Exact derivation of the Le Chatelier—Shreder equation

[a]M. MALINOVSKÝ and [b]V. SEKEROVÁ

[a]*Department of Inorganic Technology, Slovak Technical University,*
880 37 Bratislava

[b]*Department of Mathematics, School of Economics,*
886 33 Bratislava

New variant of derivation of the generalized Le Chatelier—Shreder equation which describes the course of liquidus in simple eutectic systems is presented. The derivation is based on the conditions valid for phase equilibria, *i.e.* $\bar{G}^{l}_{i,eq} = G^{0,s}_{i}$ and $d\bar{G}^{l}_{i,eq} = dG^{0,s}_{i}$ at P, $T = $ const.

Furthermore, it is taken into account that the partial molar Gibbs energy of the given component in the case of saturated solution, $\bar{G}^{l}_{i,eq}$, depends formally both on composition and temperature, but in fact for the case of phase equilibrium, these parameters are not mutually independent.

Приведен новый вариант вывода обобщенного уравнения Ле Шателье—Шредера, которое описывает ход ликвидуса в простых эвтектических системах. Вывод обоснован на условиях фазового равновесия, т.е. $\bar{G}^{l}_{i,eq} = G^{0,s}_{i}$ и $d\bar{G}^{l}_{i,eq} = dG^{0,s}_{i}$ при P, $T = $ const.

Свыше этого, учитывается обстоятельство, что парциальная мольная энергия Гиббса данного компонента в насыщенном растворе, $\bar{G}^{l}_{i,eq}$, зависит формально от состава и температуры, но для данного случая фазового равновесия оба эти параметры взаимосвязаны.

For the quantitative description of the course of liquidus curve in the systems having no solid solutions the generalized Le Chatelier—Shreder equation is of the primary importance. However, in deducing this equation [1—3] it was not taken into account that temperature and composition are not independent variables. The aim of this work is to present an exact treatment of this problem.

Thermodynamic condition for a phase equilibrium of the type $\bar{B}^{l} \rightleftharpoons B^{0,s}$

Let us consider a simple eutectic system A—B (Fig. 1). For the equilibrium $\bar{B}^{l} \rightleftharpoons B^{0,s}$ at temperature T_1 and concentration of the substance B equal to x_1 it holds (assuming that the pressure is constant) that the partial molar Gibbs energies of coexisting phases are equal
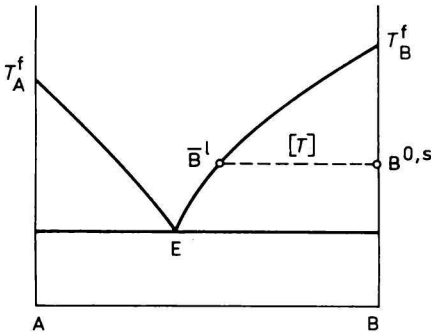
Fig. 1. Isobaric phase diagram of a simple eutectic system A—B.
Phase equilibrium $\bar{B}^l \rightleftharpoons B^{0,s}$ at temperature T

$${}^1\bar{G}^l_{B,eq} = {}^1G^{0,s}_B \tag{1}$$

It holds that $\bar{G}^l_{B,eq} = f(T, x_B)$; $G^{0,s}_B = f(T)$.

Now let us change the temperature T_1 by dT and the concentration x_1 by dx. These changes will influence also the increase in partial molar Gibbs energies by $d\bar{G}_B$, resp. $dG^{0,s}_B$. If under these new conditions ($T_2 = T_1 + dT$, $x_2 = x_1 + dx$) the equilibrium $\bar{B}^l \rightleftharpoons B^{0,s}$ is reached again it holds

$${}^2\bar{G}^l_{B,eq} = {}^2G^{0,s}_B \tag{2}$$

and further

$${}^2\bar{G}^l_{B,eq} = {}^1\bar{G}^l_{B,eq} + d\bar{G}^l_B \tag{3}$$

$${}^2G^{0,s}_B = {}^1G^{0,s}_B + dG^{0,s}_B \tag{4}$$

Combining and comparing eqns (1—4) we obtain

$$d\bar{G}^l_B = dG^{0,s}_B \tag{5}$$
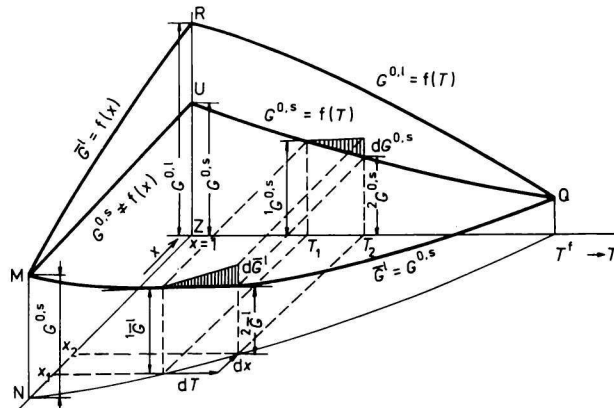

Fig. 2. Graphical illustration of the intersection of two surfaces corresponding to Gibbs functions $G^{0,s}_i = f(T)$ and $\bar{G}^l_i = f(T, x)$.
It holds $G^{0,s}_i \neq f(x)$.

