New Relationships between Thermodynamic Parameters and the Slopes of Liquidus Curves at the Eutectic Point

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Some new relationships have been derived between the enthalpies and entropies of melting and mixing of components of binary simple eutectic systems, and the slopes of the tangents to the liquidus curves at the eutectic points of the corresponding phase diagrams.

Part one

Let us consider a binary system A + B, in which an equilibrium exists between a solution and a pure solid phase (a simple eutectic system). Let us assume that this system is under a constant pressure P which is greater than the vapour pressure of this system within the considered temperature interval (a condensed system). The condition for the thermodynamic equilibrium for each component (substance) can be written as

$$\mu_i^{0,s}(T)_P = \mu_i^l(T, x_i)_P . \tag{1}$$

In equation (1),

$\mu_i^{0,s}$ is the chemical potential of a pure solid component,

μ_i^l is the chemical potential of the same component in a liquid phase which is saturated with respect to this component,

x_i is the concentration in molar fractions of the component under consideration.

Another condition of the thermodynamic equilibrium is

$$d(\mu_i^{0,s})_P = d(\mu_i^l)_P$$

or

$$d\left(\frac{\mu_i^{0,s}}{T}\right)_P = d\left(\frac{\mu_i^l}{T}\right)_P . \tag{2}$$

The total differentials in equation (2) may be written as follows

$$d\left(\frac{\mu_i^{0,s}}{T}\right)_P = \frac{\partial}{\partial T}\left(\frac{\mu_i^{0,s}}{T}\right)_P dT \tag{3}$$

and

$$d\left(\frac{\mu_i^l}{T}\right)_P = \frac{\partial}{\partial T}\left(\frac{\mu_i^l}{T}\right)_{P,\,x_i} dT + \frac{\partial}{\partial x_i}\left(\frac{\mu_i^l}{T}\right)_{P,\,T} dx_i . \tag{4}$$

Because of

$$\frac{\partial}{\partial T}\left(\frac{\mu_i^{0,s}}{T}\right)_P = -\frac{H_i^{0,s}}{T^2}, \qquad \frac{\partial}{\partial T}\left(\frac{\mu_i^l}{T}\right)_{P,\,x_i} = -\frac{\bar{H}_i^l}{T^2}$$

and

$$\frac{\partial}{\partial x_i}\left(\frac{\mu_i^l}{T}\right)_{P,\,T} \mathrm{d}x_i = R \cdot \left(\frac{\partial \ln a_i^l}{\partial x_i}\right)_{P,\,T} \mathrm{d}x_i$$

we obtain

$$RT^2\left(\frac{\partial \ln a_i^l}{\partial x_i}\right)_{P,\,T} = \Delta\bar{H}_i^{l/s} \cdot \frac{\mathrm{d}T_i}{\mathrm{d}x_i}, \tag{5}$$

where

a_i^l is the activity of the liquid substance i in the saturated solution. The reference state is the state of the pure undercooled substance i at the same temperature, $\Delta\bar{H}_i^{l/s} = \bar{H}_i^l - H_i^{0,s}$ is the partial molar differential heat of fusion, or the differential heat of the process of dissolution, of the substance i at the temperature T ([1], p. 40),

$\bar{H}_i^l$ and $H_i^{0,s}$ are the partial molar enthalpy of the substance i in a liquid saturated by this substance i, and the molar enthalpy of the pure solid substance i, respectively,

$\mathrm{d}T_i/\mathrm{d}x_i = k_i$ is the slope of the tangent to the liquidus curve of the substance i.

It should be stressed that the quantities $\mathrm{d}T_i$ and $\mathrm{d}x_i$ in the expression $\mathrm{d}T_i/\mathrm{d}x_i$ are not mutually independent, i.e., $x_i = f(T_i)$, and *vice versa*. But the variable x_i in the expression $(\partial \ln a_i/\partial x_i)_{P,\,T}$ does not depend in general on T, i.e., $a_i = f(T, x_i)_P$, where T and x_i are mutually independent variables.

Writing down equation (5) for both components A and B, multiplying in the first case by x_A and in the second by x_B and finally substracting, the following equation is obtained after rearrangement

$$x_A \cdot \Delta\bar{H}_A^{l/s} \cdot k_A - x_B \cdot \Delta\bar{H}_B^{l/s} \cdot k_B = RT^2 \cdot \left[x_A\left(\frac{\partial \ln a_A^l}{\partial x_A}\right) - x_B\left(\frac{\partial \ln a_B^l}{\partial x_B}\right)\right]_{P,\,T}. \tag{6}$$

For the eutectic point E in a phase diagram it is valid that $T = T_E$, $x_A + x_B = = 1$. Then the Gibbs—Duhem relationship can be applied to the right-hand side of equation (6). Thus for the eutectic point E we may write

$$(x_A \cdot \Delta\bar{H}_A^{l/s} \cdot k_A)_E = (x_B \cdot \Delta\bar{H}_B^{l/s} \cdot k_B)_E. \tag{7}$$

The values of the quantities x_A, k_A and k_B can be taken from the corresponding phase diagram (Fig. 1).

