the elution curves on continued use. Phenol seemed to meet these requirements and was tested quantitatively.

Spore cultures of *Aspergillus oryzae* and of *Aspergillus niger* were used for massive spore inoculation of 0.5% citric acid solution adjusted to *p*H 4.0 with ammonium hydroxide. The following concentrations (g. per 100 ml.) of phenol were added to the citrate solution; 0, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.20, 0.30, 0.50, 0.70 and 1.0. Growth was evident in the first three in twenty-four hours. After six days, there was some growth in 0.03 and a slight trace in 0.05 but no growth in the higher concentrations; the same situation was maintained after a period of about three weeks. It was decided to use 0.1% of phenol in the eluting agent giving a safety factor of about 2.

The effect of 1% phenol on column operation, a concentration ten-fold that employed as a disinfectant, was tested. The control and test columns (16 mm. in diameter and 33 cm. bed length) were charged with Amberlite IR-100 under identical conditions and the complete operation applied in processing 0.5 g. of didymium oxide. The elution curves were identical showing that a concentration of phenol as high as 1% did not interfere with the operations.

The use of 0.1% phenol in the citrate eluting agent was put into practice in the large-scale production columns. During a period of over five months there has been no growth of mold and all columns have been in continuous operation with entirely satisfactory results.

The authors wish to thank V. A. Fassel for the many spectrographic analyses which he performed during the course of this work.

V. Summary

Detailed procedures have been given for the large scale separation of the rare earths using Amberlite IR-100 and 0.5% citric acid ammonium citrate solutions as the eluant. The process employed 24 columns 4 inches in diameter and with 8 feet of resin bed length. The *p*H of the citrate eluant was 3.9; the growth of mold was eliminated by the use of 0.1% phenol. Large samples of rare earths, of high purity were obtained by these procedures, portions of which have been furnished to other members of the Manhattan Project. Examples of the quantity and quality of several fractions on hand include: (1) *Neodymium*, 800 g. 99.9% Nd_2O_3, < 0.1% Pr_6O_{11}; 770 g. 98% Nd_2O_3, 2% Pr_6O_{11}; (2) *Praseodymium*, 35 g. 99% Pr_6O_{11}, 1% Nd_2O_3; 160 g. 90% Pr_6O_{11} (impurities Ce, La, and Ca); (3) *Samarium*, 160 g. > 99.9% Sm_2O_3; 600 g. 99% Sm_2O_3, 0.5% Eu_2O_3, 0.5% Ca. In addition, considerable quantities of slightly impure heavy rare earth salts and yttrium salts have been prepared.

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[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. I. Ion-exchange Equilibria[1]

BY G. E. BOYD,[2] J. SCHUBERT[3] AND A. W. ADAMSON[4]

Introduction

The observation that extremely small quantities of dissolved radioactive species could be extensively removed by base-exchanging substances from aqueous solutions of appreciable ionic strength was the starting point for much additional research and development work on the part of many individuals associated with the Plutonium Project. As a consequence, numerous adsorption techniques have been developed for the extraction, concentration and fractionation of a wide variety of radio-isotopes. Attempts to elucidate the principles governing these systems led to the undertaking of quantitative studies of the equilibrium and rate processes governing ion-exchange adsorption. Further, these efforts led to the development of exact methods for describing adsorption processes in dynamic systems as, for example, when traces of solute are extracted from a solution flowing through a deep bed of adsorbent. The more important results from this program of basic research will be presented in a series of papers, of which the current article is the first. Here, the problem of the accurate formulation of the relations governing the equilibrium behavior of exchange adsorption systems, the experimental testing of these equations, and the generalizations concerning the adsorbability of cations arrived at will be treated.

Incidentally, the researches to be described will illustrate many of the advantages in the employment of radio-isotope techniques in dealing with physical chemical problems. By virtue of the convenience, sensitivity and accuracy with which *changes* in the amounts of radioactive substances can be estimated, the phenomenon of the exchange

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[1] This work was performed under the auspices of the Manhattan District at the Metallurgical Laboratories of the University of Chicago and at Clinton Laboratories, Oak Ridge, Tennessee, during the period April, 1942, to April, 1946.

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adsorption of ions present in extreme dilution could be studied in solutions of widely variable ionic strength.

Formulation of Heterogeneous Ion-exchange Processes According to Langmuir's Adsorption Mechanism.—The relationship which has been found to hold between the amount of base exchange and the equilibrium concentration of added electrolyte appears at first sight to be similar to an ordinary adsorption isotherm (Fig. 1). For a given amount of ion-exchanger and a fixed total volume of solution the curve has the same form. The similarity, however, seems to disappear on consideration of the equilibrium taking a constant amount of exchange adsorbent, and an increasing solution volume. The experimental results in this case reveal that the amount of uptake is *independent* of the concentration of the adsorbed electrolyte.

To explain the foregoing observations, consider the dynamic interchange of ions between the zeolite and the surrounding aqueous solution at equilibrium. Upon any unit area there will be a competition between the cations in solution for the available anionic groups structurally bound to the adsorbent. At any time, under constant conditions, then, the surface will be covered by ions both from the solution and initially in the exchanger. Consider now the most simple case of the simultaneous competitive adsorption of two singly charged cations, A^+ and B^+. By formal analogy with the Langmuir equation for adsorption from a binary gaseous mixture,[5] the equation for the adsorption of one of the ions, A^+, from a dilute electrolyte solution is then

$$\left(\frac{x}{m}\right)_{A^+} = \frac{kb_1C_{A^+}}{1 + b_1C_{A^+} + b_2C_{B^+}} \qquad (1)$$

where $(x/m)_{A^+}$ is the amount of A^+ ion adsorbed per unit weight of adsorbent; C_{A^+} and C_{B^+} are the respective equilibrium concentrations (activities) of ions A^+ and B^+ in solution; and k, b_1 and b_2 are constants.

The number of unsaturated anionic exchanging groups (*i. e.*, amount of bare surface in the Langmuir picture) must always be very small, for otherwise an appreciable free negative surface charge would be created leading to particles of adsorbent bearing a high negative charge, which is not the case. Accordingly, to a good approximation the quantity unity in the denominator of Equation (1) can be neglected relative to the quantity, $(b_1C_{A^+} + b_2C_{B^+})$

$$\left(\frac{x}{m}\right)_{A^+} = \frac{kb_1C_{A^+}}{b_1C_{A^+} + b_2C_{B^+}} = \frac{kb_1/b_2(C_{A^+}/C_{B^+})}{1 + b_1/b_2(C_{A^+}/C_{B^+})} \qquad (2)$$

For convenient application to experimental data, Equation (2) may be written in a linear form

$$\frac{C_{A^+}/C_{B^+}}{(x/m)_{A^+}} = \frac{b_2}{b_1k} + \frac{1}{k}\frac{C_{A^+}}{C_{B^+}} \qquad (3)$$

so that a $(C_{A^+}/C_{B^+})/(x/m)_{A^+}$, C_{A^+}/C_{B^+} plot should give a straight line if the treatment is valid. When very small initial concentrations of the ion A^+ are present in solutions relatively concentrated in ion B^+, even the complete adsorption of A^+ will not desorb sufficient quantities of B^+ to cause a detectable change in C_{B^+}. As a consequence, a plot of $C_{A^+}/(x/m)_{A^+}$ against C_{A^+} would be expected to be linear. An example of this is afforded by Fig. 2 which was constructed from the data of Fig. 1 obtained in preliminary experiments.

