type RR'CH$_2$ (where R and R' are alkyl) > primary and secondary chlorine > tertiary chlorine and primary hydrogen.

2. Free radicals of the type RCHCl· (in which R is alkyl) are less reactive generally, less susceptible to disproportionation, and more inclined to dimerization than the corresponding free radicals of the type RCH$_2$.

3. Free radicals of the type RR'CCl· (in which R and R' are alkyl) are less reactive generally, less susceptible to disproportionation, and more inclined to dimerization than the corresponding free radicals of the type RR'CH..

4. A disproportionation reaction involving transfer of chlorine atoms has been described.

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Gibbs–Donnan Equilibria in Ion Exchange Resin Systems

BY HARRY P. GREGOR

Two phenomena are characteristic of ion exchange reactions. The first is that equivalent amounts of ions are exchanged; the second is that there is usually a selective uptake of one ion species over another. Many theories have been reported to account for these phenomena; there is an excellent review of the older literature by Griessbach.[1]

The early attempts to formulate a theory were based on the law of mass action. For the cation exchange process

$$\mathrm{A}_{\mathrm{i}}^{+} + \mathrm{B}_{\mathrm{o}}^{+} \rightleftharpoons \mathrm{A}_{\mathrm{o}}^{+} + \mathrm{B}_{\mathrm{i}}^{+}$$

where the subscripts i and o refer to the exchange body phase and the external solution phases, respectively, the distribution constant K_{D} was defined as

$$K_{\mathrm{D}} = (\mathrm{B}^{+}/\mathrm{A}^{+})_{\mathrm{i}}(\mathrm{A}^{+}/\mathrm{B}^{+})_{\mathrm{o}} \qquad (1)$$

The terms in parentheses refer to concentrations. Experimental evidence showed, however, that in the case of univalent ions and in the absence of a chemical reaction K_{D} was not a constant for given ionic species, but varied for different concentration ratios in the external phase, for different absolute concentrations, and particularly for different ion exchange systems. Marshall and Gupta,[2] Jenny,[3] and Boyd, Schubert and Adamson[4] ascribed these variations in K_{D} with different experimental conditions as being entirely due to changes in the ratio of cationic activity coefficients within the exchange body phase, when activities rather than concentrations are used. This hypothesis was not confirmed by direct, independent experiment. The ratio of cationic activity coefficients was calculated only from experimental values of K_{D}.

Ion exchange was also considered as an adsorption process by Wiegner,[5] Rothmund and Kornfeld,[6] and others, who applied the Freundlich isotherm to the adsorption of the exchanging ion; the distribution constant K_{D} was

$$K_{\mathrm{D}} = (X_{\mathrm{B}}/X_{\mathrm{A}})_{\mathrm{i}}\,(C_{\mathrm{A}}^{+}/C_{\mathrm{B}}^{+})_{0}^{p} \qquad (2)$$

where X refers to the mole fraction of the ion in the exchange body phase, and p is a parameter. Expression (2) fits the data somewhat better than does (1), and is useful as an empirical expression.

Vanselow[7] treated exchange processes in terms of the formation of a complex between the movable ions and the exchange body. Other authors, notably Marshall and Gupta,[2] Anderegg and Lutz,[8] and Mattson and Wiklander[9] also considered the formation of associated compounds.

Mattson and Wiklander[9] as well as Bauman and Eichhorn[10] considered this phenomenon as being capable of representation as a Donnan equilibrium between the inner or exchange phase and the external solution. The expressions derived were identical with (1) except that activities were used.

Jenny[3] derived expressions for ion exchange processes on the assumption that the exchanging ions oscillated in a volume element associated with each fixed exchange group, and the probability of finding a specific ion in a volume element was calculated statistically. The size of a volume element was assumed to be a function of the nature of the ion, of the surface, and of the surface forces. The final expressions reduced to (1) for univalent ions.

The theories of ion exchange outlined above require the introduction of empirical parameters or the use of parameters which can be defined only in terms of the exchange system itself. The thermodynamic theory of ion exchange outlined in a note by Gregor[11] is an attempt to predict the behavior of various ion exchange systems from well-defined physical properties of the system, which properties are measurable apart from the ion exchange process. This theory considers the pressure–volume contributions to the free energy of the process, and here is applied to ion exchange resin systems. Cation exchange resins will be used as samples, although the theory is equally applicable to anion exchange resins.

The Physico-chemical System

Certain studies have indicated the fundamental physico-chemical nature of ion exchange systems. The cation exchange resins are high molecular weight, insoluble polyacids, usually of the sulfonic,

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[1] R. Griessbach, "Preparation and Applications of Ion Exchange Absorbents," Verlag Chemie, Berlin, 1939.

[2] C. E. Marshall and R. S. Gupta, *Soc. Chem. Ind.*, **52**, 433 (1933).

[3] H. Jenny, *J. Phys. Chem.*, **40**, 501 (1936).

[4] G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947).

[5] G. Wiegner, *J. Landw.*, **60**, 1111 (1912).

[6] Rothmund and Kornfeld, *Z. anorg. u. allgem. Chem.*, **103**, 129 (1918).

[7] A. P. Vanselow, *Soil Science*, **33**, 95 (1932).

[8] F. O. Anderegg and R. P. Lutz, *ibid.*, **24**, 403 (1927).

[9] S. Mattson and L. Wiklander, *ibid.*, **49**, 109 (1940).

[10] W. C. Bauman and J. Eichhorn, THIS JOURNAL, **69**, 2830 (1947).

[11] H. P. Gregor, *ibid.*, **70**, 1293 (1948).

carboxylic or phenolic type. The acid groups are substituents in a hydrocarbon matrix; most commercial resins contain 2 to 10 millimoles of such groups per gram of dry resin. A typical commercial resin of the sulfonic acid type contains from 2 to 6 millimoles of sulfonic acid groups per gram of dry resin; the water-equilibrated resin in the alkali metal state is about 8 molal with respect to its fixed groups.[12,13]

The electrochemical properties of the exchange groups do not appear to be affected substantially by their substitution in the resin structure. The work of Chaya also showed, in the case of sulfonic acid resins and the alkali cations, that the volumes of the resins themselves varied with the (calculated) hydrated ionic volumes of cations in the exchange positions. Furthermore, the order of selective uptake of cations follows the reverse order of hydrated ionic volumes, the smaller cation being preferred.

A plausible postulate as to the microstructure of a sulfonic acid cation exchange resin is that it consists of a flexible hydrocarbon matrix to which is attached a number of fixed anionic groups, which are compensated for electrically by movable cations. A high, internal, thermodynamic osmotic pressure is developed as a result of the high concentration of movable cations within the structure. The flexible matrix is thus expanded and the internal osmotic pressure may be calculated to be of the order of 200–300 atm., allowing for activity coefficient effects.

