[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

# The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. III. Performance of Deep Adsorbent Beds under Non-equilibrium Conditions[1]

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

## Introduction

During the past decade the importance of a quantitative understanding of the operation of adsorption towers has become increasingly evident. Usually, in the practical use of adsorbents a fluid containing the adsorbing species is swept through a granular bed at a velocity such that equilibrium conditions are far from being realized unless the rate of adsorption is extremely great. Large flow velocities are requisite, for example, when ion-exchange materials are employed in water demineralization, in the recovery and concentration of valuable traces, in purification and separations operations, etc. Presently, the factors which determine the uptake and discharge of ions by deep, cylindrical beds of base exchangers reacting under unsteady state conditions are known only partially. However, the laws of classical or rate independent chromatography would be expected to apply, if a quasi-equilibrium can be made to occur by the employment of fine adsorbent particles, elevated temperatures, and/or excessively low flow velocities. In principle, therefore, the beginning of an understanding of the more general phenomenon of rate dependent chromatography may be claimed to exist.

The first attempt to predict the extraction of ions from aqueous solutions by zeolite beds from theoretical considerations has been made only recently. In 1941, Beaton and Furnas[5] conducted an experimental study of the removal of cupric ions present in low concentration in sulfuric acid solutions by synthetic organic exchangers. In their treatment of the data the performance of the adsorbent bed was likened to a heat exchanger in which a heated (or cooled) gas was passed through a bed of broken solids. The transfer of mass in the first instance was taken as strictly analogous to the transfer to heat in the latter, and the theoretical methods used in dealing with the latter problem[6] were applied. However, no correlation of the parameters derived from the adsorption column studies with the rate and equilibrium constants determined by independent experiments was attempted.

Four subsequent attempts to understand the problem of the action of zeolites under dynamic conditions have been published. An application of the transfer theory approach to the water softening problem has been reported wherein $Ca^{++}$ ion in micro-concentrations was removed,[7] although the detailed experimental findings remain unpublished. An independent study of the same sort in which a synthetic mineral zeolite was used was described the same year.[8] In this case, however, a rate process based upon an irreversible adsorption reaction was postulated. Although the final equation which was derived could be evaluated only by trial and error, charts were provided by means of which a solution could be reached once certain dimensionless quantities were computed.

Two theoretical papers[9] have appeared wherein solutions of the general differential equations have been attempted. Each of these treatments was based upon a consideration of the rate as governed by a bimolecular mechanism formulated in accordance with the mass law equation for the exchange reaction. In the latter paper, complete solutions were given for special limiting cases of this reaction. A concise review of the status of mass transfer theories has been published recently, also.[10]

The factors governing the rate of adsorption of cations from solution by resinous base exchangers and the quantities removed at equilibrium have been discussed in two previous communications.[11] It was shown that the exchange adsorption of univalent cations could be described by the mass law when the thermodynamic activities of the ions in the exchanger were defined assuming the formation of a solid solution. The adsorption affinity was observed to be dependent upon the ionic charge, as was anticipated. In a sequence of constant ionic charge, the extent of the exchange was governed by the hydrated radius. The standard free energy per ion for the exchange of univalent cations was of the same order of magnitude as $kT$. In the rate studies it was found that the velocity of uptake of ions was governed by diffusion, either

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[2] On leave from the Department of Chemistry, University of Chicago. Present address: Clinton Laboratories, Oak Ridge, Tenn.

[3] Present address: Institute for Nuclear Studies, University of Chicago, Chicago, Ill.

[4] Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

[5] R. H. Beaton and C. C. Furnas, *Ind. Eng. Chem.*, **33**, 1501 (1941).

[6] C. C. Furnas, Bureau of Mines Bulletin No. 362 (1932); *ibid.*, **22**, 721 (1930).

[7] R. J. Myers, D. S. Herr and R. W. Atteberry, Verbal report, American Chemical Society Meeting, April, 1943.

[8] J. duDomaine, R. L. Swain and O. A. Hougen, *Ind. Eng. Chem.*, **35**, 546 (1943).

[9] (a) H. C. Thomas, THIS JOURNAL, **66**, 1664 (1944); (b) J. E. Walter, *J. Chem. Phys.*, **13**, 229 (1945).

[10] E. W. Thiele, *Ind. Eng. Chem.*, **38**, 646 (1946).

[11] (a) G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947); (b) G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., *ibid.*, **69**, 2836 (1947).

in and through the adsorbent particle, or else through a thin enveloping liquid film about the particle. For conditions of constant temperature, particle size and flow of liquid past the particle boundary, it was shown that the size of the equilibrium distribution coefficient, $\delta$, determined the rate mechanism: large values of $\delta$ favored a rate determined by film rather than particle diffusion. The rate law for film permeation was shown to be first order, resembling that for a unimolecular reaction.

This communication will report the results from an experimental study in which the exchange adsorption of micro-amounts of these same alkali metal cations by deep beds under dynamic conditions were determined. Again, by use of radioisotope indicator techniques, a quantitative estimation of the ion-exchange could be effected accurately and conveniently. A method for the continuous monitoring of the radiations emitted by the radio-isotope tracer ions contained in the solutions flowing from the adsorbent greatly facilitated these measurements. The transfer theory of Anzelius and Schuman was re-interpreted in terms of the constants occurring in the rate equation believed to be valid. The rate and equilibrium constants determined by the deep bed were compared with those obtained by independent measurement. A good agreement was found in the values obtained for the equilibrium constants in the two types of experiments; the deep bed rate constants, however, were from five to tenfold smaller than those determined by the "shallow-bed method" used previously. This variance was expected from the known variation of the rate constant with linear flow velocity.

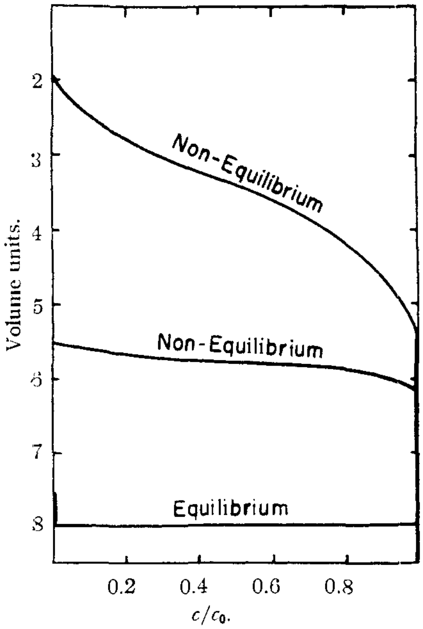

Fig. 1.—Typical concentration histories

The desorption of micro-components from a saturated bed was studied, and the transfer theory equations were found to apply also. It is therefore possible to study the changes in the shape of an adsorbed band as it is moved downward through an adsorption tower by the action of an elutriant solution.

