

# Classification of Temkin's ideal ionic solutions\*

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Classification of Temkin's ideal ionic solutions from the point of view of Raoult's and Henry's laws is presented. It was proved that in binary solutions these laws were obeyed for both components only if these components have common ions and if the stoichiometric coefficient of non-common ion equals one. In the case of components having common ions where the condition of unit stoichiometric coefficients at non-common ion is not fulfilled as well as in the case of components with non-common ions, none of these laws is valid. The exceptional behaviour of solutions formed by components  $MA_q + N_rA_r$  was analyzed.

В работе излагается классификация идеальных ионных растворов Темкина с точки зрения соблюдения законов Рауля и Генри. Было доказано, что в бинарных растворах эти законы соблюдаются для обоих компонентов в том лишь случае, если у этих компонентов имеется общий ион и если стехиометрический коэффициент у необщего иона равен единице. В случае компонентов с общим ионом, у которых условие касающееся стехиометрического коэффициента не выполняется, а также в случае компонентов без общих ионов, оба закона не соблюдаются. Было анализировано необычное поведение растворов образованных компонентами  $MA_q + N_rA_r$ .

Importance of systems of ionic melts is commonly acknowledged. In thermodynamic considerations dealing with these systems Temkin's model of ideal ionic liquids is often used [1]. This model proved to be good for example in the study of dissociation of cryolite anions in molten systems [2—5]. The possibility of application of the theory of ionic solutions and of Temkin's model on metallurgical slags has been thoroughly studied by Frohberg [6]. In the theoretical part of the quoted paper Frohberg presents the classification of solutions of ionic melts which obey Temkin's relations for activity of components in liquid phase. Frohberg divides the binary ideal ionic melts into two categories:

a) solutions formed by components having common ion. Frohberg suggests to call this type "solutions of the 1st kind" For the ideal solutions of the 1st kind it is typical that they follow Raoult's and Henry's laws in the whole concentration range. Non-ideal solutions of the 1st kind obey Raoult's law at high and Henry's law at low concentrations of component in question;

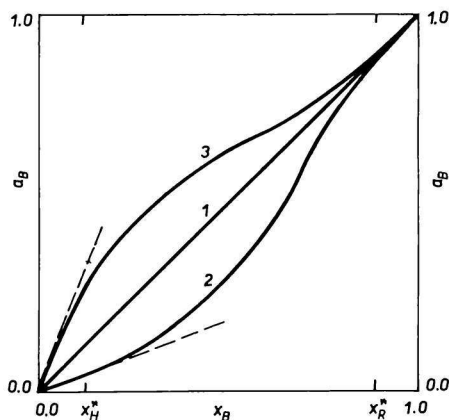
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Fig. 1. Dependence of the activity of component B in the system A—B on concentration.

1. Classic ideal solution; 2. negative deviation from ideality; 3. positive deviation from ideality.

In the concentration range  $(0; x_B^H)$  Henry's law is obeyed, in the range  $(x_B^R; 1)$  Raoult's law is valid.



b) systems formed only by components with non-common ions. Froberg suggests to call this type of solution as “solutions of the 2nd kind” These solutions do not obey Raoult's law at high concentrations and Henry's law at low concentrations.

Therefore, according to Froberg [6], the solutions formed by components having common ions obey (in comparison with the solutions having only non-common ions) the Raoult's and Henry's laws. As it will be proved in this paper this conclusion is not generally valid.

It should be stressed that using Raoult's and Henry's laws for classification of different solutions is entirely justified by importance of these laws in the thermodynamics of solutions. Mainly the importance of Raoult's law is to be stressed in this connection [7]. Importance of Temkin's model for thermodynamics of ionic melts together with systematic development of the theory of these systems makes it necessary to solve this problem.

For the solutions the components of which obey Raoult's law it generally holds that the value  $a_i$  approaches  $x_i$  when mole fraction of the  $i$ -th component approaches unit and, moreover, the tangent to the curve  $a_i = f(x_i)$  fuses with the straight line  $(a_i)_{id} = f(x_i)$ . It means that the slope of the tangent to the curve  $a_i = f(x_i)$  for  $x_i \rightarrow 1$  equals 1

$$\lim_{x_i \rightarrow 1} \frac{da_i}{dx_i} = 1 \quad (1)$$

For the components of solutions obeying Henry's law it holds that for low values of  $x_i$  the curve  $a_i = f(x_i)$  is practically identical with a straight line having origin at the point  $x_i = 0$ . The slope of this straight line has a finite positive value

$$\lim_{x_i \rightarrow 0} \frac{da_i}{dx_i} = k > 0 \quad (2)$$

The course of the dependence  $a_i = f(x_i)$  is presented in Fig. 1 for different cases.

