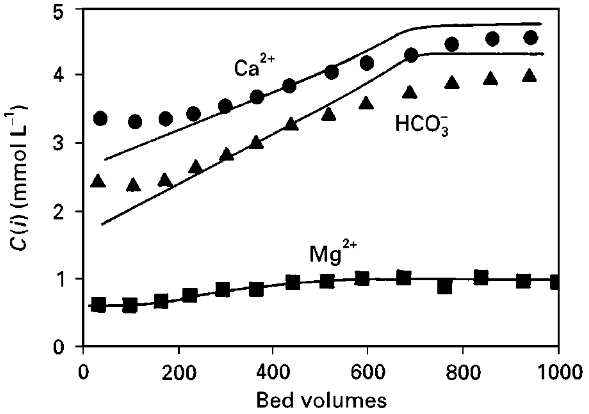

**Figure 15** Comparison of experimental (●, ▲, ■) and predicted (—) breakthrough curves during softening/dealkalization of tap water. Resin: AMBERLITE IRC 50, regenerated by carbonic acid. Volume of resin, 1 L; throughput, 6.9 BV h$^{-1}$; feed: $Ca^{2+} = 2.44$ mmol L$^{-1}$; $Mg^{2+} = 0.48$ mmol L$^{-1}$; $HCO_3^- = 4.42$ mmol L$^{-1}$.

equilibrium stages a fairly good agreement between experimental and predicted concentration histories can be obtained. **Figure 15** shows the comparison between experimental data and predicted developments of concentrations for a system with a weakly acidic resin which is applied for softening/dealkalization of tap water. Clearly a very satisfactory agreement is obtained.

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# Theory of Ion Exchange

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Proper theoretical tools are necessary at all stages in the development of ion exchange applications. Firstly, in the laboratory, when a new application is being developed, theory is helpful in the design of new materials and necessary for the interpretation and quantification of research results. Secondly, theory is needed in the design of industrial and laboratory processes. When the process is being operated, theory is again useful to keep the process under optimal control.

Ion exchangers are used in very diverse applications in the laboratory and in industry. Considering this, and the fact that a very wide range of different substances can act as ion exchangers, it is not surprising to see in the literature that various sets of nomenclature, conventions and diverse theories exist, reflecting the special features of the applications or materials involved. For instance, one finds rather different definitions for several basic terms of ion exchange in the field of water purification compared to those used in ion exchange chromatography and even diversity in the terminology can be seen within the field of ion chromatography. It is inevitable that various theories must exist for the functioning of different types of ion exchangers, but the discrepancies in the most basic definitions only lead to confusion and misconception that deter the utilization of the theory.

The theory of ion exchange is a vast subject. This article presents and discusses most of the essential theory and concepts in connection with the most common applications. There is emphasis on discussing details that are important in interpreting correctly research results and in predicting and optimizing ion exchanger performance. For simplicity, the basic equations are written for cation exchange but they are applicable to anion exchange as well, with minor modifications. Theories for the prediction of cation exchange selectivity are also discussed briefly.

## Basic Concepts

### Ion Exchange Equilibria

A binary ion exchange reaction between ion A (charge $z_A$) and ion B (charge $z_B$) may be written as:

$$z_B A^{Z_A} + z_A \bar{B}^{Z_B} \leftrightarrow z_A B^{Z_B} + z_B \bar{A}^{Z_A} \qquad [1]$$

where superscript bars refer to the ions in a solid ion exchanger. Various equilibrium quantities are used to measure and estimate the efficiency of the ion exchanger for a given separation task. The most common of these include the following.

**Selectivity coefficient (selectivity quotient)**

$$k_{A/B} = \frac{\bar{C}_A^{Z_B} C_B^{Z_A}}{\bar{C}_B^{Z_A} C_A^{Z_B}} \qquad [2]$$

where $\bar{C}$s are the concentrations of the ions in the exchanger and Cs those in solution. Various concentration units are commonly used (molar, molal, equivalent fraction, etc.). When $z_A \neq z_B$, the numerical value of $k_{A/B}$ depends on the choice of the concentration units. The selectivity coefficient ($k_{A/B}$) usually changes as a function of exchanger composition ($k_{A/B} = f(\bar{C}_A)$; see **Figure 1**) and also as a function of the total concentration (or ionic strength) of the external solution, especially in concentrated solutions.

**Corrected selectivity coefficient** By making the activity (nonideality) correction for the solution phase, the so-called corrected selectivity coefficient is obtained:

$$k'_{A/B} = \frac{\bar{C}_A^{Z_B} a_B^{Z_A}}{\bar{C}_B^{Z_A} a_A^{Z_B}} = \frac{\bar{C}_A^{Z_B} C_B^{Z_A}}{\bar{C}_B^{Z_A} C_A^{Z_B}} \frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} = k_{A/B} \frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} \qquad [3]$$

where $a_A, a_B$ are the activities of ions $A, B$ in the solution. This quantity is independent of the total concentration of the external solution by definition and thus reflects the pure exchanger–ion interactions contributing to the selectivity. In dilute solutions,

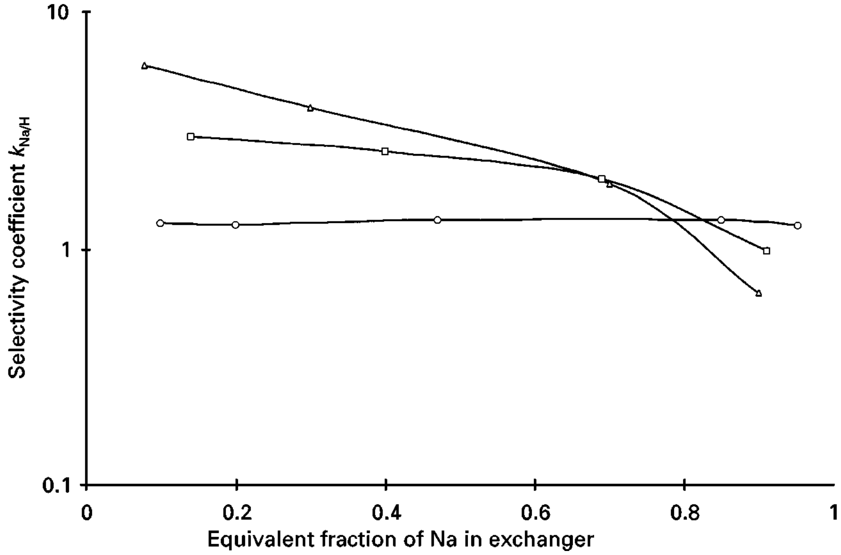

**Figure 1** Selectivity coefficient $k_{Na/H}$ (see eqn [2]) for $Na^+/H^+$ exchange is sulfonated polystyrene/divinylbenzene (DVB) resins as a function $Na^+$ equivalent fraction in resin at different degrees of cross-linking (nominal DVB content). Circles, DVB 5.5%; squares, DVB 15%; triangles, DVB 25%. (Data from Helfferich FG, 1995.)

