Relationship between the degree of thermal dissociation of a chemical compound and the radius of curvature of the liquidus curve at the melting point

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On the basis of thermodynamic relationships relation between the radius of curvature of liquidus curve at the melting point of a compound and the degree of thermal dissociation of this compound is derived. The method enables to obtain information on the degree of dissociation of compound $Z = AB$ from phase diagram data. Accuracy of the result obtained in this way depends on the accuracy of determination of temperature of solid—liquid equilibrium in the vicinity of melting point of the compound.

На основе термодинамических соотношений выведена взаимосвязь между радиусом кривизны кривой ликвидуса в точке плавления вещества и степенью термической диссоциации этого вещества. Данный метод позволяет получить информацию о степени диссоциации вещества $Z = AB$ исходя из данных фазовой диаграммы. Точность таким образом полученных результатов зависит от точности определения температуры равновесия твердой и жидкой фазы в окрестности точки плавления данного соединения.

The phenomenon of thermal dissociation of compounds plays an important role both in the theoretical and experimental study of phase equilibria. A direct experimental determination of this quantity, *e.g.* by Raman spectroscopy, needs a special apparatus and at high temperatures it is very difficult. The indirect methods for determination of the degree of thermal dissociation are based on more common experimental procedures and in many cases they provide results comparable with those obtained by the direct methods.

The determination of the degree of thermal dissociation on the basis of the curve of solid—liquid equilibrium has been for special cases investigated by LeChatelier and Rosenbaum (cited according to [1]), later by *Lewis* and *Randall* [2] and *Schottky* [3]. From the Soviet school the works of *Mlodzeevskii* [4] and *Esin* [5] should be mentioned. In this paper we will present a new treatment of this problem.

Derivation of the basic relationship

The derivation of the relationship between the degree of thermal dissociation of chemical compound and the radius of curvature of the liquidus curve is based on the application of the LeChatelier—Shreder equation to description of the liquidus curve of the compound $Z = AB$ in the system A—B. It is assumed that the system is thermodynamically ideal and no solid solutions are formed on the basis of compound Z. From the mathematical point of view we will analyze the well-known fact that in this case there is no singular point on the liquidus curve of compound Z, *i.e.* the slope of the tangent to the liquidus curve of compound Z at its melting point equals zero. The influence of temperature on the dissociation constant in the vicinity of melting point of the compound is neglected.

Let us denote the degree of dissociation of pure compound Z at its melting point as b_0. Then after melting 1 mole of compound Z it remains $(1 - b_0)$ moles of this compound in original state and b_0 moles of component A and b_0 moles of component B are formed. Because we assume an ideal behaviour the activities of components equal to the mole fractions. Thus

$$a(Z) = \frac{1 - b_0}{1 + b_0}, \qquad a(A) = a(B) = \frac{b_0}{1 + b_0} \tag{1}$$

and the equilibrium constant K° of the thermal dissociation of pure compound Z is given by the equation

$$K^\circ = \frac{a(A)\,a(B)}{a(Z)} = \frac{b_0^2}{1 - b_0^2} \tag{2}$$

In the case of mixture prepared by weighing-in x moles of compound Z and $(1 - x)$ moles of component A, the melt consists of $x(1 - b)$ moles of Z, xb moles of A, xb moles of B (these originate from dissociation of compound Z) and $(1 - x)$ moles of A which were weighed-in. The letter b denotes the degree of thermal dissociation of compound Z in the mixture Z—A. Generally it holds $b \neq b_0$.

The activities of components equal

$$a(Z—A) = \frac{x(1 - b)}{1 + xb}, \; a(A—Z) = \frac{xb + 1 - x}{1 + xb}, \; a(B—Z) = \frac{xb}{1 + xb} \tag{3}$$

and the dissociation constant of component Z in the mixture Z—A equals

$$K(Z—A) = \frac{(xb + 1 - x)b}{(1 - b)(1 + xb)} \tag{4}$$

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It follows

$$b = \frac{x-1}{2x} + \sqrt{\left(\frac{x-1}{2x}\right)^2 + \frac{1}{x}\frac{K}{1+K}} = f(x, K) \text{ for } x \neq 0 \qquad (5)$$

The generalized LeChatelier—Shreder equation for solid—liquid equilibrium states

$$T = \frac{\Delta H_{fus} T_{fus,h}}{\Delta H_{fus} - RT_{fus,h} \ln a} = \varphi(a) \qquad (6)$$

where $T_{fus,h}$ is the hypothetical temperature of fusion of absolutely undissociated chemical compound Z and ΔH_{fus} is the enthalpy of fusion of this compound.

