 and 3.8 kJ mol^{-1},

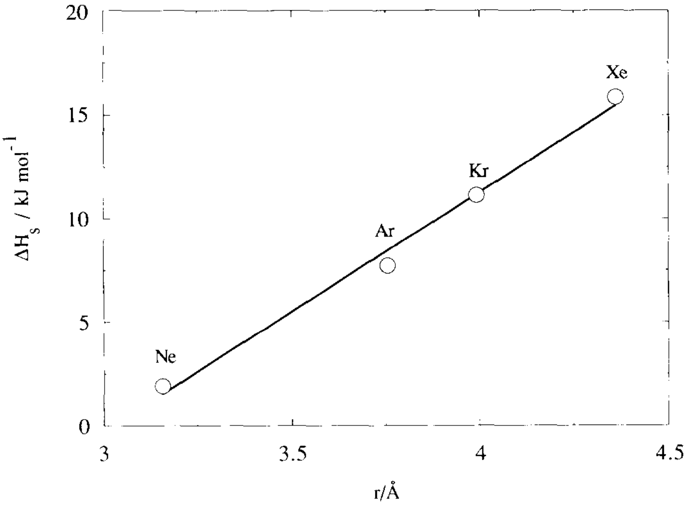

Fig. 5. Enthalpy of sublimation [21] as a function of the nearest neighbour interatomic distance [21] for Ne, Ar, Kr and Xe.

respectively. The experimental values [22] (derived from vapour pressure measurements of the solid solutions and the pure substances) are 1.3 and 2.8 kJ mol^{-1}, respectively. Considering the uncertainties in the heats of sublimation, in the lattice contants and in the experimental excess enthalpies, it can be concluded that eqn. (7) also gives a reasonable approximation for the heats of mixing of these solid solutions.

Asymmetry in the heat of mixing

Thus far we have neglected asymmetry in the heat of mixing. In order to introduce asymmetry we propose the following empirical lattice enthalpy mismatch functions for components 1 and 2

$$y_1 = \left[\frac{H_{L1} - H_{L2}}{H_{L2}}\right]^2 |H_{L1}| \tag{11}$$

and

$$y_2 = \left[\frac{H_{L1} - H_{L2}}{H_{L1}}\right]^2 |H_{L2}| \tag{12}$$

For the heat of mixing

$$H^E(x) = Cx(1-x)[(1-x)y_1 + xy_2] \tag{13}$$

or, written in two-coefficient R-K form

$$H^E(x) = x(1-x)[H_1 + (1-2x)H_2] \tag{14}$$

where the first and second R-K coefficients H_1 and H_2 are given by eqns. (15) and (16)

$$H_1 = \frac{C}{2}(y_1 + y_2) \tag{15}$$

$$H_2 = \frac{C}{2}(y_1 - y_2) \tag{16}$$

Figure 6 gives a plot of the experimental first R-K coefficients of the heats of mixing (thirteen BCIAH systems, three binary alkaline earth oxide systems, nine binary *p*-dihalobenzene systems, two binary noble gas systems, and one binary 1,3,5-trihalobenzene system) as a function of the parameter $y_1 + y_2$. The value of $C/2$ that follows from Fig. 6 is 1.37 ± 0.02.

Reliable data pertaining to the second R-K coefficient for the heats of mixing are scarce. Therefore, the best way to check the calculated second R-K coefficient is probably to compare the ratio $(H_2/H_1)_{calc}$ with $(G_2/G_1)_{exp}$. The latter were derived from phase diagram analysis of region-of-demixing data. The available data are given in Table 4. Figure 7 gives the $(G_2/G_1)_{exp}$ values as a function of $(H_2/H_1)_{calc}$. The figure shows that the ratio

