# THERMODYNAMICS OF ION EXCHANGE UNDER ISOPIESTIC CONDITIONS

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## Abstract

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# THERMODYNAMICS OF ION EXCHANGE UNDER ISOPIESTIC CONDITIONS

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An ion exchanger saturated with ions A and B may be regarded as a solid solution of swollen resinates $AR_{z_A}$ and $BR_{z_B}$, where $z_A$ and $z_B$ are the charges of ions A and B. Let us denote the chemical potentials of these resinates by $\mu_1'$ and $\mu_2'$. If an ion exchanger saturated with ions A and B is in equilibrium with an aqueous solution of the salts $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$ at constant temperature and pressure, then the equilibrium condition is the equality

$$\mu_1' - \frac{z_A}{z_B}\mu_2' = n_1\mu_1 - n_3\frac{z_A}{z_B}\mu_2, \qquad (1)$$

where $\mu_1$ and $\mu_2$ are the chemical potentials of the salts $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$ in the aqueous solution. Express the chemical potentials in terms of activities

$$\begin{aligned} \mu_i' &= \mu_{i0}' + kT\ln a_i', \\ \mu_i &= \mu_{i0} + kT\ln a_i. \end{aligned} \qquad (2)$$

Taking into account that $z_B/z_A = n_1n_4/n_2n_3 = r$, from (1) and (2) we obtain

$$\ln\overline{K} = \ln K_a - r\ln\gamma_1 + \ln\gamma_2, \qquad (3)$$

where $\overline{K}$ is the exchange constant and

$$\ln\overline{K} = \frac{1}{kT}\left(r\mu_{10}' - \mu_{20}' - n_1r\mu_{10} + n_3\mu_{20}\right); \qquad (4)$$

$$\ln K_a = n_1r\ln a_1 - n_3\ln a_2 - r\ln x_1 + \ln x_2.$$

The quantities $x_1$ and $x_2$ are the mole fractions of the resinates $AR_{z_A}$ and $BR_{z_B}$, and $\gamma_1$ and $\gamma_2$ are their activity coefficients ($a_i' = \gamma_i x_i$). In what follows, we shall choose the standard state in the ion exchanger so that $\gamma_i = 1$ at $x_i = 1$.

Differentiating equation (3), we obtain

$$d \ln K_a - r\, d \ln \gamma_1 + d \ln \gamma_2 = 0. \tag{5}$$

Since the Gibbs–Duhem equation is valid for the ion-exchanger phase,

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0, \tag{6}$$

from (5) and (6) we find

$$\begin{aligned} d \ln \gamma_1 &= \frac{x_1}{x_1 + r x_2}\, d \ln K_a, \\ d \ln \gamma_2 &= -\frac{x_1}{x_1 + r x_2}\, d \ln K_a. \end{aligned} \tag{7}$$

Applying integration by parts, we find

$$\begin{aligned} \ln \gamma_1 &= \frac{x_2}{x_1 + r x_2} \ln K_a + \int_x^1 \frac{\ln K_a}{(x_1 + r x_2)^2}\, dx_1; \\ \ln \gamma_2 &= -\frac{x_1}{x_1 + r x_2} \ln K_a + r \int_{x_1}^0 \frac{\ln K_a}{(x_1 + r x_2)^2}\, dx_1. \end{aligned} \tag{8}$$

Substituting (8) into (3), we obtain

$$\ln \overline{K} = r \int_0^1 \frac{\ln K_a}{(x_1 + r x_2)^2}\, dx_1. \tag{9}$$

The approach considered here to the equilibrium of ion exchange has been described in the literature ([1], [2]). However, equations (8) and (9), apparently, are known only for ions of equal valence ($r = 1$). Further, the given approach to the equilibrium of ion exchange assumes that the capacity of the ion exchanger remains unchanged, and that the pressure in the coexisting phases is the same.

Equations (3), (7)–(9) can be used to obtain information about the thermodynamic properties of ion exchangers. For this it is necessary to know the dependence of $K_a$ on composition. The solution of this problem is substantially simplified if the study of ion exchange is carried out under isopiestic conditions. The procedure for studying the thermodynamics of ion exchange in this case is as follows. First, an isopiestic study is carried out of ternary solutions $A_{n_1}C_{n_2} - B_{n_3}C_{n_4} - H_2O$. This study gives the dependence of the total molality $m$ on the composition of the solution; using it, with the aid of the differential equation of McKay–Perring ([3]), we find the dependence of $a_i$ on composition under isopiestic conditions (see, for example, ([4])). Then, having studied the composition of the coexisting phases under isopiestic conditions, we obtain all the necessary data for calculating $\overline{K}$, $\gamma_1$, and $\gamma_2$.

