Elucidation of structural changes and concentration fluctuations in binary mixtures using new thermodynamic relations

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Abstract. The thermodynamics associated with structural changes in binary mixtures has been examined in search of relations which connect Darken stability or the concentration–concentration fluctuations to the thermodynamic response functions. New relations have been derived. These are the counterpart of Ehrenfest relations in an extended form for second order phase transitions in binary mixtures. It has been proved that the structural change inevitably causes instability of a binary mixture with respect to the concentration fluctuations. The new relations make it possible that the instability brought about by structural change can be evaluated in terms of the thermodynamic functions.

1. Introduction

Universal thermodynamic relations associated with the phase transition have been extensively discussed (Pippard 1964). Among them, the best known are the Clapeyron–Clausius equation for the first order phase transition and the Ehrenfest relations for the second order phase transition. The latter were extended by Pippard to continuous structural transitions and called Pippard relations. According to the extension by Pippard, the constant pressure specific heat (C_P), isothermal compressibility (κ_T) and thermal expansion coefficient (α_P) diverge towards a λ-point in the same powers of temperature.

For the binary mixture, close correlation has been experimentally found between the phase transition and the stability of a binary mixture. A phase transition such as the ferromagnetic transition, order–disorder transition, superfluid transition in the liquid ^{3}He–^{4}He mixture and polymeric transition in mixtures of liquid sulphur is known to stimulate the two-phase separation (Meigering 1963, Knobler and Scott 1984, Nishizawa *et al* 1979). The miscibility gap is pulled along the Curie line which intersects to a two-melt phase boundary and consequently a horn or kink appears at the crossing, the tip of which is known to be a tricritical point in the x–T plane (Knobler and Scott 1984). The phenomena have been discussed almost independently using various specific models.

In this paper, new universal thermodynamic relations have been derived. These relations connect the constant pressure specific heat and isothermal compressibility to Darken stability. Darken stability is the reciprocal of the concentration–concentration fluctuations. The relations prove that the excess part of Darken stability caused by structural changes are definitely negative and, thus, the structural change in a binary mixture stimulates a tendency towards phase separation. It is shown that they are the counterpart of Pippard relations in a binary mixture

undergoing a structural change. The author has applied the derived relations to the Se–Te and Rb–Pb systems to estimate the extent of instability caused by a structural change due to the Peierls distortion mechanism in the former (Gaspard *et al* 1987) and by the dissociation of a poly-anion in the latter (Tumidajski *et al* 1990).

2. Thermodynamic relations

Assuming that structural change can be described by an order parameter $C(T, P, x)$, where T is temperature, P pressure and x the fraction of a constituent, the Gibbs free energy (G) for a binary mixture which undergoes structural change can be represented as (Davies and Jones 1953, Tsuchiya 1991a)

$$G = G(T, P, x, C(T, P, x)). \tag{1}$$

Further assuming that G is differentiable up to the second order with respect to any valuable of state and C. $C(T, P, x)$ can adjust itself so as to make G a minimum. Thermal equilibrium requires

$$(\partial G/\partial C)_{T,P,x} = 0. \tag{2}$$

The total differential (dG) of the Gibbs free energy is given by

$$dG = (\partial G/\partial T)_{P,x,C}\, dT + (\partial G/\partial P)_{T,x,C}\, dP + (\partial G/\partial x)_{T,P,C}\, dx = -S\, dT + V\, dP + \Delta\mu\, dx \tag{3}$$

where S, V and $\Delta\mu$ represent entropy, volume and the difference in the chemical potentials for the corresponding constituents, respectively. These thermodynamic quantities are also a function of T, P, x and C. Systematic calculation of the total differential of all of them has been done keeping one of the variables of state constant. The variable which has been taken constant is omitted so as to avoid complexity of the resulting equations.

