somewhat higher. Small differences in the measurement of the isotopic shifts produce appreciable differences in the partition function ratios and the measurement of the isotopic frequencies with a grating spectrometer would be necessary for greatest precision. As pointed out by Bigeleisen and Friedman and by McCrea, the equi-librium constant for the intramolecular equilibrium

$$N^{15}N^{14}O^{16} \rightleftharpoons N^{14}N^{15}O^{16}$$
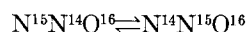
can be calculated by dividing the numbers in column two by those in column one in Table V. This results in an equilibrium constant of 1.0545 at 25°C.

Ion Exchange Kinetics. A Nonlinear Diffusion Problem*†

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Ideal limiting laws are calculated for the kinetics of particle diffusion controlled ion exchange processes involving ions of different mobilities between spherical ion exchanger beads of uniform size and a well-stirred solution. The calculations are based on the nonlinear Nernst-Planck equations of ionic motion, which take into account the effect of the electric forces (diffusion potential) within the system. Numerical results for counter ions of equal valence and six different mobility ratios are presented. They were obtained by use of a digital computer. This approach contains the well-known solution to the corresponding linear problem as a limiting case. An explicit empirical formula approximating the numerical results is given.

1. INTRODUCTION

AN ion exchange resin consists essentially of a three-dimensional cross-linked network of hydrocarbon chains carrying fixed ionic groups, the electric charge of which is compensated for by mobile ions of opposite charge ("counter ions"). These counter ions are free to diffuse within the resin network. In contact with an electrolyte solution the resin takes up solvent and some additional mobile ions (additional counter ions, and "co-ions" having the same charge sign as the fixed ionic groups). In an ion exchange process the counter ion species present initially is replaced by another species.

We consider the ion exchange between spherical ion exchange resin beads of uniform size containing the counter ion species A and a well-stirred solution containing the counter ion species B. During the process ions A diffuse out of the bead and are replaced by an equivalent amount of ions B.

It has been established that such processes are diffusion controlled: the rate determining mechanism is the interdiffusion of the two species A and B, either within the resin particles or in a Nernst diffusion layer ("film") adherent to the particle surface, which is not affected by stirring.[1] Limiting laws for film controlled exchange in ideal systems have been given previously.[2] In this paper, ideal limiting laws for particle controlled processes are calculated. Particle control is favored by concentrated

solutions, large diameter and high degree of cross-linking of the beads, and efficient stirring.[3]

The driving "force" for the flux of an ionic species is, in systems without convection, the gradient of its general chemical potential, the principal elements of which are the concentration gradient of the species and the gradient of the electric potential. Even if no external electric field is applied, a gradient of the electric potential will, as a rule, be built up by the diffusion process (diffusion potential). The corresponding differential equations are nonlinear. The interdiffusion process considered here can be described in terms of one interdiffusion coefficient which, however, is not constant but changes with the concentration ratio of the two counter ion species present. Hence, the mathematical treatment is that of a diffusion problem with varying diffusion coefficient. Hitherto, only the corresponding linear problem, i.e., with constant interdiffusion coefficient, has been solved[4] and applied to ion exchange kinetics.[5-10] In our approach the solution to the linear problem represents a limiting case: the exchange of counter ions of equal mobility. The linear solution holds rigorously for isotopic exchange processes, whereas for other cases the deviations are considerable.

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2. MODEL AND SIMPLIFYING ASSUMPTIONS

We use the simplest model conceivable and the simplest equations proved to be adequate for the description of ionic diffusion processes, the Nernst-Planck equations.[11–15]

Without respect to its actual porous structure the whole resin is treated as a quasi-homogeneous phase. Individual diffusion constants for the mobile ions present are defined correspondingly; they can be measured by tracer techniques in equilibrium systems.[1,15–18] The assumption is made with experimental support[15,16,18] that these individual diffusion constants are essentially constant for a given resin, i.e., independent of ionic composition. We make use of the ideal Einstein relation between the individual diffusion constants and the electrochemical mobilities. We neglect any coupling of ionic fluxes other than by electric forces. We assume a constant concentration of fixed ionic groups throughout the resin. Any concentration change and flux of the co-ions is disregarded, since they are small as compared with those of the counter ions if the concentration of the solution is not too high and that of the fixed ionic groups not too low.[13] We neglect changes in ionic activity coefficients and swelling condition of the resin as well as the effect of gradients of swelling pressure. Under the simple boundary condition used here, the magnitude of the selectivity coefficient is irrelevant.[19] We restrict ourselves to radial diffusion, i.e., spherical symmetry. We assume that interdiffusion within the resin beads is the rate determining mechanism throughout the process. This last assumption is not strictly valid; it leads to exchange fluxes that are infinite initially, whereas the possible diffusion rate through the film is finite. For a very short initial period film diffusion must be the rate controlling step.

The assumptions and simplification listed above are those usually made in the formulation of a model for ion exchange kinetics.[5–10]

We do not neglect the effect of the electric potential gradient on the ionic fluxes; in this respect our approach differs from previous theories.