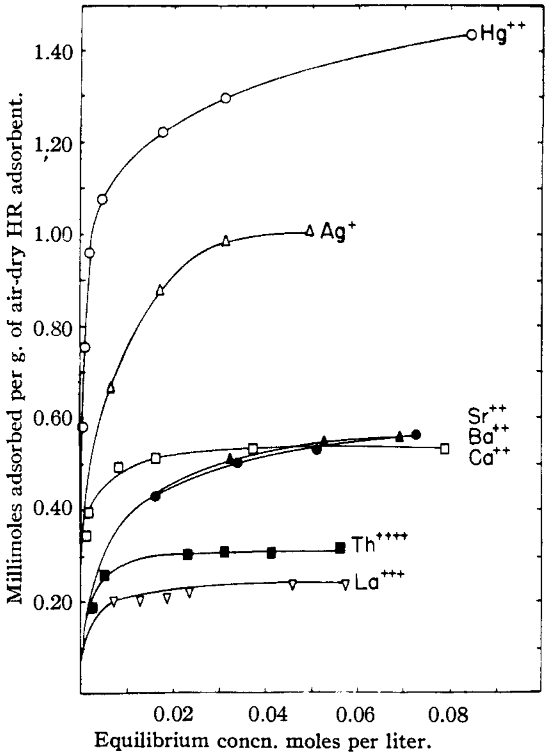

Fig. 1.—Adsorption of cations at 25° by organic ion exchanger.

Inspection of Equation (2) reveals that the amount of base exchange, $(x/m)_{A^+}$, must depend upon the *ratio* of the equilibrium concentrations of the exchanging ions, and hence that the extent of adsorption will be independent of the dilution. For $C_{B^+} \gg C_{A^+}$ the adsorption of A^+ becomes directly proportional to C_{A^+} to a good approximation; for $C_{A^+} \gg C_{B^+}$ the adsorption of A^+ becomes constant and independent of concentration. Measurement of the adsorption at $C_{A^+} = C_{B^+}$ makes possible the evaluation of the adsorption affinity, given by (b_1/b_2).

In the more general case, the exchange adsorption of two cations of unequal charge, $A^{\nu+}$ and $B^{\nu+}$, will be governed by the equation

$$\left(\frac{x}{m}\right)_{A^{\nu+}} = \frac{kb_1(C_{A^{\nu+}})^{\nu'+}}{b_1(C_{A^{\nu+}})^{\nu'+} + b_2(C_{B^{\nu'+}})^{\nu+}} \qquad (4)$$

Finally, the expression for the adsorption of a

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[5] I. Langmuir, THIS JOURNAL, 38, 2221 (1916); see H. S. Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1930, Vol. II, pp. 1073 ff.

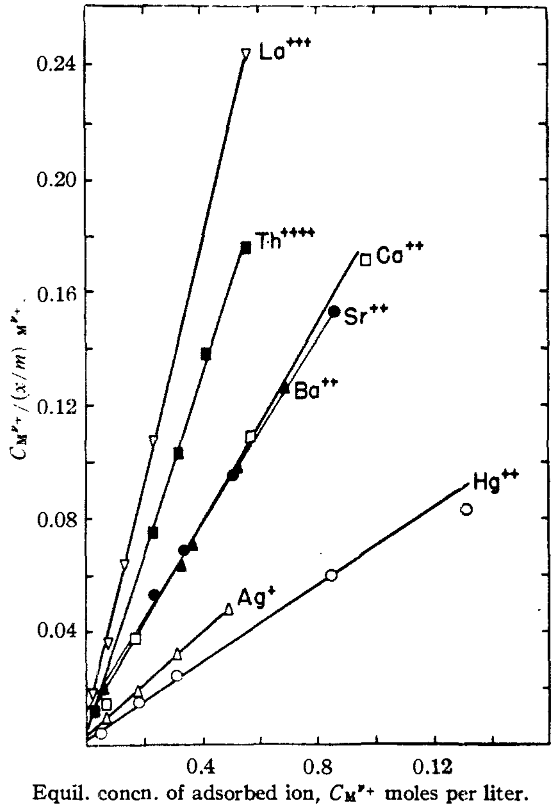

Fig. 2.—Plot of the data of Fig. 1 according to equation (3).

singly charged cation, M_i, from a mixture of singly charged cations in solution may be written:

$$\left(\frac{x}{m}\right)_{M_i} = \frac{kb_iC_{M_i}}{1 + \sum_{j=1}^{\infty} b_jC_{M_j}} \qquad (5)$$

Evidently, then, the greater ionic strength of the mixed electrolyte the less the exchange adsorption of any single cationic species held at constant concentration.

The constants b_1 and b_2 in the above equations are related to the energy of adsorption of the ions, E_{A^+} and E_{B^+}, by the relation

$$b_1/b_2 = (P_{B^+}/P_{A^+}) \exp - [(E_{B^+} - E_{A^+})/RT] \qquad (6)$$

These energies, actually free energies as will be shown later, are determined largely by electrostatic factors connected with the charge and with the size of the ion in solution. The constant, k, may be identified with the total exchange capacity, E, of the adsorbent.

The applicability of the foregoing treatment is dependent upon a number of assumptions. Several of these seem worthy of mention: Firstly, it was assumed only one type of adsorbing surface (*i. e.*, exchanging anion) was present in the exchanger. It also has been assumed that there was no interaction between neighboring adsorbed ions, which appears reasonable if the exchange positions are relatively widely spaced in the adsorbent. Further, it was taken that none of the *anions* initially present in solution was adsorbed. If a physical adsorption of anions should occur, this would be accompanied by an adsorption of cations in excess of that from base-exchange. Finally, it has been supposed that no more than one layer of cations was adsorbed, or, when the anionic groups of the zeolite are saturated no further uptake of cations occurred. When looked at in this sense, ion-exchange adsorption can be regarded as a species of chemisorption.

Since equations of the same form as the above may be derived from the law of mass action when applied to the exchange equilibrium of equally charged ions, the agreement of experimental data with Equation (2) cannot be taken as evidence that base-exchange is an "adsorption" phenomenon in any special sense.

Formulation of Heterogeneous Ion-exchange Processes According to the Law of Mass Action.—An alternative to the foregoing "adsorption" treatment is to assume that the ion-exchange is analogous to an ordinary metathesis reaction and that, at equilibrium, the Mass Law applies to the heterogeneous system: ion-exchanger + aqueous solution. The exchange reaction involving two monovalent cations, A^+ and B^+, then may be written as

$$A^+ + BR = AR + B^+ \qquad (7)$$

where R has been taken to designate the insoluble structurally bound anionic part of the organic zeolite. The thermodynamic equilibrium constant, K_a, for this reaction is defined by

$$K_a = a_{B^+}\, a_{AR}/a_{A^+}\, a_{BR} \qquad (8)$$

where a_{A^+}, a_{B^+} are the respective activities in aqueous solution of the ions A^+ and B^+, and where a_{AR} and a_{BR} are the activities in the solid state. It may be said that the Mass Law is obeyed if, for a variety of compositions of the system containing the exchanging ions plus adsorbent, the appropriate activity values when substituted into Equation (8) lead to a constant value, K_a, independent of the composition.

Further considerations must be made before Equation (8) is applied to experimental base-exchange data. First, there is the problem of the evaluation of the activities of the ions present in the aqueous phase. As is well appreciated, these may be related to the product of their concentrations in solution by their respective ionic activity coefficients. These ion activity coefficients in turn may be related to the mean activity coefficients of the electrolyte, which usually have been determined for pure aqueous solutions. The appropriate activity coefficient to be employed, however, is that for the ion in the *mixed electrolyte* in equilibrium with ion-exchanger.

The problem of the evaluation of the activities for the solid phase calls for a special treatment. If the reaction given by Equation (7) were analogous to a chemical reaction where AR and BR occur as independent solid phases, it would be possible to take their activities as constant and equal to unity. Kerr[6] reported, however, that such an assumption was not valid with the cation exchange reactions studied by him. This has been confirmed by Vanselow[7] and by the results from the present work. Actually, since the ions freely substitute for one another in the exchanger, it is better, as Vanselow pointed out, to suppose that the components of the solid phases form completely miscible solid solutions with one another. Justification for treating the organic zeolites employed in this work as solid solutions has been supplied by X-ray diffraction measurements[8] which have revealed a random distribution of the metal cations throughout the adsorbent.

