exchange on Dowex 50. Under these conditions 90% of the capacity of 20–24 Dowex 50 may be exhausted in 33 sec. in the Na–H exchange.

Additional experimental work at high solution concentrations, at various temperatures, and at various particle sizes is required to complete the study of the exchange rate of Dowex 50.

Conclusions

1. Ion exchange equilibrium and rate for Dowex 50 have been shown to be consistent with the hypothesis that the resin phase is equivalent to a highly ionized salt solution.
2. Assuming activity coefficients equivalent to those in strong chloride solutions, the ion exchange equilibrium data may be interpreted by the Donnan concept of membrane diffusion.
3. The concentration of diffusible anions in the resin phase is lower than in the solution phase, as anticipated by the Donnan theory, but quantitative agreement with the theory is not obtained ni dilute solutions.
4. At low solution concentrations the exchange rate for Dowex 50 is controlled by the mass action reaction rate between the ions at the surface of the particle. The driving force is the product of the activity of one ion in the resin phase and the activity of the second ion in the solution phase. The rate constant depends on the turbulence of the solution phase at the resin surface, the surface area, etc., and hence is constant only under a specified set of experimental conditions.
5. The diffusion rate of hydrochloric acid and sodium chloride in the resin phase is about one fifth as great as in dilute aqueous solution. This rate indicates that interdiffusion of ions in the resin phase should be controlling in the exchange rate at solution concentrations above about 0.1 molal.

MIDLAND, MICH. RECEIVED JULY 16, 1947

[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. II. Kinetics[1]

BY G. E. BOYD,[2] A. W. ADAMSON[3] AND L. S. MYERS, JR.[4]

Introduction

Although the rate factor in ion-exchange adsorption is of recognized importance in its bearing on the performance of deep adsorbent beds operating under dynamic conditions, until quite recently very little attention has been devoted to its elucidation.[5] Additional studies were deemed highly desirable since it was believed that a quantitative understanding of the kinetics of heterogeneous ion-exchange processes might reveal the mechanism of the rate controlling process, and perhaps also shed significant light on the problem of the internal physical structure of organic gel exchangers. The present investigation, therefore, was concerned first with the formulation of equations governing the velocity of ion-exchange based on diffusion and on mass action mechanisms. Three such relations were subjected to an extensive experimental testing in order to determine the validity and range of application of each of them. The alkali metal cations were employed. Depending upon the concentration existing in the aqueous phase, it was concluded that the rate of ion-exchange was determined either by diffusion in and through the adsorbent, or by diffusional transport across a thin liquid film enveloping the particle.

An important feature of the experimental work was the use of radioactive isotopes in the rate measurements. The equations were found to assume a particularly simple and readily verifiable form if the composition of the solid base-exchanger were maintained unchanged during the adsorption. In practice, this means that the cation A^+, whose adsorption is being followed, must be present in much smaller concentrations than B^+, the ion being displaced from the exchanger (*i. e.*, A^+ must be a microcomponent). This simplifying condition cannot be realized very effectively, however, owing to the paucity of highly exact general methods of trace analysis. The accurate determination of the changes in concentration of substances present in extreme dilution fortunately has been made possible by the recent feasibility of the employment of convenient radio-isotope techniques.

Also an improvement is believed to have been made in the experimental procedure used to obtain the rate data. A single stage technique, which may be termed the "shallow-bed method," made possible the determination of rates of adsorption down to very short times, a decisive advantage when the half-time for the achievement

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[1] This work was performed under the auspices of the Manhattan District at the Clinton Laboratories of the University of Chicago and the Monsanto Chemical Company at Oak Ridge, Tennessee, during the period October, 1943, to January, 1946.

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[5] F. C. Nachod and W. Wood, THIS JOURNAL, **66**, 1380 (1944); **67**, 629 (1945).

of exchange equilibrium was but one or two seconds. Further, employment of the method made possible the obtaining of rate data under conditions of constant solution concentration of the exchanging cations thereby permitting an important simplification of the mathematics in the derivation of the rate equations.

Development of the Rate Equations

In considering rates of exchange adsorption it should be remembered that the usual synthetic organic ion-exchanger consists of relatively large, porous particles, the pores or capillaries of which are filled with aqueous solution. The exchanging groups responsible for the adsorptive capacity of these materials are known, from X-ray diffraction data, to be dispersed randomly throughout the interior of the solid. In terms of the base-exchange reaction

$$A^+ + BR = AR + B^+$$

where A^+ and B^+ are the exchanging monovalent cations, and where R refers to the insoluble, non-diffusible anionic portion of the adsorbent, the over-all transport of mass, apart from that effected by the moving liquid, may be divided into five steps: (1) Diffusion of A^+ through the solution up to the adsorbent particles. (2) Diffusion of A^+ through the adsorbent particles (accompanied by the anion in solution). Two dimensional diffusion of the ion along the capillary walls of the adsorbent must be considered as a possibility. (3) Chemical exchange between A^+ and BR at the exchanging positions in the interior of the particles. (4) Diffusion of the displaced cation B^+ out of the interior of the exchanger (reverse of step 2). (5) Diffusion of the displaced cation B^+ through the solution away from the adsorbent particles (reverse of step 1). The kinetics of the exchange will be governed either by a diffusion or by a mass action mechanism, therefore, depending on which of the above steps is the slowest.

Diffusion through a Bounding Liquid Film.—Generally, an attempt is made to eliminate processes 1 and 5 experimentally by vigorous mixing, or otherwise, so as to maintain a constant concentration of adsorbing solute at the adsorbent particle–solution interface. If, however, the uptake is very rapid, it may not be possible to transport ions to the boundary at a rate sufficient to realize this desired condition. Then, a liquid film in which a concentration gradient persists may be imagined to encompass the particle.

Consider a spherical adsorbent particle of radius, r_0, surrounded by a sphere of aqueous solution of radius, r_0', in which a concentration gradient exists. Let $\Delta r_0 = r_0' - r_0$ be taken as the thickness of the film; c^l, the concentration in the bulk of the solution at any time and constant for $r \geqq r_0'$; and C^f, the concentration in the film taken to vary linearly from $C^f_{r=r_0'} = C^l$ to $C^f_{r=r_0} = C^{l*}$, the concentration in the solution adjacent to and hence in equilibrium with the solid. The concentration in the solid, C^s, is assumed constant in the region: $0 \geq r \geq r_0$. Further, denote the final or equilibrium concentrations in the solid and liquid by C^s_e and C^l_e respectively. The distribution efficient, κ, which is assumed independent of concentration, is defined by $C^s_e = \kappa C^l_e$. This assumption will, of course, apply exactly only to solutions infinitely dilute in the species being adsorbed. In order for κ to be constant within experimental error, however, it is sufficient if the adsorbate be a microcomponent of the system.

Equilibrium at the surface of the adsorbing particle is assumed for all times of contact so that for $r = r_0$

$$C^l_{r=r_0} = C^s/\kappa = \frac{Q}{4/3\ \pi r_0^3\ \kappa} \qquad (1)$$

since the total amount of adsorbate per particle, Q, is given by $(4/3)\pi r_0^3 C^s$.

If diffusion through the film is rate controlling, the rate of permeation, P (*i. e.*, quantity transferred/unit time/unit area of unit thickness under a standard concentration difference) is

$$P = -D^l(\partial C^f/\partial r)_{r=r_0'} \qquad (2)$$

and D^l is the diffusion constant in the liquid.

The total rate of flow of adsorbate across the film, $\mathrm{d}Q/\mathrm{d}t$, is given by

$$\mathrm{d}Q/\mathrm{d}t = 4\pi r_0^2 D^l\ (\partial C^f/\partial r)_{r=r_0} \qquad (3)$$

which for a linear concentration gradient

$$(\partial C^f/\partial r) = (C^l - C^l_{r=r})/\Delta r_0 \qquad (4)$$

may be written as

$$\mathrm{d}Q/\mathrm{d}t = \frac{4\pi r_0^2 D^l}{\Delta r_0}(C^l - C^l_{r=r_0}) = \frac{3D^l}{r_0 \Delta r_0 \kappa}\left[\frac{4\pi r_0^3 C^l \kappa}{3} - Q\right] \qquad (5a)$$

Defining the constant R by $3D^l/r_0\Delta r_0\kappa$, and noting that the total amount adsorbed at equilibrium, Q_∞, from a very large amount of solution kept at C^l for all time is given by $4\pi r_0^3 C^l\kappa/3$, it is seen that Equation (5a) reduces to

$$\mathrm{d}Q/\mathrm{d}t = R(Q_\infty - Q) \qquad (5b)$$

which, upon integration for the condition that $Q = 0$ when $t = 0$, becomes

$$Q = Q_\infty[1 - \exp(-Rt)] \qquad (6a)$$

Defining the fractional attainment of equilibrium, F, by Q/Q_∞, Equation (6a) may be written alternatively as

$$\log(1 - F) = -(R/2.303)t \qquad (6b)$$

Diffusion in and through the Adsorbent Particle: Constant Solution Concentration.—If an experimental arrangement can be devised for which it may be assumed that the initial concentration of adsorbate in solution, C^l_0, remains constant, the appropriate equation for diffusion through the solid may be solved.