3. FORMULATION OF THE PROBLEM

Under the assumptions mentioned, the fluxes of the two counter ion species A and B are given by the

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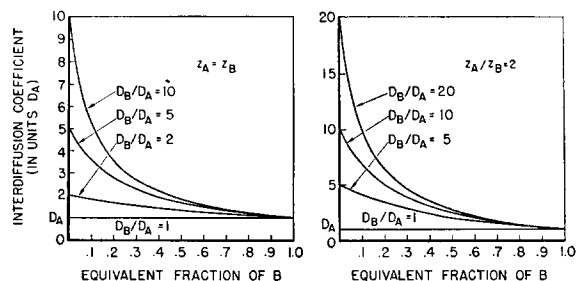[19] F. Helfferich, Discussions Faraday Soc. **21**, 83 (1956).

FIG. 1. Dependence of the interdiffusion coefficient D_{AB} on the ionic composition of the exchanger, calculated from Eq. (4), for the interdiffusion of ions of equal valence (left) and of a univalent and a bivalent ion (right). The different curves correspond to different ratios D_A/D_B.

Nernst-Planck equations[11–14]

$$\Phi_A = -D_A[\text{grad}C_A + z_A C_A(\mathfrak{F}/RT)\,\text{grad}\varphi], \quad (1a)$$

$$\Phi_B = -D_B[\text{grad}C_B + z_B C_B(\mathfrak{F}/RT)\,\text{grad}\varphi], \quad (1b)$$

where Φ is the flux, D is the individual diffusion constant, C is the molar concentration, z is the electrochemical valence, $\mathfrak{F}$ is the Faraday constant, R is the gas constant, T is the absolute temperature, φ is the electric potential, and the subscripts A and B refer to the counter ion species.

Electroneutrality requires that the total equivalent concentration of counter ions is constant throughout the bead, since the concentrations of both the fixed ionic groups and the co-ions are constant; thus

$$z_A C_A + z_B C_B \equiv C = \text{const.} \quad (2)$$

The absence of an electric current in combination with (2) gives the condition

$$z_A\Phi_A + z_B\Phi_B = 0. \quad (3)$$

By use of (2) and (3), Eqs. (1a) and (1b) may be combined to give

$$\Phi_A = -\left[\frac{D_A D_B(z_A^2 C_A + z_B^2 C_B)}{D_A z_A^2 C_A + D_B z_B^2 C_B}\right]\text{grad}C_A. \quad (4)$$

The quantity in brackets may be termed the interdiffusion coefficient D_{AB} of the process. Its value depends not only on the individual diffusion constants D_A and D_B; it is also a function of the concentration ratio C_A/C_B and therefore a function of the time and space coordinates. The dependence of the interdiffusion coefficient on ionic composition is shown in Fig. 1 for various values of the ratio D_A/D_B. For $C_A \ll C_B$, D_{AB} assumes the value D_A, and for $C_B \ll C_A$ the value D_B. The ion present in *smaller* concentration always has the stronger influence on the interdiffusion coefficient.[3,19] This simple rule is a consequence of the fact that in (1) the concentration of the species enters in the electric term. It is also physically evident since the electric field acts on every ion present and thus causes a large transference of the species present in high concentration, whereas the

flux of the species present in low concentration is hardly affected.

For the treatment of time-dependent processes the equation of continuity must be introduced

$$\partial C_A/\partial t = -\text{div}\mathbf{\Phi}_A. \tag{5}$$

In previous work on time-dependent processes, only the limiting linear case has been considered, to which (4) and (5) reduce when a constant interdiffusion coefficient D_{AB} is assumed. Analytical solutions to the linear problem have been derived for a number of systems including those with spherical symmetry with various boundary conditions.[4,20] However, Eq. (4) and Fig. 1 show that the assumption of a constant interdiffusion coefficient holds only if the individual diffusion constants D_A and D_B are equal, as is the case for example in isotopic exchange processes.

This paper deals with the general, nonlinear problem and will treat specifically systems with spherical symmetry. Upon substitution of (4) into (5) an expression is obtained which can be written conveniently in dimensionless form with the introduction of the following dimensionless variables and parameters:

$$\gamma \equiv z_A C_A/C; \quad \tau \equiv D_A t/r; \quad \rho \equiv r/r_0; \tag{6}$$
$$a \equiv z_A D_A/z_B D_B - 1; \quad b \equiv z_A/z_B - 1,$$

where t is time, r is the radial coordinate, and r_0 is the radius of the beads. The resulting equation

$$\frac{\partial \gamma}{\partial \tau} - \frac{1}{1+a\gamma}\left[(1+b\gamma)\frac{\partial^2 \gamma}{\partial \rho^2}\right.$$
$$\left. + \frac{b-a}{1+a\gamma}\left(\frac{\partial \gamma}{\partial \rho}\right)^2 + \frac{2(1+b\gamma)}{\rho}\frac{\partial \gamma}{\partial \rho}\right] = 0 \tag{7}$$

was derived in a preliminary note.[21] The fraction q_A of the species A still present in the sphere at the dimensionless time τ is expressed in terms of the solution $\gamma(\rho,\tau)$ of Eq. (7) as follows:

$$q_A(\tau) = 3\int_0^1 \gamma(\rho,\tau)\rho^2 \partial\rho. \tag{8}$$

The ion exchange rate, defined as the decrease with time of the amount Q_A of the species A (in moles) present in the spheres, may be written as

$$-\frac{dQ_A}{dt} = -VC\frac{dq_A}{dt} = -\frac{VCD_A}{r_0^2}\frac{dq_A}{d\tau}, \tag{9}$$

where V is the total volume of ion exchanger used.

