Thermodynamic analysis of thermal dissociation of complex compounds in the systems of the type A—A_rB_s and B—A_rB_s

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It is shown that thermal dissociation of complex compound A_rB_s in the mixture containing components A or B depends on the value of stoichiometric coefficients r and s. In the systems of the type A—A_rB_s for $s > 1$ and B—A_rB_s for $r > 1$ the degree of thermal dissociation of the complex compound at infinite dilution equals one ($b_\infty = 1$) and the change of mole fraction of undissociated compound with the change of composition of the system equals zero. In this case there occurs a minimum on the curve of dependence of the degree of dissociation on composition of the system.

On the contrary in the system of the type A—A_rB_s for $s = 1$ and in the system B—A_rB_s for $r = 1$ the degree of dissociation of the complex compound monotonously decreases with decreasing content of the compound in the system and at infinite dilution it approaches to a value which is generally different from one. The change of mole fraction of undissociated compound with the change of composition of the system differs from zero in this case.

Показано, что термическое разложение сложного соединения A_rB_s на смесь, содержащую компоненты A или B, зависит от значения стехиометрических коэффициентов r и s. В системах типа A—A_rB_s для $s > 1$ и B—A_rB_s для $r > 1$ степень термической диссоциации сложного соединения при бесконечном разбавлении $b_\infty = 1$, и изменение мольной доли недиссоциированного соединения при изменении состава системы равно нулю. В этом случае имеет место минимум на кривой зависимости степени диссоциации от состава.

Наоборот, в системе типа A—A_rB_s для $s = 1$ и в системе B—A_rB_s для $r = 1$ степень диссоциации сложного соединения равномерно уменьшается при снижении содержания соединения в системе и при бесконечном разбавлении приближается к величине, в общем случае отличной от единицы. Изменение мольной доли недиссоциированного соединения при изменении состава системы отлично от нуля в данном случае.

The existence of complex compounds with nonzero degree of thermal dissociation in the molten systems remarkably influences their physicochemical properties. The products of dissociation can be volatile or chemically active and this can be important for the design and control of technological processes. Knowledge on dissociation of complex compounds in molten systems as it follows from thermodynamic analysis is important also because of lack of direct experimental evidence of chemical compounds in high temperature systems by spectroscopic methods. The thermodynamic analysis is based on the data on solid—liquid equilibria, volume properties, vapour pressure, *etc.*, which are easier available than direct spectroscopic investigation.

Let us consider the system A—B in which a congruently melting compound A_rB_s is formed. This compound partly thermally dissociates under melting according to the scheme

$$A_rB_s \rightleftarrows rA + sB \qquad (A)$$

This system can be divided into two binary systems A—A_rB_s and A_rB_s—B. After this transformation of coordinates the weighed-in mole fraction of the complex compound $A_rB_s \equiv Z$ in its mixture with substance A will be denoted as x. Then the mole fraction of A in this mixture is $1 - x$. As the complex compound partly thermally dissociates under melting (the degree of dissociation will be denoted as b) it holds for the amounts of substances in 1 mol of the molten mixture

$$\begin{aligned} n_A &= 1 - x + rxb \\ n_B &= sxb \\ n_Z &= x(1 - b) \end{aligned} \qquad (1)$$

Then for mole fractions of the components in the mixture it holds

$$\begin{aligned} x_A &= \frac{1 - x + rxb}{1 + xb(r + s - 1)} \\ x_B &= \frac{sxb}{1 + xb(r + s - 1)} \\ x_Z &= \frac{x(1 - b)}{1 + xb(r + s - 1)} \end{aligned} \qquad (2)$$

x_Z is the mole fraction of undissociated complex compound. Let us denote the degree of thermal dissociation of this compound in the melt of composition corresponding to this compound ($x = 1$) as b_0. The degree of dissociation at infinite dilution ($x \rightarrow 0$) will be denoted b_Z. When we assume an ideal thermodynamic behaviour of molten mixture (this assumption does not influence conclusions about behaviour of the system at infinite dilution) the activities of components equal to their mole fractions and for the equilibrium constant of the reaction (A) it holds

$$K_{\text{dis}}(\text{Z—A}) = \frac{(xrb + 1 - x)^r (xsb)^s}{[xb(r + s - 1) + 1]^{r+s-1}\, x(1 - b)} \qquad (3)$$