$k'_{A/B} \approx k_{A/B}$. However, the corrected selectivity coefficient usually varies with the exchanger composition ($\bar{C}_A$).

**Thermodynamic equilibrium constant** The thermodynamic equilibrium constant $K_{A/B}$:

$$K_{A/B} = \frac{\bar{a}_A^{Z_B} a_B^{Z_A}}{\bar{a}_B^{Z_A} a_A^{Z_B}} = \frac{\bar{C}_A^{Z_B} C_B^{Z_A}}{\bar{C}_B^{Z_A} C_A^{Z_B}} \frac{\bar{\gamma}_B^{Z_A}}{\bar{\gamma}_A^{Z_B}} \frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} = k'_{A/B} \frac{\bar{\gamma}_B^{Z_A}}{\bar{\gamma}_A^{Z_B}} \qquad [4]$$

can be obtained by integrating the corrected selectivity coefficient as a function of exchanger composition. According to Argesinger *et al.* and Högfeldt *et al.*:

$$K_{A/B} = \int_0^1 \ln K_H \, d\bar{E}_A \qquad [5]$$

where $\bar{E}_A$ is the equivalent fraction of $A$ in the exchanger ($\bar{E}_A = z_A\bar{C}_A/(z_A\bar{C}_A + z_B\bar{C}_B)$) and $K_H$ is the corrected selectivity coefficient written with mole fractions ($\bar{X}$) as concentration units for the ions in the exchanger:

$$K_H = \frac{\bar{X}_A^{Z_B} C_B^{Z_A}}{\bar{X}_B^{Z_A} C_A^{Z_B}} \frac{\gamma_B^{Z_A}}{\gamma_A^{Z_B}} \qquad [6]$$

Gaines and Thomas supplemented the abstract thermodynamic treatment to include the contributions of salt imbibition and water activity changes, which need to be considered when ions are exchanged in concentrated solutions.

**Distribution coefficient (distribution constant, distribution ratio)** Various distribution constants and coefficients are used to measure the ion exchange equilibria. In general, the distribution coefficient $k_d$ of ion $A$ is defined as a concentration ratio in the exchanger and solution:

$$k_d = \frac{\bar{C}_A}{C_A} \qquad [7]$$

This quantity is only a constant under special conditions. In general, $k_d$ depends on the ionic composition of the exchanger and the solution. For a binary exchange, one obtains from eqns [2] and [7] that:

$$k_d = k_{A/B}^{\frac{1}{Z_B}} \left(\frac{\bar{C}_B}{C_B}\right)^{\frac{Z_A}{Z_B}} \qquad [8]$$

Under the special condition that $A$ is present in the solution and in exchanger at much lower concentration than $B$ ($C_A \ll C_B$, $\bar{C}_A \ll \bar{C}_B$), $k_{A/B}$ and $\bar{C}_B$ are essentially constant ($\bar{C}_B \approx Q$, the ion exchange capacity) and:

$$\log k_d = \frac{1}{Z_B} \log (k_{A/B} Q^{Z_A}) - \frac{Z_A}{Z_B} \log C_B \qquad [9]$$

Under these circumstances, $k_d$ depends only on the concentration of ion $B$ and, on a logarithmic scale, the slope of $k_d$ equals $-z_A/z_B$, the ratio of cation charges.

Experimentally determined graphs of $\log k_d$ vs $\log C_B$ (eqn [9]) are frequently used in research to study sorption mechanisms, the charges of the exchanging species and in the estimation of exchanger performance, e.g. in water purification (estimation of processing capacity) and in ion chromatography (estimation of retention volume). Great care should be taken, however, in the interpretation of the data and in making sure that the assumptions leading to eqn [9] are valid. Because of the widespread use of distribution coefficients in ion exchange, it is useful to emphasize this point by taking a binary uni-univalent exchange ($z_A = z_B = 1$) as an example here. For this equilibrium, eqn [9] can be further manipulated to give:

$$k_d = \frac{Q}{\dfrac{C_B}{k_{Cs/Na}} + C_A} \qquad [10]$$

This equation now shows that, in fact, the condition for linear dependence of $k_d$ on $C_A$ ($\log k_d = \log (k_{A/B}Q) - \log C_B$) is that $C_A \ll C_B/k_{A/B}$. Thus, even if $C_A \ll C_B$, the dependence may not be linear if the selectivity coefficient is very large. This feature of $k_d$ is shown as calculated examples in **Figure 2**. It can be seen that, if the selectivity coefficient is low, $k_d$ falls linearly with the concentration of the macro-ion B, on a logarithmic scale with a slope of $-1$, as eqn [9] implies. However, when the selectivity increases, the $k_d$ starts to level off at lower concentrations of B and ultimately becomes independent of $C_B$ when the selectivity is very high. In the studies of highly selective exchangers (zeolites and some other inorganic materials, chelating resins) such independence of $k_d$ on the macro-ion concentration is often observed and every now and then the incorrect conclusion is made that the uptake of trace ions is not ion exchange but some sort of surface adsorption reaction. Figure 2 also shows an interesting feature of the link between $k_d$ and selectivity: in dilute solutions the $k_d$s tend to a common value, which is determined by the ratio