If the problem is limited to the exchange of counter ions of equal valence ($z_A = z_B$), so that $b=0$, the general

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Eq. (7) may be simplified by the introduction of the new variable‡

$$u \equiv \ln(1+a\gamma), \tag{10}$$

to become

$$\frac{\partial u}{\partial \tau} - \frac{e^{-u}}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2\frac{\partial u}{\partial \rho}\right) = 0, \tag{11}$$

which is a convenient form for numerical integration. The results reported at the present time will be for this case. Determination of the solutions of Eq. (7) for non-zero values of b are planned for a later time.

We use the simplest initial and boundary conditions possible, assuming that initially the beads contain counter ions A only and the solution counter ions B only, and that no concentration changes occur in the solution.

$$0 \leqslant \rho < 1, \quad \tau = 0, \quad \gamma(\rho) = 1, \tag{12a}$$
$$\rho \geqslant 1, \quad \gamma(\rho,\tau) = 0. \tag{12b}$$

The boundary condition (12b) corresponds to infinite solution volume or to continuous renewal of the solution. The selection of a boundary condition other than (12b) would require the introduction of further parameters which, for the numerical evaluation we carried out, would have to be chosen arbitrarily and have led to results applicable in special cases only. In contrast, by using the conditions (12), more general limiting laws are obtained, which can be approached fairly closely by experimental techniques. Other initial conditions are treated in Sec. (6).

Even under the simple conditions (12) an analytical solution to the Eqs. (7) or (11) was not obtained. We have evaluated (11) numerically for six values of the ratio D_A/D_B of the individual diffusion constants:

$$D_A/D_B = 10(a=9), \quad D_A/D_B = \tfrac{1}{10}(a=-0.9),$$
$$D_A/D_B = 5(a=4), \quad D_A/D_B = \tfrac{1}{5}(a=-0.8),$$
$$D_A/D_B = 2(a=1), \quad D_A/D_B = \tfrac{1}{2}(a=-0.5).$$

The results are given in Sec. (5).

4. CALCULATION PROCEDURE

For the numerical evaluation, (11) was approximated by the finite difference form

$$u(\rho, \tau+\Delta\tau) = u(\rho,\tau) + g(\rho,\tau)$$
$$\times \{R_+(\rho)[u(\rho+\Delta\rho, \tau) - u(\rho,\tau)]$$
$$- R_-(\rho)[u(\rho,\tau) - u(\rho-\Delta\rho, \tau)]\}, \tag{13}$$

where

$$g(\rho,\tau) \equiv \exp[-u(\rho,\tau)]\Delta\tau/(\Delta\rho)^2;$$
$$R_+(\rho) \equiv [(\rho+\tfrac{1}{2}\Delta\rho)/\rho]^2;$$
$$R_-(\rho) \equiv [(\rho-\tfrac{1}{2}\Delta\rho)/\rho]^2.$$

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‡ It should be noted that the new variable u is related to the electric potential φ by $u = -(z_A\mathfrak{F}/RT)\varphi$.

By use of (13), $u(\rho, \tau+\Delta\tau)$ can be calculated from $u(\rho+\Delta\rho, \tau)$, $u(\rho,\tau)$, and $u(\rho-\Delta\rho, \tau)$. For the calculation the initial condition and the boundary conditions for $\rho=0$ and $\rho=1$ are required. The initial condition is obtained from (12a) and (10):

$$u(\rho, \tau=0) = \ln(1+a). \tag{14a}$$

The boundary conditions at the bead surface ($\rho=1$) is given by (12b) and (10):

$$u(\rho=1, \tau) = 0. \tag{14b}$$

It can be shown that the gradients of γ and u vanish at the center of the sphere:

$$(\partial u/\partial\rho)_{\rho=0} = 0.$$

Hence the condition at $\rho=0$ becomes

$$u(\rho=0, \tau) = u(\rho=0+\Delta\rho, \tau). \tag{14c}$$

By choice of $\Delta\rho$ an upper limit is given for $\Delta\tau$ by the stability condition for the numerical integration.[22] In case of (13), this condition is

$$\Delta\tau \leqslant 0.4 e^u (\Delta\rho)^2. \tag{15}$$

The function $u(\rho,\tau)$ was calculated numerically from (13) and (14) in accord with the requirement (15).