One of the ionic species, the sulfonic acid groups, are fixed and in this manner are restricted to the resin phase; this constitutes a Donnan system. When Donnan[14] originally considered membrane systems containing non-diffusible ion species, he stipulated that the osmotic pressures be equilibrated on both sides of the membrane by the addition of a non-diffusible nonelectrolyte, to avoid pressure–volume free energy effects. In later papers, Donnan and Guggenheim[15] and Donnan[16] extended the theory to consider these pressure–volume free energy contributions.

This paper applies the classical thermodynamic formulations of Gibbs and Donnan to ion exchange resin systems, and in particular considers the pressure–volume free energy changes involved in the swelling and deswelling processes. These systems are treated first as being ideal, then as non-ideal ones.

It should be pointed out that the term "thermodynamic osmotic pressure" does not necessarily mean that an actual hydrostatic pressure is present within these ion exchange gel systems. What is being considered are the pressure-volume free energy changes which accompany swelling and deswelling processes. As has been pointed out by several authors, particularly Alfrey,[17] these free energy changes are best treated from entropy considerations, although it is convenient to calculate them in terms of osmotic pressures and volume changes.

Ideal Systems

The Model.—A model which represents the essential features of a cation exchange resin is shown in Fig. 1. The resin is shown as a cylinder of variable volume, held under pressure by springs lengthened under tension. Its inner volume V_i is the total external volume V_e of the resin minus the volume V_m of the incompressible hydrocarbon matrix including the (hydrated) anionic groups fixed to the inner wall. The inner phase is in direct contact with the external solution, which is infinite in volume and under atmospheric pressure. The dotted line indicates the boundary between inner and outer solutions, not a semipermeable membrane. The force which opposes the spring tension is the thermodynamic osmotic pressure π within the resin phase. Thus, V_i will vary with π, and the simple relationship may be postulated

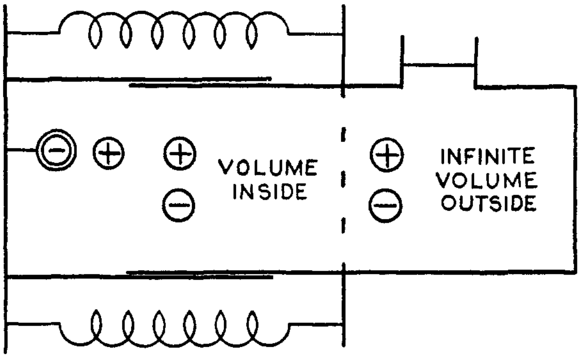

Fig. 1.—Model of cation exchange resin.

$$V_i = m\pi + b \tag{3}$$

This expression describes in a general way the elastic properties of a cross-linked resin structure at moderate pressures.[17] In calculating the behavior of this model for comparison with observed resin behavior, it must be noted that the values of m and b depend upon the specific system considered. In all cases the qualitative behavior will be the same. For purposes of illustration the values of m and b have been set arbitrarily at m = 0.00015 liter atm.$^{-1}$ mole^{-1} and b = 0.15 liter mole^{-1}; various data indicate that these are reasonable values for these parameters. The number of fixed anionic groups is taken as one mole, and the value of b is taken as the molar volume of the system when π is 0.

Thermodynamic Properties of Model.—Consider cations of a single species acting as counter ions (ions in the exchange positions) to the fixed anions, and that the external phase is pure solvent. Make the following assumptions: (1) That the hydrated volumes of all ionic and molecular constituents are constant; (2) that the fixed groups and the movable ions do not interact chemically, but are completely dissociated at all times; (3) that the volume of the fixed anionic group is constant, and is considered a part of the resin matrix; and (4) that for this ideal system all activity coefficients are

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[12] H. Chaya, Thesis, Polytechnic Institute of Brooklyn, June, 1947.

[13] H. P. Gregor and J. I. Bregman, This Journal, **70**, 2370 (1948).

[14] F. G. Donnan, *Z. Elektrochem.*, **17**, 572 (1911).

[15] F. G. Donnan and E. A. Guggenheim, *Z. physik. Chem.*, **162A**, 346 (1932).

[16] F. G. Donnan, *ibid.*, **168A**, 369 (1934).

[17] T. Alfrey, "Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York, N. Y., 1948.

unity. This case corresponds to that of a strong acid resin with alkali cations in the exchange position, immersed in water. Then n_1 moles of cations of molar volume v_1 and n_0 moles of water of molar volume v_0 make up the volume V_i.

The thermodynamic osmotic pressure of this system may be calculated from the expression

$$\pi = RT/v_o \ln (X_o)_o/(X_o)_i \qquad (4)$$

Various properties of this model have been calculated from equations (3) and (4), with the insertion of values of v_1 varying from 0.0 to 0.3. The value of n_1 is taken as 1 mole, v_0 as 0.018 l., T as 25°, $(X_o)_o = 1$, and $V_i = n_0v_0 + n_1v_1$, as defined previously. In Fig. 2 the variation in the internal volume V_i and the solvent volume n_0v_0 for various values of v_1 are shown.

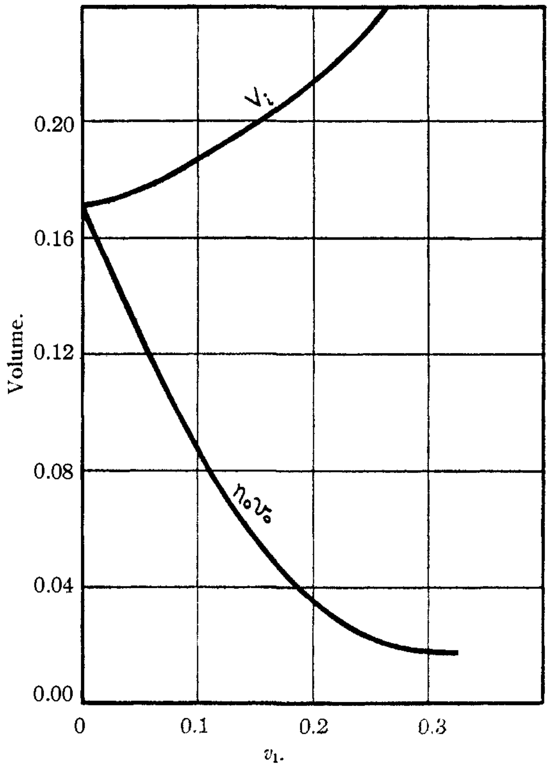

Fig. 2.—Effect of molar volume (v_1) of ion in exchange position upon total internal volume (V_i) and internal free volume or volume of free solvent (n_0v_0).

