

Influence of a complex compound on the thermodynamic activity of components in a binary ionic system

*M. MALINOVSKÝ, ^bJ. VRBENSKÁ, and *I. KOŠTENSKÁ

**Department of Inorganic Technology, Slovak Technical University,
812 37 Bratislava*

^b*Department of Electrotechnology, Slovak Technical University,
880 19 Bratislava*

Received 23 December 1981

The influence of a complex compound Z having nonzero degree of thermal dissociation on the thermodynamic activity of component A in a binary system A—Z is analyzed. It is assumed that no solid solutions are formed in the system.

It is shown that if the component A is identical with some of the products of thermal dissociation of the compound Z then its activity coefficient formally increases. This statement holds also reversely. These phenomena are caused by that the real concentration of component A in solution differs from the "weighed-in" amount of A. Therefore if the activity coefficient of component A should reflect only the character of its interaction with other substances in solution, the influence of described concentration changes is to be eliminated.

Анализируется влияние комплексного соединения Z с ненулевой степенью термической диссоциации на термодинамическую активность компонента А в бинарной системе А—Z, в которой не появляются твердые растворы.

Установилось, что если компонент А тождественный некоторому продукту термической диссоциации соединения Z, то его коэффициент активности формально увеличивается и наоборот. Эти явления вызваны тем, что фактическая концентрация компонента А в растворе в данном случае отличается от «взвешенного количества А». Если коэффициент активности компонента А должен отражать только характер взаимодействия этого вещества с другими веществами в растворе, то необходимо исключить влияние описанных изменений концентраций.

Deviations from ideality in the case of ionic molten solutions can be caused by two reasons:

a) as a result of the change of interaction of species in solution, e.g. of the first component by the presence of the second one;

b) as a result of the change in concentration of "weighed-in" amount of given component; this case occurs when components of the system form ions in the solution.

The first category of deviations from ideality is a principle one. The second is apparently only formal. If we wish to obtain activity coefficients which reflect the real character of interactions of components in solution it is necessary to eliminate in an appropriate way the deviations of the second category.

Let us consider an ionic system MA—NB. Its composition can be expressed in mole fractions $x(\text{MA}) + x(\text{NB}) = 1$. If the component NB forms ions N^+ and B^- , the solution is "diluted" with respect to the component MA because the real composition of solution is $x(\text{MA}) + x(\text{N}^+) + x(\text{B}^-) = x(\text{MA}) + 2x(\text{NB})$. Then the real concentration of the component MA, $y(\text{MA}) = x(\text{MA})/[x(\text{MA}) + 2x(\text{NB})] < x(\text{MA})$. Therefore, the activity coefficient of the component MA in the solution should not be calculated with respect to the "weighed-in" mole fraction $x(\text{MA})$ but with respect to the real mole fraction of this component $y(\text{MA})$.

A more complicated situation arises when the partner of the component MA is not a simple ionic compound of the type NB but a complex compound Z. For sake of simplicity, let us assume that the compound is of the type N_2CD , where N^+ is the cation and CD^{2-} is the complex anion. The compound is in solution electrolytically completely dissociated into the ions 2N^+ and CD^{2-} . The complex anion further dissociates partially thermally according to the scheme $\text{CD}^{2-} \rightleftharpoons \text{C}^- + \text{D}^-$. We shall limit our discussion to the most typical cases:

1. The cation of the component MA and the cation of the complex compound Z are identical ($\text{M} = \text{N}$). Further, one of the products of thermal dissociation of the anion CD^{2-} is identical with A^- , i.e. $\text{C} = \text{A}$. Then we actually deal with the system MA— M_2AD .

2. The cations of the components MA and Z are identical, i.e. $\text{M} = \text{N}$, but none of the products of thermal dissociation of the anion CD^{2-} is identical with A^- . Thus $\text{C}, \text{D} \neq \text{A}$ and we deal with the system MA— M_2CD .

1. The system MA— M_2AD

When we weigh in x moles of component MA and $(1-x)$ moles of component M_2AD then $x + (1-x)b$ moles of component MA, $(1-x)(1-b)$ moles of component M_2AD , and $(1-x)b$ moles of component MD are formed; b is the degree of thermal dissociation of the complex anion AD^{2-} in the solution.

The real mole fractions $y(i)$ of all substances which are present in the solution are given by eqns (1—3)

$$y(\text{MA}) = \frac{x + (1-x)b}{1 + (1-x)b} \quad (1)$$

$$y(\text{M}_2\text{AD}) = \frac{(1-x)(1-b)}{1+(1-x)b} \quad (2)$$

$$y(\text{MD}) = \frac{(1-x)b}{1+(1-x)b} \quad (3)$$

It can be easily proved that

$$y(\text{MA}) > x(\text{MA})$$

Physical reason is in that the real mole fraction of MA, $y(\text{MA})$ includes not only the weighed-in amount of component MA but also the amount of MA which has resulted from the partial thermal dissociation of the component M_2AD .