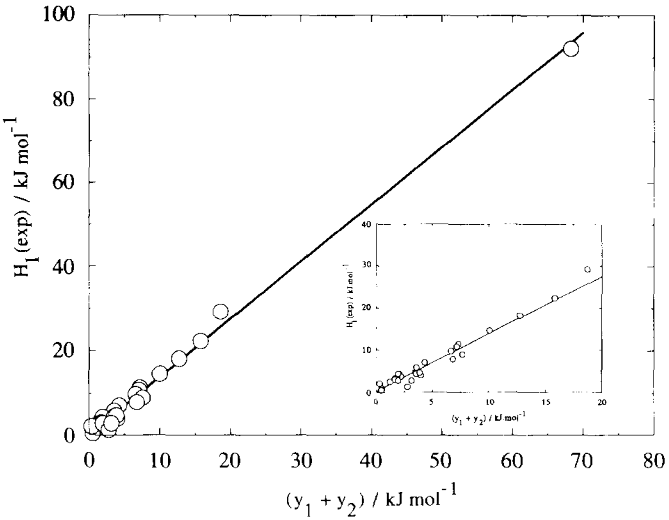

Fig. 6. Experimental first Redlich–Kister coefficients of the heats of mixing as a function of the parameter $y_1 + y_2$.

$(H_2/H_1)_{calc}$ matches well with the $(G_2/G_1)_{exp}$ ratio. It follows that the asymmetry in excess Gibbs energy is larger than the asymmetry in the heat of mixing. This could be due to a systematic error in eqns. (11)–(13) or to the effect of the excess entropy.

TABLE 4

Comparison of $(H_2/H_1)_{calc}$ and $(G_2/G_1)_{exp}$ values

No.	System	$(H_2/H_1)_{calc}$ (eqns. (15) and (16))	$(G_2/G_1)_{exp}$	T_G/K	Ref.
1	(Li,Na)Br	0.102	0.094	455	6
2	(Na,K)Cl	0.137	0.200	678	6
3	(Na,K)Br	0.124	0.130	599	6
4	(Na,K)I	0.108	0.120	444	6
5	K(Br,I)	0.085	0.120	390	6
6	Rb(Br,I)	0.078	0.111	280	6
7	(Mg,Ca)O	0.148	0.204	2250	14
8	ClCl + BrBr	0.174	0.200	150	17
9	TCB + TBB[a]	0.231[b]	0.291	0	17

[a] TCB and TBB are 1,3,5-trichlorobenzene and 1,3,5-tribromobenzene, respectively

[b] Required enthalpies of sublimation were also taken from ref. 17.

THE ESTIMATION OF CHARACTERISTIC TEMPERATURES OF BINARY SOLID SOLUTIONS

Figure 8 shows the characteristic temperatures determined by various experimental means (combinations of calorimetry, mass spectrometry,

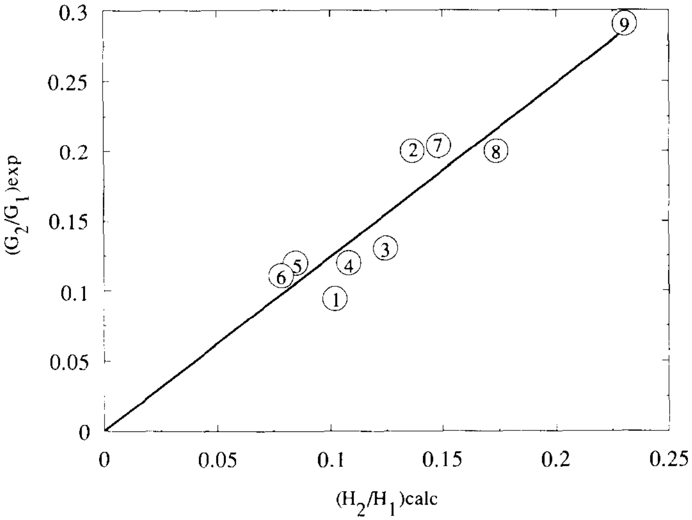

Fig. 7. Experimental G_2/G_1 values as a function of the calculated H_2/H_1 values. The numbers in the figure correspond to the system numbers in Table 4.