Quite generally, the activities of the components of the binary solid solution must be taken as complex functions of their respective mole fractions. If, however, the ions in the solid are singly charged and if they are not too widely different in size, their solid solutions may be taken as ideal. In this case a_{AR} and a_{BR} may be set equal to the mole fractions X_{AR} and X_{BR} with Equation (8) becoming

$$K_a = (a_{B^+})X_{AR}/(a_{A^+})X_{BR} = (a_{B^+})(n_{AR})/(a_{A^+})(n_{BR}) \tag{9}$$

where n_{AR} and n_{BR} are the number of moles of A and B in the solid, respectively. When the solid solution deviates from ideality, as revealed by a lack of linearity in a log a_{A^+}/a_{B^+}, log X_{AR}/X_{BR} plot, more elaborate methods must be employed. Kielland[9] has proposed an empirical method for the estimation of the activity coefficients, γ_{AR}, γ_{BR}, in the binary solid solution based upon the Duhem–Margules equation as follows

$$\text{Let} \quad \log \gamma_{AR} = CX^2_{BR} \tag{10}$$

$$\text{and} \quad \log \gamma_{BR} = CX^2_{AR} \tag{11}$$

where C is a constant for each particular system, and may be positive or negative, most commonly varying from zero to one.

Substituting Equations (10) and (11) into Equation (8)

$$\log K_a = \log (a_{B^+})(a_{AR})/(a_{A^+})(a_{BR}) =$$
$$\log (a_{B^+})(X_{AR})/(a_{A^+})(X_{BR}) + C(X^2_{BR} - X^2_{AR}) \tag{12}$$

Setting

$$\log (a_{B^+})X_{AR}/(a_{A^+})X_{BR} = \log K_c'$$

and re-writing (12)

$$\log K_c' = \log K_a - C(X^2_{BR} - X^2_{AR}) \tag{13}$$

Thus, log K_c' is a linear function of $(X^2_{BR} - X^2_{AR})$ with slope C, and log K_c' = log K_a when $X^2_{AR} = X^2_{BR}$. When the value of C is obtained, values of γ_{AR} and γ_{BR} may be computed from Equations (10) and (11), if desired. From the value of log K_a obtained it becomes possible to calculate the standard free energy of exchange adsorption, ΔF^0.

The foregoing has been based upon the exchange of two monovalent cations; a brief further discussion of the somewhat more general case of the exchange of two ions of unequal positive charge, A^{ν_+} and $B^{\nu'_+}$ where $\nu'_+ > \nu_+$ will now be given. Writing the exchange reaction

$$A^{\nu_+} + (\nu_+/\nu'_+)BR = AR + (\nu_+/\nu'_+)B^{\nu'_+} \tag{14}$$

The expression for the mass law equilibrium constant assuming ideal solid solutions is then

$$K_a = \frac{(a_{B^{\nu'_+}})^{\nu_+/\nu'_+}(X_{AR})}{(a_{A^{\nu_+}})(X_{BR})^{\nu_+/\nu'_+}} = \frac{(a_{A^{\nu'_+}})^{\nu_+/\nu'_+}(n_{AR} + n_{BR})^{(\nu_+/\nu'_+ - 1)}(n_{AR})}{(a_{A^{\nu_+}})(n_{BR})^{\nu_+\nu'_+}} \tag{15}$$

where symbols have the same meaning as in Equations (8) and (9).

In the special case when $n_{AR} \ll n_{BR}$, Equation (15) becomes

$$K_a = (a_{B^{\nu'_+}})^{\nu_+/\nu'_+}(n_{AR})/(a_{A^{\nu_+}})(n_{BR}) \tag{16}$$

As will be seen later, Equation (16) will be of particular use in those experiments wherein radioactive traces were adsorbed.

Equation (15) may be developed further by introducing the activity coefficients, $\gamma_{A^{\nu_+}}$ and $\gamma_{B^{\nu'_+}}$, for the ions in solution; thus

$$K_a = \frac{(\gamma_{B^{\nu'_+}})^{\nu_+/\nu'_+}(m_{B^{\nu'_+}})^{\nu_+/\nu'_+}(n_{AR} + n_{BR})^{\nu_+/\nu'_+ - 1}(n_{AR})}{(\gamma_{A^{\nu_+}})(m_{A^{\nu^+}})(n_{BR})^{\nu_+/\nu'_+}} \tag{17}$$

These activity coefficients are evaluated in the following manner, where X is a monovalent anion, the notation being that of Lewis and Randall[10]

$$\gamma_{A^{\nu_+}} = \gamma_{AX\nu_+}/(\gamma_X) = (\gamma_{\pm AX})^{\nu_+ + 1}/(\gamma_X)^{\nu_+} \tag{18}$$

$$\gamma_{B^{\nu'_+}} = \gamma_{BX}/(\gamma_X)^{\nu'_+} = (\gamma_{\pm BX})^{\nu'_+ + 1}/(\gamma_X)^{\nu'_+} \tag{19}$$

Substituting Equations (18) and (19) into (17)

$$K_a = \frac{[(\gamma_{\pm BX})^{\nu'_+ + 1}]^{\nu_+/\nu'_+}}{[\gamma_{\pm AX}]^{\nu_+ + 1}} \frac{(m_{B\nu'_+})^{\nu_+/\nu'_+}(n_{AR} + n_{BR})^{\nu_+/\nu'_+ - 1}(n_{AR})}{(m_{A^{\nu_+}})(n_{BR})^{\nu_+/\nu'_+}} \tag{20}$$

It is evident that the mean activity coefficients must be those for the mixed electrolyte, and that values for these must be obtained by independent procedures. In studies on the exchange adsorption of Ag$^+$ with H$^+$, and Tl$^+$ with H$^+$ ions in clays, Marshall and Gupta[11] have estimated the activities by a determination of reversible electrode potentials in the appropriate mixed electrolytes. In the present research, where generally the ionic strength of the equilibrium solutions has been low, the assumption was made that the mean activity coefficient of a salt in a mixture was the same as that of the pure salt at the same ionic strength. At high dilutions, the mean activity coefficient ratio for two electrolytes of the same

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[6] H. W. Kerr, *J. Am. Soc. Agron.*, **20**, 309 (1928).

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

[8] W. H. Zachariasen and R. C. L. Mooney, private communication, December 20, 1945.

[9] J. Kielland, *J. Soc. Chem. Ind.*, **54**, 232T (1935); A. W. Porter, *Trans. Faraday Soc.*, **16**, 336 (1921).

[10] G. N. Lewis and M. Randall, "Thermodynamics and The Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

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

valence type may be taken as unity. For solutions of high ionic strength where one salt overwhelmingly predominates, the activity coefficient of the microcomponent electrolyte will deviate from the value predicted by the ionic strength principle, and other methods must be employed to find its correct value.[12]

Several concluding remarks about the application of mass action principles to base exchange equilibria seem appropriate. In the past the apparently limited success this approach has enjoyed may have been owing to some, or all, of the following: (*a*) The chemical equations used to represent the exchange reaction were stoichiometrically incorrect, either because of partial hydrolysis of certain cations in solution and hence the simultaneous adsorption of ions of reduced positive charge, or, because of the adsorption of the products from the incomplete dissociation of the electrolyte[13]; (*b*) a rather more subtle error in this same category may have resulted from the frequent assumption that the base-exchanger contained but one chemical grouping (*i. e.*, exchanging acid) responsible for the adsorptive capacity. If the exchanger were actually a polybasic substance, then this capacity might well depend strongly on the *p*H at which the exchange experiments were performed. Consequently, in such systems, unless the *p*H were maintained closely constant, the extent of the exchange might be affected; (c) the activity coefficients of the ions in solution and/or in the solid phase were neglected. Sometimes an attempt to avoid the limitation imposed by the lack of information concerning activities in solution has been made by performing all measurements at constant ionic strength and assuming under these conditions that the activity coefficient ratio remained constant. This assumption is probably valid only to a fair degree in even dilute solutions, which, unfortunately, were rarely used by investigators employing this approximation.

From the experimental aspect, even in the most careful studies as yet performed, there have been some uncertainties in the data because changes in the composition of the zeolite were almost always computed from the difference in solution concentrations before and after exchange. When small variations in solution concentration are used to estimate concentrations in the solid phase the results frequently are subject to considerable error.

