Interpretation and Correlation of Ion Exchange Column Performance Under Nonlinear Equilibria

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Various methods are known for interpreting experimental data for linear-equilibrium cases or constant-pattern break-through curves where either external or internal diffusion alone controls the rate in the ion exchange column. The present paper provides interpretive techniques for nonlinear equilibrium cases where the rate is controlled by a combined diffusion mechanism. The techniques can be applied whether or not the value of the equilibrium constant is known.

A completely general correlational method is derived for adding the mass transfer resistances under conditions of nonlinear equilibrium. Published break-through results from numerous sources and from new measurements, evaluated by the techniques described, are used to determine the numerical constants for the general correlation.

The fundamental design of fixed-bed ion exchange columns rests upon three separate steps: first, experimental data from the laboratory or pilot plant must be evaluated to determine the rate, equilibrium, and stoichiometric-capacity coefficients for the ion exchange system of interest; second, since it is impractical to do laboratory studies under all the conditions that might be encountered in full-scale operations, a means must be available for relating these coefficients to the operating variables; and, third, rate information must be introduced into design methods for predicting the break-through behavior as outlined by other investigators (*3, 12, 22, 27, 28*) and by some of the present authors (*16, 30, 31, 32*).

It is now well known that the break-through behavior or concentration history of an ion exchange column depends upon the mass-action equilibrium constant for the exchange reaction as well as upon the rate of exchange and other measurable factors. The break-through curve becomes less sharp if either the rate coefficient or the equilibrium constant is diminished. Moreover, the break-through curve does not have the same shape when external diffusion controls as when internal diffusion controls or as when a combination of these two rate-determining mechanisms is involved. For the interpretation of data, the choice of procedures will be seen to depend upon whether the equilibrium constant and the rate-controlling mechanism are both known.

The methods by which rate and other parameters are obtained from column-break-through measurements include matching of experimental and theoretical concentration histories, fitting of the curves to derived equations, and calculation from the slope of the curve at its midpoint. One or another of these techniques has been used for external diffusion controlling (*3, 11, 14, 16, 22, 27, 28*), internal diffusion controlling (*13, 16, 30*), and a reaction-kinetic representation (*4, 5, 7, 8, 12, 16, 23, 29, 31*). The midpoint slope has been used in an approximate reaction-kinetic calculation by Gilliland and Baddour (*12*) to treat a combination of internal and external diffusion mechanisms.

This paper will provide both a more rigorous treatment of the situation where external- and internal-diffusion resistances are combined and also a method for predicting in advance which mechanism is controlling. Part I indicates the evaluation techniques available for either a known or an unknown equilibrium constant and presents some new procedures. Part II gives the exact relationship between the reaction-kinetic rate constant obtained from the midpoint slope and the individual diffusion coefficients. This information is used to correlate break-through data for twelve different ion systems and a variety of operating conditions into a general equation.

I. MIDPOINT-SLOPE INTERPRETATION OF EXPERIMENTS WITH NONLINEAR EQUILIBRIUM

An algebraic criterion will be derived for determining whether external or internal diffusion controls or whether a column operation is in the intermediate region. This criterion is applicable both for interpreting experimental results and for making design predictions. Its numerical coefficients are obtained from the correlation to be developed in Part II. Use of the midpoint-slope method for evaluating the rate parameters is facilitated by two new plots which are presented. One plot is more applicable to combined mechanisms, and a second may be preferred when a single diffusional mechanism controls. Either plot can be used when the equilibrium constant for exchange is known and also with certain types of run data when the equilibrium is not known.

Basic Definitions for Various Transfer Mechanisms

The rate relations for the diffusion mechanisms have been stated in three earlier papers (*16, 30, 31*). This paper is based especially upon reference *16*, and the results derived therein will be applied here without further proof. In terms of the individual coefficients and the interfacial concentrations, the rate equation for external (fluid-film) diffusion is [*16*, Eq. (34)]

$$\frac{dq_A}{d\tau} = (k_f)_A a_v \frac{\epsilon}{\rho_b} [c_A - (c_A)_i] \quad (1)$$

and, as a first approximation, for internal (particle) diffusion [*16*, Eq. (42) and *30*]

$$\frac{dq_A}{d\tau} = (k_p)_A a_v [(q_A)_i - q_A] \quad (2)$$

Here q_A and c_A are the concentrations of component A on the coexisting solid and fluid phases; $(k_f)_A$ and $(k_p)_A$ are the mass transfer coefficients for external and internal diffusion controlling, respectively; a_v is the transfer area per unit of volume of bed, which is given by the external-surface area of the particles; ϵ is the fraction of voids in the column, external to the particles; ρ_b is the bulk density of the resin as packed; and τ is time.

These rate equations are applied to a typical exchange reaction involving ions of equal valence. In this case the equi-

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librium resin concentration, q_A^*, is given by the explicit relation [*16*, Eq. (43)]

$$q_A^* = \frac{K_A Q c_A}{(K_A - 1)c_A + C_0} \qquad (3)$$

where K_A is the equilibrium mass-action constant;* the total ultimate exchange capacity of the resin, Q, is equal to $(q_A + q_B)$ or $(q_A^* + q_B^*)$; and the total ionic level of the solution, C_0, is equal to $(c_A + c_B)$.

If $c_A = (c_A)_i$, then $q_A^* = (q_A)_i$ in Equation (3), because equilibrium is maintained at the particle interface. Equation (3) can also be used to relate c_A^* and q_A.

Combined Diffusional Resistances. By equating the diffusional rates given by Equations (1) and (2), rearranging, and multiplying both sides of the new relation by $(q_A)_0^*/(c_A)_0$, two equivalent ratios result which are defined as a mechanism parameter ζ:

$$\zeta = \frac{\mathbf{D}_A (k_p)_A}{(k_f)_A} = \frac{(q_A)_0^*[c_A - (c_A)_i]}{(c_A)_0[(q_A)_i - q_A]} \qquad (4)$$

where

$$\mathbf{D}_A = (q_A)_0^* \rho_b / (c_A)_0 \epsilon \qquad (5)$$

and $(q_A)_0^*$ is the equilibrium exchange capacity of the resin corresponding to complete saturation with a fluid of entering composition $(c_A)_0$. [When the feed contains only one of the exchanging ions, $(q_A)_0^* = Q$ and $(c_A)_0 = C_0$.] It is noted that ζ will range from zero to infinity during the transition from internal [$(k_p)_A$ small] to external [$(k_f)_A$ small] diffusion controlling.

