

LAWS GOVERNING THE COURSE OF LIQUIDUS AND SOLIDUS CURVES OF SYSTEMS WITH UNLIMITED SOLUBILITY IN SOLID PHASE

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This paper deals with a thermodynamic analysis of the liquidus and solidus curves for binary condensed systems of the first order with unlimited solubility of components in both liquid and solid phases. The heats of fusion of both pure components of a system of this type can be calculated from the slopes of the tangents drawn to the liquidus and solidus curves in the point $x_i \rightarrow 1$. The course of these curves for an ideal system of the given type was calculated for various values of the molar entropy of fusion.

We shall consider a condensed system in which an equilibrium between the solid and liquid phases exists provided that its components are intermiscible in the liquid phase without limitation. According to the interaction of the components in the solid state, two extreme cases are distinguished: 1) The components are completely insoluble in one another, and 2) the components are intermiscible without limitation. The first category includes simple eutectic systems, which have been analyzed mainly with respect to the physical meaning of the slopes of tangents to the liquidus curve in the points corresponding to melting of pure components and in the eutectic point¹⁻³, and with respect to the inflexion points^{1,4}.

The special case of systems of the second category, with monotonous course of both liquidus and solidus curves has been studied less thoroughly^{1,5}, and it is this case which will be dealt with in the present paper.

THEORETICAL

Derivation of Equations of Liquidus and Solidus Curves

These equations were derived rigorously by van Laar¹ and can be derived more simply by the method of an isothermal ΔG cycle. We choose the standard state of pure substances A and B in the solid state $A^{0,s}$ and $B^{0,s}$ and in the liquid state $A^{0,l}$ and $B^{0,l}$. Their melting points fulfil the relation $T_B^f < T_A^f$. Then $A^{0,l}$ at a temperature T between T_B^f and T_A^f is in an undercooled state and *vice versa*, $B^{0,s}$ at the same temperature T is in an overheated state.

We shall perform an isothermal cycle first with the substance A. If 1 mol A is transferred from a solid solution of an activity $a_A^s \neq 1$ into the pure solid state ($a_A^{0,s} = 1$), the corresponding change of the free enthalpy, ΔG_1 , is equal to $-RT \ln a_A^s$. The substance is then liquefied: $\Delta G_2 = \Delta G_A^{0,1/s}$. In the third part of the cycle, 1 mol A is transferred into (liquid) solution of an activity a_A^l : $\Delta G_3 = RT \ln a_A^l$; finally it is transferred into a solid solution: $\Delta G_4 = 0$ with respect to the phase equilibrium condition at $T, P = \text{const.}$ ($\bar{G}_A^s = \bar{G}_A^l$). Since for the whole cycle $\sum \Delta G_i = 0$, we obtain:

$$RT \ln (a_A^l/a_A^s) = -\Delta G_A^{0,1/s} = -\Delta H_A^{0,1/s} + T \Delta S_A^{0,1/s}, \quad (1)$$

where $\Delta G_A^{0,1/s}$, $\Delta H_A^{0,1/s}$ and $\Delta S_A^{0,1/s}$ denote molar free enthalpy, enthalpy and entropy of the solid-liquid phase transition of the pure substance A. We shall assume for simplicity that $\Delta H_A^{0,1/s}$ is independent of temperature and equal to the molar enthalpy of fusion of A at T_A^f , which applies practically in all cases provided that T_A^f and T_B^f are not too much different. Then for the first component

$$\ln (a_A^l/a_A^s) = (\Delta H_A^f/R) (1/T_A^f - 1/T) = -N_A \Delta T_A / T T_A^f \quad (2)$$

and analogously for the second component

$$\ln (a_B^l/a_B^s) = -N_B \Delta T_B / T T_B^f, \quad (3)$$

where $N_i = \Delta H_i^f/R$, $-\Delta T_i = T - T_i^f$. We shall assume further that both the liquid and solid solutions behave ideally, hence $a_i^l = x_i^l$, and since $x_B = 1 - x_A$, we have

$$\ln (x_A^l/x_A^s) = -N_A \Delta T_A / T T_A^f, \quad (4)$$

$$\ln [(1 - x_A^l)/(1 - x_A^s)] = -N_B \Delta T_B / T T_B^f, \quad (5)$$

hence a system of two equations with two unknown variables, x_A^l and x_A^s , the temperature T being chosen. We set $-N_A \Delta T_A / T T_A^f = \ln M$ and $-N_B \Delta T_B / T T_B^f = \ln Q$ so that Eqs (4) and (5) take the form

$$x_A^l = f_1(T) = (1 - Q)M / (M - Q), \quad x_A^s = f_2(T) = (1 - Q) / (M - Q), \quad (6), (7)$$

and analogously

$$x_B^l = f_3(T) = (M - 1)Q / (M - Q), \quad x_B^s = f_4(T) = (M - 1) / (M - Q). \quad (8), (9)$$

These equations define the liquidus and solidus curves for ideal systems in dependence

on T . Some examples are shown in Fig. 1 for different values of ΔH_A^f and ΔH_B^f at constant T_A^f and T_B^f .

