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Calculation of property contour diagrams

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ABSTRACT

Contour diagrams are very useful for describing how a property changes with other variables. One such a diagram is the isothermal lines on a liquidus projection, which helps us understand how the liquidus surface changes with temperature and composition. A method has been implemented in Pandat to calculate two-dimensional property contour diagrams in multi-component systems. Property contour diagrams will be presented for various thermodynamic and physical properties such as phase fraction, partial pressure, molar volume, and driving force.

1. Introduction

Phase diagrams have been widely used in many phase equilibrium related fields such as metallurgy [1] and geology [2]. They are usually two-dimensional (2D) or three-dimensional (3D) graphs with a series of phase boundaries separating different sets of stable phase regions. Most phase diagrams are defined by their graph's axes, which are selected from the variables of temperature (T), pressure (P), and composition (x). Those types of phase diagrams provide us with the phase equilibrium stability information in a 2D or 3D state space. In a (T, P, x) space, every point represents the state of a system's determined stable equilibrium, and it is possible to obtain all the equilibrium related properties of the system as long as those properties are computable. Phase boundaries are only a subset of a (T, P, x) state space with a phase fraction of zero or one for a specified phase [3–5], and they use the property of relative phase amounts of the phases in equilibrium.

The concept of zero-phase-fraction for a 2D phase diagram [3,4] greatly enhances our understanding of phase diagrams, especially for a multi-component system. Morral et al. [4] also demonstrated the usefulness of the phase fraction contour lines. Phase fraction contour diagrams present details on how the relative phase amounts change within a phase region along with the variables of the 2D graph axes. A method to calculate phase fraction contour diagrams has been integrated with zero-phase-fraction phase diagram calculation [5]. Another typical contour diagram is the isothermal lines on a liquidus projection diagram [1]. An isothermal line is a temperature contour line where each point on the line has the same temperature. Other types of contour diagrams are also available, such as activity contour (isoactivity) diagrams [6] and pressure contour diagrams [7].

Recently, Eriksson, Bale, and Pelton [8] proposed a new type of diagram, the first-melting projection, which is a special type of contour diagram and will be discussed later.

In a contour diagram, each curve has the same value of specific property. The contour diagram will be extended in this paper to any computable property of stable phase equilibrium and presented together with a phase diagram. The function to calculate a contour diagram has been implemented in Pandat software [9].

2. Phase fraction contour diagrams

Let's first start from the phase fraction contour diagrams with a simple hypothetical binary eutectic system A–B. As shown in Fig. 1, this system has three phases: liquid, α, and β. The equilibrium condition for the two-phase equilibrium between the α phase and β phase in this system is

$$\begin{cases} \mu_A^\alpha = \mu_A^\beta \\ \mu_B^\alpha = \mu_B^\beta \end{cases} \tag{1}$$

Using the zero-phase-fraction (ZPF) concept [3], the α phase boundary of α–β phase equilibrium is the ZPF line of the β phase.

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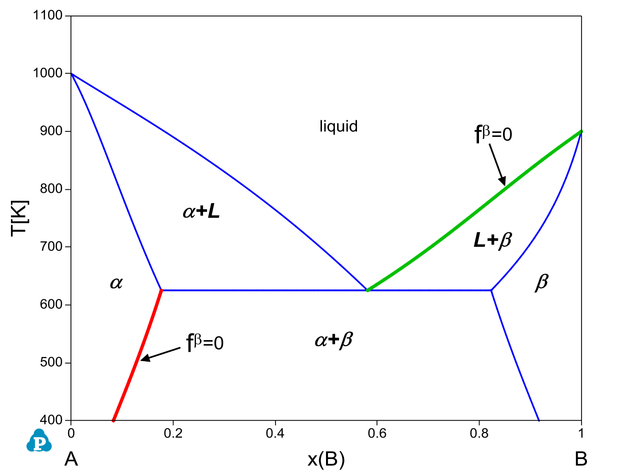

Fig. 1. Phase diagram A–B with the ZPF lines of β phase in equilibrium with liquid phase and α phase. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

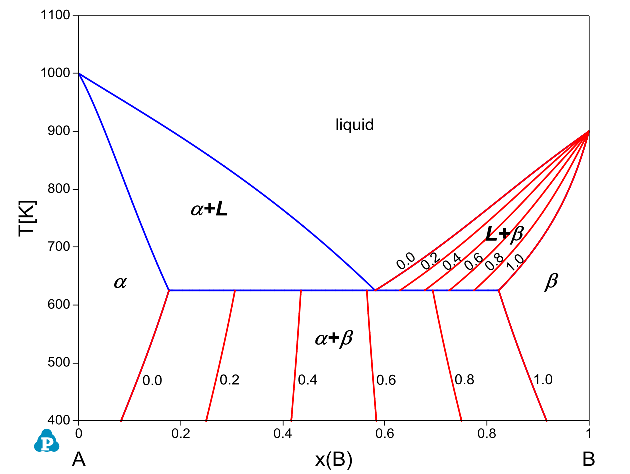

Fig. 2. Phase diagram A–B with f^{β} contour lines in red color. The contour values of f^{β} are labeled beside the corresponding lines. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Calculation of the ZPF line of the β phase in equilibrium with the α phase needs one more constraint in addition to the condition of Eq. (1),

