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THE KINETICS OF ION EXCHANGE ON SULPHONATED CATION EXCHANGERS

A. B. Sigodina, N. I. Nikolaev, and N. N. Tunitskii

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A solution to the problem of creating high-quality ion exchangers, as well as a rational approach to the selection of optimum operating conditions for ion-exchange units and the regeneration of ion exchangers, is only possible with a detailed knowledge of both equilibrium and kinetic data.

However, while many studies have been concerned with the statics of ion-exchange processes the kinetics of ion exchange and the kinetic properties of ion exchangers have been investigated to a considerably lesser extent. Of the reviews which have appeared recently, three [1,2,3] should be noted in which problems of ion-exchange kinetics have been partially discussed. In Helfferich's detailed monograph [3], where the theory of ion-exchange processes is set out fairly fully, little attention is paid to experimental data on ion-exchange kinetics and, in particular, on the coefficients of diffusion and self-diffusion in ion exchangers; in addition, the investigations by Soviet authors are not sufficiently reflected. In the present review we would like to remedy this omission and pay particular attention to reviewing the theoretical and experimental information on the kinetics of ion exchange in the processes of self-diffusion, the diffusion of microcomponent ions, complete exchange, and the exchange of large ions on strongly acid cation exchangers. In presenting the information we shall not refer back to the problems set out in Helfferich's book.

I. FUNDAMENTAL PROBLEMS IN THE THEORY OF ION-EXCHANGE KINETICS

If an ion A from a solution replaced an ion B in an ion exchanger then the exchange process takes place primarily in the following stages: the diffusion of the ion A through the layer of liquid adjacent to the ion-exchange particle, the transfer of the ion A from the solution phase to the ion-exchanger phase, the diffusion and exchange of the A and B ions within the ion exchanger, the transfer of the B ion from the ion-exchanger phase to the solution phase, and diffusion of the B ion through the layer of solution adjacent to the ion-exchange particle. It should be borne in mind that due to the necessity for preserving the electroneutrality of the solution, the transfer of the ions during diffusion is balanced by a counter flow.

In the first stages of investigating ion-exchange kinetics (up to approximately 1950) some authors attempted to use the concept of "the order of reaction" of the ion-exchange process to explain the experimental results, assuming the

existence of a chemical mechanism in ion-exchange processes. Nowadays, however, it is generally considered that chemical stages are not the rate-determining ones in all the ion-exchange processes on sulphonated cation--exchangers so far investigated, and that the exchange is a series of purely physical processes, those of transfer and diffusion. It is considered that the rate-determining steps are either the diffusion of ions in solution or diffusion within the ion-exchanger particles. In some cases both these processes affect the rate of exchange.

When analysing the kinetics of ion exchange it is usually assumed that mixing leads to an instantaneous levelling out of the concentration within the bulk of the solution but there is a thin film of immobile solution in the region of the solid surface where transfer is achieved only by diffusion. Of course, the true state of affairs is much more complicated and requires the solution of complex hydrodynamic equations but, nevertheless, the model of a film of finite thickness has been found to be extremely effective in explaining the series of processes. As the flim thickness is not a physical quantity but a fictitious one, rather, it is impossible to determine it by a direct method. From data on the rate of dissolution of solids and investigations on the kinetics of electrode processes, film thicknesses of the order of 10^{-2}–10^{-3} cm and even $\sim 10^{-4}$ cm at higher flow rates are obtained; similar values for film thickness are obtained from studies of the kinetics of ion exchange for film diffusion.

One of the characteristic features of a film diffusion exchange mechanism is the dependence of the rate of exchange on the rate of filtration of a solution or the intensity of agitation.

Diffusion within the particle will be the rate-determining process when the transfer of ions to the surface of the particle takes place more rapidly than their transfer into the solid phase. In practice the following factors will contribute to this: (a) a high concentration of the ion being exchanged in solution; (b) an effective agitation or rapid flow of the solution; (c) a large particle size; (d) a high degree of cross-linking or large and multicharged ions.

The determination of the transition from film diffusion kinetics to particle diffusion kinetics is of particular interest. Working with sulphonated cation exchangers of an average degree of cross-linking and at fairly high flow rates, Boyd *et al.*[4] showed that the rate of ion exchange in 0.1 M and more concentrated solutions is determined by particle diffusion, and in 0.001 M and less dilute solutions by film diffusion. According to the theory of Adamson and Grossman[5,6], the rate-determining step in the exchange process is film diffusion for values of the parameter $D_S R/D_i \delta k$ appreciably less than unity while for values of this parameter greater than unity it is particle diffusion. Here the parameters D_S and D_i are the diffusion coefficients in the solution and in the ion exchanger respectively, R is the radius of the particle, δ the film thickness, and k the diffusion coefficient for the diffusing particles (*i.e.* $[A]/[A_S]$). Helfferich[3] defined the form of this parameter somewhat more precisely as

$$\frac{cD_s R}{aD_i \delta}(5 + 2K_B^A),$$

where K_B^A is the concentration equilibrium constant, a the capacity of the ion exchanger, and c the concentration of the outer solution. It should be pointed out that all these relationships which define the region of transition from film diffusion to particle diffusion kinetics are approximate in nature and are mainly used for average rates of exchange.

When analysing experimental data, as further consideration will show, it must be remembered that for a film diffusion mechanism of ion exchange (this relates primarily to the processes of self-diffusion and the diffusion of micro-component ions) the relative rate of exchange is inversely proportional to the radius of the ion exchanger particle and for a particle diffusion mechanism it is inversely proportional to the square of the radius in the first stages of exchange. If the rate-determining step of the exchange were to be a chemical reaction, then the rate of exchange on ion exchangers should not depend on their grain size.

Considerable mathematical difficulties arise in expressing the diffusion process in ion exchange, some of which have still not been overcome at the present time.

From the point of view of their mathematical description the main diffusion processes of ion exchange can be divided into five cases: (1) diffusion through the film of solution adjacent to the particle of ion exchanger, with a constant concentration in the outer solution; (2) diffusion through the film with a variable concentration in the outer solution; (3) diffusion within the ion-exchanger particle at a constant concentration in the outer solution; (4) diffusion within the ion-exchanger particle with a variable concentration in the outer solution; and (5) diffusion processes taking place simultaneously both in the film of solution and in the ion-exchanger particle.

As sulphonated cation exchangers mostly consist of spherical particles we shall only deal with the case of spherical symmetry.

In the mathematical treatment of the experimental results it is assumed that the thickness of the diffusion film of solution is constant, although there have been attempts[7] to take account of the asymmetry of the film thickness in relation to the flow of solution. We shall use the following general system of notation in our subsequent account:

c = the concentration of the outer solution, mg-equiv. cm^{-3},
c_0 = the initial concentration of the outer solution,
δ = diffusion film thickness, cm,
D_S = diffusion coefficient in the solution, $cm^2\ s^{-1}$,
D_i = diffusion coefficient within the ion-exchanger particle, $cm^2\ s^{-1}$,
R = radius of ion-exchanger particle, cm,
a = capacity of the ion exchanger, mg-equiv. cm^{-3},
F = fractional attainment of equilibrium,
n = mole fraction of the displacing ion in the solution,
N = mole fraction of the displacing ion in the ion exchanger,
$1 - n$ = mole fraction of the ion being displaced, in the solution,
$1 - N$ = mole fraction of the ion being displaced, in the ion exchanger,
v_S = volume of solution,
v_i = volume of ion exchanger,
t = time, s.

For isotopic exchange at a constant concentration in the outer solution, when the transfer through a film can be characterised by a single diffusion coefficient, the equation

$$F = N = 1 - \exp\left(-\frac{3D_s c_0}{R\delta a}\, t\right) \qquad (1)$$

has been derived[4].

It is not difficult to derive also the relationship for the more general case, where $K \neq 1$. Equating the diffusion flow through the film

$$4\pi R^2 D_s \frac{c\,(n_0 - n)}{\delta}\,dt$$

to the change in the content of the ion being displaced in the ion-exchange particle

$$\frac{4\pi R^3}{3}\,a\,dN,$$

and taking into account the establishment of equilibrium at the phase boundary

$$\frac{N}{1-N} = K\frac{n}{1-n},$$

we obtain the following differential equation

$$\frac{3D_s c_0}{\delta R a}\left(n_0 - \frac{N}{K-(K-1)N}\right) = \frac{dN}{dt}. \qquad (2)$$

Integrating this equation for complete exchange, *i.e.* taking into account that $n_0 = 1$ and $N = 0$ at $t = 0$, gives the final equation

$$\frac{3D_s c_0 K}{\delta R a}\cdot t = -\ln(1-N) + (K-1)N. \qquad (3)$$

It is not possible to find $N(t)$ from Eqn. (3), but the results of certain numerical calculations based on Eqn. (3), shown in Fig. 1, give a graphical representation of the effect of the equilibrium constant on the nature of the film diffusion kinetics of exchange. At $K = 1$ Eqn. (3) is transformed into Eqn. (1). D_S in Eqn. (3) should be taken as the diffusion coefficient of the electrolyte.