Analytical solution of the relationship (3) for $b = f(x)$ is available only for the simplest case when $b_0 \neq 1$, $r = 1$, $s = 1$. Then it holds

$$b = \frac{x - 1}{2x} + \sqrt{\left(\frac{x - 1}{2x}\right)^2 + \frac{b_0^2}{x}} \qquad (4)$$

At the derivation of the relationship (4) only the values $b > 0$, which have a physical meaning, are considered.

General analytical solution for the degree of dissociation in the form $b = f(b_0, x, r, s)$ is not possible. This task can be solved only numerically for chosen values of b_0, x, r, and s. Model calculations of the dependence $b = f(x)$ were carried out for all combinations of stoichiometric coefficients changing from 1 to 5 and the values of b_0 changing from 0.1 to 0.9 with the step 0.1. For illustration in Fig. 1 there is plotted the function $b = f(x)$ in the systems A—AB_2 and A—A_2B. (Detailed numerical calculations are not presented in this paper. They are available at the authors on request.)

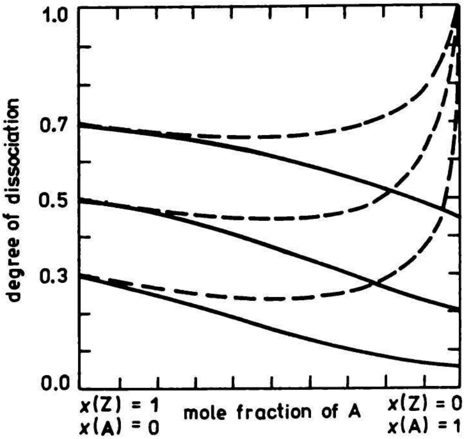

Fig. 1. Dependence of the degree of thermal dissociation of complex compound of the type Z ≡ AB_2 (dashed line) and Z ≡ A_2B (full line) on composition of the system Z A ($b_0 = 0.3$; 0.5; 0.7).

Analysis of the obtained data showed that the course of the thermal dissociation of compound Z ≡ A_rB_s in its mixture with substance A depends remarkably on the value of the stoichiometric coefficient s. (The case of the mixture B—A_rB_s is similar. Here the degree of dissociation depends on the coefficient r.)

When $s = 1$ then it holds for eqn (*3*)

$$K_{\mathrm{dis}}(\mathrm{Z{-}A}) = \frac{b(xrb + 1 - x)^r}{(xrb + 1)^r\,(1 - b)} \tag{5}$$

At infinite dilution when $x \to 0$

$$K_{\mathrm{dis}}(\mathrm{Z{-}A}) = \frac{b_\infty}{1 - b_\infty},\ \text{resp.}\ b_\infty = \frac{K_{\mathrm{dis}}(\mathrm{Z{-}A})}{K_{\mathrm{dis}}(\mathrm{Z{-}A}) + 1} \tag{6}$$

It can be shown that for decreasing x (the mole fraction of complex compound $\mathrm{A}_r\mathrm{B}$ in its mixture with substance A) the degree of thermal dissociation of this compound decreases from the value of b_0 to b_∞. It is important that in this case b_∞ differs from 1. It can be also proved (see Supplement A) that it holds

$$\lim_{x \to 0}\,(\mathrm{d}b/\mathrm{d}x) = r\,\frac{K}{(K + 1)^2} \tag{7}$$

$$\lim_{x \to 0}\,(\mathrm{d}x_{\mathrm{Z}}/\mathrm{d}x) = 1 - b_\infty \tag{8}$$

In a special case (which is, however, very frequent) when also $r = 1$ it holds

$$\lim_{x \to 0}\,(\mathrm{d}x_{\mathrm{Z}}/\mathrm{d}x) = 1 - b_0^2 \qquad (r = 1,\ s = 1) \tag{9}$$

From the derived relationships it follows that in discussed cases we can judge from the value of b_0 on the degree of dissociation of complex compound at infinite dilution. For illustration we present in Table 1 the relationships between the constants b_0 and b_∞ for some typical cases.