Recently, as a consequence of the basic discoveries of Adams and Holmes,[14] a variety of synthetic base-exchange substances have been developed industrially which permit many of the foregoing difficulties to be overcome. These high capacity organic zeolites may be used in solutions of sufficiently low *p*H to eliminate nearly all hydrolysis effects. Some, but not all, of these commercial materials contain but one structurally bound exchanging anion, and hence exhibit a capacity independent of *p*H over wide ranges.[15] Another important advantage of these organic exchangers is that a direct analysis of the equilibrium solid phase is possible.

Experimental: Materials and Procedures

In the present series of investigations the phenol-formaldehyde resinous exchanger, Amberlite IR-1,[16] was used. This synthetic organic zeolite appeared to possess the following additional advantages for use in quantitative studies: (a) a fairly well-defined chemical structure which was stable over a wide *p*H range; (b) a large adsorptive capacity which was independent of the degree of sub-division; and (c) a rapid rate of adsorption leading to a state of apparent equilibrium at low *p*H's within two hours. One possible disadvantage was observed during the course of this work, however. This was the moderate reducing action shown by Amberlite IR-1 even when it had been carefully freed of residual sulfite initially present. For example, the reduction of Ag^+ ion to metallic silver as well as Hg(II) to Hg(I) was noted; at temperatures above 75° this reducing action seemed to be enhanced. This behavior might be expected if the exchanger contains phenolic compounds. The organic exchanger was observed to be inert toward many reagents including strong acids and bases, various salt solutions and organic liquids. Only with nitric acid above 2 *N* in concentration were any effects noted. With this reagent, however, a rapid, energetic reaction occurred, and if amounts of hydrogen peroxide were also present, a complete dissolution of the adsorbent could be effected.

Since the chemical composition of this material determined the extent of its exchange adsorption, a brief resume of its mode of preparation and of its chemical structure seems desirable. Presumably, Amberlite IR-1 is the result of the condensation of polyhydric phenols and formaldehyde in the presence of sodium sulfite which is added to effect the incorporation of methylene sulfonic acid so as to increase adsorption at low *p*H. The polymerization is carried to the so-called "C-Stage" which yields an insoluble, infusible product. Analyses carried out by ourselves and by others[16b] have agreed on a sulfur content in the range of 5.5–6.5%. If the exchange capacity of the adsorbent were caused entirely by the methylene sulfonic acid groups present, this should be

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[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, pp. 444 ff.

[13] The latter difficulty may be surmounted if solutions sufficiently dilute to insure complete dissociation can be used. Radioactive isotopes have proved to be of unique value in the analysis of such systems because of the sensitivity they afford and because of the accuracy and convenience with which their concentrations can be measured.

[14] B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind.*, **54**, 1–6T (1935).

[15] W. C. Bauman, THIS JOURNAL, **69**, 2830 (1947).

[16] (a) Produced by the Resinous Products Chemical Co., Philadelphia, Pennsylvania; (b) R. J. Myers, J. W. Eastes and F. J. Myers, *Ind. Eng. Chem.*, **33**, 697, 1203, 1270 (1941).

approximately 1.7 to 2.0 milliequivalents per gram of the anhydrous acid form of the adsorbent. Actually, the observed capacity for exchange has been observed repeatedly to vary between 2.35 and 2.53 m. e./g., revealing the presence of other acidic exchanging groups. Further, as the data of Table I show, the exchange capacity is strongly dependent upon the *p*H of the solutions employed. If the capacity at *p*H 1.0 is assumed to be caused entirely by the methylene sulfonic acid anions present, then, an analysis of the data of Table I shows that the second exchanging group which is responsible for the increased capacity between *p*H 1.0 and 7.0 must have an acid dissociation constant of *ca.* 8.5×10^{-4}. This value is sufficiently close to that for salicylic acid (10.6×10^{-4}) to suggest that Amberlite IR-1 contains an appreciable number of carboxyl groups ortho to phenolic hydroxyls known to be present. It may be estimated from the data of Table I that the exchanger contains a total of about 1.6 m. e. of —COOH per gram of dry adsorbent. The still more greatly increased capacity at *p*H 8.8 must be attributed mainly to the phenolic groups whose hydrogens may now undergo exchange. At *p*H values below 7, the exchange of these phenolic groups is sufficiently repressed that they exercise virtually no role in the observed ion-exchange adsorption.

TABLE I

VARIATION OF THE ADSORPTIVE CAPACITY OF AMBERLITE IR-1 WITH *p*H

*p*H	M. e./g. anhydrous HR	Increase in capacity, m. e./g.	Concentration of NaCl used to convert exchanger, *M*
1.0	1.80	0	...
2.3	2.53	0.73	5.0
4.1	3.38[a]	1.58	5.0
8.8	5.42[a]	3.62	5.0

[a] These data were obtained by Mr. B. H. Ketelle.

The physical structure of the adsorbent is of comparable importance, since the rate of approach to exchange equilibrium and hence the practical efficiency of the extraction is profoundly influenced by this factor. Amberlite IR-1 must be regarded as an organic gel in which the water of gelation is a vital structural element. Removal of this water, as by excessive drying, results in a greatly lowered adsorptive capacity. The loss, however, is not irreversible, for upon prolonged soaking in water the adsorbent slowly regains its exchange capacity. The gel structure must be a fairly open one since the exchanging groups in the interior seem freely accessible. The observation that the capacity was independent of the particle size serves to substantiate this hypothesis. The resinous structure is cross-linked in three dimensions by methylene linkages but, in spite of this, there is appreciable elasticity, so that a sizeable swelling or shrinking occurs when the concentration of the electrolyte above the adsorbent varies widely. The relation between the moisture content and the cation form of the adsorbent is illustrated by Table II.

TABLE II

CAPACITY AND MOISTURE CONTENT OF AMBERLITE IR-1

Cation in adsorbent	% H_2O in air-dried MR	M. e. cation per g. air-dried MR	M. e. cation per g. oven-dried HR	Moles H_2O per mole of cation
H^+	33.2	(1.68)	(2.53)	11
Li^+	21.5	1.95	2.53	6.1
Na^+	15.0	2.03	2.53	4.1
K^+	13.3	2.08	2.65	3.6
NH_4^+	16.6	2.28	2.87	4.0

Experimental Procedure

Preparation of the Adsorbent.—The resinous exchanger as received from the manufacturer was in the sodium form and had an average particle size of about 0.6 mm. (−30 mesh). The moist exchanger was air-dried, ground in a pebble mill, dry-sieved to obtain a 40/60 mesh range (U.S. Standard Sieve Series) fraction, and then placed in a glass column and back-washed with demineralized water until free of fines. Three adsorption–desorption cycles were carried out using 10% sodium chloride and hydrochloric acid solutions alternately in order to "condition" the resin. These "conditioning" cycles were found necessary to remove traces of extraneous chemicals which remain with the resin after manufacture. The adsorbent was then converted to the hydrogen form by passing a large excess of 5 *N* hydrochloric acid through the bed. When other forms were desired, aliquots of the hydrogen resin were converted by passing a large excess of a 5 *M* solution of the chloride of the desired cation through the bed of adsorbent. After about sixteen hours, the converted exchanger was washed with a minimum of distilled water, air-dried and stored in glass-stoppered bottles.

The moisture contents of the various zeolite preparations were determined by drying to constant weight at 115°. The cation components were determined by dissolving a portion of the adsorbent in concentrated nitric acid to which a little hydrogen peroxide (Superoxol) had been added, and analyzing the resulting clear solution. An alternative procedure was to ash the resin in a muffle furnace at about 800° followed by subsequent solution and analysis of the ash. It was observed that unless distilled water of the very best grade was employed to wash the resin, the hydrogen form (HR) would frequently contain as much as 2% ash. When washing was carried out carefully with doubly distilled water the ash content was reduced to 0.05%.

