Influence of Compound Formation on Activity Factor Curves for Binary Mixtures

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Dolezalek[1] has shown that for liquid mixtures, deviations from Raoult's law can in some cases be explained by assuming association of one of the components or compound formation. He assumed the molecular species present to obey Raoult's law; the problem was to correctly identify the various species present and their amounts. Denoting the components by A and B he developed equations in two cases: the formation of the symmetric compound AB, and the association of A to A_2. Later on Hildebrand and Eastman[2] in their study of thallium amalgams developed expressions assuming the formation of the compound AB_2.

The present author has made an extension of Dolezalek's theory to the general case A_uB_v, this work being part of a critical comparison of a number of such simplified assumptions to the observed deviations from ideality in binary mixtures such as ion exchangers.

We make the following assumptions: we have two components A and B in a two phase equilibrium. The ideal laws are valid, but in one phase we have compound formation or association. In the following only the case of compound formation will be dealt with

A and B interact to form the compound A_uB_v according to the reaction:

$$\underset{x_1}{u\mathrm{A}} + \underset{x_2}{v\mathrm{B}} \rightleftharpoons \underset{x_3}{\mathrm{A}_u\mathrm{B}_v} \qquad (1)$$

$$k = \frac{[\mathrm{A}_u\mathrm{B}_v]}{[\mathrm{A}]^u \cdot [\mathrm{B}]^v} = \frac{x_3}{x_1^{\,u} \cdot x_2^{\,v}} \qquad (2)$$

where x_1, x_2 and x_3 are the true mole fractions of A, B and A_uB_v. The apparent mole fractions X_1 and X_2 of A and B are connected with the true mole fractions by:

$$\begin{aligned} X_1 &= (x_1 + ux_3)/(x_1 + x_2 + (u+v)x_3) \\ X_2 &= (x_2 + vx_3)/(x_1 + x_2 + (u+v)x_3) \end{aligned} \qquad (3)$$

Since the ideal laws are valid we have the following expressions for the apparent activities a_1, a_2 and activity factors g_1, g_2, if we take the pure components as standard states:

$$\begin{aligned} a_1 &= x_1 \\ a_2 &= x_2 \end{aligned} \quad (4) \qquad \begin{aligned} g_1 &= x_1/X_1 \\ g_2 &= x_2/X_2 \end{aligned} \quad (5)$$

By experimental methods it is possible to find the $g_1(X_1)$ and $g_2(X_2)$ curves. As shown below it can be seen from these curves, whether they may be due to compound formation or not. From (2), (3) and (5) we find the following limiting values for g_1 and g_2, remembering that $x_1 = 1$, $x_2 = 0$ at $X_2 = 0$ and that $x_1 = 0$, $x_2 = 1$ at $X_2 = 1$:

$$\begin{aligned} &X_2 = 0\text{: } g_1 = 1;\ g_2 = 1 \text{ for } v > 1 \text{ and} \\ &\qquad g_2 = 1\,/\,(1 + k) \text{ for } v = 1 \\ &X_2 = 1\text{: } g_2 = 1;\ g_1 = 1 \text{ for } u > 1 \text{ and} \\ &\qquad g_1 = 1\,/\,(1 + k) \text{ for } u = 1 \end{aligned} \qquad (6)$$

By setting $g_1 = g_2$ one finds:

$$X_2 = v\,/\,(u + v) \qquad (7)$$

From (6) and (7) it is seen that the point of intersection of g_1 and g_2 gives the composition of the compound and the limiting values of g_1 and g_2 will give the value of k if one of u or $v = 1$. If, however, the g curves do not have the limiting values predicted from (6), they cannot be explained by compound formation only.

In Figs. 1 and 2 the a and g values are given as functions of X_2 assuming the compound A_3B to be formed. The func-

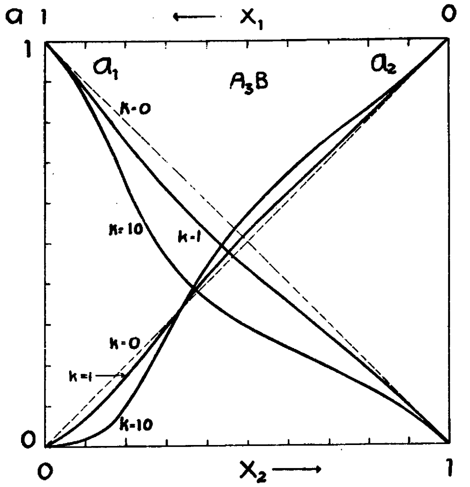

Fig. 1. The activities a_1 and a_2 are plotted against X_2, assuming the compound A_3B to be formed. The activities have been calculated for $k = 1$ and 10. The dotted lines give a_1 and a_2 when Raoult's law is valid.

tions have been calculated for $k = 1$ and 10. It may be noted that depending upon the symmetry of equations (2)—(5), the a and g functions, assuming AB_3 to be formed, are mirror images of those given in Figs. 1 and 2.

Application to ion exchange equilibria:

The equilibrium quotient λ_{21} for the ion exchange reaction:

$$z_1A_2^{z_2+} + z_2A_1R_{z_1} \rightleftharpoons z_2A_1^{z_1+} + z_1A_2R_{z_2} \quad (8)$$

is defined by:

$$\lambda_{21} = \frac{\{A_1^{z_1+}\}^{z_2} \; X_2^{z_1}}{\{A_2^{z_2+}\}^{z_1} \; X_1^{z_2}} = K_{21} \frac{g_1^{z_2}}{g_2^{z_1}} \quad (9)$$

where K_{21} is the thermodynamic equilibrium constant of (8).

