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Thermodynamic implications of drawing rectilinear phase boundaries



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ABSTRACT

For illustrative and explanatory purposes, liquidus and solidus are frequently drawn as straight lines in textbooks. Thermodynamic consequences of sketching rectilinear phase boundaries are analyzed. It is shown that although thermodynamics does not prohibit such boundaries, they result in peculiar temperature dependencies of components' lattice stabilities. An idiosyncrasy of these functions and restrictions imposed by them are worth keeping in mind if it is intended to pencil a T - x section on which all phase boundaries are straight lines.

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1. Problem formulation

In virtually any textbook on phase transformations or physical metallurgy, there is a section on solidification, in which a famous Gulliver–Scheil equation [1,2] is derived. To simplify its derivation, authors assume that an equilibrium distribution coefficient is constant. This assumption does not necessitate the linearity of liquidus and solidus, but if they are straight lines, then, of course, the distribution coefficient is constant. As Fig. 1 typifies, the authors employ this argument and consciously draw the phase boundaries as straight lines. Since the discussion in the textbooks is focused on Scheil's model and its usage for describing a redistribution of components during solidifications, the supposition of rectilinearity of the phase boundaries is tacitly accepted without paying any attention to it. It is worth mentioning that the authors never assign particular values to the slopes of liquidus and solidus. Also, nothing quantitative is said about components' melting points and enthalpies of fusion; the thermodynamic properties of liquid and solid solutions remain unspecified as well. In fact, the T - x sections exemplified by Fig. 1 are cartoons sketched for a utilitarian pedagogic purpose.

Although the straight-line liquidus and solidus look so “natural” that it is tempting to accept them without challenging, it is interesting to find whether rectilinear phase boundaries are thermodynamically feasible. If “rectilinearity” is interpreted strictly mathematically, then the investigation cannot be based on an analysis of experimentally established phase diagrams containing discrete data points burdened with random and,

sometimes, non-random errors. Consequently, such a study should be anchored to solution thermodynamics.

The examination may lead to two outcomes: either rectilinear phase boundaries are thermodynamically prohibitive or not. In the latter case, the study must reveal how the properties of pure components, on the one hand, and liquid and solid solutions, on the other hand, are interlinked.

Predictably, the present investigation hinges on expressions for calculating the slopes. Fortunately, there is no need to derive corresponding formulae from scratch; that was already done in [3–7]. However, for the sake of cohesiveness, the next two sections begin with a brief review of the “calculus of slopes”.

2. No solid-state solubility

Although this work is focused on the case illustrated by Fig. 1, let us begin by considering a simpler situation when the component 2 does not dissolve in the solid component 1. This case can be interpreted as if one drew a sketch shown in Fig. 2 and then asked: Is it possible that the slope of liquidus remains constant within a finite temperature region below the melting point? It is worth accentuating that nothing in addition to the drawing is known. In particular, there is no information on the melting point and the enthalpy of fusion of the component 1; the thermodynamic properties of the liquid phase and even a model suitable for describing it are undefined.

The condition of equilibrium between the liquid phase and the pure solid component 1 is

$$F(x, T) \equiv G(x, T) - xG_x(x, T) - G_1^S(T) = 0 \quad (1)$$

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Notations

a slope of liquidus
b slope of solidus

$$f \underbrace{aa \dots}_{m \text{ times}} \underbrace{bb \dots}_{n \text{ times}} \equiv \frac{\partial^{m+n} f}{\partial a^m \partial b^n}$$

G molar Gibbs energy of liquid phase
*G*₁^S molar Gibbs energy of solid component 1
G^{ex} excess molar Gibbs energy of liquid phase
G^L molar Gibbs energy of liquid phase
G^S molar Gibbs energy of solid phase

p slope of liquidus
q slope of solidus
R gas constant
S^{ex} excess molar entropy of the liquid phase
T temperature
*T*_{*i*} melting point of component *i*
x mole fraction of second component in liquid phase
y mole fraction of second component in liquid phase
z mole fraction of second component in solid phase
 β slope of liquidus
 $\Delta P_i^{I \rightarrow II}$ change of the molar property *P* when component *i* transforms from state I to state II

Recalling that (1) must hold along the liquidus and using implicit differentiation, one obtains $F_x + F_T(dT/dx) = 0$, from which the slope can be found:

$$dT/dx = -F_x/F_T \tag{2}$$

If, for the sake of simplicity of derivations, the solid component 1 and the liquid component 2 at the current temperature are used as reference states, then

$$G_1^S \equiv 0 \tag{3}$$

$$G = (1-x)\Delta G_1^{S \rightarrow L} + RT[(1-x)\ln(1-x) + x \ln x] + G^{ex} \tag{4}$$

By employing (1), (3) and (4) in (2), the following expression (which, of course, does not depend on a choice of the reference states) for the slope can be derived:

$$\frac{dT}{dx} = \frac{(RT/(1-x)) + xG_{xx}^{ex}}{-\Delta S_1^{S \rightarrow L} + R \ln(1-x) - S^{ex} + xS_x^{ex}}$$

If $x \rightarrow 0$, then $dT/dx \rightarrow -RT_1/\Delta S_1^{S \rightarrow L}(T_1) < 0$. Table 1 contains actual slopes calculated not for a generic “component 1”, but for real chemical elements; as this table evidences, they vary widely.