Preparation of the Solutions.—All solutions were prepared from analytical grade chemicals and laboratory distilled water. The stock solutions, and, in many cases, the actual dilutions used, were analyzed for their cation concentration by appropriate procedures. Lithium, sodium and potassium were determined by fuming with sulfuric acid and weighing as the sulfate; sodium was estimated also by the sodium zinc uranyl acetate procedure. Ammonium chloride solutions were analyzed by the Kjeldahl method, and the hydrochloric acid solutions by titration with standard base. Barium was determined gravimetrically as barium sulfate, and lanthanum by precipitating as the oxalate followed by ignition to the oxide.[17]

Radiochemical Measurements.—Radioactive isotopes were employed as tracers in the experiments where a knowledge of the behavior at very low ionic strength was desired. The 14.6 h Na^{24}, 19.5 d Rb^{86} and 1.7 y Cs^{134} activities were prepared by irradiating about 20 mg. of the nitrate, carbonate and bromide, respectively, with neu-

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(17) The authors are indebted to R. W. Bane and Group of the Metallurgical Laboratory, University of Chicago, and to W. M. Byerly, P. F. Thomason, S. W. Rasmussen and M. A. Perry of the Analysis Group of Clinton Laboratories, Oak Ridge, Tennessee, for the numerous chemical analyses required by this work.

trons in the Clinton pile. Radiochemically pure activities were obtained as indicated by the half-life with the exception of cesium bromide, which first needed to be cleaned of bromine activity by repeated silver chloride precipitations.

The quantity of the radioactive tracer in the equilibrium solution or solid was determined using a mica end-window G.-M. tube with self-quenching connected in turn to a scale of 64 counting circuit plus mechanical recorder. In assaying the 14.6 h Na^{24}, the adsorbent was transferred to a 22 mm. watch glass supported on cardboard and covered with Scotch tape. The gamma activities of these samples were counted at 8% geometry using an Al + Pb + Al sandwich of absorbers to remove the beta particles also emitted by Na^{24}. When the 19.5 d Rb^{86} or the 1.7 y Cs^{134} was used the exchanger was dissolved in a mixture of concentrated nitric acid and hydrogen peroxide, diluted to 10 ml., and a 0.5 ml. aliquot evaporated on a watch glass which was then mounted and counted without added absorber. Separate experiments showed there were no self-absorption or scattering errors detectable caused by the presence of adsorbent or salt in the samples. In the experiments using radio-sodium, it was necessary to correct for decay during the counting of the samples. This amounted to 10 to 20% and was always made.

In order that the radioactive isotopes of sodium, rubidium and cesium may be used as tracers for their respective elements, it is of course necessary that they be in the usual oxidation and/or hydrolytic states to be expected in the systems employed. Although this should certainly be the case with the alkali metal ions in view of their small degree of hydrolysis and consequent improbability of radiocolloid formation, the point was tested using the 14.6 h Na^{24} activity.

A very small quantity of freshly neutron irradiated sodium nitrate was added to 10 ml. of a 0.1 *M* sodium chloride solution. Sodium magnesium uranyl acetate was then precipitated, and collected in separate fractions. Each fraction was dried, weighed, and counted so as to determine the specific activity. Variations in this specific activity from one fraction to the next might be expected if the sodium tracer were in a different chemical state than the bulk inactive sodium ion.

Two such experiments were performed: in the first, the precipitation was made at 20°, and most of the precipitate was contained in the first fraction collected. In the second experiment, the reagent solution was first heated to 60° before being added to the sodium chloride solution. Under these conditions, the rate of precipitation was smaller and the fractions obtained were about equal size. The results are shown in Table III. In neither experiment was any significant change detected in the specific activity.

Table III

Verification of Interchange between Na^{24} and Na^{23}

	Specific activity in given fraction in cts./min.mg.				
Experiment	1	2	3	4	5
1	76.0	74.4	76.6		
2	68.3	68.8	67.6	67.4	67.5

Equilibration Procedure.—(a) Wherever possible the adsorption equilibrium was approached from both directions. For example, in the exchange between sodium and hydrogen ions, equilibrium was approached using the hydrogen form of the adsorbent (HR) in one series and the sodium form (NaR) in the other series of concentrations.

(b) Only air-dried resin of known moisture content was employed. The anhydrous weight (*i. e.*, oven-dried) of the *equilibrium form* of the exchanger was used in the calculations. This was obtained by a method of successive approximations as is illustrated below in the presentation of the results for the sodium-hydrogen exchange system.

(c) Ample time was taken for the attainment of equilibrium which was about four to six hours when the solution plus adsorbent were shaken vigorously. The results from a study of the rate processes governing the exchange adsorption will be presented in a subsequent paper. Here it will suffice to remark that usually, if not always, the exchange is diffusion rate controlled. The diffusional nature of the adsorption rate process is particularly noticeable with concentrated electrolyte solutions. As might be anticipated, the particle size of the adsorbent also plays an important role in determining this rate. Generally, in studies of ion-exchange equilibria, the more finely divided the adsorbent can be made, the better. With Amberlite IR-1 the equilibrium adsorption has always been observed to be independent of the particle size.

Experimental Results

Sodium-Hydrogen Exchange.—The equilibrium in the sodium-hydrogen exchange was approached from both directions; that is, various amounts of sodium-saturated adsorbent were shaken with dilute hydrochloric acid in one series, while various amounts of the hydrogen form were shaken with dilute sodium chloride in another sequence of experiments. This exchange proved to be fully reversible. The formulation used for the reaction was

$$Na^+ + HR = NaR + H^+ \qquad (21)$$

The equilibrium expression follows from Equation (20)

$$K_a = (a_{NaR}m_{H^+}/a_{HR}m_{Na^+})\,(\gamma^2{}_{\pm HCl}/\gamma^2{}_{\pm NaCl}) \qquad (22)$$

Since the ionic strength of the equilibrium electrolyte solutions was small, ($\mu = 0.1$), the activity coefficient ratio in Equation (22) for the 1–1 electrolytes could be taken as unity within the experimental error. In one case, however, where μ was as large as 1.08, this was not permissible, as is illustrated by Table IV. A convenient method for graphical illustration of the experimental results can be based upon writing Equation (22) as

$$\log (X_{NaR}/X_{HR}) = \log (n_{NaR}/n_{HR}) = \log K_a + \log (a_{Na^+}/a_{H^+}) \qquad (23)$$

assuming that the solid solution is ideal, and hence that the activities in the solid are equal to their respective mole fractions. Since Equation (23) is that of a straight line of unit slope, conformity of the experimental data to it, as shown in Fig. 3, affords some verification for this last assumption. It is especially of interest to note from Table IV that the mole fraction of sodium in the exchanger, X_{NaR}, varied from 0.26 up to 0.93, hence deviations from an ideal solid solution should have become apparent.

Ideal behavior may not always be observed in the exchange of sodium and hydrogen ions, however. In studies where a carbonaceous cation exchanger (Zeocarb) was employed, Walton[18] has obtained data which give a smooth curve deviating slightly negatively from a straight line of slope = 0.55 when plotted as are the data in Fig. 3. In this case, the treatment outlined by Equations (10) to (13) above may be employed to evaluate the activity coefficients in the solid. When this is done, values greater than unity for these coefficients are found, indicating positive deviations from ideality. On the basis of general considerations, this type of deviation would be anticipated.

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[18] H. F. Walton, *J. Phys. Chem.*, **47**, 371 (1943).

It should be noted also that the value for the equilibrium constant was but 0.55, showing that with this adsorbent hydrogen was much more strongly adsorbed than sodium ion.

From Fig. 3, the value log $K_a = 0.25$ or $K_a = 1.78$ is found from which the standard free energy of exchange adsorption may be computed: $\Delta F^0_{298} = -RT \ln K_a = -0.34$ kcal./mole, the negative value indicating a stronger adsorption affinity for the sodium ion with the synthetic cation-exchange adsorbent.

At this point, a brief explanation of the manner in which the mass of the equilibrium adsorbent may be approximated seems appropriate. It is evident that, as a consequence of exchange, the initial weight of the adsorbent may either increase or decrease. Of course, this equilibrium adsorbent may be recovered entirely and its weight in an anhydrous condition determined directly. However, since the equilibrium composition of the exchanger must be determined by analysis, it is possible to make use of this together with the initial weight to compute the final total adsorbent weight. The procedure may be illustrated by an example.

