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Phase diagrams: the composition of the material being instantaneously abstracted from the liquid during equilibrium crystallization in binary systems with solid solution between the end members

D. TAYLOR

15 Leigh Road, Congleton, Cheshire, CW12 2EG

ABSTRACT. A method is presented for determining the composition of the material being instantaneously abstracted from the liquid during equilibrium crystallization of a solid solution in a binary system. It shows that, except when the solidus and liquidus curves are straight and parallel, the composition of the material being instantaneously abstracted from the liquid does not lie on the straight line joining the composition of the first crystals and last liquid for that bulk composition. Despite this, the latter straight line is a reasonable approximation to the actual curve.

THE features of a ternary system are generally illustrated by a projection on to the composition plane at constant pressure. For such a projection the composition of the material being instantaneously removed from a liquid at temperature *T*, as a single crystalline phase crystallizes under equilibrium conditions, can be found by drawing a tangent to the equilibrium crystallization curve for that liquid at the point on the curve corresponding to the temperature *T*. If the tangent is extended away from the direction the liquid takes then it will intersect one of the sides, or an apex, of the ternary system at the composition of the material being instantaneously removed from the liquid at temperature *T*. A similar construction cannot be used for a binary system.

The common way of depicting a binary system is as an isobaric section with composition and temperature as the *x* and *y* axes respectively. Fig. 1 shows such a diagram for a binary system with complete solid solution between the two end members, A and B, and with no minimum of the liquidus and solidus, examples of such a system are the albite-anorthite and forsterite-fayalite systems. The question being asked for such a system is: what is the composition of the material being instantaneously abstracted from the liquid during the equilibrium crystallization of a bulk composition, such as *X*? The answer to this is known at two temperatures: the temperatures of the start and completion of crystallization. At the start of crystallization the composition of the first crystals to precipitate, C_2, is the composition of the material being instantaneously abstracted from the liquid. At the completion of crystallization the composition of the last remaining liquid, L_2, is the composition of the material being instantaneously

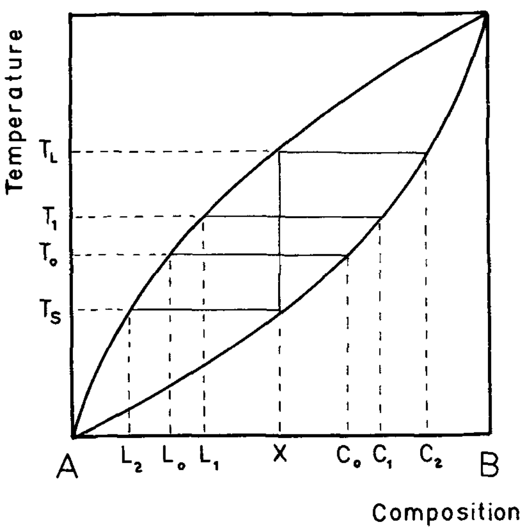

FIG. 1. Schematic diagram of an isobaric section of a binary system A-B showing complete solid solution between the end members.

abstracted from the liquid. Does, therefore, the composition of the material being instantaneously abstracted during equilibrium crystallization of X lie on the straight line joining C_2 and L_2? This question cannot be answered by inspection of the diagram, but can be resolved by recourse to the analysis of model systems.

Method of analysis. In passing from T_1 to T_0, fig. 1, the liquid changes in composition from L_1 to L_0 and decreases in proportion from $(C_1-X)/(C_1-L_1)$ to $(C_0-X)/(C_0-L_0)$. If L_0, L_1, X, C_0, and C_1 are given in terms of weight fraction of component B then the composition, M, of the material removed from the liquid and added to the crystals during the temperature interval T_1-T_0 is given by:

$$M = \frac{L_1(C_1-X)/(C_1-L_1)-L_0(C_0-X)/(C_0-L_0)}{(C_1-X)/(C_1-L_1)-(C_0-X)/(C_0-L_0)}. \tag{1}$$

If the temperature interval T_1-T_0 is decreased by moving T_1 closer to T_0 then the numerator and denominator of equation (1) decrease but their ratio continues to give the composition of the material removed from the liquid during the temperature interval T_1-T_0. If the temperature interval is now made infinitely small, that is L_1 coincides with L_0, then the numerator and denominator of equation (1) also become infinitely small and their ratio gives the composition of the material being instantaneously abstracted from the liquid at the temperature T_0 for bulk composition X. The use of equation (1) to determine M by successive approximations (making T_1-T_0 successively smaller and smaller) is unsatisfactory since the successive numerators and denominators get smaller and smaller and the accuracy of both becomes less as C_1 approaches C_0. These analytical problems can be overcome as follows.