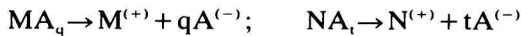
*Analysis of the validity of Raoult's and Henry's laws*

The presented classification of ionic systems is based on comparison of these systems with classic ideal solutions which were chosen as the standard state. It means that for both components of such solutions the Raoult's and Henry's laws are valid in the whole concentration range. (A possibility of using other standard states will be discussed in subsequent paper.)

*1. Systems having common ion*

A. System of the type  $MA_q - NA_t$  ( $q \geq 1, t \geq 1$ )

Let us assume that both components are completely dissociated in solution into ions



Let us denote the mole fraction and activity of the first component  $x_1$  and  $a_1$ , and of the second component  $x_2$  and  $a_2$ , respectively ( $x_1 + x_2 = 1$ ). According to Temkin's model we can write for the activity of the first component

$$a_1 = x_{M^{(+)}} \cdot x_{A^{(-)}}^q = \frac{x_1}{x_1 + x_2} \left[ \frac{x_1 + x_2}{x_1 + x_2} \right]^q = x_1,$$

$$\lim_{x_1 \rightarrow 1} \frac{da_1}{dx_1} = 1; \quad \lim_{x_1 \rightarrow 0} \frac{da_1}{dx_1} = 1$$

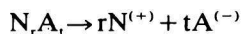
Similarly we can derive for the second component

$$a_2 = x_2; \quad \lim_{x_2 \rightarrow 1} \frac{da_2}{dx_2} = 1; \quad \lim_{x_2 \rightarrow 0} \frac{da_2}{dx_2} = 1$$

It follows that in this case both Raoult's and Henry's laws are fulfilled in the entire range of concentrations. The numerical value of stoichiometric coefficients in conjunction with common ion is not important.

B. The system  $M_pA_q - N_rA_t$  ( $p, q, r, t > 1$ )

Let us assume total dissociation of both components according to the scheme



$$a_1 = x_{M^{(+)}}^p \cdot x_{A^{(-)}}^q = \left[ \frac{px_1}{px_1 + rx_2} \right]^p = \left[ \frac{px_1}{r + x_1(p-r)} \right]^p \quad (3)$$

$$\frac{da_1}{dx_1} = p \left[ \frac{px_1}{r + x_1(p-r)} \right]^{p-1} \cdot \frac{pr}{[r + x_1(p-r)]^2}, \quad (4)$$

$$\lim_{x_1 \rightarrow 1} \frac{da_1}{dx_1} = r > 1, \quad (5)$$

$$\lim_{x_1 \rightarrow 0} \frac{da_1}{dx_1} = 0, \quad (6)$$

$$a_2 = \left[ \frac{rx_2}{px_1 + rx_2} \right]^r = \left[ \frac{rx_2}{p + x_2(r-p)} \right]^r$$

$$\frac{da_2}{dx_2} = r \left[ \frac{rx_2}{p + x_2(r-p)} \right]^{r-1} \cdot \frac{rp}{[p + x_2(r-p)]^2},$$

$$\lim_{x_2 \rightarrow 1} \frac{da_2}{dx_2} = p > 1, \quad (7)$$

$$\lim_{x_2 \rightarrow 0} \frac{da_2}{dx_2} = 0 \quad (8)$$

It follows that despite the discussed system has common ions none of the components obeys either Raoult's or Henry's laws. The dependence  $a_i = f(x_i)$  for the component  $N_rA_t$  is shown in Fig. 2.

### C. Systems of the type $MA_q - N_rA_t$ ( $q, t \geq 1, r > 1$ )

Let us assume the total electrolytic dissociation of both components. Then it holds

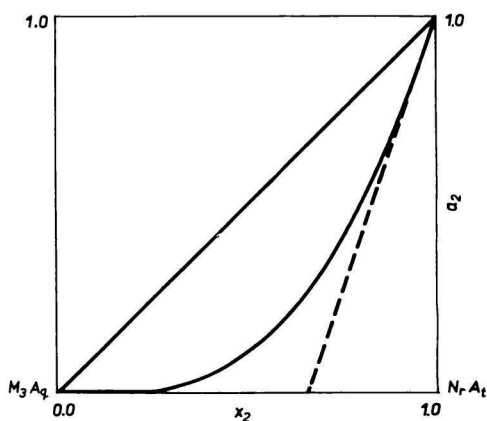


Fig. 2. Dependence of the activity of component  $N_rA_t$  of ideal ionic solution which is formed by components  $M_sA_q - N_rA_t$  on concentration of this component.

Neither Raoult's nor Henry's law is obeyed.

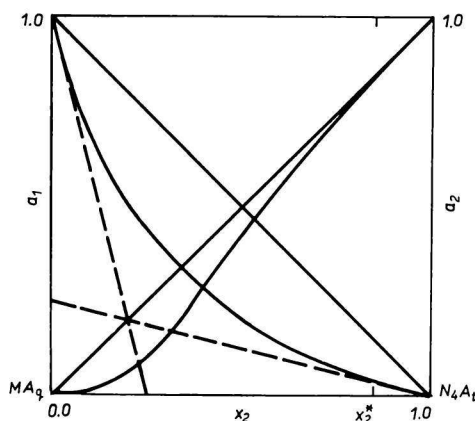


Fig. 3. Dependence of activities of components of ideal ionic solution  $MA_q$  and  $N_rA_t$ , respectively, on their concentrations.

