

AN INVESTIGATION OF BASE EXCHANGE
EQUILIBRIA

by

R. W. STOENNER
A. B. Missouri Valley College, 1942
M. A. University of Kansas, 1944

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Approved by:

Arthur W. Davidson
Instructor in Charge

William J. Argering Jr
Instructor in Charge

January, 1949

Ray Brewster
Chairman of the Department

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INVESTIGATION OF BASE EXCHANGE EQUILIBRIA

I. INTRODUCTION

The phenomenon of base or cation exchange has been known since 1850, when Way (1) observed that when a salt solution is passed through soil, a portion of the cations remains in the soil, while other cations, originally in the soil, appear in the solution. A few years later, Eichorn (2) showed that under these conditions the cations are mutually exchangeable.

These two discoveries resulted in numerous subsequent researches involving a large number of naturally occurring substances. Decaying organic matter, for instance, was found to exhibit ion exchange properties (3)(4) to a marked degree. Further, it was found that the ion exchange capacities of these substances can be increased by treatment with sulfuric acid or other oxidizing agents (5)(6)(7). Sulfonated coal, one of the best of these materials, is still being used to soften water (8), although it has been largely superseded for this purpose by more efficient synthetic materials.

Naturally occurring zeolites, as well as humus substances, were found to possess the capacity for ion exchange, and this property was soon applied in a process for the softening of water. Since these minerals are nearly insoluble, hard water can be softened by passing it through a bed of zeolite which has previously been treated with a sodium salt to convert it to its sodium form; by this means, sodium ions are exchanged for the calcium and magnesium ions contained in the hard

water, and water is obtained which no longer exhibits the property known as hardness.

All of this early work was based upon naturally occurring organic and inorganic substances of ill-defined chemical constitution. The first truly synthetic organic ion exchange materials were the resins synthesized in 1935 by Adams and Holmes (9)(10). They discovered that when a polyhydric phenol is condensed with formaldehyde in a basic solution of sodium sulfite, an insoluble polymer with cation exchange properties is formed. Similarly, they found that if amino groups are present on one of the components of the polymer, the latter substance exhibits anion exchange properties.

In the first synthetic cation exchanger, the active center at which the exchange took place was found to be the phenolate group. Numerous other active centers have since been employed in exchangers; among these are the RSO_3^- , $\text{RCH}_2\text{SO}_3^-$, and RCOO^- groups. One or several of these active groups may be incorporated into the polymer to yield a product "tailor-made" for any particular purpose.

The object of the present research project was to attempt to determine the laws which govern cation exchange on synthetic resins containing the RSO_3^- group. Considerable research has already been done in this field, and several types of correlation between the concentration of ions in solution and the composition of the solid phase have been proposed and tested. Austerweil (11) suggested an analogy to the distribution extraction of the cations between the

two immiscible phases, water and the solid resin. More commonly, adsorption isotherms (12)(13)(14)(15) and the Mass Action Law (8)(14)(16)(17)(18)(19)(20)(21) have been applied.

Inasmuch as Boyd and his coworkers (14) have derived both a Langmuir adsorption isotherm and a Mass Action equation and in the case of cation exchange on synthetic exchangers have claimed formal equivalence of the two, and since the present author is of the opinion that an appropriate equation based upon the Law of Mass Action can be applied with a considerable degree of success, only the Mass Action approach to the problem will be considered in this dissertation.

Accordingly, let it be assumed that the ion exchange process is a simple metathetical reaction in a heterogeneous system composed of two phases, solution and solid exchanger, and that at equilibrium the Law of Mass Action applies. For an exchange reaction involving two monovalent cations, A^+ and B^+ , the following equation may be written:



where Res denotes the insoluble anionic portion of the solid resin phase. The thermodynamic equilibrium constant, K_a , for this reaction is expressed by the equation.

$$K_a = \frac{(B^+)(ARes)}{(A^+)(BRes)}$$

where (B^+) and (A^+) are the respective activities of the two ions in the solution, and $(ARes)$ and $(BRes)$ are the activities of the two components in the solid phase. If the above

assumptions are valid, a variety of compositions of the system should lead to a constant value of K_a when the appropriate values for the several activities are substituted in this equation.

Before the equation may be applied to experimental data, further consideration of the activity quantities is necessary. The activity of each of the two ions in solution may be defined as the product of its concentration (experimentally determinable) and its ionic activity coefficient. The ionic activity coefficient, in turn, may be related, by means of a familiar convention, to the mean activity coefficient of the electrolyte in solution. Thus if the hypothetical activity coefficient of the two cations C^+ and C'^+ are represented by γ_{C^+} and $\gamma_{C'^+}$, respectively, and that of the common anion, A^- by γ_{A^-} then since $\gamma_{CA} = \sqrt{\gamma_{C^+} \gamma_{A^-}}$ and $\gamma_{C'A} = \sqrt{\gamma_{C'^+} \gamma_{A^-}}$, the ratio $\frac{\gamma_{C^+}}{\gamma_{C'^+}}$, is, in terms of experimentally determinable quantities, $\left(\frac{\gamma_{CA}}{\gamma_{C'A}}\right)^2$. Such mean activity coefficients have usually been determined for pure aqueous solutions; the values required, however, are those for mixed electrolyte solutions, which values are rarely available in the literature. This difficulty may be avoided by the assumption first made by G. N. Lewis (22) that in any dilute solution of a mixture of strong electrolytes of the same valence type, the activity coefficient of each electrolyte depends solely upon the total ionic strength of the solution.

The problem of the evaluation of the activities of the two components of the solid phase is much more difficult,

and, in fact, has not been satisfactorily solved. If the reaction $A + B_{Res} \rightleftharpoons B + A_{Res}$ were analogous to a chemical reaction in which B_{Res} and A_{Res} are independent solid phases, their activities could be taken as constant and equal to unity. As reported by Kerr (23), and confirmed by Vanselow (18), this assumption is experimentally valid. As pointed out by Vanselow, inasmuch as the exchanging cations freely substitute for one another throughout the solid phase, it would be more appropriate to consider that the two components of the solid phase are completely miscible; that is, that they form a solid solution. Further justification for this hypothesis is to be found in the fact that X-ray diffraction measurements on the solid phase (14) reveal a completely random arrangement of the exchanging cations. If the ions in the solid solution are both singly charged and of approximately the same size, the solid solution may be considered to be ideal, and the activities of the two components of the solid phase may accordingly be set equal to their respective mol fractions.

The expression for the equilibrium constant now becomes

$$K_a = \frac{(B^+) X_{A_{Res}}}{(A^+) X_{B_{Res}}} = \frac{(B^+) n_{A_{Res}}}{(A^+) n_{B_{Res}}}$$

where $X_{A_{Res}}$ and $X_{B_{Res}}$ are mol fractions of the two components of the solid phase and $n_{A_{Res}}$ and $n_{B_{Res}}$ are the number of moles of A and B in the solid phase.

In cases where the exchanging cations differ widely in size or are of different valences, the solid solution may no

longer be expected to behave as an ideal solution. The deviation from ideality may be detected by the non-linearity of a plot of $\log \frac{(B^+)}{(A^+)}$ vs. $\log \frac{(X_{BRes})}{(X_{ARes})}$. In this case somewhat more elaborate methods must be employed to estimate the activity coefficients of the solid phase. Kielland (24) has proposed an empirical method for evaluating the activity coefficients of the two components of the solid phase. This method is in harmony with the Duhem-Margules relation which states

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 = 0$$

where γ is the activity coefficient and is defined as the activity divided by the mole fraction; i. e.,

$$\gamma = \frac{a}{X}$$

$$\text{Let } \log \gamma_{ARes} = C X_{BRes}^2$$

$$\text{and } \log \gamma_{BRes} = C X_{ARes}^2$$

where C is a constant for any particular system and may assume either plus or minus values, but more commonly varies between 0 and 1. Returning to the original expression of the equilibrium constant $K_a = \frac{(B^+)(ARes)}{(A^+)(BRes)}$

we may write

$$\log K_a = \log \frac{(B^+)(ARes)}{(A^+)(BRes)} = \log \frac{(B^+) X_{ARes} \gamma_{ARes}}{(A^+) X_{BRes} \gamma_{BRes}}$$

$$\log \frac{(B^+) X_{ARes} \gamma_{ARes}}{(A^+) X_{BRes} \gamma_{BRes}} = \log \frac{(B^+) X_{ARes}}{(A^+) X_{BRes}} + \log \frac{\gamma_{ARes}}{\gamma_{BRes}} =$$

$$\log \frac{(B^+) X_{ARes}}{(A^+) X_{BRes}} + \log \gamma_{ARes} - \log \gamma_{BRes} .$$

Substituting from the Kielland formulation, we have

$$\log \frac{(B^+)X_{ARes}}{(A^+)X_{BRes}} + CX_{BRes}^2 - CX_{ARes}^2 = \log K_a$$

$$\log K_a = \log \frac{(B^+)X_{ARes}}{(A^+)X_{BRes}} + C (X_{BRes}^2 - X_{ARes}^2).$$

Let $\log \frac{(B^+)X_{ARes}}{(A^+)X_{BRes}} = \log K_C^1$; then from the above equation

$$\log K_C^1 = \log K_a - C(X_{BRes}^2 - X_{ARes}^2).$$

Thus it may be seen that, if the empirical hypothesis is correct, $\log K_C^1$ must be a linear function of $(X_{BRes}^2 - X_{ARes}^2)$ with a slope equal to C, and $\log K_C^1 = \log K_a$ when $X_{BRes} = X_{ARes}$. The values of $\log K_C^1$ may be plotted against the corresponding values of $(X_{BRes}^2 - X_{ARes}^2)$, and the constant C may then be obtained from the slope of the resulting straight line. With this value of C, the activity coefficients of the components in the solid phase may then be obtained from the equations

$$\log \gamma_{ARes} = CX_{BRes}^2$$

and $\log \gamma_{BRes} = CX_{ARes}^2$.

Krishnomoorthy, Davis and Overstreet (25) have recently adopted a method first suggested by Fowler and Guggenheim (26) to arrive at an expression for the equilibrium constant for an exchange reaction. In this method, the activities of the solid components are related to the numbers of mols by equations which can be derived from relatively simple statistical mechanics. The derivation need not be given here but the final result is presented in the following form. For any

system containing the ionic species A, B, C, D,, the equilibrium for the exchange reaction of any pair, for example A and B, is given by the expression:

$$K_{(A,B)} = \frac{(A)^{r_2}}{(B)^{r_1}} (q_1A + q_2B + q_3C \dots)^{r_1-r_2} \cdot \frac{(B)^{r_1}}{(A)^{r_2}}$$

where r_1, r_2, r_3, \dots are the valences of ions A, B, C,; the terms in brackets are the number of moles in the solid phase; the terms in parenthesis are the activities of the ions in solution, and

$$q_n = \frac{r_n + 1}{2} .$$

For a univalent-univalent exchange, this equation reduces to

$$K_{(A^+,B^+)} = \frac{(A)}{(B)} (A + B)^0 \cdot \frac{(B^+)}{(A^+)} = \frac{(A)}{(B)} \frac{(B^+)}{(A^+)}$$

which is exactly equivalent to the equation first derived for a simple exchange where the solid phase might be considered to be an ideal solution. However, for the divalent-univalent exchange of A^{++} and B^+ , where

$$r_1 = 2; r_2 = 1$$

and

$$q_1 = \frac{2 + 1}{2} = \frac{3}{2}; q_2 = \frac{1 + 1}{2} = 1$$

we have

$$K_{(A^{++},B^+)} = \frac{(A)}{(B)^2} (3/2A + B) \cdot \frac{(B^+)^2}{(A^{++})} = \frac{3/2(A)^2}{(B)^2} \frac{(A)(B)}{(A^{++})} \cdot \frac{(B^+)^2}{(A^{++})}$$

Hence it is evident that for other than univalent-univalent exchanges, this expression is no longer equivalent to the simple mass action equation.

Krishnamoorthy and Overstreet have tested the relation experimentally on an exchange involving lanthanum, cesium,

and hydrogen ions with Amberlite IR 100 as the synthetic exchanger. Their results, treated in the manner just described, yield an average value of $K_{(La^{3+}, Cs^+)}$ of 367, with an average deviation of -14 or 3.8%, which is somewhat lower than average deviations of 5 to 10% reported elsewhere. Additional merit must be accorded the expression of Krishnamoorthy, Davis, and Overstreet when it is considered that the experimental test involved ions of widely different valences, as well as the effect of the presence of a third ion in the exchanging solution.

Reasons for the limited success of the application of the Law of Mass Action to cation exchange reactions have been indicated by Boyd (14). Among these reasons, he suggests that the equations written to represent the exchange reaction may not necessarily be stoichiometrically correct, either because the cations may be subject to partial hydrolysis, giving rise to the adsorption of partially hydrolyzed fragments with reduced positive charge, or because the electrolyte may be incompletely dissociated, in which case not only would the calculated ion concentrations be erroneous, but additional errors would result from adsorption of the intermediate ions. Further, it has frequently been assumed that the synthetic exchanger contains active centers of only one species. If the exchanger were polybasic, the adsorptive capacity would be dependent upon the pH of the equilibrium mixture, since the several varieties of exchange centers would be expected to become active progressively, according to the

strength of the acid grouping. Recent developments in the synthesis of organic exchangers, however, have resulted in resins which contain only one structurally bound anionic grouping, so that the adsorptive capacity is independent of the pH at which the exchange reaction is carried out. At the same time, the acid strength of the active centers now employed is sufficiently high so that exchanges may be carried out at low pH values, at which the hydrolysis of the cations in the solution is negligible.

Undoubtedly an error of considerable magnitude is introduced by the assumption of the validity of the ionic strength principle in the less dilute solutions (those in which the ionic strength is greater than 0.1) used by most investigators. If this principle is employed, it must be regarded only as one which approaches validity only as the solution approaches infinite dilution.

From the experimental standpoint, the most serious error lies in the evaluation of the composition of the solid phase. Of necessity, the composition of the solid has invariably been calculated from changes in the concentrations of the ions in the solution before and after exchange, for direct analysis of the solid phase is rendered impossible by the following circumstance. In order that such an analysis might be carried out, it would be necessary first to wash the adhering equilibrium solution from the resin. During the washing, the ionic strength of the solution surrounding the solid phase would constantly be changing. But the equilibrium

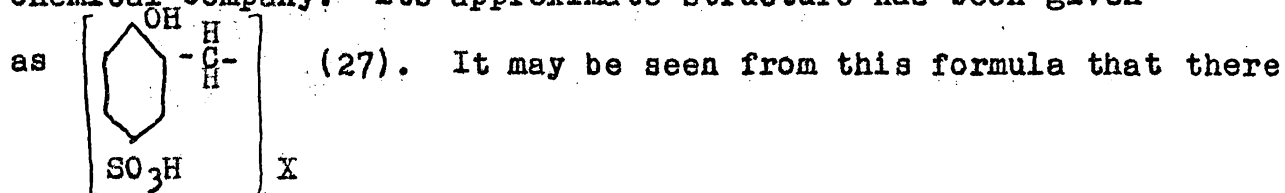
constant has been found to vary with the ionic strength of the solution. For example, Bauman and Eichorn (19), in studying the ammonium-hydrogen exchange upon Dowex-50, found the following relation between the ionic strength and the equilibrium constant

μ	K
0.01	1.20
0.1	1.20
1.0	1.15
2.0	0.83
4.0	0.51

Thus during the washing the equilibrium would be shifted in accord with the change in the equilibrium constant. Hence any analysis of the solid phase would not yield the concentrations prevailing at equilibrium. When the calculation of the composition of the solid phase at equilibrium is dependent upon small differences in the concentrations of ions in the solution, the results are inevitably subject to considerable error.

