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ALGEBRAIC METHODS FOR DETERMINING DIRECTIONS OF DECREASING TEMPERATURE ALONG ISOBARIC LIQUIDUS UNIVARIANT LINES

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ABSTRACT

Two features of temperature-composition slopes along isobaric liquidus univariant boundary lines are of particular interest. One is the direction of decreasing temperature as these lines terminate at isobaric liquidus invariant points, and the other is the existence and location of temperature maxima and minima. In systems of more than four components, these features cannot be defined by conventional geometrical procedures. Algebraic methods are necessary. For an *n*-component system, the form of the balanced equation involving the $n + 1$ phases in equilibrium at an isobaric liquidus invariant point allows a determination of the temperature–composition slopes of all the liquidus univariant lines terminating at the invariant point. To determine the existence and location of a temperature maximum or minimum along an isobaric liquidus boundary line, balanced equations are used that involve two liquids on the univariant line and the $n - 1$ crystalline phases in equilibrium with each of these two liquids.

Keywords: algebraic methods, multicomponent systems, temperature maximum, temperature minimum, liquidus boundary lines.

SOMMAIRE

Il y a deux aspects d'intérêt à propos de la température et de la composition le long des courbes univariantes cotectiques sur le liquidus. Premièrement, quelle est la direction de diminution en température là où ces courbes atteignent un point isobariquement invariant sur le liquidus? Deuxièmement, y a-t-il des minima ou des maxima en température, et où se trouvent-ils? Dans tout système à plus de quatre composants, ces aspects ne peuvent être définis au moyen de constructions géométriques conventionnelles; une approche algébrique s'impose. Pour un système à *n* composants, la forme de l'équation balancée impliquant les $n + 1$ phases à l'équilibre à un point isobariquement invariant sur le liquidus permet une détermination des pentes de toutes les lignes univariantes sur le liquidus qui terminent à ce point, en termes de température et de composition. Afin de déterminer s'il existe des maxima et des minima en température le long d'une courbe cotectique isobare sur le liquidus, et d'en trouver les coordonnées, il est nécessaire d'utiliser des équations balancées impliquant deux liquides sur cette courbe et les $n - 1$ phases en équilibre avec chacun de ceux-ci.

(Traduit par la Rédaction)

Mots-clés: méthodes algébriques, systèmes à composants multiples, maximum en température, minimum en température, liquidus, courbes cotectiques.

INTRODUCTION

Presnall (1986) presented some algebraic methods for describing and manipulating isobaric liquidus compositional relationships in multicomponent systems. The methods can be applied to systems of any number of components, but are most useful for systems of more than four components, in which the compositional relationships among the phases cannot be represented diagrammatically. Additional algebraic procedures are presented here that supplement those described earlier. Two problems related to the temperature profile along an isobaric liquidus univariant line are considered. One concerns the direction of decreasing temperature of such a line as it encounters a liquidus invariant point, and the other concerns determination of the existence and location of a temperature maximum or minimum. Invariant equilibria involving liquid immiscibility will not be considered.

SLOPES AT INVARIANT POINTS

For an *n*-component system, an isobaric liquidus invariant point can be determined to be either of the peritectic or eutectic type by balancing a chemical reaction involving the $n + 1$ phases in equilibrium at the invariant point (Presnall 1986). For a system of many components, the equation is most easily balanced by using determinants according to the procedure of Korzhinskii (1959, p. 103–106). In the case of a eutectic point, the

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balanced equation will show the liquid phase alone on one side of the equation, and all the crystalline phases on the other. For a peritectic point, the liquid phase will be joined by one or more of the crystalline phases on the same side of the equation. These two types of equations are algebraic statements of the definition of a eutectic and peritectic liquid. In the former, the composition of the liquid can be expressed by positive proportions of all the crystalline phases in equilibrium with it; in the latter, the liquid composition cannot be so expressed.

Of additional interest is a determination of which liquidus univariant lines terminating at the invariant point decrease in temperature toward the invariant point, and which increase. For a eutectic point, temperatures along all the liquidus univariant lines obviously decrease toward the invariant point, but for a peritectic point, temperatures along one or more of the univariant lines must increase.