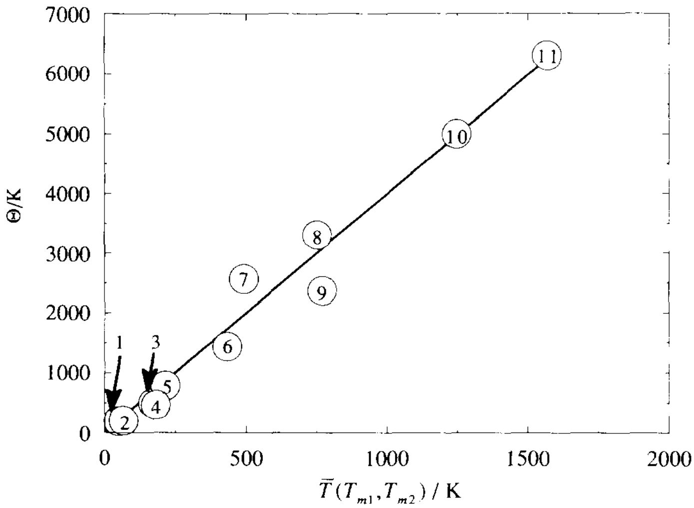

Fig. 8. Experimental characteristic temperatures of binary solid solutions as a function of the parameter $\bar{T}(T_{m1}, T_{m2})$. Pure-substance melting points were taken as given in refs. 14, 17, 18, 21, 23 and 33: 1, argon + krypton [22]; 2, krypton + xenon [22]; 3, mean value of ten binary *p*-dihalobenzene mixtures [7]; 4, 1,3,5-trichlorobenzene + 1,3,5-tribromobenzene [17]; 5, 1,2,4,5-tetrachlorobenzene + 1,2,4,5-tetrabromobenzene [23]; 6, sodium chloride + silver chloride [26–28]; 7, mean value of thirteen binary common-ion alkali halide mixtures [6]; 8, nickel + gold [24]; 9, palladium + gold [25]; 10, strontium oxide + barium oxide [8]; 11, magnesium oxide + calcium oxide [8].

vapour pressure measurements, E.M.F. measurements and phase diagram analysis) [6–8, 17, 22–28] depicted as a function of the parameter given by

$$\bar{T}(T_{m1}, T_{m2}) = \frac{T_{m1}T_{m2}}{T_{m1} + T_{m2}} \qquad (17)$$

in which T_{m1} and T_{m2} are the melting temperatures (K) of the first and second component, respectively. The parameter given by eqn. (17) has been introduced for the calculation of the characteristic temperatures of metallic liquid binary solutions by Tanaka et al. [29]. A least-squares fit of the data plotted in Fig. 8 leads to

$$\Theta = (4.0 \pm 0.16)\frac{T_{m1}T_{m2}}{T_{m1} + T_{m2}} \qquad (18)$$

DISCUSSION AND CONCLUSIONS

As Urusov has pointed out in several papers [30–32], the heat of mixing of a binary solid solution is related to the size difference and to the chemical difference in the components. For mixtures within a chemically coherent group of substances, the chemical difference, (i.e. polarizability, electronegativity), which is usually small, is related to the difference in size of the components. This makes it possible to disregard the chemical difference and to correlate the heat of mixing to the size difference alone.

The spectrum of chemical substances can be divided into a few classes according to bond type: ionic, ionic-covalent, covalent, van der Waals. It has been shown that within a chemically coherent group of substances which are members of the ionic or van der Waals class, the heats of mixing are determined by the internal energies of the pure components. Moreover, to a good approximation, the heats of mixing of binary mixtures within these different classes can be described by one ‘internal energy mismatch’ relation. Although this has been made plausible in the “General approach” section above, a thorough theoretical description of the observed phenomena, which after introducing some approximations should lead to our empirical relations, is still lacking. As far as the characteristic temperatures are concerned, excess entropies of solid solutions are mainly the effect of thermal vibrations. A more theoretical approach (statistical thermodynamics) should link lattice enthalpies and excess enthalpies to Debye temperatures and excess Debye temperatures. Once the excess Debye temperatures are known, excess specific heats and excess entropies can be calculated by means of statistical thermodynamics. If eqn. (18) is indeed valid for all kinds of binary solid solutions, as suggested by the experimental evidence depicted in Fig. 8, then eqn. (18) can be a very powerful tool in future materials research. Further work is in progress.

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