For the numerical integration corresponding to (8), which leads to the fraction q_A still present in the sphere, Simpson's rule was used:

$$q_A(\tau) = \frac{3}{a} \int_0^1 [e^{u(\rho,\tau)} - 1]\rho^2 \partial\rho$$

$$= \frac{(\Delta\rho)^3}{a} \{4 \sum_{n=1,3,5\cdots}^{1/\Delta\rho-1} n^2 [e^{u(\rho,\tau)} - 1]$$

$$+ 2 \sum_{n=2,4,6\cdots}^{1/\Delta\rho-2} n^2 [e^{u(\rho,\tau)} - 1]\}, \tag{16}$$

where

$$n \equiv \rho/\Delta\rho.$$

The dimensionless rate, $-dq_A/d\tau$, was approximated by

$$-dq_A/d\tau = [q_A(\tau-\Delta\tau) - q_A(\tau)]/\Delta\tau. \tag{17}$$

The calculation starts out with a step function. Therefore, a very fine subdivision of space and time is required initially. The initial spacing of ρ used was $\Delta\rho = 1/640$. The spacing of $\Delta\tau$ was selected in accordance with the stability condition (15). As the calculation proceeded, $\Delta\rho$ was increased stepwise to $1/320$, $1/160$, $1/80$, $1/40$ (at about $q_A=0.9$), $1/20$ (at about $q_A=0.6$), and $1/10$ (at $q_A<0.1$). $\Delta\tau$ was increased correspondingly. The estimated maximum error in q_A is ±0.01; the error in $dq_A/d\tau$ is about $\pm2\%$.

The calculations were carried out on the Datatron digital computer (manufactured by Electrodata, Inc.,

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Pasadena, California) in the computing center at the California Institute of Technology. Floating point numbers were used. The total time required was about 35 hours.

5. RESULTS AND DISCUSSION

The calculation yields the dimensionless functions $u(\rho,\tau)$, $q_A(\tau)$, and $-dq_A(\tau)/d\tau$. The first is readily converted to $\gamma(\rho,\tau)$, which gives the radial concentration profiles of the species A. In tabulating and plotting the results, we have followed general practice and given the fractional attainment of equilibrium, $F(\tau)$, rather than $q_A(\tau)$. Under the initial and boundary conditions (12), this quantity is given by

$$F(\tau) = 1 - q_A(\tau). \tag{18}$$

The representation of the data is kept in dimensionless form, since the actual values of the concentrations, the fractional attainment of equilibrium, and the rates at a given time t depend also on D_A, r_0, C, and V. They can be obtained from the tables and graphs by substituting numerical values for these quantities and using (6) and (9).

Table I gives the fractional attainment of equilibrium, $F(\tau)$, and the dimensionless rate, $-dq_A/d\tau$, for the various cases. Figure 2 shows a plot of F versus τ and includes the solution to the linear case ($D_A=D_B$) which is well known[4] to be

$$F(\tau) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\pi^2\tau). \tag{19}$$

It should be emphasized that the time coordinate τ contains the quantity D_A; hence, these results can be used for direct comparison of different processes only if the ion A initially present in the beads is the same in all cases. Figure 2 shows that the curves for different ratios D_A/D_B cannot be transformed into one another by a linear transformation of the time. If the ion B is slower, the process is slower, but not by a constant factor, because the interdiffusion coefficient increases with decreasing concentration of A. On the other hand, if B is faster, the process is faster, but the interdiffusion coefficient decreases during the process.

It is of interest to compare the rates for forward and backward exchange of two counter ion species. In Fig. 3 we have plotted the fractional attainment of equilibrium for the exchange processes H^+ against Li^+ and Li^+ against H^+, assuming a ratio $D_H/D_{Li}=10$. For direct comparison we have chosen $D_H t/r_0^2$ as the dimensionless time coordinate in both cases. It is seen that the process is faster if H^+, the faster ion, is initially present in the resin. The half-times of exchange differ by about the factor 2, the time required for 90% exchange by about the factor 3. According to previous theories, which assume a constant interdiffusion coefficient, the two curves should coincide.

The radial concentration profiles of the species A for

TABLE I. Fractional attainment of equilibrium, $F(\tau)$, and dimensionless rate, $-dq_A(\tau)/d\tau$, for six different values of the ratio D_A/D_B.