$$f^{\beta} = 0 \tag{2}$$

Eqs. (1-2) represent the condition for the ZPF of the β phase in the α–β phase equilibrium. The red line in Fig. 1 is the ZPF line of the β phase in equilibrium with the α phase. If the α phase in Eq. (1) is replaced by the liquid phase and Eq. (2) is also considered, we have a set of equations,

$$\begin{cases} \mu_A^{liq} = \mu_A^{\beta} \\ \mu_B^{liq} = \mu_B^{\beta} \\ f^{\beta} = 0 \end{cases} \tag{3}$$

which represent the condition for the ZPF line of the β phase in equilibrium with the liquid phase. The calculated ZPF line of the β phase is shown as the green line in Fig. 1.

If the phase fraction of β phase, f^{β}, is set to be d, a value between zero and one, and φ is used to represent either α or liquid, we have the equations for calculating the f^{β} contour lines,

$$\begin{cases} \mu_A^{\varphi} = \mu_A^{\beta} \quad (\varphi = liquid, \ \ \alpha) \\ \mu_B^{\varphi} = \mu_B^{\beta} \\ f^{\beta} = d \qquad (0 \le d \le 1) \end{cases} \tag{4}$$

in which the symbol φ represents either liquid or α Eq. (4) will produce the β phase fraction (f^{β}) contour lines within the equilibria of liquid–β and α–β, as shown in Fig. 2 with 0.2 as the incremental value of d. The contour property here is f^{β} and takes values between zero and one with a step size of 0.2.

In general, phase fraction contour lines can be calculated from the equilibrium conditions and contour constraint,

$$\begin{cases} \mu_j^{\varphi 1} = \mu_j^{\varphi 2} \\ f^{\varphi} = d \qquad (0 \le d \le 1) \end{cases} \tag{5}$$

where φ_1 and φ_2 are the phases in the equilibrium and φ is one of the phases.

One more component, C, is added into the A–B system to form a hypothetical ternary eutectic system A–B–C. Fig. 3 is its isothermal section at 500 K. The phase fraction contour lines f^{α}=0. 4, f^{β}=0. 4, and f^{γ}=0. 4 are calculated with Eq. (5) and are also shown in Fig. 3.

An example for a multi-component phase fraction contour diagram in Ti–Al–V–N–O system has been presented in a previous paper [5].

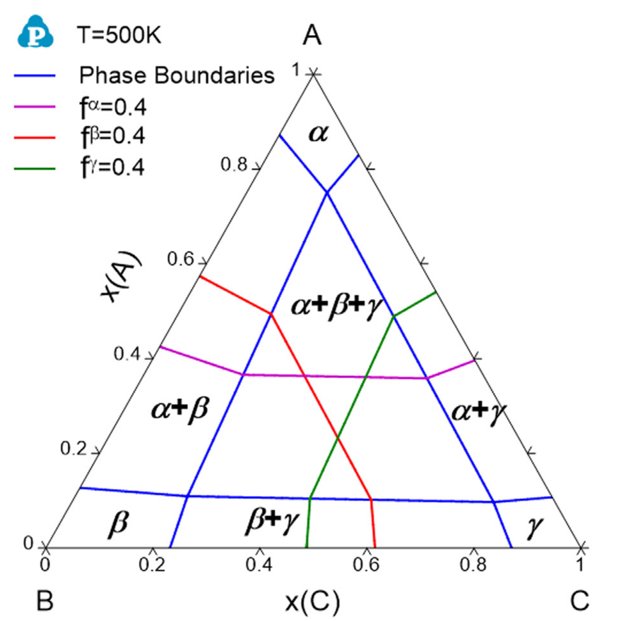

Fig. 3. Isothermal section of A–B–C at 500 K with three phase fraction contour lines for the three phases, α, β and γ.

Eriksson et al. recently proposed a new type of phase diagram, the first-melting projection [8], which consists of a set of phase boundaries with temperatures at which the liquid phase first appears while heating a system. In most situations, the first-melting projection is the solidus line/surface of the system. As they pointed out, if a catatectic invariant or retrograde solid solubility happens in a system, the first-melting projection differs from the solidus since the first-melting is a single-valued function of compositions. A solidus line/surface is a phase boundary where solid phase(s) is in equilibrium with liquid and the molar fraction of liquid phase is zero. In terms of zero-phase-fraction, a solidus line is the ZPF of the liquid phase. Fig. 4 is the Ce–Mn binary phase diagram which has several invariant reactions of the catatectic type as presented by Eriksson et al. [8] The red lines are the calculated ZPF lines of the liquid phase, i.e., the solidus lines. If the ZPF lines of the liquid phase are projected along the temperature direction onto the compositional space, they will overlap. When an overlap happens, the ZPF line with the lowest temperature is selected. Then, the

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