2.1. S and V as a function of T and P

Bearing in mind that S and V can take, respectively, the form $S(T, P, C)$ and $V(T, P, C)$, the following equations can be written.

$$dS = (\partial S/\partial T)_{P,C}\, dT + (\partial S/\partial P)_{T,C}\, dP + (\partial S/\partial C)_{T,P}\, dC. \tag{4}$$

Dividing by dT and assuming C to be constant,

$$(\partial S/\partial T)_C = (\partial S/\partial T)_{P,C} + (\partial S/\partial P)_{T,C}(\partial P/\partial T)_C. \tag{5}$$

It should be mentioned that the equation

$$(\partial u/\partial v)_w = (\partial u/\partial v)_t + (\partial u/\partial t)_v(\partial t/\partial v)_w$$

holds for a function of two variables $u(v, t)$ when the variations are taken along a path defined by $w(v, t) = $ constant. Then the left-hand side of equation (5) may be rewritten as

$$(\partial S/\partial T)_C = (\partial S/\partial T)_P + (\partial S/\partial P)_T(\partial P/\partial T)_C. \tag{6}$$

Equating the right-hand side of equations (5) and (6), and using the Maxwell relation, $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$, equation (7) is obtained.

$$(\partial S/\partial T)_P - (\partial S/\partial T)_{P,C} = \{(\partial V/\partial T)_P - (\partial V/\partial T)_{P,C}\}(\partial P/\partial T)_C. \tag{7}$$

Denoting the constant pressure specific heat and volume expansion coefficient brought about by the structural changes, respectively, as δC_P and $\delta\alpha_P$, equation (7) is rewritten as

$$\delta C_P = TV\delta\alpha_P(\partial P/\partial T)_C \tag{8}$$

where $(\partial P/\partial T)_C$ is the constant C slope in the T–P plane.

In a similar way, it is not difficult to obtain the following relation.

$$(\partial V/\partial P)_T - (\partial V/\partial P)_{T,C} = \{(\partial V/\partial T)_{P,C} - (\partial V/\partial T)_P\}(\partial T/\partial P)_C \qquad (9)$$

which can be rewritten as

$$\delta\kappa_T = \delta\alpha_P(\partial T/\partial P)_C. \qquad (10)$$

Here $\delta\kappa_T$ is the change in the isothermal compressibility caused by the structural change. Combining equations (8) and (10)

$$\delta C_P \delta\kappa_T = TV(\delta\alpha_P)^2. \qquad (11)$$

Equations (8), (10) and (11) are analogous to the Pippard relations for the second order phase transition.

It should be emphasized that the change in the compressibility, $\delta\kappa_T$, and the change in the specific heat, δC_P are always positive, while $\delta\alpha_P$ is of undetermined sign depending on the sign of $(\partial V/\partial C)_{T,P}$. A qualitative argument is as follows: $\delta\kappa_T$ takes a form $-V^{-1}(\partial V/\partial C)_{T,P}(\partial C/\partial P)_T$ (Tsuchiya 1991a). If the volume contracts upon a structural change $((\partial V/\partial C)_{T,P} < 0)$, such a structural change proceeds with an applied pressure $((\partial C/\partial P)_T > 0)$ and *vice versa*. Then $\delta\kappa_T$ is always positive and from equation (11) δC_P is also positive. The requirements arise from the thermodynamic stability condition, $(\partial^2 G/\partial C^2)_{T,P,x} > 0$, and the proof has been given by Prigogine and Defay (1954).

2.2. V and Δμ as a function of P and x

A similar argument may be applied to the volume $V(P, x, C)$ and to the difference in the chemical potential $\Delta\mu(P, x, C)$.

$$(\partial V/\partial P)_x - (\partial V/\partial P)_{x,C} = \{(\partial V/\partial x)_{P,C,} - (\partial V/\partial x)_P\}(\partial x/\partial P)_C. \qquad (12)$$

Denoting the difference in the partial volumes for the respective constituents brought about by the structural changes as $\delta\Delta V$, equation (12) is rewritten as

$$\delta\kappa_T = V^{-1}\delta\Delta V(\partial x/\partial P)_C \qquad (13)$$

where $(\partial x/\partial P)_C$ is the constant C slope in the P–x plane. The following equation is obtained for $\Delta\mu$,

$$(\partial\Delta\mu/\partial x)_P - (\partial\Delta\mu/\partial x)_{P,C} = \{(\partial\Delta/\partial P)_{x,C} - (\partial\Delta\mu/\partial P)_x\}(\partial P/\partial x)_C. \qquad (14)$$

Defining Darken stability as $D = (\partial\Delta\mu/\partial x)_{T,P}$ and denoting the contribution brought about by the structural change as δD, equation (14) is reduced to

$$\delta D = -\delta\Delta V(\partial P/\partial x)_C. \qquad (15)$$

From equations (13) and (15) we obtain

$$\delta\kappa_T \delta D = -V^{-1}(\delta\Delta V)^2. \qquad (16)$$

The original Darken excess stability is defined by $(\partial^2 G^e_{mix}/\partial x^2)_{T,P}$, where G^e_{mix} is the excess mixing Gibbs free energy (Darken 1967). It differs from D used here by the factor $RT/\{x(1 - x)\}$, the contribution coming from the ideal entropy of mixing, where R is the universal gas constant.