Thermodynamic Analysis of Liquidus and Solidus Curves

We shall concentrate ourselves on the region close to the melting points of pure components. The general equation of the liquidus curve of an ideal system is $T_i = f(x_i)$ and it is necessary to determine the value of $\lim (dT_i/dx_i)$ for $x_i \rightarrow 1$. Since Eqs (6)–(9) contain T implicitly it is more convenient to study the inverse function hence $\lim (dx_i/dT)$ for $T_i \rightarrow T_i^f$, and to take into account that $M \rightarrow 1$ for $T \rightarrow T_A^f$ and $Q \rightarrow 1$ for $T \rightarrow T_B^f$. After rearrangement we obtain

$$\lim_{T \rightarrow T_A^f} (dx_A^l/dT) = N_A q / (T_A^f)^2 (q - 1) = 1/k_A^l, \quad (10)$$

$$\lim_{T \rightarrow T_A^f} (dx_A^s/dT) = N_A / (T_A^f)^2 (q - 1) = 1/k_A^s, \quad (11)$$

$$\lim_{T \rightarrow T_B^f} (dx_B^l/dT) = N_B m / (T_B^f)^2 (m - 1) = 1/k_B^l, \quad (12)$$

$$\lim_{T \rightarrow T_B^f} (dx_B^s/dT) = N_B / (T_B^f)^2 (m - 1) = 1/k_B^s, \quad (13)$$

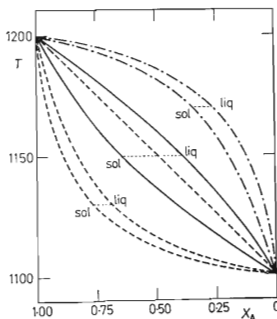


FIG. 1

Phase Diagrams of Binary Systems with Completely Intermiscible Components A and B in Solid and Liquid States

$T_A^f = 1200$ K, $T_B^f = 1100$ K, $-\cdot-\cdot-$ $\Delta H_A^f = 28.8$, $\Delta H_B^f = 4.8$; $---$ $\Delta H_A^f = 28.8$, $\Delta H_B^f = 28.8$; $- - -$ $\Delta H_A^f = 4.8$, $\Delta H_B^f = 28.8$ kcal mol $^{-1}$.

where

$$q = \lim_{T \rightarrow T_A^f} Q = \exp [N_B(1/T_B^f - 1/T_A^f)], \quad (14)$$

$$m = \lim_{T \rightarrow T_B^f} M = \exp [N_A(1/T_A^f - 1/T_B^f)]. \quad (15)$$

The coefficients k_A^1 , k_A^s , k_B^1 and k_B^s defined by Eqs (10)–(13) correspond to the slopes of tangents to the liquidus and solidus curves for substances A and B described by Eqs (6)–(9). On rearranging Eqs (10)–(13) we obtain the following relations for these slopes:

$$k_A^1/k_A^s = 1/q, \quad k_B^1/k_B^s = 1/m, \quad (16a,b)$$

$$k_A^1 - k_A^s = -(T_A^f)^2 (1 - q)^2 / N_A q, \quad (17a)$$

$$k_B^1 - k_B^s = -(T_B^f)^2 (1 - m)^2 / N_B m, \quad (17b)$$

$$k_A^1 k_A^s / (k_A^s - k_A^1) = (T_A^f)^2 / N_A, \quad k_B^1 k_B^s / (k_B^s - k_B^1) = (T_B^f)^2 / N_B, \quad (18a, b)$$

$$\ln(k_A^1/k_A^s) / \ln(k_B^1/k_B^s) = -\Delta H_B^f / \Delta H_A^f = -N_B / N_A. \quad (19)$$

It should be noted that Eqs (16)–(19) hold not only for ideal but also for real systems of the type under study since $\lim a_i = \lim \gamma_i = 1$ for $x_i \rightarrow 1$. Since the dependence of $\Delta H^{0,1/s}$ on temperature has the general form of $\Delta H^{0,1/s} = \Delta H^f + f(T^f - T)$, T approaches T^f and $\Delta H^{0,1/s} = \Delta H^f = \text{const.}$ for $x_i \rightarrow 1$. The derived equations are therefore valid regardless of whether $\Delta H^{0,1/s}$ depends on temperature or not. We assumed that both the liquid and solid solutions fulfil the so-called limiting criterion⁶, *i.e.* $\lim (da_i/dx_i) = 1$ for $x_i \rightarrow 1$, hence the solutions are of the first order according to Froberg⁷.

DISCUSSION

As can be seen from Fig. 1, the course of the liquidus and solidus curves is influenced (at constant T_A^f and T_B^f) by the values of ΔH_A^f and ΔH_B^f . If $\Delta H_A^f \gg \Delta H_B^f$ then both curves are concave with respect to the concentration axis (*i.e.* located in the whole concentration range above the straight line joining the melting points of the pure components A and B); if $\Delta H_A^f \ll \Delta H_B^f$ they are convex.

The equations derived can be utilized similarly as in the case of simple eutectic systems in calculating the values of the molar enthalpies of fusion, $\Delta H_{i,j}^f$, from measured liquidus and solidus curves for systems of the envisaged type for $x_{i,j} \rightarrow 1$. In this respect, Eqs (16a,b) are especially important since they enable to determine the molar enthalpy of fusion of the first component ΔH_i^f , only from the course of

these curves for $x_j \rightarrow 1$, hence close to the melting point of the pure second (*e.g.* lower melting) component j .

REFERENCES

1. Prigogine I., Defay R.: *Chemische Thermodynamik*, p. 379, 381 and 388. Deutscher Verlag für Grundstoffindustrie, Leipzig 1962.
2. Dodé M., Hagège R.: *Compt. Rend.* 248, 2339 (1959).
3. Malinovský M.: *Chem. zvesti* 25, 92 (1971).
4. Malinovský M.: *Chem. zvesti* 23, 809 (1969).
5. Thurmond C. D.: *J. Electrochem. Soc.* 57, 827 (1953).
6. Malinovský M.: *Chem. zvesti* 23, 801 (1969).
7. Froberg M. G.: *Arch. Eisenhüttenw.* 12, 597 (1961).

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