0.33 g. of clear sirup which crystallized spontaneously. Its rotation was $[\alpha]^{20}\text{D}$ 83.8° (*c*, 1.05, chloroform). Two recrystallizations from 2-propanol gave almost pure α-D-glucose pentaacetate, m.p. 108°, mixed m.p. 109–111°.

Pentaacetyl-1-thio-β-D-glucose.—Tetraacetyl-α-D-glucosyl bromide (4.11 g.) in chloroform (30 ml.) was treated with a mixture of potassium hydroxide (0.62 g., 10% excess) and thioacetic acid (0.9 ml., 10% excess) in ethanol (5 ml.). The solution was refluxed for 30 minutes, cooled and the potassium bromide (0.95 g.) filtered. The filtrate was washed as usual, dried and evaporated to give 3.92 g. of crude, amber, sirup. This was crystallized, with Norit decolorization, from a mixture of 2-propanol and petroleum ether to give white needles, m.p. 116–117°. After two further recrystallizations from 2-propanol the product had m.p. 118° and $[\alpha]^{21}\text{D}$ 10.7° (*c*, 1.496, chloroform).

Anal. Calcd. for $C_{16}H_{22}O_{10}S$: C, 47.40; H, 5.47; S, 7.89. Found: C, 47.27, 47.34; H, 5.49, 5.41; S, 7.88, 7.83.

This product, prepared by more cumbersome methods, has been previously reported[18] to have m.p. 120° or 121° and $[\alpha]^{22}\text{D}$ 10.17° (tetrachloroethane).

Reductive Desulfurization of Pentaacetyl-1-thio-β-D-glucose.—Pentaacetyl-1-thio-β-D-glucose (2.5 g.) was refluxed in absolute ethanol (*ca.* 40 ml.) containing Raney nickel (*ca.* 15 g.) for 3.5 hours. The mixture was cooled, filtered (Celite), and evaporated in an air stream to a volume of several ml. The residue was dissolved in ether, and the solution washed with water, dried over anhydrous sodium sulfate, filtered and the solvent distilled, leaving 1.38 g. (68%) of clear sirup. This was dissolved in a few ml. of dry ether, treated with isopentane to incipient turbidity, and seeded with tetraacetyl-1,5-anhydro-D-glucitol.[19] On standing at 0° the solution produced 0.70 g. of white needles, m.p. 68–69°. These were recrystallized from the same solvent mixture to produce a sample of m.p. 72.5°. This had $[\alpha]^{21}\text{D}$ 38.8° (*c*, 0.567, chloroform), and showed no mixed melting point depression with authentic tetraacetyl-1,5-anhydro-D-glucitol.[19]

Acetyl Sulfide, Sulfuric Acid and β-D-Glucose Pentaacetate.—Acetyl sulfide[20] (5 ml.) was treated with sulfuric acid (0.5 ml.) and the mixture, smelling somewhat of sulfur dioxide, filtered through Celite. β-D-Glucose pentaacetate (1.00 g.) was dissolved in acetyl sulfide (5 ml.), and the two solutions mixed. No significant change in the rotation of the mixture was noticed during 18 hours. The mixture was accordingly heated on the steam-bath for 20 hours. The dark solution was cooled, neutralized with sodium hydroxide solution, and steam distilled. On cooling, the residue (*ca.* 100 ml.) deposited 0.70 g. of yellow solid, m.p. 128–130°. After two recrystallizations from 2-propanol, the product had m.p. 131°, and showed no mixed m.p. depression with the starting material.

Acetic Anhydride, Sulfuric Acid and Pentaacetyl-1-thio-β-D-glucose.—Pentaacetyl-1-thio-β-D-glucose (1.00 g.) in acetic anhydride (10 ml.) containing sulfuric acid (0.3 ml.) gave a solution whose rotation changed only from 0.87 to 0.98° in 8.5 hours in a one decimeter tube. The solution was poured into water, extracted with ether, and processed as usual to give 0.70 g. of starting material, m.p. and mixed m.p. 118°.

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[18] Vogel and George, "Tabellen der Zucker und Ihrer Derivate," Julius Springer, Berlin, 1943, p. 252.

[19] The seed was obtained through the kindness of Dr. H. G. Fletcher, Jr.

[20] Bonner, THIS JOURNAL, **72**, 4270 (1950).

STANFORD, CALIFORNIA RECEIVED JULY 10, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Studies of Cation-exchange Equilibrium on a Synthetic Resin[1,2]

BY WARREN K. LOWEN, RAYMOND W. STOENNER, WILLIAM J. ARGERSINGER, JR., ARTHUR W. DAVIDSON AND DAVID N. HUME

Eight exchange systems on Dowex 50 have been investigated, involving the ions Na^+, H^+, NH_4^+, Ag^+, Tl^+, Ni^{++} and Ca^{++} in solutions of total ionic strength of approximately unity. Equivalence of exchange, as ordinarily understood, is not obtained in these systems. The apparent discrepancies between the decrease in concentration of one ion in the solution and the increase in concentration of another almost certainly arise mainly from the absorption of water by the resin. In certain systems, especially those involving either silver or thallous ion, adsorption of electrolyte by the resin occurs also.

The effect of the nature of the anion in solution on the exchange equilibrium has been found to be negligible, and hysteretic effects, in all but a very few cases, are only apparent. In every exchange system studied, the apparent equilibrium constant has been found to vary regularly with the equilibrium resin composition. Since the error involved in the assumption of constant activity coefficient ratios in the aqueous solution is presumably slight, it is concluded from this variation in equilibrium quotient that the common assumption of ideal solid solution behavior in the resin phase must be invalid.

Introduction

Although attempts have been made to formulate heterogeneous cation-exchange equilibria in terms both of the Langmuir adsorption mechanism[3] and of the Donnan membrane equilibrium,[4] the most fruitful theoretical treatments of such equilibria have been those based upon the application of the law of chemical equilibrium to the exchange, regarded as a simple metathetical reaction.[3-7]

Thus, in the simplest case, when both of the cations are univalent, let us consider the reaction to be that represented by the equation

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

where A^+ and B^+ are the cations involved in the exchange and R represents the active anionic portion of the insoluble resin. From a purely thermodynamic viewpoint, then, and regardless of the structure of the resin, the following equation should be applicable

$$\frac{a_{B^+}a_{AR}}{a_{A^+}a_{BR}} = K_a \qquad (1)$$

where a_{A^+}, a_{B^+}, a_{AR} and a_{BR} are the activities of the respective ions in the solution and of the two resin

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[1] Abstracted from independent Ph.D. theses by W. K. Lowen and R. W. Stoenner, University of Kansas, 1949. This material was presented at the 115th Meeting of the American Chemical Society, April, 1949, and is contained also in a report to the Office of Naval Research, NR057158, August, 1950.

[2] For detailed tables of data supplementary to this article, order Document 3122 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $2.25 for photocopies (6 × 8 inches) readable without optical aid.

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

[4] W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

[5] W. Juda and M. Carron, *ibid.*, **70**, 3295 (1948).