Adamson and Grossman[5,6] have proposed more complex equations than Eqn. (3) to describe the kinetics. These equations contain the different diffusion coefficients of the exchanging ions, and the electric charge balance in the flow is not introduced. Therefore the equations they suggest are not consistent and their unwieldiness is unjustified.

Taking the hydrogen–caesium and sodium–caesium exchange reactions as an example, these authors[6] established a linear relationship between $[\ln(1 - N)]/t$ and N/t. In a later paper[8] an attempt was made to take account of the effect of the diffusion electric potential on film diffusion kinetics. Starting from the Nernst–Planck equation

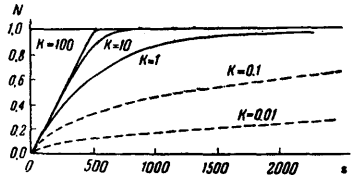


Fig. 1. Calculated curves for complete exchange at constant concentration in the external solution (at $D_i = 2 \times 10^{-5}$ cm^2 s; $\delta = 6 \times 10^{-4}$ cm; $R = 0.05$ cm; $a = 2$ mg-equiv. cm^{-3}; $c_0 = 2 \times 10^{-3}$ mg-equiv. cm^{-3} and different values of the equilibrium constant K).

and neglecting any selectivity in the exchange ($K = 1$), the authors obtained the following equation:

$$\ln\left\{\frac{y(t)-1}{(D_A/D_B)^{1/3}-1}\right\} + \frac{1}{2}\left[y^2(t) - \frac{D_A}{D_B}\right] + y(t) - \left(\frac{D_A}{D_B}\right)^{\frac{1}{3}} = -\frac{3D_A c}{R\delta a}t\,, \qquad (4)$$

$$y(t) = [D_A N + D_B(1-N)]/D_B.$$

If the exchange process takes place through a film between the ion exchanger and a solution of limited volume, then for isotopic exchange ($D_{SA} = D_{SB}$ and $K = 1$), applying Eqn. (3):

$$F = \frac{N(0) - N(t)}{N(0) - N(\infty)} = 1 - \exp\left[-\frac{3D\,(v_i a + v_s c)}{R\delta a v_s}\,t\right]. \qquad (5)$$

For other cases of exchange in a limited volume of solvent it is possible to obtain differential equations representing the process, but their solution will be fairly complicated and hardly suitable for practical application.

The process of diffusion exchange in a particle for constant concentration of the outer solution is represented by the well-known solution to the equation for diffusion in a sphere:

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp(-n^2 B t)}{n^2}; \qquad B = \frac{\pi^2 D_i}{R^2}. \qquad (6)$$

When carrying out experiments the degree of exchange F, which is dependent on time, is determined from the results of the measurements. Then from a tabulation in the literature[4], which gives the variation of F with Bt, the value of B for corresponding values of F and t are found and the diffusion coefficient D_i found from the expression $D_i = BR^2/\pi^2$.

In the case of exchange with a limited volume of solution, the concentration of the electrolyte solution is a variable in the film diffusion kinetics, and when solving the diffusion equation account should be taken of the boundary condition which expresses the conservation of the total number of ions:

$$\frac{dc}{dt} = \frac{4\pi R^2 D_i}{v_s}\left[\frac{\partial(aN)}{\partial r}\right], \qquad (7)$$

where $r = R$.

The solution of the corresponding problem for thermal conductivity has been given by Patterson[9]:

$$F = 1 - \frac{2}{3w}\sum_{n=1}^{\infty}\frac{e^{-\lambda_n^2\tau}}{1 + \lambda_n^2/9w(1+w)}, \qquad (8)$$

where $w = k(v_i/v_s)$, k is the sorption coefficient, $\tau = D_i t/R^2$ a dimensionless parameter, and λ_n are the roots of the transcendental equation

$$\lambda\coth\lambda = 1 + \frac{\lambda^2}{3w}.$$

Eqn. (8) is applicable for $\tau > 0.1$. For $\tau < 0.1$ the degree of exchange should be determined from the expression

$$u' \simeq \frac{1}{\alpha-\beta}\{\alpha e^{\alpha^2\tau}(1 + \operatorname{erf}\alpha\sqrt{\tau}) - \beta e^{\beta^2\tau}(1 - \operatorname{erf}\beta\sqrt{\tau})\}, \qquad (9)$$

where α and β are the roots of the equation $x^2 + 3\omega x - 3\omega = 0$.

From Eqn. (9), F is determined by means of the relationship

$$F = \frac{1-u'}{1 - 1/(w+1)}. \qquad (10)$$

For the practical use of Eqns. (8), (9), and (10) the variation of F with τ must first be plotted for values of ω corresponding to the experimental conditions, and then τ and the corresponding D_i found from the experimentally determined values of $F(t)$ (*cf.* Fig. 2). This method of determining the diffusion coefficient was successfully used in the studies of Soldano *et al.*[10,11,12]

As with the electrolyte solution, an electrical diffusion potential is produced within the ion-exchanger particle during the exchange of ions of different mobilities. In some papers[13,14,15] the diffusion processes of complete exchange in ion exchangers were examined, taking into account the effect of an electric field. The diffusion current can be expressed by the relationship

$$I = kTB_2 \frac{da}{dx} + BEzea, \qquad (11)$$

where B is the mobility of the ion in the ion exchanger, ze the ionic charge, E the potential of the electric field produced in the ion exchanger during the exchange of ions of different mobilities, and a the concentration expressed in g-equiv.

Taking into account the conservation of overall electroneutrality, the effective diffusion coefficient for complete exchange will be

$$D_{eff} = \frac{D_1 D_2 (a_1 z_1 + a_2 z_2)}{D_1 a_1 z_1 + D_2 a_2 z_2}, \qquad (12)$$

where $D_1 = kTB_1$ and $D_2 = kTB_2$. Here D_1 and D_2 are functions of the composition of the ion exchanger at a given point, their form being unknown, although limiting values can readily be determined.

The expression given for the effective diffusion coefficient is approximate, as it does not take into account the activity coefficients of the ions in the ion exchanger, the variations in its swelling, and the transfer of water. An examination of the expression for the effective diffusion coefficient shows that in the initial and final stages of exchange, when one of the exchanging ions is present in the ion exchanger in low amounts (a microcomponent ion), D_{eff} is determined by the mobility of this ion.

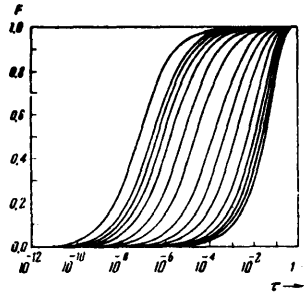


Fig. 2. Variation of F with τ for different values[9] of ω (from left to right, curves corresponding to ω = 1000; 500; 400; 300; 200; 100; 50; 20; 10; 5; 2; 1; 0.5; 0.2; 0).

The greatest complexity arises in a mathematical description of the processes of complete exchange, when the rate of the process is determined simultaneously by diffusion through the film of solution and by diffusion within the particle of ion exchanger.

Pouchlý and Erdös[16-18] examined the kinetics of adsorption from solutions, taking account of particle diffusion and film diffusion for the case of linear sorption isotherms. Even assuming a linear sorption isotherm, however, fairly unwieldy expressions are obtained for the rate of the exchange process.

Another paper[19] gives a mathematical relationship between τ, the average period of adsorption of ions from particles, the coefficients of particle and film diffusion, and other quantities which determine the rate of the ion-exchange process. For spherical particles this relationship has the form

$$\bar{\tau} = \frac{R^2}{15D_i} + \frac{R\delta\gamma}{3D_s}, \qquad (13)$$

where γ is the sorption coefficient referred to 1 cm³ and the other symbols are given above. $\bar{\tau}$ denotes the mean time of desorption from the particle of the ion exchanger and in practice is defined as:

$$\tau = \int_0^\infty \left[1 - \frac{A(t)}{A(\infty)}\right] dt,$$

where $A(t)$ and $A(\infty)$ are the quantities of ions in a spherical particle at a given moment t and $t = \infty$ respectively. It is assumed that at $t = 0$, the ions are uniformly distributed throughout the volume. This integral can be readily solved graphically from the experimentally determined values of $A(t)$. In particular, the relationship (13) enables D_i to be found from the experimentally determined value of τ and the known values of D_s and δ. For very large particles and low values of γ and δ (highly concentrated solutions and high flow rates), Eqn. (13) enables the diffusion coefficient of the ions in the ion exchanger to be determined at once.

The sharpness in the chromatographic separation of different ions depends on the elution of the zone containing these ions. For a linear sorption isotherm and an infinitely high rate of exchange, the chromatographic zones are not eluted; elution is the result of a finite rate in the diffusion processes. From a practical point of view ion-exchange kinetic data can be used for estimating the degree of elution of the chromatographic zones. The same applies to the opposite problem, *viz.* the determination of the kinetic characteristics of the exchange process from the elution of the chromatographic zones.