In this case, we begin by writing the diffusion equation for spherical particles in the form

$$(\partial u/\partial t) = D^i(\partial^2 u/\partial x^2) \qquad (7)$$

where, in addition to the symbols already defined, $u = C^s r$ where r is the radius of the spherical surface of concentration C^s in the solid, and D^i is the internal diffusion coefficient. The boundary conditions are, then

$$u = 0 \text{ at } r = 0 \text{ for } t \gg 0$$
$$u = r\kappa C^l \text{ at } r = r_0 \text{ for } t \gg 0$$
$$u = rC_0^s \text{ at } t = 0 \text{ for } 0 < r < r_0$$

The solution to Equation (7) has been given by Barrer.[6]

$$C^s = \kappa C^l + \frac{1}{r}(\kappa C^l - C_0^s)\frac{2r_0}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi r}{r_0}\, e^{-D^i n^2 t/r_0^2} \quad (8)$$

The total amount of solute entering per unit area in a given time t is

$$q = \int_0^t P\,dt = -\int_0^t D^i(\partial C^s/\partial r)_{r=r_0}\,dt \quad (9)$$

Utilizing Equation (8), and assuming that the initial concentration in the solid, C_0^s, is zero, Equation (10) is obtained

$$q = \frac{2r_0}{\pi^2}\kappa C^l\left[\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-D^i n^2\pi^2 t/r_0^2} - \sum_{n=1}^{\infty}\frac{1}{n^2}\right] \quad (10)$$

The total amount adsorbed at any time, Q, is given by $Q = 4\pi r_0^2 q$. Also remembering that $\sum_{n=1}^{\infty} 1/n^2 = \pi^2/6$, one may write Equation (10) as[7]

$$Q = \frac{4\pi r_0^3\kappa C^l}{3}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-D^i n^2\pi^2 t/r_0^2}\right] \quad (11)$$

Accordingly, the expression for the fractional attainment of equilibrium, $F = Q/Q_\infty$, where Q_∞ is the amount adsorbed at equilibrium (*i. e.*, $t = \infty$), may be written as

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D^i\pi^2 n^2 t}{r_0^2}\right) \quad (12)$$

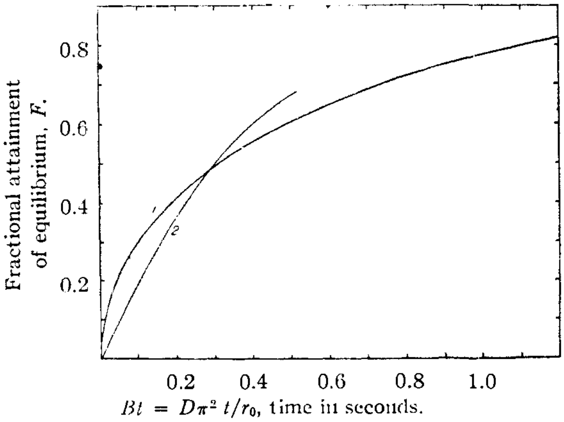

Fig. 1.—Theoretical curves for adsorption velocity: curve 1, rate determined by particle diffusion; curve 2, rate determined by film diffusion or chemical exchange reaction.

The solution has been obtained for the case where the adsorbent particles are in the form of slabs, rather than spheres. The derivation is similar to the foregoing, and only the final equation will be given

$$F = 1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\exp\left[-(2n-1)^2\frac{\pi^2 D^i t}{4x_0^2}\right] \quad (13)$$

where x_0 is the half-thickness of the slab.

Since the adsorbent particles in our experiments were far from being exact spheres, it was thought possible that a better agreement would be obtained with the slab Equation (13); consequently, solutions (12) and (13) were tested. Both were found to agree closely with the experimental data, although the equation for the spherical case represented the results better.

Equation (12) was employed most conveniently in the form of a $(Q/Q_\infty, Bt)$ plot, where $B = D^i\pi^2/r_0^2$, as illustrated by Fig. 1.[8] For each experimentally observed value of F a value of Bt is read from the curve and divided by the time of contact. If the data obey the diffusion Equation (12), the values of B should be constant; knowing the particle size, r_0, an average value of D^i can be obtained.

The series in Equation (12) converges slowly for small values of Bt so that in this region it becomes advantageous to use an approximate equation. For small values of F, and hence Bt, only the outermost spherical shell of the adsorbent contains the adsorbed ion. If this shell is approximated by a slab of area $4\pi r_0^2$, the amount of adsorbate contained will be given by an equation for diffusion into a semi-infinite solid[9]

$$C^s(x,t) = C_0^s\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2}\,dy\right] = C_0^s[1 - erf(y)] \quad (14)$$

where x = distance normal to the surface of the slab; C_0^s = concentration at $x = 0$; and $y = (x' - x)/2\sqrt{Dt}$. Integration of Equation (14) gives

$$C^s(x,t) = C_0^s\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{x}{2\sqrt{Dt}} - \frac{x^3}{3\cdot 1!\,(2\sqrt{Dt})^3} + \frac{x^5}{5\cdot 2!(2\sqrt{Dt})^5} - \cdots\right)\right] \quad (15)$$

Again, the amount diffused into the adsorbent per unit area is given by a relation of the type of Equation (9). On making use of Equation (15), then, it can be shown that the amount, q', taken up by a unit area of semi-infinite slab is given by

$$q' = 2C_0^s\sqrt{Dt/\pi} \quad (16)$$

Hence, the total amount diffused into the slab (or equivalent sphere) of area $4\pi r_0^2$ is

$$Q = 8\pi r_0^2 C_0^s\sqrt{Dt/\pi} \quad (17)$$

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(6) R. M. Barrer, "Diffusion in and through Solids," Cambridge Press, 1941, p. 29.

(7) Through some misprint, or otherwise, a slightly different final equation is given by Barrer.

(8) A table of values of Bt as a function of F is given in the appendix.

(9) Ref. 6, p. 12.

Since at equilibrium, $Q_\infty = 4/3\pi r_0^3 C_0^s$, it follows that

$$F = Q/Q_\infty = 6/r_0\sqrt{Dt/\pi} \qquad (18a)$$

or, in terms of Bt

$$F = 1.08\sqrt{Bt} \qquad (18b)$$

Equation (18b) may be used to compute values of F up to about 0.05. A parabolic rate law thus will be obeyed to a good approximation for small values of t, for small diffusion coefficients and/or for large particles.

Adsorption Kinetics as a Chemical Phenomenon.—As was pointed out in an earlier publication,[10] for the case of two monovalent ions the mass law applies to the exchange when written as

$$A^+ + BR \rightleftarrows B^+ + AR$$

If m_{A^+} and m_{B^+} denote the concentrations of the ions A^+ and B^+ in solution, and n_{AR} and n_{BR} the moles of A^+ and B^+ in the adsorbent, then one can write for the net reaction rate

$$\mathrm{d}n_{AR}/\mathrm{d}t = k_1 m_{A^+} n_{BR} - k_2 m_{B^+} n_{AR} = -n_{AR}(k_1 m_{A^+} + k_2 m_{B^+}) + k_1 m_{A^+} E \qquad (19)$$

where k_1 and k_2 are the forward and reverse specific rate constants, and E is a constant defined by $E = n_{AR} + n_{BR}$.