2.3. $\Delta\mu$ and S as a function of T and x

Let us consider the difference in the chemical potential $\Delta\mu(T, x, C)$ and the entropy $S(T, x, C)$. Equation (17) is obtained for $\Delta\mu$ as a function of T and x.

$$(\partial\Delta\mu/\partial x)_T - (\partial\Delta\mu/\partial x)_{T,C} = \{(\partial\Delta\mu/\partial T)_{x,C} - (\partial\Delta\mu/\partial T)_x\}(\partial T/\partial x)_C. \tag{17}$$

Writing the difference in the partial entropy for the respective constituents brought about by the structural changes as $\delta\Delta S$, equation (17) is rewritten as

$$\delta D = \delta\Delta S(\partial T/\partial x)_C \tag{18}$$

where $(\partial T/\partial x)_C$ is the constant C slope in the x–T plane. For S we have

$$(\partial S/\partial T)_x - (\partial S/\partial T)_{x,C} = \{(\partial S/\partial x)_{T,C} - (\partial S/\partial x)_T\}(\partial x/\partial T)_C \tag{19}$$

and

$$\delta C_P = -T\delta\Delta S(\partial x/\partial T)_C. \tag{20}$$

From equations (18) and (20),

$$\delta C_P\delta D = -T(\delta\Delta S)^2. \tag{21}$$

From equations (11), (16) and (21), δD in terms of $\delta\alpha_P$ is given by

$$(\delta D)^2 = V^{-2}(\delta\Delta V)^2(\delta\Delta S)^2/(\delta\alpha_P)^2. \tag{22}$$

The darken stability function is related to the concentration–concentration fluctuations $S_{cc}(0)$ by $D = RTS_{cc}(0)^{-1}$ (Bhatia and Thornton 1970). Hence, the negative sign of right-hand side of equations (16) and (21) proves that the structural changes in a binary mixture inevitably enhances instability with respect to the concentration fluctuations.

3. Application to the Se–Te system and Rb–Pb system

Since the test of relations analogous to the Pippard relations in 2.1 has been reported elsewhere (Tsuchiya 1991a), the author deals with the applicability of new thermodynamic relations (16) and (21). Extensive studies on the thermodynamic properties associated with structural changes in the liquid Se–Te system have been carried out. This enables the author to apply the equations to the aforesaid system. For this system the order parameter is the change of the average co-ordination number of Se and Te atoms from two to three. In figure 1 the isotherms of the isothermal compressibility (Tsuchiya 1991a), molar volume (Tsuchiya 1988) and difference in the partial volume at $600\,^\circ$C have been plotted. The temperature $600\,^\circ$C has been chosen so as to make it convenient to determine the excess quantities involved in the analysis. Effects due to structural changes (appearance of peak/dip) appear in the mid-range of composition at the above mentioned temperature. The base line for $\delta\kappa$ has been drawn with a binary hard sphere model for the compressibility evaluation (Tsuchiya 1991a). A straight line connecting the values for Se and Te has been chosen as a base for ΔV because the molar volume as a function of composition changes almost linearly in the respective sides. Figure 2 shows the results of the constant pressure specific heat (Kakinuma and Ohno 1987), mixing entropy (Tsuchiya *et al* 1996) and the difference in the partial entropy at the same temperature. The specific heat of Se has been chosen for the base line for C_P because liquid Se does not undergo structural changes at the corresponding temperature. ΔS in equation (21) consists of the contribution from the derivative of mixing entropy and the difference in the entropy of constituents. Assuming a random mixture of Se and Te, the base line for $\delta\Delta S$ is given by $-\ln[x/(1-x)]+$const, where const represents the difference in the entropy of pure Se and Te.
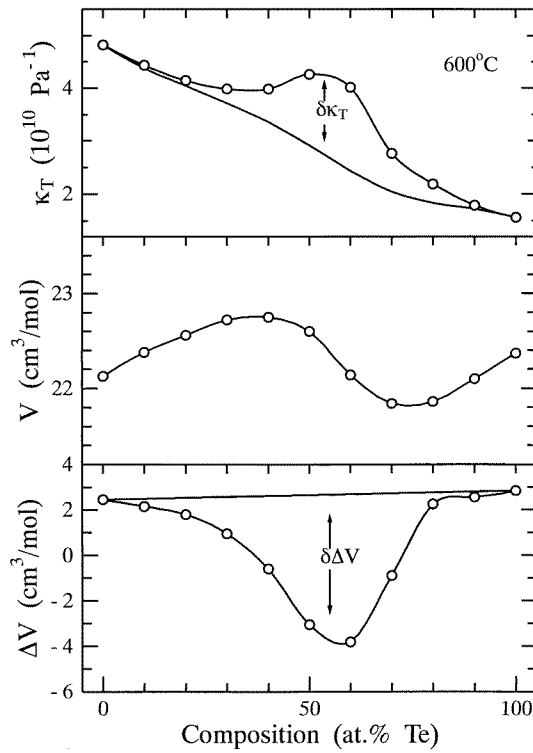
Figure 1. Isothermal compressibility κ_T (Tsuchiya 1991a), molar volume V (Tsuchiya 1986) and difference ΔV in the partial molar volumes for the liquid Se–Te system at 600 °C. $\delta\kappa_T$ and $\delta\Delta V$ represent the contribution brought about by the structural change.