[6] J. F. Duncan and B. A. J. Lister, *J. Chem. Soc.*, 3285 (1949).

[7] J. A. Marinsky, *Technical Report*, NR26001 (1949).

components when equilibrium has been attained, and K_a, the activity quotient, must by definition be constant at a fixed temperature regardless of the initial concentrations. This relationship may alternatively be expressed by the equation

$$\frac{c_{B^+}\gamma_{B^+}a_{AR}}{c_{A^+}\gamma_{A^+}a_{BR}} = K_a \tag{2}$$

where c and γ represent the molarity and the molar activity coefficient of an ion; or better, if the cations are present in solution together with the anion X^-

$$\frac{c_{B^+}\gamma^2_{\pm BX}a_{AR}}{c_{A^+}\gamma^2_{\pm AX}a_{BR}} = K_a \tag{3}$$

where $\gamma_\pm$ represents the mean activity coefficient of the electrolyte in question.

The activity coefficients of the individual electrolytes in mixed solutions are, at least in principle, determinable by experiment, although their actual values are known only in relatively few instances. On the other hand, although there appears to be ample evidence to indicate that AR and BR are to be regarded not as independent solid phases but rather as completely miscible components of a solid solution,[8] no direct method for the determination of the activities of these components is available. It has sometimes been assumed[9] that this solid solution is ideal, so that the activity of each component may be identified with its mole fraction. This assumption, of course, may not be valid, and it has been suggested[10] that the activity coefficient, f, of each resin component ($f = a/N$, where N is the mole fraction of the component in the resin) may vary with composition according to a single term Margules equation.

If the activity coefficients of the resin components are included in the expression for the thermodynamic equilibrium constant, equation (3) becomes

$$\frac{c_{B^+}\gamma^2_{\pm BX}N_{AR}f_{AR}}{c_A\gamma^2_{\pm AX}N_{BR}f_{BR}} = K_a \tag{4}$$

A point which, it seems to the authors, has not previously been sufficiently stressed is that the constancy of K_a in equation (4) is a mathematical necessity, consequent upon the definition of the several activities. Hence, provided the activity coefficients of the electrolytes AX and BX in the mixed aqueous solution are known, the constancy of K_a might be utilized for the determination of the ratio f_{AR}/f_{BR} for resins of varying composition.

It has been assumed by most workers in this field that the *over-all* process occurring when a sample of an ion-exchange resin is immersed in a solution of electrolytes can be formulated in terms of simple equivalent exchange; that is, one equivalent of B^+ has usually been supposed to enter the solution from the resin for every equivalent of A^+ that enters the resin from the solution (the volume of solution remaining constant), so that the concentrations of both ions in the equilibrium solution (as well as the equilibrium composition of the resin) can be determined from a knowledge of the original concentrations and analysis of the final solution for one of the cations only. In some of the most recent studies[4,6,7] the possibility of over-all non-equivalence of exchange has indeed been mentioned, although in the opinion of the present authors it has hardly been given sufficient consideration. Duncan and Lister mention the possible adsorption of non-exchanged material on the surface of the resin, but in their calculations assume equivalence of exchange. Marinsky presents evidence purporting to show that exchange takes place on an equivalent basis, at least under the conditions used in his experiments. In the present investigations, however, considerable departure from over-all equivalence was observed in almost every instance, and the composition of the equilibrium solution was always determined by means of an independent analysis for each of the cations. A hypothesis in terms of which this non-equivalence of exchange may be accounted for will be presented later in this paper.

Experimental Methods

Preliminary Experiments.—All of the experimental work to be described here was carried out on the resin known as Dowex 50,[11,12] which proved to be satisfactorily resistant toward hydrolysis and oxidation. No sulfate ion could ever be detected in the solutions resulting either from the washing of any form of the resin with distilled water or from its subjection to an exchange reaction. Nitric acid (1 molar) and saturated silver nitrate solution were found to have no oxidizing action upon the resin.

The sample of Dowex 50 (largely in the sodium form) obtained from the manufacturer was visibly heterogeneous, consisting of particles varying in color from light amber to dark brown; the density of the particles increased with increasing intensity of color. A portion of this commercial sample was completely converted to the sodium form by treatment with saturated sodium chloride solution, and the product was separated into a light- and a dark-colored fraction by flotation in a concentrated solution of sodium bromide. After each of these fractions had been washed free of sodium bromide, they were dried simultaneously over phosphorus pentoxide in the same desiccator. A weighed portion of each fraction was then decomposed by means of concentrated sulfuric acid, in the presence of a few tenths of a gram of metallic selenium as catalyst. After evaporation of the solution to dryness and retreatment with concentrated sulfuric acid, the dry residue, now consisting of pure sodium sulfate, was weighed. In this manner it was found that the dried lighter particles contained 8.57%, the darker ones 8.93% of sodium. However, since a complete separation of the resin into perfectly uniform fractions would not have been practicable, and since it was the purpose of the investigation to study the properties of the commercial resin as such, all further studies were carried out upon the thoroughly mixed product consisting of the 16–28 mesh screening fractions.

General Method.—For the study of each exchange reaction, two "pure" resins were prepared, one containing each of the cations involved in the exchange. These resins were dried in a vacuum desiccator over phosphorus pentoxide at room temperature. No attempt was made, however, to attain any specified moisture content. Instead, in each case, the number of grams of partially dried resin containing one gram-equivalent of exchangeable cation was designated as the equivalent weight of the resin. The equivalent weight of each resin, as thus defined, was determined by an appropriate method to be described below. In the exchange experiments, weighed samples (usually of about 4 g.) of the resins to be studied were placed in ground-glass stoppered flasks in contact with 100-ml. portions of a series of accurately analyzed aqueous solutions of appropriate salts of the two cations involved, in varying proportions but at a constant total ionic strength of 1 molar.[13] The attainment of

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[8] Ref. 3, p. 2831.

[9] *Ibid.*, p. 2824.

[10] J. Kielland, *J. Soc. Ind. Chem. Ind.*, **54**, 232T (1935),

[11] Supplied by courtesy of the Dow Chemical Company.

[12] For a discussion of the physical structure and chemical composition of this resin, see ref. 4, p. 2830.

[13] When the two cations were not of the same valence, it was necessary to adjust the initial concentrations in such manner that the total ionic strength of the *equilibrium* solution might be approximately equal to unity.

equilibrium was hastened by agitation on a mechanical shaker, which was immersed in a constant temperature bath maintained at 25.0 ± 0.2°; equilibrium was reached, in every case, within two hours. The equilibrium composition of the aqueous solution was then determined by means of analysis for each of the cations, and the equilibrium composition of the solid phase was calculated, by methods to be described, from the changes in concentration which had occurred in the solution.