As will be shown later, Equation (16), the ratio of the mass transfer coefficients, leads to

$$\zeta = \mathbf{D}_A \frac{\beta_1 (D_p)_A}{\beta_2 (D_f)_A N_{Re}^{\,m} N_{Sc}^{\,n}} \qquad (6)$$

Here $(D_f)_A$ and $(D_p)_A$ are the diffusivities of ion A against the exchanged ion in the fluid and particle, respectively; and β_1, β_2, m, and n are dimensionless constants. The Reynolds number is as given by Ergun (*9*):

$$N_{Re} = \frac{d_p R \rho}{6(1 - \epsilon) S \mu} \qquad (7)$$

with d_p the resin particle diameter, R/S the superficial solution velocity through the column, and μ/ρ the kinematic viscosity. The Schmidt number is

$$N_{Sc} = \mu / \rho (D_f)_A \qquad (8)$$

Prediction of Controlling Resistance. As developed in the correlation section to follow, $\beta_1 = 0.29$, $\beta_2 = 0.060$, and $m = n = 0.50$ in the ambient temperature range of 70° to 80°F. Hence

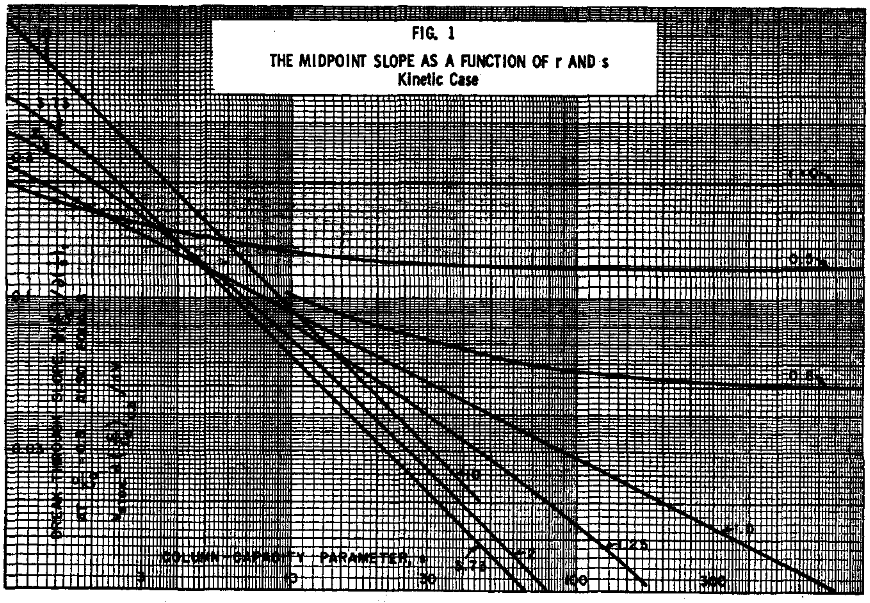
FIG. 1

THE MIDPOINT SLOPE AS A FUNCTION OF r AND s

Kinetic Case

$$\zeta = 4.8\mathbf{D}_A (N'_{Pe})^{-0.5} \frac{(D_p)_A}{(D_f)_A} \qquad (9)$$

since $N'_{Pe} = (N_{Re})(N_{Sc})$. This equation conforms to the well-known fact (*4*, *31*) that the transition from internal to external diffusion controlling will occur at low total ionic concentrations (high $\mathbf{D}$ values) and at low flow rates (low Peclet or Reynolds numbers). If ζ is less than 0.30, the exchange may be considered to be controlled entirely by internal diffusion; and if greater than 3.0, by external diffusion alone. A value of ζ between 0.30 and 3.0 indicates that the combined effect of the two mechanisms must be considered. Typical values of D_p and D_f will be given in Part II.

This evaluation of the mechanism parameter is based on the assumption that only internal and external diffusion contribute to the rate. Therefore caution must be taken that longitudinal diffusion (*1*, *19*, *21*, *28*), which can occur at low flow rates and high diffusivities, does not enter into the picture. This mechanism becomes significant at Peclet numbers of 25 or less (*31*, Figure 6), but has been ignored by some investigators.

Intermediate cases with a combined effect of internal and external diffusion will be discussed in a following section, in terms of an over-all rate coefficient, $(\kappa_{kin})_A$, which is based on a reaction-kinetic mechanism. The transfer coefficient can be replaced by a dimensionless *column-capacity parameter* derived from it, analogous to the N.T.U. (*6*), as shown previously (*16*). This parameter takes the following form:

for external diffusion controlling [*16*, Eq. (59)],

$$(\Sigma_f)_A = (k_f)_A a_p h S \epsilon / R \qquad (10)$$

for internal diffusion controlling [*16*, Eq. (60)],

$$(\Sigma_p)_A = (k_p)_A a_p \mathbf{D}_A h S \epsilon / R \qquad (11)$$

For the combined-mechanism case the reaction-kinetic result [*16*, Eq. (18)] is applicable:

$$s_A = (\kappa_{kin})_A h S \epsilon / R \qquad (12)$$

Here h is the height of the resin-packed section of the column, and S is its cross-sectional area.

Regardless of the mechanism, the break-through curve will be a function of a throughput ratio which depends upon solution volume or upon elapsed time:

$$\frac{t}{s} = \frac{\theta}{\Sigma} = \frac{R\tau - v\epsilon}{\mathbf{D} v \epsilon} \qquad (13)$$

where v is the column volume of resin ($= hS$) and t or θ is a dimensionless *solution-capacity parameter*. The steepness of a break-through curve depends also upon the equilibrium parameter:

$$r_A = \frac{1}{K_A} = \frac{c_A(Q - q_A^*)}{q_A^*(C_0 - c_A)} \qquad (14)$$

Evaluation If the Equilibrium Constant Is Known

Matching to Master Curves. This method was first used by Furnas (*10*) on problems of regenerative heat transfer and by others for ion exchange (*3*, *5*). For the curve-fitting method one first has to plot a family of theoretical break-through curves, with c/C_0 as ordinate, as obtained from cross plots of the earlier paper (*16*) for the proper controlling mechanism as indicated by Equation (9) and the appropriate value of r. With scales similar to those of the master curves, the experimental data for c/C_0 are plotted against log $(\tau - v\epsilon/R)$ or log $(V - v\epsilon)$; here $V (= R\tau)$ is the total volume of feed solution that has entered the column up to the time of measurement τ. The experimental curve is then compared with the reference family, horizontal displacement only being used, in order to find the prepared curve which best fits it and characterizes its Σ or s value.

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*If the exchanging ions do not have the same valence, the true equilibrium constant must be replaced by an apparent second-order equilibrium constant $K_A{}^{II}$ as defined previously [*16*, Eq. (55)].