If, as before, it is assumed that the concentrations of A^+ and B^+ in solution are kept constant, then, on integration, Equation (19) becomes

$$n_{AR} = \frac{k_1 m_{A^+} E}{k_1 m_A + k_2 m_{B^+}}(1 - e^{-St}) = Q \qquad (20a)$$

where $S = k_1 m_{A^+} + k_2 m_{B^+}$ and where Q has the same meaning as in the foregoing sections on diffusion. Equation (20a) may be put in a more compact form by noting that

$$Q_\infty - Q = Q_\infty\, e^{-St} \qquad (20b)$$

where Q_∞ is the equilibrium value (*i. e.*, $t = \infty$). Hence

$$\log(1 - F) = -\frac{S}{2.303}t \qquad (20c)$$

Equation (20b) predicts an exponential decay of the quantity $(Q_\infty - Q)$, and, if several mass action rate processes are occurring independently, the individual rate constants may be obtained by analyzing a [*log* $(1 - F)$, t] plot in much the same manner as for the decay of a mixture of radioactive species.

Comparison of the Mass Action and Diffusion Equations.—Plots of the mass action rate Equation (20) and the diffusion Equation (12) are quite different in shape as is illustrated by Fig. 1. Generally, the two curves will cross as may be shown by the following considerations: According to Equation (20c), $\mathrm{d}\ln(1 - F)/\mathrm{d}t = -S$, which is a constant, whereas according to Equation (12)

$$\mathrm{d}\ln(1 - F)/\mathrm{d}t = -\frac{D\pi^2}{r_0^2}\frac{\sum^{\infty} e^{-n^2Bt}}{\sum^{\infty}\frac{1}{n^2}e^{-n^2Bt}} \qquad (21)$$

Thus, the slope, constant when the rate is mass action controlled, varies between infinity initially and $-D\pi^2/r_0^2$ if the rate of adsorption is governed by diffusion. Evidently, if the magnitude of S exceeds $D\pi^2/r_0^2$, the two curves must cross, as has been indicated in Fig. 1 for $F = 0.5$. Ion exchange rate data should not be expected to obey either equation very closely in a region such as this where the diffusion and mass action velocities are comparable.

The identity in form of the rate Equation (6) for the case of diffusion through a bounding liquid film with the mass law type rate Equation (20) should be noted. Should experimental data conform to this type of equation it will be necessary to carry out experiments whereby the magnitude of the slope (R or S) is varied to determine the correct rate mechanism. Thus, if film diffusion is rate controlling, the slope will vary inversely with the particle size, r_0, the film thickness, Δr_0, and with the distribution coefficient, κ; if the exchange is chemically rate controlled, the slope will be independent of particle diameter and flow rate and will depend only on the concentrations of the ions in solution, and the temperature.

Experimental: Materials and Procedures

Preparation of Materials.—The phenol-formaldehyde resinous exchanger, Amberlite IR-1[11] was employed. The preparation of the adsorbent for the experimental measurements and of the solutions employed have been described in the preceding paper.[10] Likewise, a description of the radiochemical methods has been given previously.

However, since the computation of diffusion constants required a knowledge of the particle size r_0 [*cf.* Equation (12)] attention was devoted to its experimental determination. It was not sufficient to estimate these radii by dry screening with standard sieves, since the adsorbent particles swell appreciably on being wetted. Particle size (as size distribution) was determined therefore by wet sieving, after a preliminary grading by dry screening to obtain uniform particles. The procedure was to wash a weighed portion of the exchanger through successively finer mesh standard sieves (U. S. Standard Series) by means of a stream of distilled water. Each size range was collected, dried, and weighed, and its average particle radius computed as the arithmetic average of the sieve openings. The weight-size distribution and the arithmetic mean wet particle size for each preparation are given in Table I.

In the case of the 60/70 mesh adsorbent it is evident that there was a large increase (*ca.* 50%) in size upon wetting. This was not true of the

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[10] G. E. Boyd, J. Schubert and A. W. Adamson, This Journal, 69, 2818 (1947).

[11] Produced by the Resinous Products and Chemical Co., Philadelphia, Pennsylvania.

Table I

Wet and Dry Particle Sizes

Cation in ad-sorbent	Original dry sieve range (U. S. standard)	Av. dry particle radius, cm.	Size distribution on being wetted (as per cent. in each range) 30/40	40/50	50/60	60/70	Av. wet particle radius, cm.
H^+	60/70	0.0115	1.8	90.5	7.0	0.7	0.0178
	30/40	.0210	55.2	37.6	1.9	0.1	.0222
Li^+	60/70	.0115		82.7	17.3	1.0	.0173
Na^+	60/70	.0115		62	35	3	.0163
K^+	60/70	.0115		92	8		.0177
NH_4^+	60/70	.0115		65	35		.0165

30/40 mesh material for which very little difference was found. Possibly the larger particles underwent fragmentation upon being wet to an extent sufficient to balance the degree of swelling.

In other studies it had been noted that the adsorbent expanded less in salt solutions than in water, and that with concentrated electrolytes a shrinkage usually occurred. This effect was looked for, but, as shown in Table II, only a negligible change in the particle size occurred when electrolyte solutions of low ionic strength were used.

Table II

Effect of Ionic Strength on Particle Size

Cation in adsorbent	Dry sieve range	Composition of solution, distilled water +	Wet radius, cm.
H^+	60/70	0.1 *M* HCl	0.0178 to 0.0175
H^+	30/40	0.1 *M* HCl	0.0222 to 0.0223
K^+	60/70	0.2 *M* KCl	0.0177 to 0.0182

Experimental Procedures.—The apparatus used for the obtaining of the rate data was a shallow bed arrangement similar to that used by Domaine, Swain and Hougen.[12] A weighed portion of adsorbent was introduced into a small cell (Fig. 2) of 0.48 sq. cm. cross-section covered at each end by 200 mesh 18-8 Stainless Steel wire screen. The amount of exchanger used was 100 mg. for the studies in 0.1 *M* and 10 mg. in the case of 10^{-8} *M* solutions. A simple computation for the latter case shows that the shallow-bed was a cylinder roughly three particle diameters deep and that there were about twenty particles along a diameter.

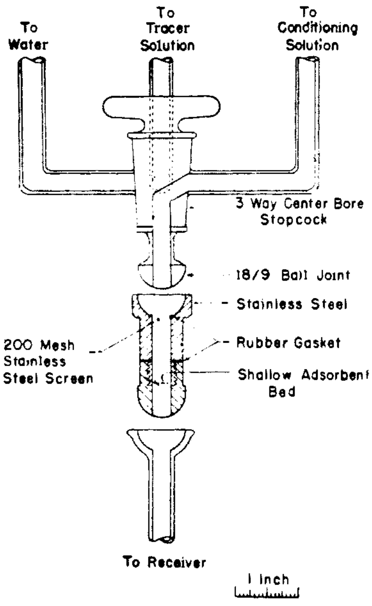

Fig. 2.—Experimental arrangement for the determination of adsorption rates with shallow beds.

The cell was flushed initially with distilled water to remove air bubbles, following which inactive salt solution (*i. e.*, containing no tracer) was passed through the bed for five minutes to "condition" the exchanger. This pretreatment served to fill the pores of the adsorbent with solution of the same composition as was to be studied, so that the subsequent rate of exchange data would not be complicated by changes in solution composition taking place in the pores of the exchanger. Five minutes "contact" time appeared sufficient since little additional effect was observed when periods up to one hour were used.

After pre-treatment, a solution of the same bulk composition but containing radioactive tracer atoms was forced through the shallow adsorbent bed for a pre-determined time, and followed immediately by a water wash. The adsorbent was then flushed from the cell, filtered on a sintered glass funnel, and dried with acetone. Separate tests showed that the washing procedure did not remove any activity from the exchanger. The time of contact of the active solution with the adsorbent was taken as the time elapsed between the opening and closing of the stopcock connecting the reservoir of active solution with the adsorption cell (Fig. 2). A stop watch was used throughout to measure these intervals.

The essential feature of this method is that the solution from which adsorption occurs flows very rapidly through a thin bed of adsorbent. By a suitable arrangement of stopcocks, the ion-exchanger may be immersed in and then swept clean of solution fast enough that "contact" periods of the order of a few seconds may be measured accurately. It should be noted that not only can the rate process be measured from the beginning, even though it may be very swift, but also that the adsorption occurs at virtually constant solution concentration. Further, this adsorption took place from highly dilute solutions of the adsorbate even though the ionic strength of the supporting electrolyte may be as large as 0.1. The experimental realization of these conditions permits the application of the diffusion Equations (6) and (12) and the mass law Equation (20). In all the measurements except those in which the flow rate was varied deliberately, a velocity of about 5 ml./sec. (*i. e.* 10 ml./sq. cm./sec.) was maintained.