Hydrogen Resin.—The pure hydrogen form of Dowex 50 was prepared by passing hydrochloric acid of constant boiling point, under a reflux condenser, through the screened commercial product in a column 5 cm. in diameter and 70 cm. in height. This treatment was continued until the effluent solution gave no further flame test for sodium ion. The product was then washed with distilled water until the washings showed only a negligible content of chloride ion, and dried as described above. In order to determine the equivalent weight of the dried resin, a weighed quantity was allowed to stand in contact with saturated sodium chloride solution, and the course of the exchange was followed by means of *p*H measurements with a glass electrode. When equilibrium had been reached, the liberated hydrogen ion in the salt solution was titrated with standard sodium hydroxide solution. The mixture was then again allowed to stand until a new equilibrium had been attained, whereupon the titration was repeated. This process of alternate equilibration and titration was continued until the *p*H of the effluent remained constant at 6.0.

In equilibrium solutions resulting from exchange reactions, the concentration of hydrogen ion was determined by titration with sodium hydroxide solution.

Sodium Resin.—The pure sodium resin was obtained by maintaining a portion of the hydrogen form in contact with a large excess of saturated sodium chloride solution for two hours. Sodium hydroxide solution was intermittently added to bring the *p*H of the solution up to that of a saturated sodium chloride solution, where it eventually remained constant. The equivalent weight of the washed and dried resin was determined by decomposition of a weighed sample with concentrated sulfuric acid and weighing of the resulting sodium sulfate, as already described.

The sodium ion in equilibrium solutions was determined also as sulfate after evaporation with sulfuric acid.

Ammonium Resin.—Pure ammonium resin was prepared from the hydrogen form in an exactly analogous manner. The equivalent weight was determined by exhaustive exchange of a weighed quantity of the resin with saturated sodium chloride solution. Pellets of sodium hydroxide were added to the resulting solution, and the ammonia formed was distilled into a measured volume of standard acid. After all of the liberated ammonia had been collected, the excess acid was titrated with sodium hydroxide solution.

The concentration of ammonium ion in equilibrium solutions was likewise determined by the liberation of ammonia with sodium hydroxide, and its distillation into standard acid.

Silver Resin.—Hydrogen resin was placed in the column previously described, and 1 molar silver nitrate solution was passed through it. The effluent solution was neutralized by vigorous agitation with an excess of freshly prepared silver oxide, filtered, and again used as influent. Conversion to silver resin was regarded as complete when the *p*H of the effluent solution showed only a negligible decrease from that of the influent. The equivalent weight of the silver resin was determined by exhaustive exchange with saturated sodium nitrate solution. An aliquot portion of the effluent solution was then titrated electrometrically with standard sodium chloride solution.

The concentration of silver ion in equilibrium solutions was likewise determined by electrometric titration with sodium chloride solution.

Thallous Resin.—Hydrogen resin was treated in the column with saturated thallous nitrate solution until the *p*H of the effluent solution remained constant. The equivalent weight of the thallous resin was determined by complete exchange with saturated sodium nitrate solution. An aliquot portion of the effluent solution was treated with hydrochloric acid to precipitate thallous chloride; the mixture was then titrated electrometrically with standard potassium bromate solution, the thallous chloride being oxidized to thallic. The concentration of thallous ion in equilibrium solutions was determined similarly by electrometric titration.

Nickel Resin.—Pure nickel resin was prepared by a method similar to that for the silver resin, the effluent being neutralized with nickel carbonate. Attempts to determine the equivalent weight of this resin by means of the replacement of nickel ion with sodium or calcium were unsuccessful because of the excessive amounts of salt solution required to bring about complete replacement. Instead, a weighed quantity of the resin was decomposed by treatment with concentrated sulfuric acid in the presence of selenium, and the nickel content of the residue was determined by precipitation with dimethylglyoxime.

The nickel content of equilibrium solutions was likewise determined by precipitation with dimethylglyoxime, except when calcium ion was also present in appreciable concentration. In this case, since the results of the conventional method were invalidated by coprecipitation, nickel was determined by electrolytic deposition on a platinum cathode.

Calcium Resin.—Pure calcium resin was prepared in an analogous manner. Because of the low solubility of calcium sulfate, digestion with concentrated sulfuric acid did not prove to be a satisfactory method for determining the equivalent weight of this resin. Instead, a weighed quantity of the resin was treated with 72% perchloric acid for 24 hr. at about 50°. The excess perchloric acid was then evaporated, and the residue of calcium perchlorate was dissolved in water. Calcium was determined by precipitation in the usual manner as oxalate; the precipitate was ignited at 600° in an atmosphere of carbon dioxide, and weighed as calcium carbonate.

The calcium content of equilibrium solutions was determined similarly by precipitation as oxalate from a strongly ammoniacal solution. However, when nickel ion was also present in appreciable concentration, it was necessary, in order to avoid errors from coprecipitation, to dissolve the precipitate of calcium oxalate in a small quantity of concentrated hydrochloric acid, and then to reprecipitate calcium oxalate by the addition of excess ammonium hydroxide.

Methods of Calculation

Equilibrium Composition of Resin.—The concentrations of the two exchanging cations in the equilibrium solution are given directly, in every case, by the experimental results, which, however, clearly indicate that the assumption—usually made in previous studies—of constancy of total concentration during the exchange process is altogether unwarranted. In almost every instance, the concentration of the solution is found to undergo an appreciable net increase during the exchange.[14] This phenomenon is believed to be due chiefly to the preferential absorption of water from the solution by the partially dried resin.[15] Since the resins used in the present work were never initially completely wet, and in fact in the several experiments had been dried to different degrees, each over-all process must have included, in addition to simple equivalent ion-exchange, absorption of variable amounts of water from the solution. Hence the decrease in solution volume resulting from such absorption must be taken into consideration in the calculation of the equilibrium composition of the resin. However, with the single almost certainly valid assumption of equivalence in the *primary* exchange process, both the water absorption and the equilibrium resin composition may be calculated with sufficient accuracy in the following manner.[16]

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[14] Such an increase might, perhaps, have been anticipated from the reported observation of Bauman and Eichhorn (ref. 4, p. 2831) that when the hydrogen form of the resin is immersed in hydrochloric acid, the chloride concentration in the external solution, when equilibrium is reached, is always found to be greater than in the solution within the resin particles, often in a ratio as great as 10:1. When dry acid resin was introduced into 1 molar hydrochloric acid, they observed a considerable increase in the chloride ion concentration of the external solution.

[15] For this explanation, we are greatly indebted to a suggestion contained in a private communication from W. C. Bauman (Feb. 23, 1949).

[16] To be entirely correct, one should include in the calculation the take-up of electrolyte by the resin, since assuredly at equilibrium the resin phase contains not pure water, but a solution of the mixed electrolytes. With the reasonable assumption, however, that the ratio of internal to external concentrations is the same for the two electrolytes, it may be shown that the final equations for the water absorption and resin composition are identical with those obtained by the simpler treatment outlined here.

Consider the simple uni-univalent exchange in which a quantity of pure B resin containing n^0 gram-equivalents is treated with the volume V^0 liters of a solution initially containing c_A^0 moles/liter of A^+ and c_B^0 moles/liter of B^+. Let the volume of the solution at equilibrium be V, and the experimentally determined equilibrium concentrations of A^+ and B^+ be c_A and c_B, respectively; further, let the number of equivalents of A resin and B resin at equilibrium be n_A and n_B, respectively, and their mole fractions be N_A and N_B. Three independent relations describing, respectively, the conservation of resin anion, A^+, and B^+ connect these quantities.

