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Computer Coupling of Phase Diagrams and Thermochemistry 32 (2008) 89–93

www.elsevier.com/locate/calphad

Undulate phase boundaries on binary T–x diagrams

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Received 28 June 2007; received in revised form 7 August 2007; accepted 14 August 2007
Available online 17 September 2007

Abstract

Usually, an inflection point on a phase boundary is considered as an unambiguous indication that one of phases participating in the equilibrium is internally unstable, i.e. that it is prone to separation. Subsequently, it is habitually deemed that the inflection point may appear only if a thermodynamic model of this phase contains an excess term.

It is shown that in contrast to this belief, inflection points on a phase boundary may appear when a pure solid component or a stoichiometric binary phase is in equilibrium with the ideal binary solution, which is internally stable, indeed.

Keywords: Binary system; Phase boundary; Inflection point; Entropy of melting

1. Introduction

The Sn–Zn system was optimized by Fries and Lukas [1]. The phase diagram resulting from that assessment is shown in Fig. 1 (solid lines). Let us notice an inflection point on the liquidus. A traditional way of explaining such a shape (known as "S-shape") is to assume that the liquid phase is prone to separation at temperatures below the liquidus. A dashed line representing a metastable miscibility gap in the liquid suggests that in this particular case, the rationalization is compelling.

In this work, it is shown that such an explanation is not universal. This is done by firstly deriving general expressions for the slope and curvature of a phase boundary for the case when a binary solution is in equilibrium with a stoichiometric binary phase. Then these expressions are simplified by assuming that the solution is ideal. Finally, through a straightforward mathematical analysis, a condition resulting in the appearance of an inflection point is formulated.

2. Slope of a phase boundary

Let us consider the equilibrium between a binary solution phase L and a binary stoichiometric phase α. For the sake of determinacy, let us assume that L is a simple (single lattice) substitutional solution. The Gibbs energies of L and α are given by (1) and (2), respectively:

$$\begin{aligned} G^L &= (1-x^L)\Delta G_1^{0L} + x^L \Delta G_2^{0L} \\ &\quad + RT((1-x^L)\ln(1-x^L) + x^L \ln x^L) + \Delta^{\mathrm{ex}} G^L \end{aligned} \tag{1}$$

$$G^\alpha = (1-x^\alpha)\Delta G_1^{0\alpha} + x^\alpha \Delta G_2^{0\alpha} + \Delta_f G^\alpha \tag{2}$$

where $\Delta G_i^{0\gamma}$ is the Gibbs energy of transformation of the i-th component from the structure associated with its reference state to the structure of the γ phase. The general expression (2) reduces to $G^\alpha = \Delta G_1^{0\alpha}$ if $x^\alpha = 0$ and to $G^\alpha = \Delta G_2^{0\alpha}$ if $x^\alpha = 1$.

The condition of equilibrium between L and α can be written as

$$G^L + (x^\alpha - x^L) G_L^L - G^\alpha = 0. \tag{3}$$

In (3) and below, the notation $\varphi_{\underbrace{LL\ldots L}_{m\text{ times}}\underbrace{TT\ldots T}_{n\text{ times}}} \equiv \frac{\partial^{m+n}\varphi}{\partial(x^L)^m \partial T^n}$ is used for making expressions shorter and easier to handle.

A great deal of attention has been paid in the literature to calculating slopes of phase boundaries [2,3]. Despite this, it seems justified to start derivations from scratch to ensure cohesiveness of the present work as well as to enforce internal logic.

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doi:10.1016/j.calphad.2007.08.002

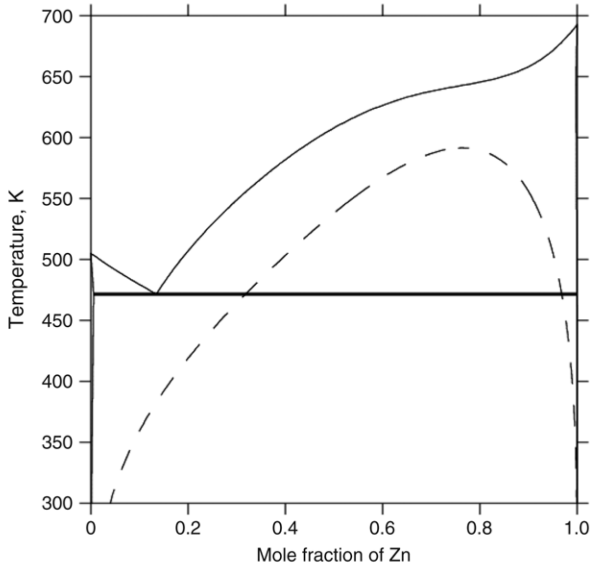

Fig. 1. A metastable miscibility gap in the liquid phase (dashed curve) superimposed on the equilibrium Sn–Zn phase diagram.