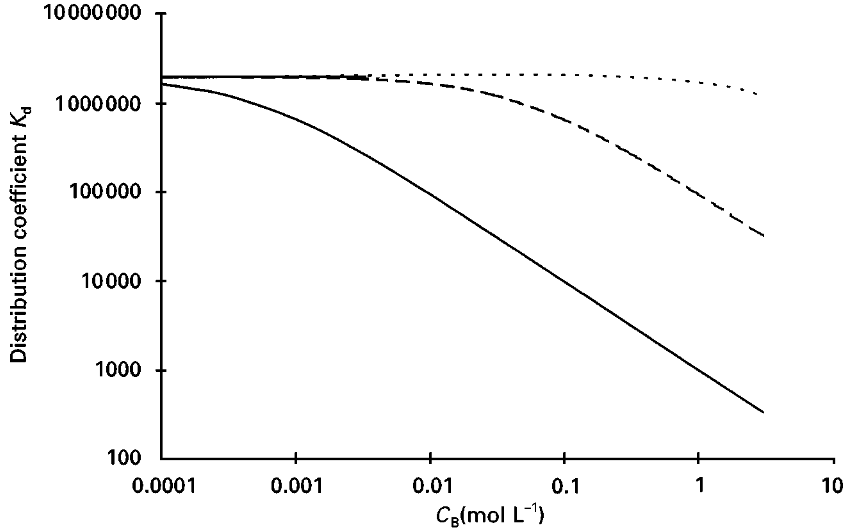

**Figure 2** Calculated values (eqn [10]) for the distribution coefficient $k_d$ for trace ion $A$ ($C_A = 10^{-6}$ mol L$^{-1}$) in binary univalent $A^+/B^+$ exchange as a function of macro-ion concentration $C_B$ at different values of the selectivity coefficient $k_{A/B}$. Dotted line, $k_{A/B} = 5\,000\,000$; dashed line, $k_{A/B} = 50\,000$; continuous line, $k_{A/B} = 500$. Ion exchange capacity of the exchanger 2.0 mmol g$^{-1}$.

of $Q/C_A$. The value of selectivity thus becomes unimportant in dilute solutions.

In general, eqn [9] is valid for several parallel trace ion exchange reactions ($A$, $C$, $D$ ...) in the presence of one common macro-ion $B$, since the ions that are present at trace level will have a negligible effect on other trace ion equilibria.

**Separation factor** Separation factor is usually used in ion exchange chromatography to estimate the separability of two trace ions. Considering the separation of two trace ions $A$ and $C$ using macro ions $B$ as an eluent, one obtains for the separation factor ($\alpha_{A/C}$):

$$\alpha_{A/C} = \frac{\bar{C}_A C_C}{C_A \bar{C}_C} = \frac{k_{d(A)}}{k_{d(C)}} = \left(\frac{k_{A/B}}{k_{C/B}}\right)^{\frac{1}{z_B}} \left(\frac{\bar{C}_B}{C_B}\right)^{\frac{z_A}{z_C}}$$
$$= \text{Constant}/C_B^{\frac{z_A}{z_C}} \qquad [11]$$

In the case that $z_A \neq z_C$, the separation factor increases as the concentration of $B$ is decreased.

**Ion exchange isotherm** An ion exchange isotherm is a function that represents the ionic composition of the exchanger ($\bar{E}_A$) as a function of the ionic composition of the solution ($E_A$), or vice versa, at constant temperature (**Figure 3**). Traditionally, the selectivity of the exchanger is estimated from the isotherm. If the isotherm is concave towards the axis representing the ion concentration in the exchanger, the ion exchanger is considered to be selective for that ion (curves a and b in Figure 3). If the isotherm lies on the diagonal of the presentation ($\bar{E}_A = E_A$), the exchanger has no preference for either ion $A$ or $B$ (curve c) and a bending of the isotherm towards the $E_A$-axis indicates that the exchanger is nonselective. The magnitude of the selectivity coefficient cannot be always deduced from the isotherm because when $z_A \neq z_B$, the shape of the isotherm depends strongly on the total ion concentration ($C_T$) in the solution. This behaviour arises from the difference between the cation charges, which can be clearly seen if the equation for the selectivity coefficient is expressed in terms of equivalent fractions and rearranged:

$$\frac{\bar{E}_A^{z_B}}{\bar{E}_B^{z_A}} = \frac{E_A^{z_B}}{E_B^{z_A}} k_{A/B} C_T^{(z_B - z_A)} \qquad [12]$$

At a given point $\bar{E}_A$ on the isotherm (the left-hand side of eqn [12] constant), the ratio $E_A/E_B$ must decrease as $C_T$ is decreased when $z_A > z_B$. Thus, the relative concentration of ion $A$ must decrease with decreasing $C_T$. This feature, the increased preference of an ion exchanger for the ion having a higher charge with the dilution of the solution, is called electroselectivity. It should be also noted that the ion exchanger may prefer ion $A$ strongly even though the value of the selectivity coefficient is equal to or less than unity (see calculated examples in Figure 3).

## Ion Exchange Kinetics

The rate of ion exchange is governed by the various diffusion processes in the system. In general,