The desired information can be derived from the balanced equation of phases in equilibrium at the invariant point. To write this equation, the compositions of all the phases must be known. The procedure applies to a system of any number of components, but examples from ternary systems are used to explain the methods so that compositional relationships can be shown both algebraically and geometrically. The presence or absence of compositional degeneracy (Zen 1966) does not affect the procedure.

Figure 1 shows liquidus boundary-lines and solidus compatibility-triangles for two hypothetical ternary phase diagrams. In Figure 1a, the reaction involving phases in equilibrium at the peritectic point p_1 can be found from the determinant,

$$\left|\begin{array}{cccc} A & 1 & 0 & 0 \\ B & 0 & 1 & 0 \\ ABC & 0.33 & 0.33 & 0.33 \\ p_1 & 0.52 & 0.17 & 0.31 \end{array}\right| = 0,$$

in which the first column gives labels for the phases involved in the peritectic reaction, and the second, third, and fourth columns give the proportions of components A, B, and C, respectively, that define the composition of each of the four phases. Solution of this determinant yields the balanced equation,

$$0.88p_1 + 0.12B = 0.82A + 0.18ABC, \qquad (1)$$

in which the coefficients on each side of the equation have been normalized to a total of one. The coefficients give useful information about the proportions of phases and would always be present when determinant solutions are used to apply the methods explained here to systems of more than four components. However, the coefficients are not necessary for an explanation of the algebraic methods and are omitted from the remainder of the discussion. Thus, equation (1) is simplified to

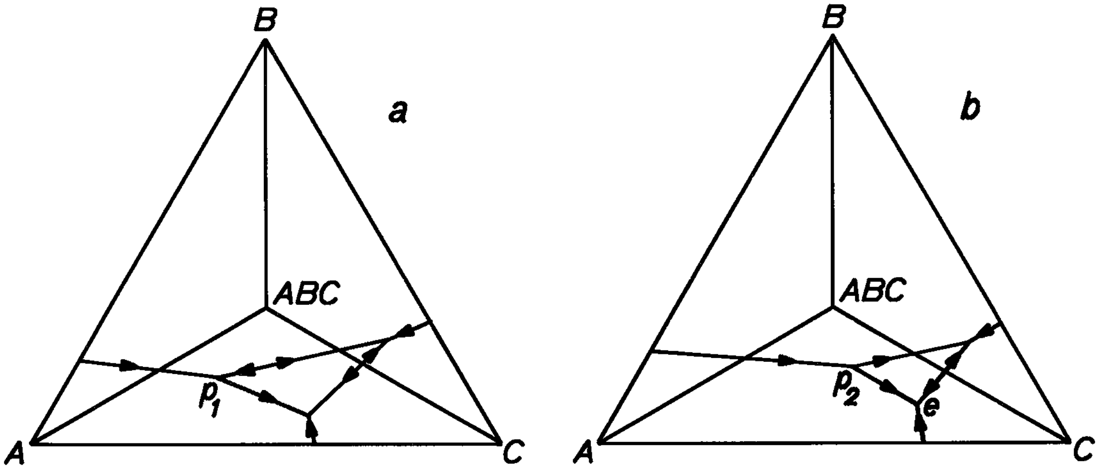

FIG. 1. Hypothetical liquidus phase diagrams for the ternary system A-B-C to illustrate slopes of liquidus univariant lines at invariant points. Lines with arrows indicating directions of decreasing temperature are liquidus boundary-lines. Lines without arrows show solidus compatibility-triangles.

$$p_1 + B = A + ABC, \quad (2)$$

which can be seen visually from Figure 1a to be correct. Similarly, in Figure 1b, the reaction for peritectic point p_2 is

$$p_2 + A + B = ABC, \quad (3)$$

and the reaction for eutectic point e is

$$e = A + ABC + C. \quad (4)$$

In general, it is evident that the amount of the phase assemblage on the side of an equation that does not contain the liquid will increase on removal of heat. Therefore, in reaction (2), the phase assemblage $A + ABC$ increases on removal of heat. This is the same assemblage of crystalline phases in equilibrium with liquid along the one univariant line that decreases in temperature away from invariant point p_1. Neither of the other two univariant lines contains the crystalline assemblage, $A + ABC$, and both lines decrease in temperature toward the invariant point.