Conservation of resin anion $n^0 = n_A + n_B$

Conservation of A^+ $c_A^0 V^0 = n_A + c_A V$

Conservation of B^+ $n^0 + c_B^0 V^0 = n_B + c_B V$

These may be combined to yield the equations

$$n_A = \frac{c_A^0 c_B - c_A c_B^0}{c_A + c_B} V^0$$

$$n_B = n^0 - \frac{c_A^0 c_B - c_A c_B^0}{c_A + c_B} V^0$$

or, in terms of mole fractions in the resin phase

$$N_A = \frac{(c_A^0 c_B - c_A c_B^0) V^0}{(c_A + c_B) n^0}$$

$$N_B = 1 - \frac{(c_A^0 c_B - c_A c_B^0)}{(c_A + c_B) n^0} V^0$$

The absorption of water is determined approximately on the assumption of negligible density differences between the initial and final solutions, and is, therefore, on a volume basis, merely the difference $\delta V = V^0 - V$ in each experiment. The above equations may be solved to give the following expression for $\delta V/n^0$, the volume of water taken up per equivalent of resin

$$\delta V/n^0 = \frac{V^0}{n^0}\left(1 - \frac{c_A^0 + c_B^0}{c_A + c_B}\right)$$

Adsorption.—In all the exchanges involving either silver or thallous ion, it was found that the apparent non-equivalence of exchange could not be accounted for by the explanation already given. The apparent discrepancy was in general smaller, and decreased, changing sign, as the concentration of silver or thallous ion in the equilibrium solution increased. This behavior seemed to indicate adsorption of the cation by the resin in addition to simple exchange and water absorption. In order to calculate the equilibrium resin composition and the cation adsorption effect, exact equivalence was assumed in the primary exchange process, and it was further assumed that the water absorption by the resin, on a volume per equivalent of resin basis, was constant throughout a series of experiments with the same initial resin and varying compositions of the external solution. The value, W, of this water absorption was determined by the previous method of calculation as the mean for those runs in which the equilibrium solution was most dilute in the adsorbable ion, the ion adsorption there being supposed negligible. The pertinent conservation equations may again be solved to obtain the composition of the resin phase and the amount of cation adsorbed by the resin. For example, for the silver–hydrogen exchange process with pure hydrogen resin as initial exchanger, the results are

$$N_{AgRes} = \frac{c_H(V^0 - Wn^0) - c_H^0 V^0}{n^0}$$

$$E/n^0 = \frac{(c_{Ag}^0 + c_H^0)V^0 - (c_{Ag} + c_H)(V^0 - Wn^0)}{n^0}$$

in which N_{AgRes} is the mole fraction of silver resin at equilibrium, E/n^0 is the number of equivalents of silver adsorbed per equivalent of resin, and the other quantities have been previously defined. Similar expressions may be obtained for the exchange on pure silver resin, and for the analogous exchanges involving thallous ion.

Equilibrium Constant.—The activities which appear in the expression for the thermodynamic equilibrium constant K_a are not directly known. The "concentration equilibrium quotient" K_c is defined for a uni-univalent exchange by the expression

$$K_c = \frac{c_B N_A}{c_A N_B}$$

This approximate quotient is related to the true equilibrium constant by the equation

$$K_a = K_c \cdot \left(\frac{\gamma_{\pm BX}}{\gamma_{\pm AX}}\right)^2 \frac{f_A}{f_B}$$

The solution activity coefficient ratio, $(\gamma_{\pm BX}/\gamma_{\pm AX})^2$, in general, varies slowly with composition at constant total ionic strength. Experimental data, however, are available for but one of the systems studied, the sodium–hydrogen exchange. For the sake of uniformity, therefore, the ionic strength principle was extended in all cases to the ionic strength employed (1 molar), the ratio of activity coefficients being assumed constant for a given exchange system at constant total ionic strength, at a value calculated from the tables in Harned and Owen[17] for pure solutions of the two individual electrolytes. Thus for each exchange, all the K_a values have been calculated from the corresponding K_c values by multiplication by a constant factor.

The resin phase is assumed to behave as an ideal solid solution; or in other words, a value of unity has been assigned to each of the two activity coefficients f_A and f_B. The inadequacy of this assumption is believed to be the principal reason for the variation of the K_a values from constancy, the assumption of constant solution activity coefficient ratio introducing only a relatively minor error. Attempts to approximate these solid-phase activity coefficients by use of the Margules expansion, as described above, were only moderately successful, and hence were not made use of in the final reported results.[18]

In the figures and the discussion which follow, the convention has been adopted always to write the equilibrium constant expression for the A–B exchange with the mole fraction of A resin in the numerator. In other words, for example, sodium–hydrogen exchange refers specifically to the reaction

$$Na^+ + HRes = H^+ + NaRes$$

With this convention, the equilibrium constant gives directly a measure of the tendency of the first named ion in the exchange process to replace the second ion in the resin.

Results and Discussion

Exchanges between Univalent Ions.—In Fig. 1 are presented the data for all the sodium–hydrogen exchange experiments; the specific conditions for each set of exchanges are indicated in the legend. With varying composition of the equilibrium resin, the K_a values range from 1.4 to 2.4. Examination of the K_a values obtained in these five sets of experiments shows a maximum of 5% hysteresis (*i.e.*, divergence between results obtained from exchanges in opposite directions). Other workers[4,6,7] have reported K_a values of 1.20, 1.52 and 1.75 for solutions much more dilute than those used in the present work; direct comparison with these apparent values of the equilibrium constant, therefore, might be misleading. Our own values, however, are self-consistent; the agreement among all sets of experiments indicates that the effects both of recycling the resin and of varying the anion present in the solution are but slight. For a given pair of cations at a fixed ionic strength, the exchange equilibrium appears to be determined primarily by the state of the resin, rather than by its history. Complete validation of this conclusion

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(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

(18) The views stated in this paragraph are substantiated by work now in progress, in which the variation of the solution activity coefficient ratio is explictly included.

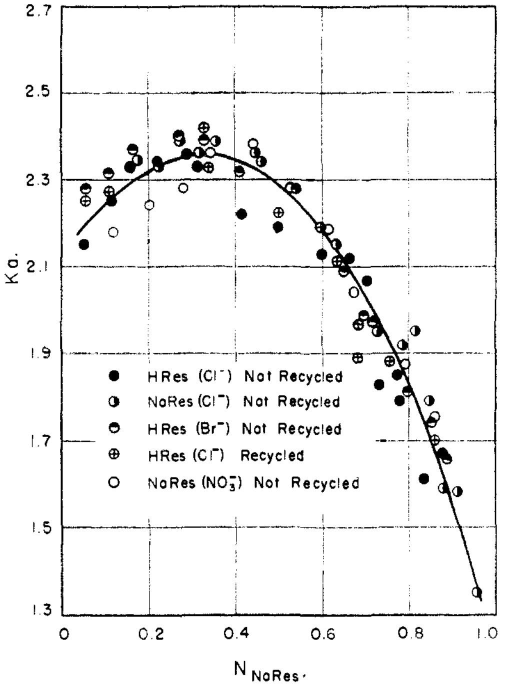

Fig. 1.—Sodium–hydrogen exchange.