In Fig. 3 log λ_{21} calculated from (9) is plotted against X_2 for $k = 10$, $K_{21} = 10$ and $z_1 = z_2 = 1$ assuming that one of

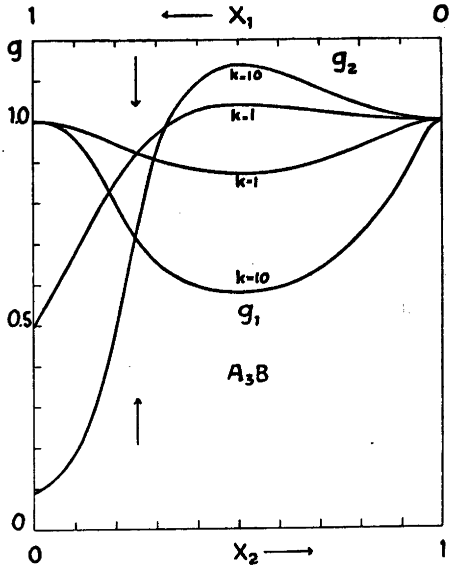

Fig. 2. The activity factors g_1 and g_2 are plotted against X_2, assuming the compound A_3B to be formed. The activity factors have been calculated for $k = 1$ and 10. The arrows indicate the points of intersection at $X_2 = 0.25$.

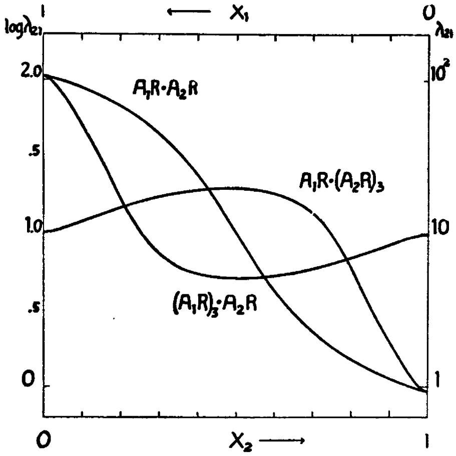

Fig. 3. Log λ_{21} is plotted against X_2, assuming one of the following compounds $A_1R \cdot A_2R$, $A_1R \cdot (A_2R)_3$ and $(A_1R)_3 \cdot A_2R$ to be formed. The equilibrium quotient has been calculated for $k = 10$, $K_{21} = 10$ and $z_1 = z_2 = 1$.

the following compounds is formed: 1) $A_1R \cdot A_2R$, 2) $A_1R \cdot (A_2R)_3$ and 3) $(A_1R)_3 \cdot A_2R$. From Fig. 3 is seen that the symmetric compound gives a decreasing $\log \lambda_{21}(X_2)$ curve, the asymmetric compounds AB_3 and A_3B give curves with maximum or minimum. For arbitrary values of z_1 and z_2 the $\log \lambda_{21}(X_2)$ curves have essentially the same form as those reproduced in Fig. 3.

By comparing Figs. 1—3 with the corresponding Figs. in the preliminary communications by Högfeldt *et. al.*[3–4] or in the full paper by Högfeldt [5] it is seen that they have the same general form. Especially the g curves calculated from Marinsky's measurements have a form almost identical with those caused by compound formation. The point of intersection gives $X_2 = 0.17$. From (6) and (7) $X_2 = 0.17$ gives $v = 1$, $u = 5$. The compound $(HR)_5 \cdot BaR_2$ has also been proposed by Marinsky and Coryell [6], who found by trial that it fitted the experimental data. The first to use this approach was probably Kielland [7], who attributed the deviations from Duhem-Margules equation he found in ion exchange systems to compound formation.

Although certainly over-simplified, the assumption of compound formation is, so far as I know, the only approach hitherto published that gives an explanation of the existence of extreme values of the equilibrium quotients. Any theory dealing with ion exchange equilibria must allow for such extremes, and the striking qualitative agreement of this simple assumption with experimental data may perhaps focus the attention on some kind of interaction between the components in the exchanger.

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Dissolving velocity of Metals in Deutero-Electrolytes

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The present paper is a preliminary report on experiments dealing with the dissolution of metals in acids and bases, the hydrogen content of which had been partly or completely replaced by deuterium.

Dissolving velocity experiments. The dissolving velocity of metals in non-oxidizing acids is usually determined by measuring the rate of hydrogen evolution. This method was also employed in the present study. Some results are given here for zinc, aluminium and iron.

1. Zinc. 2 mm wire, prepared from a very pure zinc was used. The reagents were 1 N hydrochloric acid and 2 N sulphuric acid with varying content of deuterium. Curves representing the mean values from the experiments with sulphuric acid at 25° C are shown in the diagram Fig. 1. Similar curves were obtained in the experiments with hydrochlorid acid.

Further it was attemped to etablish a sort of "model local element", the cathodic area of which could be maintained constant during the dissolving process. The anode of the element, 2 mm zinc wire, was fixed axially in a nickel cylinder, and the ends of the wire connected to the cylinder.

When this element was immersed in acid practically all the hydrogen liberation took place at the inside area of the nickel cylinder.

The curves obtained were of a different character than those shown in Fig. 1. There