Similarly, in reaction (3), phase ABC increases upon removal of heat. This phase occurs as part of both phase assemblages for the univariant lines that decrease in temperature away from the invariant point ($p_2 + ABC + A$ and $p_2 + ABC + B$). Also, ABC is not part of the phase assemblage for the one univariant line ($p_2 + A + B$) that decreases in temperature toward the invariant point.

In reaction (4), the phase assemblage $A + ABC + C$ increases upon removal of heat. This assemblage is not part of any of the univariant lines that join at invariant point e. None of these lines decrease in temperature away from the invariant point.

From these three examples, the following rule can be formulated with reference to the balanced equation defining the phases reacting at an invariant point. All liquidus univariant lines terminating at the invariant point and containing the phase assemblage that increases in amount on removal of heat (that is, the phase assemblage not containing the liquid phase) must decrease in temperature away from the invariant point. Conversely, all liquidus univariant lines that do not contain the phase assemblage that increases in amount on removal of heat must decrease in temperature toward the invariant point.

TEMPERATURE MAXIMA AND MINIMA

The temperature–composition profile of an isobaric liquidus univariant line shows either a continuously decreasing slope in one direction, a temperature maximum, or a temperature minimum. For a ternary system, the existence of a temperature

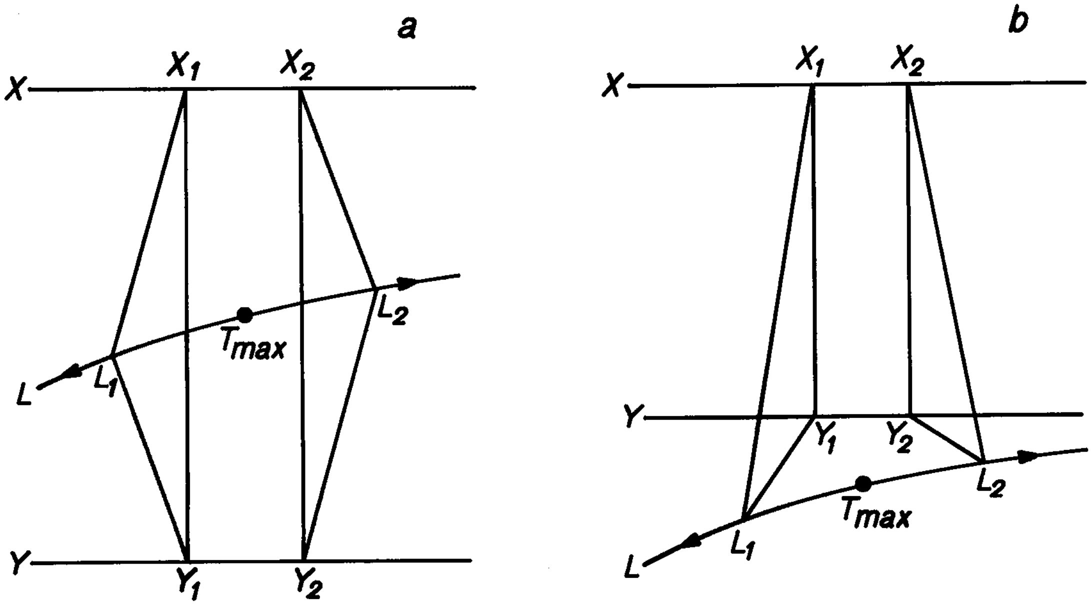

FIG. 2. Ternary isobaric liquidus boundary-lines with a temperature maximum (T_{max}). X and Y are solid solutions in equilibrium with liquids along the boundary line L.

maximum or minimum is evident when the compositions of the liquid and its two coexisting crystalline phases become collinear. This is indicated by collapse of the three-phase triangles to a line and corresponds to a unique point on the boundary line. In this section, criteria will be described for the algebraic determination of the existence and location of a temperature maximum or minimum. As before, ternary systems are used for illustrative purposes, but the method is applicable to a system of any number of components. The solution to the problem of a temperature maximum has been presented by Mukhopadhyay (1991), and for continuity of the more general discussion presented here, the solution given by Mukhopadhyay is repeated.