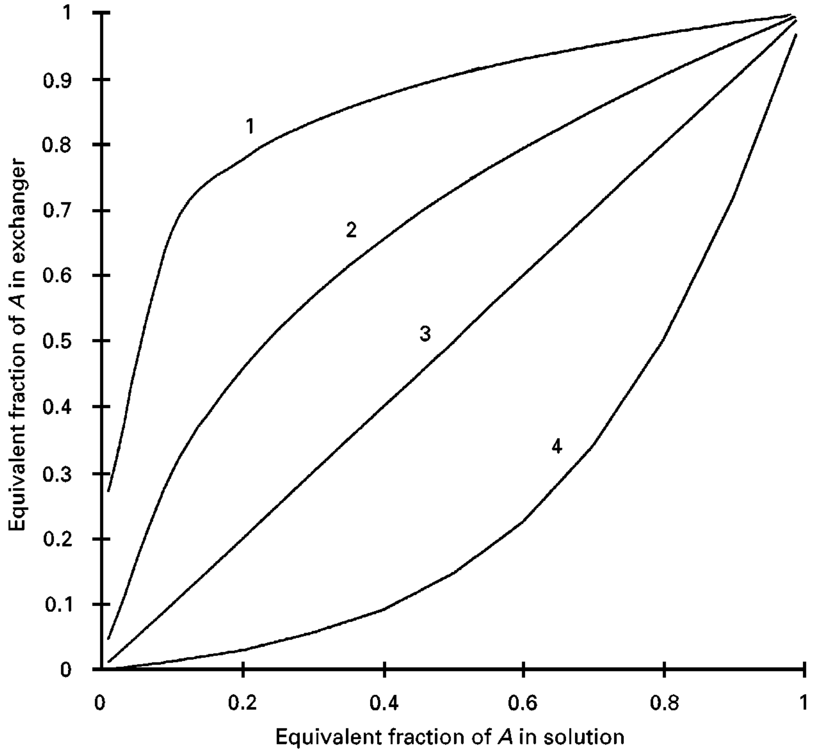

**Figure 3** Calculated ion exchange isotherms for a hypothetical di-univalent ($A^{2+}/B^{+}$) exchange having a selectivity coefficient $k_{A/B} = 1$. The isotherms have been generated using constant total ion concentrations: 1, 0.01 mol L$^{-1}$; 2, 0.1 mol L$^{-1}$; 3, 1 mol L$^{-1}$; 4, 5 mol L$^{-1}$. The isotherms show increasing preference of the ion exchanger for ion *A* with increasing dilution of the solution (electroselectivity effect.)

diffusion can be described by Fick's first law. The flux of ion $A(J_A)$ is given by:

$$J_A = -D \operatorname{grad} C_A \qquad [13]$$

where $D$ is the diffusion coefficient. This equation describes purely statistical diffusion that is driven by the concentration gradient. In ion exchangers it is usually necessary to consider also the electric potential ($\varphi$) and then the flux of ion $A$ ($J_A$) is given by the Nernst–Planck equation:

$$J_A = -D\left(\operatorname{grad} C_A + z_A C_A \frac{F}{RT} \operatorname{grad} \varphi\right) \qquad [14]$$

where $F$ is the Faraday constant. Most commonly, the kinetics of ion exchange reactions are interpreted in the terms of external or internal diffusion. As the external solution is usually agitated, there is essentially no concentration gradient in the bulk of the external solution. Gradients arise, however, within a thin layer of solution adhering to the surface of the exchanger particle. Diffusion across this layer is called film diffusion. This concept, developed first by Nernst, often satisfactorily describes the diffusion processes at solid–solution interfaces. The internal diffusion of the ions in the exchanger phase is called particle diffusion. Most often, the particle is considered homogeneous, so that the different diffusional processes within the particle (pore diffusion, matrix diffusion) are represented by a single particle diffusion coefficient. Either particle or film diffusion may be the rate-determining step for the exchange process or both may contribute to the rate in intermediate cases. In general, film diffusion may dominate at early stages of exchange (*A* low in exchanger, *B* low in solution) when the concentration gradient in the particle is large (fast rate in particle). However, as the exchange proceeds further, the concentration gradients in the particle decrease and particle diffusion may become the rate-determining step.

In the exchange process, ions *A* and *B* move in opposite directions. Therefore, generally, the so-called interdiffusion coefficient ($D_{A/B}$) must be used in eqns [13] and [14]. For particle diffusion:

$$\bar{D}_{A/B} = \frac{\bar{D}_A \bar{D}_B (z_A^2 \bar{C}_A + z_B^2 \bar{C}_B)}{z_A^2 \bar{C}_A \bar{D}_A + z_B^2 \bar{C}_B \bar{D}_B} \qquad [15]$$

Normally, the interdiffusion coefficient is not constant, but changes with the ionic composition ($\bar{C}_A$) of the exchanger. To calculate ion exchange rates in a given ion exchange system, the Nernst–Planck equations must be solved simultaneously for each diffusing species under boundary conditions specific to the system. In general, the resulting equations are nonlinear differential equations, which have analytical solutions only in some special cases. Such a case, for instance, is isotopic ion exchange, for which a so-called self-diffusion constant can be used. Assuming also that the solution has indefinite volume – the concentration of ion in the solution remains essentially constant – it is obtained for the half-time ($t_{1/2}$) of the exchange reaction. In the case of particle diffusion:

$$t_{1/2} = 0.030 \frac{r_0^2}{\bar{D}} \qquad [16]$$

where $r_0$ is the radius of the exchanger particle and $\bar{D}$ is the particle diffusion coefficient. For film diffusion:

$$t_{1/2} = 0.23 \frac{r_0 \delta Q}{DC} \qquad [17]$$

where $\delta$ is the film thickness, $Q$ the ion exchange capacity, $D$ the film diffusion coefficient and $C$ is the ion concentration. For particle diffusion (eqn [16]), the rate of exchange increases ($t_{1/2}$ decreases) as the particle radius decreases, being proportional to $1/r_0^2$. For film diffusion (eqn [17]), the rate increases less strongly as $r_0$ is decreased (the proportionality is to $1/r_0$). In film diffusion the exchange rate can also be increased by increasing the efficiency of agitation, which will decrease the film thickness. In real applications of ion exchange the exchange rates do not usually follow the simple relationships of eqns [16] and [17] and the equations are presented here just to give a simple view of the factors that can affect the ion exchange rates.

The values of film diffusion coefficients are of the same order of magnitude as the diffusion coefficients of ions in the external salt solution ($D \approx 10^{-5}\,\mathrm{cm^2\,s^{-1}}$). The values of particle diffusion coefficients depend strongly on the charge of the ion and on the structure and porosity of the exchanger matrix. In sulfonated polystyrene resins $\bar{D}$ decreases with increasing degree of cross-linking, being in the range of $10^{-5}$–$10^{-7}\,\mathrm{cm^2\,s^{-1}}$ for univalent cations. For multivalent cations, the values are much lower, falling in the range of $10^{-7}$–$10^{-10}\,\mathrm{cm^2\,s^{-1}}$. In weakly acidic resins and in crystalline inorganic ion exchangers, cation diffusion coefficients are typically 2–5 orders of magnitude lower.

## Basic Ion Exchange Operations

Ion exchange reactions can be carried out as either batch or column operations. Column operation is far more common and efficient than batch operation. Batch operation is however used in research, because the experiment is simple to carry out and a large number of experiments can be carried out in parallel.