This important relationship which has been derived for the first time in 1959 in a slightly different way by *Dodé* and *Hagège* [2] seems to have fallen into an undeserved oblivion. It can be used, *e.g.*, for computing one of the terms

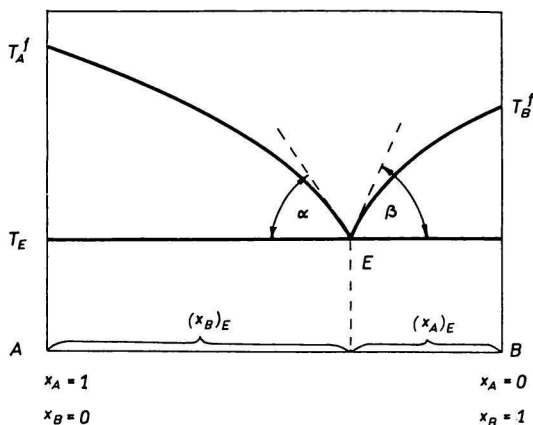$$(\Delta\bar{H}_A^{l/s})_E, \quad (\Delta\bar{H}_B^{l/s})_E,$$

Fig. 1. The phase diagram of a simple eutectic system A + B.
The slopes of the liquidus curves at the eutectic point E are plotted where
$$\text{tg } \alpha = (k_\text{A})_E, \text{ tg } \beta = (k_\text{B})_E.$$

if the other is known. But some more important information can be obtained if equation (7) is combined with the following equation

$$\Delta H_E^{\text{l/s}} = (x_\text{A} \cdot \Delta \bar{H}_\text{A}^{\text{l/s}})_E + (x_\text{B} \cdot \Delta \bar{H}_\text{B}^{\text{l/s}})_E . \qquad (8)$$

In equation (8),

$\Delta H_E^{\text{l/s}}$ is the molar enthalpy change for the process "solid → liquid" at the eutectic composition and temperature. Other terms hold their previous meaning.

From equation (7) and (8) we obtain

$$(\Delta \bar{H}_\text{A}^{\text{l/s}})_E = \frac{k_\text{B}}{x_\text{A} \cdot (k_\text{A} + k_\text{B})} \cdot \Delta H_E^{\text{l/s}}, \qquad (9)$$

$$(\Delta \bar{H}_\text{B}^{\text{l/s}})_E = \frac{k_\text{A}}{x_\text{B} \cdot (k_\text{A} + k_\text{B})} \cdot \Delta H_E^{\text{l/s}}. \qquad (10)$$

Further

$$\Delta \bar{H}_i^{\text{l/s}} = \bar{H}_i^\text{l} - \bar{H}_i^{0,\text{s}} = (\bar{H}_i^\text{l} - H_i^{0,\text{l}}) + (H_i^{0,\text{l}} - H_i^{0,\text{s}})$$

or

$$(\Delta \bar{H}_i^{\text{l/s}})_E = (\Delta \bar{H}_i^{\text{mix}})_E + (\Delta H_i^{0,\text{l/s}})_E , \qquad (11)$$

where

$(\Delta \bar{H}_i^{\text{mix}})_E$ is the partial molar enthalpy of mixing of the substance i at the eutectic composition and temperature,

$(\Delta H_i^{0,\text{l/s}})_E = (H_i^{0,\text{l}} - H_i^{0,\text{s}})_E$ is the molar enthalpy change in the process "solid → → liquid" of the pure substance i at the eutectic temperature T_E.

Because $\mathrm{d}\Delta H_i^{0,l/s} = \Delta C_{P,i}^{0,l/s} \cdot \mathrm{d}T$ we obtain

$$(\Delta H_i^{0,l/s})_E = \Delta H_i^f - \int_{T_E}^{T_i^f} \Delta C_{P,i}^{0,l/s} \cdot \mathrm{d}T \qquad (12)$$

in which

ΔH_i^f is the molar enthalpy of fusion of the pure substance i at its melting point, T_i^f. $\Delta C_{P,i}^{0,l/s} = C_{P,i}^{0,l} - C_{P,i}^{0,s}$ is the difference between the molar heat capacities of the pure liquid and pure solid substance i, respectively.