## Theoretical Considerations

**General.**—Consider the dynamic system obtained by passing a solution containing an adsorbate through a deep bed of unsaturated adsorbent; in the regular development of such a case the solution becomes progressively impoverished in solute as it passes through the bed, and the adsorbent becomes correspondingly enriched. This continuous sequence of changes may be approximated by a series of single-stage adsorption steps where the solution and adsorbent are divided into portions and each portion of solution is shaken in turn with each portion of adsorbent. The larger the number of fractions (each correspondingly smaller) the closer, in principle, the conditions within the column may be approached. Adsorption column operation may be equilibrium or non-equilibrium. In terms of the foregoing "single-stage" approximation, equilibrium conditions would correspond to the shaking of each portion of the solution with each aliquot of adsorbent until equilibrium was reached, whereas non-equilibrium operation would correspond to the employment of a limited shaking time. Non-equilibrium operation has been observed with deep adsorbent beds particularly wherever the adsorbent particle size was large, and/or wherever high flow rates were used.

On passing a solution through a bed of adsorbent, the concentration, $C^l$, of adsorbable solute in the first portion of liquid to emerge will be lower than the influent concentration, $C^l_0$, but will gradually rise to this value with progressively larger volumes. The plot of the effluent concentration against the throughput volume, $V$ (or the time $t$, for a constant flow rate), is termed a "concentration history." Since generally there is a period during which an imperceptible amount of adsorbate emerges, followed by a more or less sharp rise in concentration, bed performances may be compared qualitatively using these "break-through curves." Concentration histories typical of equilibrium and of *non*-equilibrium column operation are shown in Fig. 1. The infinitely sharp rise predicted for equilibrium operation may be regarded as the limiting case of the *S*-shaped, non-equilibrium curve. Similar curves may be obtained for the plot of concentration in the adsorbent against the distance from the top of the bed.

**Derivation of the Equations.**—If it is assumed that a lamina of solution passing through an adsorbent bed encounters an infinite number of particles, the actual physical system can be treated by the methods of calculus, and a basic general differential equation may be formulated. Let

$x$ = distance from top of column (cm.)
$t$ = time in seconds
$V$ = volume of solution in ml.
$f$ = fractional void space in the adsorbent bed (*i. e.*, intergranular space)
$v$ = linear velocity of flow of the solution in the bed (cm./sec.)
$W$ = volume flow rate (cc./sq. cm./sec.)($W = vf$)
$C^s$ = amount of adsorbate per cc. of adsorbent bed (moles/cc.)
= $\phi(C^l, t)$
$C^l$ = concentration of adsorbate in solution (moles/cc.)
$\delta$ = equilibrium distribution coefficient
$= \dfrac{\text{moles adsorbate per cc. adsorbent bed}}{\text{moles adsorbate per cc. solution}}$

Further, it will be assumed that the concentration of adsorbate is such that the distribution coefficient, $\delta$, is independent of this concentration (*i. e.*, $C^s = \delta C^l$.)

The conservation of matter relates the following processes which occur in an element of fluid contained in a portion of the adsorbent bed of unit cross section and length, d$x$

$$\left\{\begin{matrix}\text{Adsorbate imparted to}\\ \text{the fluid element by}\\ \text{the solid in time, d}t\end{matrix}\right\} + \left\{\begin{matrix}\text{Adsorbate carried}\\ \text{in by the flowing}\\ \text{liquid}\end{matrix}\right\} = \left\{\begin{matrix}\text{Change in amount}\\ \text{of adsorbate in the}\\ \text{fluid}\end{matrix}\right\}$$

or

$$-(\partial C^s/\partial t)\mathrm{d}x\mathrm{d}t - (\partial C^l/\partial x)vf\mathrm{d}x\mathrm{d}t = (\partial C^l/\partial t)f\mathrm{d}x\mathrm{d}t \quad (1)$$
$$(\partial C^l/\partial t) + v(\partial C^l/\partial x) + (1/f)(\partial C^s/\partial t) = 0$$

Solutions to Equation (1) for systems containing a single adsorbate have been reported for equilibrium conditions, and these form the current basis of the theory of chromatography. The equation may be put into the form in which it occurs in this theory by remembering that $V = vft$

$$f(\partial C^l/\partial V) + (\partial C^l/\partial x) + (\partial C^s/\partial V) = 0 \quad (2)$$

In the case where the adsorption, $C^s$, is a linear function of the equilibrium solution concentration, $C^l$, integration of Equation (2) yields a discontinuous function,[12,13] corresponding physically to the infinitely sharp break-through Curve 1 shown in Fig. 1.

In the most general case of non-equilibrium operation the amount adsorbed per unit bed volume depends both on the concentration and on time, or, $C^s = \phi(C^l,t)$. For the present purposes this function will be considered as factorable, so that, $\phi(C^l,t) = \mathrm{f}(C^l)\ \mathrm{F}(t)$. Further, as indicated above, only the special case when $\mathrm{f}(C^l) = \delta C^l$ will be examined.

To integrate Equation (1) for the non-equilibrium problem, an expression for $(\partial C^s/\partial t)$ must be known. As was demonstrated in the kinetic studies, wherein a single-stage or shallow-bed technique was employed, the adsorption of the alkali metal cations from dilute electrolyte solutions (*i. e.*, $< 0.003\ M$) may be described by a first order differential rate equation. Therefore, for the adsorption of these ions from such solutions passing through *any arbitrarily chosen lamina of a deep adsorbent bed* we shall write

$$(\partial C^s/\partial t) = [3D^l/r_0\Delta r_0\delta](\delta C^l - C^s) = k\delta(C^l - S) \quad (3)$$

where

$\delta C^l$ = equilibrium concentration in the solid corresponding to the actual concentration in the liquid, $C^l$
$C^s$ = actual concentration in the solid ($S = C^s/\delta$)
$D^l$ = diffusion coefficient of the ion in the mixed electrolyte
$r_0$ = adsorbent particle radius
$\Delta r_0$ = thickness of fluid film enveloping particle

Substituting Equation (3) into (1) the equation to be solved may be written as

$$(\partial C^l/\partial t) + v(\partial C^l/\partial x) = -(1/f)k\delta(C^l - S) \quad (4)$$

The boundary conditions which restrict the solutions to Equation (4) are

$C^l = C^l_0$ at $x = 0$ for $t \geq 0$ where $C^l_0$ = influent concentration

$$S = 0 \text{ at } x \geq 0 \text{ for } t = 0$$

Changing the variables in Equation (4) by the substitutions

$$y = (k\delta/f)(x/v) \quad (5a)$$

and

$$z = k(t - x/v) \quad (5b)$$

the problem resolves into the equations

$$(\partial S/\partial z) = (C^l - S) \quad (6a)$$
$$(\partial C^l/\partial y) = (S - C^l) \quad (6b)$$

The solution for this system of equations has been reached by several investigators for the analogous problem of heat transfer,[14,15] and their results are applicable to the case at hand provided the conditions specified are met (*i. e.*, the isotherm is linear, and the rate of transfer of solute between solid and fluid is proportional to the difference between the actual concentration in the fluid and the concentration corresponding to equilibrium with the solid.) Thus, when the initial concentrations in the solid and in the fluid are uniform and when the concentration in any adsorbent particle is uniform at any one time, we have[16]

$$S/C_0 = e^{-y-z}\sum_{n=1}^{\infty} z^n M_n(yz) \quad (7a)$$

$$C/C_0 = e^{-y-z}\sum_{n=0}^{\infty} z^n M_n(yz) \quad (7b)$$

The quantity $M_n(yz)$ is a modified Bessel function which is related to the Bessel function of zero order for an imaginary argument, $J_0$, by the relation

$$M_n(yz) = \mathrm{d}^n M_0(yz)/\mathrm{d}(yz)^n \quad (8a)$$

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(12) (a) J. N. Wilson, THIS JOURNAL, **62**, 1583 (1940); (b) D. DeVault, *ibid.*, **65**, 532 (1943).