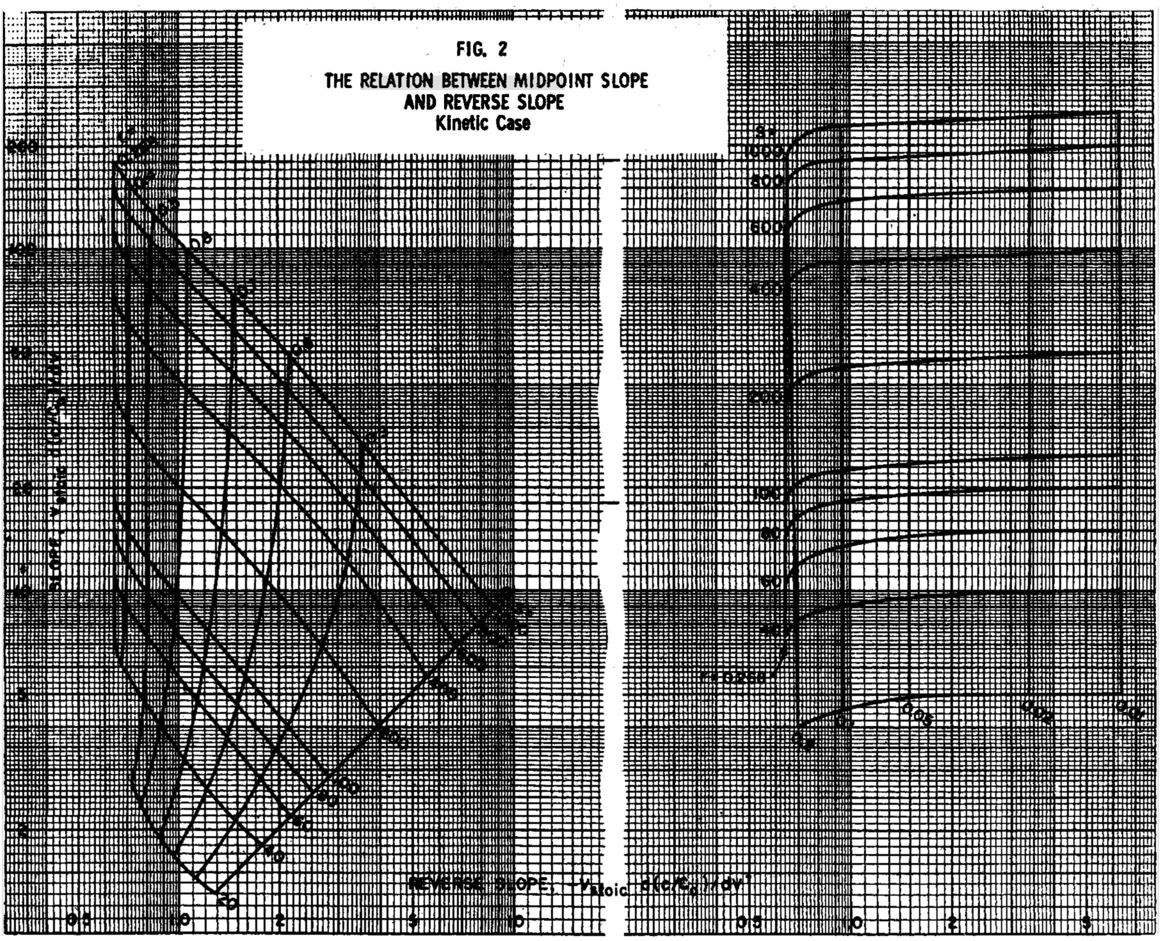
FIG. 2
THE RELATION BETWEEN MIDPOINT SLOPE
AND REVERSE SLOPE
Kinetic Case

Fitting of Equations in the Constant-pattern Region. If the equilibrium constant K for the exchange is substantially greater than unity, and break-through curves therefore exhibit constant-pattern behavior, the experimental data can be interpreted through the use of analytic relations. For an intermediate mechanism, the kinetic relation [*8, 28*, or *16*, Eq. (69)] can be applied; similar relations are available for external [*11, 22*, or *16*, Eq. (70)] and internal diffusion [*30*, Eq. (35)]. This relation permits the determination of s or Σ from two values of the concentration ratio c/C_0, each at a different elapsed time.

To estimate the reliability of rate coefficients calculated in this manner, it is necessary to determine whether constant-pattern conditions are fulfilled. The technique for predicting limits of this type is shown in reference *24* [Eq. (43) and Figure 3, which is based on 1% accuracy].

Fitting of Midpoint Slopes. Thomas (*29*) and Gilliland and Baddour (*12*) have given special attention to the determination of the experimental slope at the "midpoint" ($c/C_0 = 0.5$). The slope, $[d(c/C_0)/d\tau]/R$ or $d(c/C_0)/dV$, is usually measured graphically on a linear plot of the concentration history. The present paper gives for the first time a single master plot for diffusional mechanisms and a single plot for the reaction-kinetic treatment, each of which shows all possible values of the calculated slopes, $d(c/C_0)/d(t/s)$ or $d(c/C_0)/d(\theta/\Sigma)$, as functions of the column-capacity parameter and the equilibrium parameter.

Through the use of Equation (13), the measured slope can be converted to a dimensionless form by multiplying it by $\mathbf{D}v\epsilon$:

$$\mathbf{D}v\epsilon\,\frac{d(c/C_0)}{dV} = \frac{d(c/C_0)}{d(t/s)} \text{ or } \frac{d(c/C_0)}{d(\theta/\Sigma)} \quad (15)$$

The term $\mathbf{D}v\epsilon$ gives the volume of solution that contains just as much ion A as the column will eventually take up, that is, the stoichiometric volume V_{stoic}.

The midpoint slopes for the kinetic case will illustrate the behavior. Figure 1 is a plot of V_{stoic} $[d(c/C_0)/dV]_{0.5}$ against s, as a function of r. The subscript 0.5 indicates that the functions are evaluated at the midpoint concentration. For a known slope and a known r, Figure 1 is seen to give directly a unique value of s.

The construction of Figure 1 has been based upon slopes determined graphically from numerical solutions for c/C_0 and upon slopes calculated by differentiation of the break-through relation [*16*, Eq. (29), and A.D.I. document 4953].

The authors have replotted the kinetic case data of Figure 1 in another form, Figure 2, which serves an additional use, to be described below. Figure 3 is an analogous plot for the cases where either external or internal diffusion solely controls.

Evaluation If the Equilibrium Constant Is Unknown

Use of Data for Two Bed Lengths at Equal Flow Velocity. Runs on beds of two different lengths with a particular resin and solution will sometimes be found to give break-through curves having the same (constant) pattern. For such curves r is known to fall between zero and unity and usually between zero and 0.5. Although unique values of r and s cannot be obtained from such curves, the product $(1 - r)s$ or $(1 - r)\Sigma$ can be calculated analytically as shown by Ekedahl and Sillén (*8*), and may then be used directly in design calculations for other columns.

It is found more often that two bed lengths give break-through curves of different shapes, each with c/C_0 practically zero during the early part of the run, even though the other operating conditions are equal. In this situation the following procedure may prove useful. For each curve, several values of r are assumed; the values of s (or Σ) are determined from the shapes of the theoretical curves corresponding to these values of r (by matching curves or midpoint slopes), and the apparent values of s are calculated *per unit length*. If these values are plotted against the assumed r on a single graph, the curves for the two runs will be found to intersect at the true value of r.

The use of differential beds, in which the effluent c/C_0 is very close to unity,