Let us consider this method using as an example the equilibrium of the ion exchanger KU-2 with the solutions $NaCl - KCl - H_2O$, $NaCl - CaCl_2 - H_2O$, and $NaCl - LaCl_3 - H_2O$. Data from isopiestic studies of these solutions at 25° are known ([5], [6]). Analysis of these data shows that, in the first approximation (the common ion is indistinguishable),

$$\ln \frac{a_i}{a_{i0}} = K(1-y_i)^2 \ln \frac{1}{a_w} + \ln y_i, \qquad [a_w] \tag{10}$$

where $y_i$ is the mole fraction of the salt without taking water into account; $a_i = a_{i0}$ at $y_i = 1$; $K$ is a constant equal to 0.90 for $NaCl - KCl - H_2O$, 0.33 for $NaCl - CaCl_2 - H_2O$, and 0.22 for $NaCl - LaCl_3 - H_2O$. In what follows, subscript 1 will always refer to NaCl, and subscript 2 to the other salt.

Substituting (10) into the equation for $K_a$, we find

$$\lg K_a = n_4 \lg a_{10} - \lg a_{20} + (n_4 y_2^2 - y_1^2) K \ln \frac{1}{a_w} +$$

$$+ n_4 \lg \frac{y_1}{x_1} + \lg \frac{x_2^2}{y_2}. \qquad [a_w] \tag{11}$$

For the case under consideration, equation (3) takes the form

$$n_4 \lg \gamma_1 - \lg \gamma_2 = \lg K_a - \lg \overline{K}, \qquad [a_w] \tag{12}$$

$$\lg \overline{K} = n_4 \int_0^1 \frac{\ln K_a}{(x_1 + n_4 x_2)^2}\, dx_1, \qquad [a_w] \tag{13}$$

$$d \lg \gamma_2 = -\frac{x_1}{x_1 + n_4 x_2}\, d \lg K_a. \qquad [a_w] \tag{14}$$

For the systems studied by us, ternary solutions were prepared according to data from isopiestic studies in such a way that the mole fraction of each salt varied from 0 to 1 at constant water activity. Then, 50 ml portions of the prepared solutions were each charged with samples of ion exchanger of not more than 2 g. The total amount of cations in the ion-exchanger sample was always much less than the total amount of cations in the solution. Therefore, the change in the composition of the solution during the exchange process may be neglected, and it may be assumed that the composition

of the final solution is equal to the composition of the initial one. The solutions with the samples of resin were stirred in a thermostat at $25.0 \pm 0.1°$ for 24 h. After the experiment was completed, the ion exchanger was quantitatively separated from the solution, washed with distilled water, and analyzed for the content of cations.

(Figure: Fig. 1)

**Fig. 1.** Dependence of $\lg \gamma_i$ on $(1 - x_i)^2$ for resins in the Na–Ca form (*a*) and in the Na–La form (*b*). Curves 1 refer to Na, curves 2 to Ca and La.

For the analysis of ion exchangers in the Na–Ca and Na–La forms, a definite amount of ion exchanger was washed with an excess of hydrochloric acid, and the amount of Ca or La ions in the resulting filtrate was determined. The content of the Na ion was calculated from the capacity of the given sample. In view of the difficulty of the quantitative determination of sodium and potassium when present together, the isopiestic method was used for the analysis of resins in the Na–K form; it is based on the fact that the absorption of water by samples of ion exchanger under isopiestic conditions is a linear function of composition.

In our experiments the initial ion exchanger was used in the Na form. The stirring time adopted by us is sufficient for the attainment of equilibrium. This was checked by approaching equilibrium "from above" and "from below." For this purpose, an ion exchanger of identical composition was immersed in solutions in different forms, i.e., in the Na and K forms, in the Na and Ca forms, and in the Na and La forms. A sufficient agreement of the results was found to justify the conclusion that equilibrium is attained completely within the time adopted by us.