(13) (a) J. Weiss, *J. Chem. Soc.*, 297 (1943); (b) J. E. Walter, *J. Chem. Phys.*, **13**, 229 (1945)

(14) T. E. W. Schumann, *J. Frank. Inst.*, **208**, 407 (1929).

(15) A. Anzelius, *Z. ang. Math. Mech.*, **6**, 291 (1926).

(16) A confirmation of the solution to Equation (6) has been obtained recently by Mr. R. Scalettar in an application of Laplace transformation theory methods to this problem.

where

$$M_0(yz) = J_0(2i\sqrt{yz}) = [1 + yz + (yz)^2/(2!)^2 + (yz)^3/(3!)^2 + \ldots] \quad (8b)$$

Numerical values of $S/C_0$ and $C/C_0$ have been calculated from Equation (7) by Schumann[14] for values of $y$ and $z$ ranging from zero to ten, and by Furnas[6] for selected values in the interval from 9 to 500. The curves resulting when the values for $C/C_0$ are plotted are illustrated by Fig. 2. Although similar curves for $S/C_0$ exist, they are of less interest than those shown, because the influent to and the effluent from the exchanger bed can be analyzed more easily than can the exchanger itself.

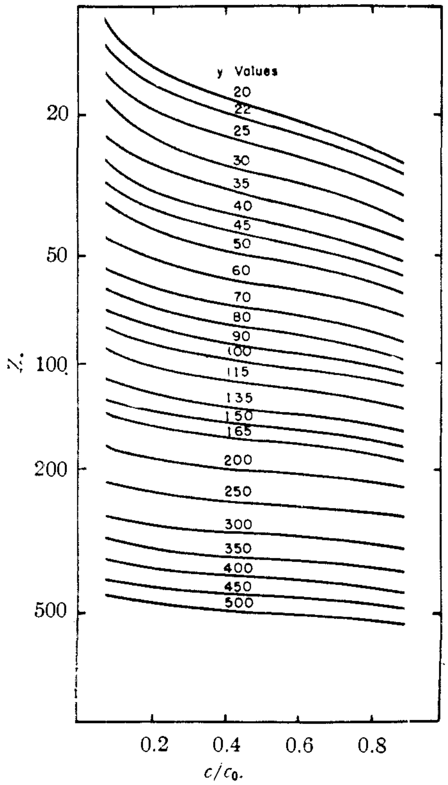

Fig. 2.—Representative transfer theory curves taken from C. C. Furnas, ref. 6.

Evidently the behavior of an adsorption tower may be described by the dimensionless quantities $S/C_0$, $C/C_0$, $y$ and $z$. Charts of the type of Fig. 2 are of universal application to those transfer problems which may be formulated as above no matter what the actual constants involved may be. In its formal aspect, therefore, the problem of the prediction of the behavior of adsorbent beds under dynamic conditions has relevance to other fields. It is known that the same type of problem is met with in the drying of solids, in the dehumidification of air, in the action of catalyst beds, and in gas mask performance to cite only a very few examples.

It is from the family of curves of Fig. 2 that the values of $y$ and $z$ are actually determined from experimental data. The procedure developed by Furnas will be described: (1) Plot the experimental concentration history as $C/C_0$ *vs.* log $t$. From Equation (5b), which may be written as

$$\log z = \log k + \log (t - x/v) \quad (9)$$

it is seen that log $t$ differs from log $z$ only by a constant.[17] If a plot of experimental values of $C/C_0$ against log $t$ is made, the resulting curve will differ from the theoretical plot of $C/C_0$ against log $z$ by a constant displacement. (2) Fit the experimental curve to one of the theoretical ones by sliding one graph over the other, keeping the base lines superimposed, and then read the numerical value of $y$. Values of $t$ and $z$ are obtained at the same time by reading them from the experimental and best fitting theoretical curves for a selected $C/C_0$ value. The particular relative concentration, $C/C_0$, chosen is immaterial since the ratio $z/(t - x/v)$ will remain unchanged. (3) Compute values for $k$ and $\delta$ from the equations

$$k = z/(t - x/v) \quad (10a)$$

$$\delta = yf/k(x/v) = yV/kx \quad (10b)$$

The results obtained from the treatment of the adsorption data observed with deep beds along the foregoing lines are limited, of course, by the correctness and the completeness of the assumptions upon which the mathematical treatment is based, and by the inaccuracies due to the subjective judgment as to the best congruence between the experimental and theoretical curves. With reasonable care and a certain amount of experience this latter cause may be reduced to less than a ±10% variation.[18] The only reliable way to determine the adequacy of the assumptions appears to be by experimentation. Several criteria may be employed to test the validity of the theory when applied to the description of rate dependent ion-exchange adsorption phenomena: (a) each experimentally determined "break-through curve" should have the shape of but one of the curves computed from theory; (b) as the adsorbent bed depth varies the same values of $k$ and $\delta$ should be obtained; (c) the numerical values of $k$ and $\delta$ observed with adsorption towers should be in agreement with experimental error with independent experimental determinations of these quantities; (d) the value of $k$ should depend upon the flow rate, particle size and distribution coefficient in a manner predictable from Equation (3).

Other implicit approximations in the theory, some of which are not readily amenable to an ex-

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[17] The term $x/v$ in the expression $(t - x/v)$ is a correction, almost always negligibly small, for the time required for the first portion of the solution to traverse the bed.

[18] An alternative to the curve-matching procedure of Furnas has been suggested by Mr. G. F. Quinn who has constructed a cross-plot of the theoretical curves by first plotting $y$ against $z/y$ for selected values of $C/C_0$ using Fig. 2, and then plotting $y$ against $X = \theta/\theta_r = (z/y)/(z/y)_r$ where the reference value $(z/y)_r$ is taken for $C/C_0 = 0.1$. The latter graph is employed to find $k$ and the former to obtain $\delta$ after a best value of the rate constant is determined.

perimental testing, may be enumerated: (1) It was assumed that the volume of solution and solid do not change with concentration. This assumption should be obeyed closely in the ion-exchange system. (2) The assumption that the distribution coefficient, $\delta$, is independent of the adsorbate concentration will be true strictly only for infinitely dilute solutions. On the other hand, it may be taken as an approximation valid within experimental error for dilute solutions, or, for solutions in which the adsorbing ion is present in low thermodynamic activity. (3) In the derivation of the equations above it was assumed that the fluid advanced uniformly through all the interstices in the bed (*i. e.*, rate of flow does not vary across any given plane normal to the long axis of the bed). It is likely that this assumption will not be valid for flow through beds made up of nonspherical particles, since in this case the interstices will be quite irregular in shape. (4) Any effects arising from the nature of the surface of the adsorbent particles are ignored (*i. e.*, surface roughness, etc.). (5) The effect of longitudinal or axial diffusion has been assumed to be negligible. (6) The performance of the cylindrical bed was assumed to be independent of its diameter. Owing to the finite particle size, however, there must be some minimum value of the diameter below which this assumption will not be good. The inaccuracy thus resulting is related to the violation of the assumption made by the application of the methods of differential calculus to a physical system containing a finite number of adsorbent particles. (7) Diffusion in and through the adsorbent particles is assumed to be sufficiently rapid that any particle may be considered as being at a uniform concentration at any instant. (8) The transfer of adsorbing ion to the exchanger by streaming at the particle boundary is assumed to be negligible compared to the uptake by diffusion through the thin fluid film.