II. SODIUM-HYDROGEN EXCHANGE ON DOWEX-30

The first exchanger selected for investigation was Dowex-30, a sulfonate-type resin manufactured by the Dow Chemical Company. Its approximate structure has been given



are two functional groups present on the unit structure, but these two acid groups are of widely different strength, the phenol group becoming active only in alkaline solutions. The substance as received, is a moist mixture of sodium and hydrogen resins, possibly containing traces of other cations. The particles are of irregular shape, but sufficiently uniform in size so that no advantage is to be gained by a preliminary screening.

The first exchange system to be studied was the sodium-hydrogen exchange. Pure hydrogen resin was prepared by placing the resin, as received, in a glass column 5 cm. in diameter, and 70 cm. long. Constant boiling hydrochloric acid was then refluxed through the column until the effluent was free of sodium ion, as indicated by a flame test. The resin was then removed from the column and washed until free of chloride ion, after which it was air dried for a day, then oven dried at 110°C ., and stored at this temperature until used. The equivalent weight of the resin was first determined by maintaining a weighed quantity in contact with a large excess of saturated sodium chloride solution until no

further exchange took place. The liberated hydrogen ion was then titrated with a standard alkali solution. The time required to liberate all the replaceable hydrogen ions was inconveniently long (4 to 5 days); consequently a more rapid method was desirable. If the only sulfur contained in the resin is in the active sulfonate group, an analysis for sulfur should yield the same value of the equivalent weight as did the titration of the liberated hydrogen ion. For the sulfur analysis, the resin was decomposed by evaporation with a mixture of concentrated nitric and perchloric acids. The sulfate ion was precipitated as barium sulfate, which was filtered off, ignited, and weighed. This determination gave a value of 295 for the equivalent weight of the resinate ion, as compared to 297 from the hydrogen titration method. It was assumed that this difference was sufficiently small to warrant the use of the sulfur analysis for the subsequent determinations of the equivalent weight of hydrogen resin.

Pure sodium resin was prepared from pure hydrogen resin by placing it in contact with a very large excess of saturated sodium chloride solution. Sodium hydroxide was then added to the solution until the pH of the mixture was approximately that of a saturated sodium chloride solution. As in the determination of the equivalent weight of the hydrogen resin, this conversion was extremely slow in the latter stages, again requiring 4 to 5 days. The sodium resin was washed and dried in the same manner as the hydrogen resin. For the determination of the equivalent weight, the decomposition of

the resin was accomplished as before with nitric and perchloric acids. Two ml. of concentrated sulfuric acid was added to the residue, and the whole evaporated to dryness. The samples were then ignited and weighed as sodium sulfate. The equivalent weight of the resinate ion by this method was found to be 298, which is in close agreement with the values obtained from the hydrogen and sulfur determinations.

All equilibrium studies in this investigation were carried out batchwise. Weighed quantities of resin were placed in glass stoppered Erlenmeyer flasks in contact with 100 ml. of aqueous solutions of compounds of the two exchanging cations with a common anion in various proportions, the total ionic strength of each solution being unity. These reaction flasks were shaken in a 25° C. thermostatically controlled water bath for a period never less than two hours, in order to insure sufficient time for equilibrium to be reached. Aliquot portions of the equilibrium effluent were then removed and analyzed for the two exchanging cations. All pipets used were calibrated in the usual manner, water being used as the calibration liquid.

The 100 ml. exchange solutions were prepared by one of the two following methods: a) For univalent-univalent exchanges, 1 N stock solutions of the two exchanging cations were prepared and analyzed. The 100 ml. exchange solutions were then made up from aliquot portions of these stock solutions. b) For divalent-univalent exchanges, and for cases in which a contraction in volume upon mixing was observed, each

of the exchange solutions was prepared individually, and was analyzed prior to the exchange reaction.

The hydrogen ion concentrations were determined by titration with standard sodium hydroxide solution; sodium ion was determined by weighing as sodium sulfate after evaporation with sulfuric acid, and ignition to 750° C. to insure complete removal of the excess sulfuric acid.

If simple exchange is the only reaction involved, solutions placed in contact with the hydrogen form of the resin should undergo a decrease in sodium ion content exactly equivalent to the gain in hydrogen ion. Likewise, in experiments with the sodium form of the resin, the loss in hydrogen ion from the solution should be equivalent to the gain in sodium ion. However, the large deviations from equivalent exchange that were observed clearly indicated that some reaction other than simple exchange was involved in these preliminary exchange studies.

As an explanation of these results, adsorption of hydrogen chloride by the hydrogen resin and of sodium chloride by the sodium resin was quickly discarded because of the magnitude of the deviations from equivalent exchange. Further, chloride determinations before and after exchange revealed no change in the chloride ion concentration, such as would be the result if physical adsorption on the solid resin were occurring.

A search for the anion accompanying the excess cation revealed the presence of sulfate ion. Quantitative determin-

ations showed that at equilibrium an amount of sulfate ion was present which corresponded to the difference between the sodium ion gained and the hydrogen ion lost on the one hand, and between the hydrogen ion gained and the sodium ion lost, on the other. A portion of the resin was then treated with pure water. Analysis of the resulting solution showed that at equilibrium the sodium resin yielded appreciable and equivalent quantities of sodium and sulfate ions, while the hydrogen resin yielded appreciable and equivalent quantities of hydrogen and sulfate ions. Furthermore, these amounts were comparable with the previously observed deviations from equivalent exchange that had been observed.

It was thought that the maintenance of the resin at 110° C. for a period of two months during storage may have caused partial decomposition of the sulfonate group in such a manner as to yield sulfate ion upon contact with water. It was therefore decided to prepare some fresh samples of resins by the usual method, but to dry them in a vacuum desiccator with either phosphorus pentoxide or "Drierite" as the desiccant, instead of at an elevated temperature. After drying for an arbitrary period of time, the resins were stored in a sealed container.

From the resins which had been prepared in this manner, a series of samples were brought in contact with aqueous solutions of sodium chloride and hydrogen chloride of ionic strength equal to unity, and allowed to come to equilibrium. Portions of the effluent were removed and analyzed for sodium

and hydrogen ions as before.

Table I contains the data for the exchange study on hydrogen resin, while Table II contains the data for the sodium resin exchange. In these and all subsequent tables, (except Tables IV, V, VI, VII, VIII and X in which the order was inadvertently reversed) the first of the two columns headed Δ , is the increase (number of moles) in the solution of the cation originally present on the resin, while the second column marked Δ contains the decrease (number of moles) in the solution of cation entering the resin. The column headed $\frac{\Delta H - \Delta Na}{\text{eq. res.}}$ is the difference between the two observed changes in concentrations divided by the number of equivalents of resin originally present.

Examination of the values of $\frac{\Delta H - \Delta Na}{\text{eq. res.}}$ shows that the gain in hydrogen ion always exceeds the loss in sodium ion from the solution. This fact indicates that even unheated hydrogen resin is unstable in aqueous solutions, undergoing partial hydrolysis of the sulfonate group similar to that encountered with the heated resin; the magnitude of the difference between the gain in hydrogen ion and the loss in sodium ion, however, is appreciably smaller than in the case of the heated resin. This deviation from equivalent exchange, since it seems to result from a hydrolysis reaction of some sort, will be referred to hereafter as the hydrolytic effect.

Since, on the other hand, the corresponding quantities $\frac{\Delta Na - \Delta H}{\text{eq. res.}}$ listed in Table II are all negligibly small, and since they assume both negative and positive values, it may be concluded that they are attributable entirely to

Dowex-30

Table I

HRes + NaCl + HCl

No.	Original Solution	Weight of Resin	Equivalents of Resin	ΔH^+	ΔNa^+	$\frac{\Delta H - \Delta Na}{\text{eq. res.}}$	N_{NaRes}	K_c	K_a
1.	$Na^+ = 0.1953M$ $H^+ = 0.7377M$	5.0879	0.01271	0.00336	0.00203	0.104	0.180	0.91	1.37
2.	$Na^+ = 0.2923$ $H^+ = 0.6473$	4.3913	0.01098	0.00350	0.00243	0.097	0.245	0.82	1.23
3.	$Na^+ = 0.3845$ $H^+ = 0.5596$	4.5823	0.01148	0.00422	0.00343	0.069	0.320	0.86	1.29
4.	$Na^+ = 0.4846$ $H^+ = 0.4638$	4.6683	0.01165	0.00509	0.00417	0.079	0.390	0.79	1.19
5.	$Na^+ = 0.5780$ $H^+ = 0.3742$	3.7668	0.00942	0.00490	0.00425	0.069	0.480	0.74	1.11
6.	$Na^+ = 0.6848$ $H^+ = 0.2730$	4.8149	0.01202	0.00715	0.00630	0.071	0.560	0.72	1.08
7.	$Na^+ = 0.7755$ $H^+ = 0.1846$	3.9473	0.00985	0.00643	0.00590	0.054	0.630	0.60	0.90
8.	Pure Water	4.4806	0.01121	0.00029	-----	0.014	-----	-----	-----

Dowex-30

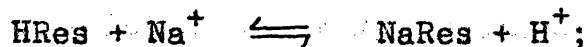
Table II

NaRes + HCl + NaCl

No.	Original Solution	Weight of Resin	Equivalents of Resin	ΔNa^+	ΔH^+	$\frac{\Delta\text{Na} - \Delta\text{H}}{\text{eq. res}}$	N_{NaRes}	$-K_c$	K_a
1.	$\text{H}^+ = 0.7377\text{M}$ $\text{Na}^+ = 0.1953\text{M}$	4.6430	0.00938	0.00668	0.00654	0.015	0.28	1.07	1.61
2.	$\text{H}^+ = 0.6476$ $\text{Na}^+ = 0.2923$	4.5448	0.00918	0.00588	0.00571	0.019	0.37	0.98	1.47
3.	$\text{H}^+ = 0.5594$ $\text{Na}^+ = 0.3845$	4.3007	0.00868	0.00494	0.00493	0.001	0.43	0.90	1.35
4.	$\text{H}^+ = 0.4638$ $\text{Na}^+ = 0.4846$	4.6931	0.00947	0.00462	0.00456	0.006	0.53	0.84	1.26
5.	$\text{H}^+ = 0.3742$ $\text{Na}^+ = 0.5780$	5.2670	0.01063	0.00420	0.00429	-0.009	0.60	0.81	1.21
6.	$\text{H}^+ = 0.2730$ $\text{Na}^+ = 0.6848$	5.5727	0.01123	0.00336	0.00337	-0.001	0.61	0.78	1.17
7.	$\text{H}^+ = 0.1846$ $\text{Na}^+ = 0.7755$	4.8506	0.00980	0.00249	0.00233	0.016	0.75	0.62	0.93

experimental error, rather than to any hydrolysis of the sulfonate group.

All values of K shown in Tables I and II are for the reaction



that is,

$$K_c = \frac{(\text{H}^+)(\text{NaRes})}{(\text{Na}^+)(\text{HRes})}$$

where (H^+) and (Na^+) are the concentrations of the ions in the water phase and (NaRes) and (HRes) are the mol fractions of the two components in the solid phase which are, of course, proportional to the numbers of mols of the components. In the case of the sodium resin study, where no hydrolytic effect was observed, the composition of the resin at equilibrium was established from the mean of the changes in concentration of sodium ion and hydrogen ion occurring in the exchange process. In the hydrogen resin study, (H^+) is the hydrogen ion concentration as determined by titration of a portion of the equilibrium effluent; (Na^+) is the sodium ion concentration as determined by sodium analysis on the equilibrium effluent. (NaRes) is equal to the number of equivalents of sodium ion lost from the solution. (HRes) is equal to the number of equivalents of hydrogen resin originally present, minus the quantity $(\Delta \text{H}^+ - \Delta \text{Na}^+)$, minus the number of equivalents of sodium ion lost from the solution, or more simply, the number of equivalents of hydrogen resin originally present minus the increase in hydrogen ion concentration in the solution. In using this method of establishing the

composition of the solid phase in the hydrogen resin study, it is assumed that a portion of the resin equivalent to the excess gain in hydrogen ion over the loss in sodium ion, has been rendered inactive toward exchange. Values of K_a are derived by multiplying the K_c value by the ratio of the squares of the mean activity coefficients of hydrogen chloride and sodium chloride at unit ionic strength; i. e.,