In experiment 1 of Table IV the weight of the starting oven-dry NaR was 0.855 g., which thus contained 2.24 × 0.855 = 1.92 millimoles of sodium. After exchange with hydrogen ion, it was found by analysis that 1.40% of the weight of the oven-dry adsorbent was due to sodium. As a first approximation, take 0.855 g. as the weight of the anhydrous equilibrium resin. Hence, 1.92 − 0.52 = 1.40 mmol. of sodium, equivalent to 32 mg., had been released from the solid. Since 1.40 mmol. of hydrogen ion must have entered the exchanger, its weight must therefore have increased by 1.4 mg. Accordingly, the weight of the equilibrium adsorbent is given to a first approximation by: 0.855 − (0.032 − 0.001) = 0.824 g.

Repeating the foregoing it is found that: 0.014/23 × 0.824 = 0.50 mmol. sodium remained in the exchanger, or, 1.42 mmol. left the solid. The weight of the equilibrium exchanger from the second approximation then is: 0.855 − (0.033 − 0.001) = 0.823 g. One approximation, therefore, sufficed to give the equilibrium mass. When the two exchanging ions differ widely in atomic weight, two approximations may be necessary.

Exchange Adsorption of the Alkali Metal Cations.—The equilibrium constants for a number of monovalent ion systems were obtained for systems of constant ionic strength ($\mu = 0.1$) in which one of the exchanging ions was maintained at micro-concentration levels. The adsorption of the microcomponent was determined by means of radioactive isotope techniques with the results shown in Table V. Here, the designation of a system as $A^+ + BR$ means that A^+ was the microcomponent whose adsorption was followed by an appropriate radioisotope, and B was the macrocomponent, present as the chloride at an equilibrium concentration of 0.1 or 0.001 *M*, respectively.

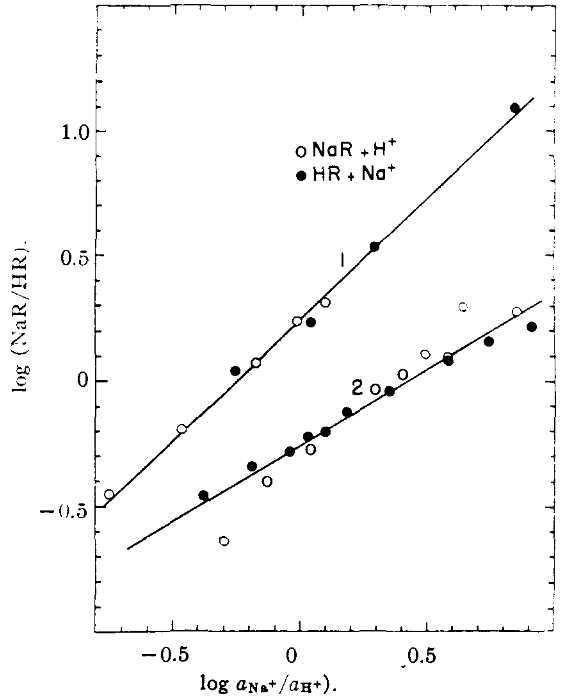

Fig. 3.—The exchange adsorption of sodium and hydrogen ions on Amberlite IR-1 (curve 1) and Zeocarb (curve 2); data for curve 2 from ref. 15.

With the exception of the data on the $Na^+ + HR$ exchange systems, the agreement shown by Table V between the values of K_c determined at 0.1 and 0.001 *M* can be regarded as satisfactory. Owing, however, to the very great interference caused by traces of polyvalent cation impurities in the distilled water used to prepare the more dilute solutions, the results from the latter experiments are regarded as somewhat less reliable than those found with the more concentrated alkali metal cation solutions. Accordingly, in our discussion of these data the equilibrium constant values for the 0.1 *M* solutions will be employed. Although values of K_c, the concentration product ratio, are given in Table V, actually these approximate the thermodynamic equilibrium constants quite closely. The activity coefficient corrections in the case of the 0.1 *M* solutions result in less than a 5% lowering of the K_c values listed; with the 0.001 *M* solutions this correction is negligible, and the values given would be superior for the estimation of ΔF^0 were it not for the experimental uncertainties mentioned.

Sodium–Barium Exchange.—In the exchange adsorption of sodium ion by the barium zeolite or of barium ion by the sodium zeolite the equilibrium may be described by

$$Ba^{++} + 2NaR = BaR + 2Na^+$$

TABLE IV[a]

EXPERIMENTAL DATA FOR IR-1 FOR THE REACTION $Na^+ + HR \rightleftharpoons NaR + H^+$

(All concentrations given in moles/liter × 10^3)

					Initial concentrations by analysis				Final concentrations by analysis			
Sample	Cation in solid	Air-dried resin, g.	Resin on oven-dry basis, g.	Solution, ml.	Na^+	H^+	NaR	HR calcd. from NaR assuming equiv exch.	Na^+	H^+	NaR	HR calcd. from NaR by diff.
1	Na^+	1.000	0.855	100	0	94.0	19.16	0	14.2	79.5	5.0	14.2
2	Na^+	2.000	1.710	100	0	94.0	38.32	0	23.7	69.0	14.9	23.4
3	Na^+	4.000	3.420	100	0	94.0	76.64	0	37.8	56.5	41.7	34.9
4	Na^+	6.000	5.130	100	0	94.0	115.0	0	46.9	48.5	73.0	42.0
5	Na^+	8.000	6.840	100	0	94.0	153.3	0	53.4	42.0	103	50.2
7	H^+	2.000	1.545	100	89.9	0	0	36.3	59.0	30.0	28.2	8.1
8	H^+	4.000	3.090	100	89.9	0	0	72.6	43.2	48.0	45.9	26.7
9	H^+	6.000	4.635	100	89.9	0	0	109	32.8	59.5	57.0	52.0
10	H^+	6.000	4.635	100	1070	0	0	109	972	107	101	8.0

where, by Equation (20)

$$K_a = \frac{(n_{NaR} + n_{BaR})(n_{BaR})}{(n_{NaR})^2}\left(\frac{m^2_{Na^+}}{m_{Ba^{++}}}\right)\left(\frac{\gamma^4_{\pm NaCl}}{\gamma^3_{\pm BaCl_2}}\right) = K_c\left(\frac{\gamma^4_{\pm NaCl}}{\gamma^3_{\pm BaCl_2}}\right) \quad (24)$$

As may be seen from Fig. 4 the exchange adsorption apparently obeyed Equation (24), which assumes the formation of ideal solid solutions over the range investigated. There was indication of a slight although real hysteresis in the equilibrium. The average value of log K_a may be taken from Fig. 4 as 1.07 or K_a = 11.8.

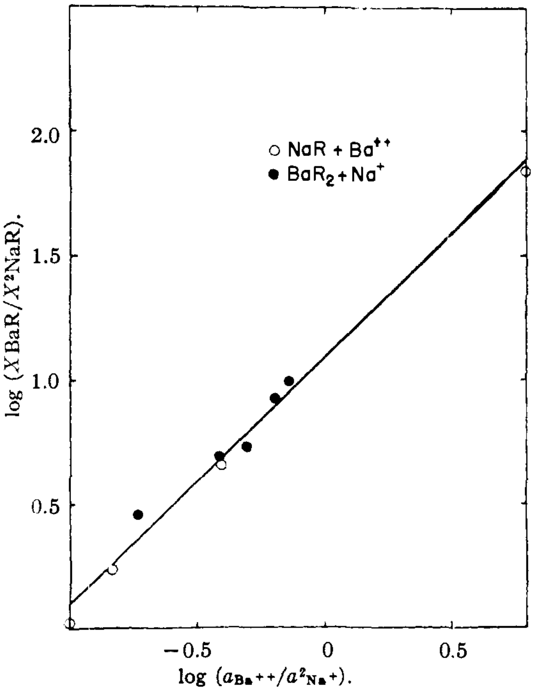

Fig. 4.—The exchange adsorption of barium and sodium ions on Amberlite IR-1.