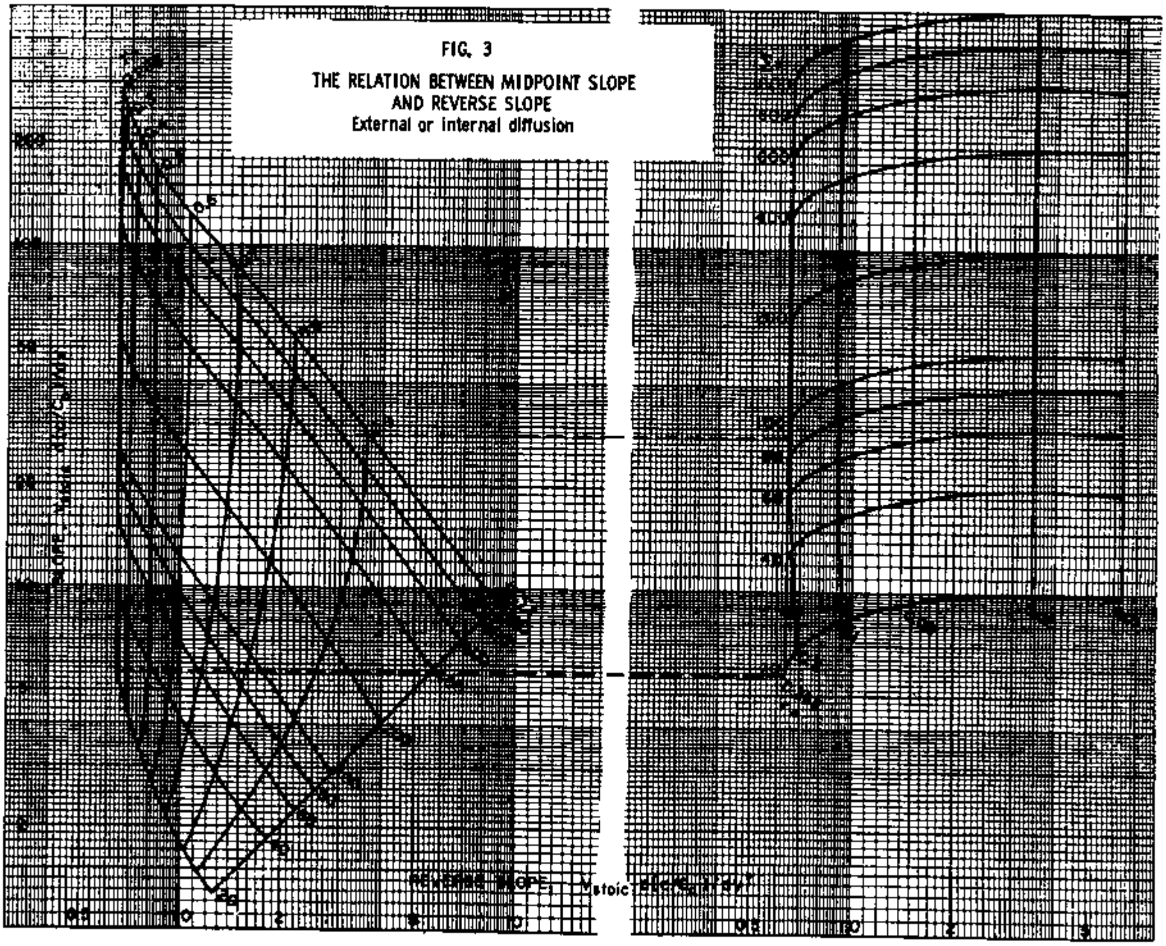

FIG. 3

THE RELATION BETWEEN MIDPOINT SLOPE AND REVERSE SLOPE

External or internal diffusion

is well known from the work of DuDomaine, Swain, and Hougen (7) and Boyd, Adamson, and Myers (4) to be a means of obtaining the rate constants without consideration of the equilibria.

Saturation and Elution Curves from a Single Column at Equal Concentrations and Flow Rates. The mass-action equilibrium constant for a reverse exchange is evidently the reciprocal of the constant for exchange in the forward direction, as discussed by Thomas (*29*) and expanded by the present authors (*31*). Hence, if $r\dagger$ denotes the equilibrium parameter for elution, $r\dagger = 1/r$ where r applies to the saturation step. Since r and $r\dagger$ are not equal unless they are both unity, the break-through curves for saturation and elution will usually differ in shape and slope. In the kinetic case it is noted that $s\dagger = rs$ and $s = r\dagger s\dagger$; in the diffusion-controlled cases, $\Sigma\dagger = \Sigma$.

The equilibrium parameter can be determined readily on an exchange system by continuing the saturation-step break-through run to a concentration ratio approaching complete exchange ($c/C_0 \sim 1.0$). The column is then regenerated by a solution of the ion initially present on the resin, at the same concentration level C_0 and at the same flow rate as used in the saturating run.

If the saturation data are fitted against one of the standard curves for a given r value and the elution data are likewise fitted on the related $r\dagger$ chart, apparent values of s and $s\dagger$ will be obtained. This procedure can be repeated for other r values. Then, if $s\dagger/s$ is plotted against the assumed r, intersection of the curve with a line $s\dagger/s = r$ will indicate the correct value of r.

The midpoint-slope method is even more efficient when applied to such data. Because the designations of saturation and elution refer to process requirements rather than to the special problem of column performance, it will be convenient to designate the exchange with favorable equilibrium as the A step ($r_A < 1$; $K_A > 1$) and the reverse exchange as the B (or $A\dagger$) step. Each value of r_A and s_A then corresponds both to a particular value of slope $[d(c_A/C_0)/d(t_A/s_A)]_{0.5}$ for the A step as indicated by Figure 1 and to a particular value of $-[d(c_A/C_0)/d(t_A\dagger/s_A\dagger)]_{0.5}$, termed the reverse slope, for the B step. In Figure 2 the slope and the reverse slope are used as ordinate and abscissa on log-log coordinates, and the values of r_A and s_A are used as contours. Use of this plot involves calculating the dimensionless slopes [*cf.* Equation (15)] from the experimental data for both A and B steps, locating the corresponding point on Figure 3, and reading off both the r_A and s_A values.

The minimum slope which occurs at $r_A = 3.73$ produces a double plot in Figure 2. The left side corresponds to r_A values between 0.268 (= 1/3.73) and 1.0, and the right side to r_A between zero and 0.268. A choice may be made between these two ranges by comparing the experimental throughput volumes $(V\dagger - v\epsilon)_{0.5}$ and $(V - v\epsilon)_{0.5}$ for the two steps. Normally the latter will approach V_{stoic}, and the former may be appreciably smaller. Figure 4 shows the dimensionless ratio of these two corrected volumes, which is also the ratio of $(t\dagger/s\dagger)_{0.5}$ to $(t/s)_{0.5}$ as a function of r_A and s_A. With this chart the observed ratio of volumes will usually serve as a criterion for determining whether r_A is greater or less than 0.268. Similar considerations apply to Figure 3.

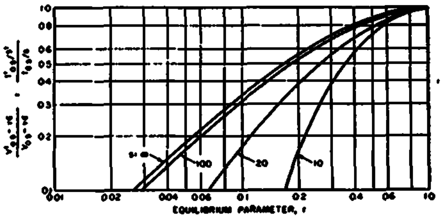

Fig. 4. The ratio of throughput volumes at the midpoint.

II. THEORY AND CORRELATION FOR COMBINED FLUID- AND PARTICLE-PHASE RESISTANCES

Definitions

As was pointed out above, the correlation now to be derived involves both internal and external diffusion as rate-controlling mechanisms and thus permits a continuous transition from one region to the other. The rate relations for these two mechanisms have been stated above in Equations (1) and (2).

The mass transfer coefficients in these equations can be related to the operating variables and characteristics of the resin-ion system as shown previously (*15*). Combining Equations (24 to 26), (29), and (30) of that reference gives the film coefficients as

$$(k_f)_A a_p = \frac{6(1-\epsilon)(D_f)_A}{\beta_1 d_p^2} N_{Re}^{\,m} N_{Sc}^{\,n} \quad (16)$$

$$(k_p)_A a_p = \frac{6(1-\epsilon)(D_p)_A}{\beta_2 d_p^2} \quad (16a)$$

The interrelationship of these coefficients with the measured over-all rate constant will then enable the mass transfer data to be correlated with the system variables.*

Interrelation of Transfer Coefficients

In terms of the reaction-kinetic coefficient the rate of exchange can be expressed [*16*, Eq. (2) and (13)] as

$$\frac{dq}{d\tau} = \frac{(\kappa_{kin})_A \epsilon}{Q \rho_b}\left[c_A(Q - q_A) - \frac{1}{K_A} q_A(C_0 - c_A)\right] \quad (17)$$

The basic relation between the individual film coefficients is obtained by equating the rates given in Equations (1), (2), and (17).

$$\frac{dq}{d\tau} = \frac{c_A - (c_A)_i}{\left[\dfrac{\rho_b}{(k_f)_A a_p \epsilon}\right]} = \frac{(q_A)_i - q_A}{\left[\dfrac{1}{(k_p)_A a_p}\right]} = \frac{c_A(Q - q_A) - q_A(C_0 - c_A)/K_A}{\left[\dfrac{Q\rho_b}{(\kappa_{kin})_A \epsilon}\right]} \quad (18)$$