## Experimental—Materials and Procedures

In order to test the theory developed above it is necessary to obtain the ratio of the concentration of the adsorbing ion in the effluent from the bed to that in the influent as a function of time. If a large reservoir of solution at constant concentration be employed for the influent, then, all that is necessary experimentally is to obtain the concentration history in the effluent.

**Preparation of Adsorbent**.—The adsorbent employed was the phenol-formaldehyde synthetic cation exchanger, Amberlite IR-1. This material, received as the sodium form in a wet condition in a 40/60 mesh particle size range, was placed in large glass columns and successively converted to the hydrogen form with 6 $N$ hydrochloric acid and then back to the sodium form with 6% sodium chloride in order to be certain that the exchanger was free from all soluble reaction products. After removal from the column and air-drying, aliquots were pulverized in a ball-mill and sieved until sufficient quantities of 70/80 mesh particles were produced. Quantities of this latter product were placed in glass tubes of 10 mm. diameter (0.79 sq. cm.) until various adsorbent beds of approximately the desired depth were formed. In each case, the lower end of the glass cylinder was fitted with a one-hole rubber stopper carrying a glass outlet tube. The bed was supported above this stopper by a small plug of glass wool covered with a disc of heavy, coarse-weave glass filter cloth. The flow rate was regulated by means of a screw clamp placed upon a section of Transflex tubing in the effluent line. Employment of a no. 0000 Rotameter in series permitted a convenient control and accurate measurement of this flow. The top of the column was fitted also with a one-hole rubber stopper containing a glass inlet tube which was normally connected by means of tubing to the large glass storage bottle used as the reservoir for the influent solutions. The influents, maintained at an approximately constant hydrostatic head of six feet, consisted of either: (a) 0.001 $M$ $HClO_4$ containing 14.8 h $Na^{24}$ or 19.5 d $Rb^{86}$ tracer; or, (b) 0.001 $M$ CsCl or 0.1 $M$ CsCl containing 14.8 h $Na^{24}$ tracer. These influents were allowed to percolate downflow through the adsorbent bed.

**Preparation and Analysis of Solutions**.—Considerable care must be exercised in the purification of all the reagents employed, owing to the possibility of very great effects caused by minute amounts of cationic impurities. For example, the laboratory distilled water could not be used because of the presence of several p. p. m. of $Cu^{++}$ and $Fe^{+++}$ ions; consequently, it was further demineralized using large columns of the resinous exchangers, Amberlite IR-1 and IR-4 in the recommended manner. The perchloric acid was of A. R. grade (J. T. Baker & Co.) and was diluted to prepare solutions of the desired concentration. The cesium chloride, purchased from Maywood Chemical Co., was purified by successive recrystallization. The sodium and rubidium tracers were prepared by a sixty-hour irradiation of A. R. grade sodium carbonate with slow neutrons in the former case, and by a sixty to ninety day irradiation of rubidium carbonate in the latter. The rubidium salts used were purified by successive re-precipitation and recrystallization. The radiochemical purity of the radioactivities used was established by means of half-life and beta-ray energy determinations.

The chemical analyses for perchloric acid and for cesium were made using standardized procedures. In the experiments where the concentration history was measured by assaying the radioactivity contained in aliquots of the effluent, a standardized[19] mounting and counting technique was employed.

**Experimental Procedure**.—The adsorbent bed, containing a pre-determined amount of either the hydrogen or cesium form of the exchanger, was first back-washed with demineralized water to remove the "fines" (or color) and to ensure the removal of any air so as to prevent channeling. Next, the adsorbent was "pre-conditioned" by allowing solution of the same composition as was to be employed in the experiment, except containing no radioactivity, to pass through the bed until the effluent was of the same composition as the influent. The desired tracer was added then to the influent reservoir, and the thin-walled Transflex tube carrying the effluent was coiled about a glass-walled G. M. tube (Eck and Krebs) mounted inside a heavy lead shield so that the growth of the radioactivity in the effluent could be detected and recorded. A schematic diagram of the experimental arrangement and of the components of the measuring and recording units is given by Fig. 3. The continuous record of the break-through of tracer activity was obtained by use of a pen and ink electronic recorder (Esterline-Angus). Owing to the very great sensitivity with which small quantities of certain radio-isotopes may be detected, it was possible to estimate relative concentrations down to $5 \times 10^{-4}\%$ and smaller. With the $Na^{24}$ and $Rb^{86}$ the minimum value recorded for $C/C_0$ was usually about 0.01. In the preparation of the concentration history plots for comparison with the theoretical curves, the recorded data were corrected for counter background, counting losses, changes in counter sensitivity and for radioactive decay. A small

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[19] G. E. Boyd and D. N. Hume, Chapter VI, Manhattan Technical Series (to be published).

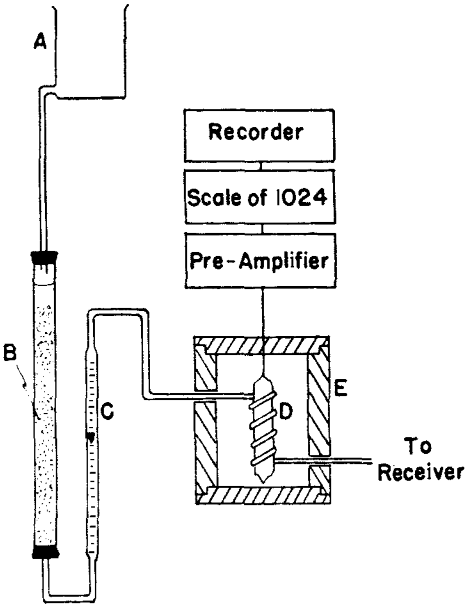

Fig. 3.—Experimental arrangement for adsorption column studies: A, solution reservoir; B, adsorbent bed; C, flowmeter; D, Geiger–Mueller counting tube; E, lead shield.

correction for the time required for the displacement of the hold-up in the adsorbent bed after the start of the passage of active solution was applied. The value of the depth of the bed, $x$, employed below was measured while the solution containing the radio-isotope was flowing. At the conclusion of the experiment, the adsorbent was removed from the tube, washed, dried, and its mass determined by heating for two hundred hours at 110°. This datum together with the computed bed volume made possible the calculation of the factor required to convert the value of the distribution coefficient found in an equilibrium experiment so that it might be compared with the value of $\delta$ obtained from the column.