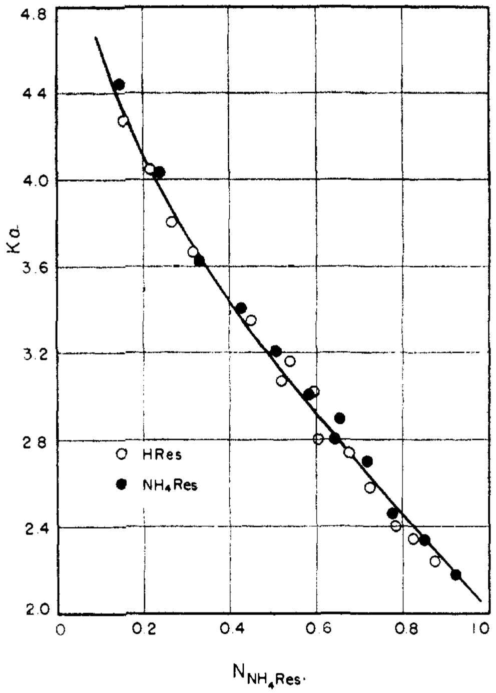

Fig. 2.—Ammonium–hydrogen exchange.

would require exchange data at various ionic strengths, which are now being obtained in this laboratory. The observed variation of the K_a values with resin composition, however, is certainly significant, and casts considerable doubt on the common assumption of ideal solid solution behavior in the resin phase.

Figure 2 gives the results for two sets of ammonium–hydrogen exchanges at unit ionic strength. Figure 3 shows the results for the series of experiments with pure hydrogen resin as initial exchanger in ammonium chloride–hydrochloric acid solutions of varying ionic strength.

In the ammonium–hydrogen exchange, as is shown in Fig. 2, hysteresis is again very slight. The range of values of K_a for this exchange, 2.2 to 4.4, is higher than the corresponding range, 1.4 to 2.4, for the sodium–hydrogen exchange, as might have been expected from the larger size of the exchanging cation. Bauman and Eichhorn[4] reported the single value 1.15 for K_a for the ammonium–hydrogen exchange at unit ionic strength.

The results shown in Fig. 3 definitely indicate a decrease in K_a, the apparent equilibrium constant, with decreasing ionic strength, an effect contrary to that found by Bauman and Eichhorn. The similarity in shape of the curves at the several ionic strengths lends support to the belief that the variation of K_a from constancy arises primarily from the assumption of ideal solid solution behavior in the resin phase, while the increasing range with increasing ionic strength is probably due to the assumption of constancy of ionic activity coefficients at constant total ionic strength, an assumption which decreases in validity as the ionic strength increases. Unfortunately, no data are at present available for the variation of activity coefficient ratios in ammonium chloride–hydrochloric acid mixtures at constant ionic strengths.

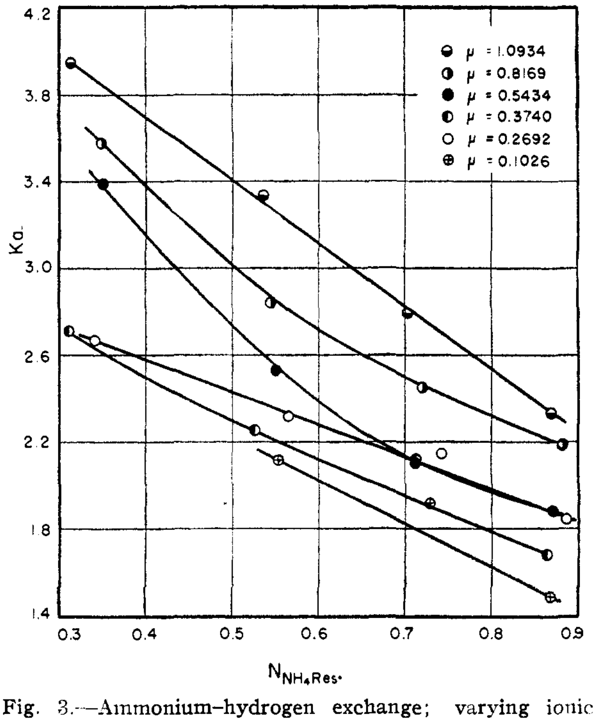

Fig. 3.—Ammonium–hydrogen exchange; varying ionic strength.

The results of experiments on the silver–hydrogen exchange at constant total ionic strength of approximately unity are given in Fig. 4, which shows the variation of K_a for this exchange as a function of the composition of the equilibrium resin.

Here the experimental results indicated, in addition to simple exchange of cation and absorption of water, adsorption of silver ion by the resin. The equilibrium constants, calculated as previously outlined for this system, indicate no hysteresis within

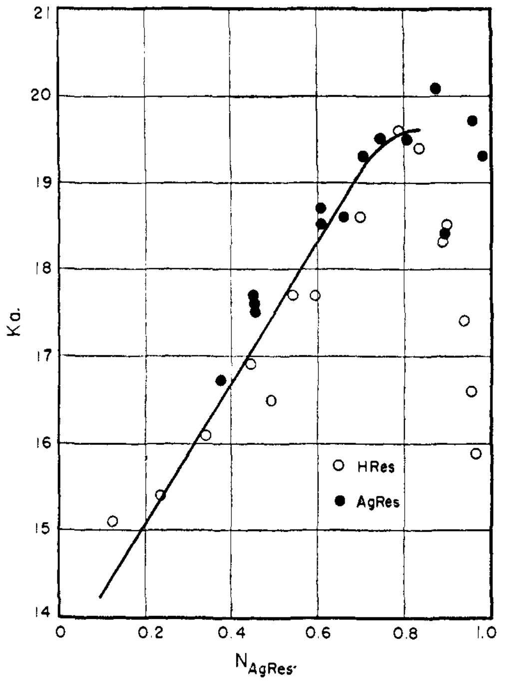

Fig. 4.—Silver–hydrogen exchange.

experimental error. The relatively large values of K_a, ranging from 15 to 20, are such as might be expected for an exchange involving one ion capable of forming covalent bonds.

The calculated amounts of adsorption of silver ion by the resin are of reasonable magnitude, and increase, as might be expected, with increasing concentration of silver ion in the equilibrium solution. Figure 5 shows this variation; the curves for the two sets of runs have the general shape of adsorption isotherms. The smaller calculated amount of adsorption with silver resin may be due to the presence of some adsorbed silver ion on the resin even after thorough washing during its preparation. Further evidence for this hypothesis is the observed fact that apparent adsorption on the silver resin does not occur until an appreciable initial concentration of silver ion has been attained, whereas the pure hydrogen resin exhibits adsorption even in the influent solutions most dilute in silver ion.