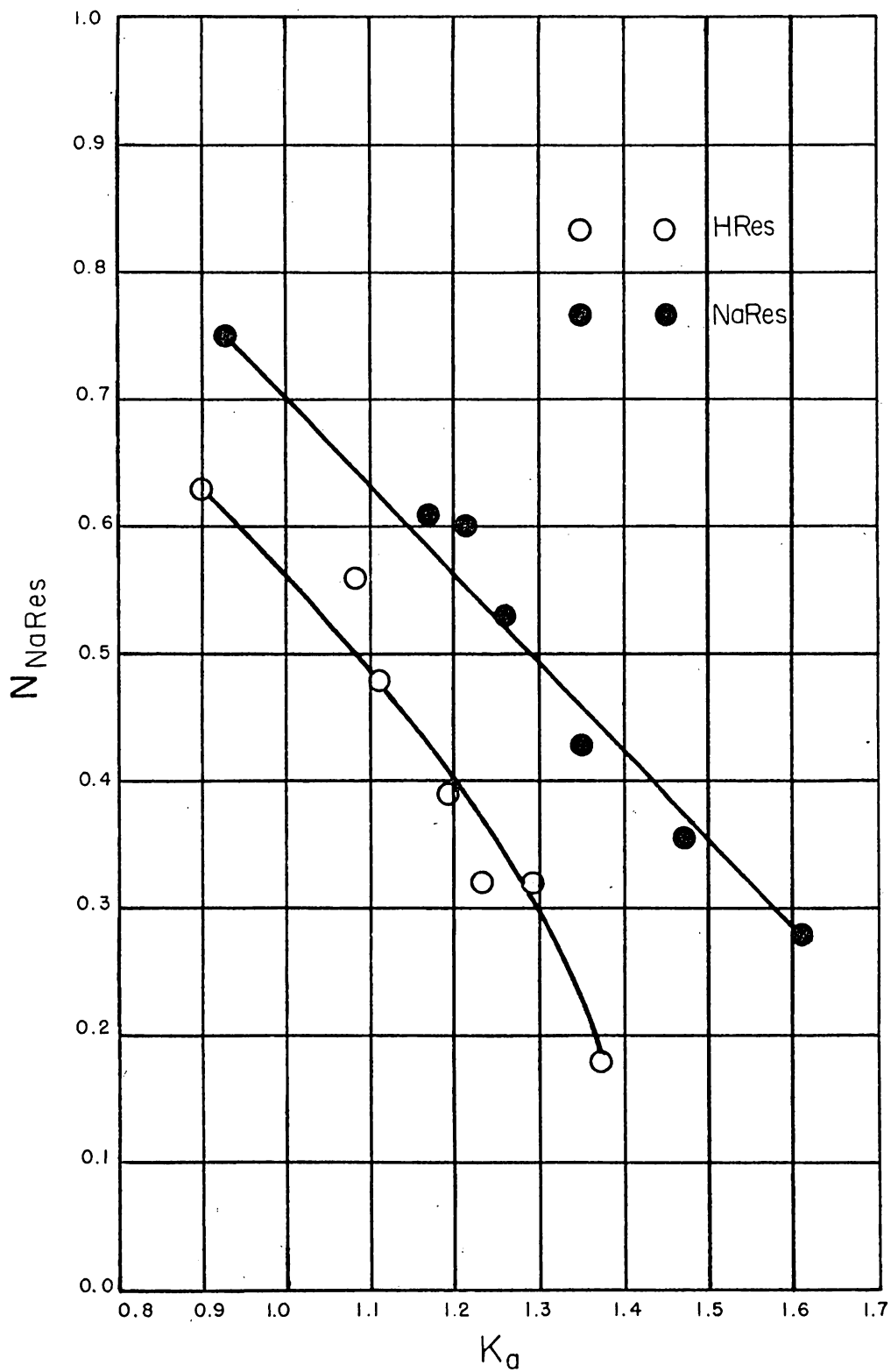
$$K_a = K_c \cdot \frac{\gamma_{\text{HCl}}^2}{\gamma_{\text{NaCl}}^2} .$$

When values of the equilibrium quotient from Tables I and II are plotted against the corresponding mol fractions, the curves of Figure I are obtained.

It will be noticed that the values of K_a increase with increasing proportion of hydrogen resin in the solid phase. In order to use the Mass Action expression for K_a , two assumptions were made. The first was that the "ionic strength" principle was valid in solutions of unit ionic strength; secondly, in the absence of any method of evaluating activity coefficients in the solid phase, this phase was assumed to be an ideal solid solution of hydrogen resin and sodium resin, the activity of each of which was taken as equal to its respective mol fraction. It is believed that in this second assumption lies the largest source of deviation from constancy of the values of K_a .

Juda (21), in making a similar investigation of several carbonaceous exchangers, noted that when the hydrogen form of Dowex-30 was brought in contact with water, an appreciable

Figure 1



amount of hydrogen ion from the resin appeared in the water phase. A correction term was therefore introduced by him into the Mass Action expression, to take account of excess cation coming from the solid phase. As was the case in the present investigation, he did not observe this same hydrolysis when the sodium form was employed as the initial exchanger. Sodium resin was considered by him to be entirely stable in aqueous solutions, so that no correction term in the Mass Action equation was necessary.

The work of Juda is not exactly comparable to the present investigation, in that solutions of ionic strength varying from 0.001 to more than 1 were employed by him, while the present study was confined to solutions of unit ionic strength. His results are tabulated in Table III.

Table III

A						B				
#	a	w _H	v _{Na}	X _e	K _{H/Na}	K _{H/Na}	X _{e'}	v _H	w _{Na}	c
1	1.16	0.080	104.9	0.70	1.03	1.07	1.25	104.9	0.167	1.97
2	4.08	.339	104.9	2.61	0.98	1.28	2.83	104.9	.278	6.04
3.	9.19	.879	104.8	6.35	1.12	1.09	6.18	104.8	.896	9.34
4.	15.84	.731	105.0	7.93	1.01					
5.	49.0	2.50	102.1	26.24	1.03					
6.	103.3	4.01	96.85	48.6	0.95	1.50	229.1	90.76	18.82	554.2
7.	1188.	16.93	33.8	570.6	0.93	0.87	345.5	89.24	20.95	901.8

A = studies with HRes as the initial exchanger.

B = studies with NaRes as the initial exchanger.

a = millequivalents of NaCl/liter original solution.

c = millequivalents of HCl/liter original solution.

w_H } = weight in grams of solid exchanger.

w_{Na} }

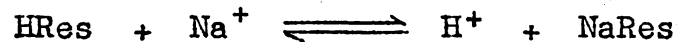
v_{Na} } = volume in cc. of solution placed in contact with solid exchanger.

v_H }

X_e } = hydrogen ion and sodium ion concentrations respectively at equilibrium.

X_{e'} }

K_{H/Na} = "Concentration" equilibrium constants for the reaction



III. SILVER-SODIUM EXCHANGE ON DOWEX-30

The study of the exchange between silver ion and sodium ion was next undertaken. The choice of this exchange pair was made partially because of the application, during the latter part of the war, of a silver ion exchanger to the desalting of sea water, and partially in the hope of obtaining data as to the effect of the radius of the exchanging cation on the point of equilibrium.

An attempt was made to prepare the silver resin in a manner analogous to that used for pure sodium resin. Pure hydrogen resin was placed in a saturated solution of silver nitrate, and the progress of the exchange was followed with a pH meter. Freshly prepared silver oxide was added to the solution as the exchange took place, in order to maintain the pH at a level between 6.0 and 6.5. Suitable precautions were taken to prevent the actinic reduction of the silver ion. The conversion to silver resin was considered to be complete when no further change in the pH of the solution was observed. Examination of the resulting resin and of the supernatant liquid, however, clearly revealed the presence of a considerable quantity of metallic silver, evidently resulting from the reduction of silver ion by the resin.

Such reduction of the silver ion was further demonstrated by treatment of a sample of sodium resin with a solution containing silver ion and sodium ion as nitrate, and analysis of the effluent after 24 hours. The results are

shown in the following representative data.

Wt. of NaRes = 5.5362 g.

Solution placed on resin: $(\text{Ag}^+) = 0.491 \text{ M}$

$(\text{Na}^+) = 0.494 \text{ M}$

Equilibrium concentrations: $(\text{Ag}^+) = 0.397 \text{ M}$

$(\text{Na}^+) = 0.576 \text{ M}$

Decrease in concentration of silver ion = 0.094 mole per
liter

Increase in concentration of sodium ion = 0.082 mole per
liter

These data show that the loss of silver ion from solutions, in equivalents, exceeded the gain of sodium ion by 14.6%. A discrepancy of this order would be expected only if a portion of the silver ion was being reduced by the solid exchanger.

From these considerations, it was concluded that quantitative studies of any equilibria involving silver ion and Dowex-30 are not feasible.

IV. DOWEX-50

Because of the instability exhibited by Dowex-30 toward hydrolysis and oxidation, experiments on this resin were discontinued and attention was turned toward Dowex-50, a more recent product of the Dow Chemical Company. In this resin, as in Dowex-30, the sulfonate group serves as the active exchange center, but the unit structure of Dowex-50 does not contain the phenol group; this difference might be expected to render Dowex-50 less susceptible to oxidation than is Dowex-30.

The resin as received from the manufacturer is a moist mixture of the sodium and hydrogen forms. The particles are small and all approximately spherical in shape; their color, however, ranges from light amber to dark brown. In view of this variation in physical appearance, experiments were undertaken to determine the degree of chemical homogeneity of the different colored particles.

The solid resin, as received, was air dried and screened through a series of standard sieves. Major fractions obtained were 12-14, 16-20, and 20-28 mesh. The portion larger than 12 mesh was selected for the homogeneity investigation, since it seemed to contain a larger proportion of the light colored particles. This portion was then converted to pure sodium resin in the same manner as that described for Dowex-30. The mixture was separated into light and dark fractions by flotation in a solution of sodium bromide of such

concentration that the lighter colored particles floated on the solution, while the darker colored particles sank to the bottom of the container. Each of the fractions was then washed free of sodium bromide and the two were dried simultaneously over phosphorus pentoxide in the same vacuum desiccator. The sodium ion content of each fraction was determined by decomposition with sulfuric acid in the presence of a small amount of selenium as catalyst.* The sodium content of the

*In the case of Dowex-30, decomposition of the resin could be brought about by means of heat alone, or by oxidation with nitric acid, perchloric acid or aqua regia. None of these methods proved satisfactory in the case of Dowex-50, which, however, could be completely decomposed by digestion with concentrated sulfuric acid, in the presence of a few tenths of a gram of metallic selenium.

lighter particles was 8.57%, while that of the dark ones was 8.93%; the equivalent weights of the sodium resins calculated from these sodium analyses are 269 and 232 respectively.

From this study, it was concluded that the light and dark particles of Dowex-50 are not chemically identical, or at least that they are sufficiently different physically that they exhibit different rates of drying under the same conditions of desiccation. However, since a complete separation would not have been practicable, the 16-28 mesh portions were recombined and thoroughly mixed; the resulting product was regarded as being homogeneous with respect to its ion-exchanging properties. Justification for this assumption is to be found in the reproducibility of results encountered in later exchange studies.

V. SODIUM-HYDROGEN EXCHANGE ON DOWEX-50

The sodium and hydrogen forms of Dowex-50 were prepared in the manner already described for Dowex-30. Since it had been determined that oven drying was undesirable, and since it did not seem worthwhile to establish a standard drying procedure, the equivalent weight of each batch of the sodium resin was individually determined by analysis for sodium as described above. The equivalent weight of each batch of the hydrogen resin was determined by treatment of a weighed quantity of the resin with a saturated solution of sodium chloride, followed by titration of the liberated hydrogen ion with standard alkali. This method had already been tried in the work with Dowex-30, but had then been discarded because of the inconveniently long time (4 to 5 days) required for complete replacement of the hydrogen ion; in the case of Dowex-50, however, complete exchange occurred within thirty minutes.

As in the previous study, a series of samples were treated with aqueous solutions of sodium chloride and hydrogen chloride, of ionic strength approximately equal to unity. Portions of the equilibrium effluent were removed and analyzed for sodium and hydrogen ions.

Table IV contains the data for the exchange study on hydrogen resin, while Table V contains those for the sodium resin exchange. From the values of $\frac{\Delta H - \Delta Na}{\text{eq. res}}$ contained in Table IV, it may be observed that, as in the case of Dowex-30, the hydrogen resin is subject during exchange to a partial

Dowex-50

Table IV

Hydrogen Resin (NaCl+HCl)

No.	Original Solution	Weight of Resin	ΔNa^+	ΔH^+	$\frac{\Delta\text{H} - \Delta\text{Na}}{\text{eq.res.}}$	N_{NaRes}	K_c	K_a
1.	$\text{Na}^+=0.9540\text{M}$ $\text{H}^+=0.0$	4.0139	0.01223	0.01255	0.022	0.878	1.08	1.62
2.	$\text{Na}^+=0.9604$ $\text{H}^+=0.0429$	4.3836	0.01264	0.01307	0.028	0.839	1.15	1.72
3.	$\text{Na}^+=0.8554$ $\text{H}^+=0.09267$	5.1797	0.01373	0.01455	0.045	0.784	1.22	1.83
4.	$\text{Na}^+=0.8073$ $\text{H}^+=0.1401$	3.9404	0.01044	0.01095	0.038	0.777	1.23	1.84
5.	$\text{Na}^+=0.7624$ $\text{H}^+=0.1822$	4.1732	0.01054	0.01095	0.028	0.735	1.23	1.84
6.	$\text{Na}^+=0.7100$ $\text{H}^+=0.2323$	4.4417	0.01070	0.01133	0.040	0.710	1.39	2.08
7.	$\text{Na}^+=0.6575$ $\text{H}^+=0.2851$	4.3257	0.00995	0.01043	0.031	0.671	1.42	2.13
8.	$\text{Na}^+=0.5783$ $\text{H}^+=0.3644$	4.4526	0.00909	0.00979	0.044	0.603	1.44	2.16
9.	$\text{Na}^+=0.4633$ $\text{H}^+=0.4771$	4.2934	0.00734	0.00817	0.055	0.511	1.49	2.24
10.	$\text{Na}^+=0.3704$ $\text{H}^+=0.5730$	4.1807	0.00611	0.00637	0.018	0.423	1.52	2.28
11.	$\text{Na}^+=0.2843$ $\text{H}^+=0.6848$	5.3770	0.00579	0.00687	0.057	0.323	1.59	2.38
12.	$\text{Na}^+=0.2376$ $\text{H}^+=0.7058$	4.1057	0.00407	0.00479	0.049	0.295	1.60	2.40
13.	$\text{Na}^+=0.1885$ $\text{H}^+=0.7965$	4.4132	0.00332	0.00444	0.072	0.229	1.61	2.42
14.	$\text{Na}^+=0.1399$ $\text{H}^+=0.8472$	5.1289	0.00285	0.00385	0.035	0.166	1.59	2.38
15.	$\text{Na}^+=0.09581$ $\text{H}^+=0.8960$	4.1022	0.00160	0.00246	0.059	0.117	1.54	2.31
16.	$\text{Na}^+=0.0447$ $\text{H}^+=0.9472$	4.5867	0.00080	0.00182	0.063	0.053	1.49	2.24

Dowex-50

Table V

Sodium Resin (NaCl + HCl)

No.	Original Solution	Weight of Resin	ΔH^+	ΔNa^+	$\frac{\Delta Na - \Delta H}{eq. res.}$	N_{NaRes}	K_c	K_a
1.	$H^+ = 0.9462$	3.7209 g	0.01028	0.01124	0.071	0.175	1.57	2.36
2.	$H^+ = 0.9472$ $Na^+ = 0.0441$	4.0209	0.01027	0.01145	0.081	0.229	1.58	2.37
3.	$H^+ = 0.8960$ $Na^+ = 0.0958$	3.6502	0.00887	0.00972	0.065	0.280	1.63	2.44
4.	$H^+ = 0.8472$ $Na^+ = 0.1399$	3.7534	0.00829	0.00942	0.083	0.333	1.62	2.43
5.	$H^+ = 0.7968$ $Na^+ = 0.1885$	2.8672	0.00590	0.00693	0.099	0.367	1.66	2.49
6.	$H^+ = 0.7058$ $Na^+ = 0.2376$	4.2538	0.00780	0.00884	0.068	0.455	1.61	2.42
7.	$H^+ = 0.6848$ $Na^+ = 0.2843$	3.0509	0.00534	0.00625	0.082	0.471	1.62	2.43
8.	$H^+ = 0.5735$ $Na^+ = 0.3704$	2.7249	0.00407	0.00482	0.076	0.552	1.56	2.34
9.	$H^+ = 0.4771$ $Na^+ = 0.4633$	3.6991	0.00443	0.00551	0.081	0.640	1.49	2.24
10.	$H^+ = 0.3644$ $Na^+ = 0.5783$	4.3394	0.00404	0.00519	0.072	0.723	1.38	2.07
11.	$H^+ = 0.2851$ $Na^+ = 0.6575$	5.9399	0.00420	0.00549	0.060	0.793	1.31	1.96
12.	$H^+ = 0.2323$ $Na^+ = 0.7100$	4.7742	0.00278	0.00380	0.059	0.829	1.31	1.96
13.	$H^+ = 0.1822$ $Na^+ = 0.7624$	4.1405	0.00203	0.00302	0.066	0.854	1.20	1.80
14.	$H^+ = 0.1401$ $Na^+ = 0.8073$	4.8073	0.00190	0.00335	0.083	0.880	1.17	1.76
15.	$H^+ = 0.0927$ $Na^+ = 0.8554$	4.0362	0.00109	0.00232	0.084	0.918	1.05	1.58
16.	$H^+ = 0.0429$ $Na^+ = 0.9069$	4.6902	0.00067	0.00181	0.067	0.959	0.88	1.32
17.	$Na^+ = 0.9540$	2.8296	0	0.00047	0.046	-	-	-

hydrolysis, the extent of which, however, is appreciably less than in the previous study. It may be noted also that there is a marked difference in the magnitude of the values of $\frac{\Delta Na - \Delta H}{\text{eq. res.}}$ given in Table V, and those in Table II for the sodium hydrogen exchange on the sodium form of Dowex-30. In the latter case, the difference between the gain of sodium ion and the loss of hydrogen ion was negligibly small and was attributed entirely to experimental error. In the case of Dowex-50, however, the values of $\frac{\Delta Na - \Delta H}{\text{eq. res.}}$ are so large as to indicate that a reaction other than simple exchange is taking place. This behavior is analogous to the hydrolytic reaction found to occur in studies involving the hydrogen forms of both Dowex-30 and Dowex-50. In the case of Dowex-30, the anion corresponding to the loss of cation from the resin was readily found to be sulfate ion. Attempts to identify the anion associated with the cation lost from Dowex-50, however, were unsuccessful.