(a) $D_A/D_B = 10$

τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$
0.00001831	0.006		0.08187	0.477	2.52
0.00007690	0.012		0.08937	0.495	2.37
0.0003113	0.023		0.09687	0.512	2.24
0.001717	0.051	27.60	0.1044	0.528	2.12
0.002185	0.063	25.33	0.1119	0.544	2.02
0.002654	0.074	23.10	0.1231	0.566	1.88
0.003122	0.084	20.97	0.1306	0.580	1.80
0.003592	0.093	19.02	0.1456	0.606	1.65
0.004060	0.102	17.31	0.1606	0.629	1.53
0.004529	0.110	15.88	0.1756	0.652	1.42
0.004998	0.117	14.72	0.1906	0.672	1.33
0.005935	0.130	13.02	0.2056	0.691	1.24
0.006873	0.141	11.84	0.2206	0.709	1.16
0.007810	0.152	10.94	0.2356	0.726	1.11
0.008748	0.161	10.20	0.2506	0.742	1.03
0.01062	0.179	9.04	0.2656	0.757	0.976
0.01437	0.213	7.37	0.2806	0.771	0.923
0.01812	0.237	6.42	0.2956	0.785	0.874
0.02187	0.259	5.77	0.3106	0.798	0.829
0.02562	0.280	5.27	0.3331	0.815	0.766
0.02937	0.299	4.87	0.3556	0.832	0.710
0.03312	0.317	4.53	0.3781	0.847	0.658
0.03687	0.333	4.24	0.3856	0.852	0.642
0.04062	0.348	3.99	0.4156	0.870	0.582
0.04437	0.363	3.77	0.4456	0.887	0.527
0.04812	0.376	3.58	0.4756	0.902	0.476
0.05187	0.389	3.41	0.5056	0.915	0.430
0.05562	0.402	3.26	0.5656	0.939	0.346
0.05937	0.414	3.12	0.6256	0.957	0.273
0.06312	0.425	3.00	0.6856	0.971	0.206
0.06687	0.436	2.89	0.7456	0.982	0.147
0.07437	0.457	2.69	0.8356	0.991	0.075

(b) $D_A/D_B = 5$

τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$
0.00001831	0.010		0.06219	0.503	3.39
0.00007690	0.020		0.06969	0.527	3.12
0.0003113	0.041		0.07719	0.550	2.90
0.001718	0.095	27.11	0.08469	0.571	2.70
0.002186	0.107	23.37	0.09219	0.590	2.53
0.002655	0.117	20.97	0.09969	0.609	2.38
0.003124	0.127	19.35	0.1072	0.626	2.25
0.003593	0.135	18.13	0.1147	0.644	2.13
0.004061	0.144	17.12	0.1222	0.658	2.02
0.004999	0.158	15.43	0.1297	0.673	1.91
0.005963	0.172	14.06	0.1372	0.687	1.82
0.006874	0.185	12.96	0.1447	0.700	1.74
0.007811	0.197	12.06	0.1597	0.725	1.59
0.008750	0.208	11.31	0.1747	0.748	1.45
0.009686	0.218	10.67	0.1897	0.769	1.34
0.01062	0.228	10.13	0.2047	0.788	1.23
0.01156	0.237	9.65	0.2197	0.806	1.14
0.01297	0.250	9.04	0.2347	0.822	1.05
0.01437	0.262	8.51	0.2497	0.837	0.977
0.01578	0.274	8.06	0.2647	0.851	0.906
0.01766	0.289	7.55	0.2872	0.870	0.810
0.01953	0.302	7.11	0.3097	0.888	0.724
0.02141	0.315	6.73	0.3322	0.903	0.645
0.02328	0.328	6.39	0.3622	0.921	0.555
0.02516	0.342	6.03	0.3922	0.936	0.471
0.02844	0.358	5.66	0.4222	0.949	0.395
0.03219	0.379	5.24	0.4522	0.960	0.328
0.03969	0.414	4.58	0.5122	0.976	0.215
0.04719	0.448	4.10	0.5722	0.986	0.133
0.05469	0.477	3.70	0.6622	0.994	0.059

(c) $D_A/D_B = 2$

τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$
0.00001831	0.013		0.05281	0.561	4.23
0.00007690	0.026		0.05656	0.576	4.01
0.0003113	0.051		0.06031	0.591	3.81
0.001249	0.101		0.06406	0.605	3.63
0.001718	0.118	33.55	0.06781	0.618	3.47
0.002186	0.133	29.52	0.07156	0.631	3.32
0.002655	0.146	26.61	0.07531	0.643	3.18
0.003124	0.157	24.36	0.07906	0.655	3.05
0.003593	0.168	22.56	0.08281	0.666	2.92
0.004062	0.178	21.07	0.08656	0.677	2.81
0.004530	0.188	19.30	0.09031	0.687	2.70
0.004999	0.197	18.76	0.09406	0.697	2.61
0.005963	0.214	17.03	0.1016	0.716	2.43
0.006874	0.229	15.66	0.1091	0.733	2.26
0.007811	0.243	14.55	0.1166	0.750	2.12
0.008749	0.256	13.62	0.1241	0.765	1.98
0.009686	0.268	12.83	0.1316	0.779	1.86
0.01062	0.280	12.15	0.1391	0.793	1.74
0.01203	0.296	11.28	0.1466	0.805	1.64
0.01344	0.312	10.55	0.1541	0.817	1.54
0.01484	0.326	9.93	0.1616	0.828	1.45
0.01625	0.340	9.42	0.1691	0.839	1.37
0.01812	0.357	8.80	0.1841	0.858	1.21
0.02000	0.373	8.27	0.1991	0.875	1.07
0.02187	0.388	7.80	0.2141	0.890	0.957
0.02375	0.402	7.40	0.2291	0.904	0.848
0.02656	0.422	6.87	0.2441	0.916	0.753
0.03031	0.446	6.29	0.2591	0.926	0.666
0.03406	0.469	5.81	0.2891	0.944	0.518
0.03781	0.490	5.40	0.3191	0.958	0.399
0.04156	0.509	5.05	0.3641	0.972	0.266
0.04531	0.528	4.74	0.4091	0.982	0.175
0.04906	0.545	4.47	0.4691	0.990	0.099

