

The Slope Calculation of Tangent Line to the Liquidus Curve at Dystectic Melting Point of a Compound A_qB_r in a Phase Diagram of an $A-A_qB_r$ System

I. NERÁD, J. STREČKO, I. PROKS, K. ADAMKOVIČOVÁ, and L. KOSA

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
SK-842 36 Bratislava*

Received 1 March 1994

The generalized form of the LeChatelier—Shreder equation and relation for the limiting value (for x_{eq} approaching to 1) of temperature variation of the degree of dissociation of A_qB_r in an $A-A_qB_r$ system at the dystectic melting point were used to calculate the limit of temperature variation of "weighted-in" mole fraction of A_qB_r at the dystectic melting point during permanent phase equilibrium. It was proved that this limit is infinite and thus the tangent line to the liquidus curve at the dystectic melting point is parallel to the composition axis.

The LeChatelier—Shreder equation describing equilibrium coexistence of melt in a system $A-A_qB_r$ with crystalline phase of a binary compound A_qB_r , which has a dystectic melting point, was derived in [1]. In contradiction to using of hypothetical temperature of fusion and hypothetical enthalpy of fusion [2—4] this equation does not contain any hypothetical thermodynamic quantities and was written in the form

$$\left[\frac{d \ln a(A_qB_r, x_{\text{eq}}, T)}{dT} \right]_{p, \text{eq}} = \frac{\Delta_{\text{fus}} H(A_qB_r, T)}{RT^2} \quad (1)$$

where $\Delta_{\text{fus}} H$ is the experimentally determinable enthalpy of fusion of A_qB_r , R is the gas constant and $a(A_qB_r, x_{\text{eq}}, T)$ is the activity of the compound A_qB_r in the melt of the composition expressed using its weighted-in mole fraction $x_{\text{eq}} = n(A_qB_r) / \{n(A_qB_r) + n(A)\}$ at the corresponding equilibrium temperature T . $n(A_qB_r)$ and $n(A)$ are weighted-in amounts of substances of A_qB_r and A , respectively. Quantities related to phase equilibrium are denoted by the subscript eq.

$a(A_qB_r, x_{\text{eq}}, T)$ can be expressed as follows

$$\begin{aligned} a(A_qB_r, x_{\text{eq}}, T) &= \frac{f(A_qB_r, x_{\text{eq}}, T)}{f_+(A_qB_r, T)} \\ &= \frac{\nu(A_qB_r, x_{\text{eq}}, T) k_{\text{H}}(A_qB_r, x_{\text{eq}}, T) y(A_qB_r, x_{\text{eq}}, T)}{\nu_+(A_qB_r, T) k_{\text{H},+}(A_qB_r, T) y_+(A_qB_r, T)} \end{aligned} \quad (2)$$

Symbols f , ν , k_{H} , and y denote the fugacity, the fugacity coefficient, the Henry constant, and the true mole fraction of undissociated constituent A_qB_r ,

$y = n(A_qB_r) / \{n(A_qB_r) + n(A) + n(B)\}$, respectively, at the same chosen temperature T . $n(A_qB_r)$, $n(A)$, and $n(B)$ are amounts of substances of constituents A_qB_r , A , and B in the melt, respectively. Quantities related to the melt of pure compound A_qB_r ($x_{\text{eq}} = 1$) are denoted by the subscript +.

Because activity $a(A_qB_r)$ is a function of x_{eq} , the limit of temperature variation of x_{eq} at the dystectic melting point of A_qB_r has to be involved in the limit for $x_{\text{eq}} \rightarrow 1$ of the left-hand side of eqn (1). The zero value of the slope of tangent line to the liquidus curve at the dystectic melting point of a compound A_qB_r in a phase diagram of an $A-A_qB_r$ system is a well-known experimental fact. Semiquantitative explanations have been generally accepted. In the case of ideal solution of optical antipodes and their 1:1 racemic phase, the problem was cleared by *Mauser* [5]. The aim of the present paper is the exact general thermodynamic verification of this experimental experience.