The values of K shown in Tables IV and V are for the reaction



$$K_c = \frac{(\text{NaRes})(\text{H}^+)}{(\text{HRes})(\text{Na}^+)}$$

The data of Table IV were treated in the same manner as those of Table I, while the data of Table V were treated in an entirely analogous manner; that is, (H^+) and (Na^+) are the hydrogen and sodium ion concentrations, respectively, as determined by analysis of the effluent. (HRes) is equal to

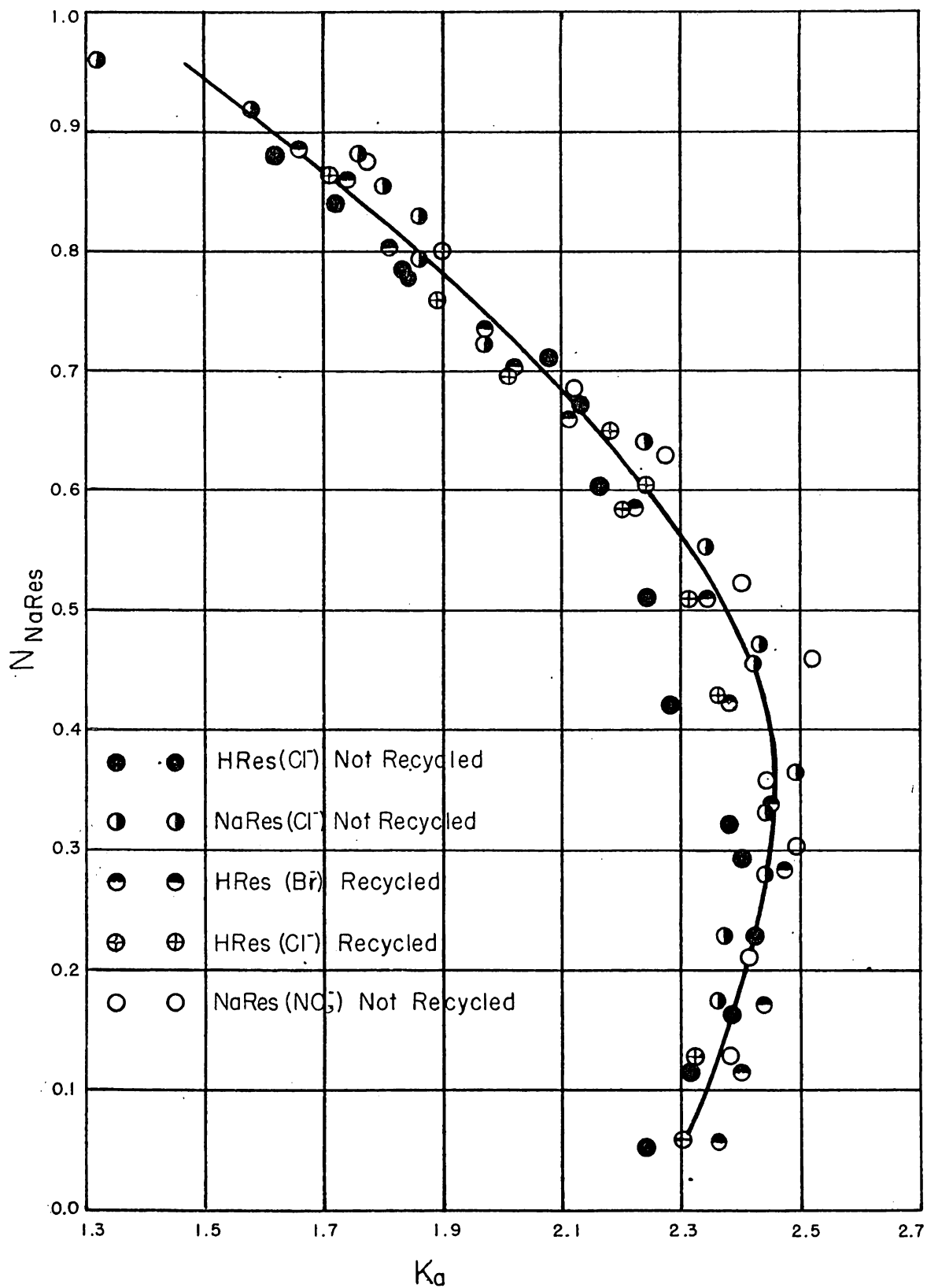
ΔH^+ , while (NaRes) is the number of equivalents of sodium resin initially present, minus the increase in sodium ion concentration in the solution. Values of K_a are derived by multiplying the K_c value by the ratio of the squares of the mean activity coefficients of hydrogen chloride and sodium chloride at unit ionic strength; i. e.,

$$K_a = K_c \cdot \frac{\gamma_{\text{HCl}}^2}{\gamma_{\text{NaCl}}^2}$$

Values of mean activity coefficients used in this dissertation were obtained from two sources: a) Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943. b) Latimer, W. M., "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

Values of the equilibrium quotient are shown plotted against the equilibrium mole fractions of sodium resin in Figure II. It is apparent from this plot that the values of K_a increase with increasing mole fraction of hydrogen resin to a maximum of approximately 2.4 when N_{HRes} is about 0.7. Further increase in the proportion of hydrogen resin in the solid phase is accompanied by a slight decrease in the values of K_a . As stated before, it is believed that the largest source of deviation from constancy of K_a lies in the assumption that the solid phase is an ideal solid solution, in which the activities of the two components are equal to their respective mole fractions. It may be seen from Figure II

Figure II



that no apparent hysteresis was encountered in this study; i.e., that the values of K_a derived from hydrogen resin and from sodium resin are in good agreement with each other throughout the range of the investigation.

In an attempt to discover whether or not the magnitude of the differences between the gain of hydrogen ion and loss of sodium ion might be diminished by previous treatment of the resin, a sample was "conditioned" by recycling ten times, and the investigation of the sodium-hydrogen exchange repeated with the "conditioned" resin. The results are given in Table VI and are shown graphically in Figure II. Instead of being decreased, the magnitude of the differences was actually considerably increased by the recycling procedure. However, when the values of K_a are calculated and plotted as before, the curve obtained coincides with that for the "unconditioned" resin.

A study of the effect of anions upon the sodium-hydrogen exchange was next undertaken. Hydrogen resin was employed for the exchange studies in bromide media, and sodium resin for those in nitrate media. A series of batch studies in solutions of approximately unit ionic strength were made as described previously for the chloride media. Results of these two investigations are presented in Tables VII and VIII, and are shown graphically in Figure II. From these experiments, it was concluded that the results sodium-hydrogen exchange on Dowex-50 are independent of the anion present.

Dowex-50

Table VI Recycled Hydrogen Resin (NaCl + HCl)

No.	Original Solution	Weight of Resin	ΔNa^+	ΔH^+	$\frac{\Delta\text{H}^+ - \Delta\text{Na}^+}{\text{eq. res.}}$	N_{NaRes}	K_c	K_a
1.	$\text{Na}^+ = 0.0503\text{M}$ $\text{H}^+ = 0.9476$	4.3903	0.00095	0.00224	0.076	0.061	1.53	2.30
2.	$\text{Na}^+ = 0.09556$ $\text{H}^+ = 0.8976$	4.6859	0.00189	0.00327	0.077	0.128	1.55	2.32
3.	$\text{Na}^+ = 0.2843$ $\text{H}^+ = 0.6848$	4.4536	0.00524	0.00664	0.082	0.333	1.62	2.43
4.	$\text{Na}^+ = 0.3816$ $\text{H}^+ = 0.5677$	4.5168	0.00700	0.00807	0.062	0.429	1.57	2.36
5.	$\text{Na}^+ = 0.4633$ $\text{H}^+ = 0.4771$	4.3078	0.00767	0.00922	0.094	0.511	1.54	2.31
6.	$\text{Na}^+ = 0.5724$ $\text{H}^+ = 0.3785$	4.0508	0.00932	0.01026	0.056	0.583	1.47	2.20
7.	$\text{Na}^+ = 0.5783$ $\text{H}^+ = 0.3644$	4.4310	0.00964	0.01072	0.063	0.604	1.49	2.24
8.	$\text{Na}^+ = 0.6575$ $\text{H}^+ = 0.2851$	5.1796	0.01225	0.01329	0.052	0.649	1.45	2.18
9.	$\text{Na}^+ = 0.7155$ $\text{H}^+ = 0.2386$	4.3157	0.01080	0.01166	0.064	0.695	1.34	2.01
10.	$\text{Na}^+ = 0.7554$ $\text{H}^+ = 0.2494$	4.6102	0.01154	0.01266	0.063	0.695	1.34	2.01
11.	$\text{Na}^+ = 0.8073$ $\text{H}^+ = 0.1401$	4.5420	0.001242	0.01351	0.062	0.759	1.26	1.89
12.	$\text{Na}^+ = 0.9540$ $\text{H}^+ = 0.0$	4.3922	0.01393	0.01469	0.045	0.864	1.14	1.71

Dowex-50

Table VII

Hydrogen Resin (NaBr + HBr)

No.	Original Solution	Weight of Resin	ΔNa^+	ΔH^+	$\frac{\Delta\text{H} - \Delta\text{Na}}{\text{eq. res.}}$	N_{NaRes}	K_c	K_a
1.	$\text{Na}^+ = 1.023 \text{ M}$ $\text{H}^+ = 0.0$	3.5003	0.01117	0.01209	0.068	0.887	1.03	1.66
2.	$\text{Na}^+ = 1.023$ $\text{H}^+ = 0.0$	4.6809	0.01480	0.01564	0.046	0.858	1.08	1.74
3.	$\text{Na}^+ = 0.9898$ $\text{H}^+ = 0.1005$	4.3975	0.01270	0.01385	0.068	0.802	1.12	1.81
4.	$\text{Na}^+ = 0.8796$ $\text{H}^+ = 0.2009$	4.6704	0.01256	0.01348	0.051	0.733	1.22	1.97
5.	$\text{Na}^+ = 0.8250$ $\text{H}^+ = 0.2508$	4.5934	0.01174	0.01272	0.055	0.701	1.25	2.02
6.	$\text{Na}^+ = 0.7156$ $\text{H}^+ = 0.3014$	4.1780	0.01004	0.01099	0.059	0.663	1.31	2.11
7.	$\text{Na}^+ = 0.6129$ $\text{H}^+ = 0.4021$	4.4148	0.00934	0.01046	0.066	0.585	1.38	2.22
8.	$\text{Na}^+ = 0.5115$ $\text{H}^+ = 0.5010$	4.4649	0.00820	0.00939	0.069	0.511	1.45	2.34
9.	$\text{Na}^+ = 0.4092$ $\text{H}^+ = 0.6018$	4.4291	0.00684	0.00787	0.060	0.425	1.48	2.38
10.	$\text{Na}^+ = 0.3074$ $\text{H}^+ = 0.7010$	4.2375	0.00512	0.00634	0.075	0.338	1.52	2.45
11.	$\text{Na}^+ = 0.2558$ $\text{H}^+ = 0.7523$	4.5050	0.00455	0.00595	0.080	0.284	1.53	2.47
12.	$\text{Na}^+ = 0.1534$ $\text{H}^+ = 0.8585$	4.8218	0.00294	0.00447	0.082	0.172	1.51	2.44
13.	$\text{Na}^+ = 0.1023$ $\text{H}^+ = 0.9090$	4.6321	0.00188	0.00361	0.097	0.116	1.49	2.40
14.	$\text{Na}^+ = 0.05096$ $\text{H}^+ = 0.9521$	4.3232	0.00088	0.00276	0.112	0.059	1.46	2.36

Dowex-50

Table VIII

Sodium Resin ($\text{NaNO}_3 + \text{HNO}_3$)

No.	Original Solution	Weight of Resin	ΔH^+	ΔNa^+	$\frac{\Delta\text{Na} - \Delta\text{H}}{\text{eq. res.}}$	N_{NaRes}	K_c	K_a
1.	$\text{H}^+ = 0.9847\text{M}$	3.0912 g	0.00890	0.00978	0.079	0.132	1.39	2.38
2.	$\text{H}^+ = 0.9355$ $\text{Na}^+ = 0.0495$	3.8709	0.01029	0.01116	0.062	0.214	1.40	2.41
3.	$\text{H}^+ = 0.8861$ $\text{Na}^+ = 0.0992$	4.9538	0.01155	0.01301	0.087	0.304	1.46	2.49
4.	$\text{H}^+ = 0.7869$ $\text{Na}^+ = 0.1990$	3.1452	0.00673	0.00760	0.077	0.359	1.42	2.44
5.	$\text{H}^+ = 0.6860$ $\text{Na}^+ = 0.2968$	3.3461	0.00593	0.00698	0.087	0.463	1.48	2.52
6.	$\text{H}^+ = 0.5868$ $\text{Na}^+ = 0.3971$	3.2125	0.00481	0.00589	0.093	0.543	1.40	2.40
7.	$\text{H}^+ = 0.4898$ $\text{Na}^+ = 0.4953$	4.1183	0.00508	0.00625	0.078	0.629	1.33	2.27
8.	$\text{H}^+ = 0.3927$ $\text{Na}^+ = 0.5935$	3.1027	0.00323	0.00416	0.083	0.686	1.24	2.12
9.	$\text{H}^+ = 0.2449$ $\text{Na}^+ = 0.7431$	3.8757	0.00258	0.00376	0.085	0.798	1.11	1.90
10.	$\text{H}^+ = 0.1469$ $\text{Na}^+ = 0.8420$	2.5873	0.00113	0.00196	0.089	0.869	1.03	1.77

Further, since the values of $\frac{\Delta H - \Delta Na}{\text{eq. res.}}$ and $\frac{\Delta Na - \Delta H}{\text{eq. res.}}$ have approximately the same values as those previously observed in the chloride media, it may be assumed that the hydrolytic effect is not in any way related to the anion employed. It may also be noted that whereas Dowex-30 is partially oxidized by 1 M nitric acid, as evidenced by the odor of oxides of nitrogen observed in the reaction flask, Dowex-50 is entirely stable toward this reagent.