(d) $D_A/D_B = \tfrac{1}{2}$

τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$
0.00001221	0.014		0.03002	0.539	7.07
0.00005127	0.027		0.03252	0.556	6.64
0.0001802	0.049		0.03502	0.572	6.25
0.0006489	0.092		0.03752	0.587	5.91
0.0009614	0.113	58.73	0.04002	0.601	5.60
0.001274	0.130	50.17	0.04252	0.615	5.31
0.001586	0.145	44.36	0.04502	0.628	5.05
0.001899	0.157	40.08	0.04752	0.640	4.82
0.002211	0.169	36.78	0.05002	0.652	4.60
0.002524	0.180	34.12	0.05252	0.663	4.39
0.002836	0.190	31.92	0.05502	0.674	4.20
0.003149	0.200	30.07	0.05752	0.684	4.03
0.003774	0.218	27.08	0.06002	0.694	3.86
0.004399	0.234	24.77	0.06252	0.703	3.71
0.005024	0.248	22.91	0.06752	0.721	3.43
0.005649	0.262	21.37	0.07252	0.738	3.17
0.006274	0.275	20.07	0.07752	0.753	2.95
0.006899	0.288	18.95	0.08252	0.767	2.75
0.007524	0.299	17.97	0.08752	0.780	2.57
0.008774	0.320	16.31	0.09252	0.792	2.40
0.01002	0.340	15.03	0.09752	0.804	2.24
0.01127	0.358	13.95	0.1025	0.815	2.10
0.01252	0.375	13.04	0.1075	0.825	1.97
0.01377	0.390	12.26	0.1125	0.835	1.85
0.01502	0.405	11.57	0.1225	0.852	1.63
0.01627	0.419	10.96	0.1325	0.867	1.45
0.01752	0.433	10.42	0.1475	0.887	1.21
0.01877	0.445	9.94	0.1625	0.904	1.02
0.02002	0.457	9.50	0.1825	0.922	0.827
0.02127	0.469	9.10	0.2025	0.937	0.664
0.02252	0.480	8.73	0.2225	0.949	0.535
0.02377	0.491	8.40	0.2625	0.966	0.351
0.02502	0.501·	8.08	0.3225	0.981	0.189
0.02752	0.520	7.53	0.4025	0·992	0.084

TABLE I.—Continued.

(e) $D_A/D_B = \frac{1}{5}$

τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$
0.000006104	0.011		0.02532	0.543	8.18
0.00002564	0.023		0.02782	0.562	7.58
0.00008423	0.039		0.03032	0.580	7.05
0.0004749	0.090	93.11	0.03282	0.597	6.95
0.0006311	0.103	79.96	0.03532	0.613	6.18
0.0007874	0.115	70.94	0.03782	0.628	5.81
0.0009436	0.125	64.26	0.04032	0.642	5.47
0.001100	0.135	59.07	0.04282	0.656	5.17
0.001412	0.152	51.42	0.04532	0.668	4.89
0.001725	0.167	45.98	0.04782	0.680	4.66
0.002037	0.181	41.85	0.05032	0.692	4.42
0.002506	0.199	37.18	0.05282	0.702	4.21
0.002975	0.216	33.68	0.05782	0.722	3.82
0.003444	0.231	30.92	0.06282	0.740	3.49
0.004069	0.249	28.02	0.06782	0.757	3.19
0.004694	0.266	25.72	0.07282	0.772	2.94
0.005318	0.281	23.84	0.07782	0.786	2.71
0.005944	0.296	22.27	0.08282	0.799	2.50
0.006569	0.309	20.93	0.08782	0.811	2.32
0.007819	0.334	18.80	0.09532	0.828	2.08
0.009069	0.356	17.10	0.1028	0.843	1.87
0.01032	0.376	15.71	0.1103	0.856	1.68
0.01157	0.395	14.55	0.1178	0.868	1.52
0.01282	0.413	13.56	0.1253	0.879	1.38
0.01407	0.429	12.71	0.1398	0.889	1.25
0.01532	0.444	11.97	0.1441	0.902	1.09
0.01657	0.459	11.31	0.1591	0.917	0.917
0.01782	0.473	10.72	0.1741	0.929	0.769
0.01907	0.486	10.20	0.1891	0.940	0.649
0.02032	0.498	9.72	0.2191	0.956	0.463
0.02159	0.510	9.29	0.2641	0.972	0.286
0.02282	0.521	8.89	0.3091	0.982	0.179
0.02407	0.532	8.52	0.3691	0.994	0.097

