thus

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

Since the standard states are the same as with I:

$$\left\{A_1 R_{z_1}\right\} = \left\{(A_1)_{\frac{1}{z_1}} R\right\}^{z_1} \text{ or } g_1 x_1 = (\gamma_1 \beta_1)^{z_1}$$
$$\left\{A_2 R_{z_2}\right\} = \left\{(A_2)_{\frac{1}{z_2}} R\right\}^{z_2} \text{ or } g_2 x_2 = (\gamma_2 \beta_2)^{z_2} \quad (8)$$

The reaction can be written:

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

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:

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

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

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

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).

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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_1x_2), equilibrium quotients (I $\varkappa$; II λ), and activity factors (I $\gamma_1\gamma_2$; 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 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

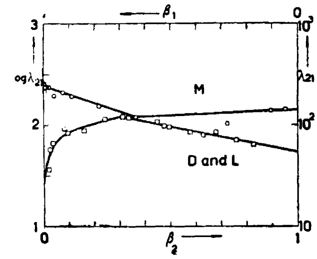


Fig. 1. Log λ_{21} as function of β for $Ba^{2+}-H^+$ exchange on Dowex 50. O: *Marinsky* [3]. □: *Duncan and Lister* [4].

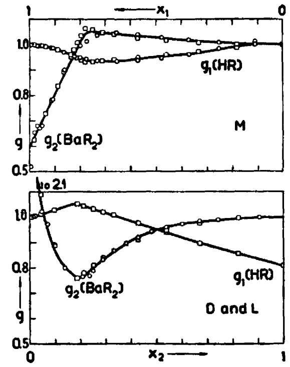


Fig. 2. Activity factors g_1 and g_2. O: *from (6) and (8),* □: *from (11). Fig. 2 a gives g from Marinsky's measurements and 2 b from Duncan's and Lister's.*

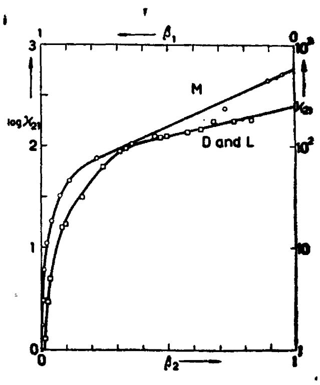
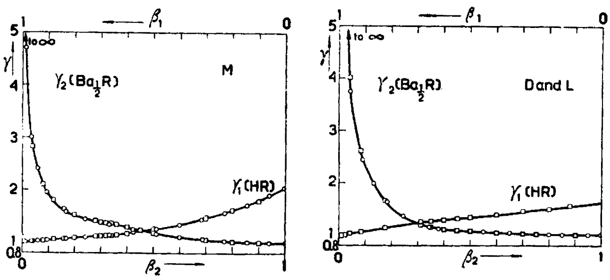


Fig. 3. Log $\varkappa_{21}$ as function of β. O: *Marinsky,* □: *Duncan and Lister.*

compound $BaR_2(HR)_5$ proposed by Marinsky and Coryell [3]. At almost the same composition, Duncan's and Lister's values give a minimum in g_2 (maximum in g_1)!

Fig. 3 gives $\varkappa_{21}(\beta)$, and Figs. 4—5 give γ_1 and γ_2 calculated from (6) and from (11) and (8). This way of representation II, with molar sizes BaR_2 and HR, and the corresponding equilibrium quotient λ_{21} and activity factors g_1 and g_2, rather than I (with $Ba_{\frac{1}{2}}R$, $\varkappa_{21}$, γ_1 and γ_2). The curves obtained with II, by the way, resemble more those for univalent ions [1] (where I and II are of course identical).



Figs. 4—5. Activity factors γ_1 and γ_2. O: *from (11) and (8),* □: *from (6). Fig. 4 gives γ from Marinsky's measurements and Fig. 5 from Duncan's and Lister's.*

does not bear out the difference between the two sets of measurements, since they give curves of essentially the same form.

Moreover, for $\beta_1 \to 1$, log $\varkappa_{21}$ seems to tend towards $-\infty$, and $\gamma_2 \to +\infty$. This is to be expected since λ_{21} seems to have a finite value at $\beta_1 = 1$ (*cf.* (11) and (8)).

In this case it seems preferable to use

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