A repetition of a particular experiment usually gave duplicate results with good agreement; the primary cause of variation seemed to result from changes in bed density presumably caused by slightly different conditions during the backwashing and settling of the particles under gravity. Although usually smooth concentration histories were observed which corresponded to a single transfer theory curve over the entire range of relative concentration, occasionally irregularities suggestive of the onset of channeling were noted. Such effects were especially evident when $C/C_0$ exceeded 0.85. Another rather more common peculiarity was the finding that the relative concentration exceeded unity (*i. e.*, effluent greater than influent concentration). Instead of $C/C_0$ becoming constant and equal to one, this ratio rapidly increased to 1.10 after which it gradually decreased toward unity as more solution was passed through the column. Very small amounts of a chemically similar impurity could produce this phenomenon.

## Experimental Results

Typical data obtained in a series of adsorption experiments are presented by Figs. 4 and 5 where the effluent concentrations are given in terms of $C/C_0$ with $C_0$ representing the influent concentration maintained constant.

**Influence of Adsorbent Bed Dimensions.**—Figure 4 illustrates the increasing time required for penetration of $Na^+$ ion as the bed depth was increased. Qualitative agreement with the prediction from theory may be seen in the sense that the breakthrough curve becomes progressively steeper as the depth, $x$, increases. If the rate constant, $k$, were truly independent of bed thickness, the observed $y$ value should increase linearly with $x$, all other variables being held unchanged. The data of Table I for this series of experiments reveals this was not the case, for the rate constant decreased approximately five-fold when the depth increased nine-fold. The distribution coefficient, $\delta$, likewise should be constant within experimental error, although clearly a trend seems to be present.

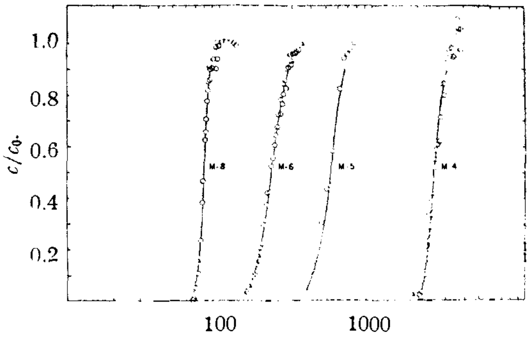

Fig. 4.—Effluent concentration of radio-sodium activity as a function of time and length of adsorbent bed.

Table I

Variation of Transfer Theory Constants with Bed Depth for the Adsorption of Micro-amounts of Sodium Ion from 0.001 $M$ Cesium Chloride Solutions

Flow rate, 0.10–0.12 cc./sq. cm./sec.; adsorbent particle size, 70–80 mesh; temperature, *ca.* 25°.

| Expt. | Bed depth, cm. | $y$ | $k \times 10^3$, sec.$^{-1}$ | $\delta$ $\left(\frac{\text{moles/cc. bed}}{\text{moles/cc. solution}}\right)$ |
|---|---|---|---|---|
| M-6 | 5.0 | 50 | 4.2 | 290 |
| M-5 | 9.3 | 50 | 1.6 | 330 |
| M-4 | 46.9 | 115 | 0.74 | 360 |

The variation of the rate constant with depth is believed to be real for it has been observed to occur previously with other systems studied in these laboratories in greater detail. Beaton and Furnas[1] likewise observed this same effect.

The influence of bed diameter was not investigated, although other experiments have revealed that the operating performance, as measured by the dimensionless parameters $y$ and $z$, is not changed except for relatively small diameters. As an empirical rule, it has been found that the rate constant will be independent of this variable so long as the particle size is sufficiently small that twenty or more granules are needed to extend from one wall to the opposite along any diameter.

**Influence of Flow Rate.**—According to Equation (3), $k$ would be expected to increase approximately directly with the linear flow rate, $v$ (assuming that $\Delta r_0$ varies inversely as $v$; [illegible] is a consequence, $y$ should be found virtually independent of flow. The data of Table II and Fig. 5 show how well this prediction holds over the narrow range examined.

TABLE II

VARIATION OF TRANSFER THEORY CONSTANTS WTH FLOW RATE FOR THE ADSORPTION OF MICRO-AMOUNTS OF SODIUM ION FROM 0.001 $M$ CESIUM CHLORIDE SOLUTIONS

Adsorbent particle size, 70/80 mesh; temperature, *ca.* 25°

| Expt. | Bed depth, cm. | Flow rate, cc./sq. cm./sec. | $y$ | $k \times 10^3$, sec.$^{-1}$ | $\delta$ $\left(\frac{\text{moles/cc. bed}}{\text{moles/cc. soln.}}\right)$ |
|---|---|---|---|---|---|
| M-5 | 9.3 | 0.099 | 50 | 1.6 | 330 |
| M-7 | 10.3 | .25 | 60 | 4.5 | 270 |

The rate constant it is seen increased nearly proportionately with the flow whereas the distribution coefficient either remained constant or decreased slightly. It is believed that the value of $y$ was constant within the experimental errors involved. The dependence of $k$ on the flow velocity is in agreement with previous findings with other systems and with the observations of Myers, Herr and Atteberry.[7] On the other hand, Beaton and Furnas[5] and duDomaine, Swain and Hougen[8] have reported the reaction velocity to be independent of the flow rate. If diffusion of adsorbate in and through the adsorbent particles were rate controlling, flow would not be expected to be an important factor.

**Influence of the Magnitude of the Distribution Coefficient.**—According to Equation (3), the magnitude of the rate constant should vary inversely as the distribution coefficient, $\delta$. Maintaining all other variables constant, but increasing the cesium ion concentration from 0.001 to 0.1 $M$ should decrease $\delta$ one-hundred fold and therefore increase $k$ by a corresponding factor. The data presented by Table III show this to be true roughly.

TABLE III

VARIATION OF TRANSFER THEORY CONSTANTS WITH MACRO-COMPONENT ION CONCENTRATION FOR THE ADSORPTION OF MICRO-AMOUNTS OF SODIUM ION FROM CESIUM CHLORIDE SOLUTIONS

Adsorbent particle size, 70/80 mesh; adsorbent bed depth, 47 cm.; temperature, *ca.* 25°

| Expt | Flow rate, cc./sq. cm./sec. | Cesium chloride concn., $M$ | $y$ | $k \times 10^3$, sec.$^{-1}$ | $\delta$ $\left(\frac{\text{moles/cc. bed}}{\text{moles/cc. soln.}}\right)$ |
|---|---|---|---|---|---|
| M-4 | 0.11 | 0.001 | 115 | 0.74 | 360 |
| M-8 | .048 | .1 | 400 | 85.5 | 4.7 |

In predicting the behavior of adsorption columns from changes in $\delta$ it is to be remembered that the results will be valid only for linear isotherms. However, within this range the performance will not change with changing microcomponent concentration, and this has been verified in other experiments where the concentration varied by $10^4$. Since the dimensionless parameter $y$ is proportional to the product $k\delta$, it is to be expected that the action of the bed will be independent of $\delta$, and hence of the concentration of the macro-component ion. The magnitude of $\delta$ is dependent, of course, upon the exchange capacity of the adsorbent and upon the nature and concentrations of the components in the system.