In the concentration range  $(x_2^*; 1)$  the first component obeys Henry's and the second component Raoult's law.

$$a_1 = \frac{x_1}{r - x_1(r-1)}, \quad (9)$$

$$\frac{da_1}{dx_1} = \frac{r}{[r - x_1(r-1)]^2}, \quad (10)$$

$$\lim_{x_1 \rightarrow 1} \frac{da_1}{dx_1} = r > 1, \quad (11)$$

$$\lim_{x_1 \rightarrow 0} \frac{da_1}{dx_1} = \frac{1}{r} > 0, \quad (12)$$

$$a_2 = \left[ \frac{rx_2}{1 + x_2(r-1)} \right]^r$$

$$\frac{da_2}{dx_2} = r \left[ \frac{rx_2}{1 + x_2(r-1)} \right]^{r-1} \cdot \frac{r}{[1 + x_2(r-1)]^2},$$

$$\lim_{x_2 \rightarrow 1} \frac{da_2}{dx_2} = 1, \quad (13)$$

$$\lim_{x_2 \rightarrow 0} \frac{da_2}{dx_2} = 0 \quad (14)$$

Therefore, the first component obeys only the Henry's law but not the Raoult's law. The behaviour of the second component is just opposite (Fig. 3). Formal reason for that is apparently caused by the fact that the expression  $[px_1/r + x_1(p-r)]^{p-1}$  (which occurs in the expression  $da_1/dx_1$  for systems with common ion — see eqn (4)) identically equals one for  $p = 1$ . Consequently, eqns (10–12) are valid and eqn (12) corresponds to Henry's law for the first component. However, if this law is fulfilled for the first component in the range  $(0; x_1^*)$  then the Raoult's law must be valid for the second component in the concentration range  $(x_2^*, 1)$ . (We should bear in mind that  $x_1^* + x_2^* = 1$ .)

## 2. Systems with non-common ion of the type $M_pA_q - N_rB_t$ ( $p, q, r, t > 1$ )

$$a_1 = \left[ \frac{px_1}{r + x_1(p-r)} \right]^p \left[ \frac{qx_1}{t + x_1(q-t)} \right]^q \quad (15)$$

$$\begin{aligned} \frac{da_1}{dx_1} = & p \left[ \frac{px_1}{r + x_1(p-r)} \right]^{p-1} \cdot \frac{pr}{[r + x_1(p-r)]^2} \left[ \frac{qx_1}{t + x_1(q-t)} \right]^q + \\ & + q \left[ \frac{qx_1}{t + x_1(q-t)} \right]^{q-1} \cdot \frac{qt}{[t + x_1(q-t)]^2} \left[ \frac{px_1}{r + x_1(p-r)} \right]^p \end{aligned} \quad (16)$$

$$\lim_{x_1 \rightarrow 1} \frac{da_1}{dx_1} = r + t, \quad (17)$$

$$\lim_{x_1 \rightarrow 0} \frac{da_1}{dx_1} = 0 \quad (18)$$

Simultaneously

$$\lim_{x_2 \rightarrow 1} \frac{da_2}{dx_2} = p + q, \quad (19)$$

$$\lim_{x_2 \rightarrow 0} \frac{da_2}{dx_2} = 0 \quad (20)$$

The relations of components of ideal binary ionic solutions towards Raoult's and Henry's laws are summarized in Table 1. It should be mentioned that cations are denoted with letters M, N, and anions with letters A, B. However, all the derived expressions and conclusions hold their validity also if the cations and anions are mutually replaced.

Table 1

Summary of relations of components of ideal ionic solutions towards Raoult's and Henry's laws

System	Component	Raoult's law	Henry's law
MA <sub>q</sub> —NA <sub>t</sub>	MA <sub>q</sub>	yes	yes
	NA <sub>t</sub>	yes	yes
M <sub>p</sub> A <sub>q</sub> —N <sub>r</sub> A <sub>t</sub>	M <sub>p</sub> A <sub>q</sub>		
	N <sub>r</sub> A <sub>t</sub>		
MA <sub>q</sub> —N <sub>r</sub> A <sub>t</sub>	MA <sub>q</sub>		yes
	N <sub>r</sub> A <sub>t</sub>	yes	
M <sub>p</sub> A <sub>q</sub> —N <sub>r</sub> B <sub>t</sub>	M <sub>p</sub> A <sub>q</sub>		
	N <sub>r</sub> B <sub>t</sub>	no	no

Since the derived relations have been obtained for  $x_i$  approaching zero or one, it may be expected that they have a general validity and are not restricted to the Temkin's model only.

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