The amount of radioactive tracer in the solid was estimated by standard beta and gamma counting procedures, using a bell-type, mica end-window Geiger–Müller counting tube. The manner of the preparation of the samples and other details were given in the first paper of this series. The following radioisotopes were employed: 14.6 h Na^{24}, 19 d Rb^{86} and 1.7 y Cs^{134}.

All of the experiments were performed at room temperature (*ca.* 30°), except for the temperature dependence studies. These latter were performed in an air conditioned room which could be kept at the desired temperature.

Calculation of Results.—The general procedure for the calculation of the experimental results will be illustrated in the section on Experimental Results. However, owing to non-ideal experimental conditions, several small corrections were applied to the primary data: (1) In the case of the experiments with 0.1 *M* solutions, the exchange adsorption was so rapid that there was some drop in the concentration of the tracer in solution even when it passed through the

(12) J. du Domaine, R. L. Swain and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

cell at 5–6 ml./sec. This diminution in activity was estimated from the total amount removed by the exchanger and the volume of solution passed through the cell. For the shortest times of contact this amounted to about a 5% decrease. (2) In the experiments with 10^{-3} *M* solutions, since the same solution was used over and over again, a 5–10% decrease in solution concentration occurred during a series of successive determinations of points for a given rate of uptake curve. This change was allowed for in computing the values for the fractional attainment of equilibrium.

Conformity of Rate Data with Equations.—In the theoretical discussion it was postulated that the rates of exchange adsorption would be governed either by diffusion through a thin liquid film [Equation (6)], by diffusion in and through the adsorbent particle [Equation (12)], or by the velocity of the chemical exchange [Equation (20)], occurring at the adsorbing sites in the interior of the particle. Actually, these equations were found, under certain conditions, to fit the observations rather closely, as is shown by Fig. 3 which gives the velocities of uptake of Na^+ ion from 0.1 and 0.001 *M* potassium chloride solutions using the 14.6 h Na^{24} as tracer.

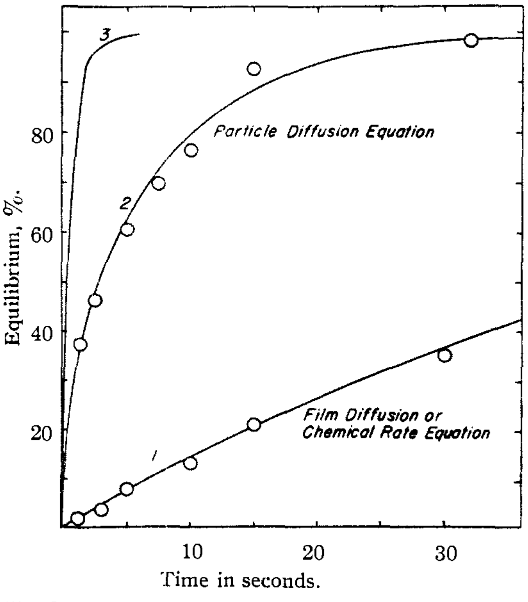

Fig. 3.—Rate of exchange adsorption of sodium ion at 30° from 0.001 *M* (curve 1) and 0.1 *M* (curve 2) aqueous potassium chloride solutions by 60/70 mesh adsorbent (solid lines represent best fitting theoretical curves).

Agreement of the data with a relation represented by Equation (6) or (20) was found in the more dilute solutions, as is illustrated by the correlation between the experimental points and the theoretical curve, Curve 1, computed from Equation (6). In 0.1 *M* potassium chloride, the rate of exchange, if governed either by Equation (6) or (20), should be one hundred times greater than that found with the 0.001 *M* solution, as shown by Curve 3. The observed rate was much smaller than this prediction, however. The agreement between the experimental points and Curve 2, computed from Equation (12) suggests that diffusion in and through the solid is rate determining for the more concentrated solutions.

The complete data for these two experiments, with the values of *R* (or *S*) and *B* calculated for each point, are given in Tables III and IV. In Table III, the values of $B = D\pi^2/r_0^2$ remain nearly constant, whereas values of *R* (or *S*) vary about three-fold. The picture is reversed in Table IV, however, where nearly constant values of *R* are obtained, while values of *B* vary one-hundred fold. It is to be remembered that each point was determined using a separate aliquot of the adsorbent.

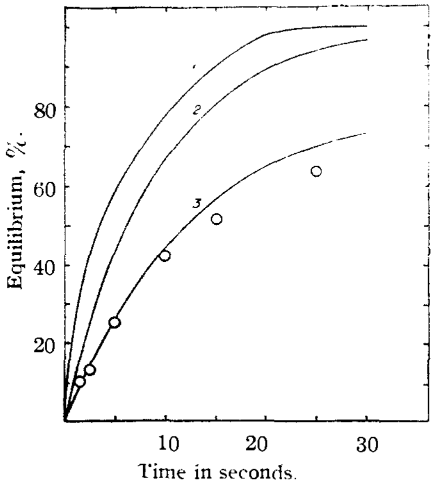

Fig. 4.—Rate of exchange adsorption of sodium ion at 30° from a solution 0.001 *M* in potassium chloride and 0.01 *M* in sodium chloride: curve 1, predicted rate for particle diffusion; curve 2, predicted rate for film diffusion or for chemical exchange.

In an attempt to determine the boundary between the two rate processes more closely, an experiment was conducted at a concentration intermediate between 0.001 and 0.1 *M*. Surprisingly it was found, as shown by Fig. 4, that the velocity of exchange was less than predicted by either Equation (6) or (12). It should be noted, however, that the predicted rates are of comparable magnitude. Now, since these two rate processes act in series, it is possible to understand why the observed rate should be slower than either acting alone. On the basis of a "resistance concept," the time to achieve a given fraction of equilibrium should be the sum of the times required by each process when it occurs independently. Using this hypothesis Curve 3 in Fig. 4 was computed, and it

TABLE III

EXCHANGE ADSORPTION OF SODIUM ION FROM 0.1 M POTASSIUM CHLORIDE SOLUTIONS (EXPERIMENT R-3)

Mesh size of adsorbent, 60/70 (r_0 = 0.0177 cm.); temperature, *ca.* 30°; composition of solution, 8×10^{-5} M NaCl 0.111 M KCl

Time of contact, seconds	Activity in adsorbent γcts./min./0.1 g. air-dried KR	% Equilibrium	Corrected[a] % equilibrium	Bt	B[b] (sec.$^{-1}$)	Calculated[c] % equilibrium	ln (1 − F) (Eq. 6 or 20)	R or S (sec.$^{-1}$)
1.3	555	34.7	37.2	0.159	0.122	35.5	−0.470	0.360
2.5	705	44.1	46.2	.248	.099	48.0	−0.618	.247
5.0	940	58.7	60.4	.50	.100	62.7	−0.93	.185
7.5	1095	68.3	69.7	.72	.096	73.0	−1.17	.156
10.0	1200	75.0	76.4	.96	.096	79.5	−1.44	.144
15	1460	91.2	92.6	2.1	.140	88.5	−2.60	.173
30	1560	97.5	98.3	~3.5	.117	98.0	−4.10	.136
60	1600	~100	~100					

[a] Sample calculation of this correction: for five second point, total counts/minute adsorbed = 940; initial activity of solution = 1066 cts./m./ml., thus, activity lost by solution equal to activity contained in 0.9 cc. Volume through shallow bed (6 cc./sec.) = 30 cc. Fraction activity removed = 100 × 0.9/30 = 3%. Corrected % equilibrium = 1.03 × 58.7 = 60.4. [b] Average B = 0.110 ± 0.010; average $D^i = 3.5 \times 10^{-6}$ sq. cm. sec.$^{-1}$. [c] Calculated using $D^i = 3.5 \times 10^{-6}$ sq. cm. sec.$^{-1}$.