The displacement and elution of the zones in a chromatographic column containing the ions of one of the elements being separated in microquantities may be represented by the following equation:

$$\frac{(\Delta\bar{v})^2}{v} = \frac{2R^2u}{15D_i} + \frac{2\Gamma\delta u}{S_s\rho D_s} + \frac{2Q^2D_l l}{u}, \qquad (14)$$

where $\bar{v}$ is the average volume of eluant required to transfer an ion through the column, $(\Delta\bar{v})^2 = \overline{(\bar{v} - \bar{v})^2}$ the mean square fluctuation of v, u the volume flow rate of the solution through the column, D_l the diffusion coefficient of ions, dependent on the longitudinal mixing of the solution in the column, Γ the adsorption coefficient referred to 1 cm³ of the granular layer, $S_s\rho$ the surface area of 1 cm³ of the granular layer, and Q the cross-sectional area of the column.

If it is assumed as an approximation that $\delta \simeq 1/u$ and the effect of longitudinal mixing is neglected, then Eqn. (14) may be written as

$$\frac{(\Delta\bar{v})^2}{v} = i + bv,$$

where

$$i = \frac{2cT}{S_{sp}D_s}; \quad b = \frac{2R^2}{15D_i}. \qquad (15)$$

The relationship (15) is also approximately true in those cases where the role of film diffusion is low. Thus, with these assumptions $(\Delta\bar{v})^2/v$ is a linear function of velocity. From the slope of the straight lines which give the variation of $(\Delta\bar{v})^2/v$ with the rate of flow through the column, and using the expression for b, the value of the diffusion coefficient can be readily found. In those cases where the role of the processes in solution appreciably affects the elution of the chromatographic zones, the contribution of film diffusion may also be taken into account more accurately, as has been done in an earlier paper [19].

II. EXPERIMENTAL METHODS OF INVESTIGATION

Two principal methods are used to study ion-exchange kinetics, *viz.* the shallow-bed technique (with a constant concentration in the outer solution) and the exchange between the solution and the ion exchanger in a limited volume of solvent (with a variable concentration of the solution). The first method has been most widely used, as considerable mathematical difficulties arise when dealing with the results obtained from experiments in a limited volume of solution. Some investigators consider that the main drawback to the further development and improvement in the "exchange in limited volume" method is the absence of a mathematical solution to certain basic equations which represent the exchange process under these conditions.

1. The Shallow-Bed Technique [4,10,13,20-23]

A diagram of the apparatus which was used in experiments on the kinetics of ion exchange in solutions [13,20,21,24] is shown in Fig. 3. 50 mg air-dried cation exchanger were charged into the cuvette, the base of which consisted of a fine mesh. A mesh was also fixed above the cation exchanger and the cuvette was placed in a stainless steel casing completely enclosed by a cover. The solution was passed through the cation exchanger at a rate of $\sim 8-10$ m s^{-1}. The measurements were carried out both on adsorption and desorption. When using the adsorption method the cation exchanger was first washed with a solution containing the same cation as in the cation exchanger. Then a solution containing the substituting cation (labelled with a radioactive isotope) was passed through over a known period of time, after which the cation exchanger was washed with distilled water and dried with acetone. The radioactivity of the cation exchanger after the known period of contact with the active solution was measured with an end-window counter. When using the desorption method the radioactive solution was first passed through the cation exchanger at a rate of ~ 0.2 cm s^{-1} until it was completely saturated with the radioactive isotope. Then the cation exchanger was washed over a known period of time at a high rate with a solution containing the substituting cation and the decrease in the activity of the cation exchanger measured as a function of the contact time with the non-active solution.

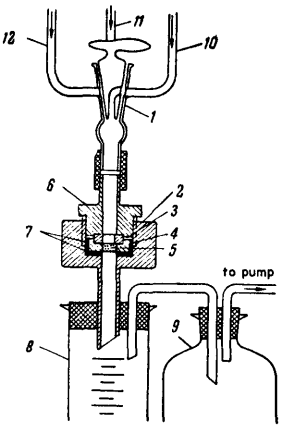


Fig. 3. Apparatus for measuring the diffusion coefficient in cation exchangers [24]: 1) four-way cock; 2) stainless steel casing; 3) washer for pressing nickel mesh against cell; 4) cation-exchanger cell; 5) cation-exchanger granules; 6) cover; 7) rubber washer; 8) measuring cylinder; 9) ballast vessel; 10), 11), and 12) connecting tubes.

2. The "Exchange in a Limited Volume of Solvent" Method

This was first used by Boyd and Soldano [12,25] to study self-diffusion and also by Dryden and Kay [26]. A weighed amount of ion exchanger was placed in a solution containing a radioactive isotope. After the tracer was uniformly distributed in the ion exchanger, the solution was removed and the ion exchanger washed with water and suspended in 150 ml distilled water in a vessel held in a thermostat. After reaching thermal equilibrium (after several hours) a volume (~ 50 ml) of the electrolyte at the same temperature and containing the same ion as the ion exchanger was added to the solution. The addition was made rapidly over 1–3 s. Then samples were removed from the solution and analysed until the activity of the sample remained constant. This method can also be used without radioactive tracers. For all its experimental simplicity, however, a fairly complex treatment of the results is needed to calculate the diffusion coefficients.

The diameter of the ion-exchanger particles must be known accurately to calculate the diffusion coefficient. In an earlier paper [20] the diameters of the ion-exchanger particles were measured in the swollen state under the microscope and the average of 400 measurements taken. The particles of an ion exchanger with an increased divinylbenzene content had a true spherical shape, but the particles of an ion exchanger with a low divinylbenzene content had an irregular shape, and the size of the particles was therefore determined from measurements in two directions.

III. SELF-DIFFUSION IN CATION EXCHANGERS

The self-diffusion coefficient of ions depends on a number of factors, primarily the degree of cross-linking [10,12,22,24], the nominal divinylbenzene (DVB) content, the temperature, and the ionic charge.

Boyd and Soldano[12] investigated the variation of the self-diffusion coefficients of Na^+, Zn^{2+}, and La^{3+} with cross-linking in an ion exchanger, using a wide range of DVB contents, 2–24% (Table 1).

Soldano[10] obtained similar results for the self-diffusion coefficients of the Na^+, Zn^{2+}, and Y^{3+} for a change in DVB content from 5 to 25%. For example, the self-diffusion coefficient of Y^{3+} decreases by more than two orders of magnitude with this change in DVB content.

It has been shown[24] that with a decrease in the DVB content of a cation exchanger from 12 to 7%, the self-diffusion coefficient of the Na^+ ion increases by a factor of 2.5 and that of Sr^{2+} by a factor of 8.

The variation of the self-diffusion coefficient with the charge on the ion has been studied[10,12,24,27-34]. The results of the first two papers[10,12] show good agreement and may be considered together (Table 2).

From the self-diffusion coefficients given above it may be seen that the self-diffusion coefficient varies approximately tenfold for a unit difference in the charge.

On investigating the Na^+, Ca^{2+}, and Sm^{3+} ions in Dowex-50 at 25° Holm[27] found that an increase of unity in the charge reduces the self-diffusion coefficient by a factor of ~ 4.

However, the self-diffusion coefficient is not determined solely by the charge on the ion but still depends on its nature. From other data[24] it follows that the self-diffusion coefficient of the Na^+ ion in a cation exchanger containing 7% DVB is eighteen times greater than the self-diffusion coefficient of the Sr^{2+} ion and in a cation exchanger containing 12% DVB it is sixty times greater.

In a comparison of the self-diffusion coefficients for ions having the same charge the following values of $\overline{D}$ (in $cm^2\ s^{-1}$) were obtained for the alkali metals[12] under almost identical conditions (DVB content 8.6%, temperature 0.3°): Na^+ 3.50×10^{-7}, K^+ 6.28×10^{-7}, Rb^+ 6.36×10^{-7}, and Cs^+ 6.61×10^{-7}; *i.e.* in the decrease in their rate of self-diffusion, $Cs^+ \geq Rb^+ > K^+ > Na^+$, the order of the alkali metal ions corresponds to the decrease in their radii.

The effect of temperature on the self-diffusion coefficients has been studied[10,12,35-40]. The values of $\overline{D}$ shown in Table 1 for two temperatures (0.3° and 25°) indicate an increase in the self-diffusion coefficient with a rise in temperature.

TABLE 1. Variation of the self-diffusion coefficient with the degree of cross-linking of an ion exchanger[12].