Sodium–Lanthanum Exchange.—Preliminary experiments were performed on the exchange of sodium ion with lanthanum zeolite. This reaction may be written.

$$La^{+3} + 3\,NaR = LaR + 3\,Na^+$$

whence

$$K_a = K_c \times \gamma^6_{\pm NaCl}/\gamma^4_{\pm LaCl_3} \quad (25)$$

where

$$K_c = (n_{LaR})(n_{LaR} + n_{NaR})^2/(n_{NaR})^3 \times m_{Na^+}/m_{La^{+++}}$$

Owing to analytical difficulties, it was not possible to obtain values for the exchange constant when lanthanum ion was allowed to react with the sodium form of the adsorbent. However, when equilibrium was approached using the lanthanum form, an average value of K_a = 16.2 ± 1.1 was found.

Small errors in the analytical determinations of the concentrations in both solution and solid may be seen by Equation (25) to produce an appreciable uncertainty in the computed value of the equilibrium constant. Since the equilibrium concentrations in this particular exchange system were quite small, the K_a value reported must be considered as approximate. Further, the mole fraction of LaR in the adsorbent varied only from 0.69 to 0.79, which was too small a range for the detection of any deviations from ideality in the solid solutions formed.

Qualitatively, the values of K_a observed when the adsorbent was initially in the sodium form were much smaller than the average value given above. The magnitude of this hysteresis appeared to be appreciably greater than that encountered in the Ba^{++} + NaR exchange system.

The Variation of Adsorption with Temperature.—A preliminary determination of the magnitude of the variation of exchange adsorption with temperature was carried out in the case of the equilibrium

$$Na^+ + KR = NaR + K^+$$

with the results presented in Table VI

Evidently, the enthalpy of adsorption is either zero or very small in the neighborhood of room temperatures as might be expected for the ex-

TABLE IV (*Continued*)

Ionic strength, μ	Activity coefficient ratio, $\frac{\gamma^2 \pm \text{HCl}}{\gamma^2 \pm \text{NaCl}}$	pH of solution at equil.	Equil. const.		Mole fractions		Na in oven-dried resin at equil., %	Oven-dried resin cor. for exchange, g.	Material balance	
			K_0	K_a	NaR	HR			Final	Initial
0.094	1.0	1.12	1.97	1.97	0.26	0.74	1.40	0.823	113	113
.093	1.0	1.18	1.86	1.86	.39	.61	2.06	1.658	132	131
.094	1.0	1.28	1.79	1.79	.55	.45	2.87	3.346	171	171
.095	1.0	1.35	1.81	1.81	.64	.36	3.34	5.04	209	210
.095	1.0	1.40	1.63	1.63	.67	.33	3.53	6.73	247	249
.089	1.0	1.55	1.77	1.77	.78	.22	4.04	1.605	126	125
.091	1.0	1.33	1.91	1.91	.63	.37	3.31	3.192	163	164
.092	1.0	1.23	1.99	1.99	.52	.48	2.75	4.757	199	201
1.08	1.33	0.84	1.39	1.85	.93	.07	4.77	4.85	1179	1188

[a] Sodium resin contained 2.24 milliequivalents of sodium per gram of oven-dry NaR, from analysis of ash. Assuming equivalent exchange, hydrogen resin contained 2.35 milliequivalents of exchangeable hydrogen per gram oven-dry HR. The air dried NaR contained 14.5% moisture, and air-dried HR contained 22.8% moisture. The solution was analyzed for sodium by precipitation of sodium–magnesium uranyl acetate from an aliquot of the original solution while HCl was found by titration with standard base. The resins were prepared for analysis by dry ashing of a given amount and dissolving the residue with hydrochloric acid. The ash content of the HR was 0.052%.

TABLE V

EXCHANGE OF MONOVALENT CATIONS AT 30°

System	Initial solution concentrations		K_0
	Macrocomponent, M	Microcomponent, $M \times 10^5$	
$Na^+ + HR$	0.100	8.0	1.65
$Na^+ + LiR$	.0904	8.0	1.51
$Na^+ + NaR$	.0992	0.1	1.00
$Na^+ + NH_4R$	.1005	9.5	0.86
$Na^+ + KR$	.111	8.0	0.70
$Rb^+ + KR$	.0982	5.0	1.15
$Cs^+ + KR$	.0982	5.0	1.74
$Na^+ + HR$	10.0×10^{-4}	6.58	1.40
$Na^+ + LiR$	9.04	6.58	1.72
$Na^+ + NaR$	9.92	0.1	1.00
$Na^+ + NH_4R$	10.0	9.5	0.79
$Na^+ + KR$	9.82	8.0	0.62
$Rb^+ + KR$	9.92	5.0	1.37
$Cs^+ + KR$	9.82	5.1	1.88

TABLE VI

TEMPERATURE COEFFICIENTS FOR THE $Na^+ + KR$ SYSTEM

Mesh size of adsorbent, 60–70; NaCl concentration, 8×10^{-5} M

KCl, M	T, °C.	K	ΔH, kcal./mole
0.111	30.0	0.70	2 ± 2
0.0982	13.5	.58	
9.82×10^{-4}	30.0	.62	0 ± 2
9.82×10^{-4}	20.5	.63	

change of such very similar cations as sodium and potassium.

Discussion

To facilitate the intercomparison of the experimentally determined mass law constants the following treatment was applied: First, each exchange reaction was resolved into its respective pair of "half-reactions"; next, the equilibrium constant of the half-reaction for the formation of the hydrogen organolite, $H^+ + R^- = HR$, was taken arbitrarily as unity; then, a set of self-consistent relative equilibrium constants, $K_{rel.}$, and standard free energies of formation, ΔF^0_{MR} for each metallic organolite was computed. The first three columns of Table VII list the derived information. One by-product from systematizing the experimental data in this way is that in principle quantitative information about a much larger number of exchange reactions may be obtained merely by the addition of their component half-reactions.

A comparison of the free energies of organolite formation for the ions of cesium, barium and lanthanum, which are roughly of the same size and also possess the electron structure of xenon, reveals the primary role of ionic charge in determining base exchange adsorption. Within a series of constant charge and analogous electronic configuration, ionic size appears as the decisive factor. This is illustrated in the table by the alkali metal cations, and by the trivalent rare earth ions of lanthanum and yttrium. The existence of such a lyotropic series has been recognized in the colloid sciences for many years. Base exchange measurements on clays and mineral zeolites have given approximately the same adsorption series as found here with the resinous exchangers, excepting for the position of hydrogen ion. Since charge exerts a dominant influence in the exchange adsorption of ions from aqueous solutions, the phenomenon must be controlled largely by electrostatic forces, presumably coulombic in nature. According to this view, adsorbability would then increase with a decrease in ionic radius, and on this basis, if crystal radii are used, lithium would be more strongly

Table VII

Correlation of Equilibrium Data

Reaction	$K_{rel.}$	$-\Delta F^0_{MR}$ (298.1°) cal./mole	Ion	Crystal ionic radii after Goldschmidt	$-\Delta F^0_{Hyd.}$, kcal./mole	Distance of closest approach a^0(Å.)	Ref.
$H^+ + R^- = HR$	1.00	0	H^+	..	...	5.6	[a]
$Li^+ + R = LiR$	0.91	−60	Li^+	0.78	114.6	6.9	[b]
$Na^+ + R^- = NaR$	1.71	320	Na^+	0.98	89.7	5.2	[c]
$NH_4^+ + R^- = NH_4R$	1.99	410	NH_4^+	..	...	4.5	[b]
$K^+ + R^- = KR$	2.44	530	K^+	1.33	73.5	4.1	[d]
$Rb^+ + R^- = RbR$	2.81	615	Rb^+	1.49	67.5	3.2	[a]
$Cs^+ + R^- = CsR$	4.24	860	Cs^+	1.65	60.8	2.6	[e]
$Ba^{++} + R^= = BaR$	15.5	1680	Ba^{++}	1.43	...	...	.
$Y^{+++} + R^≡ = YR$	21.8	1830	Y^{+++}	1.06	...	...	.
$La^{+++} + R^≡ = LaR$	34.8	2110	La^{+++}	1.22	...	3.9	[f]