THEORETICAL

Limit of Temperature Variation of Dissociation Degree for a Substance A_qB_r in Melt Coexisting with a Crystalline Phase A_qB_r

The degree of dissociation of A_qB_r to its constituents is a function of both composition and temperature. A relation for equilibrium of a reaction of "total dissociation"



can be written in the form

$$\begin{aligned} \Delta_{\text{dis}}G(x_{\text{eq}}, T) &= \Delta_{\text{dis}}H(x_{\text{eq}}, T) - \\ -T \left\{ \Delta_{\text{dis}}S_{\text{inconf}}(x_{\text{eq}}, T) - R \ln \left[\left[y(A, x_{\text{eq}}, T) \right]^{s(X)} \right] \right\} &= \\ &= \Delta_{\text{dis}}H(x_{\text{eq}}, T) - \\ -T \left[\Delta_{\text{dis}}S_{\text{inconf}}(x_{\text{eq}}, T) - R \ln K_y(T) \right] &= 0 \end{aligned} \quad (3)$$

where $\Delta_{\text{dis}}G$, $\Delta_{\text{dis}}H$, and $\Delta_{\text{dis}}S_{\text{inconf}}$ are the increases of the Gibbs energy, enthalpy, and the configurational entropy of dissociation according to the scheme (A) [1], respectively. X represents constituents A_qB_r , A , and B , $s(X) = 1, q$, and r .

Rewriting eqn (3) an expression for $\ln K_y(T)$ can be obtained

$$\begin{aligned} \ln K_y(T) &= \ln \frac{[y(A, x_{\text{eq}}, T)]^q [y(B, x_{\text{eq}}, T)]^r}{y(A_qB_r, x_{\text{eq}}, T)} = \\ &= - \frac{\Delta_{\text{dis}}H(x_{\text{eq}}, T) - T\Delta_{\text{dis}}S_{\text{inconf}}(x_{\text{eq}}, T)}{RT} \end{aligned} \quad (4)$$

Substituting the true mole fractions of respective constituents in eqn (4) by

$$y(A_qB_r, x_{\text{eq}}, T) = \frac{(1-\alpha)x_{\text{eq}}}{x_{\text{eq}}\alpha(q+r-1)+1} \quad (5)$$

$$y(A, x_{\text{eq}}, T) = \frac{x_{\text{eq}}(\alpha q - 1) + 1}{x_{\text{eq}}\alpha(q+r-1)+1} \quad (6)$$

and

$$y(B, x_{\text{eq}}, T) = \frac{x_{\text{eq}}\alpha r}{x_{\text{eq}}\alpha(q+r-1)+1} \quad (7)$$

after deriving $\ln K_y(T)$ with respect to T one obtains (The derivatives of all quantities with respect to T are denoted by a prime.)

$$\begin{aligned} \left[\ln K_y(T) \right]' &= \\ &= \frac{[r(x'_{\text{eq}}\alpha + x_{\text{eq}}\alpha')(1-\alpha) - x'_{\text{eq}}\alpha(1-\alpha) + x_{\text{eq}}\alpha'\alpha]}{[x_{\text{eq}}\alpha(q+r-1)+1][x_{\text{eq}}(\alpha q - 1) + 1]} \cdot \\ &\quad \cdot \frac{[x_{\text{eq}}\alpha(q+r-1)+1][x_{\text{eq}}(\alpha q - 1) + 1]}{x_{\text{eq}}\alpha(1-\alpha)} - \\ &\quad - \frac{(q+r-1)^2(x'_{\text{eq}}\alpha + x_{\text{eq}}\alpha')[x_{\text{eq}}(\alpha q - 1) + 1]x_{\text{eq}}\alpha(1-\alpha)}{[x_{\text{eq}}\alpha(q+r-1)+1][x_{\text{eq}}(\alpha q - 1) + 1]x_{\text{eq}}\alpha(1-\alpha)} + \end{aligned}$$

$$\begin{aligned} &+ \frac{q[x'_{\text{eq}}(\alpha q - 1) + x_{\text{eq}}\alpha q'] [x_{\text{eq}}\alpha(q+r-1)+1]x_{\text{eq}}\alpha(1-\alpha)}{[x_{\text{eq}}\alpha(q+r-1)+1][x_{\text{eq}}(\alpha q - 1) + 1]x_{\text{eq}}\alpha(1-\alpha)} = \\ &= \left[- \frac{\Delta_{\text{dis}}H(x_{\text{eq}}, T) - T\Delta_{\text{dis}}S_{\text{inconf}}(x_{\text{eq}}, T)}{RT} \right]' \end{aligned} \quad (8)$$