TABLE IV

EXCHANGE ADSORPTION OF SODIUM ION FROM 0.001 M POTASSIUM CHLORIDE SOLUTIONS (EXPERIMENT R-4)

Mesh size of adsorbent, 60/70; temperature, *ca.* 30°; composition of solution, 8×10^{-5} M NaCl + 9.82×10^{-4} M KCl

Time of contact, sec.	Adsorbent activity γcts./min./0.01 g. air-dried KR	Adsorbent activity γcts./min./0.01 g.[a] at equilibrium	% Equilibrium	ln (1 − F) (Eq. 6 or 20)	R or S[b] (sec.$^{-1}$)	Calculated[c] % equilibrium	Bt	B, sec.$^{-1}$
1.2	150	7840	1.91	−0.0193	0.0161	1.82	3.0×10^{-4}	2.5×10^{-4}
2.5	283	7840	3.61	− .0369	.0147	3.7	1.1×10^{-3}	4.4×10^{-4}
5.0	618	7860	7.87	− .0821	.0164	7.4	8.0×10^{-3}	1.6×10^{-3}
10.0	1120	7860	14.3	− .155	.0155	14.1	0.025	2.5×10^{-3}
15	1650	7880	21.0	− .236	.0158	20.5	.052	3.5×10^{-3}
30	2780	7900	35.2	− .434	.0145	36.8	.140	4.7×10^{-3}
60	4770	8570	55.7	− .814	.0135	60.3	.40	6.7×10^{-3}
120	7330	8570	85.2	−1.91	.0159	84.1	1.40	0.012
300	7550	8460	89.3	−2.13	.0071	~99	~4	0.013

[a] Slightly different equilibrium values were used for each point because of the change in solution concentration. [b] Average R (or S) = 0.0153 ± 0.0008 sec.$^{-1}$. [c] Calculated using R (or S) = 0.0153 sec.$^{-1}$.

is seen to be in reasonable agreement with the experimental points.[13]

Verification of the Rate Mechanisms.—Although the data presented thus far suggest the existence of two rate mechanisms depending upon the ionic strength of the solution from which exchange adsorption takes place, mere agreement with Equations (6), (12) or (20) cannot be accepted as proof for the nature of the rate mechanism. In fact, as was mentioned earlier, two of the mechanisms give equations of identical form [*e. g.*, Equations (6) and (20)] so that critical experiments were necessary to determine the process controlling the exchange in dilute solutions.

With solutions of 0.1 M concentration, or greater, only one mechanism, namely, particle diffusion, has seemed to apply. However, here again, to exclude the possibility of other unknown rate processes, an experimental testing of the assumptions underlying Equation (12) seemed most desirable. In the derivation of the relation for diffusion in and through the adsorbent particle, a number of implicit assumptions were made: it was assumed for example that at the center of the spherical adsorbent particle that: $(\partial C^s/\partial r)_{r=0} = 0$. It is believed that the manner of conduct of the experiments satisfied this condition, although in nearly all cases, including those which appeared to obey Equation (6), deviations were observed when a relatively long time of contact was employed. Under these circumstances, however, the equilibrium point was approached rather closely ($1 - F < 0.2$), and the experimental data were subject to large error so that no very definite conclusions can be drawn.

A second approximation in the derivation was the assumption that the diffusion constant, D^i, was independent of the concentration. Accordingly, the effect of a two-fold change in potassium chloride concentration on the rate of the exchange of sodium ion was measured. As shown in Table

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[13] This "resistance" concept has been used by W. L. McCabe (J. H. Perry, "Chemical Engineers Handbook," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 1773) in treating the dissolution of crystals; here the net specific rate of dissolving k is given as: $1/k = 1/k' + L/D$ where k' is the chemical reaction rate constant, L the thickness of the diffuse layer surrounding the crystal, and D the constant for the diffusion of ions through this layer.

V, the rate was found independent of the concentration over this range.

TABLE V

ADSORPTION OF SODIUM ION FROM SOLUTIONS OF DIFFERING POTASSIUM CHLORIDE CONCENTRATION

Temperature, *ca.* 30°; NaCl concentration, 8×10^{-5} *M*; 14.6 h Na^{24} used as indicator; particle mesh size: 60/70 (r_0 = 0.0178 cm.)

Expt.	KCl, *M*	$B \times 10^3$, sec.$^{-1}$	$D_i \times 10^6$ sq. cm. sec.$^{-1}$
R-3	0.111	110	3.5
R-7	0.197	110	3.5

Since the diffusion constant for sodium chloride in its own aqueous solutions changes by less than ten per cent. ($D^i \sim 17 \times 10^{-6}$ sq. cm. sec.$^{-1}$ at zero molality) in the ionic strength range employed,[14] the test afforded by these experiments was not sufficiently accurate to eliminate a possible dependence of D^i on concentration.

A preliminary study of the temperature dependence of the exchange rate in 0.1 *M* solutions was conducted. If the velocity of the process were controlled by the rate of diffusion through the interior of the particle, then the change of the diffusion constant with temperature might be expected to give an activation energy of about 5–10 kcal. Experimental results on the exchange of Na^+ ion in 0.1 *M* potassium chloride solutions at 13.5 and at 30° are given in Table VI.

TABLE VI

TEMPERATURE VARIATION OF THE RATE OF SODIUM ION ADSORPTION

Adsorbent mesh size, 60/70 (r_0 = 0.0178 cm.); NaCl concentration, 8×10^{-5} *M*; 14.6 h Na^{24} used as tracer

Expt.	KCl, *M*	Temperature, °C.	$B \times 10^3$ (sec.$^{-1}$)	$D_i \times 10^6$ sq. cm. sec.$^{-1}$)	$E_{act.}$, kcal. mole^{-1}
R-3	0.111	30	110	3.5	
					8 ± 2
R-12	0.0982	13.5	51	1.6	

The value found for the activation energy is perhaps slightly larger than would be expected if the values of D^i measured are related to the diffusion constant of sodium ion in aqueous solution.

If diffusion in and through the adsorbent particle were rate determining, variations in the velocity of flow of the solution from which adsorption occurs should be without effect so long as the concentration is not changed by the adsorption. Thus, if Equation (12) may be used to describe the data, the constant $B = D^i\pi^2/r_0^2$ should be found independent of flow. The results from four experiments in which the flow was changed, maintaining the time of contact constant, are summarized by Table VII.

TABLE VII

THE EFFECT OF FLOW VELOCITY ON THE RATE OF ADSORPTION OF RUBIDIUM ION FROM POTASSIUM CHLORIDE SOLUTIONS

Adsorbent mesh size, 40/50 (r_0 = 0.0199 cm.); KCl concentration, 0.1 *M*; 19.0 d Rb^{86} used as tracer; total adsorption time, 5.3 seconds

Flow velocity ml./sec.	Fractional attainment of equilibrium, *F*	$B \times 10^3$ (sec.$^{-1}$)	$D_i \times 10^6$ sq. cm. sec.$^{-1}$
2.4	0.377	30	1.2
8.5	.454	45	1.8
10.0	.465	47	1.9
11.9	.476	52	2.1

As may be seen, the flow rate probably plays a role, for as the flow was increased to larger and larger velocities, the quantity *B* steadily increased. This observation suggested that even with the relatively concentrated solutions each particle is made effectively slightly larger by the presence of a surrounding liquid film. The thickness of this film should be an inverse function of the flow velocity; the thinner the film the faster the rate of adsorption. The adsorption rate should therefore increase with flow until turbulence sets in, after which, it should increase much less rapidly. It is an interesting, and as yet unexplained, fact that, in spite of the presence of a flow rate effect, the adsorption rate data for 40/50 mesh particles in 0.1 *M* KCl conformed rather well with Equation (12).

The one explicit prediction contained in the particle diffusion Equation (12) is that the rate of uptake is determined by the quantity $D\pi^2/r_0^2$. Accordingly, the time to achieve a given fraction of equilibrium should vary inversely as r_0^2. This was found to be the case, as is shown by the results given in Table VIII.

TABLE VIII

EFFECT OF PARTICLE SIZE ON THE RATE OF ADSORPTION OF SODIUM ION FROM HYDROCHLORIC ACID SOLUTIONS

Temperature, *ca.* 30°; composition of solution, 0.1 *M* HCl + 8×10^{-5} *M* NaCl

Expt.	Wet radius, r_0, cm.	$B \times 10^3$, sec.$^{-1}$	$D_i \times 10^6$, sq. cm. sec.$^{-1}$
R-1	0.0222	65	3.2
R-2	0.0178	114	3.6

A point to be mentioned in this connection is the uncertainty of the r_0 values themselves. The adsorbent particles were only approximately spherical, hence, the average equivalent spherical radius as determined by wet sieving may well be different from that for diffusion. These irregularities in shape were not sufficient, however, to cause any departures of the rate data from Equation (12) except in the region of $F > 0.8$, where the experimental error is greatly magnified.