For the equilibrium constant K^{dis} of the complex compound M_2AD it holds

$$K^{\text{dis}} = \frac{a(\text{MA}) \cdot a(\text{MD})}{a(\text{M}_2\text{AD})} \approx \frac{y(\text{MA}) \cdot y(\text{MD})}{y(\text{M}_2\text{AD})} \quad (4)$$

which can be written as

$$K^{\text{dis}} = \frac{[x + (1-x)b]b}{(1-b)[1 + (1-x)b]} \quad (5)$$

If $x \rightarrow 1$, $K^{\text{dis}} \rightarrow K_{\infty}^{\text{dis}} = b_{\infty}/(1-b_{\infty})$. If $x \rightarrow 0$, $K^{\text{dis}} \rightarrow K_0^{\text{dis}} = b_0^2/(1-b_0^2)$. The symbols b_{∞} and b_0 denote the degree of thermal dissociation of the compound M_2AD at its infinite dilution and in the pure compound M_2AD , respectively. For ideal systems it holds $K_{\infty}^{\text{dis}} = K_0^{\text{dis}}$ and therefore also $b_{\infty} = b_0^2$ assuming that the quantities are compared at equal (or nearly equal) temperature. Because $b_0 < 1$ it holds also

$$0 < b_{\infty} < b < b_0 < 1 \quad (6)$$

From the equality $K^{\text{dis}} = K_0^{\text{dis}}$ we can derive for b

$$b = -\frac{x}{2(1-x)} + \left[\frac{x^2}{4(1-x)^2} + \frac{b_0^2}{1-x} \right]^{1/2} \quad (7)$$

Theoretical conclusions obtained in the first part of this paper will now be applied to the system $\text{NaF}-\text{Na}_3\text{FSO}_4$ the phase diagram of which has been recently verified [1]. It can be checked that at partial thermal dissociation of compound Na_3FSO_4 into NaF and Na_2SO_4 the real mole fraction of NaF is expressed by relation which is identical with eqn (1). We shall calculate the value of the activity coefficient of NaF at the eutectic point E in this system. The experimentally found coordinates of the point E are as follows: $x(\text{NaF}) = 0.305$; $x(\text{Na}_3\text{FSO}_4) = 0.695$; $T(\text{E})/\text{K} = 1054$.

From eqn (8)

$$\ln a(\text{NaF}, E) \approx \frac{\Delta H^f(\text{NaF})}{R} \cdot \frac{T(E) - T^f(\text{NaF})}{T(E) \cdot T^f(\text{NaF})} \quad (8)$$

we found that for $T(E)$ $a(\text{NaF}, E) = 0.52810$. In eqn (8) $\Delta H^f(\text{NaF})$ denotes the molar enthalpy of fusion of NaF (it equals $33.35 \text{ kJ mol}^{-1}$ [2]), $T^f(\text{NaF})$ is the temperature of fusion of NaF (it equals 1266.5 K). Temperature dependence of $\Delta H^f(\text{NaF})$ can be neglected in this case.

Thus a "classical" activity coefficient of NaF at the point E equals

$$\gamma(\text{NaF}, E) = a(\text{NaF}, E)/x(\text{NaF}, E) = 1.73148$$

High positive value of the activity coefficient would indicate that there is a strong repulsion between components of the system $\text{NaF}-\text{Na}_3\text{FSO}_4$, which is highly unprobable.

However, if we take into account the thermal dissociation of Na_3FSO_4 then the real mole fraction of NaF is expressed by eqn (1). The quantity b can be calculated from eqn (7). It has been found that $b_0 = 0.70$ [3]. Thus $b = 0.64844$ and $y(\text{NaF}, E) = 0.52091$. Then it follows

$$\gamma^*(\text{NaF}, E) = a(\text{NaF}, E)/y(\text{NaF}, E) = 1.0138$$

The symbol $\gamma^*(\text{NaF}, E)$ denotes the activity coefficient of NaF at eutectic point which was obtained after elimination of the increase of content of NaF in solution resulting from the thermal dissociation of Na_3FSO_4 .

Therefore, it follows that the behaviour of NaF in the eutectic mixture $\text{NaF} + \text{Na}_3\text{FSO}_4$ is almost ideal.