DVB, %	Diffusing ion	Diffusion coefficient, D, $cm^2\ s^{-1}$	
		0.3°	25°
4	Na^+	$6.66 \cdot 10^{-7}$	$1.41 \cdot 10^{-6}$
8.6		$3.50 \cdot 10^{-7}$	$9.44 \cdot 10^{-7}$
Dowex-50		$1.15 \cdot 10^{-7}$	$2.88 \cdot 10^{-7}$
16		$6.58 \cdot 10^{-8}$	$2.40 \cdot 10^{-7}$
24		$2.69 \cdot 10^{-8}$	$1.00 \cdot 10^{-7}$
2	Zn^{2+}	$2.95 \cdot 10^{-7}$	$7.37 \cdot 10^{-7}$
8		$2.06 \cdot 10^{-8}$	$6.30 \cdot 10^{-8}$
Dowex-50		$8.77 \cdot 10^{-9}$	$2.89 \cdot 10^{-8}$
16		$3.12 \cdot 10^{-9}$	$1.16 \cdot 10^{-8}$
24		$5.52 \cdot 10^{-10}$	$2.63 \cdot 10^{-9}$
2	La^{3+}	$5.18 \cdot 18^{-8}$	$1.30 \cdot 10^{-7}$
4		$2.96 \cdot 10^{-8}$	$6.85 \cdot 10^{-8}$
8		$3.01 \cdot 10^{-9}$	$9.20 \cdot 10^{-9}$
16		$1.53 \cdot 10^{-10}$	$5.10 \cdot 10^{-10}$

TABLE 2. Effect of ionic charge on the self-diffusion coefficient.

Diffusing ion	Self-diffusion coefficient, at 25°, D, $cm^2\ s^{-1}$	Degree of cross-linking in resin
Na^+	$2.76 \cdot 10^{-7}$	10% DVB. Ref. 10
Zn^{2+}	$2.89 \cdot 10^{-8}$	
Y^{3+}	$3.18 \cdot 10^{-9}$	
Na^+	$2.88 \cdot 10^{-7}$	Dowex-50. Ref. 12
Zn^{2+}	$2.89 \cdot 10^{-8}$	
Y^{3+}	$3.18 \cdot 10^{-9}$	
Th^{4+}	$2.15 \cdot 10^{-10}$	
Na^+	$1.00 \cdot 10^{-7}$	24% DVB. Ref. 10
Zn^{2+}	$2.63 \cdot 10^{-9}$	
Y^{3+}	$2.18 \cdot 10^{-10}$	

The study of the effect of cation-exchanger capacity on the self-diffusion coefficient is of great interest. Unfortunately, it is difficult to prepare ion-exchanger samples having a different capacity but a constant cross-linking which, as we have seen, greatly affects the rate of self-diffusion. Self-diffusion has been investigated for samples of cation exchangers prepared from the desulphonation of a sulphonated polystyrene cation exchanger by prolonged heating in water above 100°.[10] The investigations showed (Table 3) that the self-diffusion coefficients drop considerably with a decrease in capacity, but the activation energies increase. In order to find out how the cross-linking of an ion exchanger is altered on desulphonation, experiments on the sorption of water were carried out. These experiments led to the conclusion that at the first stages of desulphonation a rupture of the bonds takes place, and at the later stages it is compensated by the formation of new bonds. Thus, it may be assumed that samples desulphonated to a capacity below 4 mg-equiv. g^{-1} of dry resin have approximately the same cross-linking.

The ionic strength of the external electrolyte solution has a very interesting effect on the self-diffusion coefficient[12,41,46]. Measurements of the self-diffusion coefficient at 25° for the Na^+ ion in a cation exchanger containing 8.6% DVB[12] gave the values $\overline{D} = 9.44 \times 10^{-7}$ $cm^2\ s^{-1}$ at an electrolyte concentration of 0.22 *N* and $\overline{D} = 11.1 \times 10^{-7}$ $cm^2\ s^{-1}$ at a concentration of 1.0 *N*. On increasing the ionic

TABLE 3. Effect of cation-exchanger capacity on the self-diffusion coefficient and the activation energy[10].

Capacity, mg-equiv. per g dry resin in H form	Self-diffusion coefficient, $cm^2\ s^{-1}$		Activation energy, cal $mole^{-1}$
	0.3°	25°	
4.3	$1.23 \cdot 10^{-7}$	$3.32 \cdot 10^{-7}$	6600
3.2	$6.84 \cdot 10^{-8}$	$1.9 \cdot 10^{-7}$	6660
2.5	$2.24 \cdot 10^{-8}$	$6.98 \cdot 10^{-8}$	8180

strength of the solution from 0.26 M to 0.53 M the self-diffusion coefficient of Y^{3+} in Dowex-50 cation exchanger fell from 3.18×10^{-9} to 2.83×10^{-9} cm^2 s^{-1}. However, the experimental measurement of diffusion coefficients at low concentrations is very difficult. Boyd and Soldano [12] also considered the effect of the nature of the anion on the self-diffusion coefficient at a constant ionic strength in the solution. For the Ag^+ ion at a concentration of 0.22 N in the external solution, and with 16% and 25% cross-linking, $\overline{D} = 2.85 \times 10^{-7}$ cm^2 s^{-1} in $AgClO_4$ solution and in $AgNO_3$ solution $D = 2.62 \times 10^{-7}$ cm^2 s^{-1}, *i.e.* the nitrate ion reduces the self-diffusion coefficient somewhat. This effect was not observed for the La^{3+} ion. The authors explained the effect of the ionic strength of the external electrolyte solution as a relative contribution of two processes: (1) the compressing action of the external electrolyte, which, on increasing the concentration, will increase the density of the spherical ion-exchanger particles and decrease the rate of the process, and (2) the penetration of the diffusing anions from the external solution into the exchanger, which may cause a decrease in the activation energy and therefore an increase in the diffusion coefficient.

The quantitative interpretation of the diffusion processes of ions in an ion exchanger is usually based on Eyring's theory of absolute rates of reaction [47], according to which the diffusion coefficient is

$$D = e\lambda^2 \frac{kT}{h} e^{\frac{\Delta S^{\neq}}{R}} e^{-\frac{E}{RT}}, \qquad (16)$$

where D is the diffusion coefficient, λ the distance between two equilibrium positions, k Boltzmann's constant, h Planck's constant, $\Delta S^{\neq}$ the entropy of activation, and E the activation energy.

Eyring's equation connects the value of the diffusion coefficient with the activation energy and entropy of activation of the process, the greater the entropy of activation the higher the diffusion coefficient.

At first glance it would seem natural to take the value of λ [12] as the distance between the active groups, *i.e.* a value of the order of 10×10^{-8} cm. However, this is too high. It is impossible to determine λ without certain further assumptions. Assuming that the entropy of activation for the K^+, Rb^+, Cs^+, and Ag^+ ions is zero (or close to zero), it seems to be more accurate to take $\lambda = 1.5 \times 10^{-3}$ cm, *i.e.* the value found by Wang [48] for self-diffusion in water.

The activation energy of self-diffusion depends on a number of fundamental factors characteristic of the cation exchanger and the cation taking part in the exchange process, *viz.* the degree of cross-linking of the cation exchanger [10,12,23], the temperature [12], and the charges and dimensions of the cations [12,23,29,38]. The effect of these factors may be inferred from the data in Table 4.

For the alkali metal series an increase in the activation energy with a decrease in the dimensions of the ions is observed. In their decrease in activation energy the alkali metals fall into a series of the following type: $Na^+ > K^+ > Rb^+ > Cs^+$. In the main, the activation energy also rises with an increase in the ionic charge.

The temperature dependence of the activation energy may be shown taking the Na^+ and Zn^{2+} ions as examples [12]. For temperatures of 6°, 18.35°, and 36.9° the activation energy for the Na^+ ion in a cation exchanger containing 8.6% DVB falls, being 7100, 6280, and 4640 cal mole^{-1} respectively. For the Zn^{2+} ion the activation energy in a cation exchanger containing 16% DBV varied from 8580 (6.6°) to 8440 (19°) and 7800 (37.5°) cal mole^{-1}. Similar data on the change in activation energy with the change in the degree of cross-linking have been reported elsewhere [10]. For the Zn^{2+} ion the activation energy is 5200, 7700, 8500, and 10 000 cal mole^{-1} for DVB contents of 4, 10, 16, and 24% respectively.

TABLE 4. Variation of the activation energy of self-diffusion with the degree of cross-linking of the cation exchanger and the charge on the cation [12].

Ion	Cross-linking, % DVB	Activation energy, cal mole^{-1}	Ion	Cross-linking, % DVB	Activation energy, cal mole^{-1}
Na^+	8.6	6500	Ag^+	8.6	5895
	16	8400		16	6590
	24	8620		24	7200
Cs^+	8.6	4790	Sr^{2+}	4	5640
	24	5205		16	10 980
Zn^{2+}	8	7040	La^{3+}	4	5520
	16	8520		8	7310
	24	10 250		16	7870

Soldano [10] associates the activation energy of the exchange process with two principal factors: the work of creating a passage for the diffusing particles in the exchange medium (in the majority of ionic systems in an aqueous medium this work is relatively constant and is independent of the size of the cation) and the work against the electrostatic interaction, which depends on the dielectric permeability of the medium, the degree of association of the ions, and the distances between them. However, it is impossible to explain the great changes in diffusion coefficient with change in the ionic charge as being due only to activation energies, as they depend to a considerable extent on changes in the entropy of activation. With an increased degree of cross-linking of the cation exchanger the value of $\Delta S^{\neq}$ rises and it is also increased by the multicharged ions themselves which can act as auxiliary cross-linking agents and thereby increase the density and the complexity of the system.