In order to determine whether or not the magnitude of the hydrolytic effect is dependent upon the ionic strength of the solution, an investigation of the ammonium-hydrogen exchange on hydrogen resin was undertaken at ionic strengths of approximately 1, 0.75, 0.50, 0.375, 0.25, and 0.1. The ammonium ion concentrations in the exchange solutions were determined by the addition of concentrated sodium hydroxide solution to the sample, followed by distillation of the liberated ammonia into a sample of standard acid. The excess acid was then titrated with a standard sodium hydroxide solution. Hydrogen ion concentrations were determined as before. These results are contained in Table IX; a plot of the average values of $\frac{\Delta H - \Delta NH_4}{\text{eq. res}}$ against the average ionic strengths is shown in Figure III. From this curve it may be observed that the hydrolytic effect does indeed vary in the same direction as the ionic strength. From the highest value of 0.091 equivalents per equivalent of resin when the ionic strength is approximately 1.1, the hydrolytic effect decreases slowly

$\mu = 1.0933$

Table IX

HRes + NH₄Cl + HCl

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔH^+	ΔNH_4^+	$\frac{\Delta H - \Delta NH_4}{\text{eq. res.}}$	$N_{NH_4 \text{ Res}}$	K_c	K_a
1.	NH ₄ ⁺ =1.0997M H ⁺ =	4.3446	0.01860	0.01641	0.01459	0.0978	0.869	1.15	2.38
2.	NH ₄ ⁺ =0.8247 H ⁺ =0.2594	4.3834	0.01877	0.01376	0.01225	0.0805	0.710	1.38	2.86
3.	NH ₄ ⁺ =0.5498 H ⁺ =0.5188	4.4177	0.01891	0.01107	0.00953	0.0814	0.549	1.68	3.48
4.	NH ₄ ⁺ =0.2749 H ⁺ =0.7782	4.3596	0.01866	0.00762	0.00570	0.103	0.340	2.03	4.20

ave.=0.0907

 $\mu = 0.8169$

1.	NH ₄ ⁺ =0.8266 H ⁺ =	3.1102	0.01332	0.01186	0.01111	0.0570	0.884	1.25	2.19
2.	NH ₄ ⁺ =0.6200 H ⁺ =0.1929	3.0375	0.01300	0.00976	0.00862	0.0878	0.726	1.44	2.52
3.	NH ₄ ⁺ =0.4133 H ⁺ =0.3858	3.2444	0.01389	0.00828	0.00707	0.0872	0.557	1.72	3.01
4.	NH ₄ ⁺ =0.2067 H ⁺ =0.5787	3.0313	0.01298	0.00551	0.00424	0.0986	0.362	2.19	3.83

ave.=0.0826

 $\mu = 0.5434$

1.	NH ₄ ⁺ =0.5481 H ⁺ =	2.2501	0.009633	0.00851	0.00789	0.0645	0.876	1.28	1.92
2.	NH ₄ ⁺ =0.4111 H ⁺ =0.1292	2.1623	0.009257	0.00687	0.00609	0.0843	0.718	1.44	2.16
3.	NH ₄ ⁺ =0.2740 H ⁺ =0.2580	2.1120	0.009042	0.00539	0.00468	0.0786	0.562	1.77	2.66
4.	NH ₄ ⁺ =0.1370 H ⁺ =0.3875	2.3733	0.01016	0.00395	0.00319	0.0748	0.340	2.09	3.14

ave.=0.0755

$\mu = 0.3740$

Table IX (continued)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔH^+	ΔNH_4^+	$\frac{\Delta H - \Delta NH_4}{\text{eq. res.}}$	$N_{NH_4 \text{ Res}}$	K_c	K_a
1.	$NH_4^+ = 0.3687$ $H^+ =$	1.6211	0.006940	0.00610	0.00552	0.0836	0.867	1.28	1.71
2.	$NH_4^+ = 0.2766$ $H^+ = 0.0928$	1.6699	0.007149	0.00519	0.00499	0.0280	0.719	1.62	2.16
3.	$NH_4^+ = 0.1844$ $H^+ = 0.1856$	1.6464	0.007049	0.00403	0.00352	0.0724	0.538	1.76	2.35
4.	$NH_4^+ = 0.0922$ $H^+ = 0.2784$	1.6045	0.006869	0.00258	0.00213	0.0655	0.332	2.13	2.84

ave. = 0.0624

 $\mu = 0.2663$

1.	$NH_4^+ = 0.2736$ $H^+ =$	1.1271	0.004825	0.00429	0.00424	0.0104	0.889	1.49	1.89
2.	$NH_4^+ = 0.2052$ $H^+ = 0.0648$	1.0826	0.004635	0.00345	0.00344	0.0022	0.740	1.65	2.09
3.	$NH_4^+ = 0.1368$ $H^+ = 0.1296$	1.0946	0.004686	0.00275	0.00258	0.0363	0.571	1.88	2.38
4.	$NH_4^+ = 0.0684$ $H^+ = 0.1944$	1.1373	0.004869	0.00180	0.00163	0.0349	0.347	2.16	2.74

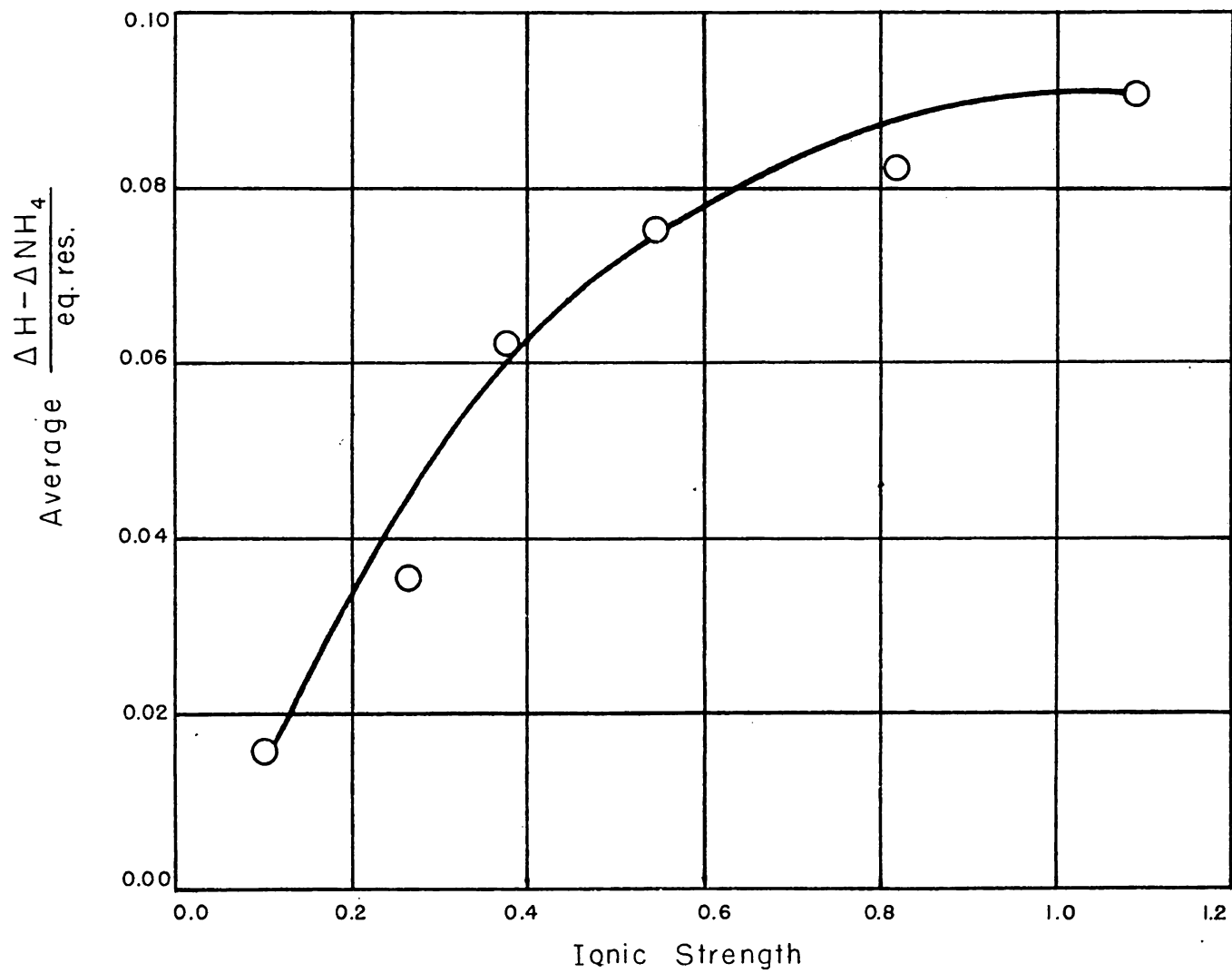
ave. = 0.0356

 $\mu = 0.1026$

1.	$NH_4^+ = 0.1026$ $H^+ =$	0.4411	0.001889	0.001654	0.001596	0.0306	0.872	1.30	1.50
2.	$NH_4^+ = 0.07701$ $H^+ = 0.02537$	0.4302	0.001842	0.001337	0.001348	-0.0060	0.729	1.64	1.90
3.	$NH_4^+ = 0.05134$ $H^+ = 0.05074$	0.4256	0.001822	0.001028	0.000997	0.0170	0.556	1.85	2.14

ave. = 0.0155

Figure III



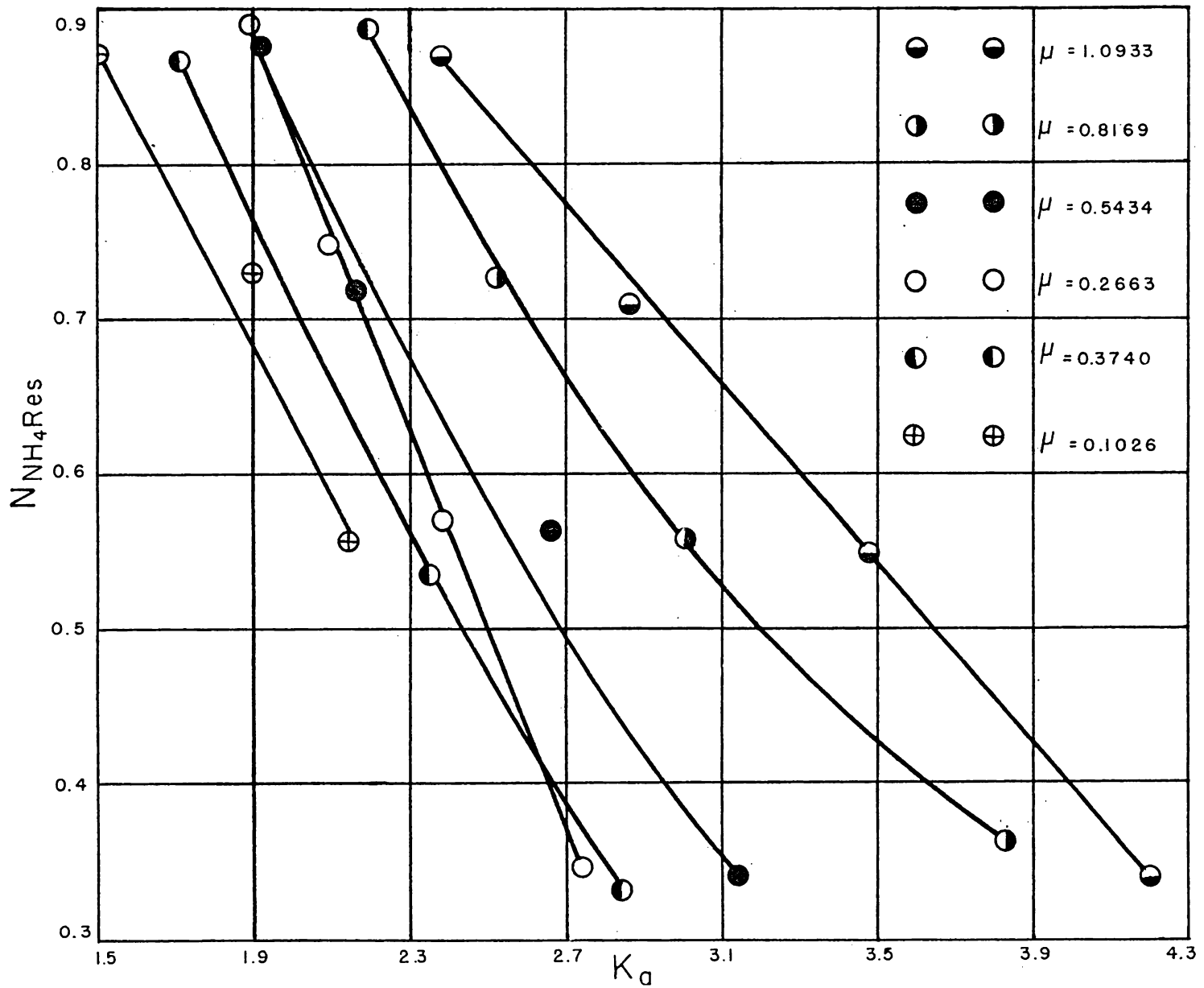
with decreasing ionic strength. At an ionic strength of approximately 0.5, the curve turns rather sharply, however, and the magnitude of the hydrolytic effect decreases more rapidly, attaining a value of only 0.015 equivalent per equivalent of resin at an ionic strength of 0.1.

The evidence presented by this study seems to indicate that the method of correction for the hydrolytic effect used by Juda and Carron (21) is in error, since the magnitude of hydrolytic effect which they used was determined for the resin in pure water instead of in solutions of electrolytes.