The validity of eqn (5) can be demonstrated graphically (Fig. 2). The function $\bar{G}_B^l(T, x_B)$ is represented by the surface RMQ, the function $G^{0,s}(T)$ by the surface UMQ. Because $G^{0,s}$ does not depend on x it holds that the surface UMQ can be constructed by shifting abscissa MU in such a way that the point U follows the line UQ and the abscissa MU is all the time parallel to the base ZNT. The plane ZNT will serve as a base for measuring the magnitude of Gibbs functions. The surface $\bar{G}^l = f(T, x)$ intersects the surface $G^{0,s} = f(T)$ in the line $\widehat{MQ}$. If eqn (1) holds at (T_1, x_1) and eqn (2) at (T_2, x_2) then the elementary vectors dT and dx are not independent but their relative lengths obey the condition that the sum of the vectors must lay on the line $\widehat{NT'}$, which is an orthogonal projection of the line $\widehat{MQ}$ in the plane base ZNT.

However, in this case it must hold $d\bar{G}_B^l = dG_B^{0,s}$.

Derivation of the Le Chatelier—Shreder equation on the basis of relation $\ln a_{i,\,eq}^l = f[T, x_i(T)]$

By deducing the equation in question from the differential form of the function $\ln a_i^l = f(T, x_i)$ it is assumed that the activity of the i-th component in a binary liquid solution, a_i^l, is (at constant pressure P) a function of absolute temperature T and concentration x_i of this substance in solution.

This assumption is generally correct. However, in those cases when we deal with a liquid solution saturated with the i-th component (*i.e.* the solution is in thermodynamic equilibrium with the pure solid component i) the corresponding binary system "i—j" possesses only one degree of freedom as it follows from Gibbs phase rule

$$v = k - f + 1 = 2 - 2 + 1$$

Two coexisting phases are the pure solid substance i and the liquid solution saturated with this substance. Therefore, only one of the parameters T, x is independent.

At first, let us consider the case when at solid—liquid equilibrium the independent variable is absolute temperature T and thus $x_i = f(T)$.

In this case $a_{i,\,eq}^l = F[T, x_i] = F[T, x_i(T)]$, or $\ln a_{i,\,eq}^l = f[T, x_i(T)]$. For the differential of a function of multiple variable of the given type it holds

$$d \ln a_{i,\,eq}^l = \left(\frac{\partial \ln a_{i,\,eq}^l}{\partial T}\right)_{x_i} dT + \left(\frac{\partial \ln a_{i,\,eq}^l}{\partial x_i}\right)_T \frac{dx_i}{dT} dT \qquad (6)$$

We need to determine both partial derivatives in this equation. (In the next the index "i" will be omitted to simplify the relations.) In order to determine the

relation $(\partial \ln a_{i,\,eq}^l / \partial T)_x$ we shall use for activity the identity

$$\bar{G}^l = G^{0,l} + RT \ln a^l \qquad (P = \text{const}) \tag{7}$$

As a standard state, the state of pure liquid (undercooled liquid) substance at the temperature of the system will be chosen. Considering that we deal with the activity of the substance in a liquid phase which is saturated with this substance, eqn (7) will be written in the following way

$$\ln a_{i,\,eq}^l = \frac{1}{R} \frac{(\bar{G}_i^l - G_i^{0,l})_{eq}}{T} \tag{8}$$

Then for the searched partial derivative it follows

$$\left(\frac{\partial \ln a_{eq}^l}{\partial T}\right)_x = \frac{1}{R} \frac{\partial}{\partial T}\left[\frac{(\bar{G}^l - G^{0,l})_{eq}}{T}\right]_x \tag{9}$$

Now it is necessary to rearrange the right side of eqn (9). Generally it holds

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P = -\frac{H}{T^2} \tag{10}$$

For $\bar{G}_{eq}^l = f(T, x)$, $G^{0,l} = f(T)$ $(P = \text{const})$ we get from eqn (10)

$$\frac{\partial}{\partial T}\left(\frac{\bar{G}_{eq}^l}{T}\right)_{P,x} = -\frac{(\bar{H}^l)_{x,\,eq}}{T^2} \tag{11}$$

and

$$\frac{\partial}{\partial T}\left(\frac{G^{0,l}}{T}\right)_P = -\frac{H^{0,l}}{T^2} \tag{12}$$

