Short Communications

Activities of the Components in Ion Exchangers with Multivalent Ions

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A cation exchanger, R^-, containing two ionic species, A_1 and A_2, can be regarded as a solid solution of the components A_1R and A_2R. The activities of these components can be calculated from exchange equilibrium data, as we have recently shown for the case of univalent ions[1].

We shall now consider the general case with two ions: $A_1^{z_1+}$ and $A_2^{z_2+}$. We can choose the molecular weight of the components in two ways:

I. $(A_1)_{\frac{1}{z_1}}R$ and $(A_2)_{\frac{1}{z_2}}R$, using the *equivalent fractions* β_1 and β_2.

II. $A_1(R)_{z_1}$ and $A_2(R)_{z_2}$, using what we shall call the *molar fractions* x_1 and x_2. The activities are in both cases chosen so that they are unity in the pure components.

I. With I the reaction can be written:

$$z_1 A_2^{z_2+} + z_1 z_2 (A_1)_{\frac{1}{z_1}}R \rightleftharpoons z_2 A_1^{z_1+} + z_1 z_2 (A_2)_{\frac{1}{z_2}}R \tag{1}$$
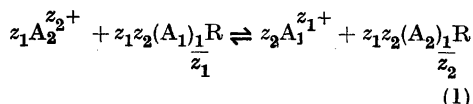
Introducing the capacity s_0 in arbitrary units, and the activity factors γ_1 and γ_2:

$$[(A_1)_{\frac{1}{z_1}}R] = \beta_1 s_0; \quad [(A_2)_{\frac{1}{z_2}}R] = \beta_2 s_0; \quad \beta_1 + \beta_2 = 1 \tag{2}$$

$$\{(A_1)_{\frac{1}{z_1}}R\} = \gamma_1 \beta_1; \quad \{(A_2)_{\frac{1}{z_2}}R\} = \gamma_2 \beta_2 \tag{3}$$

Now, assuming that we know the activities of the ions in the aqueous solution, equilibrium measurements give the equilibrium quotient $\varkappa_{21}$, which is related to the thermodynamic equilibrium constant K_{21} of (1) by:

$$\varkappa_{21} = \varkappa_{21}^{-1} = \frac{\{A_1^{z_1+}\}^{z_2}}{\{A_2^{z_2+}\}^{z_1}} \cdot \left(\frac{\beta_2}{\beta_1}\right)^{z_1 z_2} =$$
$$= K_{21} \cdot \left(\frac{\gamma_1}{\gamma_2}\right)^{z_1 z_2} \tag{4}$$

as is easily seen from (1), (2) and (3). Gibbs-Duhem's law gives:

$$\beta_1 \, d\ln \gamma_1 \beta_1 + \beta_2 \, d\ln \gamma_2 \beta_2 = 0 \tag{5}$$

From (5), (2) and (4) we find, remembering that K_{21} is a constant:

$$d\ln \gamma_1 = \frac{\beta_2}{z_1 z_2} \, d\ln \varkappa_{21};$$
$$d\ln \gamma_2 = -\frac{\beta_1}{z_1 z_2} \, d\ln \varkappa_{21} \tag{6}$$

Thus, as for univalent ions, γ_1 and γ_2 can be obtained by graphical integration of the curve $\log \varkappa_{21}$ (β).

II. If the "moles" chosen are $A_2R_{z_1}$ and $A_2R_{z_2}$, with molar fractions x_1 and x_2 and activity factors g_1 and g_2:

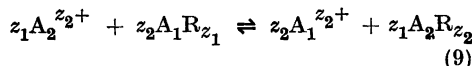$$\beta_1 + \beta_2 = x_1 + x_2 = 1; \quad \beta_1 : \beta_2 = x_1 z_1 : x_2 z_2,$$

thus

$$x_1 = \beta_1 z_2 (\beta_1 z_2 + \beta_2 z_1)^{-1};$$
$$\beta_1 = x_1 z_1 (x_1 z_1 + x_2 z_2)^{-1} \text{ etc.} \qquad (7)$$