### Batch Operation

In batch operation, a given amount ($m$) of ion exchanger is contacted with a given volume ($V$) of solution. The mixture is agitated until equilibrium has been attained. In typical binary batch process used for ion exchange studies (e.g. determination of $k_{A/B}$ as a function $\bar{C}_A$, Figure 1), the exchanger is initially in a homoionic form (e.g. the $B$ form) and the solution initially contains only the ion $A$. Considering the simple uni-univalent exchange as an example, the ratio of ion concentrations at equilibrium is given by:

$$\frac{\bar{C}_A}{\bar{C}_B} = k_{A/B}\left(\frac{C_A}{C_B}\right) \qquad [18]$$

In general, to achieve a high conversion to the $A$ form in a single batch equilibration, the selectivity coefficient $k_{A/B}$ and the ratio $C_A/B_B$ must be high. In practice, the degree of conversion to the $A$ form is controlled by adjusting the initial concentration of $A$ ($C_{A0}$) in the solution and the solution to solid ratio ($V/m$), often also called the batch factor (BF):

$$\bar{C}_A = (C_{A0} - C_A)\frac{V}{m} \qquad [19]$$

At constant $C_{A0}$, the degree of conversion increases as $V/m$ is increased (**Figure 4**). It is usually difficult to obtain a high conversion in a single batch equilibration, since the selectivity often decreases with increasing conversion and there is always ion $B$ in the solution released from the exchanger. Removing $B$ from the solution can enhance conversion. This can be achieved by equilibrating the ion exchanger successively with fresh portions of solution $A$.

### Column Operation

There are several types of column operation, classified according to the technical design of the apparatus

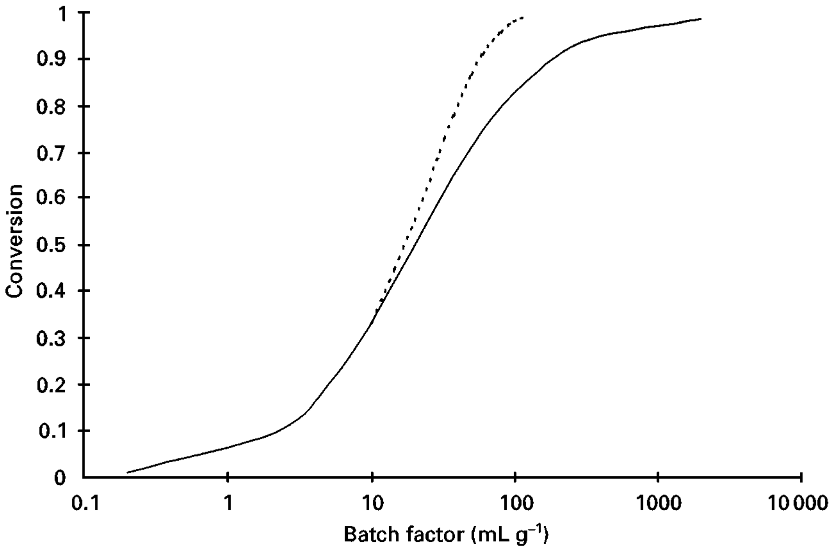

**Figure 4** Batch ion exchange: calculated degree of conversion from the $B^+$ form to the $A^+$ form as a function of solution volume to exchanger mass ratio (batch factor). Selectivity coefficient $k_{A/B} = 1$, ion exchange capacity 2 mmol g$^{-1}$. The solid line represent the conversion in single batch equilibration. The broken line represents successive batch equilibrations with a constant batch factor of 10 mL g$^{-1}$.

(e.g. fixed-bed or floating-bed operation) or according to the purpose of the application (e.g. column chromatography or column separation).

**Column separation** Column separation usually involves elimination of undesirable ions from water (deionization, softening, decontamination). Taking the binary exchange discussed earlier as an example, a solution containing harmful ions (*A*) is passed through the column that contains an exchanger in the *B* form. The *A* ions are then taken up by the exchanger and *B* ions are released into the solution. Because *B* ions are constantly removed from the system, the operation is much more efficient than batch exchange in removing *A* ions from the solution (see eqn [18]). The column effluent is first free of ion *A*, but when a given amount of solution has been passed through, *A* starts to emerge in the effluent and its concentration increases gradually to that in the influent solution (**Figure 5**). The graph of the concentration of *A* in effluent as a function of effluent volume is called the breakthrough curve.

The area above the breakthrough curve gives the total volume of solution that has been freed from ion A. Dividing this volume by bed mass or volume gives the total processing capacity, or theoretical capacity ($Q_T$), of the column (L kg$^{-1}$ or L L$^{-1}$). In this simple example, $Q_T = Q/C_A$ ($Q$ = ion exchange capacity in mmol L$^{-1}$ or mmol mL$^{-1}$) since at equilibrium *A* ions have taken up all of the ion exchange capacity. In general, $Q_T$ is equal to $k_d$, which can be easily calculated in binary systems from eqn [9] for trace ions to be separated, provided that selectivity coefficients are known. However, because ion *A* is considered harmful, operation is not continued until total processing capacity has been used, but the feed is discontinued when the concentration of *A* in the effluent reaches a measurable or a regulated value. The capacity at this point is called the processing capacity, or breakthrough capacity ($Q_B$). The ratio $Q_B/Q_T$ is called the column utilization factor, $F_U$. For efficient separation process $F_U$ should be maximized.

**Column chromatography** In column chromatography ions are separated from each other for analysis or for chemical production purposes. Considering a simple example in which ions *A* and *C* are separated for analysis, a sample solution containing *A* and *C* is passed into the column containing an exchanger in the *B* form. The sample volume is so low that *A* and *C* take up only a very small fraction of the column capacity near the inlet. After sample injection, an eluent solution containing ion *B* is passed through the column. *A* and *C* in the exchanger are exchanged for *B* and begin to move through the column at different velocities. At a given volume, the less preferred ion *A* first emerges in the eluent as a concentration peak followed by ion *C*. The eluent volumes at which *A* and *C* emerge, i.e. the volumes at the peak maxima, are called the retention volumes ($V_R$) and they can be obtained from the relation:

$$V_R = k_d V_S + V_M \qquad [20]$$

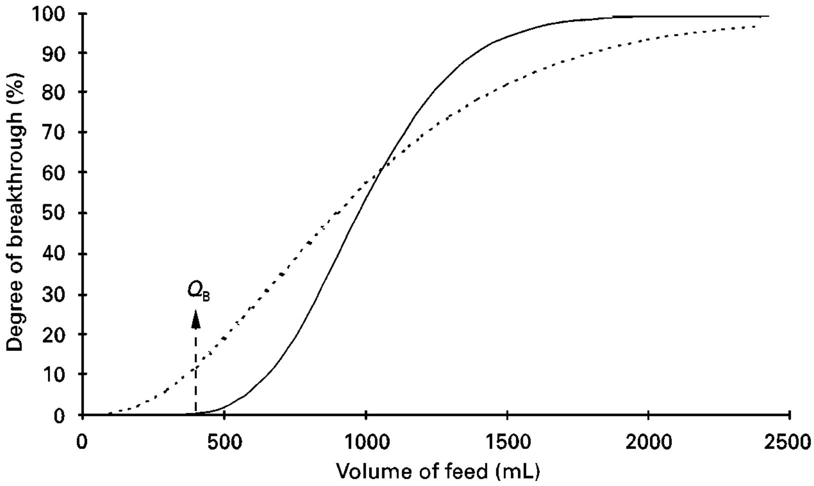

**Figure 5** Examples of column breakthrough curves generated for different number of theoretical plates $N$ (see eqns [22]–[27]). In this example, the capacity of the exchanger ($Q$) is 1 mmol mL$^{-1}$ and the exchanger bed volume is 1 mL. The exchanger is initially in the $B^+$ form and the feed contains only ion $A^+$ at a concentration of 0.001 mmol mL$^{-1}$ ($C_A$). The total processing capacity $Q_T$ is thus $Q/C_A = 1000$ mL mL$^{-1}$ exchanger and the area above the breakthrough curves is 1000 mL for the 1 mL bed. The breakthrough capacity $Q_B$ depends on $N$, which is affected by the operating conditions. Continuous line, $N = 30$; broken line, $N = 10$.

where $V_S$ is the volume of ion exchanger bed and $V_M$ is the free solution volume in the bed. In analytical separations $A$ and $C$ are present at trace levels, so $k_d$ values are again easily calculated from eqn [9]. In analytical work, efficient operation requires that the concentration peaks of $A$ and $B$ are well separated (the peaks are sharp). The retention volumes $V_R$ should not be too large, because this leads to a long analysis time and to broadening of the peaks.

## Theory of Column Exchange

Most models for ion exchange column operation are based on the concept of effective plates or transfer units. Martin and Synge first used this concept for chromatography and the theory was refined by Glueckauf, who obtained for the material balance in the ion exchange column, under linear equilibrium ($k_d$ constant):

$$\left(\frac{\partial C_i}{\partial z}\right)_V + q(k'_d + \beta)\left(\frac{\partial C_i}{\partial V}\right)_Z - \frac{H}{2}\left(\frac{\partial^2 C_i}{\partial z^2}\right)_V = 0 \qquad [21]$$

where $z$ is the longitudinal coordinate in the column, $q$ is the cross-sectional area of the bed, $k'_d$ is the column distribution coefficient in which the exchanger phase concentration of species $i$ is calculated per unit volume of the bed, i.e. $k'_d$ is obtained from the $k_d$ of eqn [7] as $k'_d = k_d\,(1 - \beta)$, where $\beta$ is the bed void fraction. $H$ is the effective height of the theoretical plate given by:

$$H = H_0 + H_P + H_F + H_L \qquad [22]$$

$H_0$, $H_P$, $H_F$ and $H_L$ are the contributions of particle size, particle diffusion, film diffusion and longitudinal diffusion to the effective height:

$$H_0 = 1.64\, r_0 \qquad [23]$$

$$H_P = \frac{k'_d}{(k'_d + \beta)^2}\,\frac{0.14\, r_0^2\, u}{\bar{D}} \qquad [24]$$

$$H_F = \left(\frac{k'_d}{k'_d + \beta}\right)^2 \frac{0.266\, r_0^2\, u}{D(1 + 70 r_0 u)} \qquad [25]$$

$$H_L = \frac{D\beta\sqrt{2}}{u} \qquad [26]$$

where $u$ is the linear flow rate. The number of theoretical plates ($N$) in the column is then obtained by dividing the column length $L$ by $H$:

$$N = \frac{L}{H} \qquad [27]$$

In general, the column performance improves as $N$ is increased. In column separations the increase in $N$ makes the breakthrough curve steeper (breakthrough capacity $Q_T$ increases). In column chromatography, increase in $N$ makes the elution peaks sharper and so increases the separation of two peaks. For a column with a constant length $Z$, $N$ can be increased by decreasing the plate height $H$. The easiest way of doing this is to decrease the particle radius (see eqns [23]–[25]), but there is a practical lower limit for $r_0$, because the hydrodynamic pressure increases with decrease in $r_0$. Another way to increase $N$ is to decrease flow rate (eqns [24] and [25]), but a very low rate is not usually acceptable due to the effect of longitudinal diffusion (eqn [26]), which causes poor separation.

## Equilibrium Theories

Much theoretical work has been carried out to explain the nonideality of the ion exchange systems, e.g. for the calculation of ion exchange equilibria and to understand the factors that give rise to ion exchange selectivity. For ions in solution, sufficient theories exist to calculate the nonideality (activities) in the liquid phase. For the ions in the exchanger phase, no generally valid theories exist. For the calculation of ion exchange equilibria, it is always possible to measure the nonideality of the exchanger phase, e.g. the corrected selectivity coefficient $k'_{\mathrm{A/B}}$ as a function of exchanger ion composition at a given total solution concentration ($C_{\mathrm{T}}$) and then use the measured function for the calculation of equilibria at other $C_{\mathrm{T}}$ values from equation:

$$k'_{\mathrm{A/B}} \frac{\bar{E}_{\mathrm{B}}^{Z_{\mathrm{A}}}}{\bar{E}_{\mathrm{A}}^{Z_{\mathrm{B}}}} = \frac{E_{\mathrm{B}}^{Z_{\mathrm{A}}}}{E_{\mathrm{A}}^{Z_{\mathrm{B}}}} \frac{\gamma_{\mathrm{B}}^{Z_{\mathrm{A}}}}{\gamma_{\mathrm{A}}^{Z_{\mathrm{B}}}} C_{\mathrm{T}}^{(Z_{\mathrm{A}} - Z_{\mathrm{B}})} \qquad [28]$$