Then from eqns (11) and (12) it follows

$$\frac{\partial}{\partial T}\left[\frac{(\bar{G}^l - G^{0,l})_{eq}}{T}\right]_x = -\frac{(\bar{H}^l - H^{0,l})_{x,\,eq}}{T^2} \tag{13}$$

After introducing from eqn (13) into eqn (9) we obtain

$$\left(\frac{\partial \ln a_{eq}^l}{\partial T}\right)_x = -\frac{1}{R} \frac{(\bar{H}^l - H^{0,l})_{x,\,eq}}{T^2} \tag{14}$$

Thus we have determined one of the partial derivatives in eqn (6). For determining the second partial derivative in this equation, *i.e.* the expression $(\partial \ln a_{eq}^l / \partial x)_T$, we shall utilize the condition for the phase equilibrium of this type described by eqns (1) and (5).

It holds $(P = \text{const})$

$$\bar{G}_{eq}^l = f[T, x(T)]$$

$$G^{0,s} = f(T)$$

and therefore

$$d\bar{G}_{eq}^{l} = \left(\frac{\partial \bar{G}_{eq}^{l}}{\partial T}\right)_{x} dT + \left(\frac{\partial \bar{G}_{eq}^{l}}{\partial x}\right)_{T} \frac{dx}{dT} dT \tag{15}$$

$$dG^{0,s} = \left(\frac{\partial G^{0,s}}{\partial T}\right) dT \tag{16}$$

With regard to eqn (5) it holds

$$\left(\frac{\partial \bar{G}_{eq}^{l}}{\partial T}\right)_{x} dT + \left(\frac{\partial \bar{G}_{eq}^{l}}{\partial x}\right)_{T} \frac{dx}{dT} dT = \left(\frac{\partial G^{0,s}}{\partial T}\right) dT \tag{17}$$

For $P = $ const, it generally holds

$$dG = -S \, dT$$

from which it follows for our case

$$d\bar{G}_{eq}^{l} = -\bar{S}_{eq}^{l} \, dT$$

$$dG^{0,s} = -S^{0,s} \, dT$$

and thus

$$\left(\frac{\partial \bar{G}_{eq}^{l}}{\partial T}\right)_{x} = -(\bar{S}^{l})_{x,eq} \tag{18}$$

$$\left(\frac{\partial G^{0,s}}{\partial T}\right) = -(S^{0,s}) \tag{19}$$

Combining eqns (17—19) we obtain

$$-(\bar{S}^{l})_{x,eq} \, dT + \left(\frac{\partial \bar{G}_{eq}^{l}}{\partial x}\right)_{T} \frac{dx}{dT} \, dT = -(S^{0,s}) \, dT \tag{20}$$

and after rearranging

$$\left(\frac{\partial \bar{G}_{eq}^{l}}{\partial x}\right)_{T} = (\bar{S}^{l} - S^{0,s})_{x,eq} \, dT \frac{dT}{dx} \frac{1}{dT}$$

or

$$\left(\frac{\partial \bar{G}_{eq}^{l}}{\partial x}\right)_{T} = (\bar{S}^{l} - S^{0,s})_{x,eq} \frac{dT}{dx} \tag{21}$$

From the definition relation (7) we get for the case of phase equilibrium in question the equality

$$\left(\frac{\partial \bar{G}_{eq}^{l}}{\partial x}\right)_{T} = RT \left(\frac{\partial \ln a_{eq}^{l}}{\partial x}\right)_{T} \tag{22}$$

After introducing from eqn (22) into eqn (21) we obtain

$$RT \left(\frac{\partial \ln a_{eq}^l}{\partial x}\right)_T = (\bar{S}^l - S^{0,s})_{x,eq} \frac{dT}{dx}$$

or

$$\left(\frac{\partial \ln a_{eq}^l}{\partial x}\right)_T = \frac{1}{R} \frac{(\bar{S}^l - S^{0,s})_{x,eq}}{T} \frac{dT}{dx} \tag{23}$$

This relation can be further treated. It holds by definition that $dH = V\,dP + T\,dS$ and therefore at the constant pressure $dH = T\,dS$. For an infinitesimal change of the amount of the i-th substance in solution which is saturated with this substance at temperature T it holds

$$(d\bar{H}^l)_{eq} = T(d\bar{S}^l)_{eq}$$

For 1 mole of the i-th substance in the saturated solution having the same composition and the same temperature it holds

$$(\bar{H}^l)_{x,eq} = T(\bar{S}^l)_{x,eq} \tag{24}$$

where $(\bar{H}^l)$, $(\bar{S}^l)$ are partial molar functions. Similarly, for 1 mole of the pure i-th solid substance at the same temperature T

$$H^{0,s} = T\,S^{0,s} \tag{25}$$

From a comparison of eqn (24) with eqn (25) it follows that $(\bar{H}^l - H^{0,s})_{x,eq} = T(\bar{S}^l - S^{0,s})_{x,eq}$ or

$$(\bar{S}^l - S^{0,s})_{x,eq} = \frac{(\bar{H}^l - H^{0,s})_{x,eq}}{T} \tag{26}$$