Since the standard states are the same as with I:

$$\{A_1 R_{z_1}\} = \left\{(A_1)_{\frac{1}{z_1}} R\right\}^{z_1} \text{ or } g_1 x_1 = (\gamma_1 \beta_1)^{z_1}$$

$$\{A_2 R_{z_2}\} = \left\{(A_2)_{\frac{1}{z_2}} R\right\}^{z_2} \text{ or } g_2 x_2 = (\gamma_2 \beta_2)^{z_2} \qquad (8)$$

The reaction can be written:

$$z_1 A_2^{z_2+} + z_2 A_1 R_{z_1} \rightleftharpoons z_2 A_1^{z_2+} + z_1 A_2 R_{z_2} \qquad (9)$$

The thermodynamic constant of (9) is the same as that of (1), K_{21}, because of (8). An equilibrium quotient λ_{21} for (9) may be defined by:

$$\lambda_{21} = \frac{\left\{A_1^{z_1+}\right\}^{z_1} x_2^{z_1}}{\left\{A_2^{z_2+}\right\}^{z_1} x_1^{z_2}} = K_{21} \cdot \frac{g_1^{z_2}}{g_2^{z_1}} \qquad (10)$$

and from (10) and Gibbs-Duhem's law we can derive:

$$\text{dln } g_1 = \beta_2 z_2^{-1} \text{dln } \lambda_{21};$$
$$\text{dln } g_2 = -\beta_1 z_1^{-1} \text{dln } \lambda_{21} \qquad (11)$$

To find γ_1, γ_2, g_1 and g_2 one need only make *one* graphical integration, either finding one of γ_1 and γ_2 with (6) and the other with (4), or one of g_1 and g_2 with (11) and the other with (10).

The other set of activity factors can be found from (8).

1. Ekedahl, E., Högfeldt, E., and Sillén, L. G. *Acta Chem. Scand.* 4 (1950) 556.

Activities of the Barium and Hydrogen Forms of Dowex 50

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Högfeldt, Ekedahl and Sillén have recently developed equations for calculating the activities of the components in ion exchangers [1], [2].

For multivalent ions there is a choice whether to consider (I) equivalents $Ba_{\frac{1}{2}}R$, $Al_{\frac{1}{3}}R$ etc. or (II) molecules BaR_2, AlR_3 etc. Dependent on the choice, different mole fractions (I $\beta_1 \beta_2$; II $x_1 x_2$), equilibrium quotients (I $\varkappa$; II λ), and activity factors (I $\gamma_1 \gamma_2$; II $g_1 g_2$) should be used.

There are in literature very few measurements on ion exchange equilibria with multivalent ions. We have applied our formulae to two sets of measurements [3], [4] on the exchange H^+ (= 1) — Ba^{2+} (= 2) on Dowex 50. Marinsky [3] used Dowex 50 which had been treated with 6 C NaOH at 95° C for 48 hours, whereas Duncan and Lister [4] mention no pretreatment of their resin.

Fig. 1 gives log λ_{21} as a function of β, not of x, to facilitate the integration of equation (11). (For the numbers of equations see Högfelt at al [2]). The equilibrium quotient λ_{21} from Duncan's and Lister's measurements is seen to differ considerabl from Marinsky's, which is probably due to the pretreatment.

In Fig. 2 a and b, the g values have been calculated both from λ_{21} with (11) and from $\varkappa_{21}$ (Fig. 3) with (6) and (8). The deviations are small. They are of course due to the fact that the smoothed curves $\varkappa_{21}(\beta)$ and $\lambda_{21}(\beta)$ are not exactly equivalent.

It is interesting to note that Marinsky's values give a maximum in the activity factor g_2 of BaR_2, (and a minimum in g_1) not far from the composition of the