The values of the equilibrium constants for this series of exchanges, calculated in the same manner as that used in the sodium-hydrogen exchange on Dowex-50, are shown graphically in Figure IV. The results appear as a family of curves, in which the highest values of K_a occur at unit ionic strength. An exception to the foregoing statement must be made for the series at ionic strengths of 0.25 and 0.375, the curves for which are in reverse order. This fact may possibly be due to the increased validity of the ionic strength principle at the lower ionic strengths. The assumption regarding the activities of the two components of the solid phase remains the primary cause for the lack of constancy in the values of K_a .

It has been observed that although the method of preparation of the pure resin has no effect upon the value of the equilibrium constant, K_a , for a particular exchange,

Figure IV



the magnitude of the hydrolytic effect is greater for recycled resin than for resin which has not received such extensive conditioning treatment. This increased discrepancy was considered to be due to the repeated treatments with 6 M hydrochloric acid, which might conceivably have exerted some deleterious effect on the stability of the resin. Accordingly, a sample of resin as received from the manufacturer, with no preliminary treatment other than size screening, was changed to the pure hydrogen form by treatment with 1 M hydrochloric acid, reconverted to sodium resin by means of a saturated sodium chloride solution, and finally changed back to hydrogen resin with 1 M hydrochloric acid. A series of exchanges of sodium and hydrogen ions at unit ionic strength was studied as in previous work.

As before, it was observed that this mode of preparation of the resin had no effect on the value of the equilibrium constant, K_a . The value of the hydrolytic effect, $\frac{\Delta H - \Delta Na}{\text{eq. res.}}$, however, was no lower than those encountered previously, but assumed approximately the same magnitude. It was concluded, therefore, that treatment with 6 M hydrochloric acid was not a contributing cause of the hydrolytic effect.

VI. SILVER-HYDROGEN EXCHANGE ON DOWEX-50

Inasmuch as Dowex-50 does not contain the phenol group which presumably brings about the reduction of silver ion to metallic silver by Dowex-30, and since Dowex-50 is not noticeably attacked by 1 M nitric acid, it was decided to attempt again the investigation of the silver-hydrogen exchange, with Dowex-50 as the solid exchanger. The approach to the problem was essentially that employed in the sodium-hydrogen exchange.

The hydrogen resin was prepared and its equivalent weight determined as before. For the preparation of pure silver resin, pure hydrogen resin was placed in a column 5 cm. wide and 70 cm. long, and a 1 N solution of silver nitrate was passed through it. The liberated hydrogen ion in the effluent solution was neutralized by vigorous agitation with an excess of freshly prepared silver oxide. After filtration, the solution was thus ready for another passage through the column. When the pH of the effluent solution showed no more than a negligible decrease from that of the influent solution, the conversion to silver resin was considered to be complete. The resin was then removed from the column and washed with distilled water until free of silver ion, as evidenced by the fact that the addition of chloride ion to the wash water yielded no precipitate. The resin was then dried in the usual manner. The equivalent weight of the silver resin was determined by placing a weighed quantity of

resin in a small column, through which a saturated solution of sodium nitrate was passed to displace the silver ion. An aliquot portion of the effluent solution was then titrated with a standard sodium chloride solution to the potentiometric equivalence point.

As in previous studies, a series of samples were treated with aqueous solutions of silver nitrate and nitric acid of total ionic strength approximately equal to unity. As a precaution against the photochemical reduction of silver ion, the reaction flasks were painted black. Portions of the equilibrium solutions were removed and analyzed for hydrogen and silver ions as before.

Table X contains the data for the silver-hydrogen exchange on hydrogen resin, and Table XI contains the data for the silver-hydrogen exchange on silver resin. Examination of the values of $\frac{\Delta H - \Delta Ag}{\text{eq. res.}}$ in Table X and of $\frac{\Delta Ag - \Delta H}{\text{eq. res.}}$ in Table XI reveals that in neither of these studies may the data be treated in a manner similar to that used for the sodium-hydrogen exchange. Whereas the quotient $\frac{\Delta H - \Delta Na}{\text{eq. res.}}$ always assumed positive values of approximately the same magnitude, the values of $\frac{\Delta H - \Delta Ag}{\text{eq. res.}}$ range from positive at the lower concentrations of silver ion to the rather large negative quantities found for higher concentrations of silver ion. The same is true as well for values of $\frac{\Delta Ag - \Delta Na}{\text{eq. res.}}$ listed in Table XI. It is to be expected that the hydrolytic action on the hydrogen resin, as previously discussed, would be encountered again in this study, and the initial

Dowex-50

Table X

HRes ($\text{AgNO}_3 + \text{HNO}_3$)

No.	Wt. Resin	Original Solution	ΔH^+	ΔAg^+	$\frac{\Delta\text{H} - \Delta\text{Ag}}{\text{eq. res.}}$	N_{AgRes}	K_c	K_a	$\frac{\text{Eq. Ag}^+ \text{ Ads.}}{\text{eq. res.}}$
1.	3.7911	$\text{Ag}^+ = 0.9869$ $\text{H}^+ =$	0.01326	0.01405	-0.058	0.976	6.50	21.0	0.118
2.	4.6133	$\text{Ag}^+ = 0.9871$ $\text{H}^+ =$	0.01607	0.01691	-0.051	0.964	6.73	21.8	0.111
3.	4.4872	$\text{Ag}^+ = 0.8884$ $\text{H}^+ = 0.0979$	0.01535	0.01604	-0.043	0.954	7.10	23.0	0.103
4.	4.3197	$\text{Ag}^+ = 0.7403$ $\text{H}^+ = 0.2447$	0.01425	0.01490	-0.042	0.918	7.27	23.5	0.102
5.	4.9700	$\text{Ag}^+ = 0.7402$ $\text{H}^+ = 0.2442$	0.01624	0.01685	-0.034	0.909	7.03	22.8	0.094
6.	4.5225	$\text{Ag}^+ = 0.5922$ $\text{H}^+ = 0.3914$	0.01405	0.01419	-0.0086	0.860	7.22	23.4	0.069
7.	3.7737	$\text{Ag}^+ = 0.4935$ $\text{H}^+ = 0.4894$	0.01122	0.01123	0.0000	0.821	7.22	23.4	0.060
8.	4.2694	$\text{Ag}^+ = 0.3946$ $\text{H}^+ = 0.5873$	0.01134	0.01118	+0.010	0.727	6.58	21.3	0.050
9.	4.0480	$\text{Ag}^+ = 0.2959$ $\text{H}^+ = 0.6852$	0.00927	0.00890	+0.025	0.617	6.06	19.6	0.035
10.	4.8173	$\text{Ag}^+ = 0.2467$ $\text{H}^+ = 0.7341$	0.00940	0.00879	+0.036	0.530	5.88	19.0	0.024
11.	4.0853	$\text{Ag}^+ = 0.1975$ $\text{H}^+ = 0.7828$	0.00727	0.00663	+0.044	0.465	5.67	18.4	0.016
12.	4.3548	$\text{Ag}^+ = 0.1480$ $\text{H}^+ = 0.8319$	0.00618	0.00546	+0.046	0.358	5.33	17.3	0.014
13.	4.4174	$\text{Ag}^+ = 0.0988$ $\text{H}^+ = 0.8807$	0.00466	0.00381	+0.054	0.250	5.10	16.5	0.006
14.	4.4843	$\text{Ag}^+ = 0.0492$ $\text{H}^+ = 0.9299$	0.00295	0.00198	+0.060	0.132	4.96	16.1	0.000

Dowex-50

Table XI

Silver Resin ($\text{AgNO}_3 + \text{HNO}_3$)

No.	Wt. Resin	Original Solution	ΔAg^+	ΔH^+	$\frac{\Delta\text{Ag} - \Delta\text{H}}{\text{eq. res.}}$	N_{AgRes}	K_c	K_a	$\frac{\text{Eq. Ag}^+\text{Ads.}}{\text{eq. res.}}$
1.	5.7802	$\text{H}^+ = 0.9858$ $\text{Ag}^+ =$	0.01029	0.00909	+0.074	0.394	5.65	18.3	-----
2.	6.4970	$\text{H}^+ = 0.9562$ $\text{Ag}^+ = 0.0279$	0.01018	0.00888	+0.071	0.475	6.05	19.6	-----
3.	5.6798	$\text{H}^+ = 0.9365$ $\text{Ag}^+ = 0.0465$	0.00878	0.00764	+0.072	0.483	5.98	19.4	-----
4.	5.5989	$\text{H}^+ = 0.9365$ $\text{Ag}^+ = 0.0465$	0.00867	0.00756	+0.070	0.481	6.00	19.4	-----
5.	6.5268	$\text{H}^+ = 0.8872$ $\text{Ag}^+ = 0.0929$	0.00839	0.00727	+0.061	0.570	6.07	19.6	0.0109
6.	6.6207	$\text{H}^+ = 0.8379$ $\text{Ag}^+ = 0.1394$	0.00732	0.00620	+0.060	0.640	6.48	21.0	0.0119
7.	5.9497	$\text{H}^+ = 0.8379$ $\text{Ag}^+ = 0.1394$	0.00674	0.00563	+0.066	0.636	6.59	21.3	0.0060
8.	7.6009	$\text{H}^+ = 0.8078$ $\text{Ag}^+ = 0.1859$	0.00714	0.00600	+0.054	0.695	6.60	21.4	0.0183
9.	5.6986	$\text{H}^+ = 0.7394$ $\text{Ag}^+ = 0.2323$	0.00471	0.00392	+0.049	0.735	6.95	22.5	0.0226
10.	5.3129	$\text{H}^+ = 0.6901$ $\text{Ag}^+ = 0.2788$	0.00378	0.00312	+0.044	0.775	7.13	23.1	0.0266
11.	5.7115	$\text{H}^+ = 0.6059$ $\text{Ag}^+ = 0.3717$	0.00307	0.00243	+0.040	0.838	7.40	24.0	0.0318
12.	6.7308	$\text{H}^+ = 0.4929$ $\text{Ag}^+ = 0.4647$	0.00244	0.00182	+0.033	0.895	8.35	27.0	0.0392
13.	6.4029	$\text{H}^+ = 0.4039$ $\text{Ag}^+ = 0.5576$	0.00175	0.00140	+0.020	0.916	7.39	23.9	0.0525
14.	5.7725	$\text{H}^+ = 0.2020$ $\text{Ag}^+ = 0.7434$	0.00066	0.00044	+0.014	0.970	8.71	28.2	0.0581
15.	6.6389	$\text{H}^+ = 0.1010$ $\text{Ag}^+ = 0.8364$	0.00046	0.00023	+0.013	0.988	8.70	28.2	0.0597

positive values of $\frac{\Delta H - \Delta Ag}{\text{eq. res.}}$ may indeed be accounted for in this manner. As the concentration of silver ion is increased, however, a second deviation, opposite in sign, becomes the predominant term in the value of $\frac{\Delta H - \Delta Ag}{\text{eq. res.}}$.

It was at first supposed that this latter deviation resulted from the reduction of an appreciable quantity of silver ion to metallic silver in the more concentrated solutions. In order to test this supposition, investigations were undertaken to reveal the presence of metallic silver, either in suspension in the equilibrium solutions or on the resin itself, after a typical batch study of the silver-hydrogen exchange. Since all such attempts failed to yield a quantitative silver balance, it was thought that finely divided metallic silver might have been lost in the removal of original equilibrium solution from the solid phase. A quantitative column study was therefore carried out, in which a measured quantity of hydrogen resin was converted into silver resin in a micro-column wrapped with heating wire and with glass tape for insulation against loss of heat and entry of actinic rays. After the quantity of silver ion taken up by the resin had been accurately determined, the silver ion was completely eluted with saturated sodium nitrate solution. The quantity of silver ion recovered by this elution was found to be equal to that taken up by the resin. Furthermore, if any finely divided silver had been present, it must have been retained either on the resin or on the fritted glass filter at the bottom of the column. Accordingly,

after the elution with sodium nitrate, the column was filled with concentrated nitric acid, which was heated to boiling by means of the column heater. This nitric acid was then removed and tested for silver ion; the result was completely negative. In view of these experiments, it was concluded that the new type of deviation encountered in the silver-hydrogen system could not be the result of partial reduction of the silver ion by the resin.

An explanation of the results in terms of adsorption of silver ion by the resin was next considered. In addition to true exchange between the solution and the solid, it appears to be possible also for adsorption of ions from the solution on the solid resin to take place. If this were true, the number of equivalents of silver ion lost from the solution might well exceed the number of equivalents of hydrogen ion gained from the resin. It would be expected, furthermore, according to this hypothesis, that the values of $\frac{\Delta H - \Delta A_g}{\text{eq. res.}}$ would be increasingly negative as the initial concentration of the silver ion was increased. This is precisely the trend observed in the experimental results presented in Table X.

In order further to test this new hypothesis, pure silver nitrate solutions were allowed to stand in contact with pure silver resin, and a decrease in silver ion concentration in the equilibrium solution was observed in every case. Since the possibility of reduction of silver ion to metallic silver has already been eliminated, and since true

exchange is obviously ruled out by the conditions of this experiment, it was concluded that this decrease in silver ion concentration must be due to adsorption. With various concentrations of silver ion in contact with the resin, the decrease in silver ion concentration was found to increase with increasing initial concentration. This fact is regarded as further evidence of the adsorption of silver ion by the resin.

In view of these facts, the experimental results already presented were treated as if true equilibrium exchange were accompanied by adsorption of silver ion. These calculations were carried out in such a manner as to distinguish between the extent of exchange and the extent of adsorption, each of which separately could be quantitatively determined.

In this method of calculation, two phenomena, in addition to true exchange, must be considered. First, the hydrogen resin, when brought into contact with aqueous solutions of electrolytes, has been shown to be partially decomposed by some hydrolytic reaction. Since there is no reason to suppose that this sort of effect would not occur also in the silver-hydrogen exchange, the positive values of $\frac{\Delta H - \Delta Ag}{\text{eq. res.}}$ in the solutions of very low silver ion concentrations are attributed to the hydrolytic effect. Secondly, the result of adsorption of silver ion by the resin would be in the opposite direction, and thus, if the hydrolytic effect did not exist, would make $\frac{\Delta H - \Delta Ag}{\text{eq. res.}}$ negative. The fact that, as the

original silver ion concentration is increased, a progressive decrease from positive to negative values of the deviations is observed, is in line with the hypothesis of combined hydrolytic and adsorption effects.

In the investigation of the silver-hydrogen exchange on hydrogen resin, it was assumed that no adsorption occurred in the batch study with the lowest original silver ion concentration. The extent of the hydrolytic effect may thus be evaluated from the difference between the number of equivalents of hydrogen ion gained by the solution and of silver ion lost by the solution in this instance. The extent of the hydrolytic effect was further assumed to be constant throughout the series of solutions with varying proportions of silver and hydrogen ions. This assumption seemed justified in view of the results obtained for the sodium-hydrogen exchange.