As larger ions assume the exchange positions, the volume of the system increases slightly due to the high swelling modulus; at the same time, the solvent volume n_0v_0 decreases considerably, causing a sharp increase in π.

Cation Exchange.—Consider now the behavior of the model described above for the exchange process occurring under the above ideal conditions

$$A_o^+ + B_i^+ = B_o^+ + A_i^+$$

where two species of cations are present in the resin phase, and in dilute solution (as salts) in V_o. Under these conditions, the movable anions will be almost completely excluded from the resin phase by Donnan effects, and negligible counter osmotic pressures will be established. This case corresponds to the exchange of alkali cations, involving dilute solutions and a strong acid resin.

When ions enter or leave this system, a certain amount of solvent also enters or leaves concomitantly with the change in the thermodynamic osmotic pressure. Thus, for the process $A_0^+ \rightarrow A_i^+$, let f moles of solvent move $o \rightarrow i$, and for $B_i^+ \rightarrow B_0^+$, g moles of solvent move $i \rightarrow o$. Then the total process which occurs in the system is

$$A_0^+ + fS_0 + B_i^+ + gS_i = A_i^+ + fS_i + B_0^+ + gS_0$$

where S does not include solvent of solvation; as stated above, the volume of the ion (v_1, v_2) is the effective solvated volume. Then if the terms with the subscripts 0, 1 and 2 refer to those for the solvent, cation A^+ and cation B^+, respectively, the equilibrium constant for the process is

$$K_x = \left(\frac{X_1}{X_2}\right)_i \left(\frac{X_2}{X_1}\right)_o \left(\frac{(X_0)_i}{(X_0)_0}\right)^{f-g} \qquad (5)$$

The equation of Donnan[16] which applies to this ideal system and exchange process, considering only univalent cations, is

$$RT \ln \left[\left(\frac{X_1}{X_2}\right)_i \left(\frac{X_2}{X_1}\right)_o \left(\frac{(X_0)_i}{(X_0)_0}\right)^{f-g}\right] = \pi\ (v_2 - v_1 - (f - g)v_0) \qquad (6)$$

However, in view of equation (4) this expression can be simplified. Then, letting n refer to numbers of moles, equation (6) becomes

$$RT \ln \left[\left(\frac{n_1}{n_2}\right)_i \left(\frac{n_2}{n_1}\right)_0\right] = \pi\ (v_2 - v_1) \qquad (7)$$

Considering the over-all reaction described by the equilibrium constant K_x and equation (6), the standard free energy change for the process is

$$\Delta F^0 = -RT \ln K_x = -\pi\ (v_2 - v_1 - (f - g)v_0) \qquad (8)$$

Since the term $(v_2 - v_1 - (f - g)v_0)$ is the actual decrease in volume which takes place during the exchange reaction, ΔF^0 can be calculated in this manner.

Equation (7) represents the thermodynamic behavior of an ion exchange system in which the parameters are all defined quite independently of the ion exchange process itself. Here $((n_1)/(n_2))_i\ ((n_2)/(n_1))_0 = K_D$ is the conventionally defined distribution constant or selectivity coefficient. It differs from the true equilibrium constant K_x by the solvent term. It is evident that if $v_2 > v_1$, when $(n_2 = n_1)_0$, then $(n_1 > n_2)_i$, or the smaller ion is accumulated by the model. Various properties of the model can be calculated by the simultaneous solution of equations (7), (3) and (4), with $V_i = \Sigma(n_jv_j)_i$ and $n_1 + n_2 = 1$. The term v_1 is set equal to zero to simplify the calculation, for these equations can be solved readily only by graphical means. Thus, v_2 represents the difference in the volumes of the two ionic species, Δv.

In Fig. 3 the ionic concentration ratios inside are plotted against those outside for different values of Δv. The slope of the lines is not constant, but is smallest when the model is in the "relaxed" or "small ion, low π" state, and the accumulation ratio or slope is greatest in the "stretched state." This effect is also shown in Fig. 4, where K_D is shown as a function of log Δv for different ionic concentration ratios in the external phase.

Figures 3 and 4 allow the prediction of a number of experimental results: (1) the volume of an ion exchange resin should vary directly with the volume of (hydrated) ions in the exchange positions; (2) the selectivity ratio K_D should increase as Δv increases at a constant ion concentration ratio in the external solution; (3) K_D should increase as the value of $(n_1/n_2)_0$ decreases; (4) K_D will increase as π increases for systems which constitute "stiffer springs" or have smaller values for the modulus "m," and will decrease as π decreases, as may result from the establishment of a counter-osmotic pressure.

Counter-Osmotic Effects.—Consider the same model as described above but with only a single species of cation being present in the system, and with a variable concentration of electrolyte in the external phase. The effect upon the model of high concentrations of electrolytes in the external solution is being considered. Measurable amounts of non-exchange electrolyte, which consists of movable anions and an equivalent amount of movable cations (of the same species but not identical with exchange cations), will enter the inner phase under these conditions.

Let F be the number of moles of fixed anionic groups in the model (F is equal to one for the molar system), let the subscript 1 refer to cations, and 2 refer to movable anions. In order to simplify the calculations, let $v = v_1 = v_2$, and n (number of moles) be equal to $n_2 = n_1 - F$, all in the resin phase. Then the total number of moles of movable ionic species inside is $n_1 + n_2 = F + 2n$. The inside volume is $V_i = n_0v_0 + v\ (2n + F)$, and is also defined by equation (3). Thus n is the number of moles of non-exchange electrolyte within the resin phase, or the moles of cations present which are compensated for electrically by movable rather than fixed anions. Consider the process

$$A_0^+ + B_0^- + qS_0 \longrightarrow A_i^+ + B_i^- + qS_i$$

where q moles of solvent enter the resin system with the cations and anions. For this system the Gibbs–Donnan equation is

$$RT \ln \left[\frac{(X_1X_2)_i}{(X_1X_2)_0}\right] = -\pi\,(v_1 + v_2) \qquad (10)$$

Substituting

$$RT \ln \left[\frac{n(F + n)}{(n + 2n + F)^2} \times \frac{1}{(X_c)^2_0}\right] = -2\pi v \qquad (11)$$

where $(X_c)_0$ refers to the mole fraction of neutral salt in the external solution.