By introducing from eqn (26) into eqn (23) we obtain

$$\left(\frac{\partial \ln a_{eq}^l}{\partial x}\right)_T = \frac{1}{R} \frac{(\bar{H}^l - H^{0,s})_{x,eq}}{T^2} \frac{dT}{dx} \tag{27}$$

The relation (27) is the searched partial derivative in eqn (6).

The expression $(\partial \ln a_{eq}^l/\partial x)_T$ can be determined also in another way. From the definition relations $G = H - TS$ and $dG = V\,dP - S\,dT$ it follows that $(\partial G/\partial T)_P = -S = G/T - H/T$. If these relationships are applied to our problem it holds

$$(\partial \bar{G}_{eq}^l/\partial T)_x = \bar{G}_x^l/T - \bar{H}_x^l/T \qquad [P] \tag{28}$$

$$(\partial G^{0,s}/\partial T)_P = G^{0,s}/T - H^{0,s}/T \tag{29}$$

After substituting from eqns (28) and (29) into eqn (17) we obtain

$$\frac{\bar{G}_x^l}{T}\,dT - \frac{\bar{H}_x^l}{T}\,dT + \left(\frac{\partial \bar{G}^l}{\partial x}\right)_T \frac{dx}{dT}\,dT = \frac{G^{0,s}}{T}\,dT - \frac{H^{0,s}}{T}\,dT \qquad [P, eq] \tag{30}$$

and because $\bar{G}_x^l = G^{0,s}$

$$\left(\frac{\partial \bar{G}^l}{\partial x}\right)_T \frac{dx}{dT}\,dT = \frac{(\bar{H}^l - H^{0,s})_x}{T}\,dT \tag{31}$$

With respect to eqn *(22)* it holds

$$RT\left(\frac{\partial \ln a^l}{\partial x}\right)_T \frac{dx}{dT}\,dT = \frac{(\bar{H}^l - H^{0,s})_x}{T}\,dT \qquad [P,\text{ eq}] \tag{32}$$

and therefore

$$\left(\frac{\partial \ln a^l_{eq}}{\partial x}\right)_T = \frac{(\bar{H}^l - H^{0,s})_{x,eq}}{RT^2}\frac{dT}{dx} \qquad [P] \tag{33}$$

which is identical with the relationship *(27)*. Now we can introduce from eqns *(14)* and *(27)* into eqn *(6)*

$$d \ln a^l_{eq} = -\frac{1}{R}\frac{(\bar{H}^l - H^{0,l})_{x,eq}}{T^2}\,dT +$$

$$+\frac{1}{R}\frac{(\bar{H}^l - H^{0,s})_{x,eq}}{T^2}\frac{dT}{dx}\frac{dx}{dT}\,dT$$

or

$$d \ln a^l_{eq} = \frac{(-\bar{H}^l + H^{0,l} + \bar{H}^l - H^{0,s})_{x,eq}}{RT^2}\,dT$$

The quantities $H^{0,l}$ and $H^{0,s}$ are functions of T only. Therefore it holds

$$d \ln a^l_{eq} = \frac{H^{0,l} - H^{0,s}}{RT^2}\,dT = \frac{\Delta H^{0,l/0,s}}{RT^2}\,dT \tag{34}$$

From the formal point of view the result is the same as when we considered the parameters T and x as mutually independent. In the present treatment we considered T to be the independent parameter. In principle it would be possible to carry out the derivation in an opposite way, *i.e.* to choose x as independent variable. However, this is not practical because the thermodynamic functions related to pure component ($G^{0,l}$, $G^{0,s}$, $H^{0,l}$, $H^{0,s}$) do not depend on x.

The presented proceeding is a new variant of derivation of the generalized Le Chatelier—Shreder equation.

References

1. Denbigh, K., *The Principles of Chemical Equilibrium,* 2nd Ed., p. 258 Cambridge University Press, London, 1966.
2. Malinovský, M. and Svobodová-Kašíková, S., *Transactions of the Institute of Mining and Metallurgy,* Ostrava; *Metallurgical Series 18,* No. *1,* 33 (1972).
3. Malinovský, M., *Chem. Zvesti 30,* 721 (1976).

Translated by P. Fellner