In general, $k'_{\mathrm{A/B}}$ and $\gamma_{\mathrm{A}}/\gamma_{\mathrm{B}}$ are not known simultaneously, so iteration must be used to solve eqn [28]. The same approach can be extended to systems containing more than two counterions, e.g. for the ternary system the corrected selectivity coefficients $k'_{\mathrm{A/BC}}$, $k'_{\mathrm{B/CA}}$ and $k'_{\mathrm{C/AB}}$ can be measured and used for the calculation of the equilibria. For instance, $k'_{\mathrm{A/BC}}$ is defined as:

$$k'_{\mathrm{A/BC}} = \frac{\bar{E}_{\mathrm{A}}^{2Z_{\mathrm{B}}Z_{\mathrm{C}}}\, C_{\mathrm{B}}^{Z_{\mathrm{A}}Z_{\mathrm{C}}} C_{\mathrm{C}}^{Z_{\mathrm{A}}Z_{\mathrm{B}}}}{\bar{E}_{\mathrm{B}}^{Z_{\mathrm{A}}Z_{\mathrm{C}}} \bar{E}_{\mathrm{C}}^{Z_{\mathrm{A}}Z_{\mathrm{B}}}\, C_{\mathrm{A}}^{2Z_{\mathrm{B}}Z_{\mathrm{C}}}} \frac{\gamma_{\mathrm{B}}^{Z_{\mathrm{A}}Z_{\mathrm{C}}} \gamma_{\mathrm{C}}^{Z_{\mathrm{A}}Z_{\mathrm{B}}}}{\gamma_{\mathrm{A}}^{2Z_{\mathrm{B}}Z_{\mathrm{C}}}} \qquad [29]$$

for the exchange reaction:

$$2z_{\mathrm{B}}z_{\mathrm{C}}A + z_{\mathrm{A}}z_{\mathrm{C}}\bar{B} + z_{\mathrm{A}}z_{\mathrm{B}}\bar{C} \leftrightarrow 2z_{\mathrm{B}}z_{\mathrm{C}}\bar{A} + z_{\mathrm{A}}z_{\mathrm{C}}B + z_{\mathrm{A}}z_{\mathrm{B}}C \qquad [30]$$

$k'_{\mathrm{B/CA}}$ and $k'_{\mathrm{C/AB}}$ are defined accordingly. It is intrinsic to this method that it gives precise results provided that the selectivity coefficients are measured and described precisely within the exchanger composition range of interest. In practice this requires large number of measurements, which makes the method very laborious. Less effort is associated with approaches in which the solid-phase activity coefficients in multicomponent systems are estimated from the binary interaction parameters ($\Lambda$), e.g. from the Wilson equation it is obtained that:

$$\ln \bar{\gamma}_i = 1 - \ln\left(\sum_{j=1}^{M} \bar{X}_i \Lambda_{ij}\right) - \sum_{k=1}^{M} \left(\frac{\bar{X}_k \Lambda_{ki}}{\sum_{j=1}^{M} \bar{X}_j \Lambda_{kj}}\right) \qquad [31]$$

Parameter $\mathit{\Lambda}$ can be determined from the measurements of the corrected selectivity coefficients of the binary equilibria $i/j$, $k/i$ and $k/j$ by curve fitting. Activity coefficients obtained by eqn [31] are then used in the binary equations of thermodynamic equilibrium constant (eqn [4]) for the calculation of ion exchange equilibria. This method has given accurate results even in four-component systems (e.g. Na/K/Ca/Mg in a strong acid cation resin). Several other related approaches have been developed.

The theories above are based on the measurements of nonideality and make no assumptions about the interactions that give rise to the selectivity. Thus, they do not allow the calculation of $K_{\mathrm{A/B}}$, $k'_{\mathrm{A/B}}$ or $\bar{\gamma}_{\mathrm{i}}$ from the fundamental data or explain the changes of $k'_{\mathrm{A/B}}$ or $\bar{\gamma}_{\mathrm{i}}$. The first theory to explain the nonideality of the exchanger phase was developed by Kielland (the graphical presentations of Figure 1 are often called Kielland plots), who considered van der Waals-type interactions and showed that for the solid-phase activity coefficients:

$$\bar{\gamma}_{\mathrm{AR}} = c\bar{X}_{\mathrm{AR}}^2 \qquad [32]$$

$$\bar{\gamma}_{\mathrm{BR}} = c\bar{X}_{\mathrm{BR}}^2 \qquad [33]$$

Here, AR and BR denote the salt forms of the exchanger, R being the common anion. This theory predicts that the function $k'_{\mathrm{A/B}} = f(\bar{X}_{\mathrm{A}})$ is linear, which is in agreement with the observed behaviour in many cases. Quite often, the $k'_{\mathrm{A/B}}$ functions are not linear, but slightly, or even strongly, curved (see Figure 1). Some of these nonlinear functions can be explained by assuming that the exchanger has several types of exchange sites, each subsite having a characteristic selectivity coefficient $k'_{\mathrm{i}}$. The measured overall $k'_{\mathrm{A/B}}$ decreases with $\bar{X}_{\mathrm{A}}$ as sites with higher selectivity are filled first. If these subsites behave ideally, sigmoidal curves are obtained for $k'_{\mathrm{A/B}} = f(\bar{X}_{\mathrm{A}})$. By assuming nonideal behaviour for the subsites, the $k'_{\mathrm{A/B}}$ functions exhibit a wide variety of different forms. This theory has been found to be consistent with the behaviour of several zeolite systems.