The effect of varying external concentrations (in terms of molarity) upon the volume of the model for a salt where $v = 0.03$, as calculated from equation (10), is shown in Fig. 5. Terms other than n have the same meaning and numerical values as before. The number of moles of non-exchange electrolyte (n) within the resin phase is also shown in the same figure. Thus the volume of the model is reduced as the external concentration increases, due to the counter Donnan osmotic pressure set-up as a result of the partial exclusion of non-exchange electrolyte from the inner phase. The existence of the pressure gradient between the inner and outer phase serves to increase the exclusion of non-exchange electrolyte over that due to the purely electrical effects.

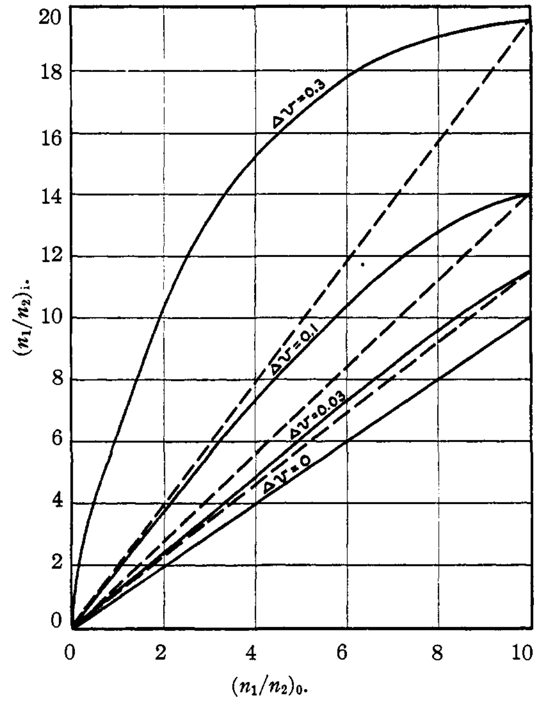

Fig. 3.—The variation in the ratio of the number of cations inside the resin model $(n_1/n_2)_i$ with changes in the same ratio existing in the external solution $(n_1/n_2)_0$, for different values of molar ionic volume differences, Δv.

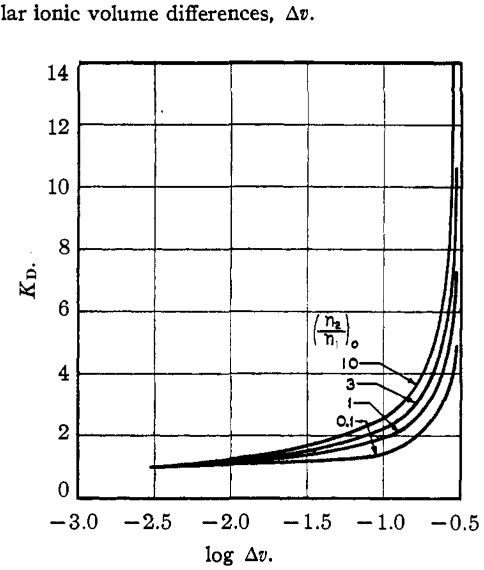

Fig. 4.—Effect of differences in the molar ionic volume Δv upon the accumulation ratio K_D for various values of ion ratios in external phase, $(n_1/n_2)_0$.

This de-swelling effect is not significant until, as shown in Fig. 5, the external concentration of electrolyte is an appreciable fraction of the concentration of fixed groups within the resin structure. In the case described the osmotic pressure is reduced 20% when the external concentration is approximately 15% of the internal concentration. When both concentrations are equal, the osmotic pressure is but one-third of its original value. One consequence of the de-swelling of the resin structure with a resultant decrease in π is that the selectivity of the system should decrease.

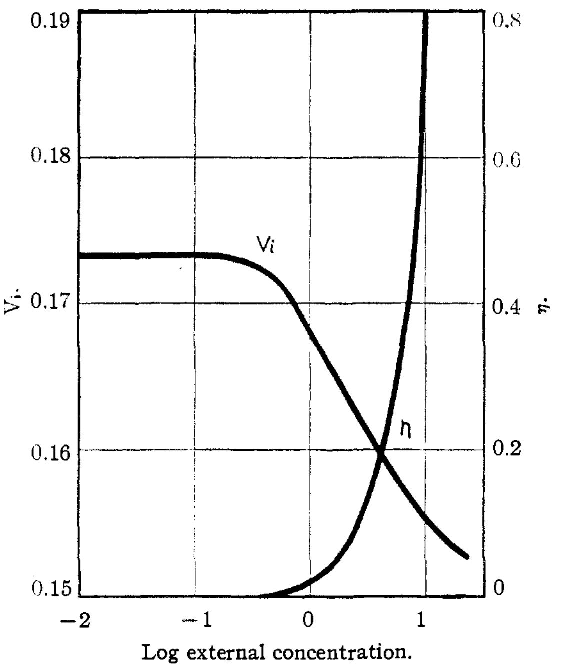

Fig. 5.—De-swelling of the resin model as a function of the logarithm of the external molar concentration of electrolyte, as a result of counter osmotic pressure. The moles of non-exchange electrolyte which have entered the resin phase (n) is also shown.

Non-ideal or Real Systems

The behavior of non-ideal systems is best discussed by first considering the exact thermodynamic expression for cation exchange processes

$$RT \ln \left[\left(\frac{X_1}{X_2}\right)_i \left(\frac{\gamma_1}{\gamma_2}\right)_i \left(\frac{A_2}{A_1}\right)_0 \left(\frac{(A_0)_i}{(A_0)_0}\right)^{f-g}\right] = \int_0^{\pi} (\bar{V}_2 - \bar{V}_1 - (f - g)\bar{V}_0)\mathrm{d}\pi \quad (13)$$

where the γ's refer to rational activity coefficients and the $\bar{V}$'s to partial molar volumes. A_0 refers to the activity of water, and $(A_1)_0$ and $(A_2)_0$ refer to the activities of the cations in the external phase.

For uni-univalent electrolytes, the value of the ratio $(A_2/A_1)_0$ is equal to the concentration ratio in dilute solution. In more concentrated solutions, a good approximation can be arrived at by using the mean activity coefficient of each of the two salts having a common anion, these coefficients being assumed to be functions of the total ionic strength only. The value of $(A_0)_0$ can be taken from the literature, or can be determined. The values of $(X_1/X_2)_i$ and $(f - g)$ can be determined by direct analysis, and thus, in addition to the right-hand term in the expression, values of $(\gamma_1/\gamma_2)_i$ and $(A_0)_i$ need to be determined or calculated.