One of the useful algebraic properties of equal fractions is that the sum of the numerators divided by the sum of the denominators is the same fraction. Application of this principle, along with a conversion of solution concentrations to dimensions of q through multiplication by $(q_A)_0^*/(c_A)_0$ in both numerator and denominator, leads to

$$\frac{dq}{d\tau} = \frac{[c_A - (c_A)_i][(q_A)_0^*/(c_A)_0] + [(q_A)_i - q_A]}{[(q_A)_0^* \rho_b/\epsilon (c_A)_0 (k_f)_A a_p] + [1/(k_p)a_p]}$$

$$= \frac{[(q_A)_0^*/(c_A)_0][c_A(Q - q_A) - q_A(C_0 - c_A)/K_A]}{[Q(q_A)_0^* \rho_b/(c_A)_0 (\kappa_{kin})_A \epsilon]} \quad (19)$$

Rearrangement leads to the usual reciprocal form, but modified by a correction term **b**:

$$\frac{\mathbf{b}_A}{(\kappa_{kin})_A} = \frac{1}{(k_f)_A a_p} + \frac{1}{\mathbf{D}_A (k_p)_A a_p} \quad (20)^*$$

where

$$\mathbf{b}_A = \frac{\{c_A - (c_A)_i + [(q_A)_i - q_A](c_A)_0/(q_A)_0^*\}Q}{c_A(Q - q_A) - q_A(C_0 - c_A)/K_A} \quad (21)$$

Equation (20) leads, with substitution of Equations (16) and (16*a*), to

$$\frac{\mathbf{b}}{(\kappa_{kin})_A} = \frac{\beta_1 d_p^{\,2} N_{Re}^{\,-m} N_{Sc}^{\,-n}}{6(1-\epsilon)(D_f)_A} + \frac{1}{\mathbf{D}} \cdot \frac{\beta_2 d_p^{\,2}}{6(1-\epsilon)(D_p)_A} \quad (22)$$

The following rearranged form of Equation (22) provides a more convenient basis for the final correlation

$$\mathbf{bD}\,\frac{(D_p)_A}{(D_f)_A}\cdot\frac{6(1-\epsilon)(D_f)_A}{d_p^{\,2}(\kappa_{kin})_A} = \beta_1 \mathbf{D}\,\frac{(D_p)_A}{(D_f)_A} N_{Re}^{\,-m} N_{Sc}^{\,-n} + \beta_2 \quad (23)$$

As pointed out earlier, the term involving β_1 (external diffusion) will predominate over β_2 (internal diffusion) at low solution concentrations (high **D**) and at low flow rates (low N_{Re}).

Effect of Exchange Conditions. Before β_1 and β_2 in the correlation can be determined from experimental data **b** must be evaluated from theoretical considerations. Likewise, when the correlation is used, the applicable value of **b** must be calculated.

Inspection of Equation (21) indicates that a range of **b** values will occur as $(c_A)_i$ varies between c_A (for internal diffusion controlling) and c_A^* (for external diffusion controlling). For each intermediate value of $(c_A)_i$, the ratio of the controlling resistances, ζ, can also be calculated from Equation (4). It follows that **b** and ζ will be related in a manner that depends upon the particular values of c_A/C_0 (usually 0.5, since most interpretive methods emphasize the data at the midpoint) and q_A/Q at which **b** is to be evaluated and upon their equilibrium relations.

For a single ion in the feed, Equation (21) becomes

$$\mathbf{b} = \frac{[c_A - (c_A)_i]Q + [(q_A)_i - q_A]C_0}{c_A(Q - q_A) - q_A(C_0 - c_A)/K_A} \quad (24)$$

since then $(c_A)_0/(q_A)_0^* = C_0/Q$. Further simplification can be achieved by replacing the resin driving force by that of the solution through Equation (4) and the resin concentration by the concentrations of the solution through Equation (3). Thus

$$\mathbf{b} = \frac{K_A C_0(\zeta + 1)[(K_A - 1)c_A^* + C_0]}{K_A C_0^{\,2}\zeta + [(K_A - 1)c_A^* + C_0][(K_A - 1)(c_A)_i + C_0]} \quad (25)$$

Evaluation of Special Terms

Among the terms contained in Equation (23), **D**, d_p, and N_{Re} can be determined from the known resin properties and the operating conditions used experimentally (or specified for design purposes). $(\kappa_{kin})_A$ is determined by the methods already given (or is the final result of the correlation as computed for design). The liquid-phase diffusivity $(D_f)_A$—or, strictly, $(D_f)_{AB}$—is estimated from physico-chemical tabulations as the mean of the self-diffusion coefficients for the salt pairs *A*- and *B*-anion that are involved.

Only the correction term **b** and the diffusivity ratio $(D_p)_A/(D_f)_A$ impose a real difficulty of evaluation. These will be discussed in the following paragraphs.

Correction Term. As stated above, the value of **b** depends upon the values of c_A and q_A and the applicable equilibrium constant. The resin concentration q_A can be determined exactly by extensive trial-and-error calculations; however, for most purposes it will suffice to assume two types of limiting behavior. At $r < 1$ $(K > 1)$, the limit of constant-pattern behavior [*16*, Eq. (67)] will be assumed. Likewise, at $r > 1$ $(K < 1)$, the limit of equilibrium-limited exchange [*16*, Eq. (31*a*)] will be used.

For $K > 1$, $q_A/Q \approx 0.5$. The value of c_A^* can be obtained through Equation (3) and equals $C_0/(1 + K_A)$; this plus Equation (25) leads to

$$\mathbf{b} = \frac{2K_A C_0(\zeta + 1)}{(K_A + 1)C_0\zeta + 2[(K_A - 1)(c_A)_i + C_0]} \quad (26)$$

Assumption of a value of $(c_A)_i$ between c_A and c_A^* permits calculation of $(q_A)_i$ through Equation (3) and thus ζ from

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*The ratio $(d_w/d_p)^{1/3}$ was introduced previously (*31*) to account empirically for the apparent effect of channeling flow in wide beds. Although this correction may possibly be necessary when longitudinal diffusion is involved, further study has shown that it does not improve the correlation of the present data in the regions where external or internal diffusion controls.

*Equation (48), reference *16*, which was derived by inference, is seen to be in error in omitting the term analogous to **b**.

Equation (4). Then Equation (26) is used to obtain **b**.

For the limit at which $(c_A)_i = c_A$, $(q_A)_i$ must equal q_A^*; internal diffusion controls, $\zeta = 0$, and in this case $\mathbf{b} = 2K_A/(K_A + 1)$. For the limit at which $(c_A)_i = c_A^*$, q_A must equal $(q_A)_i$; external diffusion controls, $\zeta = \infty$, and $\mathbf{b} = 2K_A/(K_A + 1)$.

Slightly higher values of **b** will occur under intermediate rate-controlling conditions. Figure 5 shows some typical values of ζ and **b** for $K > 1$, $c_A/C_0 = 0.5$, and s large, calculated from Equation (26). These may also be used as approximate values when s_A is too small to fall within the constant-pattern region.