Before calculation of limits in eqn (8) it is advantageous to introduce the following substitutions

$$l = q + r - 1 \quad (9a)$$

$$J = 1 - \alpha_{+, \text{eq}} \quad (9b)$$

$$L = \alpha_{+, \text{eq}}(q+r-1)+1 \quad (9c)$$

$$M = q\alpha_{+, \text{eq}} - 1 \quad (9d)$$

$$\begin{aligned} N &= \lim_{x_{\text{eq}} \rightarrow 1} \left[\ln K_y(T) \right]' = \\ &= \lim_{x_{\text{eq}} \rightarrow 1} \left[- \frac{\Delta_{\text{dis}}H(x_{\text{eq}}, T) - T\Delta_{\text{dis}}S_{\text{inconf}}(x_{\text{eq}}, T)}{RT} \right]' \end{aligned} \quad (9e)$$

For ideal solutions the last substitution can be written as

$$N_{\text{id}} = \lim_{x_{\text{eq}} \rightarrow 1} \left[\ln K_{y, \text{id}}(T) \right]' = \frac{\Delta_{\text{dis}}H_{\text{id}}(x_{\text{eq}}, T_{\text{fus}}(A_qB_r))}{R[T_{\text{fus}}(A_qB_r)]^2} \quad (9f)$$

In addition, the following relations are valid

$$\lim_{x_{\text{eq}} \rightarrow 1} \alpha = \alpha_{+, \text{eq}} = \alpha_{+}[T_{\text{fus}}(A_qB_r)] \quad (10)$$

and

$$\lim_{x_{\text{eq}} \rightarrow 1} T = T_{\text{fus}}(A_qB_r) \quad (11)$$

Calculating the limit of expressions occurring in eqn (8) taking into account the substitutions (9) and relations (10) and (11), the limit of temperature variation of the degree of dissociation for A_qB_r can be expressed as follows

$$\begin{aligned} \lim_{x_{\text{eq}} \rightarrow 1} \alpha' &= \\ &= \frac{J \left[\alpha_{+, \text{eq}} LN - (Lr\alpha_{+, \text{eq}} - L\alpha_{+, \text{eq}} - l^2\alpha_{+, \text{eq}}^2 + LM) \lim_{x_{\text{eq}} \rightarrow 1} x'_{\text{eq}} \right]}{LJr + L\alpha_{+, \text{eq}} - l^2J\alpha_{+, \text{eq}} + LJq} \end{aligned} \quad (12)$$

Limiting Value of Temperature Variation of Weighted-in Mole Fraction of the Component A_qB_r

At compositions close to that of a pure undissociated substance A_qB_r, the relations

$$v(A_q B_r, x_{eq}, T) = v_+(A_q B_r, x_{eq}, T) \quad (13)$$

and

$$k_H(A_q B_r, x_{eq}, T) = k_{H,+}(A_q B_r, x_{eq}, T) \quad (14)$$

are valid. Substituting (13) and (14) into the Le-Chatelier—Shreder equation (1) one obtains

$$\begin{aligned} \lim_{x_{eq} \rightarrow 1} \frac{d}{dT} \ln y(A_q B_r, x_{eq}, T) &= \\ &= \frac{\Delta_{fus} H^\circ(A_q B_r, T_{fus}(A_q B_r))}{RT_{fus}^2(A_q B_r)} + \\ &+ \lim_{T \rightarrow T_{fus}(A_q B_r)} \frac{d}{dT} \ln y_+(A_q B_r, T) = P \end{aligned} \quad (15)$$

P is a temperature function concerning the second term of the middle part of eqn (15).

Using relations (5) and (9) the limit of the left-hand side of eqn (15) can be written in the form

$$\frac{J(L - k_{+,eq}) \lim_{x_{eq} \rightarrow 1} x'_{eq} - (L + JI) \lim_{x_{eq} \rightarrow 1} \alpha'}{JL} \quad (16)$$

Substituting the expressions (16) and (12) into (15) one obtains the relation

$$\begin{aligned} &(L - k_{+,eq}) \lim_{x_{eq} \rightarrow 1} x_{eq} + \\ &+ \frac{(L + JI)(L\alpha_{+,eq} - L\alpha_{+,eq} - I^2\alpha_{+,eq}^2 + LM)}{LJr + L\alpha_{+,eq} - I^2\alpha_{+,eq} + LJq} \lim_{x_{eq} \rightarrow 1} x'_{eq} = \\ &= LP + \frac{(L + JI)\alpha_{+,eq}LN}{LJr + L\alpha_{+,eq} - I^2\alpha_{+,eq} + LJq} \end{aligned} \quad (17)$$