The procedure is to choose compositions of two liquids spaced at a small interval along a liquidus univariant boundary-line. Then a balanced equation is written that includes the compositions of the two liquids and the two crystalline phases in equilibrium with one of the liquids. A second equation is written that includes compositions of the same two liquids and the slightly different compositions of the same two crystalline phases in equilibrium with the other liquid. On the basis of the form of these two equations, the boundary line between the two liquid compositions can be determined to contain a temperature maximum, a temperature minimum, or neither.

Consider first the case of a temperature maximum. Figure 2a shows a temperature maximum on a liquidus boundary-line, L, liquids along this line being in equilibrium with two crystalline phases, X and Y, that show solid solution. No reaction relationship (dissolution of one of the crystalline phases during cooling) occurs along the boundary line. Figure 2b shows a similar situation, except that a reaction relationship occurs in which X reacts with liquid to form Y on cooling. In Figure 2a, a balanced equation can be written that involves the two liquids on the boundary line, L_1 and L_2, and the two crystalline phases, X_1 and Y_1, in equilibrium with L_1. A second equation can be written that involves L_1 and L_2 and the two crystalline phases, X_2 and Y_2, in equilibrium with L_2. These two equations are:

$$L_1 + L_2 = X_1 + Y_1$$
$$L_1 + L_2 = X_2 + Y_2$$

The corresponding pair of equations for Figure 2b is:

$$Y_1 = L_1 + L_2 + X_1$$
$$Y_2 = L_1 + L_2 + X_2$$

Note that in both pairs, L_1 and L_2 occur together on one side of the equation, and a temperature maximum, T_{max}, lies on the boundary line between L_1 and L_2.

Figure 3 shows diagrams similar to those in Figure 2 except that a temperature minimum occurs instead of a temperature maximum. The pair of equations for Figure 3a is:

$$L_1 = L_2 + X_1 + Y_1$$

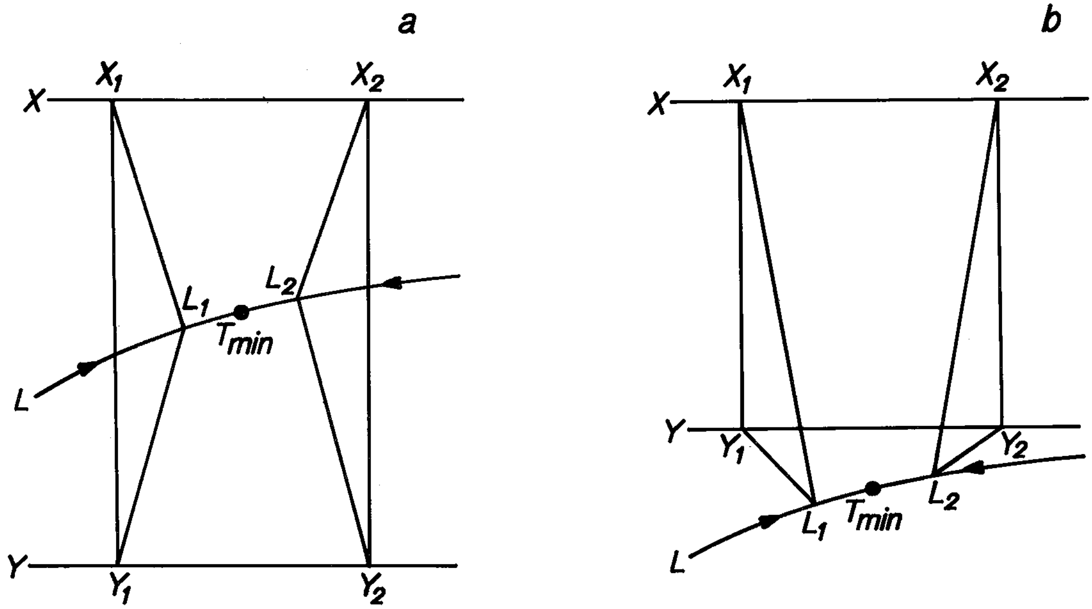

FIG. 3. Ternary isobaric liquidus boundary-lines with a temperature minimum (T_{min}). X, Y, and L are as in Figure 2.