It was noted earlier that either Equation (6) or (20) served equally well to describe the rate of exchange adsorption of ions from solutions approximately 0.001 *M* in concentration. Since the basic rate mechanisms from which they were derived are radically different in nature, it was necessary to examine the dependence of the constants *R* or *S* upon the variables in the system to determine which of these (if either) is correct.

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(14) B. W. Clack, *Proc. Phys. Soc.* (*London*), **36**, 313 (1924).

The rate constant R, it will be recalled, was defined by: $R = 3D^l/r_0\Delta r_0\kappa$, where D^l is the film diffusion constant, r_c, the particle radius, Δr_0, the film thickness, and κ, the distribution constant, defined by the ratio of the concentration of the adsorbing ion A^+ in the adsorbent to that in the solution. This distribution coefficient is determined, as may be shown by the mass law, by the ratio of the concentration of the macrocomponent ion, m_{B^+}, in solution and in the adsorbent, n_{BR}, so that, $\kappa = K_c\rho(n_{BR}/m_{B^+})$ where K_c is the mass law equilibrium constant, and ρ the particle density. The quantity R will depend linearly upon the macro-ion concentration, then, for constant D^l, r_0, and Δr_0.

The quantity, S, in the chemical rate Equation (20), it will be remembered, was defined by: $S = k_1m_{A^+}, + k_2m_{B^+}$, where m_{A^+} and m_{B^+} denoted the concentrations of the ions A^+ and B^+ in solution, and k_1 and k_2 were the forward and reverse specific rate constants. It will be seen that S will vary with m_{B^+} in the same manner as does R when $m_{A^+} << m_{B^+}$, since k_1 and k_2 are of the same order of magnitude. Variations in the bulk ion concentration, therefore, will not serve to differentiate the rate mechanisms. A verification of the predicted dependence on the macrocomponent ion concentration, however, would serve to establish the applicability of an equation of the type of (6) or (20). The results from such a study are brought together in Table IX.

TABLE IX

EFFECT OF CONCENTRATION CHANGES ON THE RATE OF ADSORPTION OF SODIUM ION BY POTASSIUM ORGANOLITE

Adsorbent mesh size, 60/70 (r_0 = 0.0178 cm.); temperature, *ca.* 30°

Expt.	KCl, $M \times 10^3$	NaCl, $M \times 10^3$	R or $S \times 10^3$, sec.$^{-1}$	k_1, liters mole^{-1} sec.$^{-1}$
R-4	0.982	0.08	15.3	8.0
R-5	1.97	0.08	28.1	8.0
R-9	0.982	2.0	27.4	7.7

The values of k_1 presented in the fifth column were computed using the equilibrium constant for the exchange: $K_c = k_1/k_2 = 0.62$. A satisfactory confirmation of the predicted dependence of the rate of adsorption of sodium ion on the concentration of potassium ion is indicated by experiments R-4 and R-5. The result from R-9 may be seen to be in fair agreement with the prediction with the mass action rate hypothesis, and is not in disagreement with the film diffusion predictions, although a value for K at a sodium ion concentration of 0.002 M is not available.

Some indication of a chemically controlled rate process might be found in the temperature variation of the speed of adsorption. A provisional estimate of the activation energy can be made from two measurements of the change in the specific rate constants as summarized by Table X.

The low order of magnitude of the activation energy appears to suggest that the exchange rate may not be chemical in its ultimate mechanism, but this is not conclusive.

TABLE X

TEMPERATURE DEPENDENCE OF THE RATE OF ADSORPTION OF SODIUM ION FROM DILUTE KCl SOLUTIONS

Mesh size of adsorbent, 60/70 (r_0 = 0.0178 cm.); composition of solution, 9.82×10^{-4} M KCl + 8×10^{-5} M NaCl

Expt.	Temperature, °C.	k_2, liters mole^{-1} sec.$^{-1}$	E_{act} cal. mole^{-1}
R-4	30	15.3	4.5 ± 2.0
R-11	20.5	11.7	

If the adsorption were controlled by a chemical exchange process the particle size of the adsorbent should be without influence on the rate, so long as the mass was kept constant. Actually, as is reported in Table XI, a clear dependence on particle size was found.

TABLE XI

EFFECT OF PARTICLE SIZE ON THE RATE OF ADSORPTION OF SODIUM ION FROM POTASSIUM CHLORIDE SOLUTIONS

Temperature, *ca.* 30°; composition of solution, 9.82×10^{-4} M KCl + 8×10^{-5} M NaCl

Expt.	Wet radius, r_0, cm.	R or $S \times 10^3$, sec.$^{-1}$	k_2, liter mole^{-1} sec.$^{-1}$	$R \times r_0$, cm. sec.$^{-1}$
R-6	0.0222	8.4	8.2	0.187
R-4	.0177	15.3	15.3	.280
R-10	.0161	17.5	17.3	.282

The demonstration of a particle size effect would seem to exclude the chemical rate picture in a decisive fashion. However, the film hypothesis cannot be regarded as established, thereby, unless the particle size dependence can be predicted from it. From its definition, for constant D^l, Δr_0 and κ, the quantity R will vary inversely with the particle radius, r_0. In the fifth column of Table XI, the required constancy of $R \times r_0$ is seen to be fairly well satisfied over a narrow size range. The smaller value in experiment R-6 can be explained partly on the basis that the value of r_0 may be too low, owing to the wide size distribution in this preparation. This distribution was assymmetric and favored particle sizes appreciably greater than r_0 = 0.0222 cm., as may be seen in the second row of Table I.

The demonstration of the dependence of the adsorption velocity on the rate of flow through the shallow bed supplied additional evidence against a chemically controlled rate process. If the exchange were governed by a mass law mechanism, variations in flow should not cause any change in S. The results summarized by Table XII show this was not the case.

Again, it does not follow from these data that the film hypothesis is validated unless it is possible by it to account for the variations noted. The rate constant, R, from its definition should vary inversely with the film thickness, Δr_0, when D^l, r_0 and κ are maintained constant. The film thickness might be expected to vary inversely

TABLE XII

THE EFFECT OF FLOW RATE ON THE ADSORPTION OF RUBIDIUM ION FROM DILUTE POTASSIUM CHLORIDE SOLUTIONS

Temperature, *ca.* 30°; adsorbent mesh size, 40/50; composition of solution: 0.001 M KCl + 8 × 10^{-5} M RbCl; total adsorption time, 150 seconds

Flow rate, ml./sec.	Fractional attainment of equilibrium, F	R or S × 10^3, sec.$^{-1}$
1.8	0.288	2.3
4.9	.399	3.4
11.3	.525	5.0
14.1	.577	5.7
1.8[a]	.297	2.3
3.8	.410	3.5
8.3	.491	4.5
12.7	.657	7.1

[a] Upflow experiments.

with increasing flow; hence, R should increase directly with the linear velocity.[15] A plot of the data of Table XII in Fig. 5 illustrates the degree of realization of this prediction. The observations made using down-flow through the shallow-bed are regarded, for experimental reasons, as more reliable than those taken with upflow. The latter, however, with the exception of the value at 25.4 cm./sec. are in reasonably good agreement with the indicated best fitting straight line.

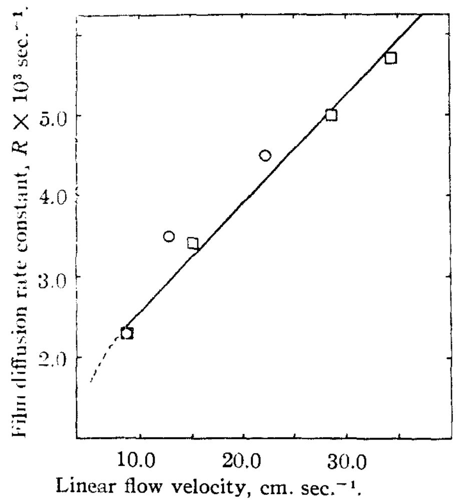

Fig. 5.—Variation of film diffusion rate constant with linear flow velocity: ☐, downflow; ○, upflow.

Discussion

All of the experimental findings obtained in this study have appeared to support the view that the rate of ion-exchange adsorption of the alkali metal cations by Amberlite IR-1 is diffusion controlled. In solutions of 0.1 M, or greater, the velocity of adsorption was governed by diffusion inside the particle, whereas, in solutions of 0.001 M, or lower, the rate of uptake was determined by permeation through a thin, enveloping liquid film. It is the purpose of the discussion which follows to examine certain consequences of each of these two pictures.