On multiplication by an expression $(LJr + L\alpha_{+,eq} - I^2\alpha_{+,eq} + LJq)$, and after introducing a substitution

$$\begin{aligned} LP(LJr + L\alpha_{+,eq} - I^2\alpha_{+,eq} + LJq) + \\ + \alpha_{+,eq}LN(L + JI) = Q(T_{fus}(A_q B_r)) \end{aligned} \quad (18)$$

this expression yields

$$\begin{aligned} &(L^2 Jr + IL\alpha_{+,eq}^2 - I^2LJ\alpha_{+,eq} + L^2 Jq - \\ &- ILJq\alpha_{+,eq} + L^2 r\alpha_{+,eq} - ILJ\alpha_{+,eq} - I^2L\alpha_{+,eq}^2 + \\ &+ L^2 M + ILJM) \lim_{x_{eq} \rightarrow 1} x'_{eq} = Q(T_{fus}(A_q B_r)) \end{aligned} \quad (19)$$

Q is a temperature function regarding the quantities I , J , L , and M into the left-hand side of eqn (19), this equation will simplify to the form

$$\begin{aligned} &(q + r - 1)[\alpha_{+,eq}(q + r - 1) + 1]U \left[\lim_{x_{eq} \rightarrow 1} x'_{eq} \right] = \\ &= Q(T_{fus}(A_q B_r)) \end{aligned} \quad (20)$$

where

$$\begin{aligned} U = \lim_{x_{eq} \rightarrow 1} (q\alpha_{+,eq} + r\alpha_{+,eq} - \alpha_{+,eq} + 1 - q\alpha_{+,eq} - \\ - r\alpha_{+,eq} + \alpha_{+,eq} - 1 + \alpha_{+,eq}^2 - \alpha_{+,eq}^2) = 0 \end{aligned} \quad (21)$$

Introducing again the substitutions (9) for $(q + r - 1)$ and $[\alpha_{+,eq}(q + r - 1) + 1]$ into eqn (20), it reduces to

$$U \lim_{x_{eq} \rightarrow 1} x'_{eq} = \frac{Q(T_{fus}(A_q B_r))}{IL} \quad (22)$$

which implies

$$\lim_{x_{eq} \rightarrow 1} x'_{eq} = \frac{Q(T_{fus}(A_q B_r))}{ILU} = \pm \infty \quad (23)$$

provided the value of $Q(T_{fus}(A_q B_r))$ is not zero.

In a special case when the value of $Q(T_{fus}(A_q B_r))$ is equal to zero, using l'Hospital's rule the same result is achieved.

If the degree of dissociation does not depend upon temperature and its value is equal to zero, *i.e.* if $y_+(A_q B_r) = 1$ and $K_y = 0$, for the presumable finite value of $\Delta_{dis} S_{inconf}(x_{eq}, T)$ $\Delta_{dis} H(x_{eq}, T) = \infty$ and thus $N = \infty$ by eqns (4) and (9), respectively. In such a case the quantity $Q(T_{fus}(A_q B_r))$ and thus also $Q(T_{fus}(A_q B_r))/ILU$ is equal to indefinite expressions by eqns (18) and (23), respectively, and the compound A_qB_r has not the dystectic melting point.

If the degree of dissociation does not depend upon temperature and its value is equal to one, *i.e.* if $y_+(A_q B_r) = 0$ and $K_y = \infty$, for the presumable finite value of $\Delta_{dis} S_{inconf}(x_{eq}, T)$ $\Delta_{dis} H(x_{eq}, T) = -\infty$ and thus $N = -\infty$ by eqns (4) and (9), respectively. In this case the quantity $Q(T_{fus}(A_q B_r))$ and thus also

$Q(T_{\text{fus}}(A_qB_r))/ILU$ is equal to $-\infty$ by eqns (18) and (23), respectively.

work was partly supported by the Slovak Grant Agency for Science (Grant No. 2/999436/93).

CONCLUSION

According to eqn (23), the slope of tangent line to the liquidus curve is equal to zero at the dystectic melting point of the compound A_qB_r in the phase diagram of an $A-A_qB_r$ system provided $\alpha \in (0, 1)$ and thus this line is parallel to the composition axis.

Acknowledgements. We are grateful to RNDr. P. Šajgalík, CSc. for comments and constructive review. This

REFERENCES

1. Proks, I., Daněk, V., Kosa, L., Nerád, I., Strečko, J., and Adamkovičová, K., to be published.
2. Kremann, R., *Z. Elektrochem.* 12, 259 (1906).
3. Daněk, V. and Cekovský, R., *Chem. Papers* 46, 161 (1992).
4. Fellner, P., Gabčová, J., Danielik, V., and Láska, M., *Chem. Papers* 47, 215 (1993).
5. Mauser, H., *Chem. Ber.* 90, 299 (1957).

Translated by J. Strečko