The entropies of activation have been considered as functions of the contribution from two opposing processes [12]: (1) the disturbance in the medium caused by the diffusing ion (the positive contribution), and (2) the electrical interaction of water (the negative contribution). The authors assume that the first effect will predominate for large diffusing ions and slight association with the ionic group, and the second effect will predominate with an increase in the degree of hydration. Eqn. (16) shows that the diffusion coefficient also depends on the activation energy and the entropy of activation. The effect of these two quantities is so complex that it was found impossible to determine the relative contribution from each of them. Nevertheless, Soldano [10] concludes that the activation energies of self-diffusion processes are comparable with the activation energies observed for the majority of aqueous systems, in contrast to the higher activation energies for ionic diffusion in solids. It is of interest to compare the self-diffusion coefficients of corresponding ions in water and in a cation exchanger. It has been noted in many papers [10-12,25,27,32,44,50-52] that the mobility of counter-ions in an ion exchanger is considerably less than the mobility of the same ions in water, particularly for multivalent ions. Summarising the available data, we may say that the absolute values of the diffusion coefficients for singly-charged counter-ions in averagely cross-linked cation exchangers are 0.3 to 0.1 of their values in aqueous solutions; for doubly-charged ions these figures are 0.2 to 0.01, and for triply-charged ions they are 0.1 to 0.001. [44]

The self-diffusion coefficients and activation energies of water in ion exchangers in various forms have been determined and compared with the same quantities in pure water [11]. The self-diffusion coefficient of water in pure water at 25° was found to be 30.1×10^{-6} cm^2 s^{-1} [11] and $23.4 \times \times 10^{-6}$ cm^2 s^{-1};[49] in a cation exchanger in the H form containing 4% DVB it was 9.14×10^{-6} cm^2 s^{-1} (25°) and in a cation exchanger in the La^{3+} form it was 8.20×10^{-7} cm^2 $\times$ $\times$ s^{-1} (3.4°). The activation energy for pure water is 4410 cal mole^{-1} and for a cation exchanger in the H form it is 4600 and 5200 (4% and 8% DVB respectively). Thus, the self-diffusion coefficients of water in an ion exchanger decrease with an increase in the degree of cross-linking and are less than the self-diffusion coefficients in water. In addition, they depend on the ionic form of the cation exchanger. The activation energy of the process increases little with an increase in the degree of cross-linking of the cation exchanger. Similar results on the self-diffusion coefficient of water have been presented elsewhere [10].

IV. DIFFUSION OF MICROCOMPONENT IONS

The cationic form of an ion exchanger remains practically unaltered during the diffusion in it of ions at microconcentrations. This enables the diffusion coefficient to be considered constant and to be calculated comparatively easily.

The rate of diffusion of microcomponent ions depends mainly on the same factors as the rate of self-diffusion, *viz.* the degree of cross-linking of the cation exchanger [21,24,25], the charge on the diffusing ion [24,25,53], and the temperature during diffusion [4,25], and also on factors peculiar to the given type of exchange, such as the effect of the cationic form and composition of the cation exchanger [4,13,21,24,25,34] and the concentration of the macrocomponent ion in solution [4,21,24,53].

Boyd and Soldano [25] considered the diffusion of a number of microcomponent ions in sulphonated polystyrene cation exchangers cross-linked with 8.6% and 16% DVB. Using as an example the diffusion of Na^+ microcomponent ions in a substantially hydrogen form of a cation exchanger, and of Na^+ in the Cs form of the resin, they showed that the diffusion coefficient decreases with an increase in the degree of cross-linking, but the activation energy for diffusion of microcomponent ions increases. For example, for the diffusion of sodium in the H form of a cation exchanger containing 8.6% DVB, $D = 8.82 \times 10^{-7}$ cm^2 s^{-1} and $E_{act} = 5320$ cal mole^{-1}, and for a DVB content of 16% $D = 3.90 \times 10^{-7}$ cm^2 s^{-1}, $E_{act} = 6880$ cal mole^{-1}.

Fedoseeva [24] obtained similar results for the effect of DVB content on the rate of diffusion of microcomponent ions.

An approximately linear relationship was found [24] for the variation of the diffusion coefficients of Na^+ and Sr^{2+} microcomponent ions with the degree of cross-linking in cation exchangers containing 7, 10, and 12% DVB. With an increase from 7% to 12% in DVB content the diffusion coefficients of Na^+ and Sr^{2+} microcomponent ions were reduced by factors of 2.5 and 4.8 respectively. Table 5 gives data for the effect of cross-linking in a cation exchanger on the diffusion of microcomponent ions [21].

Boyd *et al.* [53] noted a retardation in the exchange process with an increase in the charge on the microcomponent ion. The diffusion coefficients for Na^+, UO_2^{2+}, and Ce^{3+} ions from HCl solutions are 3.7×10^{-6}, 3.6×10^{-7}, and 9.4×10^{-9} cm^2 s^{-1} respectively. The effect of temperature on the diffusion coefficients of microcomponent ions is probably similar to the effect on the self-diffusion coefficients, although fewer studies have been concerned with this problem. The diffusion of Na^+ microcomponent ions from KCl solution at 30° and 13.5° has been studied [4], diffusion coefficients of 3.5×10^{-6} and 1.6×10^{-6} cm^2 s^{-1} respectively being obtained. An increase in the diffusion coefficient with temperature rise has also been found for Na^+ microcomponent ions in the caesium, potassium, and zinc forms of a cation exchanger [25].

TABLE 5. Variation of the diffusion coefficient of a microcomponent ion with the cross-linking of a cation exchanger [12]. External solution 1.0 *N*.

Form of cation exchanger	Diffusing ion	DVB content, %	D, cm^2 s^{-1}
RH	Sr^{2+}	12	$6.25 \cdot 10^{-8}$
RH	Sr^{2+}	7	$2.81 \cdot 10^{-7}$
RNa	Sr^{2+}	12	$5.50 \cdot 10^{-8}$
RNa	Sr^{2+}	7	$2.30 \cdot 10^{-7}$

The effect of particle size of a cation exchanger on the rate of absorption of microcomponent ions was studied, taking the extraction of Na^+ ions from HCl solutions as an example [4]. It was shown that the diffusion coefficient is virtually independent of the particle size. The diffusion coefficients have been measured for Na^+ and Rb^+ microcomponent ions from 0.1 *N* HCl solutions on to cation-exchanger granules 0.26 and 0.48 mm in diameter. The diffusion coefficient of the Na^+ ion was found to be $3.2 \times \times 10^{-6}$ cm^2 s^{-1} for both grain sizes, and diffusion coefficients virtually independent of granulation were obtained for the Rb^+ ion.

The effect of the cationic form of an ion exchanger on the diffusion coefficient is peculiar to the exchange of microcomponent ions [25]. Boyd and Soldano established that the diffusion coefficient of the Na^+ microcomponent ion in an ion exchanger containing an alkali metal ion or a hydrogen ion is higher than in an ion exchanger in the pure sodium form. In hetero-ionic exchangers, *i.e.* those containing ions of two or more types, the diffusion coefficient of sodium may reach the value of the self-diffusion coefficient of the principal ion, when the fraction of the sodium ion becomes very low (< 5%). For example, in a predominantly potassium form (96.7% K^+, 16% DVB) $D_{Na^+} = = 3.63 \times 10^{-7}$ cm^2 s^{-1} at 25°, which is close to the value of $D_{K^+} = 3.74 \times 10^{-7}$ cm^2 s^{-1}. This is also observed for the Cs^+ ion in the sodium form of the cation exchanger. For 90% sodium at 16% DVB the activation energy for the Cs^+ ion was 8220 cal mole^{-1}, and the activation energy of the Na^+ ion in the pure sodium form was 8400 cal mole^{-1}, *i.e.* a value not much greater. In a study of the mutual effect of the contents of Zn^{2+} and Na^+ ions in a cation exchanger on their diffusion, an almost linear relationship of D_{Na^+} and $D_{Zn^{2+}}$ with its composition was noted.