It was determined by fitting the curve to the experimental data along the Se side. Its value is $0.66(R^{-1})$. The value obtained is not in contradiction with the one expected from the entropy difference in the structural change in liquid Te (Tsuchiya 1991b).

From the excess quantities denoted in figures 1 and 2, δD can be readily calculated either from equation (16) or (21). The results have been presented in figure 3. Keeping in view, the uncertainty of assignments of baselines and experimental procedures undertaken by other authors, δD values obtained through relations (16) and (21) are in good agreement. The sign of δD is negative as predicted by equations (16) and (21) and the phase separation tendency develops in the liquid Se–Te system at the composition where the constant specific heat and isothermal compressibility have a peak.

In the previous paper (Tsuchiya 1997), it was shown that the concentration–concentration fluctuations $S_{cc}(0)$ for a binary alloy undergoing a structural change are given by

$$S_{cc}(0)^{-1} = (RT)^{-1}\{(\partial^2 G/\partial x^2)_{T,P,C} + \partial((\partial G/\partial x)_C/\partial C)_{T,P}(\partial C/\partial x)_{T,P}\}. \tag{23}$$

This equation is equivalent to equation (17) and the second term is equal to δD. The first term represents expected Darken stability if there were no structural change. This can be estimated at low temperatures which are far from the transitional temperature region. The lower part of figure 3 compares $S_{cc}(0)$, one with the present δD together with the Gibbs free energy at low temperatures (Tsuchiya 1986) and the other calculated at 600 °C with a inhomogeneous structure model (Tsuchiya *et al* 1996). Both results agree very well.
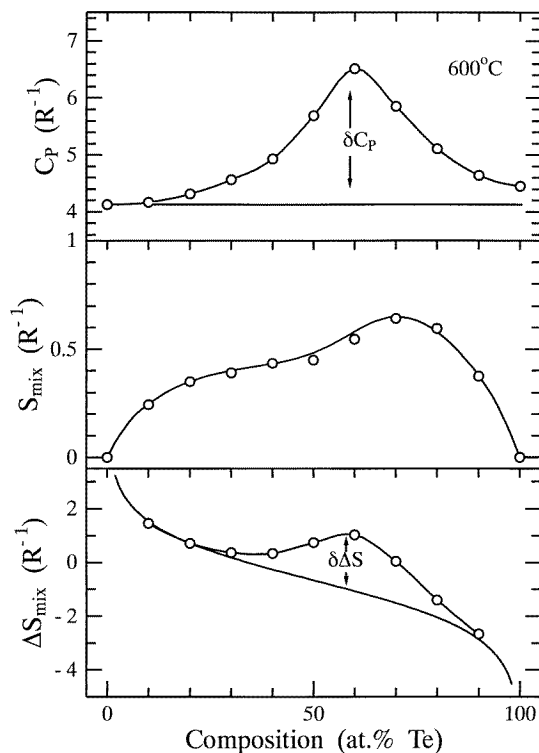
Figure 2. Constant pressure specific heat C_P (Kakinuma and Ohno 1987), mixing entropy S_{mix} (Tsuchiya *et al* 1996) and difference ΔS_{mix} in the partial mixing entropy for the liquid Se–Te system at 600 °C, where R is the universal gas constant. δC_P and $\delta \Delta S$ represent the contribution brought about by the structural change.