(f) $D_A/D_B = \frac{1}{10}$

τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$\dfrac{dq_A(\tau)}{d\tau}$
0.000004272	0.010		0.02408	0.551	8.47
0.00001794	0.019		0.02583	0.565	7.99
0.00007263	0.037		0.02758	0.579	7.56
0.0003461	0.078	115.6	0.02933	0.592	7.16
0.0004554	0.090	99.31	0.03108	0.604	6.80
0.0005648	0.101	88.32	0.03283	0.616	6.48
0.0006742	0.111	80.22	0.03458	0.627	6.17
0.0007836	0.119	73.92	0.03720	0.643	5.78
0.001002	0.134	64.61	0.03983	0.658	5.41
0.001221	0.148	57.94	0.04245	0.672	5.08
0.001440	0.160	52.87	0.04508	0.684	4.79
0.001659	0.171	48.84	0.04770	0.696	4.52
0.001987	0.186	44.09	0.05033	0.708	4.27
0.002315	0.200	40.39	0.05558	0.729	3.84
0.002643	0.213	37.41	0.06258	0.754	3.36
0.003080	0.230	34.21	0.06958	0.776	2.96
0.003955	0.258	28.87	0.07658	0.796	2.63
0.004830	0.282	25.68	0.08533	0.818	2.29
0.005705	0.304	23.22	0.09408	0.836	2.00
0.006580	0.324	21.26	0.1028	0.853	1.76
0.007455	0.342	19.64	0.1116	0.867	1.56
0.008330	0.359	18.28	0.1203	0.880	1.38
0.009205	0.375	17.12	0.1291	0.892	1.23
0.01008	0.391	16.11	0.1378	0.902	1.10
0.01096	0.404	15.22	0.1553	0.919	0.90
0.01183	0.416	14.44	0.1728	0.933	0.73
0.01358	0.440	13.10	0.1903	0.945	0.55
0.01533	0.463	11.99	0.2078	0.954	0.49
0.01708	0.483	11.07	0.2253	0.962	0.40
0.01883	0.502	10.27	0.2603	0.973	0.27
0.02058	0.519	9.58	0.2953	0.981	0.19
0.02233	0.535	9.01	0.3378	0.991	0.11

25%, 50%, 75%, and 90% exchange are shown in Fig. 4. The profiles for the linear case $(D_A = D_B)$ given by[4]

$$\gamma(\rho,\tau) = -\frac{2}{\pi\rho} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin(n\pi\rho) \exp(-n^2\pi^2\tau), \quad (20)$$

are included. The shape of the profiles depends strongly on the ratio D_A/D_B. If the ion present in the sphere initially is much the faster one, a comparatively sharp

boundary moves in toward the center of the bead [Fig. 4(a)]. If the ion present in the bead initially is much the slower one, the boundary is diffuse and the process reaches the center rapidly [Fig. 4(b)]. Again, the explanation is straightforward. In the first case the concentration of the faster ion is small near the surface and large near the center of the bead. Hence, the interdiffusion coefficient decreases toward the center. Therefore the outer shells of the bead are exhausted
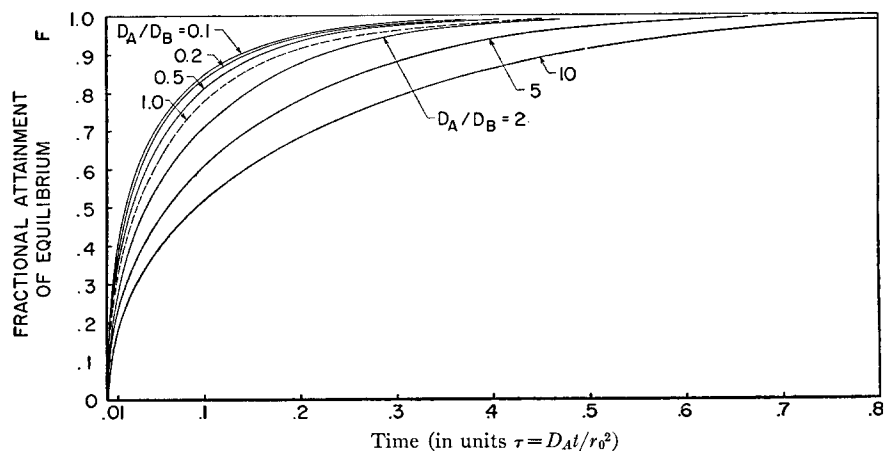