The rate of diffusion in and through the solid, if it differs from that for aqueous solutions, might be expected to give information about the internal structure of the adsorbent. Consider the results presented by Table XIII taken from these experiments wherein particle diffusion occurred.

TABLE XIII

RATE OF EXCHANGE ADSORPTION OF MONOVALENT CATIONS FROM 0.1 M SOLUTIONS AT 30°

Adsorbent mesh size: 60/70

Expt.	System	Solution concentrations Macro-component M	Micro-component, M × 10^5	$D_{i_{obs}}$ × 10^6 sq. cm. sec.$^{-1}$
R-2	$Na^+ + HR$	0.100	8.0	3.7
R-17	$Na^+ + LiR$	.0904	8.0	3.0
R-20	$Na^+ + NaR$	.0992	~0.1	2.1
R-25	$Na^+ + NH_4R$	.1005	9.5	2.9
R-3	$Na^+ + KR$	.111	8.0	3.5
R-18	$Rb^+ + KR$	.0982	5.0	2.8
R-13	$Cs^+ + KR$	.0982	5.0	2.0

Several implications of these data, when taken together, seem worthwhile noting: First, it is seen that the magnitude of the internal diffusion constants are from five to ten-fold smaller than the diffusion coefficients for the same ions in aqueous solution. In the latter case, values at 25° for the 0.1 M solutions of the chlorides of lithium,[16] sodium,[14] potassium,[17] rubidium,[17] cesium[17] and hydrogen[16] are: 11.5, 15.5, 18.2, 18.6, 19.1, 25.4 × 10^{-6} sq. cm. sec.$^{-1}$. A difference between the rate of diffusion of ions through an organic-gel adsorbent and through a corresponding volume of solution was expected, and is, of course, a reflection of the internal structure and composition of the former. A second point to be noticed in Table XIII is that sodium ion diffuses through the adsorbent slowest when present initially in 0.1 M sodium chloride solutions. Thus, the rate of uptake is nearly doubled when adsorption occurs either from 0.1 M hydrochloric acid or from 0.1 M potassium chloride. This same interaction of solutes is observed in the diffusion of ions in solution: the diffusion of a microcomponent ion is speeded up if present in a solution of a macro-component ion having a larger diffusion coefficient. A second expectation is that the internal diffusion of an ion through an adsorbent will vary *inversely* as the equilibrium distribution ratio, or, more strongly adsorbed ions will diffuse more slowly through the organolite. Since the relatively more strongly adsorbed alkali cations also show higher diffusion coefficients in their aqueous solutions, the above mentioned factors will tend to counter-balance

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(15) Generally a relation of the type: $\Delta r_0 = (a/v)^n$ where a is a constant, v the linear flow rate and n a constant ranging between $^1/_2$ and 1 would be expected depending on the magnitude of v.

(16) J. R. Vinograd and J. W. McBain, THIS JOURNAL, **63**, 2008 (1941).

(17) "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1926, p. 63 ff.

each other so that, approximately speaking, all the internal diffusion constants will be of the same order of magnitude, as is borne out by the table. The adsorption of sodium ions from solutions in which hydrogen ion is the macrocomponent might be expected to be exceptionally rapid because of the high diffusion rate of the latter. On the other hand, the adsorption of trace amounts of sodium ion is also greatest from acid solutions, thereby reducing the *over-all* internal diffusion rate.

To correlate the observed internal diffusion constants with the physical structure of the adsorbent, a number of remarks need be made. In the first place, an appreciable internal porosity must be attributed to the resinous zeolite. Further, to account for the fact that the adsorbent particles will hold 15 to 30% moisture by weight in equilibrium with the atmosphere, these pores must be assigned a rather small average diameter. The gel structure need not, however, consist of capillaries all of the same diameter.

Consider a model based upon a system of macropores plus micropores wherein the latter penetrate the walls and feed into the former. According to this picture, the major portion of the adsorptive capacity will be resident in the micropores. The macropores will serve merely as conduits for the transport of ions to and from the micropores. A simple relationship between the internal diffusion coefficient, D^i, the diffusion constant for the ion in the mixed aqueous solution, D^l, and the internal equilibrium distribution coefficient, α, can be derived. It is necessary, however, to define this latter quantity in terms of directly measurable quantities. Thus, for the adsorption of a microcomponent ion, A^+, from a solution containing relatively very large amounts of B^+, the internal equilibrium distribution ratio is given by

$$\alpha = \frac{\text{millimoles } A^+ \text{ per cc. of solid}}{\text{millimoles of } A^+ \text{ per cc. of pore solution}}$$

or

$$\alpha = \frac{K_d}{4.18 r_0^3 n} = \frac{K_d}{V} \qquad (22)$$

where

$K_d = \dfrac{\text{millimoles of } A^+ \text{ per g. air-dry adsorbent}}{\text{millimoles of } A^+ \text{ per cc. of solution}}$

= fractional void space due to pores in the wet adsorbent

r_0 = radius of the wet particle

n = number of particles per g. of air-dry adsorbent

V_p = specific volume of wet adsorbent particles

The rate of chemical exchange is considered to be much faster than the diffusion rate; hence, it follows that an equilibrium distribution is always maintained between the concentration of A^+ in any element of the pore solution and the neighboring exchange groups. The diffusion equation can now be derived as follows:

The permeation of A^+ is given by Fick's first equation

$$P = -fD^l \frac{\partial C^l}{\partial x} = -\frac{fD^l}{\alpha}\frac{\partial C^s}{\partial x}$$

where C^l is taken as the concentration of A^+ in the pore solution and C^s as the concentration per cc. of adsorbent.

If diffusion is considered to be taking place in the positive x-direction in a cylinder of unit cross-section, the accumulation of A^+ in an element of volume of length dx, bounded by planes 1 and 2, will be

$$\frac{\partial C^s}{\partial t}\,\mathrm{d}x = P_1 - P_2 = -\frac{fD^l}{\alpha}\frac{\partial C^s}{\partial x} + \frac{fD^l}{\alpha}\frac{\partial}{\partial x}\left(C^s + \frac{\partial C^s}{x}\,\mathrm{d}x\right)$$

or

$$\frac{\partial C^s}{\partial t} = \frac{fD^l}{\alpha}\frac{\partial^2 C^s}{\partial x^2} \qquad (23)$$

On comparing Equations (22) and (7) it is seen that

$$D^i = fD^l/\alpha \qquad (24)$$

The observed and predicted values of D^i are summarized in Table XIV. Owing to the absence of data for D^s, the coefficient for the diffusion of a microcomponent ion in a chloride solution of ionic strength of 0.1 M, values for the diffusion constant of the macrocomponent ion when present in its own pure solutions at that concentration were used.

The observed values of D^i, it is seen, are about three times greater than those predicted. It is necessary to conclude therefore that diffusion through the macropores will not account for the observed rapid rate of uptake of ions by the resinous adsorbent.

An alternative model for which, however, it has not been possible to devise a crucial test, was one where a vein-like structure may occur. Here, a three-dimensional network of interpenetrating microcapillaries filled with aqueous solution and possessing exchanging groups upon their walls was postulated. Adsorbing ions may then be transported either by diffusion through the liquid in the capillary, or along the capillary walls. In the latter case a surface diffusion coefficient, D^σ, will be of importance. The internal diffusion constant, D^i, will be given by

$$D^i = \left(\frac{D^l + \alpha D^\sigma}{1 + \alpha}\right) f \qquad (25a)$$

if the capillaries may be taken as cylinders. For relatively large values of α, Equation (25a) reduces to

$$D^i = fD^l/\alpha + fD^\sigma \qquad (25b)$$

If Equation (25) is applicable, it is possible to conclude from Table XIV that diffusion along capillary walls may be the rate controlling mechanism in those cases where the particle resistance determines the adsorption velocity. Generally, surface diffusion is characterized by a relatively large temperature dependence for an energy

TABLE XIV

COMPARISON OF PREDICTED AND OBSERVED VALUES OF D^i

(60/70 mesh adsorbent)

System	$n \times 10^4$ (particles g.$^{-1}$)	$V_p - V_r$ (cc. g.$^{-1}$)	K_d	α	f	$D^l \times 10^6$	$D^i_{\text{calc.}} \times 10^6$	$D^i_{\text{obs.}} \times 10$
$Na^+ + HR$	7.70	1.80	25.4	14.1	0.8	25.4	1.4	3.7
$Na^+ + LiR$	8.48	1.83	37.5	20.5	.8	11.5	0.5	3.0
$Na^+ + NaR$	8.27	1.49	23.5	15.7	.7	15.5	0.7	2.1
$Na^+ + NH_4R$	8.87	1.67	19.4	11.6	.7	18.0	1.1	2.9
$Na^+ + KR$	6.95	1.60	15.0	9.37	.7	18.2	1.4	3.5
$Rb^+ + KR$	6.95	1.60	27.9	17.4	.7	18.6	0.8	2.8
$Cs^+ + KR$	6.95	1.60	45.2	28.2	.7	19.1	0.5	2.0

roughly equal to the heat of adsorption must be available to create the activated complex. However, since the ΔH for the heterogeneous ion-exchange is roughly 6000–7000 cal. mole^{-1}, the activation energy should be of the same order of magnitude. This was indicated by the data of Table VI.