Another application has been made to the Rb–Pb system in which the polyanion compound $Rb_4^+Pb_4^{4-}$ plays an important role in the physico-chemical properties and structure (Tumidajski *et al* 1990). Figure 4 shows the experimental excess specific heat C_p^{mix} and the mixing entropy S_{mix} (Tumidajski *et al* 1990). C_p^{mix}, defined as the deviation of the specific heat from a linear interpolation between those for Pb and Rb, has a large maximum and S_{mix} has a pronounced minimum around 50 at.% Rb. The results have been interpreted as being due to the polyanion compound in the melt. It is also known (Tumidajski *et al* 1990) that the excess stability for the equiatomic alkali plumbides is rather small (about 300 kJ mol^{-1} or less) as compared with, for example, the value for Tl$_2$Te, about 2500 kJ mol^{-1} at 600 °C (Nakamura and Shimoji 1971). A model assuming a dissociation of Pb$_4^{4-}$ anions has been proposed to account for anomalous behaviour of the specific heat of the Pb–Rb system as a function of both composition and temperature (Geertsma and Saboungi 1995). In the course of calculations, it has been shown that the dissociation of the clusters gives a negative contribution to the Darken stability. They have suggested that the negative contribution would explain the small value of the stability. However, the exact amount of the contribution has not been obtained either experimentally or theoretically so far.

The lower graph in figure 4 shows the difference ΔS_{mix} in the partial entropy for Pb and Rb. In the calculations of ΔS_{mix}, S_{mix} on the Pb and Rb sides were, respectively, fitted to fourth order and second order polynomials. The solid curve in the figure for ΔS_{mix} shows a
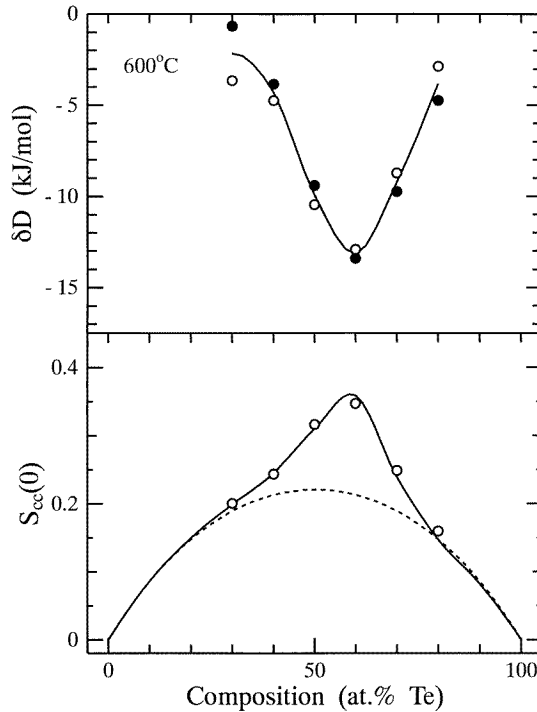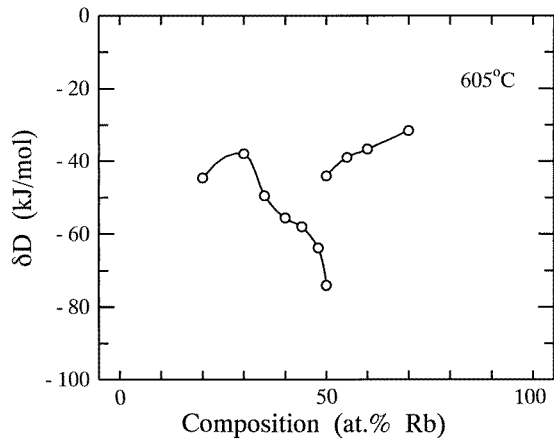
Figure 3. The Darken instability δD brought about by the structural changes in the Se–Te system at 600 °C. Solid circles and open circles have been estimated, respectively, from equations (16) and (21). $S_{cc}(0)$ (circles) obtained by the present δD together with the Gibbs free energy G_0 expected if there were no structural changes (Tsuchiya 1986) is compared with the theoretical results with an inhomogeneous structure model (solid curve) (Tsuchiya *et al* 1996). The dotted curve represents $S_{cc}(0)$ corresponding to G_0 (the first term of equation (23)).