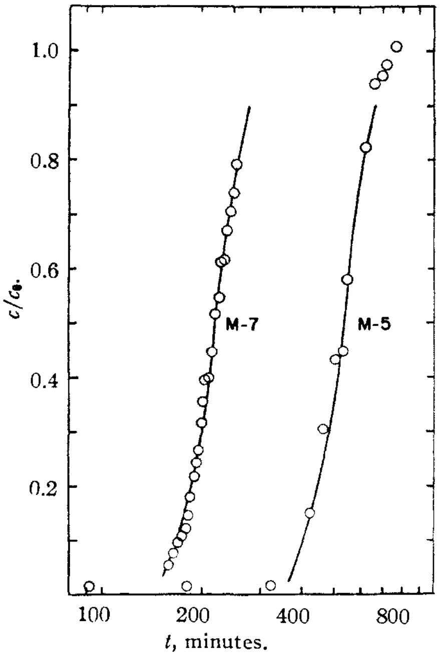

Fig. 5.—Effluent concentrations of radio-sodium activity as a function of time and flow rate.

**Influence of Adsorbent Particle Size.**—The effect of adsorbent particle size was not determined in this study although it is known to exist from other studies and from the work of Hougen, *et al.*[8] From Equation (3) it might be expected that $y$ would increase linearly with decreasing particle size. Changing the particle shape will act to change the rate constant by changing the magnitude of the void space, $f$, also.

**Influence of Temperature.**—Although temperature must be recognized as an important factor in determining the performance of deep adsorbent beds, it was not examined in this work. The value of $y$ would be expected to increase with temperature, since $y = (3D^l/r_0\Delta r_0 f)(x/v)$, and since the diffusion coefficient, $D^l$, will increase with temperature with an activation energy of approximately 5 kcal. mole$^{-1}$.

**Intercomparison of Values for Rate Constants and Distribution Coefficients.**—It is important to compare the values of the characteristic constants obtained in column experiments with those found by independent measurements. This is afforded by Table IV where the independently estimated rate constants listed were measured by the shallow bed method.[11b] Values for the distribution coefficients were determined in equilibrium experiments in which a small amount of the adsorbent was shaken for twelve to twenty-four hours with an aliquot of the solution used in the particular column experiment with which comparison was being made.

Table IV

Comparison of Rate and Equilibrium Constants Found by the Application of the Transfer Theory to Deep Adsorbent Bed Data and by Independent Measurement

| System | Transfer theory constants $k \times 10^3$ | Transfer theory constants $\delta$ | Independently determined constants $k \times 10^3$ | Independently determined constants $\delta$ |
|---|---|---|---|---|
| $Na^+$ + HR | 1.4 | 1000 | 13.5 | 900 |
| $Rb^+$ + HR | 1.5 | 2685 | 7.0 | 2950 |
| $Na^+$ + CsR | 0.7-4.5 | 270-340 | 30.4 | 310 |

An examination of Table IV reveals the values of $\delta$ to be the same within experimental error whether determined by the adsorption column or by an equilibrium experiment. Values of the rate constant, $k$, from the deep bed, however, were five to ten-fold smaller than those observed in the "shallow-bed" measurements. This discrepancy was to be expected, and, qualitatively, is in agreement with previous observations of the dependence of $k$ upon the flow rate (see Table II also). The flow (5–10 cm./sec.) in the thin bed was roughly 50 to 100 times greater than with the deep bed (0.05 to 0.35 cm./sec.). Since the value for $k$ is finite even with an unagitated system, the magnitude of this quantity determined by the deep bed would not be expected to be vanishingly small.

## Measurements on the Desorption of Microcomponents from Deep Adsorbent Beds

**Presentation of Data.**—A series of desorption experiments were conducted using adsorbent beds previously saturated with 19 d $Rb^{86}$ activity in order to determine whether the transfer theory approach could be applied in this instance. In these experiments, a sufficient quantity of the previously described stock 70/80 mesh adsorbent (HR) to make up five deep beds was placed in a large container and vigorously agitated with an aqueous 0.001 *M* $HClO_4$ solution containing added $Rb^{86}$ tracer activity. After the equilibrium adsorption had been established, the resinous exchanger was rinsed to remove any occluded activity and then packed into ten mm. diameter glass tubes to give beds of varying depths as before. The experimental procedure consisted in passing dilute perchloric acid solutions at varying flow rates through these beds until most of the adsorbed radioactivity had been removed. Consecutive aliquots of the effluent were collected from the beginning of the flow, and 0.5-ml. samples from these were analyzed for $Rb^{86}$ by evaporation, mounting and counting following a standardized procedure. At the completion of the experiment the weight of adsorbent contained by the column was determined in a manner identical with that described in the adsorption studies.

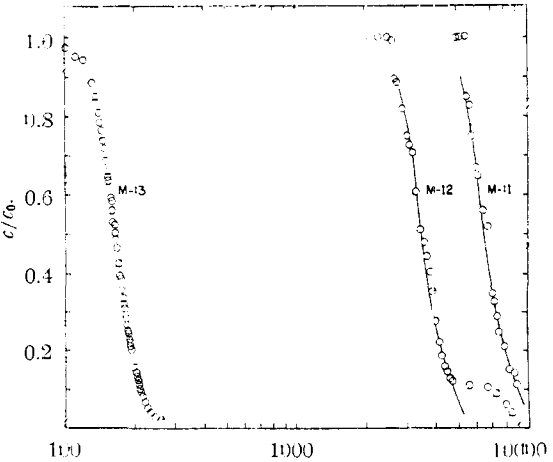

Fig. 6.—Effluent concentrations of desorbed radio-rubidium activity as a function of time and flow rate.

**Influence of Flow Rate of Elutriant.**—The observed variation of the effluent radioactivity as a function of the time and of the flow rate of the 0.001 *M* $HClO_4$ elutriant is given by Fig. 6. An increase in flow, it is seen, leads to a slightly more diffuse desorption together with an increased rate constant, $k$, as indicated in Table V. However, the increase in the rate constant was not sufficient to maintain $y$ unchanged as was the case in adsorption.

Table V

Variation of Transfer Theory Constants with Elutriant Flow Rate for the Desorption of Microamounts of Rubidium Ion by 0.001 *M* $HClO_4$

Adsorbent mesh size, 70/80; temperature, *ca.* 25°

| Expt. | Bed depth, cm. | Flow rate, ml./sq. cm./sec. | $y$ | $k \times 10^3$, sec.$^{-1}$ | $\delta$ $\left(\frac{\text{moles/cc. bed}}{\text{moles/cc. solution}}\right)$ |
|---|---|---|---|---|---|
| M-11 | 9.5 | 0.13 | 60 | 0.15 | 5600 |
| M-12 | 10.4 | .26 | 45 | .20 | 5500 |

**Influence of Elutriant Concentration.**—The concentration of the dilute perchloric acid elutriant was varied from 0.001 to 0.1 *M* in two experiments (see Fig. 6, M-13). Since bed depth and flow rate were varied also, it was not possible to estimate the role of the concentration quantitatively. Qualitatively, however, an increase in $k$, as in the adsorption case, may be inferred (see Table VI).