Multiply the numerator and denominator of equation (1) by $(C_1-L_1)(C_0-L_0)$. This is permissible as neither term converges on zero as T_1 approaches T_0. Now let $C_1 = C_0+k$ and $L_1 = L_0+l$, and expand the numerator and denominator. The denominator simplifies to $l(C_0-X)-k(L_0-X)$ and the numerator can be written

$$L_0\, l(C_0-X)-k(L_0-X)+l(C_0+k-X)(C_0-L_0)$$

and hence

$$M = L_0+\frac{l(C_0+k-X)(C_0-L_0)}{l(C_0-X)-k(L_0-X)}. \tag{2}$$

Now while l and k both converge to zero as C_1 and L_1 approach C_0 and L_0, the ratio k/l remains finite and actually converges to $(dC/dT)/(dL/dT)$, which is the ratio of the slopes of the tangents to the solidus and the liquidus curves. Hence we can proceed by dividing numerator and denominator of equation (2) by l, getting

$$M = L_0+\frac{(C_0-X)(C_0-L_0)}{(C_0-X)-\frac{k}{l}(L_0-X)}. \tag{3}$$

If now C_1 approaches C_0, or $k \to 0$, the equation becomes

$$M = L_0+\frac{(C_0-X)(C_0-L_0)}{(C_0-X)-p(L_0-X)} \tag{4}$$

where $p = (dC/dT)/(dL/dT)$. Given model systems for which the curves $C = f(T)$ and $L = f(T)$ are known, then p may be calculated. For real systems p can be obtained by measuring the slopes of the tangents to the solidus and the liquidus curves at T_0. Note that when $p = 1.0$ the equation (4) reduces to

$$M = L_0+C_0-X. \tag{5}$$

Model systems. This method of analysis was applied to six model systems for which the solidus and liquidus curves were defined by relatively simple formulae. The equations for the six models are given in Table I and the resulting liquidus and solidus curves are shown in fig. 2.

TABLE I. *Equations for the solidus and liquidus curves of the six model systems*

Model	T_L	T_S	L	C
A	$0.2+X$	$X-0.2$	$T-0.2$	$T+0.2$
B	X	$0.5X$	T	$2T$
C	X	$2X-1$	T	$(T+1)/2$
D	X	X^2	T	$\sqrt{T}$
E	$1-(1-X)^2$	X	$1-\sqrt{(1-T)}$	T
F	$1-(1-X)^2$	X^2	$1-\sqrt{(1-T)}$	$\sqrt{T}$

X is the bulk composition (wt. fraction B), T is temperature, T_L is the liquidus temperature and T_S the solidus temperature, L the composition of the liquid and C the composition of the crystals (wt. fraction B).

The results are shown in fig. 2 as a series of points, one for each determination. These results indicate that the composition of the material being instantaneously abstracted from the liquid during equilibrium crystallization lies on the line joining the first crystals and last liquid when the liquidus and solidus curves are straight and parallel, fig. 2A. For non-parallel and curved liquidus and solidus curves the composition of the material being instantaneously abstracted lies close to the same line, but its actual composition depends on the relative rates of change of the liquid and crystal compositions as a function of temperature and the relative amounts of the two phases.

