thus

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

(7)

Since the standard states are the same as with \( I: \)

\[ \{A_1 R z_1\} = (A_1 z_1 R)^{z_1} \text{ or } g_1 x_1 = (\gamma_1 \beta_1)^{z_1} \]
\[ \{A_2 R z_2\} = (A_2 z_2 R)^{z_2} \text{ or } g_2 x_2 = (\gamma_2 \beta_2)^{z_2} \]  

(8)

The reaction can be written:

\[ z_1 A_2^{2+} + z_2 A_1 R z_1 \leftrightarrow z_2 A_1^{2+} + z_1 A_2 R z_2 \]  

(9)

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

\[ \lambda_{21} = \frac{(A_1^{2+})^z_1 x_1^{z_1}}{(A_2^{2+})^z_2 x_2^{z_2}} = K_{21} \frac{g_1^{z_1}}{g_2^{z_2}} \]  

(10)

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

\[ \ln g_1 = \beta_{21}^{z_2} - \ln \lambda_{21}; \]
\[ \ln g_2 = - \beta_{12}^{z_1} - \ln \lambda_{21} \]  

(11)

To find \( \gamma_1, \gamma_2, g_1 \) and \( g_2 \) one need only make one graphical integration, either finding one of \( \gamma_1 \) and \( \gamma_2 \) 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).


Received June 21, 1950.

Activities of the Barium and Hydrogen Forms of Dowex 50

ERIK HÖGFELDT, ERIK EKEDahl, and LARS GUNNAR SILLÉN

FOA 1, Ulriksdal; Institute of Inorg. Chem., University of Stockholm and Chalmers' Institute of Technology, Gothenburg, Sweden

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\(4R\), Al\(4R\) etc. or (II) molecules BaR\(_2\), AlR\(_2\) etc. Dependent on the choice, different mole fractions (I \(I_1, I_2\); II \(x, A\)), equilibrium quotients (I \(K, A\)), and activity factors (I \(\gamma_1\gamma_2, I_1, I_2\); II \(g_1g_2\)) should be used.

There are in literature very few measurements on ion exchange equilibria with multivalent ions. We have applied our formulæ to two sets of measurements\(^3,^4\) on the exchange \(II^+ (= 1) – Ba^{2+} (= 2)\) 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 \(\lambda_{21}\) as a function of \(\beta\), not of \(x_i\), to facilitate the integration of equation (11). (For the numbers of equations see Högfeldt at \(\alpha\)). The equilibrium quotient \(\lambda_{21}\) from Duncan's and Lister's measurements is seen to differ considerably from Marinsky's, which is probably due to the pretreatment.

In Fig. 2 a and b, the \(g\) values have been calculated both from \(\lambda_{21}\) with (11) and from \(x_{21}\) (Fig. 3) with (6) and (8). The deviations are small. They are of course due to the fact that the smoothed curves \(x_{21}(\beta)\) 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
compound BaR₄(HR)₅ proposed by Marinsky and Coryell. At almost the same composition, Duncan's and Lister's values give a minimum in g₃ (maximum in g₂!).

Fig. 3 gives κ₂₁(β₁), and Figs. 4—5 give γ₁ and γ₂ calculated from (6) and from (11) and (8). This way of representation does not bear out the difference between the two sets of measurements, since they give curves of essentially the same form.

Moreover, for β₁→1, log κ₂₁ seems to tend towards −∞, and γ₂→+∞. This is to be expected since λ₂₁ seems to have a finite value at β₁ = 1 (cf. (11) and (8)). In this case it seems preferable to use II, with molar sizes BaR₄ and HR, and the corresponding equilibrium quotient λ₂₁ and activity factors g₁ and g₂, rather than I (with Ba₄R, κ₂₁, γ₁, and γ₂). The curves obtained with II, by the way, resemble more those for univalent ions (where I and II are of course identical).


Received June 22, 1950.