baseline for $\delta \Delta S$ which has been calculated using equation (2.3) of Geertsma and Saboungi (1995) and together with the degree of dissociation as a function of composition therein. It is noted that $\delta \Delta S$ jumps from negative to positive at 50 at.% of Rb in contrast to the results for the Se–Te system shown in figure 2. From these results $(\partial x/\partial T)_C$ in equation (20) is positive on the Pb side and negative on the Rb side, because δC_p is always positive. Since $(\partial x/\partial T)_C = -(\partial C/\partial T)_x(\partial x/\partial C)_T$ and $(\partial C/\partial T)_x > 0$ (the dissociation proceeds with increasing temperature), $(\partial C/\partial x)_T$ changes its sign from negative to positive around 50 at.% Rb and thus C as a function of composition takes a minimum at there. This prediction agrees with the model by Geertsma and Saboungi (1995) in which the calculated composition dependence of the degree of dissociation actually takes a minimum around 50 at.% Rb. By definition δC_p is slightly different from C_p^{mix}. However, the difference can be neglected to a first approximation because C_p^{mix} arises mainly from the dissociation of polyanion compound of Pb and Rb. δD evaluated using equation (21) is plotted in figure 5. The scanty data for numerical differentiation on the Rb rich side and the fairly large uncertainty ($\pm 20\%$) in C_p^{mix} (Tumidajski *et al* 1990) would result in a large difference in δD values at 50 at.% Rb evaluated in both composition ranges. Anyway it can be suggested that δD is -50 to -60 kJ mol^{-1} around 50 at.% Rb and the contribution from the dissociation of the polyanion compound is about 20% of the experimental Darken excess stability. It would be of interest to compare the present δD with the numerical calculations of equation (B5) in Geertsma and Saboungi (1995)
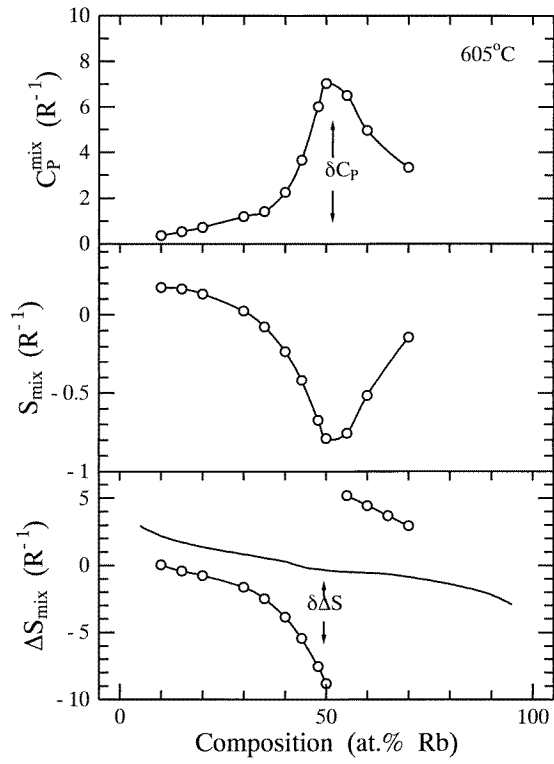
Figure 4. Excess specific heat C_p^{mix}, mixing entropy S_{mix} (Tumidajski *et al* 1990) and difference ΔS_{mix} in the partial mixing entropy for the liquid Pb–Rb system at 605 °C, where R is the universal gas constant. δC_P and $\delta \Delta S$ represent the contribution brought about by the dissociation of polyanion Pb_4^{-4}.

Figure 5. The Darken instability δD brought about by the dissociation of polyanion Pb_4^{-4} in the Pb–Rb system at 605 °C estimated from equation (21).

to confirm their model and to obtain further insight into a dissociation scheme of the polyanion compound in liquid alkali group IV alloys.