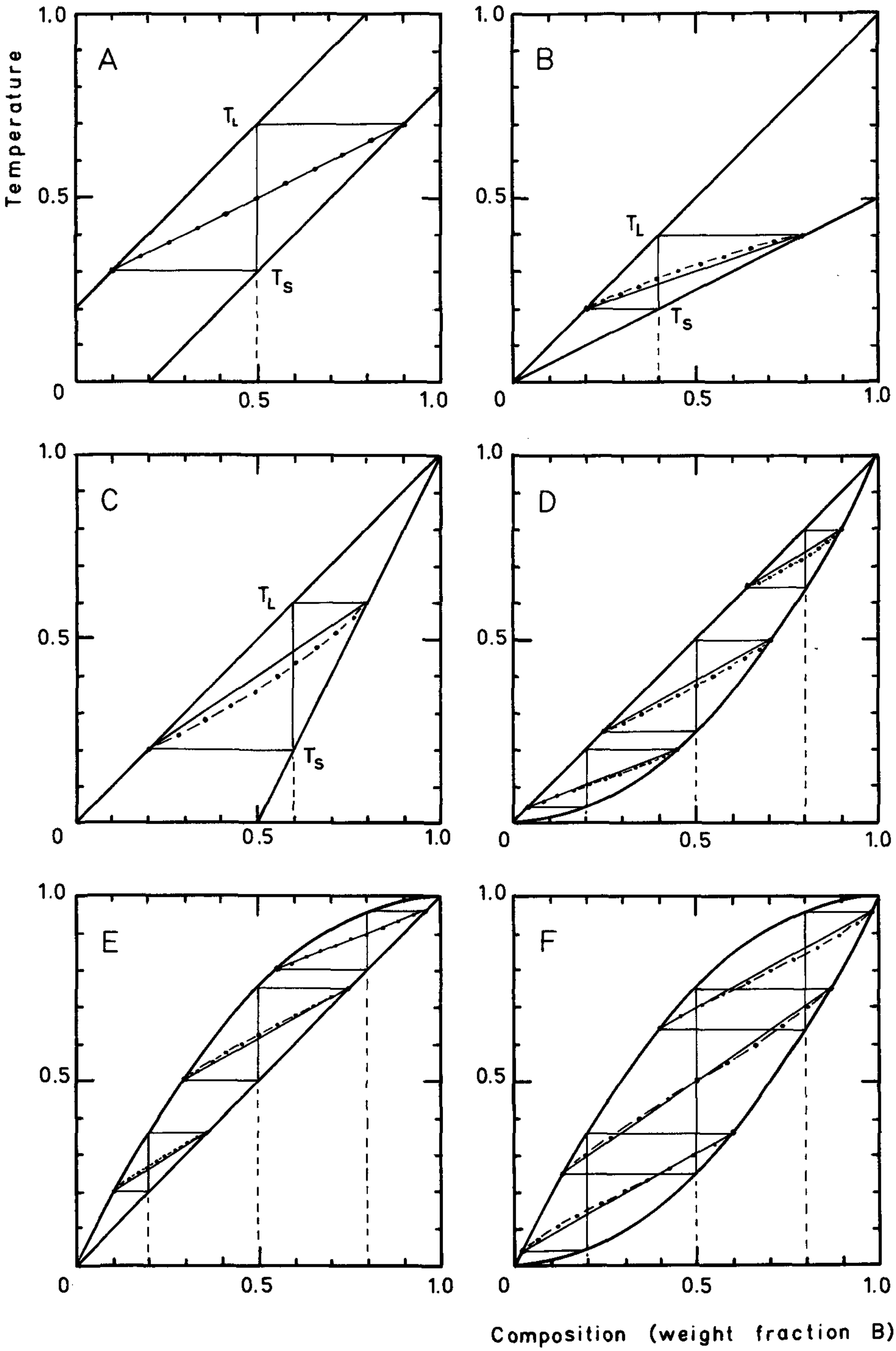

FIG. 2. Isobaric sections for the six model systems A to F. For each system one (systems A to C) or three (systems D to F) bulk compositions are shown with horizontal lines at the liquidus and solidus temperatures and a straight line joining the first crystals and last liquid for each bulk composition. The points show the composition of the material being instantaneously abstracted from the liquid during equilibrium crystallization.

For the majority of binary systems with solid solution, and taking into account the accuracy with which the solidus and liquidus curves are known, it is probably sufficiently accurate to assume that the material being instantaneously abstracted from the liquid lies on the straight line joining the first crystals to the last liquid.

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