The activity of compound Z in the molten mixture with the other component (eqn (3)) will be denoted as

$$a(Z) = \frac{x(1-b)}{1+xb} = \psi(x, b) \qquad (7)$$

Thus it holds

$$T = \varphi(a) = \varphi[\psi(x, b)] = \phi[x, f(x, K)] \qquad (8)$$

When we assume that the dissociation constant K does not depend on temperature in the vicinity of melting point, it holds for the maximum on liquidus curve

$$\frac{dT}{dx} = \frac{dT}{da}\frac{da}{dx} = 0 \qquad (9)$$

We can derive that

$$\frac{dT}{da} = R\Delta H_{fus} T_{fus,h}^2 a^{-1}(\Delta H_{fus} - RT_{fus,h} \ln a)^{-2} \neq 0 \qquad (10)$$

$$\frac{da}{dx} = \frac{\partial a}{\partial x}\frac{dx}{dx} + \frac{\partial a}{\partial b}\frac{db}{dx} = 0 \qquad (11)$$

It follows that

$$\frac{da}{dx} = \frac{1-b}{(1+xb)^2} - \frac{1+x}{(1+xb)^2}\frac{C + \dfrac{x-1}{2x} - \dfrac{K}{K+1}}{2xC} = 0 \qquad (12)$$

where

$$C = \left[\left(\frac{x-1}{2x}\right)^2 + \frac{1}{x}\frac{K}{K+1}\right]^{1/2} \qquad (13)$$

From eqn (5) it follows

$$\lim_{x \to 1} b = b_0 = \sqrt{\frac{K}{K+1}} \tag{14}$$

By solving eqns (12) and (14) we obtain

$$x^2(1 - b_0^2) - x(1 - b_0^2) = 0 \tag{15}$$

According to the assumption which has already been given at the relationship (5) $x \neq 0$. Therefore eqn (15) can be divided by x and we obtain

$$x(1 - b_0^2) - (1 - b_0^2) = (1 - b_0^2)(x - 1) = 0 \tag{16}$$

For $b_0 \in (0, 1)$ the expression $1 - b_0^2$ differs from zero and therefore eqn (15) is fulfilled only for $x = 1$. It means that the maximum exists on the liquidus curve only at the melting point of compound Z.

In the next we will analyze the maximum and calculate the radius of curvature of the liquidus curve at the point $x = 1$.

As it is known it holds

$$\frac{d^2 T}{dx^2} = \frac{d^2 T}{da^2}\left(\frac{da}{dx}\right)^2 + \frac{dT}{da}\frac{d^2 a}{dx^2} \tag{17}$$

Thus for $x \to 1$ $da/dx = 0$ and it follows

$$\lim_{x \to 1} \frac{d^2 T}{dx^2} = \lim_{x \to 1}\left[\frac{dT}{da}\frac{d^2 a}{dx^2}\right] \tag{18}$$

The term dT/da can be readily determined from eqn (6). Calculation of the term $d^2 a/dx^2$ is more complicated and therefore we will present only the final result. It holds

$$\lim_{x \to 1} \frac{d^2 a}{dx^2} = \frac{b_0 - 1}{2b_0(b_0 + 1)} \tag{19}$$

After introducing eqn (19) into eqn (18) we obtain

$$\lim_{x \to 1} \frac{d^2 T}{dx^2} = -R\Delta H_{\text{fus}}\, T_{\text{fus,h}}^2 \left[\Delta H_{\text{fus}} - RT_{\text{fus,h}}\ln\frac{1 - b_0}{1 + b_0}\right]^{-2} \frac{1}{2b_0} < 0 \tag{20}$$

This proves that the analyzed extreme is a maximum. Simultaneously it follows that the liquidus curve of the system A—AB cannot have an inflex point at $x = 1$.

The absolute value of the radius of curvature of the analyzed liquidus curve for $x \to 1$ can be determined from the relationship

$$\lim_{x \to 1} r = \lim_{x \to 1}\left|\left(\frac{d^2 T}{dx^2}\right)^{-1}\right| \tag{21}$$

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After introducing from (20) we obtain

$$\lim_{x \to 1} r = \frac{2b_0 \left[\Delta H_{fus} - RT_{fus.h} \ln \dfrac{1 - b_0}{1 + b_0} \right]^2}{R\Delta H_{fus} T_{fus.h}^2} \qquad (22)$$

We may multiply the expression (22) by $\Delta H_{fus}/\Delta H_{fus}$. After rearrangement and simplification we obtain

$$\lim_{x \to 1} r = r_0 = \frac{2b_0 \Delta H_{fus}}{RT_{fus,exp}^2} \qquad (23)$$

where $T_{fus,exp}$ is the temperature of fusion of compound Z determined experimentally. It follows that eqn (23) allows us to determine the degree of thermal dissociation b_0 of pure compound when we know r_0.