The case when $s > 1$ is from the mathematical point of view more complicated than the former case because we cannot get rid of the term x^{s-1} in numerator of the relationship (*3*).

In infinite dilution we obtain the relationship

$$\lim_{x \to 0} K_{\mathrm{dis}}(\mathrm{Z{-}A}) = \frac{0}{1 - b_\infty} \tag{10}$$

As the equilibrium constant differs from zero denominator in eqn (*10*) must be equal to zero and thus $b_\infty = 1$.

Mathematical analysis of the dependence $b = f(x)$ shows that this function has an extremum (for $s > 1$). Coordinates of the extremum can be found from the condition $\mathrm{d}b/\mathrm{d}x = 0$ (see Supplement B). There exists no general analytical solution of this problem and thus the coordinates have to be determined numerically. It can be proved that at the limit for $x \to 0$ it holds

Table 1

Relations between the degrees of dissociation b_∞ and b_0 for chosen types of complex compound A_rB

Compound	r	s	$b_\infty = f(b_0)$
AB	1	1	$b_\infty = b_0^2$
A_2B	2	1	$b_\infty = \dfrac{4b_0^3}{1 + 3b_0}$
A_3B	3	1	$b_\infty = \dfrac{27b_0^4}{18b_0^2 + 8b_0 + 1}$
A_4B	4	1	$b_\infty = \dfrac{256b_0^5}{1 + 15b_0 + 80b_0^2 + 160b_0^3}$
A_5B	5	1	$b_\infty = \dfrac{3125b_0^6}{1 + 24b_0 + 225b_0^2 + 1000b_0^3 + 1875b_0^4}$

$$\lim_{x \to 0} (\mathrm{d}x_\mathrm{Z}/\mathrm{d}x) = 0 \qquad (11)$$

The proof of the statement *(11)* is briefly discussed in Supplement B. (This conclusion can be understood when we take into account that in similar relationship *(8)* b_∞ approaches to one.)

Discussion

From the physical point of view the phenomenon of the dependence of dissociation on the stoichiometry of complex compound can be explained on the basis of following model. Let us consider the system of the type A—A_rB_s with $s = 1$. At infinite dilution of the complex substance there is only a negligible amount of molecules B in the system. Thus in the neighbourhood of each molecule B there is sufficient amount of molecules A for formation of complexes A_rB. However, in the case that $s > 1$ formation of the complex requires in addition to molecules A also s molecules of substance B. When the substance B is present only in a small amount formation of this compound is not probable. It corresponds to the total dissociation of the complex compound.

Similar reasoning can be used for explanation of total dissociation of complex compound A_rB_s at infinite dilution in the melt of substance C which contains neither molecules A nor B. This case is well-known and it has been discussed in literature. As example we can give the case of dissociation of

Supplement A

The derivation $\mathrm{d}b/\mathrm{d}x$ can be obtained by implicit derivation of the relationship (*3*).

$$\frac{\mathrm{d}b}{\mathrm{d}x} = \frac{-\dfrac{\partial F}{\partial x}}{\dfrac{\partial F}{\partial b}} \tag{12}$$

$$F(x, b) = K[bxr + 1]^r x(1 - b) - [x(rb - 1) + 1]^r xb = 0 \tag{13}$$

$$\frac{\mathrm{d}b}{\mathrm{d}x} = -\frac{Kr[bxr + 1]^{r-1} br(1 - b) - r[x(rb - 1) + 1]^{r-1}(rb - 1)b}{Kr[bxr + 1]^{r-1} xr(1 - b) - K[bxr + 1]^r - r[x(rb - 1) + 1]^{r-1} bxr - [x(rb - 1) + 1]^r} \tag{14}$$

In the limit for $x \to 0$ we obtain from the relationship (*14*) the result (*7*).