[a] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943. [b] W. M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, New York, N. Y., 1938. [c] A. S. Brown and D. A. MacInnes, This Journal, 57, 1357 (1935). [d] T. Shedlovsky and D. A. MacInnes, *ibid.*, 59, 503 (1937). [e] H. S. Harned and O. E. Schupp, *ibid.*, 52, 3886 (1930). [f] T. Shedlovsky and D. A. MacInnes, *ibid.*, 61, 200 (1939).

adsorbed than cesium ion. That such is not the case may be seen immediately from Table VII. In fact, a comparison with the energies of hydration of the gaseous ions reported by Latimer, Pitzer and Slansky[19] shows that the smaller the free energy of hydration the greater the adsorption. A correlation of the adsorption of ions by colloidal aluminum silicates with the hydrated ionic radii at infinite dilution derived from hydrodynamic data has been described by Jenny.[20]

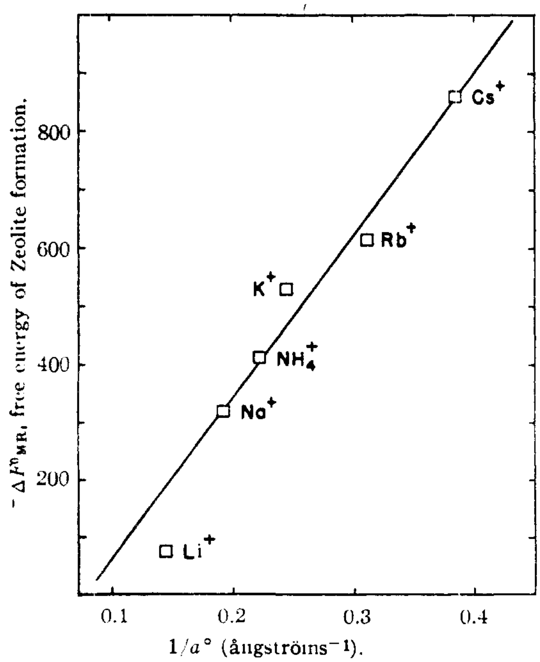

Fig. 5.—Correlation of free energy of zeolite formation with the Debye–Hückel parameter a^0.

Alternatively, the distance of closest approach, a^0, given in the relation

$$\log \gamma_{\pm} = -A\sqrt{\mu}/(1 + Ba^0\sqrt{\mu}) \qquad (26)$$

may be chosen as an index of ionic hydration. Numerical estimates of this parameter given in Table VII were computed from the indicated experimental activity coefficient data for metal chlorides using Equation (26) with the values: 0.505, 1.74, and 3.71; and 0.330, 0.570, and 0.805 for 1–1, 2–1, and 3–1 salts, respectively, for A and B.[21] It is believed this extension of the Debye–Hückel theory applies satisfactorily to the concentration range over which the adsorption measurements were performed. Little significance can be attributed to the absolute numerical values of a^0 since they may vary with the type of equation used, of which there are several. On the basis of the foregoing considerations, a relationship of the type, $-\Delta F^0_{MR} \backsimeq Ne^2/2a^0$, might be expected between the standard free energy of zeolite formation, ΔF^0_{MR}, and the parameter a^0. The plot shown in Fig. 5 may serve to confirm this hypothesis, although the position of lithium ion is admittedly anomalous.

If values of $1/a^0$ are accepted as an empirical guide to the adsorption affinity of ions, either positive or negative, which participate in base exchange reactions, it becomes possible to use activity coefficient data to predict the relative adsorbability of ions of the same charge. Actually, a ready qualitative evaluation of the relative magnitudes of a^0 may be found directly from activity coefficient–concentration plots. The higher these curves lie in the plot, the larger the magnitude of a^0. Accordingly, from activity coefficient data the sequence of adsorption among the alkaline earth cations will be: $Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}$; whereas with the divalent ions of the transition metals the series will be: $Zn^{++} > Cu^{++} > Ni^{++} > Co^{++} > Fe^{++}$. The activity

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(19) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939); see also E. J. W. Verwey, *Rec. trav. chim. Pay-Bas*, **61**, 127 (1942).

(20) H. Jenny, *J. Phys. Chem.*, **36**, 2217 (1932); see also G. Wiegner, *Kolloid Z.*, **36**, 341 (1925) (Ergänzungsband).

(21) Reference 12, pp. 379 ff.

coefficient plots for the rare earths, using the data of C. M. Mason,[22] all lie very close to each other. Even so, it is possible to predict the following series of decreasing adsorbability: $\mathrm{La}^{+++} > \mathrm{Ce}^{+++} > \mathrm{Pr}^{+++} > \mathrm{Nd}^{+++} > \mathrm{Sm}^{+++} > \mathrm{Eu}^{+++} > \mathrm{Y}^{+++} > \mathrm{Sc}^{+++} > \mathrm{Al}^{+++}$ for the trivalent ions of the third group of the Periodic Table. In general, the lyotropic series for monovalent and divalent cations recorded in the literature for various base exchange materials are in accord with expectations based on relative a^0 values. It is realized that an over-simplified picture of the nature of the adsorption affinity has been presented. Almost certainly the electronic structure of the ion must be a factor. On the other hand, a given value of a^0 is itself the resultant of a variety of complex interactions.

To a first approximation, then, the exchange adsorption of cations from strong electrolytes is governed by the magnitudes of their charges and by the radii of their hydrated ions. An important exception, however, may arise in the case of the adsorption of hydrogen ion, which apparently can be taken up as H_3O^+ or simply as H^+ depending upon the strength of the acid of the base exchanger. With the synthetic resinous exchangers where either structurally incorporated methylene or nuclear sulfonic acids are responsible for the adsorptive properties, hydrogen ion is one of the most weakly adsorbed of all cations in sharp contrast with clays, proteins and many other substances. Since hydrogen ion in solution is probably the most strongly hydrated of all singly charged ions, it is logical to suppose that the species adsorbed by the synthetic ion-exchanger is the stable hydronium ion, H_3O^+. With naturally occurring base exchangers both organic and inorganic where the adsorptive property derives from the presence of weak organic acids as —COOH, or very weak inorganic acids as H_2SiO_3, H_3AlO_3, etc., hydrogen ion is invariably one of the most strongly adsorbed cations. In this latter case, it seems probable that the ion is nearly completely dehydrated and hence adsorbed as H^+. According to this hypothesis the irregular position of H^+ ion in the lyotropic series is an expression of the varying acidity of the structurally bound anionic groups responsible for base-exchange.

For purposes of intercomparison in Table VII, the free energy of formation of the hydrogen organolite, HR, was set equal to zero. Such a choice is not altogether unreasonable, for it will be remembered that HR in this case is the strong acid, —CH_2SO_3H, which doubtless is ionized extensively. On the other hand, since the anionic groups are structurally bound and hence non-diffusible, only a small fraction (*ca.* 5%) of these hydrogen ions will be free to pass from the adsorbent into the body of an aqueous solution.

Although accurate data for the enthalpy change, ΔH, in ionic exchange adsorption are not as yet available, preliminary results suggest this to be small, in which case the entropy change must be taken to play an important role in the adsorption. Assuming the cations to be adsorbed in a hydrated condition (see Table II), the exchange of equally charged species must be accompanied by a change in the number of water molecules in the adsorbent. According to Table VII, ions of smaller hydration displace those of higher hydration, or entropy, so that an over-all entropy *decrease* occurs.

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Summary

1. The equations describing base-exchange reactions may be formulated either on the basis of an adsorption mechanism or according to the law of mass action. These relations can be shown to be formally equivalent.

2. Results from experimental measurements of the standard free energy of formation, ΔF^0_{MR} of the metallic zeolite salt gave the following order of adsorption affinity: $\mathrm{La}^{+++} > \mathrm{Y}^{+++} \gg \mathrm{Ba}^{++} \gg \mathrm{Cs}^{+} > \mathrm{Rb}^{+} > \mathrm{K}^{+} > \mathrm{Na}^{+} > \mathrm{H}^{+} > \mathrm{Li}^{+}$.

3. Adsorption affinities were shown to be determined chiefly by the magnitude of the charge and the hydrated radius of the ions in solution.

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[22] C. M. Mason, THIS JOURNAL, **60**, 1638 (1938); **63**, 220 (1941).