4. Discussion and conclusions

It may be observed that there is a marked similarity between the new equations derived in 2.2 and 2.3, and those in section 2.1. The latter are analogous to Ehrenfest relations or their extension, i.e. Pippard relations. The reason is that all these equations are related to the second partial derivatives of the Gibbs free energy $G(T, P, x, C(T, P, x))$ with respect to any pair of the variables of state in which an order parameter $C(T, P, x)$ plays a role of constraint. The relations have been derived without any specification on the structural change. 'Structural change' rather than 'phase transition' has been used because the relations derived may be applied to rapid structural changes which can be interpreted as crossover in the restricted sense. The only assumption is that the Gibbs free energy can be differentiable to the second order with respect to the variable of state. In this sense the validity of the new thermodynamic relations (equations (16), (21) and (22)) is quite obvious, and it may be possible to apply them to any structural transition in a binary mixture except in the close vicinity of a sharp transition like a λ-point. It is, therefore, concluded that the structural change in a binary mixture inevitably leads to the instability with respect to the concentration fluctuations. This gives a thermodynamic explanation for the interference between Curie lines and binary miscibility gaps. It explains why the miscibility gap is pulled along a Curie line to result in a horn or a kink in the boundary of two-melt separation. In equation (23), it could happen that the magnitude of the second term δD becomes large enough to exceed the first. This may lead to the appearance of a two-melt phase in the x–T plane; otherwise, the miscibility gap could not be expected. A very small two-melt phase with a looped boundary in the liquid S–Te system is an example (Tsuchiya 1994).

From the experimental side, on the one hand, it is not easy to directly measure the constant pressure specific heat at high temperatures and, hence, to determine the isothermal compressibility which requires estimation of the dilatation term or the difference in the isothermal and adiabatic compressibility. On the other hand, the measurements of S_{mix} by an EMF method and density at high temperatures are comparatively not so difficult. For such a situation the new thermodynamic relations have potential for evaluation of δC_P and $\delta \kappa_T$ in such a way that firstly δD can be determined from equation (22), and then δC_P and $\delta \kappa_T$ through equations (16) and (21) in terms of δD. They would provide useful information on structural changes in the melt at high temperatures.

It is not difficult to derive equations for the free energy involving the external magnetic field H. The excess contribution in the magnetization and magnetic susceptibility brought about by structural changes or magnetic transitions can be related to other thermodynamic quantities in the same way.

In summary, new thermodynamic relations have been derived that connect the excess constant pressure specific heat and the excess isothermal compressibility to the excess Darken stability caused by structural change. It has been proved that the contribution to the Darken stability caused by structural change is definitely negative. This implies that structural changes always cause instability of a binary mixture with respect to the concentration fluctuations. New relations make it possible that the excess contribution in the Darken stability caused by the structural change can be evaluated quantitatively using thermodynamic quantities. Many applications of new defined relations would be expected to a wide variety of continuous structural changes. This also includes dissociation processes in compounds forming binary mixtures at high temperatures to the superfluid transition in the liquid ^{3}He–^{4}He system at low temperatures.

References

Bhatia A B and Thornton D E 1970 *Phys. Rev.* B **2** 2004
Darken L S 1967 *Trans. AIME* **329** 80
Davies R O and Jones G O 1953 *Adv. Phys.* **2** 370
Gaspard J P, Marinelli F and Pellegatti 1987 *Europhys. Lett.* **3** 1095
Geertsma W and Saboungi M-L 1995 *J. Phys.: Condens. Matter* **7** 4803
Kakinuma F and Ohno T 1987 *J. Phys. Soc. Japan* **56** 619
Knobler C M and Scott C M 1984 *Phase Transition and Critical Phenomena* vol 9, ed C Domb and J C Lebowitz
        (London: Academic) p 163
Meijering J L 1963 *Philips Res. Rep.* **18** 318
Nakamura Y and Shimoji M 1971 *Trans. Faraday Soc.* **67** 1270
Nishizawa T, Hasebe M and Ko M 1979 *Acta Metall.* **27** 817
Pippard A B 1964 *Elements of Classical Thermodynamics* (Cambridge: Cambridge University Press)
Prigogine I and Defay R 1950 *Chemical Thermodynamics* transl. D Everett (London: Longmans)
Tsuchiya Y 1986 *J. Phys. C: Solid State Phys.* **19** 2865
——1988 *J. Phys. Soc. Japan* **57** 3851
——1991a *J. Phys. Soc. Japan* **60** 960
——1991b *J. Phys.: Condens. Matter* **3** 3163
——1994 *J. Phys.: Condens. Matter* **6** 2451
——1997 *J. Chem. Phys.* **94** 998
Tsuchiya Y, Kakinuma F and Bergman C 1996 *J. Non-Cryst. Solids* **143–146** 143
Tumidajski P J, Petric A, Takenaka T, Pelton A D and Saboungi M-L 1990 *J. Phys.: Condens. Matter* **2** 209