It was also noted that the rate of diffusion of both ions becomes less as the cation exchanger becomes saturated with the Zn^{2+} ion. The diffusion coefficient of the microcomponent Na^+ ion in the zinc form of the exchanger is

8.56×10^{-8} cm^2 s^{-1} and that of Zn^{2+} in the sodium form is 2.21×10^{-8} cm^2 s^{-1}. From these results the qualitative conclusion was arrived at, that the more mobile cations are slowed down and the less mobile cations are accelerated. This is also confirmed by the fact that in homo-ionic salt forms of an ion exchanger $\overline{D}_{Na^+} : \overline{D}_{Zn^{2+}} = 20$ but for hetero-ionic forms the same ratio is ~ 8. In this study the rate of diffusion of the Na^+ ion in a predominantly lanthanum form of the cation exchanger was measured. Although the $\overline{D}_{Na^+} : \overline{D}_{La^{3+}}$ ratio in pure salt forms is about 500 the diffusion of Na^+ for a sodium content of less than 10% in the ion exchanger decreased by a factor of 6 compared with the diffusion coefficient in the pure sodium form. All these results again confirm the conclusion that in hetero-ionic salt forms of an ion exchanger the more mobile ions are retarded and the less mobile ions are accelerated.

The diffusion of Rb^+ and Na^+ ions in various salt forms of KU-2 cation-exchanger resin† has been studied[13,34]. Table 6 shows that the highest diffusion coefficient for Rb^+ is observed for the H form of the exchanger ($3.7 \times \times 10^{-6}$ cm^2 s^{-1}) and the lowest for the Ca form ($1.5 \times \times 10^{-6}$ cm^2 s^{-1}). Thus, these studies[13] show that a cationic form has a marked effect on the mobility of the cation being studied. From the diffusion coefficients of the microcomponent Rb^+ ion in various cationic forms of an ion exchanger, the following series of cationic forms can be constructed in decreasing order of diffusion coefficients: H > K ≥ Na > Ca. A similar sequence has been noted for the microcomponent Na^+ ion: H > K > Na.[4]

It has been shown[21] that the diffusion coefficient of a microcomponent ion in a cation exchanger containing doubly-charged ions is rather low compared with a cation exchanger containing singly-charged ions, although this effect is small. Similar relationships have been noted elsewhere[24], some of the data on the diffusion coefficients of microcomponent ions in a cation exchanger containing 10% DVB being given in Table 7.

From the data given above it may be concluded that both singly- and doubly-charged cations diffuse more rapidly in a cation exchanger containing singly-charged cations than in one containing doubly-charged cations. The effect of

TABLE 6. Effect of the form of KU-2 cation-exchange resin on the diffusion coefficient of ^{24}Na, ^{86}Rb, and ^{45}Ca microcomponent ions[13,34].

Form of cation exchanger	$10^6 D_{Na^+}$, cm^2 s^{-1} Ref. 13	$10^6 D_{Rb^+}$, cm^2 s^{-1} Ref. 13	$10^6 D_{Ca^{2+}}$, cm^2 s^{-1} Ref. 34
H	2.6	3.7	0.43
K	—	1.6 (25°)	—
K	—	2.1 (28°)	—
Na	2.2	1.45 (20°)	—
Na	—	2.0 (26°)	—
Ca	—	1.15	0.16

† KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

TABLE 7. Variation of the diffusion of microcomponent ions with the form of the cation exchanger[24].

Form of cation exchanger	Diffusing ion	D_0, cm^2 s^{-1}	Concentration of external solution, N
Rb	Rb^+	$2.64 \cdot 10^{-6}$	0.165
H		$1.46 \cdot 10^{-6}$	0.165
Na	Na^+	$1.80 \cdot 10^{-6}$	0.165
Ca		$1.45 \cdot 10^{-6}$	0.165
Ca	Ca^{2+}	$0.98 \cdot 10^{-7}$	0.25
Na		$1.20 \cdot 10^{-7}$	0.25
Sr	Sr^{2+}	$1.0 \cdot 10^{-7}$	0.25
Na		$1.39 \cdot 10^{-7}$	0.25

the form of a cation exchanger on the rate of diffusion of ions becomes greater the higher the degree of cross-linking of the cation exchanger and the higher the charge on the diffusing ion. For example[21], if Sr^{2+} ions diffuse in a cation exchanger in the hydrogen form, then the diffusion coefficient of these ions in a cation exchanger containing 12% DVB is 2.9 times greater than the self-diffusion coefficient, but in a cation exchanger containing 7% DVB it is only 1.6 times as high. In a study of diffusion in a cation exchanger containing 12% DVB [24] it was noted that if the self-diffusion coefficient of an ion is 1.4 times as high as the diffusion coefficient of the microcomponent Na^+ ion in the strontium form of the cation exchanger, then the self-diffusion coefficient of the Sr^{2+} ions is less than the diffusion coefficient of the microcomponent Sr^{2+} ion in the sodium form of the cation exchanger by a factor of 2.5.

It has been stated in the literature that the diffusion coefficient apparently depends on the concentration of the external electrolyte solution. However, during a study of the absorption of Na^+ ions from KCl solutions in relation to concentration, it was found[4] that on changing the macrocomponent ion concentration from 0.1 M to 0.2 M the diffusion coefficient of the Na^+ ion remained constant ($3.5 \times \times 10^{-6}$ cm^2 s^{-1}). The diffusion coefficients measured for the Sr^{2+} microcomponent ion into the sodium form of a cation exchanger from 0.25 N and 1.0 N NaCl solutions differed quite insignificantly (2.62×10^{-7} and 2.34×10^{-7} cm^2 s^{-1} respectively). Attention should also be paid to the fact that the values for diffusion coefficients of microcomponents of 0.165 N, 0.25 N, and 1.0 N are in good agreement with other results[21,24]: 2.91×10^{-7} cm^2 s^{-1} (0.25 N) and $2.80 \times \times 10^{-7}$ cm^2 s^{-1} (1.0 N).

V. KINETICS OF COMPLETE EXCHANGE

We have considered the simplest cases of ion exchange, *i.e.* the processes of self-diffusion and the diffusion of microcomponent ions. In these processes there are virtually no changes in the form of the cation exchanger, so that it is assumed that the processes take place with constant values for the diffusion coefficients. In the case of complete exchange, the ionic form of the cation exchanger alters, so that it is impossible to assume that the diffusion coefficient is constant, for the exchanging ions may have substantially differing mobilities. In addition, the swelling of a cation exchanger alters with a change in its form. To characterise the processes in complete exchange, the concept of the effective diffusion coefficient is introduced, *cf.* Eqn.(12).

It is evident that in most cases the rates of complete exchange correspond to the rates of diffusion of the cations whose concentrations are low, *i.e.* to the rates of diffusion of the microcomponent ions. Therefore, a comparison of the rate of complete exchange with the rate of exchange of the same ions present in microconcentrations is advisable.

Of the cases of complete exchange, those in which the hydrogen ion participates[13,20,55-57] are of special interest. In the papers cited the effects of the following factors on the rate of exchange were studied: the concentrations of the exchanging ions in solution, the degree of cross-linking and the particle sizes of the ion exchanger, and the temperature of the process; the activation energy was determined. A study has been carried out[56] of the complete exchange between sodium and hydrogen ions on two sulphonated polystyrene cation exchangers having different degrees of cross-linking (5 and 17% DVB). Reichenberg[56] established that in the exchange of the H^+ ion from a resin with Na^+ from solution, the rate of exchange at high Na^+ concentrations in solution ($> 1.0\ N$) does not depend on the concentration of this ion, and is inversely proportional to the square of the radius of the exchanger particles. At low ion concentrations in solution ($< 0.05\ N$) the rate was proportional to the concentration of Na^+ ions in solution and inversely proportional to the radius of the exchanger particle. Thus, at low concentrations, the exchange process was limited by diffusion through the film of solution adjacent to the ion-exchanger particle. In the same investigation a study was made of the effect of temperature and the degree of cross-linking of the cation exchanger on the effective diffusion coefficient for the process, which was limited by particle diffusion. For a cation exchanger containing 5% DVB and a particle diameter of 544 μm, $D = 7.3 \times 10^{-6}$ cm^2 s^{-1} at 25° and 1.7×10^{-5} cm^2 s^{-1} at 50°, for a cation exchanger containing 17% DVB and a particle diameter of 546 μm, $D = 1.1 \times 10^{-6}$ cm^2 s^{-1} (25°) and 2.4×10^{-6} cm^2 s^{-1} (50°), and for the same cation exchanger but with a particle size of 893 μm, $D = 1.2 \times 10^{-6}$ cm^2 s^{-1} (25°). Thus, with an increase in the degree of cross-linking of the ion exchanger and for complete exchange there is a decrease in the diffusion coefficient. With a rise in temperature the usual increase in the diffusion coefficient is observed; the activation energy for both cation exchangers was ~ 5.9 kcal mole^{-1}. The diffusion coefficient did not depend on the size of the cation-exchanger particles.