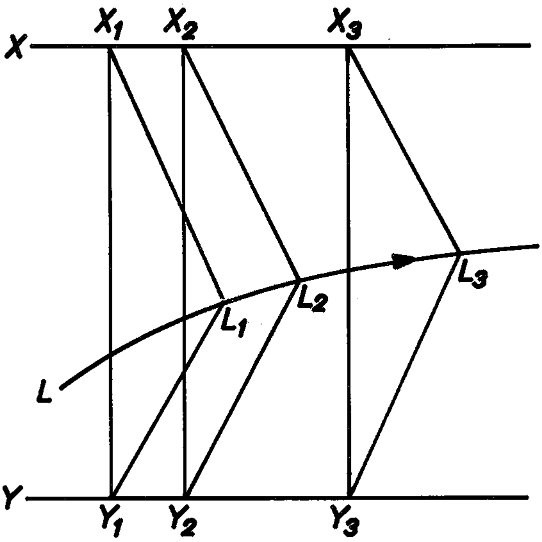

FIG. 4. Ternary isobaric liquidus boundary-line with no minimum or maximum temperature. X, Y, and L are as in Figure 2.

$$L_1 + X_2 + Y_2 = L_2$$

In Figure 3b, the pair of equations is:

$$L_1 + X_1 = L_2 + Y_1$$
$$L_1 + Y_2 = L_2 + X_2$$

For each pair of equations, two characteristics are evident. First, L_1 and L_2 appear on opposite sides of each equation. Second, substitution of X_2 for X_1 and Y_2 for Y_1 causes the substituted phases to move to the opposite side of the equation.

Figure 4 shows a case in which no maximum or minimum temperature occurs. Two possibilities are illustrated, one for liquids L_1 and L_2 in which the two three-phase triangles overlap, and one for liquids L_2 and L_3 in which they do not. The pair of equations for L_1 and L_2 is:

$$L_1 = X_1 + Y_1 + L_2$$
$$L_1 = X_2 + Y_2 + L_2$$

The two liquids, L_1 and L_2, are in each case on opposite sides of the equation, but when X_2 and Y_2 are substituted, respectively, for X_1 and Y_1, no shifts to the opposite side of the equation occur. The pair of equations for L_2 and L_3 is:

$$L_2 = X_2 + Y_2 + L_3$$
$$L_2 + L_3 = X_3 + Y_3$$

Here, L_2 and L_3 are on opposite sides of the first equation, but on the same side of the second equation.

These examples illustrate a simple set of rules that apply generally for a system of any number of components.

(1) A temperature maximum occurs on the univariant line between L_1 and L_2 if, for both equations, L_1 and L_2 occur together on the same side of the equation.

(2) A temperature minimum occurs on the univariant line between L_1 and L_2 if (a) for both equations, L_1 and L_2 occur on opposite sides of the equation, and (b) each substituted crystalline phase in the second equation moves to the opposite side of the equation from that of its counterpart in the first equation. Both of these conditions must occur.

(3) All other configurations of the two equations indicate that the univariant line slopes continuously in one direction.

If the compositions of the two chosen liquids are far apart, and if the phase relationships along the boundary line change abruptly with composition or temperature, incorrect conclusions can occur. Therefore, in regions of a phase diagram where rapid changes occur, reliable application of the method would in some cases require tests of short segments of the boundary line. This, in turn, would require a high density of data. The procedures presented here can reveal features of a phase diagram only to the extent that these features are manifest in the data used.

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REFERENCES

GREENWOOD, H.J. (1967): The *N*-dimensional tie-line problem. *Geochim. Cosmochim. Acta* **31**, 465-490.

KORZHINSKII, D.S. (1959): *Physicochemical Basis of the Analysis of the Paragenesis of Minerals*. Consultants Bureau, New York.

MUKHOPADHYAY, B. (1991): Forsterite - diopside - spinel - liquid equilibria in the system CaO-MgO-Al_2O_3-SiO_2 at 20 kbar and petrological applications. *Contrib. Mineral. Petrol.* **106**, 253-264.

PRESNALL, D.C. (1986): An algebraic method for determining equilibrium crystallization and fusion paths in multicomponent systems. *Am. Mineral.* **71**, 1061-1070.

ZEN, E-AN (1966): Construction of pressure - temperature diagrams for multicomponent systems after the method of Schreinemakers - a geometric approach. *U.S. Geol. Surv., Bull.* **1225**.

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