For $K < 1$, in the equilibrium-limited region, $c_A^* = (c_A)_i = c_A = 0.5C_0$ and so Equation (25) becomes

$$\mathbf{b} = \frac{2K_A(K_A + 1)(\zeta + 1)}{4K_A\zeta + (K_A + 1)^2} \quad (27)$$

and only the mechanism parameter affects **b** for a given K_A. When external diffusion only controls, $\zeta = \infty$ and $\mathbf{b} = (K_A + 1)/2$, and for internal diffusion $\zeta = 0$, and so $\mathbf{b} = 2K_A/(1 + K_A)$. Values in the range of $K < 1$ are also shown in Figure 5.

Diffusivity Ratio. The data available for counterdiffusivities in the resin phase, $(D_p)_{AB}$, are rather limited, both with respect to ions exchanged and resins involved. However, Boyd et al. (*4*) have supplied resin conterdiffusivities for a number of alkali-metal ion pairs. The values that they found for the exchange reaction shown in Equation (3), using Amberlite IR-1 (sulfonated phenol-formaldehyde resin), are given in Table 1.

The ratio $(D_p)_{AB}/(D_f)_{AB}$ was studied with respect to the ionic radii for the exchanging ion pairs, but the data showed no relative trend. Apparently the resin gel can be considered as a viscous medium which reduces the diffusivity uniformly if the ions are univalent and small. For this reason it is assumed that the average ratio is 0.168 ($\sim$ 0.17) for Amberlite IR-1.

The data of Reichenberg (*26*) for sodium-hydrogen exchange on Dowex 50 (sulfonated polystyrene) can be interpolated to obtain a $(D_p)_{AB}/(D_f)_{AB}$ ratio of 0.189 for an 8 to 10% cross-linked resin. For the same type of resin, Bauman and Eichhorn (*2*) measured the diffusion of sodium chloride and hydrochloride into the gel. Averaging their diffusivity values to get $(D_p)_{AB}$ leads to a ratio of 0.185. As this checks Reichenberg's result closely, the diffusivity ratio for Dowex 50 (a sulfonated polystyrene resin) will be taken as 0.187 ($\sim$ 0.19)*.

Typical Experimental Data. Column data for exchange under both trace and gross conditions at ambient temperatures (70° to 80°F,) are available in the literature.

Boyd, Adamson, and Myers (*4*, *5*) studied both shallow and deep beds and were the main source of data in the trace region. Work under gross exchange conditions was performed by Sillén and coworkers (*8*, *17*, *28*), Gilliland and Baddour (*12*), Michaels (*22*), and Nelson (*23*).

The details of the interpretation of data are given in the supplement to this paper.† Typical results from Boyd and coworkers are given in Table 2†.

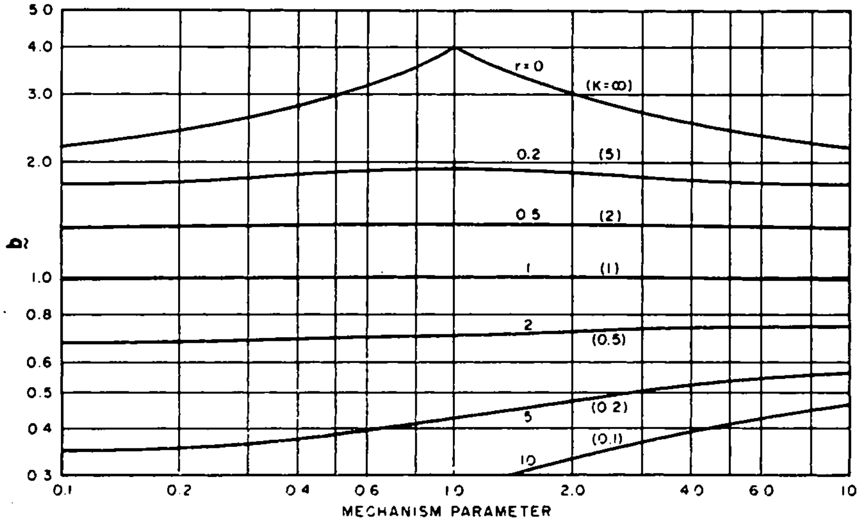

Fig. 5. Correction term b for combining diffusion resistances, as a function of the mechanism parameter ζ.

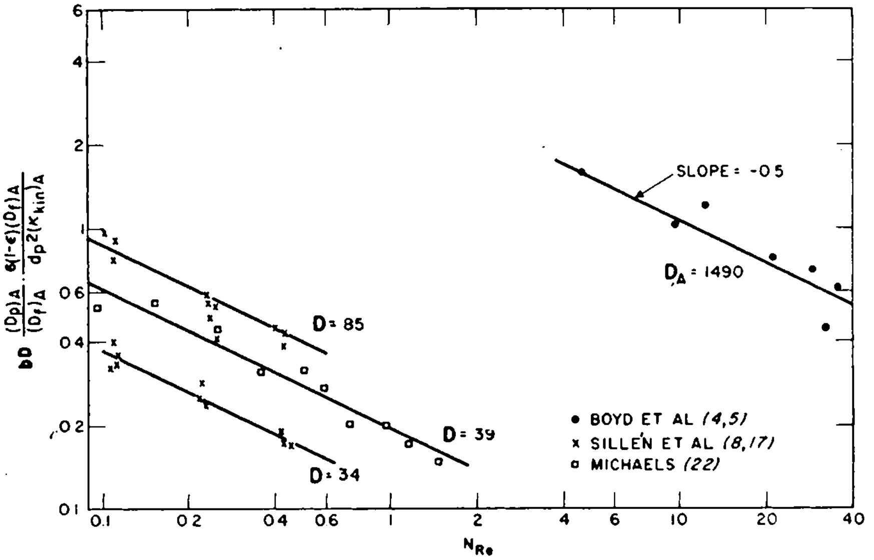

Fig. 6. Determination of Reynolds number exponent.

Table 1. Ratio of Particle Diffusivities to Liquid Diffusivities

Exchanging ions		$(D_p)_{AB}$	$(D_f)_{AB}$	$\frac{(D_p)_{AB}}{(D_f)_{AB}}$	$r^0_A + r^0_B$
A	B	10^{-6} sq. cm./sec.	10^{-5} sq. cm./sec.		10^{-8} cm.
Na	Li	3.0	1.35	0.222	12.1
Na	H	3.7	2.05	0.181	10.8
Na	Na	2.1	1.56	0.135	10.4
Na	NH_4	2.9	1.68	0.173	9.7
Na	K	3.5	1.69	0.207	9.3
Rb	K	2.8	1.84	0.152	7.3
Cs	K	2.0	1.87	0.107	6.7
Average				0.168	

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*The present commercial grade of Dowex 50 is more highly crosslinked and has been shown by Boyd and Soldano, *J. Am. Chem. Soc.* **75**, 6091 (1953), to have a substantially lower ratio.

†Complete supplementary data and tabular matter may be obtained as document 4953 from the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., for $3.75 for photoprints or $2.00 for 35-mm. microfilm.

Constants for the Correlation

Reynolds Number Exponent, m. Reference to Equation (23) shows that, if all variables but the flow rate are held constant, the left-hand term less β_2 (the internal-diffusion film ratio) can be plotted against N_{Re} on log-log coordinates, and the slope ($= -m$) determined. Since β_2 is still unknown, the data used must be selected from the external-diffusion controlling region, i.e., at high **D** and low N_{Re} values, where the effect of internal diffusion is negligible. Such data are plotted in Figure 6, and lines of -0.50 slope are drawn through the various groups of points. This slope is comparable to a value of -0.5 used by Hagerty and Bliss (*14*), to -0.4 used by Vermeulen and Hiester (*31*), to -0.6 used by Lapidus and Amundson (*20*), and to exponents in the same range found in general mass transfer studies (*11, 18, 25, 33*).