FIG. 2. Fractional attainment of equilibrium as a function of the dimensionless time coordinate $\tau = D_A t/r_0^2$. The different curves correspond to different ratios D_A/D_B. The solution to the linear problem $(D_A = D_B)$ calculated from Eq. (19) is given as a broken line.
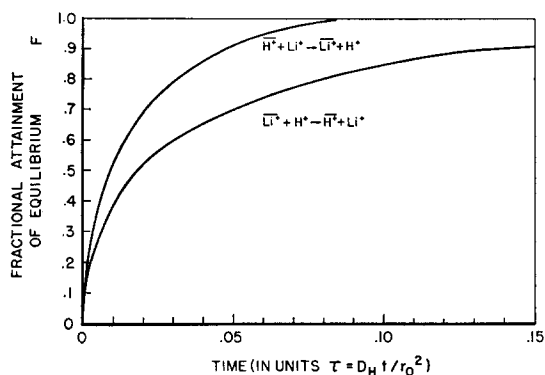
Fig. 3. Fractional attainment of equilibrium for the exchange processes H^+(resin) + Li^+(solution) → Li^+(resin) + H^+(solution), and Li^+(resin) + H^+(solution) → H^+(resin) + Li^+(solution, assuming a ratio $D_H/D_{Li} = 10$. In the first case (upper curve) the exchange is faster.

rapidly, whereas the exchange near the center remains slow. In the second case, the opposite holds. The interdiffusion coefficient increases toward the center; therefore the exhaustion is more uniform. Previous theories lead to one set of curves for all cases [Fig. 4(g)].

For practical purposes, an explicit expression for $F(\tau)$ which approximates the numerical results will be useful. The relation

$$F(\tau) = (1 - \exp\{\pi^2[f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3]\})^{\frac{1}{2}}, \quad (21)$$

where $\alpha \equiv D_A/D_B$ and the coefficients $f_1(\alpha)$, $f_2(\alpha)$, and $f_3(\alpha)$ are given by

$$1/f_1(\alpha) = -0.570 - 0.430\alpha^{0.775},$$
$$1/f_2(\alpha) = 0.260 + 7.82\alpha, \quad (21a)$$
$$1/f_3(\alpha) = -0.165 - 0.177\alpha,$$

fits all the numerical results within an error of ±0.01 in $F(\tau)$, with the exception of $\alpha = 0.1$, where the maximum error is −0.02. It should hold equally well for intermediate values of the ratio D_A/D_B. Equation (21) was developed as an extension of a simpler but less accurate approximation given by Vermeulen[23] for the linear case.

We wish to emphasize again that the results represent ideal limiting laws only, from which the behavior of actual systems may be expected to show more or less pronounced deviations. However, the comparison with the solution for the linear case demonstrates conclusively that the effect of the electric potential included in our approach is an essential feature of the process which no theory can omit.

6. EXTENSION TO OTHER INITIAL DISTRIBUTIONS

The numerical results and the empirical formula given above may be used to determine the solution for

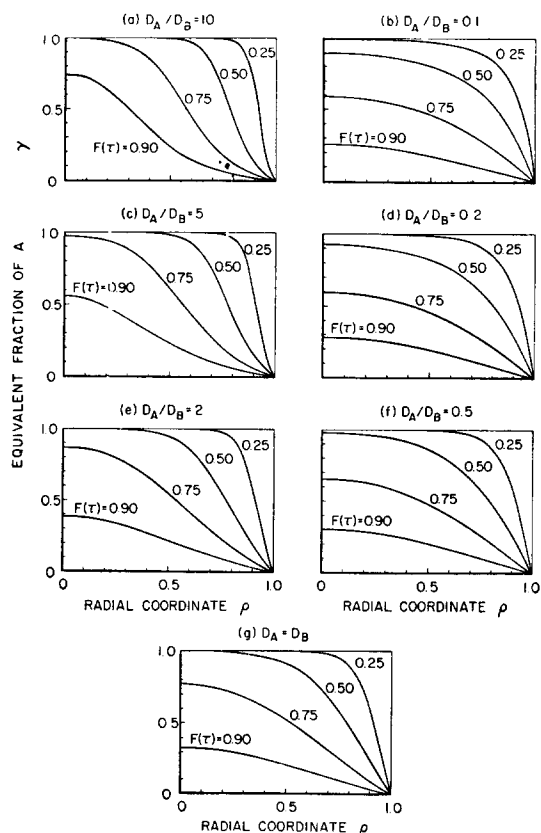[23] T. Vermeulen, Ind. Eng. Chem. **45**, 1664 (1953).

Fig. 4. Concentration profiles of the species A in the bead for 25%, 50%, 75%, and 90% exchange ($F = 0.25$, 0.50, 0.75, and 0.90) for seven different ratios D_A/D_B. The profiles for the linear case ($D_A = D_B$) were calculated from Eq. (20).

the problem in which the distribution is

$$0 \leq \rho < 1, \quad \tau = 0, \quad \gamma(\rho) = \gamma_0$$
$$\rho \geq 1, \quad \gamma(\rho, \tau) = 0$$

where γ_0 may have any constant value in the range $0 < \gamma_0 \leq 1$. The procedure is as follows. One replaces γ by $\gamma' = \gamma/\gamma_0$ and a by $a' = a\gamma_0$. Then γ' satisfies the same differential equation and the same boundary values as in the problem already described. The solution for the new problem as presented in (21) and in the numerical tables is now in terms of a' and γ'. In this way, the solution is available for any uniform initial value of γ in the sphere.

7. ACKNOWLEDGMENTS