It is of interest to note that a conclusion consistent with both Equations (24) and (25), is that much smaller internal diffusion rates should be observed with strongly adsorbed di- and trivalent ions. If surface diffusion is rate controlling with these ions then a much larger temperature dependence will be observed also.

Consider next the problem of the correlation of the rates of adsorption from dilute solutions. Here, it will be remembered, permeation in and through a thin bounding film appeared to govern the exchange velocity. The data taken from experiments of this sort are presented by Table XV.

TABLE XV

RATE OF EXCHANGE ADSORPTION OF MONOVALENT CATIONS FROM 0.001 M SOLUTIONS AT 30°

Adsorbent mesh size: 60–70

		Solution concentrations		
Expt.	System	Macro-component, $M \times 10^4$	Micro-component, $M \times 10^6$	$R \times 10^3$ (sec.$^{-1}$)
15	$Na^+ + HR$	10.0	6.6	9.3
16	$Na^+ + LiR$	9.04	6.6	6.7
21	$Na^+ + NaR$	9.92	*ca.* 0.1	9.5
26	$Na^+ + NH_4R$	10.0	9.5	9.8
4	$Na^+ + KR$	9.82	8.0	15.3
19	$Rb^+ + KR$	9.82	5.0	9.6
14	$Cs^+ + KR$	9.82	5.5	6.2

The existence of a trend in the rate constant, R, is apparent, and, with the exception of lithium ion, parallels that for the more concentrated solutions exhibited by Table XIII. Since the temperature, particle size and flow rate were maintained constant in the above series, and since R is given by $3D^l/r_0\Delta r_0\kappa$, it should, in principle, be possible to compute the trend in the rate of uptake by using the correct values for D^l and κ. Conversely, constant values of $D^l/\Delta r_0$ should result if known values of r_0 and κ are employed.[18]

The results from this type of treatment of the data of Table XV are summarized by Table XVI where a reasonable constancy of $D^l/\Delta r_0$ is shown for the first five systems.

TABLE XVI

DEMONSTRATION OF FILM DIFFUSION RATE DEPENDENCE ON THE EQUILIBRIUM DISTRIBUTION COEFFICIENT

System	$K_d \times 10^{-3}$	$\kappa \times 10^{-2}$	$D^l/\Delta r_0 \times 10^2$, cm. sec.$^{-1}$
$Na^+ + HR$	1.81	7.5	4.1
$Na^+ + LiR$	2.56	10.6	4.1
$Na^+ + NaR$	1.78	7.4	3.8
$Na^+ + NH_4R$	1.60	6.6	3.6
$Na^+ + KR$	1.12	4.6	4.2
$Rb^+ + KR$	2.39	9.9	5.6
$Cs^+ + KR$	3.28	13.6	5.0

When the foregoing values of $D^l/\Delta r_0$ are employed together with values of D^l known to range between 10 and 25 $\times 10^{-6}$ sq. cm./sec., a film thickness varying from 2.8 to 6.1 $\times 10^{-4}$ cm. is found. This hypothetical spherically symmetric bounding film must be regarded as an idealization of the actual conditions which exist in the shallow bed. It is almost certain that highly turbulent flow occurs here, for usually linear rates of 10 cm./sec. were employed. Such a film is better thought of, as C. V. King[19] has pointed out in his admirable discussion of the Nernst theory of the rate of heterogeneous reactions, as a region where flow in a direction *normal* to the surface is either very small or is absent. Across such a region, therefore, mass transfer must take place by diffusion. The film will not maintain a spherically symmetric shape under these conditions. Rather, on the upstream side it will be thinner than on the downstream, so that the film will probably be considerably streamlined. Consequently, the computed value of Δr_0 will be the average or kinematic film depth.

One interesting and possibly valuable consequence of the ideas developed in this paper will be mentioned in conclusion. It has been shown that particle diffusion was seemingly rate controlling with solutions 0.1 M or higher in univalent cation, where the rate constant was defined by the ratio, $B = D^i\pi^2/r_0^2$. Now, if all other conditions are kept invariant whereas the particle size, r_0, is reduced steadily, the inverse square dependence

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[18] It is assumed then that Δr_0 is independent of r_0 which, of course, can be valid only approximately.

[19] C. V. King, THIS JOURNAL, **57**, 828 (1935).

of B on this quantity indicates that the rate of uptake must increase rapidly. Under these conditions, at some critical minimum radius, permeation through the film will become the slowest and hence rate controlling process, since here the rate constant varies inversely only as the *first power* of the particle radius ($R = 3D^l/r_0\Delta r_0\kappa$). A further semi-quantitative discussion may be based upon a consideration of the ratio: $B/R = (\pi^2/3)(D^i/D^l)\Delta r_0(\kappa/r_0)$. Values of this ratio less than unity signify that particle diffusion will control the adsorption rate; conversely, film diffusion will be determining. At a given temperature and flow rate, the quantities (D^i/D^l) and Δr_0 will be constant so that the nature of the rate mechanism will be determined by the ratio of the distribution constant, κ, to the particle size, r_0. Large particles and relatively weak adsorption will tend to make particle diffusion the slower process. Strong adsorption favors a film controlled adsorption rate, in general.

Appendix

Table XVII

Solution to Equation (12)

The values in the first two columns were obtained from the approximate equation (Equation 18b). The values of F are given to three significant figures, but the last figure may be in error

$Bt \times 10^4$	F	$Bt \times 10^2$	F	Bt	F
0.10	0.0035	0.2	0.035	0.8	0.720
.20	.0050	1.0	.090	1.0	.775
.40	.0070	2.0	.125	1.2	.818
.60	.0083	3.0	.155	1.5	.865
.80	.0095	4.0	.180	2.0	.915
1.00	.0105	5.0	.205	2.5	.950
1.50	.0130	6.0	.225	3.0	.970
2.00	.0153	8.0	.265	3.5	.98
3.00	.0191	10.0	.300		
4.00	.0228	15.0	.365		
5.00	.0240	20.0	.420		
6.00	.026	25.0	.462		
8.00	.030	30.0	.497		
10.0	.034	40.0	.555		
15.0	.042	50.0	.605		
20.0	.048	60.0	.650		
30.0	.059	70.0	.690		

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Summary

1. Equations capable of describing the rate of the exchange adsorption of the alkali metal cations by the resinous zeolite Amberlite IR-1 have been formulated on the basis of a diffusion mechanism or according to a bimolecular chemical rate process based on the law of mass action.

2. The experimental results have revealed two rate processes governing the adsorption velocity: (a) With solutions 0.1 M in total electrolyte or greater the rate was controlled by diffusion in and through the adsorbent particle and could be described by an equation containing a single constant, B, whose magnitude was determined by the ratio of the internal diffusion constant, D^i, for the particle to the square of the particle radius. (b) With solutions 0.003 M or less the rate was limited by diffusion through a liquid film at the periphery of the particle, and could be described also by an equation containing a single constant, R, whose magnitude was determined by the ratio, $D^l/r_0\Delta r_0\kappa$, where D^l was the diffusion constant for the adsorbing ion in the mixed electrolyte, Δr_0, the film thickness parameter, and κ, the equilibrium distribution ratio.

3. The primary factors determining the nature of the rate controlling mechanism were shown to be distribution constant, κ, and the particle radius, r_0. Large values of κ, and/or small values of r_0 favor a rate determined by film diffusion, if the temperature and flow rate are kept constant.

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