For the change of model mole fraction of component Z with the change of weighed-in mole fraction of this component it holds

$$\frac{\mathrm{d}x_\mathrm{Z}}{\mathrm{d}x} = \frac{[1 - b + x(-b')]\,[1 + xb(r + s - 1)] - x(1 - b)\,[b(r + s - 1) + xb'(r + s - 1)]}{[1 + xb(r + s - 1)]^2} \tag{15}$$

b' in the relationship (*15*) denotes the derivation $\mathrm{d}b/\mathrm{d}x$. In the limit for $x \to 0$ we obtain the relationship (*8*).

Supplement B

At the extremum of the function $b = f(x)$ it must hold $\mathrm{d}b/\mathrm{d}x = 0$ and thus also $\partial F/\partial x = 0$.

$$\frac{\partial F}{\partial x} = K(1 - b)[bx(r + s - 1) + 1]^{r+s-2}[bx(r + s - 1)(r + s) + 1] - [x(rb - 1) + 1]^{r-1}(sb)^s x^{s-1}[x(rb - 1)(r + s) + s] \tag{16}$$

$$\mathrm{d}b/\mathrm{d}x = \frac{A + B}{C} \tag{17}$$

where

$$A = -K(1 - b)[bx(r + s - 1) + 1]^{r+s-2}[bx(r + s - 1)(r + s) + 1]$$
$$B = [x(rb - 1) + 1]^{r-1}(sb)^s x^{s-1}[x(rb - 1)(r + s) + s]$$
$$C = Kx[bx(r + s - 1) + 1]^{r+s-2}\{(r + s - 1)^2 + x(1 - b) - [bx(r + s - 1) + 1]\} -$$
$$- x[x(rb - 1) + 1]^{r-1}x^{s-1}(sb)^{s-1}\{r^2(xsb) + s^2[x(rb - 1) + 1]\}$$

Because for $x \to 0$ the numerator and denominator in the relationship (*17*) equal zero the limit of the expression (*17*) has to be calculated using the l'Hospital rule. For x approaching zero the value of expression (*17*) differs from zero. Then from the relationship (*15*) it follows that

$$\lim_{x \to 0}(\mathrm{d}x_{\mathrm{Z}}/\mathrm{d}x) = 1 - \lim_{x \to 0} b = 1 - b_z = 0 \tag{18}$$

Na_3AlF_6 in the melt of NaCl [1]. Molten sodium cryolite Na_3AlF_6 yields seven new (foreign) species in the melt of sodium chloride.

As an example of the system A—A_rB where the degree of thermal dissociation of infinitely diluted complex compound differs from one the system NaF—Na_2SO_4 [2] can be quoted. In this system the complex compound Na_3FSO_4 is formed. Degree of dissociation of pure compound at its melting is $b_0 = 0.73$—0.75. At infinite dilution in molten NaF the degree of dissociation approaches 0.55, which is close to b_0^2 (Table 1). This confirms good agreement between theory and experiment.

It is difficult to find suitable example for the case of the system A—A_rB_s with $s > 1$. The reason is that in this case besides the complex compound A_rB_s with $s > 1$ also a compound with $s = 1$ is formed. As example one can present the system NaF—$NaAlF_4$ in which the following complex compounds are formed: Na_3AlF_6 (type A_2B) and $Na_5Al_3F_{14}$ (type A_2B_3). Thermodynamic analysis and calculation of model composition of this system have been published by *Cochran* [3]. The results of cited paper are in agreement with conclusions about dissociation of complex compounds which are presented in this work.

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