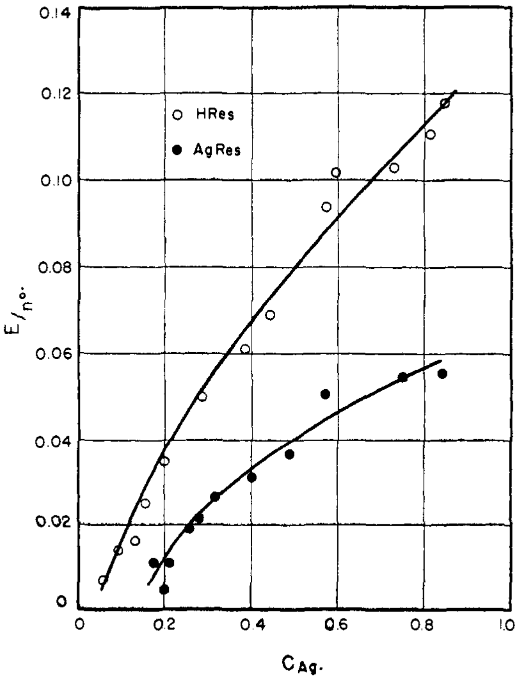

Fig. 5.—Adsorption of silver ion.

The results for the thallous-hydrogen exchanges are presented in Fig. 6; the exchanges were carried out in nitrate solutions at constant total ionic strength of approximately unity. Since adsorption of thallous ion by the resin was indicated by the experimental results, the equilibrium constants and amounts of adsorption were calculated just as for the silver–hydrogen exchange. The adsorption data yield curves of the usual shape, shown in Fig. 7.

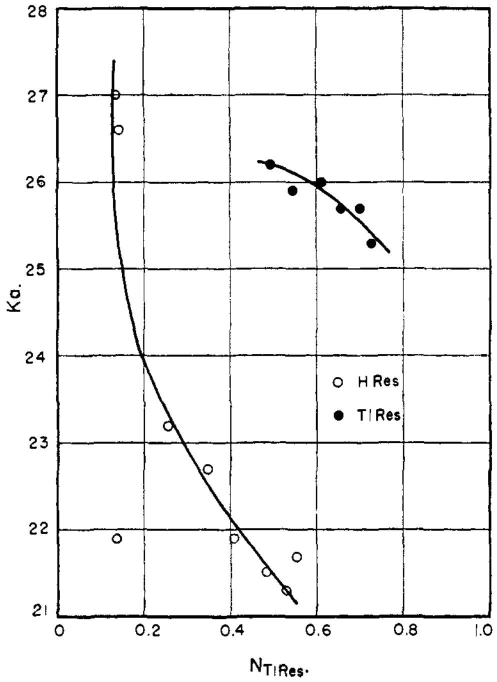

Fig. 6.—Thallous-hydrogen exchange

Figures 8 and 9 present the analogous results for the thallous–ammonium exchange in nitrate solutions at approximately unit ionic strength. The assumption of negligible adsorption in the solutions of lowest thallous ion concentration is apparently in error, especially in the series of expts. with thallous resin, since the K_a values calculated on this assumption for the solutions most dilute in thallous ion are obviously much too high. If the extent of adsorption here were known and could be taken into account, the result would be to decrease the calculated values of K_a for these cases and to increase the other K_a values.

The apparent hysteresis in this exchange is probably due to this same assumption. The range of K_a values is 5.1 to 7.4, as compared to 21 to 27 for the thallium–hydrogen exchange, which seems reasonable in view of the larger size of the ammonium ion as compared to hydrogen.

Logarithmic Additivity of Equilibrium Constants.—If the ion exchange process results in a true equilibrium, it should be possible, just as in the

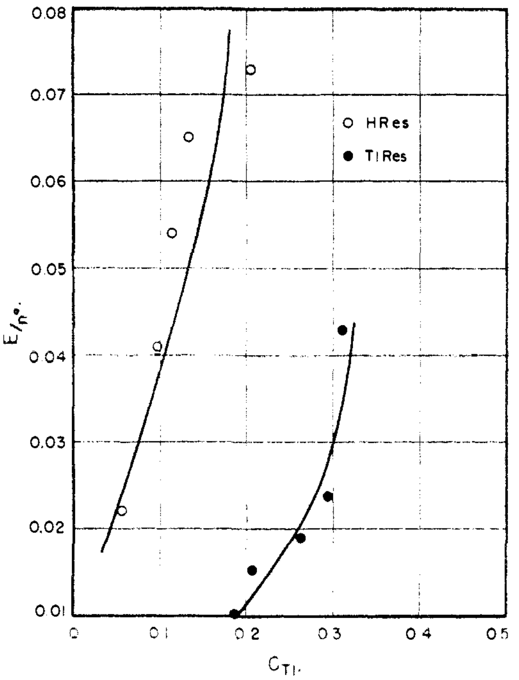

Fig. 7.—Adsorption of thallous ion.

case of other chemical changes, to calculate the equilibrium constant for a given reaction from those of two other reactions. Thus, in the three exchanges

$$A^{+} + BR = AR + B^{+} \tag{1}$$
$$C^{+} + AR = CR + A^{+} \tag{2}$$
$$C^{+} + BR = CR + B^{+} \tag{3}$$

which for convenience we shall refer to as a "triangular" system of exchanges, if K_1, K_2 and K_3 are the respective equilibrium constants, the following relationships must be valid

$$\log K_3 = \log K_1 + \log K_2$$
$$K_3 = K_1 \times K_2$$

The validity of this relationship for a triangular system may be tested with the experimental data for the ammonium–hydrogen, thallous–ammonium, and thallous–hydrogen exchanges—a trio which is especially suitable because the equilibrium constants for each pair differ by a factor of at least two. Since the apparent equilibrium constant has been found to be a function of resin composition, it was decided to select for each exchange the average value corresponding to an equimolar mixture of the two forms of the resin at equilibrium, from the two sets of data obtained with the different initial resins. This choice of the value for a resin of 0.5 mole fraction corresponds to the use of a first order approximation in treating the activity coefficients of the resin phase by means of a Margules expansion, as has often been done in ion exchange studies. Whatever may be the actual activity coefficients of the two resin components, their ratio must be unity at 0.5 mole fraction if the one-term Margules expansion is valid; hence, at this composition the apparent equilibrium constant should nearly equal the true thermodynamic equilibrium constant for the exchange. The data and calculated result are

$$K_1 = \frac{(\mathrm{NH_4Res})(\mathrm{H^+})}{(\mathrm{HRes})(\mathrm{NH_4^+})} = 3.18$$
$$K_2 = \frac{(\mathrm{TlRes})(\mathrm{NH_4^+})}{(\mathrm{NH_4Res})(\mathrm{Tl^+})} = 6.35$$
$$K_3 = \frac{(\mathrm{TlRes})(\mathrm{H^+})}{(\mathrm{HRes})(\mathrm{Tl^+})} = 23.8 \text{ (obsd.)}$$
$$K_1 \times K_2 = K_3 = 20.2 \text{ (calcd.)}$$

In view of the rather pronounced variation of the K_a values with resin composition in each case, and the fact that further calculation shows that the one-term Margules expansion for the solid phase activ-