Determination of the radius of curvature

The radius of curvature of the liquidus curve at the melting point can be determined either from experimental data in numerical form or from the graph of the liquidus curve in phase diagram.

For determination of r_0 from numerical experimental data the liquidus curve can be approximated at the vicinity of point $x = 1$ by parabola (Fig. 1). Axis of the parabola is parallel with the axis y (this is the axis of temperature) and its vertex has coordinates $(1, T_{fus, exp})$. Equation of the parabola is $(x - m)^2 = -2p(y - n)$. In our case $m = 1$, $n = T_{fus, exp}$ and therefore

$$(x - 1)^2 = -2p(y - T_{fus, exp}) \qquad (24)$$

After rearrangement and substituting $1/p = c$ we obtain
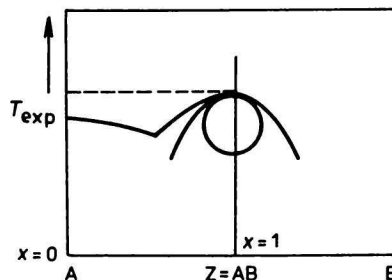
$$y = T_{fus, exp} + c(-0.5x^2 + x - 0.5) \qquad (25)$$

Because the radius of curvature at the extreme equals $r = |1/y''|$ it holds

$$r = p = 1/c \qquad (26)$$

Fig. 1. Part of the phase diagram of the system A—B in which a congruently melting compound Z = AB is formed. In the vicinity of melting point of the compound liquidus curve is approximated by parabola.
Circle is drawn with the radius r_0.

The corresponding values of the parameters p or c can be determined using the least-squares method. When we denote the experimental points on liquidus curves (x_i, T_i) (they must lie in the vicinity of extreme) we can obtain for the radius of curvature the relationship

$$r_0 = \frac{\sum\limits_{i=1}^{n} (0.5x_i^2 - x_i + 0.5)^2}{\sum\limits_{i=1}^{n} (T_{fus,exp} - T_i)(0.5x_i^2 - x_i + 0.5)} \qquad (27)$$

n is the number of experimental data used in the calculation.

Test of application of the derived relationship

Correctness of the proposed method of calculation of the degree of thermal dissociation of a compound from the radius of curvature of the liquidus curve was numerically tested for the model system having these properties: the system consists of two components A and B which form congruently melting compound $Z = AB$. The system can be divided into two simple eutectic subsystems A—Z and Z—B. The following values of the temperatures and enthalpies of fusion of components were assumed: $T_{fus,A} = 1300\ K$, $T_{fus,B} = 1200\ K$, $\Delta H_{fus,A} = 32\,800\ J\ mol^{-1}$, $\Delta H_{fus,B} = 25\,200\ J\ mol^{-1}$. $\Delta H_{fus,Z}$ was estimated to be $58\,800\ J\ mol^{-1}$. $T_{fus,exp,Z} = 1700\ K$ (this approximately corresponds to the rule that for each atom in compound the change of entropy of fusion $\Delta S_{fus} = 8.5\ J\ K^{-1}\ mol^{-1}$). The degree of thermal dissociation of pure compound was chosen to be $b_0 = 0.5$. Using these data the liquidus curve of component Z was calculated using the procedure described in [6]. On the basis of these data the radius of curvature of liquidus curve at the melting point was calculated according to eqns (23) and (27). The latter relationship gives the value $b_0 = 0.49925$ which may be considered as proof of correctness of the presented approach.

The method was tested for the case of the system NaF—Na$_2$SO$_4$ in which a congruently melting compound Na$_3$FSO$_4$ is formed. In paper [7] the degree of thermal dissociation of this compound was determined to be $b_0 = 0.73$. Using the experimental data [8] and the relationships derived in this work we obtained $b_0 = 0.62$. It follows that the accuracy of determination of the degree of thermal dissociation remarkably depends on the precision of measurements of the temperature of solid—liquid equilibrium. A more detailed analysis showed that the method gives satisfactory results when the temperature is determined with precision better than $\pm 0.5\ K$.

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