Turning first to the determination of the osmotic pressure π of the system as a function of V_e, the external volume of the resin, several different methods of attack are available. One is to determine the external volume of resin particles in the solution equilibrated and the dry states, and then calculate the pore volume as being equal to the external volume minus the dry volume (matrix) minus the volume of the hydrated cationic species. Then π can be calculated from the equation

$$\pi = \frac{n_1RT}{V_i - n_1v_1} = \frac{n_1RT}{\text{pore volume}}$$

Since activity coefficients have been neglected and because of the large uncertainty in the ion volumes, this calculated value of π is subject to variation by a factor of 2 or 3. However, this equation may be useful for the prediction of qualitative comparisons.

Another method of approach which may yield values of $(A_0)_i$ (and thus π) as well as $(\gamma_1/\gamma_2)_i$ is carried out by measuring the activity of the solvent (from vapor pressure measurements) of a linear polymer of the same composition as that of the resin. In the absence of cross-linking agents and at the same molality as that of the resin in its various states, the thermodynamic properties of the poly-electrolyte should be very similar to those of the resin. The effect of pressure upon these thermodynamic quantities in going from the linear polymer to the resin is readily calculated, although as a rule it is a minor correction. Then by the application of the Gibbs–Duhem equation, mean activities of the movable cation–fixed anion system can be calculated. Since for different cations only the ratio $(\gamma_1/\gamma_2)_i$ is needed, the single ion activity coefficients of the anionic species cancel out.

Another promising method of attack, which is also being investigated in this Laboratory, is the utilization of equation (7), using neutral molecules instead of ions. The resin is equilibrated with a solution containing two species of neutral molecules (urea is an example) whose molar volumes are fairly independent of electrolyte concentration, and the concentration ratios in the resin phase and in the external solution determined directly. If it can be assumed that the activity coefficients are unity, this allows a direct calculation of π. Other lines of investigation include a determination of the volume as a function of relative humidity, direct swelling pressure measurements, and a calculation of π from thermochemical data. However, all of these latter methods depend on certain assumptions as to mechanical structure, which themselves are not available for direct measurement.

Approximate thermodynamic osmotic pressures may also be calculated from deswelling curves which result from the establishment of counter osmotic pressures. If the assumption is made that the volume of an ion exchange system is proportional to the thermodynamic osmotic pressure, as in equation (3), then the external osmotic activity at which a specific percentage decrease in volume takes place indicates the magnitude of the osmotic pressure. By fitting a calculated curve to the experimental data, it is possible to evaluate the parameters m, b and also π.

It is not possible to evaluate the individual partial molar ion volumes within the resin phase directly. However, the differences in the partial molar volumes can be determined by direct experiment. By plotting the external volume of the resin as a function of X_1 (or X_2), and taking the slope at the desired point

$$\frac{\partial V_e}{\partial n_2} - \frac{\partial V_e}{\partial n_1} - (f - g)\frac{\partial V_e}{\partial n_0} = \Delta V$$

the value of ΔV can be determined.

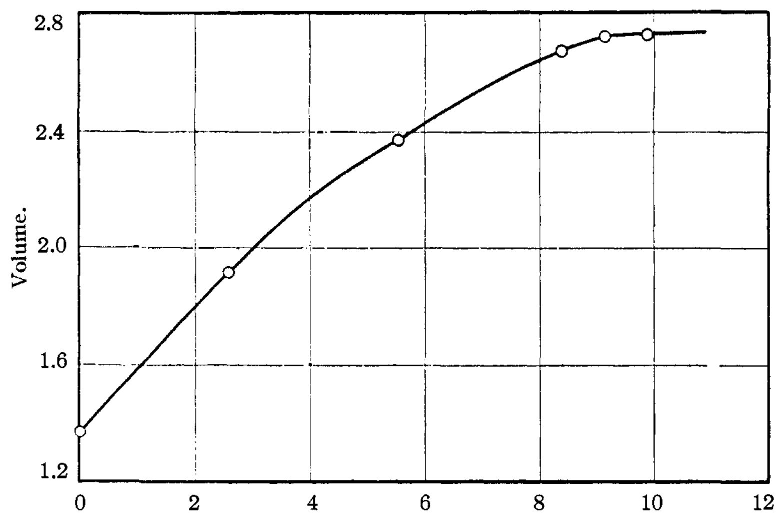

Fig. 6.—The specific volume of a carboxyl resin as a function of millimoles of sodium hydroxide absorbed by the resin.

If π is then known as a function of V_e, the value of $\pi\Delta V$ can be readily calculated. This calculation assumes that ΔV is independent of π, and in view of the incompressibility of these systems, this is a valid assumption. If the value of $\pi\Delta V$ is determined as shown above, the value of $(A_0)_i$ must be calculated; fortunately, for even very concentrated systems this parameter is not strongly dependent upon ionic concentration.

For those systems where the cations are not strongly hydrated as in the case of the potassium and quaternary ammonium compounds, then the apparent molar volumes can be substituted for the partial molar ones without serious error. Under these conditions, the free energy term for the solvent cancels out, and an expression similar to equation (7) can be used, except that ionic activity coefficients must be included.

If hydrated ions are considered, then it is possible to use the hydrated ionic volumes as calculated from conductance data by Gorin.[18] At infinite dilution, these are: K^+, 0.020; Na^+, 0.043; Li^+, 0.076; Mg^{++}, 0.165; La^{+++}, 0.217; $(CH_3)_4N^+$, 0.081; $(C_2H_5)_4N^+$, 0.219 liter mole^{-1}. Under these conditions, equation (7) cannot be used, and the term $(A_0)_i$ is not defined.

The quantitative verification of the theory outlined above must await extensive experimentation. However, sufficient data have already been assembled which give qualitative support to salient points of the theory.

Gregor and Gutoff[19] have measured the external volume of sulfonated polystyrene cation exchange resin particles (with 8% cross-linking) in various states, in 0.001 M solution. For potassium–tetramethylammonium exchange with the same resin, it was found in dilute solution that V_e varied linearly with X_{K^+}, and $-\partial V_e/\partial X_{K^+}$ was 58.6 ml. mole^{-1}. This value compares with 61 ml. mole^{-1} for the difference in the molar ionic volumes. The difference must be due to solvent transport and corresponds to the transport of 0.13 mole of water, having a molar volume of 18 ml., out of the resin phase. The contribution of the pressure–volume free energy term to K_D can be calculated if one assumes a value of π for this system. Since this resin system is approximately 9 molal in the potassium state, a value of $(A_0)_i$ can be compared with the activity of water in 3 molal (9 osmolal) sulfuric acid, where it is 0.85. The resultant average osmotic pressure is 223 atm. Neglecting ionic activity coefficients, the value of $\pi\Delta V$ which is equal to $RT \ln [(X_{K^+}/X_{R_4N^+})_i (A_0)_i^{(f-g)}]$ is 13.1 liter atm. when $(A_2/A_1)_0 = 1.0$. Thus, $(X_{K^+}/X_{R_4N^+})_i$ is calculated to be 1.70. The experimental value of K_D for this resin is 2.55. This agreement is acceptable and similar calculations on comparable systems show reasonable agreement.[20]