2. The system MA—M₂CD

In this case when x moles of component MA and $(1-x)$ moles of component M₂CD are weighed-in the following numbers of moles are formed: x moles MA, $(1-x)(1-b)$ moles M₂CD, $(1-x)b$ moles MC, and $(1-x)(1-b)$ moles MD. Real mole fractions $y(i)$ of all substances present in solution equal

$$y(\text{MA}) = \frac{x}{1 + (1-x)b} \quad (9)$$

$$y(\text{M}_2\text{CD}) = \frac{(1-x)(1-b)}{1 + (1-x)b} \quad (10)$$

$$y(\text{MC}) = y(\text{MD}) = \frac{(1-x)b}{1 + (1-x)b} \quad (11)$$

In contradistinction to the former case now $y(\text{MA}) < x(\text{MA})$. Therefore a "diluting effect" takes place here. For the equilibrium constant K^{dis} of the compound $Z = \text{M}_2\text{CD}$ it holds

$$K^{\text{dis}} = \frac{(1-x)b^2}{(1-b)[1+(1-x)b]} \quad (12)$$

At infinite dilution of the compound Z the degree of thermal dissociation b_∞ approaches unit. Thus it holds

$$0 < b_0 < b < b_\infty = 1 \quad (13)$$

From the equality $K^{\text{dis}} = K_0^{\text{dis}}$ we found for b the following relationship

$$b = -\frac{xb_0^2}{2(1-x)} + \left[\frac{x^2b_2^4}{4(1-x)^2} + \frac{b_0^2}{1-x} \right]^{1/2} \quad (14)$$

The obtained results will be demonstrated on an example of the system $\text{NaCl}-\text{Na}_3\text{FSO}_4$ the phase diagram of which has been recently verified [4]. We shall determine the value of the activity coefficient of NaCl at the eutectic point E in this system. The experimentally found coordinates of the point E are as follows: $x(\text{NaCl}) = 0.68$; $x(\text{Na}_3\text{FSO}_4) = 0.32$; $T(\text{E})/K = 900$. From equation similar to eqn (8) we find that $a(\text{NaCl}, \text{E}) = 0.54354$. The value of $\Delta H^f(\text{NaCl})$ equals $28.158 \text{ kJ mol}^{-1}$ [2] and $T^f(\text{NaCl}) = 1074 \text{ K}$.

The "classical" activity coefficient of NaCl at the point E equals

$$\gamma(\text{NaCl}, \text{E}) = a(\text{NaCl}, \text{E})/x(\text{NaCl}, \text{E}) = 0.800 \quad (15)$$

The obtained value of the "classical" activity coefficient of NaCl corresponds to a remarkably negative deviation from ideality. However, taking into account almost ideal behaviour of liquidus curves of NaCl in the systems $\text{NaCl}-\text{NaF}$ and $\text{NaCl}-\text{Na}_2\text{SO}_4$ [5, 6] this strong negative deviation seems to be rather improbable.

If, however, we consider the thermal dissociation of Na_3FSO_4 , then the real mole fraction of NaCl is given by eqn (9). The quantity b can be calculated from eqn (14). Then for $x = 0.68$ and $b_0 = 0.70$ we obtain $b = 0.78225 > b_0$. It follows that $\gamma(\text{NaCl}, \text{E}) = 0.54386$ and

$$\gamma^*(\text{NaCl}, \text{E}) = 0.54354/0.54386 = 0.99941 \approx 1.000 \quad (16)$$

Thus the liquidus curve of NaCl in the system $\text{NaCl}-\text{Na}_3\text{FSO}_4$ goes practically ideally up to the eutectic point E.

Theoretical analysis of the problem discussed clearly proved that a change in concentration of a given component influences (and distorts) the value of the activity coefficient of this component. Therefore if this coefficient has to charac-

terize the nature of interaction of the component in solution it is necessary to eliminate the influence of an increase or decrease of its concentration which is caused by a thermal dissociation of complex compounds present in the system.

References

1. Koštenská, I. and Malinovský, M., *Chem. Zvesti* 36, 159 (1982).
2. Stull, D. R. and Prophet, H., *JANAF Thermochemical Tables*, 2nd Edition. Natl. Bur. Stand., Washington, 1971.
3. Koštenská, I. and Malinovský, M., *Chem. Zvesti* 36, 151 (1982).
4. Malinovský, M. and Koštenská, I., *Zh. Prikl. Khim.*, in press.
5. Malinovský, M. and Gabčová, J., *Chem. Zvesti* 30, 783 (1976).
6. Gabčová, J., Koštenská, I., and Malinovský, M., *Chem. Zvesti*, to be published.

Translated by P. Fellner