Similar results were obtained in another investigation[57]. It was shown that for complete exchange between alkali metal ions in solution and the hydrogen ion in a cation exchanger at an external solution concentration less than 1.0 *N* the effective diffusion coefficient is independent of the grain size of the ion exchanger and increases with temperature. It was established that for complete exchange the alkali metals can be arranged in the following order, according to the effective diffusion coefficient in the exchange with the hydrogen ion: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The activation energy for the exchange of the H^+ ion with the Na^+ ion was estimated as ~ 5 kcal mole^{-1}.

A study of complete exchange has been made[13] in the replacement of the H^+ ion in a cation exchanger by the Na^+ ion from 0.1 *N* NaCl. Fig. 4 shows the kinetic curves for the diffusion of the microcomponent Na^+ ion from 0.1 *N* HCl into a cation exchanger in the hydrogen form at 18°.

For complete exchange the diffusion coefficient of the Na^+ ion is 5×10^{-6} cm^2 s^{-1} and for the exchange of the microcomponent Na^+ ion it is 2.6×10^{-6} cm^2 s^{-1}, *i.e.* twice as high, which is perfectly explicable, as the mobility of the H^+ ion is much higher than that of the Na^+ ion.

Complete exchange between H^+ and Na^+ ions, and between H^+ and Rb^+ ions, has been studied in other investigations[20,24]. Some of the results for complete exchange between H^+ and Na^+ ions are given in Fig. 5 and Table 8. The most rapid process is the exchange of H^+ ions from the cation exchanger with Na^+ ions from the solution, the slowest process being the diffusion of microcomponent Na^+ ions into the cation exchanger in the hydrogen form. Complete exchange between Na^+ and H^+ ions takes place with effective diffusion coefficients lying between these two limiting values.

The results obtained[20] confirm the theoretical conclusions that the effective diffusion coefficients have their highest values in exchange processes involving hydrogen ions at low H^+ ion contents in a cation exchanger. At these stages, apparently, the effective diffusion coefficients are close to the diffusion coefficient of the microcomponent H^+ ion in the sodium or rubidium forms of the cation exchanger.

The kinetics for the complete exchange of the singly-charged ions Li^+, Na^+, and K^+ with the H^+ ion in 1.0 *N*

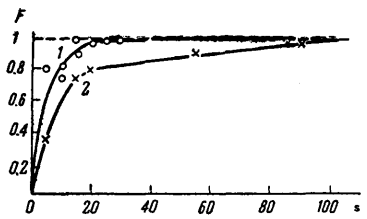


Fig. 4. Kinetic curves for complete exchange of hydrogen ions with sodium on KU-2 cation-exchange resin[13]: 1) 0.1 *N* NaCl + ^{24}NaCl (tracer) [? 2) 0.1 *N* HCl + + ^{24}NaCl [tracer], see text (Ed. of Translation)], cation exchanger in the hydrogen form.

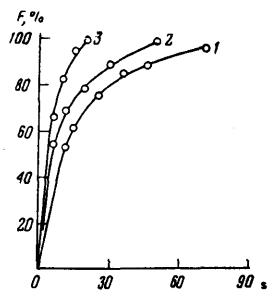


Fig. 5. Cation exchanger with a decreased DVB content[20]: 1) diffusion of Na^+ microcomponent ion in hydrogen form of cation exchanger; 2) exchange of sodium ions from the cation exchanger with hydrogen ions from solution; 3) exchange of hydrogen ions from the cation exchanger with sodium ions from solution.

TABLE 8. Effective diffusion coefficients in the exchange of sodium and hydrogen ions (sulphonated cation exchanger containing 7% DVB).[20]

System	Exchange period, s	Degree of exchange, F, %	$10^6 D_{eff}$, $cm^2 s^{-1}$
RNa—H^+	5	53.7	5.99
	10	69.0	5.50
	20	77.6	3.80
	30	88.2	4.18
	40	91.5	3.80
RH—Na^+	6	65.0	8.2
	10	81.0	10.2
	15	94.6	13.2
	20	97.0	13.0

TABLE 9. Effective diffusion coefficients for complete exchange between strontium and sodium ions[21].

System	Period of contact between solution and cation exchanger, s	Degree of exchange, F, %	D_{eff}, $cm^2 s^{-1}$	System	Period of contact between solution and cation exchanger, s	Degree of exchange, F, %	D_{eff}, $cm^2 s^{-1}$
RSr—Na^+	30	50.5	$9.6 \cdot 10^{-7}$	RNa—Sr^{2+}	10	51.0	$2.8 \cdot 10^{-6}$
	60	64.5	$9.1 \cdot 10^{-7}$		15	65.9	$3.3 \cdot 10^{-6}$
	80	73.0	$8.5 \cdot 10^{-7}$		25	77.2	$3.0 \cdot 10^{-6}$
	140	79.0	$7.3 \cdot 10^{-7}$		40	86.5	$2.94 \cdot 10^{-6}$
	180	80.0	$6.1 \cdot 10^{-7}$		60	90.5	$2.70 \cdot 10^{-6}$
	400	85.0	$2.8 \cdot 10^{-7}$		90	97.5	$2.85 \cdot 10^{-6}$
	520	91.0	$2.5 \cdot 10^{-7}$		120	99.3	—
	760	93.5	$2.3 \cdot 10^{-7}$		200	100	—

aqueous and aqueous alcoholic solutions have been studied[58]. The authors assumed also that in the initial stages of the exchange process the diffusion coefficients are constant, and therefore used for their calculations the equation for diffusion in a sphere involving a constant diffusion coefficient, *cf.* Eqn. (6). The diffusion coefficients thus found for aqueous solutions were, respectively. Li^+ 2.96×10^{-7}, Na^+ 4.55×10^{-7}, and K^+ 4.60×10^{-7} $cm^2 s^{-1}$. In addition, it was noted that in the exchange of the H^+ ion with the Li^+ ion the coefficient for diffusion from lithium sulphate solution is higher than from lithium chloride solution.

The complete exchange between singly-charged and doubly-charged ions has been studied[21,24]. In this case the kinetic characteristics are determined to a considerable extent by the difference in the properties of cation exchangers containing singly- and doubly-charged ions,

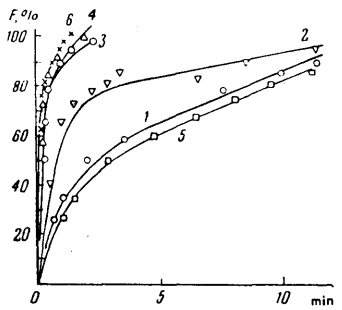


Fig. 6. Cation exchanger with a decreased DVB content. Exchange in 0.25 *N* solutions at 19–20°:[21] 1) diffusion of strontium microcomponent ions in the sodium form of cation exchanger; 2) exchange of strontium ions from the cation exchanger with sodium ions from solution; 3) exchange of sodium ions from the cation exchanger with strontium ions from solution; 4) diffusion of sodium microcomponent ions in the strontium form of cation exchanger; 5) self-diffusion of strontium ions; 6) self-diffusion of sodium ions.

particularly in swelling. The curves in Fig. 6 show that in the first stages the exchange of ions from a cation exchanger with the Na^+ ions from solution takes place much more rapidly than the diffusion of the microcomponent Sr^{2+} ion in the sodium form of the cation exchanger, but in later stages the rates of both processes approach each other. The calculated effective diffusion coefficients are shown in Table 9.

Thus, during the exchange process in the RSr–Na^+ system the effective diffusion coefficient falls and becomes an order of magnitude lower than the effective diffusion coefficient for complete exchange in the RNa–Sr^{2+} system, whereas for exchange in the RNa–Sr^{2+} system the effective diffusion coefficient is almost constant over the whole exchange process, being close to the diffusion coefficient of the microcomponent Na^+ ion in the strontium form of the cation exchanger. It should be noted that, at first, the exchange of Sr^{2+} ions in the cation exchanger with hydrogen ions takes place more rapidly than the exchange of Sr^{2+} ions with Na^+ ions, but in the later stages the rates of both processes become approximately equal. The initial difference in the rates of exchange is probably due to the higher mobility of the hydrogen ions in the cation exchanger, but at the later stages the rate of exchange is governed by the diffusion of the microcomponent strontium ion in the hydrogen or sodium forms of the cation exchanger.

VI. KINETIC FEATURES OF THE EXCHANGE OF LARGE ORGANIC IONS

The study of the kinetics of ion exchange processes during the sorption of large multicharged organic ions on a cation exchanger has a certain interest. Bruns *et al.*[59-66] showed that the rate of sorption of streptomycin ions on cation exchangers is determined by particle diffusion. It was established that the rate of exchange depends on a number of factors: the degree of cross-linking of the cation exchanger, the temperature, the concentration of ions in the solution, and the cationic form of the cation exchanger. It was found[59-61,63,64] that with an increase in the degree of cross-linking, diffusion in the cation exchanger is retarded and the amount of large ions absorbed becomes less than the total exchange capacity of the ion exchanger. Yakhontova *et al.* applied the concept of "pseudo-equilibrium" to this phenomenon. The establishment of "pseudo-equilibrium" was explained by the formation of a "streptomycin crust" on the surface of the grain of cation exchanger, it being assumed that the streptomycin form of the cation exchanger is only slightly permeable to streptomycin ions.