Schmidt Number Exponent, n. This exponent could normally be determined by plotting the intercepts of Figure 6 (obtained at constant N_{Re}) against N_{Sc} on log-log paper. Because of the limited data, this was not possible in the present study. It is assumed for convenience that the powers of N_{Re} and N_{Sc} are identical; thus, that $n = m = 0.50$. Recent work by Gaffney and Drew (*11*) indicated a value of 0.58 for n. Choosing n and m to be the same permits simplification of the relations, as the product of N_{Re} and N_{Sc} is the N'_{Pe} group in which viscosity and density changes have no effect. This type of simplification is justified by the fact that the correlation is solely to be derived from and is intended to be applied to aqueous solutions.

Slope and Intercept of Correlation Plot. The remaining constants, β_1 and β_2 in Equation (23), are now rather easily found. If the left-hand side of this equation is plotted against the independent variable $\mathbf{D}[(D_p)_A/(D_f)_A](N'_{Pe})^{-0.5}$, the slope of the best line through the data is β_1 and its intercept is β_2. This has been done in Figure 7 and on two similar plots expanding the region near the origin tenfold and hundredfold, the data from the authors previously listed being used. The values of β_1 and β_2 found were 0.29 and 0.060 respectively.

The choice of these constants is confirmed by replotting the data in the same form on logarithmic coordinates, as shown in Figure 8. It is seen that the majority of the points fit the curve well with only a small amount of spread.* A ζ scale, based on Equation (6), has also been indicated on the abscissa of this plot, to facilitate the proper choice of **b** in design problems.

The two diffusional regions are clearly revealed in Figure 8. In the horizontal portion of the curve, at abscissa values less than 0.06, internal diffusion controls; at abscissa values greater than 0.60, the 45° line represents the region where external diffusion controls.

Final Form of Relation. With the constants now determined, the correlation can be written in terms of h/s_A and N'_{Pe}, by use of Equations (14) and (30), as

$$\mathbf{bD}\,\frac{(D_p)_A}{(D_f)_A}\cdot\frac{h/(s_A)}{d_p}\cdot\frac{\epsilon}{N'_{Pe}} \tag{28}$$

$$= 0.29\mathbf{D}\,\frac{(D_p)_A}{(D_f)_A}\,(N'_{Pe})^{-0.5} + 0.060$$

and this is the equation of the solid curve on Figure 8. Rearrangement leads to a simple form relating the Colburn number to other dimensionless parameters:

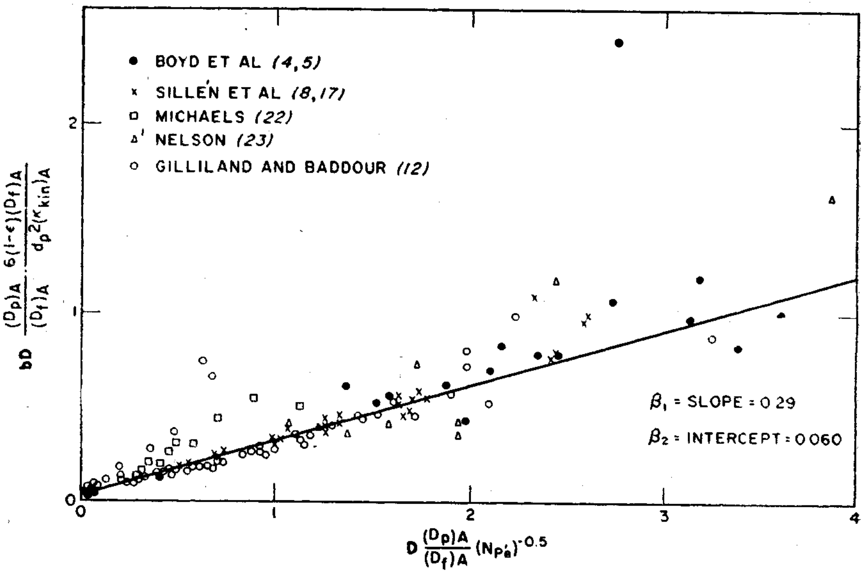

Fig. 7. Linear correlation plot.

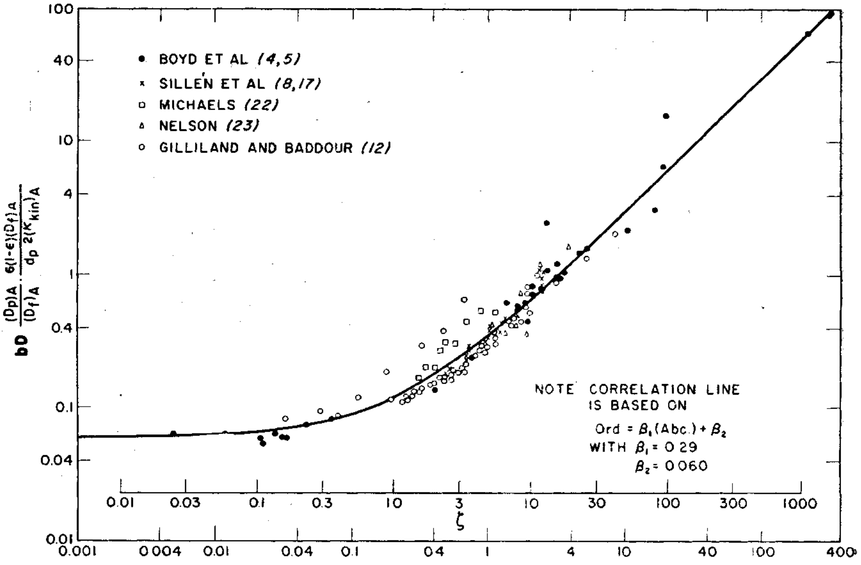

Fig. 8. Logarithmic correlation plot.

TABLE 2. RANGE OF EXPERIMENTAL VARIABLES IN BOYD'S DATA ON TRACE EXCHANGE (*4*)

Run	Trace ion	Gross ion	$(1/\kappa_{kin})_A$	N_{Re}	$\mathbf{D}_A$
R-7	Na	K	3.24 sec	11	2.3
R-5	Na	K	0.103	11	344
XV-19	Rb	K	0.0700	11	1,490
M-8	Na	Cs	0.980	440	11.8
M-5	Na	Cs	0.675	0.10	825
M-10	Rb	H	0.492	1190	14,300

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*The recent results of Sujata, Banchero, and White, *Ind. Eng. Chem.*, **47**, 2193 (1955), also agree with this correlation to within experimental error.

$$\frac{h}{(s_A)d_p} = \frac{0.29(N'_{Pe})^{0.5}}{\mathbf{b}\epsilon} + \frac{0.060(N'_{Pe})}{\mathbf{b}\epsilon\mathbf{D}_A(D_p)_A/(D_f)_A} \quad (29)^*$$

These data cover a thousandfold range of concentration, a large range of equilibrium constants, a six-hundredfold range of flow velocities, and bed heights varying from 0.04 to 20 in. (0.1 to 50 cm.).