**The Application of the Transfer Theory to Desorption Data.**—Before undertaking to make further remarks about the desorption results summarized in Table VI, a brief discussion of the manner in which the transfer theory may be applied to desorption data seems in order. In the application of the theory to *adsorption* data, the transfer curves were plotted with $C/C_0$ as ordinate and log $z$ as abscissa. The quantity $z$ was a dimensionless parameter and $C$ and $C_0$ were the effluent and influent concentrations of adsorbate, respectively, in the solution which percolated through the adsorbent bed. However, to consider the more general case, which includes desorption as well as adsorption processes, it is desirable to formulate the concentration coördinate, $f(C)$, differently. Specifically, $f(C)$ should be taken as a function of $z$ such that its magnitude varies from zero at zero time to unity at infinite time. Furthermore, at $t = 0$, $f(C)$ must be taken as proportional to the difference $C - C_0$ or $C - S_0$. Physically, this last condition implies that the concentration history of the effluent from the column is determined by the difference between the concentration in the leading edge of liquid emerging from the column and the input. The concentration in the leading edge is zero for the *adsorption* case, whereas it is equal to $S_0$ for *desorption*. The quantity, $S_0$, is defined by the relation: $S_0 = C_0^s/\delta$, where $C_0^s$ is the initial amount adsorbed (moles/cc. adsorbent bed). It is evident from this definition that $S_0$ actually possesses the units of solution concentration, and that numerically it is equal to the concentration in the solution which would be in equilibrium with the initial concentration, $C_0^s$, in the adsorbent. It follows from these considerations that

$$f(C) = (C - S_0)/(C_0 - S_0) = F(z)$$

In the adsorption case, since initially there was no adsorbate in the adsorbent, $S_0 = 0$ and $f(C) = C/C_0$. For desorption, however, since the initial concentration of adsorbate in solution, $C_0$, was zero, $f(C) = 1 - C/S_0$. In the treatment of the foregoing experimental desorption data then, the quantity, $1 - C/S_0$, was plotted with log $t$ and the resulting curve matched with the best theoretical curve in a manner analogous to the procedure used in the treatment of the adsorption data. Numerical values of $1 - C/S_0$ may be found readily since $S_0$ is equal to the constant activity of the first portions of the effluent. Table VI summarizes the findings from the desorption studies.

TABLE VI

DESORPTION OF $Rb^{86}$ ACTIVITY FROM DEEP ADSORBENT BEDS

| Expt. | Macro-component concn., ($M$ $HClO_4$) | Bed depth, cm. | Flow rate, cc./sq. cm./sec. | $y$ | $k \times 10^3$, sec.$^{-1}$ | $\delta \left(\frac{\text{moles/cc. bed}}{\text{moles/cc. soln.}}\right)$ | Comments |
|---|---|---|---|---|---|---|---|
| M-9 | 0.001 | 6.2 | 0.13 | .. | .. | .. | Not a transfer theory curve |
| M-10 | .001 | 9.6 | .13 | 60 | 0.13 | 5700 | |
| M-11 | .001 | 9.5 | .13 | 60 | .15 | 5600 | |
| M-12 | .001 | 10.4 | .26 | 45 | .20 | 5500 | Poor curve |
| M-13 | .1 | 16.7 | .060 | 50 | 5.5 | 32.6 | |

In four of the five experiments, concentration histories resembling transfer theory curves were obtained. Experiments M-10 and M-11 were performed in as nearly the same way as was possible, and serve to indicate the degree of reproducibility in separate experiments. In experiment M-9, the "retention time" may have been too short to permit a transfer curve to be established.

## Discussion

Both the adsorption and desorption results now presented show that, even in moderately concentrated solutions of the bulk ion, concentration histories of the shape of those predicted by theory were observed. However, the unexpected variation of the rate constant, $k$, with bed depth suggests there are factors involved not considered by the theory. In view of the probably constant values for $\delta$, a completely satisfactory explanation of the immediate cause is lacking. Channeling in the bed should give rise to sizable variations in the adsorptive capacity, which was not the case. The possibility of an effect caused by a back-exchange reaction can be excluded, for only microamounts of $Na^+$ ion were adsorbed in these experiments. Changes in the fractional void space, $f$, with bed depth should, if present, exert an action such as to increase, rather than decrease, $k$ (see Equation (3)). The occurrence of longitudinal diffusion in the front edge of the adsorption band must be admitted, although from other experiments the influence of this factor is believed to have been almost negligibly small.

As the length of the adsorption column increases, it is possible that the nature of the fluid flow through the porous bed may alter. Since it is likely, even with the relatively small throughput velocities employed in the above experiments, that turbulent together with laminar flow exists in the bed, variations in the mixture of these types may well be reflected by variations in the over-all bed rate constant. The observed change of $k$ with flow velocity, $v$, as well as bed depth, $x$, has suggested that conceivably the ratio of these variables, $x/v$, may be the proper function. This ratio may, for the sake of convenience, be termed the "retention time," for its value is a measure of the time required for a thin lamina of fluid to traverse the length of the bed. Since the fractional bed void space, $f$, is not readily estimated, values for the retention time in the above experiments will not be given. However, since the void must be the same for a given adsorbent form and particle size, the quantity $x/v = xf/W$ may be employed in the estimation of relative values. Experiments M-6 and 7 (Tables I and II) form a set which may be used to give a test of this retention time correlation. The latter experiment had the same retention time as M-6, which had a 5 cm. deep bed. It is seen that the values of the rate constants observed were the same within the experimental error, suggesting that possibly this variable may be more appropriate for the description of the performance of long adsorption columns. Further work is in progress to determine bed depth effects more completely.

In the light of the principles now delineated, an elementary discussion of the process of non-equilibrium elutriation will be attempted in conclusion. The release of a single species is effected generally by passing a solvent through the adsorbent bed containing the displaceable constituent which is then observed in the effluent. In the more usual, and more complex, situation a narrow band of mixed cations may be adsorbed initially at the top of the bed, and it is desired that this mixture be separated by washing the column with a desorbing solution. Under optimum conditions, each cation forms a separate narrow band which moves through the bed at a characteristic constant rate. If these cations are all present in the system as micro-constituents, the speed of each band will be independent of the presence of the others.

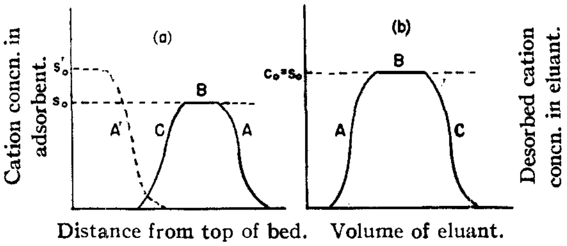

Fig. 7.—Band shapes in elutriation.

Consider any single band being displaced through the bed by a wash solution. It is observed that *both* the leading and trailing edges are diffuse (Fig. 7) in contrast to the shape found in rate-independent adsorption (*i. e.*, classical chromatography) where the leading edge is sharp and the training either diffuse or sharp. When the band reaches the exit end of the adsorption tube, the desorbed species becomes detectable in the effluent solution, and, if a plot of the breakthrough curve is made, a typical shape is found (Fig. 7b). Two special cases may be imagined: (a) when the band is sufficiently broad to exhibit a flat middle region, B; and (b) when this is not the case and branches A and C overlap. In the first of these cases, the shape of the band in the adsorbent formed by the initial adsorption step has been indicated by the broken line in Fig. 7a. Here, the equilibrium concentration in the bed is given by $S_0'$, and the diffuse portion, A′, corresponds to a theoretical transfer curve as discussed above. If a desorbing solution is passed through the column, the equilibrium concentration in the adsorbent will change to a new value, $S_0$, determined by the nature of the elutriant, and the branch A′ will change in shape to correspond to a new transfer curve of $y$ value determined by the new values of $k$ and $\delta$. As the adsorption wave reaches the bottom of the column, a breakthrough curve, shown by branch A in Fig. 7b, is observed. This concentration history should again be of the same form as one of the transfer theory curves, unless the column is not long enough for the change in shape in A′ to be complete.