Inserting equation (12) into (11) and then (11) into (9) and (10) we easily obtain for the component A

$$(\Delta \bar{H}_A^{\mathrm{mix}})_E = \frac{k_B}{x_A \cdot (k_A + k_B)} \cdot \Delta H_E^{l/s} - \Delta H_A^f + \int_{T_E}^{T_A^f} \Delta C_{P,A}^{0,l/s} \cdot \mathrm{d}T . \qquad (13)$$

Similarly, one obtains for the component B

$$(\Delta \bar{H}_B^{\mathrm{mix}})_E = \frac{k_A}{x_B \cdot (k_A + k_B)} \cdot \Delta H_E^{l/s} - \Delta H_B^f + \int_{T_E}^{T_B^f} \Delta C_{P,B}^{0,l/s} \cdot \mathrm{d}T . \qquad (14)$$

Part two

If one takes into account that $\Delta \bar{H}_i^{l/s} = T \cdot \Delta \bar{S}_i^{l/s}$, where $\Delta \bar{S}_i^{l/s} = \bar{S}_i^l - S_i^{0,s}$ is the partial molar entropy of fusion of the substance i in a solution saturated by i at T, then equation (7) yields the following relationship which is valid for the composition and temperature of the eutectic point E

$$(x_A \cdot \Delta \bar{S}_A^{l/s} \cdot k_A)_E = (x_B \cdot \Delta \bar{S}_B^{l/s} \cdot k_B)_E . \qquad (15)$$

This relationship seems to be obtained for the first time.
Further we can write

$$\Delta \bar{S}_i^{l/s} = \bar{S}_i^l - S_i^{0,s} = (\bar{S}_i^l - S_i^{0,l}) + (S_i^{0,l} - S_i^{0,s})$$

or

$$(\Delta \bar{S}_i^{l/s})_E = (\Delta \bar{S}_i^{\mathrm{mix}})_E + (\Delta S_i^{0,l/s})_E , \qquad (16)$$

where

$(\Delta \bar{S}_i^{\mathrm{mix}})_E$ is the partial molar entropy of mixing, or the differential entropy of the process of dissolution, of the substance i at the eutectic composition and temperature, $(\Delta S_i^{0,l/s})_E$ is the molar entropy change in the process "solid → liquid" of the pure substance i at the eutectic temperature T_E.

Because $\mathrm{d}\Delta S_i^{0,l/s} = \Delta C_{P,i}^{0,l/s} \cdot \mathrm{d}\ln T$, after some rearrangement we obtain

$$(\Delta \bar{S}_A^{\mathrm{mix}})_E = \frac{k_B}{x_A \cdot (k_A + k_B)} \cdot \Delta S_E^{l/s} - \Delta S_B^f + \int_{T_E}^{T_A^f} \Delta C_{P,B}^{0,l/s} \cdot \mathrm{d}\ln T, \qquad (17)$$

$$(\Delta \bar{S}_{\mathrm{B}}^{\mathrm{mix}})_E = \frac{k_{\mathrm{A}}}{x_{\mathrm{B}} \cdot (k_{\mathrm{A}} + k_{\mathrm{B}})} \cdot \Delta S_E^{\mathrm{l/s}} - \Delta S_{\mathrm{B}}^{\mathrm{f}} + \int_{T_E}^{T_{\mathrm{B}}^{\mathrm{f}}} \Delta C_{P,\mathrm{B}}^{0,\mathrm{l/s}} \cdot \mathrm{d} \ln T . \qquad (18)$$

The analogy between equation (13), (14), on the one hand, and (17), (18) on the other hand, is obvious.

A practical application of the derived equations will be considered in a subsequent paper.

Part three

The relationships (7) and (15) are valid for all simple binary eutectic systems, whether ideal or non-ideal. If we only confine ourselves to ideal systems then both mentioned equations can be derived in a simpler manner.

For ideal systems it is valid that $a_i = x_i$ and further, $\Delta \bar{H}_i^{\mathrm{l/s}} = \Delta H_i^{0,\mathrm{l/s}}$, because the term $\Delta \bar{H}_i^{\mathrm{mix}}$ is equal to zero (see equation (11)). Then the differential equation (5) written for the substances A and B of an ideal binary system yields.

$$RT^2 \cdot \frac{1}{x_{\mathrm{A}}} = \Delta H_{\mathrm{A}}^{0,\mathrm{l/s}} \cdot \frac{\mathrm{d}T_{\mathrm{A}}}{\mathrm{d}x_{\mathrm{A}}} , \qquad (19)$$

$$RT^2 \cdot \frac{1}{x_{\mathrm{B}}} = \Delta H_{\mathrm{B}}^{0,\mathrm{l/s}} \cdot \frac{\mathrm{d}T_{\mathrm{B}}}{\mathrm{d}x_{\mathrm{B}}} . \qquad (20)$$

For the same eutectic temperature T_E we obtain immediately equation (7) and from this, also equation (15).

The derived equations are valid not only for the equilibrium "solid ↔ liquid", but — mutatis mutandis — for arbitrary two different phases at equilibrium.

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References

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