A qualitative, experimental vertification of the postulated relationship between the volume and the concentration of movable ions in the resin phase may be obtained by a study of the swelling of a carboxyl resin, Amberlite IRC-50.[21] Gregor and Becher[22] added various amounts of sodium hydroxide to the resin, originally in the acid state, and obtained the data shown in Fig. 6. Here the volume of one gram of resin is plotted against the amount of –COOH groups converted to the salt state. The total capacity of the material is 9.5 mmoles per gram. The volume of the resin matrix was obtained from density measurements of dry material in n-octane, and the pore volume was calculated at

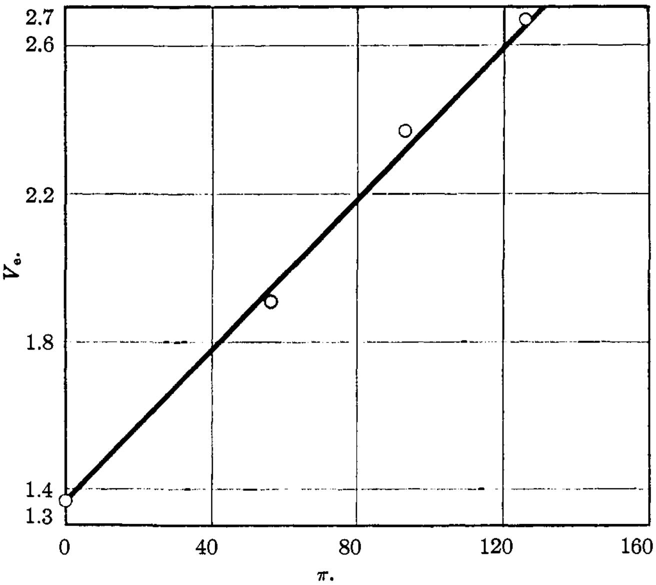

Fig. 7.—Calculated relationship between external volume V_e and internal thermodynamic osmotic pressure π.

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[18] M. H. Gorin, *J. Chem. Phys.*, **7**, 405 (1939).

[19] H. P. Gregor and Fradelle Gutoff, in preparation.

[20] H. P. Gregor and J. I. Bregman, in preparation.

[21] Rohm and Haas Co., Philadelphia, Pa.

[22] H. P. Gregor and J. Becher, in preparation.

zero osmotic pressure by subtracting this dry volume from the volume of the water-wetted resin before the addition of base, assuming a very low degree of dissociation of the acid groups.

In the calculations, it was assumed that the external volume V_e could be expressed as a power series

$$V_e = a + b\pi + c\pi^2 + d\pi^3$$

where V_e is the external volume. The osmotic pressure was calculated using the approximate expression

$$\pi = \frac{n_{Na^+}\,RT}{V_e - V_M - n_{Na^+}\,v_{Na^+}}$$

where n_{Na^+} is the number of moles of sodium ions, V_M the matrix volume, and v_{Na^+} the molar volume of the sodium ions (0.043 l.). All ionic activity coefficients are assumed to be unity. A plot of the calculated values of π *vs.* V_e is shown in Fig. 7. The values of the coefficients in the general expression for V_e are $a = 1.37$, $b = 2.3 \times 10^{-2}$, $c = -4.1 \times 10^{-4}$ and $d = 3.0 \times 10^{-6}$, for this system. Thus it appears as a first approximation that the calculated osmotic pressure is linearly related to the external volume.

The direct determination of the external volume of resin particles can be made pycnometrically, and is of sufficient accuracy to detect small differences. The volume results reported in this paper are given in terms of ml. per gram of dry resin in the hydrogen state, and are designated as specific resin volumes.

According to equations (3) and (4), the volume of an ion exchange resin should increase as the volume of (hydrated) ions in the exchange positions increases, as shown in Fig. 2. Since the volume of the hydrocarbon resin matrix may be assumed to be constant, the external volume of the particles should be a linear function of the internal volume. In Fig. 8 a plot of the specific volume of a sulfonated polystyrene resin, Dowex 50,[23] equilibrated with 0.001 M solutions of various univalent cations (as their chloride salts), is shown plotted against the molar cationic volumes taken from conductivity data. The qualitative agreement between theory and experiment is good.

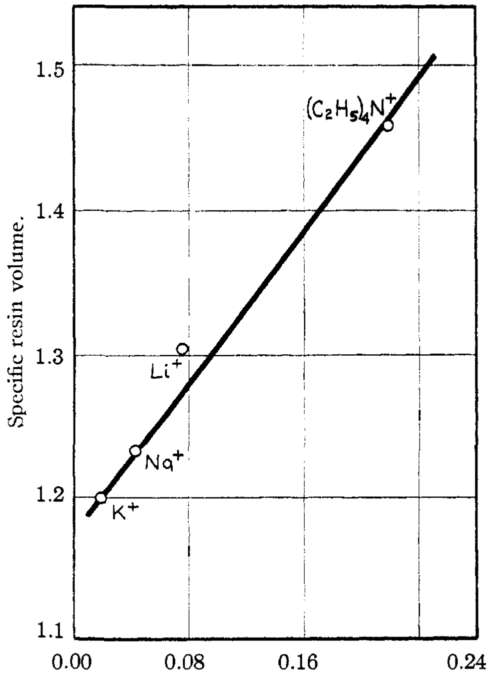

Fig. 8.—Correlation of the specific resin volume with the molar ionic volume of various cations, for a sulfonic acid cation exchange resin in equilibrium with dilute solutions of these cations.

According to equation (8) and Fig. 4, the selectivity constant K_D should increase as the difference in the volumes of cations in the exchange positions increases. Experimental data for this effect is given in Fig. 9, where K_D values for equilibria with the sodium ion and other cations are given. It should be noted that Δv is negative for potassium–sodium exchange. This work also utilized Dowex 50, and was carried out in dilute (0.01 M) solution.