A related approach is to consider the different states that a given counterion may assume depending on the neighbouring counterions. In a polymer chain (as in an organic ion exchange resin), considering the two nearest neighbours, each counterion can have three different energetic levels. As a consequence, in general $k'_{A/B} = f(\bar{X}_A)$ is a second-order polynomial function in $\bar{X}_A$, which is often the observed trend in organic resins (Figure 1). If two of the three energy levels are close to each other, the selectivity function is linear. Theories of this type are helpful in the calculation of ion exchange equilibria and in presenting the equilibria in a mathematical form, but they give no information about the magnitude of selectivity. In organic resins, various osmotic theories have been developed to estimate the relative magnitude of selectivity. The base in these theories is that:

$$K_{A/B} = \frac{\Pi}{RT}(z_B v_B - z_A v_A) \qquad [34]$$

where $\Pi$ is the osmotic pressure difference between the external solution and exchanger pore liquid and $v_A$ and $v_B$ are the partial molar volumes of *A* and *B* in the exchanger. The osmotic theory predicts the selectivity trend (I):

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

observed in strong-acid cation resins, i.e. ions with smaller hydrated radius (smaller partial molar volume) are preferred, because replacing larger ions with smaller ones will reduce the swelling pressure. The same selectivity trend can also be predicted from purely electrostatic calculations. The dielectric theory:

$$\ln K_{A/B} = \frac{-e^2}{8\pi kT}\left[\left(\frac{z_A}{r_A} - \frac{z_B}{r_B}\right)\left(\frac{1}{\varepsilon_Z} - \frac{1}{\varepsilon_S}\right)\right] \qquad [35]$$

where $\varepsilon_Z$ and $\varepsilon_S$ are the macro-permittivities of the exchanger and solution phases, respectively, predicts that in uni-univalent exchange, the selectivity decreases as the framework charge density increases for selective exchange ($K_{A/B} > 1$). This trend is commonly observed for zeolite ion exchange.

The selectivity sequence I for alkali metal ions, shown above, is common in organic resins have a low degree of cross-linking and in zeolites with low framework charge density. Other selectivity sequences appear as the degree of cross-linking or framework charge density increases:

II. Cs > K > Rb > Na > Li
III. K > Cs > Rb > Na > Li
IV. K > Cs > Na > Rb > Li
V. K > Na > Cs > Rb > Li
VI. K > Na > Rb > Cs > Li
VII. Na > K > Rb > Cs > Li
VIII. Na > K > Rb > Li > Cs
IX. Na > K > Li > Rb > Cs
X. Na > Li > K > Rb > Cs
XI. Li > Na > K > Rb > Cs

Most of these sequences have been observed in ion exchangers and they can be predicted from Eisenman theory, originally developed for selective glass electrodes. The theory considers cation exchange site and cation water (hydration) interaction energies. The free energy of exchange is obtained from:

$$\Delta F^0_{AB} = (\bar{F}^{el}_A - \bar{F}^{el}_B) - (\bar{F}^{hyd}_A - \bar{F}^{hyd}_B) \qquad [36]$$

where $F^{el}$ is the coulombic interaction energy between cation and the anionic exchange site and $F^{hyd}$ is the hydration energy of the cation. The coulombic interaction energy for a univalent cation can be calculated for widely separated sites from:

$$\bar{F}_{el} = -332/(r_+ + r_-) \qquad [37]$$

and for closely spaced sites:

$$\bar{F}_{el} = -1.56 * 332/(r_+ + r_-) \qquad [38]$$

where $r_+$ is the cation radius and $r_-$ is the radius of the anionic exchange site. The anionic field strength decreases as $r_-$ increases. Selectivity pattern I is exhibited by exchangers having a low field strength and cations are exchanged in the hydrated state with a preference for a smaller hydrated radius. As the field strength is increased, the less hydrated cations become desolvated and the selectivity patterns start to change. At high field strength, pattern XI is exhibited and cations are exchanged as bare cations.

## Conclusions

Rather simple theoretical concepts are available to describe ion exchange phenomena and applications in a qualitative manner. In some cases these concepts may give a good quantitative agreement, but generally more rigorous theories are required, considering the specific details of given systems. The application of even the simplest theories usually involves much experimental and computational effort when systems comprising more than two exchanging ions are involved.

*See also:* **II/Ion Exchange:** Historical Development.

## Further Reading

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# MASS SPECTROMETRY

## Spectrometry–Mass Spectrometry Ion Mobility

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### Introduction

The principle of mass spectrometry (MS) is the separation of ions in a vacuum, using an electrical or magnetic field or a combination of both. The ions may be formed through a variety of processes, but it is perhaps the fragmentation of the molecular ion that produces much of the analytical power of the technique. Mass-to-charge ratios are recorded and the structure of the parent ion may be determined from the ion molecular mass and the pattern of the fragment ions recorded. Experienced mass spectrometrists can recognize typical fragment ion patterns, however, although there are libraries available for the automated identification of mass spectra, careful judgement must be used in the final assignment of the compound's identity. The theory and uses of MS have been well documented as an analytical technique both as a standalone and a hyphenated technique, for example coupled with gas chromatography (GC-MS).

Less is known about the chemistry within ion mobility spectrometers, which are used in the field to monitor for contraband substances such as explosives, drugs, and on the battlefield to detect chemical warfare agents. Originally referred to as plasma chromatography, ion mobility spectrometry (IMS) is a technique concerned with the formation of ion-molecule clusters in air and their movement in an electric field, at or close to atmospheric pressure. The average ion velocity of an ion species in an electric field, $v_d$, is the product of that electric field, $E$, and a constant of proportionality, $K$, i.e. $v_d = KE$. $K$ is called the mobility of the ions, and is characteristic of a particular ion species in a specified drift gas. $K$ may be calculated indirectly from drift time, $t_d$, from the equation $t_d = l_d/v_d$, where $l_d$ is the drift length. The theory of ion mobility and reaction chemistry is covered in two monographs listed in the Further Reading section, and need not be reproduced here. Notably, the Mason–Schamp equation for mobility (an equation that attempts to reconcile fundamental properties of ions with their mobility) includes a term containing a collision integral, to which mobility is inversely proportional. The value of the collision integral is determined by the cross-section. Therefore, the mobility, and consequently the ion drift velocity, is dependent upon mass, size, shape, and polarizability. The mobilities observed for ions are weighted averages of the mobilities of all the cluster ions participating in a localized equilibrium between the ion swarm and the neutral molecules they encounter as they traverse the drift region. If the drift gas, electric field gradient, temperature, pressure, and therefore the molecular number density remain constant, mobility depends only on ion charge, reduced mass, and collision cross-section. The collision processes undergone by ions during their drift time are very complicated, and are much too complicated to go into here. However, it must be noted that these processes are affected by variations in temperature and pressure in the drift region. Ion cluster formation and fragmentation are also governed by temperature. Therefore, to simplify the situation, and to allow easy comparison between different systems, mobility of an ion is normalized for temperature and pressure, the corrected term being referred to as reduced mobility, $K_0$ ($\mu_0$ in some texts).

The initial distribution of ions immediately following ionization is modified by various chemical