The quantity of hydrogen ion gained by the solution through true exchange was calculated by subtracting the constant hydrolytic effect from the total gain in hydrogen ion. The actual hydrolytic effect deducted in any particular member of the series of experiments is the product of the hydrolytic effect per equivalent of resin and the number of equivalents of resin actually used in the experiment. Further, as in the sodium-hydrogen exchange, a quantity of hydrogen resin equivalent to the extent of hydrolytic decomposition was assumed to be inactivated. The loss of silver ion from

the solution can then be separated into that due to true exchange and that due to adsorption. The number of equivalents of silver ion lost from the solution by exchange must be equal to the corrected number of equivalents of hydrogen ion gained by the solution. The excess loss of silver ion over that corresponding to true exchange represents the amount of silver ion adsorbed. It was further assumed that the adsorbed silver ion should not be included in the mol fraction of silver resin in the solid solution of silver and hydrogen resins which results at equilibrium.

As shown in Table X, sample 14, the value taken for the constant hydrolytic effect, obtained from the particular exchange study in which the influent silver ion concentration was a minimum, is 0.060 equivalent per equivalent of original hydrogen resin. Further support for the above assumptions is gained from the fact that the average hydrolytic effect for this same batch of hydrogen resin, when employed for the sodium-hydrogen exchange study, was 0.065 equivalent per equivalent of original hydrogen resin.

Similar reasoning may be used to explain the decreasing positive values of $\frac{\Delta Ag - \Delta H}{\text{eq. res.}}$ for the silver resin, which are presented in Table XI. In this case, the hydrolytic effect alone would cause the gain of a solution in silver ion from the resin to be greater than its loss in hydrogen ion to the resin. If it is assumed that this hydrolytic effect remains constant, and further that increasing amounts of silver ion

are adsorbed as the influent silver ion concentration increases, the over-all values of $\frac{\Delta Ag - \Delta H}{\text{eq. res.}}$ would be expected to decrease as the influent silver ion concentration increases. The fact that in the case of silver resin the adsorption effect never exceeds the hydrolytic effect, may be related to the observation that the hydrolytic effect for silver resin is greater than for hydrogen resin. Also, in the preparation of the silver resin, there may remain on the resin adsorbed silver ion which repeated washing with distilled water has failed to remove. This would decrease the adsorptive capacity of the resin in the batch studies.

Calculations of K_0 values for the true exchange on silver resin were made in a manner similar to that used for the same reaction on hydrogen resin. However, these calculations are here simplified by the fact that the loss of hydrogen ion by the solutions is a direct measure of the quantity of hydrogen resin at equilibrium. The quantity of silver resin at equilibrium was calculated as the difference between the number of active equivalents of original resin and the number of equivalents of hydrogen resin at equilibrium. Once again, the original weighed quantity of resin was corrected for that inactivated by the constant hydrolytic effect. The equilibrium concentrations of silver ion and hydrogen ion in solution were obtained by direct analysis. The quantitative estimation of the magnitude of the adsorption effect was obtained from the difference between the hydrolytic effect and the actual quantity, $\frac{\Delta Ag - \Delta H}{\text{eq. res.}}$. The constant hydrolytic

effect per equivalent of original resin was again obtained from the value of $\frac{\Delta Ag - \Delta H}{\text{eq. res.}}$ for an influent solution of minimum silver ion concentration. It is of interest to note the surprisingly close agreement of the average hydrolytic effect for the sodium and silver resins; these values are 0.073 and 0.072 equivalents per equivalent, respectively. Samples of the calculations of values of K_a contained in Tables X and XI are presented below.

1. Silver-hydrogen exchange on pure hydrogen resin.

(a) Data of item 7, Table X:

Wt. resin used = 3.7737 grams = 0.01350 equivalent
 Original silver ion concentration = 0.4935 M
 Original hydrogen ion concentration = 0.4894 M
 Equilibrium silver ion concentration = 0.3812 M
 Equilibrium hydrogen ion concentration = 0.6016 M

(b) Determination of K_c and K_a :

- (1) Total ΔH^+ = 0.6016 - 0.4894 = 0.1122 mole per l.
 Actual hydrogen ion gained in 100 mls. = 0.01122 equivalent
- (2) Hydrolytic gain in hydrogen ion = 0.060 x 0.01350
 = 0.0008 equivalent
- (3) Effective number of equivalents of resin =
 0.01350 - 0.00081 = 0.01269
- (4) Hydrogen ion gained by true exchange = 0.01122 -
 0.00081 = 0.01041 equivalent
- (5) Number of equivalents of AgRes = number of equivalents of Ag^+ lost from the solution by true exchange = gain of hydrogen ion, in actual equivalents, by exchange = 0.01041 equivalent
- (6) Number of equivalents of hydrogen resin = 0.01269 -
 0.01041 = 0.00228 equivalent

$$(7) K_c = \frac{(AgRes)(H^+)}{(HRes)(Ag^+)} = \frac{0.01041}{0.00228} \times \frac{0.6016}{0.3812} = 7.22$$

$$K_a = K_c \times \frac{(\% HNO_3 \text{ in 1 molar sol.})^2}{(\% AgNO_3 \text{ in 1 molar sol.})^2} = K_c \left(\frac{0.72}{0.40} \right)^2$$

$$= 23.4$$

(c) Quantity of silver ion adsorbed:

- (1) Total Ag^+ concentration = 0.3812 - 0.4935 = -0.1123 M
 = -0.01123 actual equivalent in 100 mls.
- (2) Ag^+ lost by the solution through true exchange =
 0.01041 eq.

(3) Number of equivalents of Ag^+ lost by adsorption
 = $0.01123 - 0.01041 = 0.00081$ eq.

(4) Eq. of Ag^+ lost/eq. resin = $\frac{(0.00081 \times 279)}{3.7737}$
 = 0.060 eq.

2. Silver-hydrogen exchange on pure silver resin:

(a) Data of item 12, Table XI:

Wt. resin = 6.7308 grams = 0.01882 equivalent

Original silver ion concentration = 0.4647 M

Original hydrogen ion concentration = 0.4929 M

Equilibrium silver ion concentration = 0.4891 M

Equilibrium hydrogen ion concentration = 0.4747 M

(b) Determination of K_c and K_a :

(1) Total $\Delta H^+ = 0.4929 - 0.4747 = 0.0182$ mole per liter
 Actual hydrogen ion lost by the 100 mls = 0.00182 equivalent

(2) Effective equivalents of resin = $0.01882 - 0.072 \times 0.01882 - 0.01882 - 0.00135 = 0.01747$ equivalent

(3) Hydrogen resin at equilibrium = equivalents of hydrogen ion lost by solution by true exchange = actual equivalents hydrogen ion lost = 0.00182 eq.

(4) Silver resin at equilibrium = $0.01747 - 0.00182 = 0.01565$ eq.

(5) $K_c = \frac{0.01565}{0.00182} \times \frac{0.4747}{0.4891} = 8.35$

$$K_a = K_c \times \left(\frac{\sqrt{\pm \text{HNO}_3 \text{ in 1 molar sol.}}}{\sqrt{\pm \text{AgNO}_3 \text{ in 1 molar sol.}}} \right)^2 = K_c \times \left(\frac{0.72}{0.40} \right)^2 = 27.0$$

(c) Quantity of silver ion adsorbed

(1) Total $\text{Ag}^+ = 0.4891 - 0.4647 = 0.0244$ M
 = 0.00244 actual eq. in 100 mls.

(2) Ag^+ gained by the solution through hydrolytic effect = 0.00135 equivalent

(3) Actual excess of ΔAg^+ over ΔH^+ in the exchange = $0.00244 - 0.00182 = 0.00062$ equivalent

(4) Number of equivalents of Ag^+ adsorbed by the resin = $0.00135 - 0.00062 = 0.00073$ equivalent

(5) Number of equivalents of Ag^+ adsorbed/eq. resin = $\frac{0.00073 \times 357}{6.7308} = 0.039$ equivalent

The values of K_c contained in Tables X and XI are for the reaction



where

$$K_c = \frac{(\text{H}^+)(\text{AgRes})}{(\text{Ag}^+)(\text{HRes})}$$

The quantities in parentheses have the same significance as in the case of the sodium-hydrogen exchange. Values of K_a are presented in Figure V as a function of the equilibrium mole fraction of silver resin. Except when the mole fraction of AgRes at equilibrium exceeds 0.90, the two sets of data agree within 3%. This agreement, it is believed, is sufficiently good to lend considerable support to the several assumptions upon which the above calculations are based.

In Figure VI the quantity of silver ion adsorbed per equivalent of original resin is expressed as a function of the equilibrium silver ion concentration for the studies both with silver and with hydrogen resins. Both curves have the general shape of adsorption isotherms, approaching constant adsorption with increasing equilibrium concentration of silver ion. A possible explanation for the smaller amounts of adsorption observed with silver resin may be found in the hypothesis that some adsorbed silver ion still adheres to the resin after thorough washing during the preparation of the pure silver resin. Further evidence for this hypothesis is the fact that a minimum initial concentration of silver ion is required before adsorption on the silver resin begins, whereas pure hydrogen resin exhibits adsorption even from the influent solutions of lowest silver ion concentration.

As was illustrated by the sodium-hydrogen exchange, the actual hydrolytic effect of the resins involved is not constant, and in order to obtain the most accurate value of the

Figure V

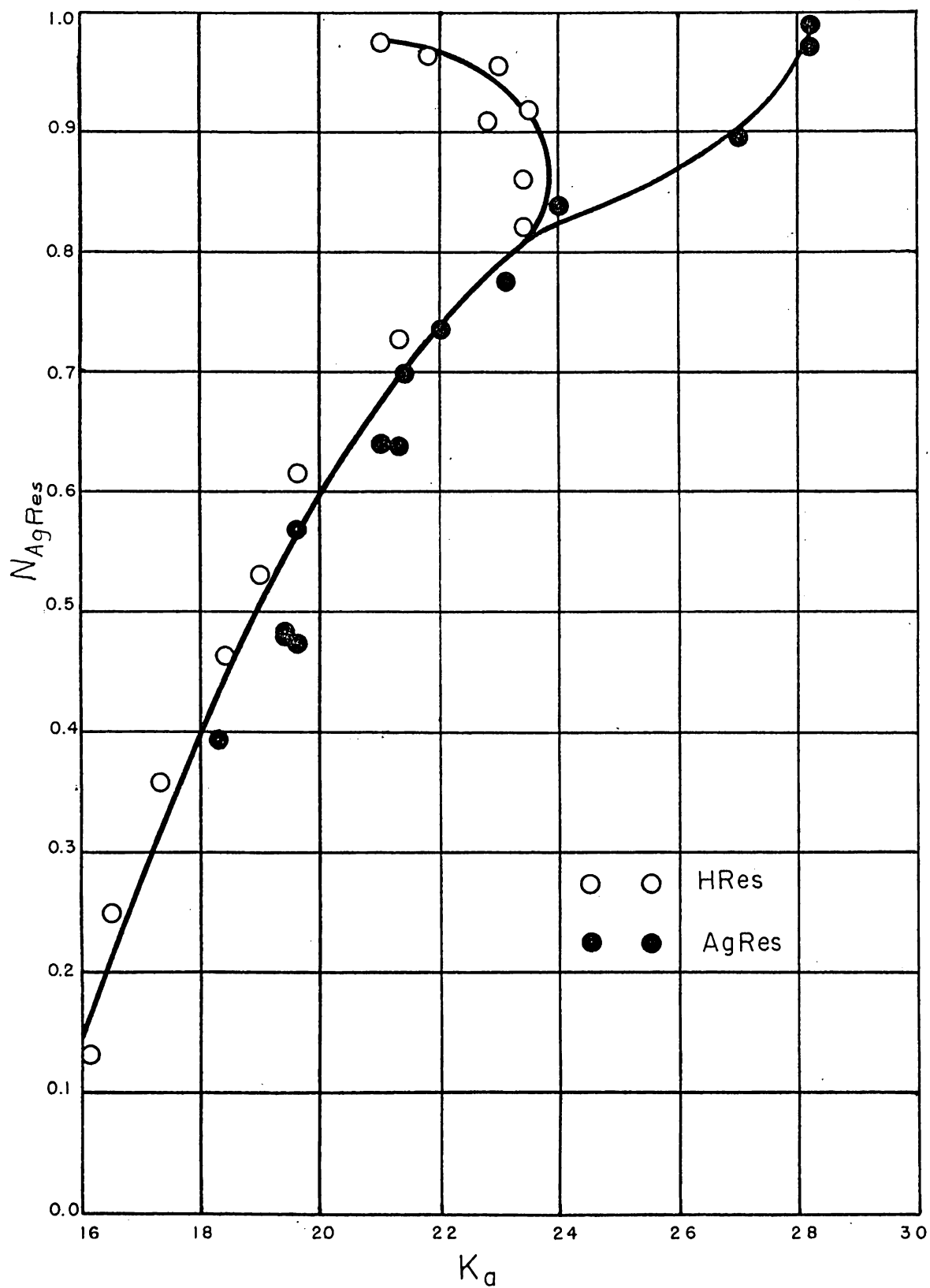
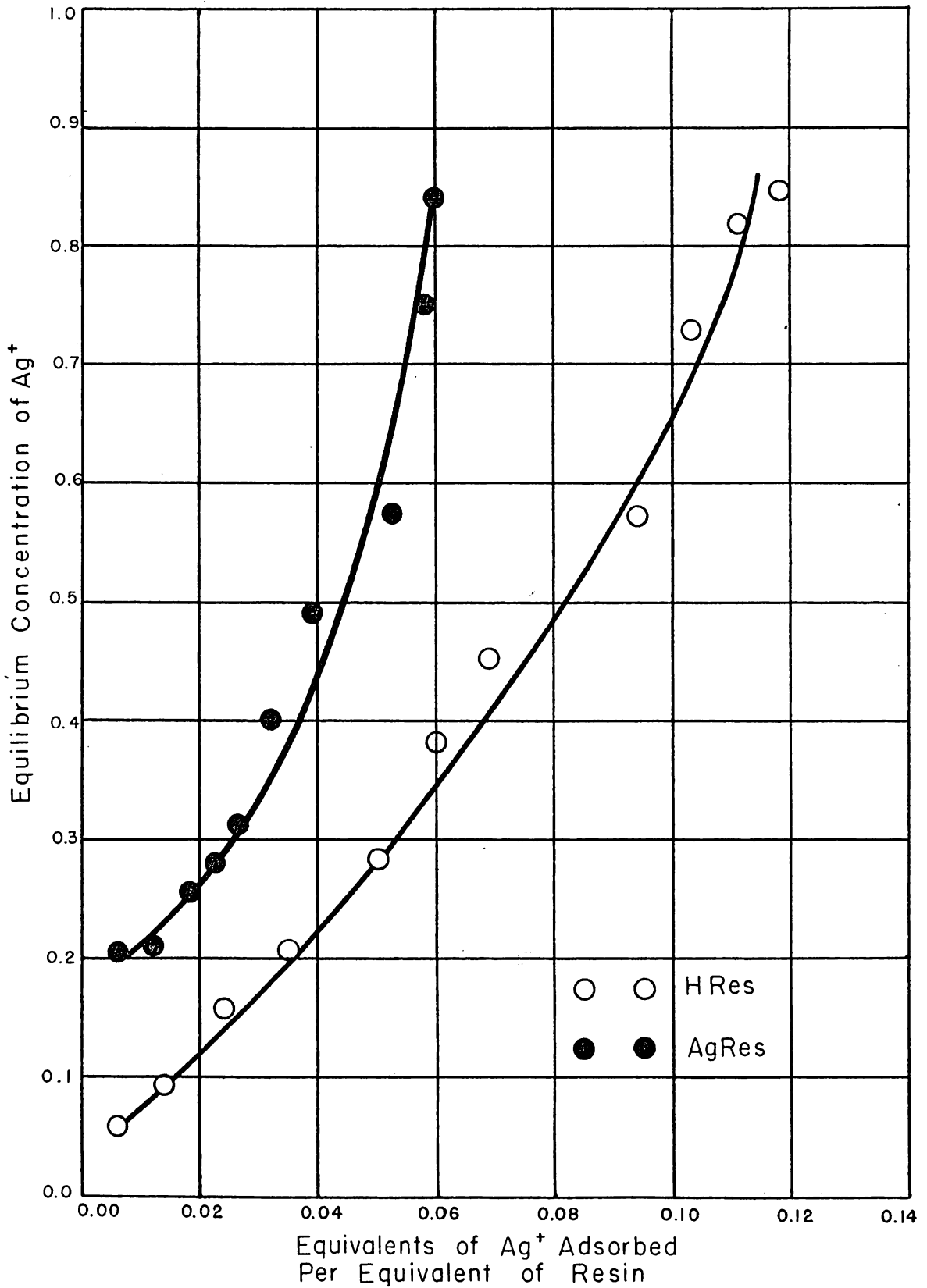