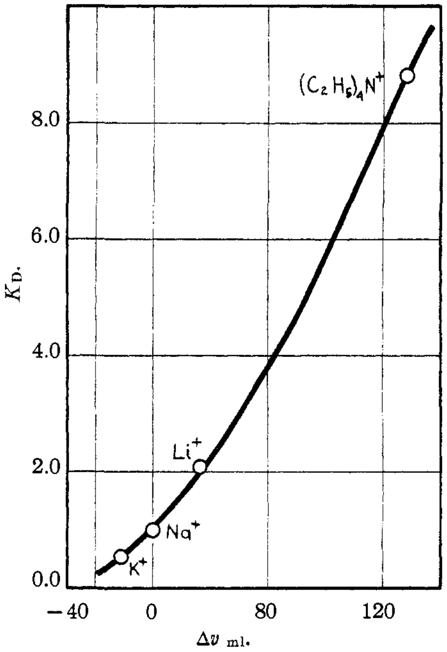

Fig. 9.—The effect of differences in molar cationic volume upon K_D, for exchange processes involving the sodium ion.

According to equation (7) and Fig. 3, the plot of $(n_1/n_2)_i$ against $(n_1/n_2)_0$ should not be linear, but the slope, or K_D should decrease as the resin moves from the stretched state to the less stretched state. This effect is shown in Fig. 10, for sodium–potassium exchange with Dowex 50. The total external concentrations are 0.2 M.

According to equation (7) the theory predicts that for a given pair of cations, the value of log K_D (and thus K_D) should increase as π increases. This can be effected by increasing the degree of cross-linking of the resin matrix. Values of K_D for the exchange of potassium and tetramethylammonium ions and for potassium and sodium ions in sulfonated polystyrene cation exchange resins with different degrees of cross-linking are shown in Fig. 11.

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(23) Dow Chemical Co., Midland, Mich.

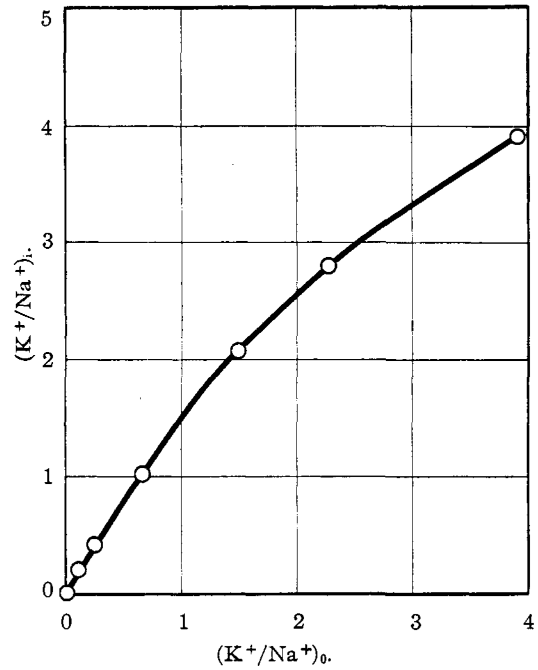

Fig. 10.—The molar ratio of potassium to sodium in the resin phase (of a sulfonic acid cation exchange resin) as a function of that same ratio in the external solution, at a constant total concentration of 0.2 *M*.

For the lightly cross-linked resins, there is no selectivity ($K_D = 1$). As the degree of cross-linking increases, K_D increases sharply.

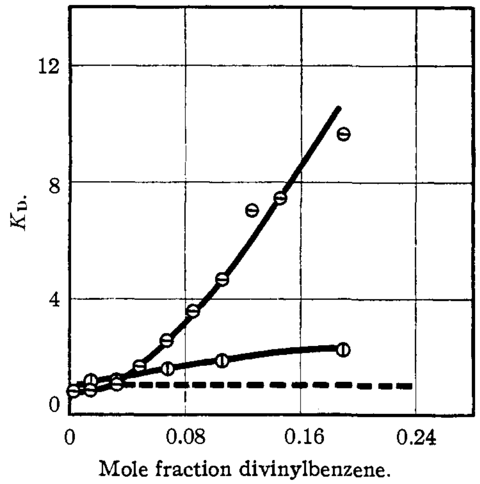

Fig. 11.—Effect of varying the degree of cross-linking in a sulfonic acid resin upon K_D for potassium–tetramethylammonium (⊖) and potassium–sodium (⦶) exchange from solutions where each ion is 0.01 *M*. The dotted line represents unity.

The effect of increasing the external ionic concentration upon the specific volume and the number of moles of non-exchange electrolyte within the resin phase for a Dowex 50 resin, using lithium chloride as electrolyte, is shown in Fig. 12. Here the experimental results show excellent qualitative agreement with the theory, as described previously in Fig. 5.

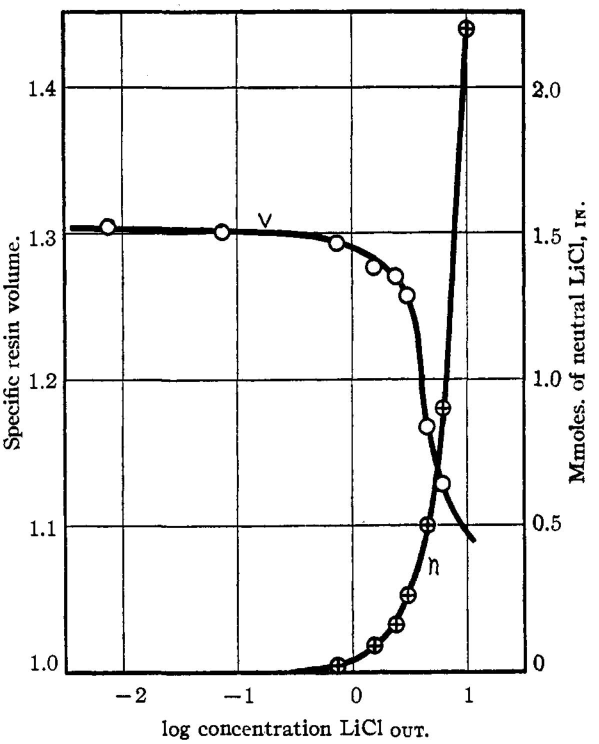

Fig. 12.—Specific resin volume for a cation exchange resin in equilibrium with lithium chloride solutions of various concentrations. The mmoles of non-exchange lithium chloride contained in the same volume of resin is also shown.

Discussion

The thermodynamic theory of exchange processes which has been presented attempts to predict ion exchange phenomena, in particular distribution coefficients, from measurable physical quantities which are defined apart from the exchange processes themselves. Qualitative comparisons between theory and experiment have been presented for a limited number of cases; in general, agreement is good. A series of publications on the quantitative aspects of these phenomena is in preparation.