The results of the experiments were treated by equations (11)–(14). The quantities $a_{10}$ and $a_{20}$ were calculated from the data given in the monograph by Robinson and Stokes (7). For solutions $NaCl–KCl–H_2O$ at $a_w = 0.8516$, $\lg a_{10} - \lg a_{20} = 0.15$; for solutions $NaCl–CaCl_2–H_2O$ at $a_w = 0.8312$, $2 \lg a_{10} - \lg a_{20} = 0.72$; for solutions $NaCl–LaCl_3–H_2O$ at $a_w = 0.9030$, $3 \lg a_{10} - \lg a_{20} = 2.25$. In accordance with these data, graphical integration of the experimental data by equation (13) gives, for the ion exchanger in the Na–K form, $\lg \overline{K} = 0.33$ ($\overline{K} = 2.2$), for the ion exchanger in the Na–Ca form, $\lg \overline{K} = 1.3$ ($\overline{K} = 20$), and for the ion exchanger in the Na–La form, $\lg \overline{K} = 3.5$ ($\overline{K} = 3.2 \cdot 10^3$). Next, from equation (14), the value of $\gamma_2$ was calculated, and then, with the aid of equation (12), $\gamma_1$.

The results of the calculations of the activity coefficients are given in Table 1. The correctness of the calculated values of the activity coefficients was checked by the Redlich–Kister relation

$$\int_0^1 \lg \frac{\gamma_1}{\gamma_2} \, dx_1 = 0. \tag{15}$$

Relation (15) is satisfied quite satisfactorily for our data.

The theory of regular solutions can formally be applied to a solution of resinates $AR_{z_A}$ and $BR_{z_B}$, according to which

$$\lg \gamma_i = K(1 - x_i)^2, \tag{16}$$

where $K$ is a constant. In Fig. 1 the experimental values obtained by us are plotted in the coordinates of equation (16). We see that the experimental points do not fall on straight lines, i.e.,

equation (16) does not describe the experimental results with sufficient accuracy.

The quantity $\overline{K}$ is a thermodynamic constant and, within the adopted assumptions, should be constant. For NaCl—KCl—$H_2O$ solutions we determined the quantity $\overline{K}$ at other water activities. It turned out that the dependence of $x_1$ on $y_1$ is the same in all cases, but the quantity $\overline{K}$ has different values. For a water activity equal to 0.8516,

**Table 1**

| $x_1$ | Na—K, $a_w$ = 0.8516 | | | Na—Ca, $a_w$ = 0.8312 | | | Na—La, $a_w$ = 0.9030 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $y_1$ | $\gamma_1$ | $\gamma_2$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
| 0.1 | 0.17 | 1.16 | 1.01 | 0.30 | 1.78 | 1.02 | 0.65 | 3.30 | 1.04 |
| 0.2 | 0.28 | 1.05 | 1.03 | 0.47 | 1.48 | 1.05 | 0.74 | 2.05 | 1.15 |
| 0.3 | 0.38 | 1.02 | 1.04 | 0.58 | 1.30 | 1.10 | 0.79 | 1.56 | 1.26 |
| 0.4 | 0.48 | 1.01 | 1.05 | 0.66 | 1.18 | 1.16 | 0.83 | 1.30 | 1.39 |
| 0.5 | 0.58 | 1.01 | 1.05 | 0.74 | 1.11 | 1.21 | 0.87 | 1.17 | 1.53 |
| 0.6 | 0.67 | 1.00 | 1.05 | 0.81 | 1.06 | 1.29 | 0.91 | 1.08 | 1.70 |
| 0.7 | 0.75 | 1.00 | 1.05 | 0.86 | 1.04 | 1.38 | 0.94 | 1.04 | 1.96 |
| 0.8 | 0.84 | 1.00 | 1.05 | 0.91 | 1.01 | 1.48 | 0.96 | 1.02 | 2.28 |

0.8956 and 0.9225, the quantity $\overline{K}$ is respectively equal to 2.2, 2.1, and 1.9, which is evidently due to the inaccurate observance of the second of the assumptions indicated above. In this connection, in a rigorous treatment the obtained values of $\overline{K}$, as well as $\gamma_1$ and $\gamma_2$, should be referred to a definite water activity.

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*Note: Figure translations are in progress. See original paper for figures.*