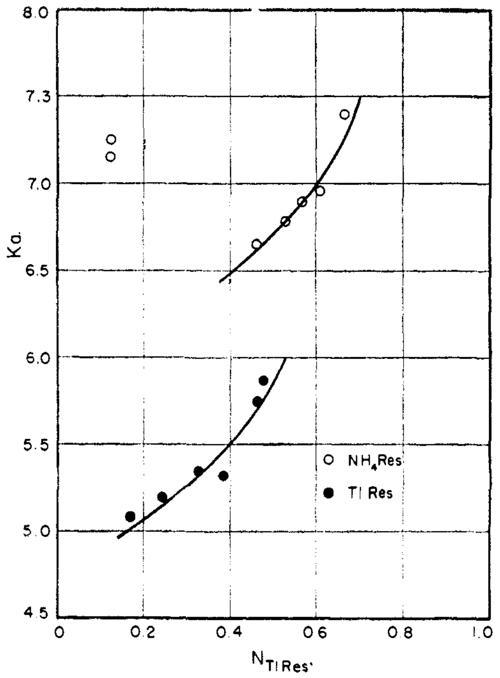

Fig. 8.—Thallous–ammonium exchange.

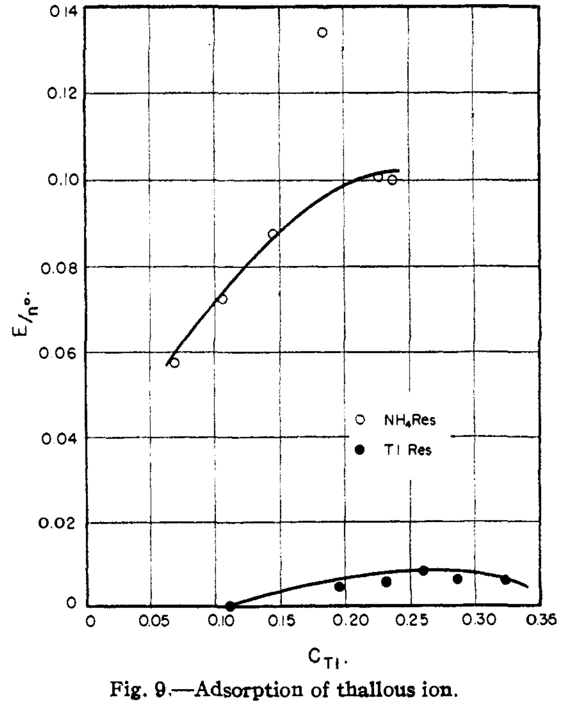

Fig. 9.—Adsorption of thallous ion.

ity coefficients is generally inadequate, the agreement between observed and calculated equilibrium constants, within 15% of the observed value, may be regarded as providing additional support for the new concepts and assumptions, particularly that of adsorption of thallous ion, involved in the determination of resin composition and equilibrium constants from the experimental data.

Exchanges Involving Bivalent Ions.—The values of K_a for the nickel–hydrogen exchange, in mixtures of nickel chloride and hydrochloric acid of total ionic strength of approximately unity,[13] are presented in Fig. 10. Since the nickel–hydrogen exchange involves ions of unlike valence, the concentration equilibrium quotient takes the form

$$K_c = \frac{c^2_{H^+} N_{NiRes2}}{C_{Ni^{++}} N^2_{HRes}}$$

Similarly, the true equilibrium constant is related to K_c by the equation

$$K_a = K_c \cdot \frac{\gamma^4_{\pm HCl} \cdot f_{NiRes2}}{\gamma^3_{\pm NiCl2} f^2_{HRes}}$$

As in the earlier exchanges, the activities in the solid resin have been approximated by the mole fractions.

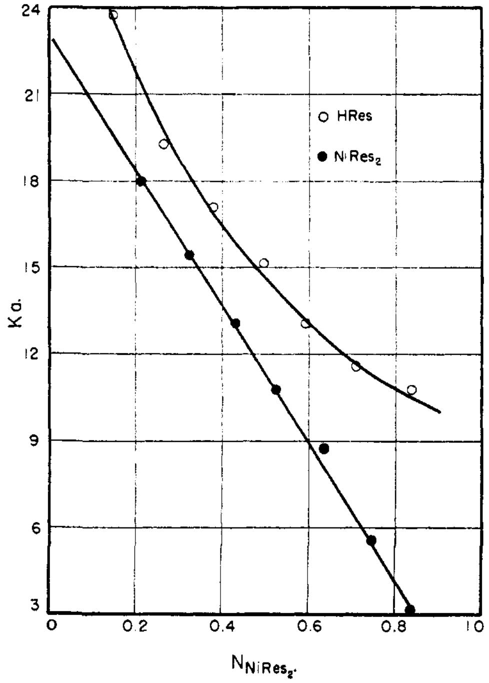

Fig. 10.—Nickel–hydrogen exchange.

Figure 10 indicates a marked apparent hysteretic effect, increasing with increasing proportion of nickel resin in the equilibrium exchanger. Neither this hysteresis nor the deviation from constancy would disappear if the mole fraction were to be replaced by the equivalent fraction as a measure of activity, a procedure which, furthermore, it would be difficult to justify on purely thermodynamic grounds. The apparent hysteresis may signify that the methods used to calculate the resin phase composition from the measured solution concentrations are somewhat in error. The primary causes of the large deviation of K_a from constancy, however, are believed to be the approximations used for the activity coefficient ratios in both phases.

Other methods of correlating these data, particularly that of Krishnamoorthy, Davis and Overstreet,[19] were tested, but none was found to give a more nearly constant value of K_a than the mass law relationship involving mole fractions in the solid phase. In nearly every case pronounced apparent hysteresis was evident, and in some instances the K_a values did not even exhibit a regular trend with varying resin composition. It should be mentioned, however, that the arbitrary substitution of equivalent fraction for mole fraction in the resin phase, in the equilibrium expression given by these authors (which may possibly be justified on the basis of the statistical nature of the exchange of ions among resin sites), results in decreased apparent hysteresis and more nearly constant values of K_a.

The results obtained in the investigation of the calcium–hydrogen exchange in solutions containing calcium chloride and hydrochloric acid at unit ionic strength are presented in Fig. 11. The methods of calculation of K_a values for this system were the same as for the nickel–hydrogen exchange. In neither system was adsorption of electrolyte indicated by the exchange data. The extent of apparent hysteresis, although greater than that observed for the uni-univalent exchanges, is nevertheless much less than in the nickel–hydrogen system. The variation of the K_a values from constancy may again be ascribed to the activity coefficient approximation for the solid phase. The higher range of values of K_a for the exchange of hydrogen with the relatively large calcium ion, as compared with those for exchange with the much smaller nickel ion, is in

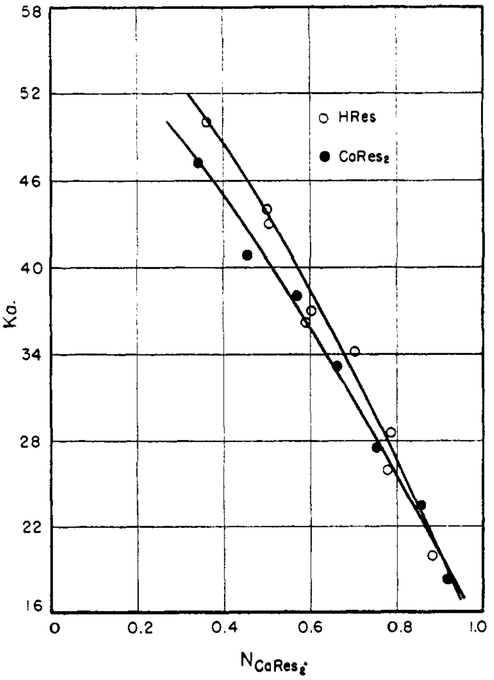

Fig. 11.—Calcium–hydrogen exchange.