Let us denote the LHS of (3) as F. Since F remains equal to zero along the phase boundary, one can use implicit differentiation and write

$$F_L + F_T(\mathrm{d}T/\mathrm{d}x^L) = 0. \tag{4}$$

The expression for the slope of the phase boundary immediately follows from (4):

$$\mathrm{d}T/\mathrm{d}x^L = -F_L/F_T \tag{5}$$

where

$$F_L = (x^\alpha - x^L)G^L_{LL} \tag{6}$$

$$F_T = G^L_T + (x^\alpha - x^L)G^L_{LT} - G^\alpha_T. \tag{7}$$

Having expressions (1) and (2), one can write partial derivatives of the Gibbs energies in (6) and (7) as

$$G^L_{LL} = RT/((1-x^L)x^L) + \Delta^{\mathrm{ex}}G^L_{LL} \tag{8}$$

$$\begin{aligned} G^L_T = &-(1-x^L)\Delta S^{0L}_1 - x^L\Delta S^{0L}_2 \\ &+ R((1-x^L)\ln(1-x^L) + x^L\ln x^L) - \Delta^{\mathrm{ex}}S^L \end{aligned} \tag{9}$$

$$G^L_{LT} = \Delta S^{0L}_1 - \Delta S^{0L}_2 + R\ln(x^L/(1-x^L)) - \Delta^{\mathrm{ex}}S^L_L \tag{10}$$

$$G^\alpha_T = -(1-x^\alpha)\Delta S^{0\alpha}_1 - x^\alpha\Delta S^{0\alpha}_2 - \Delta_f S^\alpha. \tag{11}$$

Substitution of (8) in (6) gives

$$F_L = (x^\alpha - x^L)(RT/((1-x^L)x^L) + \Delta^{\mathrm{ex}}G^L_{LL}). \tag{12}$$

Substitution of (9)–(11) in (7) yields

$$\begin{aligned} F_T = &\, R((1-x^\alpha)\ln(1-x^L) + x^\alpha\ln x^L) \\ &- (1-x^\alpha)\Delta S^{0\alpha\to L}_1 - x^\alpha\Delta S^{0\alpha\to L}_2 \\ &- \Delta^{\mathrm{ex}}S^L - (x^\alpha - x^L)\Delta^{\mathrm{ex}}S^L_L + \Delta_f S^\alpha. \end{aligned} \tag{13}$$

By inserting (12) and (13) in (5), the slope can be computed. It is worth mentioning that since there are no fundamental restrictions preventing F_T in (13) from being equal to zero, infinite slopes are not prohibited by thermodynamics. Slopes tending to $+\infty$ or $-\infty$ are inevitable if $T \to 0$, because all entropies of formations and transformations become infinitesimally small. It may happen than both the numerator and denominator in (5) are equal to zero. An analysis of this exotic and interesting situation is beyond the scope of the present contribution.

In a particular case when $x^\alpha = 0$ and $x^L \to x^\alpha$, it can easily be shown (finiteness of $\Delta^{\mathrm{ex}}G^L_{LL}$ should be recalled) that $\mathrm{d}T/\mathrm{d}x^L = -RT_1/\Delta S^{0\alpha\to L}_1(T_1) < 0$, where T_1 is the melting point of the first component when it is in the α structure. If $x^\alpha = 1$ and $x^L \to x^\alpha$, then $\mathrm{d}T/\mathrm{d}x^L = RT_2/\Delta S^{0\alpha\to L}_2(T_2) > 0$. These two expressions for limiting slopes are well known, in fact [3].

If $x^L \to x^\alpha$ and if $0 < x^\alpha < 1$, then F_L tends to zero. Since F_T becomes equal to the entropy of melting of α taken with the opposite sign, i.e. since it is always negative, an indeterminacy $0/0$ is never encountered in (5). Consequently, it can be concluded that $(\mathrm{d}T/\mathrm{d}x^L)_{x^L=x^\alpha} = 0$.

3. Curvature of a phase boundary

In contrast to slopes, the calculation of curvatures of phase boundaries did not acquire much attention in the literature. An excellent work [4] is the only publication known to the authors in which this problem was deeply and extensively discussed. Despite the unquestionable relevance of that paper, the derivations below have a different mathematical and conceptual flavor, which is not surprising since the objective of this contribution differs quite significantly from that of [4].

Let us start with a terminological clarification. The curvature of the function $\psi(z)$, which is $\frac{\mathrm{d}^2\psi/\mathrm{d}z^2}{[1+(\mathrm{d}\psi/\mathrm{d}z)^2]^{3/2}}$, cannot be identified with its second derivative. In this work, however, for the sake of brevity, $\mathrm{d}^2T/\mathrm{d}(x^L)^2$ is named the curvature. A justification of such a terminological frivolity is that the curvature and the second derivative either have the same sign or are both equal to zero.

Let us denote the LHS of (4) as Φ and recall that like F it remains equal to zero along the phase boundary. By using implicit differentiation again, one obtains

$$\Phi_L + \Phi_T(\mathrm{d}T/\mathrm{d}x^L) = 0 \tag{14}$$

where

$$\begin{aligned} \Phi_L &= \frac{\partial}{\partial x^L}(F_L + F_T(\mathrm{d}T/\mathrm{d}x^L)) \\ &= F_{LL} + F_{LT}(\mathrm{d}T/\mathrm{d}x^L) + F_T(\mathrm{d}^2T/\mathrm{d}(x^L)^2) \end{aligned} \tag{15}$$

$$\begin{aligned} \Phi_T &= \frac{\partial}{\partial T}(F_L + F_T(\mathrm{d}T/\mathrm{d}x^L)) \\ &= F_{LT} + F_{TT}(\mathrm{d}T/\mathrm{d}x^L). \end{aligned} \tag{16}$$

By inserting (15) and (16) in (14), the following expression for the second derivative can be arrived at:

$$\frac{\mathrm{d}^2T}{\mathrm{d}(x^L)^2} = -\frac{F_{LL} + 2F_{LT}(\mathrm{d}T/\mathrm{d}x^L) + F_{TT}(\mathrm{d}T/\mathrm{d}x^L)^2}{F_T}. \tag{17}$$