If the slope does not change, then the following must hold:

$$\frac{(RT/(1-x)) + xG_{xx}^{ex}(x, T)}{-\Delta S_1^{S \rightarrow L}(T) + R \ln(1-x) - S^{ex}(x, T) + xS_x^{ex}(x, T)} = -\frac{RT_1}{\Delta S_1^{S \rightarrow L}(T_1)} \equiv \beta \tag{5}$$

In order to make Eq. (5) linking the properties of the component 1 and the liquid phase usable, the lattice stability of the first component and the excess Gibbs energy of liquid have to be defined. However, as mentioned above, the only information available is the sketch shown in Fig. 2 per se. In other words, neither $\Delta G_1^{S \rightarrow L}(T)$ nor $G^{ex}(x, T)$ is known. Of course, the assumption of liquidus' linearity mathematically expressed by (5) will never allow one to restore these two functions in

a unique manner or even decide what kind of mathematical expressions should be used for describing $\Delta G_1^{S \rightarrow L}(T)$ and $G^{ex}(x, T)$. One cannot escape an ambiguity without making further simplifications. In view of a complete absence of usable information, let us treat the liquid phase as an ideal solution and then investigate what the assumption of rectilinearity does to the lattice stability of the first component.

Without the excess terms, (5) becomes

$$\frac{RT/(1-x)}{-\Delta S_1^{S \rightarrow L} + R \ln(1-x)} = \beta \tag{6}$$

A requirement that the liquidus is rectilinear translates in

$$\Delta S_1^{S \rightarrow L} = R \left(\ln \frac{\beta - T + T_1}{\beta} - \frac{T}{\beta - T + T_1} \right) \tag{7}$$

The fact that $x = (T - T_1)/\beta$ is utilized for deriving (7) from (6).

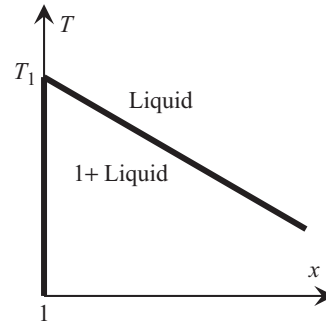


Fig. 2. Straight-line liquidus sketched for the case when component 2 does not dissolve in solid component 1.

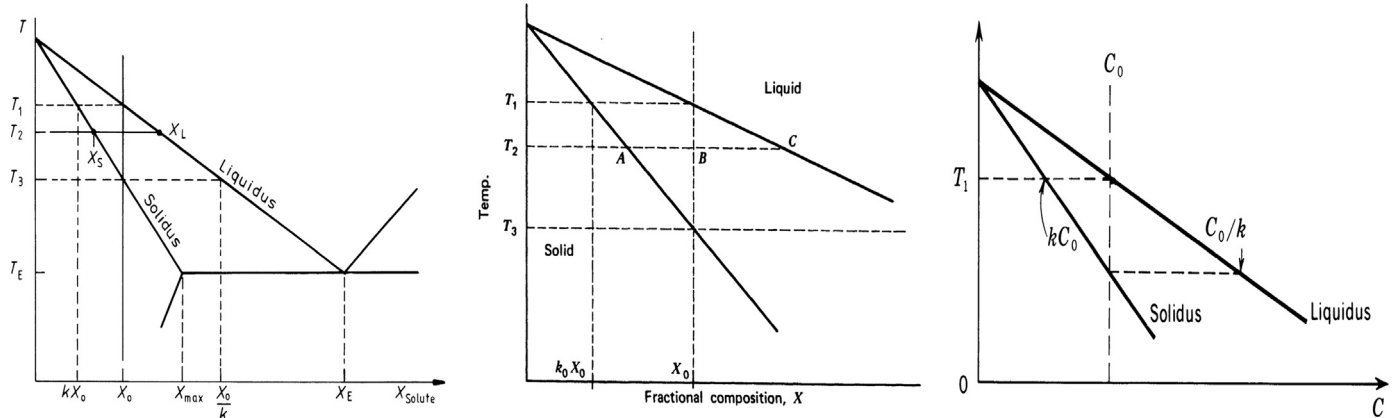


Fig. 1. Illustrations from [9, p. 209], [10, p. 246] and [11, p. 167].

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