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[19] C. Krishnamoorthy, L. E. Davis and A. Overstreet, *Science* **108**, 439 (1948).

agreement with the generally observed dependence of exchange equilibrium constant upon ionic radius.

The study of the calcium–nickel exchange was carried out with solutions containing calcium and nickel chlorides at an approximately constant ionic strength of unity, *i.e.*, a molarity of approximately 0.33. The exchange constants calculated from the results of this study are plotted in Fig. 12. The K_a values were calculated with no allowance for electrolyte adsorption by the resin. The appropriate expressions are

$$K' = \frac{c_{\mathrm{Ni}^{++}} N_{\mathrm{CaRes2}}}{c_{\mathrm{Ca}^{++}} N_{\mathrm{NiRes2}}}, \text{ and } K_a = K_{c'} \left(\frac{\gamma_{\pm \mathrm{NiCl2}}}{\gamma_{\pm \mathrm{CaCl2}}}\right)^3 \cdot \frac{f_{\mathrm{CaRes2}}}{f_{\mathrm{NiRes2}}}$$

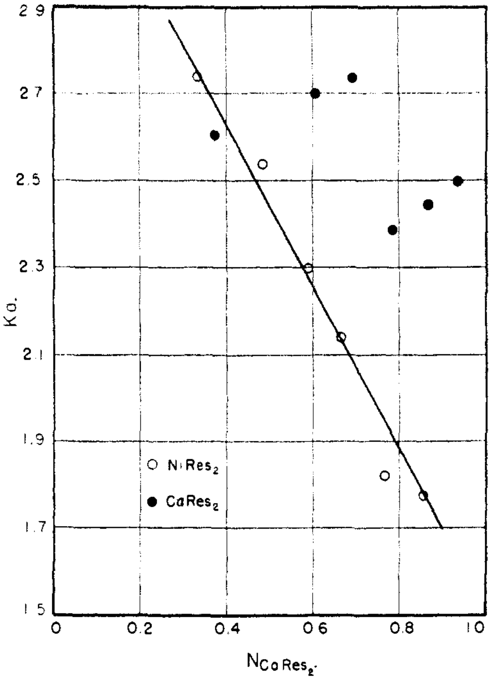

Fig. 12.—Calcium–nickel exchange.

Because of the difficulties inherent in the analytical methods for the two ions concerned, arising principally from coprecipitation, the precision of the results, particularly in the experiments with calcium resin as initial exchanger, is relatively low. Nevertheless, the rather large apparent hysteretic effect, of the order of that observed in the nickel–hydrogen exchange, seems to indicate that the magnitude of hysteresis depends more on difference in bond type than on difference in valence, since the two ions here involved have the same valence but differ in bonding character. As is to be expected, the range of K_a values is intermediate between those for the nickel–hydrogen and the calcium–hydrogen exchanges. A semi-quantitative correlation may again be observed in the triangular relationship among the three systems; the K_a values corresponding to equimolar equilibrium resin mixtures were chosen for the reasons given earlier. The results are

$$K_1 = \frac{(\mathrm{NiRes_2})(\mathrm{H}^+)^2}{(\mathrm{HRes})^2(\mathrm{Ni}^{++})} = 13.4$$

$$K_2 = \frac{(\mathrm{CaRes_2})(\mathrm{Ni}^{++})}{(\mathrm{NiRes_2})(\mathrm{Ca}^{++})} = 2.58$$

$$K_3 = \frac{(\mathrm{CaRes_2})(\mathrm{H}^+)^2}{(\mathrm{HRes})^2(\mathrm{Ca}^{++})} = 42.4 \text{ (obsd.)}$$

$$K_1 \times K_2 = K_3 = 34.6 \text{ (calcd.)}$$

The agreement between observed and calculated K_a values, within 20% of the observed value, is not so good as in the thallous–ammonium–hydrogen system. In view, however, of the experimental difficulties encountered in analysis, this agreement may be regarded as further validation for the treatment of the exchange results by mass law methods.

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LAWRENCE, KANSAS RECEIVED SEPTEMBER 11, 1950

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Condensation Products of Ethylene Chlorohydrin and Boron Trichloride[1]

BY DONALD RAY MARTIN AND LEONA SCHAFER MAKO*[1]

When one mole of anhydrous ethylene chlorohydrin is added dropwise with vigorous stirring to one mole of boron trichloride at −78°, boron (III) bis-(β-chloroethoxy)-chloride and tris-(β-chloroethyl)-borate are obtained in yields of 15 and 38 per cent., respectively. Boron (III) bis-(β-chloroethoxy)-chloride is a colorless liquid which forms a glass upon cooling. The liquid density, vapor pressure, heat of vaporization, boiling point, Trouton's constant and percentage composition of this compound were determined. A few chemical properties are reported. Tris-(β-chloroethyl)-borate was prepared by a new procedure.

Berzelius[2] observed that boron trichloride reacts with ethanol to yield a volatile product possessing an ether-like odor. Later Councler[3] observed that hydrogen chloride is evolved when boron trichloride reacts with allyl alcohol, benzyl alcohol or ethylene glycol. More recently, Wiberg and co-workers[4] synthesized the series of compounds $\mathrm{ROBCl_2}$, $\mathrm{(RO)_2BCl}$ and $\mathrm{(RO)_3B}$ (in which R is a methyl or an ethyl group) by allowing the alcohol to react with boron trichloride at −90 to −60°. Similarly, boron (III) bis-(isoamyloxy)-chloride has been prepared.[5]

This investigation was undertaken to observe if

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society on September 6, 1950, at Chicago, Illinois.

[2] J. J. Berzelius, *Ann. Physik.*, **78**, 113–150 (1824).

[3] C. Councler, *Ber.*, **10**, 1655–1657 (1877); **11**, 1106–1109 (1878); *J. prakt. Chem.*, [2] **18**, 371–402 (1878).

[4] E. Wiberg and W. Ruschmann, *Ber.*, **70B**, 1393–1402 (1937); E. Wiberg and H. Smedsrud, *Z. anorg. Chem.*, **225**, 204–208 (1935); E. Wiberg and W. Sütterlin, *ibid.*, **202**, 1–21 (1931); **202**, 31–36 (1931).

[5] C. R. Kinney, H. T. Thompson and L. C. Cheney, THIS JOURNAL, **57**, 2396–2397 (1935).