Even in case (b) when branches A and C overlap these curves will be related to the theoretical forms. Frequently, however, the peak is so narrow that the maximum value is not defined easily. Furthermore, the value of this maximum probably diminishes as the band moves down the column and becomes more diffuse. Owing to these effects it has been difficult to obtain reliable theory constants in this case. In principle, however, it is now possible to make useful predictions concerning the dependence of the shapes of adsorption bands upon such experimental variables as flow rate, particle size, temperature, concentration of macro-components, and on bed depth. The application of some of these ideas to the problem of the separation of small quantities of the heavy rare earths will be discussed in the next paper.

**Acknowledgments.**—The authors desire to express gratitude to their colleagues mentioned in Paper I for the aid and encouragement they have have given. Particular thanks are made to A. R. Brosi and J. A. Swartout for the help received from their previous comprehensive testing of several aspects of the transfer theory. The authors also wish to acknowledge the assistance given by Q. V. Larson in the performance of several of the "thin-bed" rate experiments reported above and to thank him, together with Miss H. D. Martin, for their help in the completion of the time consuming column experiments.

## Summary

1. The transfer theory of Anzelius and Schumann has been reformulated using a first order rate equation found to apply in the description of the adsorption velocity in single-stage experiments. The dependence of the rate constant on particle size, flow rate and macro-component concentration is made explicit in this modified theory. In principle, this theory should permit the prediction of the behavior of deep adsorbent beds reacting under non-equilibrium conditions to be made in terms of the rate and equilibrium constants for the system.

2. An experimental method for the continuous recording of the concentration history of the effluent from a deep bed has been described utilizing radioactive isotope tracer equipment and techniques. The employment of these methods for the control of continuous flow type processes on a much larger scale should be of value.

3. The experimental concentration histories were observed to possess the same shape as the curves predicted by theory over a wide range of relative concentration. The observed dependence of the rate constant on bed depth was not anticipated from the theory, although the variation with flow rate and macro-component concentration were in fair accord.

4. Good agreement between the values of the distribution coefficient determined by the application of the theory to the adsorption column data and by independent equilibrium experiments was found. However, the rate constants estimated from the deep bed performances were approximately five to ten-fold smaller than those measured by a shallow-bed technique. Much of

this difference was attributed to the large difference in flow rate in the two types of experiments.

5. Application of the transfer theory procedure to column desorption data was shown to be possible. A dependence of the desorption rate on flow and on macro-component ion concentration was indicated.

P. O. BOX W, OAK RIDGE, TENN. RECEIVED JULY 7, 1947

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[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

# Ion Exchange as a Separations Method. III. Equilibrium Studies of the Reactions of Rare Earth Complexes with Synthetic Ion Exchange Resins[1]

BY EDWARD R. TOMPKINS AND STANLEY W. MAYER

## Introduction

From the early investigation of the column separations method,[2] it was apparent that the separation efficiency which could be achieved was dependent upon a number of factors (such as *p*H and concentration of the complexing agent, type of complexing agent, concentrations of cations being separated, ionic strength of the eluant, type of resin, resin particle size, flow rate of eluant, column diameter and column length). Some of these variables were studied by Tompkins, *et al.*, in a process development program whose purpose was the design of an all-column fission product factory.[3] During this same period, similar studies were undertaken by F. H. Spedding, *et al.*, in their application of this separations method to large scale rare earth separations.[4]

These empirical studies resulted in the solution of a very difficult problem (*i. e.*, the separation of rare earths), but the fundamental knowledge concerning the column process was not greatly increased. Being able to get good results was more of an art than a science. It had not been possible to study most of the variables over a wide range because of the long time required to make a column run. For this reason there was a tendency to arbitrarily fix one or more conditions, without studying each extensively, and then to study the effects of varying other factors and to choose those conditions which gave the best results. Because of the exceedingly long time required to study the effect of flow rate in the lower range, Spedding, *et al.*, after studying it down to $\sim$2 ml./sq. cm./min., arbitrarily chose this rate for their rare earth separations.[4] In the studies of Tompkins, *et al.*,[3] the flow rate was varied from 10 to 0.02 ml./sq. cm./min. The results of the latter investigation indicated the importance of operating columns as near to equilibrium conditions as possible.

The above considerations indicated the need for a more thorough understanding of the column reactions. It appeared that the studies which needed to be undertaken were: (1) a determination of the effects of various factors (*i. e.*, the *p*H and concentration of the complexing agent, the type of complexing agent, the concentration of the cations being separated, the ionic strength of the eluant and the type of resin) on the equilibrium constants of the reactions involved in column separations; (2) development of a simple theory which would predict column behavior from a knowledge of these equilibrium constants; (3) a study of the kinetics of column reactions to determine the effect of non-equilibrium conditions on column separations.

Equilibrium studies of this type had already been completed by Boyd, *et al.*, for systems involving ion exchange in which no complexing agents were used.[5] They had shown that the distribution of a substance between the exchanger and any solution in equilibrium with it can be predicted from the mass law.[5]

At the time this work was initiated, ion-exchange techniques had been employed in the elucidation of some of the equilibria occurring when the alkaline and rare earth cations were adsorbed from citrate buffers by the resinous exchanger, Amberlite IR-1. Thus, by applying the mass law, Schubert and Richter[6] had obtained values for the dissociation constants of the strontium and barium citrate complex ions, and for the strontium tartrate complex which were in agreement with those determined by electrometric and by other methods. L. S. Myers[7] had measured the exchange adsorption from dilute acid solutions of the trivalent La, Ce and Y ions over the concentration range from 0.1 to $10^{-9}$ *M*. Here it was observed that the distribution coefficient, $K_d$, became independent of rare earth concentration when the latter was less than $10^{-6}$ *M*. A preliminary study of the nature of the predominant rare earth citrate complex ion in the *p*H range from 2.0 to 3.0 had indicated the yttrium complex to be appreciably more stable than that of lanthanum.[8]

The purpose of the investigation, described

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[1] This document is based on work done under Contract W-35-059-eng-71 for the Atomic Energy Project, and the information contained therein will appear in Division IV of the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the Clinton Laboratories.

[2] E. R. Tompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947).

[3] E. R. Tompkins, *et al.*, to be published.

[4] F. H. Spedding, *et al.*, THIS JOURNAL, **69**, 2777 (1947)

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

[6] J. Schubert and J. W. Richter, May, 1945, to be published.

[7] L. S. Myers, Jr., July, 1945, to be published.

[8] B. H. Ketelle and J. W. Richter, October, 1945, to be published.