The observed retardation in sorption is most likely explained by the effect of a steric factor and the value of the ionic charge (the streptomycin ion is triply-charged).

A retardation in diffusion was also observed[67,68] when the sorption of the organic dyes Methylene Blue and Antipyridine Red and of other large organic ions was studied. The photomicrographs of sections obtained by these authors[67] show that intensive staining is observed only in the external layer of a granule, the central part remaining completely unstained.

The effect of the particle size of a cation exchanger on the rate of sorption was studied[59,60,64-73], it being shown that the greatest quantity of large organic ions is sorbed by a finely-dispersed cation exchanger, and a decrease in the amount of streptomycin absorbed is observed with an increase in the granule diameter. In particular[60], on using a cation exchanger in the hydrogen form containing 9% DVB and having grain sizes of 0.25–0.5 mm, the amount of streptomycin absorbed was half that absorbed on a cation exchanger having grain sizes of 0.03–0.06 mm. Furthermore, on crushing large grains after establishing a "pseudo--equilibrium" state on them, an additional absorption of streptomycin was observed. These phenomena may be explained by the fractional volume occupied by the "streptomycin crust" being considerably higher in the finer ion--exchanger particles.

The results concerning the effect of temperature on the sorption of streptomycin on a cation exchanger are interesting[59,61,63]. It was shown that a rise in temperature from 6° to 37° leads to an increase in the rate of diffusion by a factor of 2–4. The increase in temperature also leads to a displacement in the "pseudo-equilibrium", causing further sorption.

The form of the cation exchanger and the concentration of additional cations in solution have a substantial effect on the rate of sorption of large ions[59-66,68]. The authors[59-66] noted that the sodium form of the cation exchanger absorbs streptomycin better than the hydrogen form and that "pseudo--equilibrium" is shown most clearly by the hydrogen form of a cation exchanger (referring to a weakly acid cation exchanger). The exchange of streptomycin on the hydrogen form of a cation exchanger containing an average number of cross-links was investigated in solutions containing varying concentrations of sodium sulphate[60]. It was found that an increase in sodium ion concentration up to 0.3 N produced an increase in the sorption of streptomycin, but that a further increase to 1.0 N and 2.0 N led to a decrease in sorption. The time required for the completion of the exchange process fell considerably as the concentration was raised. Bruns *et al.* attributed this phenomenon to the mixed sodium–streptomycin form of the cation exchanger being more permeable to the streptomycin ion, *i.e.* the highly mobile, univalent sodium ion stimulates the diffusion of the tervalent streptomycin in the cation exchanger.

The diffusion coefficients of Methylene Blue ions in KU-2 sulphonated cation exchangers containing 2 and 6% DVB were studied for the initial periods of sorption[68], part of the hydrogen ions of the original exchangers being previously replaced by dye ions. It was established that in the sorption of dye ions on the exchanger containing 2% DVB, the diffusion coefficients of Methylene Blue ions in the cation-exchanger phase at 40° and 75° are approximately halved by an increase from 0 (the hydrogen form) to 0.8 (80% of the hydrogen ions replaced by dye ions) in the equivalent fraction of the dye ions in the initial ion exchangers. Precisely the same thing occurs for the sorption of the dye on the cation exchanger containing 6% DVB at 75°. On carrying out sorption at lower temperatures the diffusion of Methylene Blue ions in KU-2 containing 6% DVB decreased by from one to two orders of magnitude with the increase from 0 to 0.8 in the equivalent fraction of dye ions in the initial ion exchanger. In the latter case a large increase in the activation energy is observed and a "pseudo-equilibrium" state established.

Thus, the principal feature in the sorption of large organic ions should be considered, the decrease in the permeability of the cation exchanger towards the ion being absorbed during the exchange process (the "pseudo-equilibrium" state). This decrease in permeability is expressed as a decrease in the diffusion coefficients of large ions in the ion-exchanger phase and an increase in the activation energy with the conversion from one form to the other in the ion exchanger, the introduction of a univalent mobile ion in the exchange system leading to the liquidation of the "pseudo-equilibrium" state, an increase in the diffusion coefficient, and a decrease in the activation energy.

VII. THE RELATIONSHIP BETWEEN DIFFUSION AND ELECTRICAL CONDUCTIVITY IN ION EXCHANGERS

In conclusion we would like to dwell on the determination of the self-diffusion coefficients of ions in an ion exchanger by the direct measurement of electrical conductivity.

As is well known, the diffusion coefficient and mobility of the ions are connected by the relationship

$$D = \frac{R_T T B}{zF}, \qquad (17)$$

where T is the temperature in °K, B the mobility of the ion, R_T the gas constant, z the charge of the ion, and F Faraday's constant.

If the mobility of the ion is expressed in terms of the specific electrical conductivity and the transport number, the Nernst–Einstein relationship is written in the form

$$D = \frac{R_T}{zF} \times T \times \frac{1000 \kappa t}{aF}, \qquad (18)$$

where t is the transport number, κ the specific conductivity, and a the capacity of the ion exchanger calculated for 1 cm^3.

In electrolyte solutions placed in an electric field an external force proportional to the field strength acts on the ions, as well as two internal retarding forces, *viz.* an electrophoretic force, arising from the electric field which, in pulling the ion in one direction, draws off its ion atmosphere in the opposite direction, and a relaxation force arising from the loss of spherical symmetry in the ion atmosphere on moving.

Due to the presence of the retarding forces, the Nernst–Einstein relationship is satisfied only at infinite dilution in electrolyte solutions. For a cation exchanger it is to be expected that this relationship would be correct to a large extent, as a cation exchanger may be considered as a large immobile matrix to which anions and mobile cations are attached. The transport number of the cations in relation to such a matrix is close to unity.

It should be noted at once that according to the available experimental data the Nernst–Einstein relationship is satisfied for ion exchangers saturated with doubly- and multi-charged ions.

TABLE 10. Diffusion coefficients calculated from electrical conductivity data[72].

Capacity of cation exchanger, mg-equiv. × g^{-1}	Form of exchanger	Specific conductivity, Ω^{-1} cm^{-1}	Self-diffusion coefficient, $10^{-6}D$, cm^2 s^{-1} (calculated)
0.18	K	0.00063	0.022
4.5	H	0.092	18.7
4.5	Na	0.024	4.1
4.5	K	0.045	7.9
4.5	Sr	0.010	0.86

Many attempts to measure the electrical conductivity have been made on ion-exchange materials in the form of membranes or solid columns, but in a number of cases the preparation of materials in such a form is difficult, so that studies in which the electrical conductivity of ion exchangers in the form of granules has been determined[69-72] are of particular interest. For example, the specific conductivity of a KU-2 sulphonated cation exchanger having different capacities has been studied[72]. The measurements were carried out at 19° with chloride solutions. The basic idea behind the method is to find an electrolyte solution concentration whose electrical conductivity should equal the electrical conductivity of a cation exchanger particle in equilibrium with it. Using the values obtained for the electrical conductivity, the self-diffusion coefficients of the appropriate ions were calculated from Eqn. (18) (Table 10). In the calculations from the measured electrical conductivities a correction was made for the additional conductivity due to the Donnan effect. Here one should note the satisfactory agreement between the value of the self-diffusion coefficient for the Na^+ ion obtained by using a radioactive isotope on the same sample of cation exchanger ($D = 3.5 \times 10^{-6}$ cm^2 × × s^{-1}) and that calculated from the electrical conductivity data.

For K^+ too high a value of $\bar{D}$ seems to be obtained, while for Sr^{2+} a reasonable value is obtained. The low value of $\bar{D}$ for the K^+ ion in a low-capacity cation exchanger agrees with the decrease in self-diffusion coefficients observed on desulphonation[10]. The diffusion coefficients obtained for the hydrogen ion are anomalously high, but similar results were observed elsewhere[73]. It was found that in the exchange of the H^+ ion of an ion exchanger with Na^+ from solution, the effective diffusion coefficients are very high (up to 13 × × 10^{-6} cm^2 s^{-1}) and the hydrogen ion has an increased mobility in ion exchangers, as in aqueous solutions of electrolytes.

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Karpov Physico-chemical Institute

U.D.C. 541.1

ALPHA RADIOLYSIS OF AQUEOUS SOLUTIONS

M. V. Vladimirova

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I. INTRODUCTION

Recent advances in nuclear chemistry, and in particular in the chemistry of the transuranium elements, have created a need for a better understanding of the effects of α-radiation on the physicochemical properties of a system. Furthermore, the high ionisation density of the α-radiation from radioactive elements offers a convenient simulation of the radiochemical processes occurring in solutions irradiated by fission residues. Hence the need for coordinating the experimental data relating to α-radiolysis is self-evident, particularly since the published results of different authors are often contradictory.