The theory as presented applies particularly to systems where no interaction between fixed groups and movable ions takes place. As such, it applies in particular to strong acid cation exchange resins and non-reacting univalent cations. An extension of the theory to polyvalent ions is in preparation. The theory also applies to anion exchange systems, where the same restrictions apply, such as strong base anion exchange resins or weak base resins in the presence of strong acids only.

The fundamental exchange reaction equation (13) may be utilized to determine swelling pressures in any system in which two species of particles having different molar volumes can be equilibrated. For example, swelling pressures within cellulose fibers could be evaluated, using this technique.

The next paper in this series will deal with cases where interaction between movable groups and fixed groups can take place, with ion-pair formation. Complex ion formation will also be considered.

The author wishes to express thanks to his colleagues at the Polytechnic Institute of Brooklyn for their comments and suggestions on this work. Particular thanks are expressed to H. Mark and T. Alfrey, Jr., and B. R. Sundheim for their valuable criticism, and to Mr. M. Pope for his invaluable assistance. The author is also indebted to the Office of Naval Research for the considerable support rendered to this work.

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[24] Original manuscript received March 31, 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Differential Diffusion Coefficients of Lithium and Sodium Chlorides in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND CLARENCE L. HILDRETH, JR.

Recent accurate measurements[1,2,3] of the diffusion coefficients of potassium chloride in water from 4 to 30° have shown excellent agreement with the theory[4] at concentrations from 0 to 0.3 molar. As a further test of the theory for 1–1 electrolytes, we have employed the conductometric method for measuring the diffusion of lithium and sodium chlorides in dilute aqueous solutions. The results obtained by this method for potassium chloride solutions have received excellent verification by their agreement with values obtained by Gosting[3] who employed the Gouy layer optical method. This agreement increases our confidence in the value of the conductometric method for the investigation of the theoretical aspects of electrolytic diffusion in dilute solution.

Theoretical Calculations

The theoretical values of the diffusion coefficients were computed by the following equations[5] applicable to 1–1 electrolytes:

$$\mathfrak{D} = 16.629 \times 10^{10}\, T\,\frac{\overline{\mathrm{M}}}{c}\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \qquad (1)$$

$$\frac{\overline{\mathrm{M}}}{c} \times 10^{20} = 1.0748\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right) - \frac{22.148}{\eta_0(DT)^{3/2}}\left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{9.304 \times 10^7}{\eta_0(DT)^2}\, c\phi(A'\sqrt{c}) \qquad (2)$$

where $\Lambda_0 = \lambda_1^0 + \lambda_2^0$; $\kappa a = A\sqrt{\Gamma} = A'\sqrt{c}$; $A = a35.559 \times 10^8/(DT)^{1/2}$. $\mathfrak{D}$ is the diffusion coefficient in cm.^{2} sec.$^{-1}$, λ_1^0 and λ_2^0 and the equivalent limiting ionic conductances of the cation and anion, η_0 is the viscosity of the solvent, D is the dielectric constant of water, T is the absolute temperature, $\phi(A'\sqrt{C})$ is an exponential integral function which can be obtained from a table,[5,6] κ is the reciprocal distance of the Debye and Hückel theory, a is the mean distance of approach of the ions in cm. and Γ is the ional concentration. The thermodynamic term in equation (1) was calculated by the equations

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514\, \mathcal{S}_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 2.303(2B)c - c\psi(d) \qquad (3)$$

$$\psi(d) = \frac{\partial d/\partial c + 0.001\,(2\mathrm{M}_1 - \mathrm{M}_2)}{d + 0.001c(2\mathrm{M}_1 - \mathrm{M}_2)} \qquad (4)$$

$$d = d_0 + \frac{(\mathrm{M}_2 - d_0\phi_{\mathrm{v}}^0)}{1000}\, c - \frac{S_{\mathrm{v}} d_0}{1000}\, c^{3/2} \qquad (5)$$

where $y_\pm$ is the mean activity coefficient of the electrolyte on the molar concentration scale, $\mathcal{S}_{(f)}$ is the limiting theoretical expression of the Debye and Hückel theory for activity coefficients, and B is an empirical constant. The density term, $c\psi(d)$, in equation (3), was calculated by equations (4) and (5)[6a] in which d is the density of the solution, d_0 the density of the solvent, M_1 and M_2 are the molecular weights of the solvent and solute, respectively, ϕ_{v}^0 is the apparent molal volume at infinite dilution and S_{v} is the experimental slope of the apparent molal volume *versus* $\sqrt{c}$.

The limiting value of the diffusion coefficient, $\mathfrak{D}_0$, may be obtained from

$$\mathfrak{D}_0 = 17.872 \times 10^{-10}\, T\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda_0}\right) \qquad (6)$$

and the slope, $\mathcal{S}_{(\mathrm{D})}$, of the limiting law

$$\mathfrak{D} = \mathfrak{D}_0 - \mathcal{S}_{(\mathrm{D})}\sqrt{c} \qquad (7)$$

may be computed by

$$\mathcal{S}_{(\mathrm{D})} = \frac{3.754 \times 10^{-8}}{D^{3/2}T^{1/2}}\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda_0}\right) + \frac{3.683 \times 10^{-8}}{D^{1/2}T^{-1/2}}\left(\frac{\lambda_1^0 - \lambda_2}{\Lambda_0}\right) \qquad (8)$$

The numerical coefficients in these equations were evaluated by using the universal constants of Birge.[7] The quantities required for the calculations and their sources are recorded in Table I.

TABLE I

CONSTANTS AND PARAMETERS EMPLOYED IN THEORETICAL CALCULATIONS

			LiCl	NaCl
T	298.16	λ_1^0	38.69^c	50.11^c
$\mathcal{S}_{(f)}$	0.5091^a	λ_2^0	76.34^c	76.34^c
d_0	0.97707^b	$a \times 10^8$	4.25^a	4.0^a
η_0	$8.949 \times 10^{-3a,b}$	$4.606B$	0.2740	0.1287
D	78.54^d	M_2	42.40	58.45
		S_{v}	1.488^a	2.153^a
		ϕ_{v}^0	17.00^a	16.40^a

[a] Ref. (6). [b] "International Critical Tables," Vol. 3, p. 24 (1928), McGraw-Hill Book Co., Inc., New York, N. Y. [c] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932). [d] Wyman, *Phys. Rev.*, **35**, 613 (1930).

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(1) Harned and Nuttall, THIS JOURNAL, **71**, 1460 (1949).

(2) Harned and Blake, *ibid.*, **72**, 2265 (1950).

(3) Gosting, *ibid.*, in press.

(4) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(5) Harned, *Chem. Revs.*, **40**, 461 (1947).

(6) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 130.

(6a) Ref. (6), p. 250.

(7) Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).