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NOTATION

Dimensions of the variables are indicated by a typical self-consistent set of units.

a_p = effective area for mass transfer, sq, ft./cu. ft.
A, B, etc. = ionic species
b = correction factor for computing reaction-kinetic coefficients, dimensionless; *see* Equations (20), (21), and (24) to (27).
c_A, c_B, etc. = concentration of ion in the solution phase at a specified point in the column, lb.-equiv./cu. ft.
C_0 = total concentration of ions in the solution entering the column, lb.-equiv./cu. ft.; replaces symbol c_0 used in references *16*, *30*, and *31*.
D = partition parameter, or ratio of concentrations in resin phase and solution phase at saturation, dimensionless
D = effective ionic diffusivity for counterdiffusion of two components, sq. ft./min.
d_p = mean diameter of resin particles, ft.
G = gross component, in exchange involving trace components
h = height or length of column, ft.
H_t = height of column equivalent to one mass transfer unit, ft.
k = mass transfer coefficient, ft./min.
$K(= K^{II})$ = chemical equilibrium constant for exchange, dimensionless
m, n = exponents
N'_{Pe} = Peclet number for mass transfer, $N_{Re} \cdot N_{Sc}$
N_{Re} = Reynolds number, $d_pR\rho/6(1 - \epsilon)S\mu$, consistent with reference *9*
N_{Sc} = Schmidt number, $\mu/\rho(D_f)_A$
q_A, q_B, etc. = concentration of ion in the resin phase at a specified point in the column, lb.-equiv./lb. dry resin
Q = total ionic concentration in the resin phase (i.e., ultimate capacity), lb.-equiv./lb. dry resin
$r(= 1/K)$ = equilibrium parameter, dimensionless
r^0 = ionic radius, ang.
R = volumetric flow rate, cu. ft./min.
s = column-capacity parameter for the kinetic case, dimensionless
S = cross-sectional area of column, sq. ft.
t = solution-capacity parameter for the kinetic case, dimensionless; $t = (\kappa_{kin})_A(V - v\epsilon)/\mathbf{D}R$
t/s = throughput parameter, dimensionless
u = average linear flow rate through the packed column, ft./min.; $u\epsilon$ is the superficial linear flow rate.
$v(= hS)$ = bulk-packed volume of column, cu. ft.
V = volume of saturating solution fed to column, cu. ft.; $V - v\epsilon$ is the volume that has reached the resin at a bulk volume v downstream from the column inlet
V_{stoic} = volume of saturating fluid which has contained a quantity of solute just equivalent to the exchange capacity of the column, cu. ft.
β_1, β_2 = correlation constants, dimensionless; *see* Equations (6) and (16).
ϵ = ratio of void space outside resin particles to total volume of packed column, dimensionless
θ = solution-capacity parameter for diffusional cases, dimensionless; $(k_fa_p/\mathbf{D})(V - v\epsilon)/R$, or $k_pa_p(V - v\epsilon)/R$
$\theta/\Sigma(= t/s)$ = throughput parameter, dimensionless
κ = general rate coefficient, min.$^{-1}$
μ = viscosity of the solution, lb./(ft.)(min.)
ρ = density of the solution, lb./cu. ft.
ρ_b = bulk density of dry resin, lb./cu. ft. packed volume
Σ = column-capacity parameter for diffusional cases, dimensionless; $k_fa_pv\epsilon/R$, or $k_pa_pDv\epsilon/R$
τ = time, min.
ζ = mechanism parameter, dimensionless; *see* Equation (6).

Subscripts

0 = initial condition
A, B, etc. = ionic species; or process step. A may represent the exchange of species A with species B, etc.
f = fluid (solution) film or phase
i = interface
p = particle (resin) film or phase

Superscripts

† = reverse of reference reaction, i.e., elution
* = value in equilibrium with the actual value for the coexisting phase

LITERATURE CITED

1. Barrow, R. F., C. J. Danby, J. G. Davoud, C. N. Hinshelwood, and L. A. K-Stavely, *J. Chem. Soc.*, 401 (1947).
2. Bauman, W. C., and Jacob Eichhorn, *J. Am. Chem. Soc.*, **69**, 2830 (1947).
3. Beaton, R. H., and C. C. Furnas, *Ind. Eng. Chem.*, **33**, 1500 (1941).
4. Boyd, G. E., A. W. Adamson, and L. S. Myers, Jr., *J. Am. Chem. Soc.*, **69**, 2836 (1947).
5. *Ibid.*, p. 2849.
6. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **27**, 255 (1935).
7. Du Domaine, John, R. L. Swain, and O. A. Hougen, *loc. cit.*, **35**, 546 (1943).
8. Ekedahl, Erik, and L. G. Sillén, *Arkiv. Kemi, Mineral, Geol.*, **25A**, No. 4, 1 (1947).
9. Ergun, S. K., *Chem. Eng. Progr.*, **48**, 227 (1952).
10. Furnas, C. C., *Trans. Amer. Inst. Chem. Engrs.*, **24**, 142 (1930).
11. Gaffney, B. J., and T. B. Drew, *Ind. Eng. Chem.*, **42**, 1120 (1950).
12. Gilliland, E. R., and R. F. Baddour, *loc. cit.*, **45**, 330 (1953).
13. Glueckauf, Eugen, *Trans. Faraday Soc.*, **51**, 1540 (1955).
14. Hagerty, P. F., II, and Harding Bliss, *Ind. Eng. Chem.*, **45**, 1253 (1953).
15. Hiester, N. K., E. F. Fields, Jr., R. C. Phillips, and S. B. Radding, *Chem. Eng. Progr.*, **50**, 139 (1954).
16. Hiester, N. K., and Theodore Vermeulen, *Chem. Eng. Progr.*, **48**, 505 (1952).
17. Hogfeldt, Erik, Erik Ekedahl, and L. G. Sillén, *Acta Chem. Scand.*, **4**, 1471 (1950).
18. Johnson, Frederick, Robert Bentley, and Robert Maurer, Atomic Energy Commission declassified document *MDDC-990* (July 4, 1945).
19. Lapidus, Leon, and N. R. Amundson, *J. Phys. Chem.*, **56**, 984 (1952).
20. *Ibid.*, p. 373.
21. Ledoux, Edward, *J. Phys. Colloid Chem.*, **53**, 960 (1949).
22. Michaels, A. S., *Ind. Eng. Chem.*, **44**, 1922 (1952).
23. Nelson, R. L., Jr., M.S. thesis Univ. California, Berkeley (1951).
24. Opler, Ascher, and N. K. Hiester, "Tables for Predicting the Performance of Fixed Bed Ion Exchange and Similar Mass Transfer Processes," Stanford Research Institute, Stanford, Calif. (1954).
25. Ranz, W. E., *Chem. Eng. Progr.*, **48**, 247 (1952).
26. Reichenberg, D., *J. Am. Chem. Soc.*, **75**, 589 (1953).
27. Selke, W. A., and Harding Bliss, *Chem. Eng. Progr.*, **46**, 509 (1950).
28. Sillén, L. G., *Arkiv. Kemi. Mineral, Geol.*, **22A**, No. 15 (1946).
29. Thomas, H. C., *Ann. N. Y. Acad. Sci.*, **49**, 161 (1948).
30. Vermeulen, Theodore, *Ind. Eng. Chem.*, **45**, 1664 (1953).
31. ———, and N. K. Hiester, *Ind. Eng. Chem.*, **44**, 636 (1952).
32. ———, *J. Chem. Phys.*, **22**, 96 (1954).
33. Wilke, C. R., and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **41**, 455 (1945).

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*When the column feed contains one or more minor trace constituents with respect to a single major component present in both solution and resin ($c_A \ll C_0$, $q_A \ll Q$), each trace constituent exhibits linear-equilibrium behavior (*32*), and therefore **b** = 1. In applying Equation (29), **D** must be used as defined in reference *31*.