Figure VI



equilibrium quotient, the individual hydrolytic effect in each separate experiment should be employed in the calculation. In the silver-hydrogen exchange, however, such individual hydrolytic effects cannot be measured; hence the use of a single value was adopted as the best possible approximation. These fixed values in the silver-hydrogen exchange as described above are not far from the average of the individual values of the sodium, ammonium, and hydrogen resins. It is believed, therefore, that values of K_c in the silver-hydrogen exchange are nearly as reliable as those falling on the smooth curve obtained in the other two systems.

VII. AMMONIUM-HYDROGEN EXCHANGE ON DOWEX-50

A more extensive investigation of the ammonium-hydrogen exchange was next undertaken, in which equilibrium was approached from both directions: i.e., hydrogen resin and ammonium resin were each treated with solutions containing ammonium and hydrogen ions.

The ammonium resin was prepared by immersing the pure hydrogen resin in a saturated solution of ammonium chloride, and adding ammonium hydroxide solution until the pH of the entire mixture remained constant at 7 for an indefinite period. The resulting resin was washed until free of chloride ion, and dried in the usual manner. The equivalent weight of the ammonium resin was determined by bringing a weighed quantity of the resin in contact with a saturated solution of sodium chloride. An excess of concentrated sodium hydroxide solution was then added, and the displaced ammonia was distilled over into a known volume of standard acid. The excess acid was titrated with standard alkali solution, and the equivalent weight of the resin was then obtained from the number of equivalents of standard acid neutralized by the ammonia.

The equilibrium studies were conducted in the same manner as the previous investigations. A series of samples were treated with aqueous solutions of ammonium chloride and hydrochloric acid, of total ionic strength approximately equal to unity. Portions of the equilibrium effluent were then

removed and analyzed for hydrogen and ammonium ions as before.

Table XII contains the data for the study in which hydrogen resin was used as the starting material, while in Table XIII are tabulated data for the study involving ammonium resin as the initial exchanger. Examination of the values of $\frac{\Delta H - \Delta NH_4}{\text{eq. res.}}$ in Table XII reveals that the values are nearly constant, with no obvious trend. In contrast to the conclusion drawn from the silver-hydrogen exchange studies, this deviation is attributed entirely to a reaction resembling hydrolysis of the resin; i.e., there is no adsorption of ammonium ion on the resin. The average value of the hydrolytic effect is 0.063 equivalent per equivalent of resin. This figure may be compared with the value of 0.065 obtained for the hydrogen resin used in the sodium-hydrogen exchange studies, and with the value of 0.060 obtained from the silver-hydrogen exchange studies. It may be noted that the previous investigation of the ammonium-hydrogen exchange on hydrogen resin, made for the purpose of determining the relationship between the hydrolytic effect and the ionic strength, yielded a value of 0.091 equivalent per equivalent of resin. This last value, however, is the average of results obtained on four samples only, and may thus be considered less significant than the three values reported above, each of which was the average of results obtained on about sixteen samples. Another

Dowex-50

Table XII

Hydrogen Resin (NH₄Cl + HCl)

No.	Original Solution	Weight of Resin	ΔH^+	ΔNH_4^+	$\frac{\Delta\text{H} - \Delta\text{NH}_4}{\text{eq.res.}}$	$N_{\text{NH}_4\text{Res.}}$	K_c	K_a
1.	H ⁺ = NH ₄ ⁺ = 1.0350	4.5590	0.01434	0.01360	0.045	0.874	1.11	2.24
2.	H ⁺ = 0.1000 NH ₄ ⁺ = 0.9313	3.3908	0.01013	0.00940	0.066	0.827	1.15	2.32
3.	H ⁺ = 0.1497 NH ₄ ⁺ = 0.8797	3.5560	0.01021	0.00937	0.066	0.789	1.19	2.40
4.	H ⁺ = 0.2000 NH ₄ ⁺ = 0.8276	5.3056	0.01410	0.01295	0.060	0.726	1.30	2.62
5.	H ⁺ = 0.2992 NH ₄ ⁺ = 0.7247	4.2654	0.01073	0.00968	0.069	0.680	1.38	2.78
6.	H ⁺ = 0.3992 NH ₄ ⁺ = 0.6210	3.8984	0.00896	0.00787	0.078	0.611	1.42	2.87
7.	H ⁺ = 0.3992 NH ₄ ⁺ = 0.6210	5.3629	0.01197	0.01092	0.054	0.602	1.53	3.08
8.	H ⁺ = 0.4991 NH ₄ ⁺ = 0.5175	4.2920	0.00884	0.00785	0.064	0.546	1.61	3.24
9.	H ⁺ = 0.4991 NH ₄ ⁺ = 0.5175	5.3532	0.01068	0.00931	0.071	0.524	1.58	3.19
10.	H ⁺ = 0.5993 NH ₄ ⁺ = 0.4136	5.0965	0.00884	0.00781	0.056	0.454	1.70	3.43
11.	H ⁺ = 0.7487 NH ₄ ⁺ = 0.2588	4.1981	0.00555	0.00467	0.059	0.330	1.88	3.79
12.	H ⁺ = 0.7982 NH ₄ ⁺ = 0.2074	4.6586	0.00534	0.00428	0.063	0.274	1.95	3.94
13.	H ⁺ = 0.8485 NH ₄ ⁺ = 0.1552	4.4915	0.00439	0.00333	0.066	0.221	2.08	4.20
14.	H ⁺ = 0.8982 NH ₄ ⁺ = 0.1037	4.3245	0.00334	0.00231	0.067	0.160	2.13	4.42

Dowex-50

Table XIII

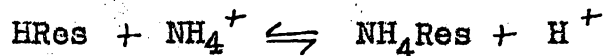
Ammonium Resin ($\text{NH}_4\text{Cl} + \text{HCl}$)

No.	Original Solution	Weight of Resin	ΔH^+	ΔNH_4^+	$\frac{\Delta\text{NH}_4 - \Delta\text{H}}{\text{eq.res.}}$	$N_{\text{NH}_4\text{Res}}$	K_c	K_a
1.	$\text{NH}_4^+ =$ $\text{H}^+ = 0.9982$	2.2421	0.00620	0.00727	0.127	0.156	2.39	4.83
2.	$\text{NH}_4^+ =$ $\text{H}^+ = 0.9982$	4.6208	0.01214	0.01346	0.076	0.243	2.09	4.22
3.	$\text{NH}_4^+ = 0.1036$ $\text{H}^+ = 0.8983$	4.7031	0.01063	0.01205	0.080	0.346	1.86	3.76
4.	$\text{NH}_4^+ = 0.2072$ $\text{H}^+ = 0.7984$	4.7585	0.00940	0.01057	0.066	0.437	1.75	3.53
5.	$\text{NH}_4^+ = 0.3103$ $\text{H}^+ = 0.6989$	4.4270	0.00734	0.00883	0.090	0.515	1.67	3.37
6.	$\text{NH}_4^+ = 0.4139$ $\text{H}^+ = 0.5990$	4.6435	0.00664	0.00780	0.066	0.592	1.58	3.19
7.	$\text{NH}_4^+ = 0.5175$ $\text{H}^+ = 0.4991$	4.6637	0.00561	0.00692	0.075	0.653	1.42	2.87
8.	$\text{NH}_4^+ = 0.5175$ $\text{H}^+ = 0.4991$	4.3484	0.00520	0.00633	0.069	0.658	1.48	2.98
9.	$\text{NH}_4^+ = 0.6210$ $\text{H}^+ = 0.3992$	4.5685	0.00437	0.00572	0.079	0.723	1.37	2.76
10.	$\text{NH}_4^+ = 0.7246$ $\text{H}^+ = 0.2993$	4.3902	0.00326	0.00475	0.090	0.782	1.25	2.52
11.	$\text{NH}_4^+ = 0.8278$ $\text{H}^+ = 0.1998$	4.8256	0.00243	0.00389	0.080	0.854	1.18	2.38
12.	$\text{NH}_4^+ = 0.9312$ $\text{H}^+ = 0.0999$	4.5936	0.00123	0.00265	0.082	0.921	1.08	2.18

possible cause for the difference is the fact that in the ionic strength investigation a different batch of resin was used, of somewhat smaller particle size than that used in the exchange studies.

Comparison of the values of $\frac{\Delta NH_4 - \Delta H}{eq. res.}$ in Table XIII with those of $\frac{\Delta Na - \Delta H}{eq. res.}$ obtained from the sodium-hydrogen exchange on sodium resin shows that the behavior of the ammonium and the sodium resins is very similar. The average value of the hydrolytic effect for ammonium resin is 0.077, as against 0.073 for sodium resin.

In view of these marked similarities, the equilibrium constants were calculated exactly as previously described for the sodium-hydrogen exchange. The values of the equilibrium constant are for the reaction

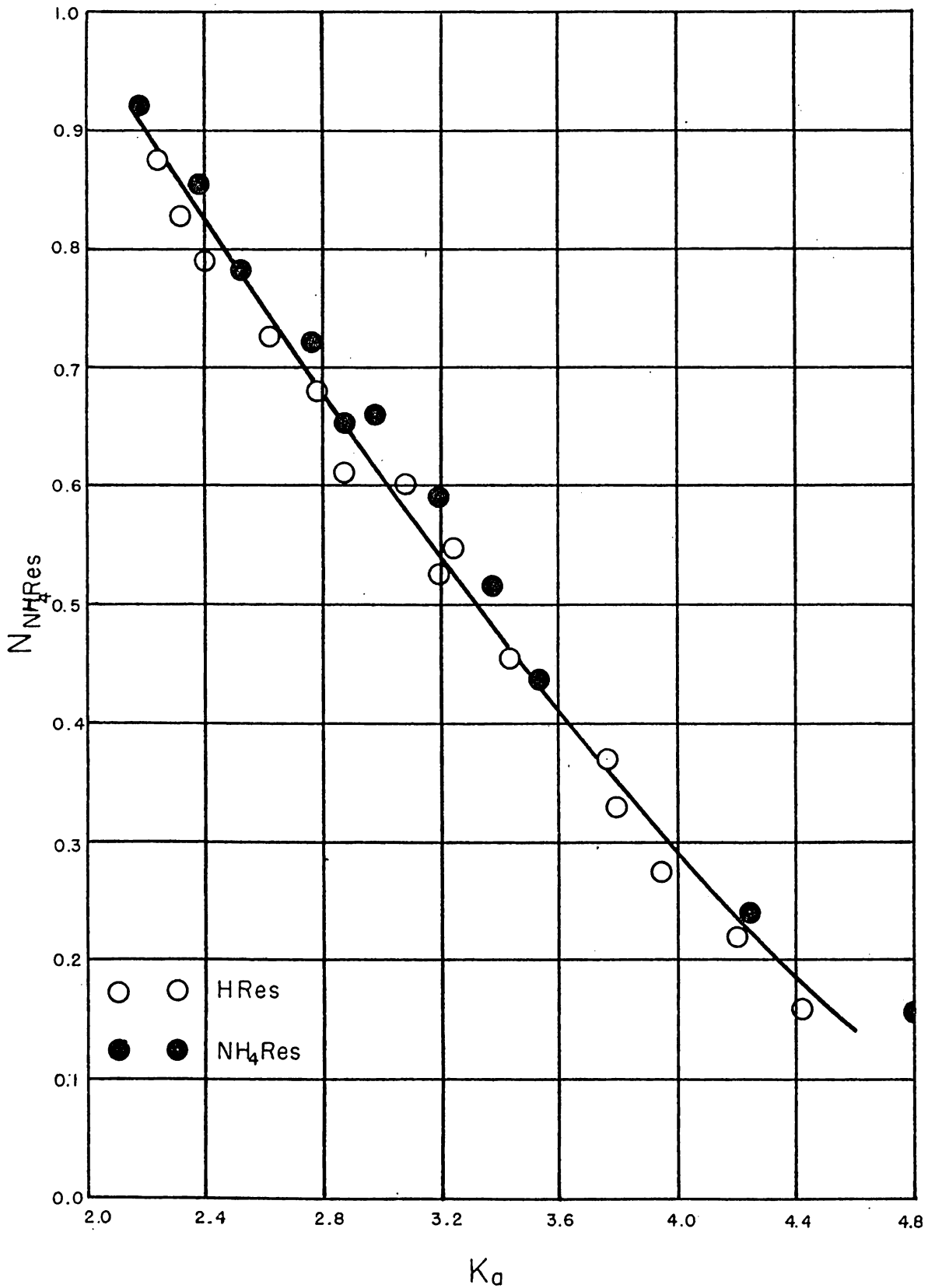


that is,

$$K = \frac{(H^+)(NH_4Res)}{(NH_4^+)(HRes)}$$

where the quantities in parentheses have the usual significance. Values of K_a vary from 2.2 to 4.8, a range which is almost the same as that covered by the equilibrium quotient for the sodium-hydrogen exchange. In Figure VII, the values of K_a are plotted against the mole fraction of ammonium resin in the solid phase. It will be noted that the hysteretic effect is very small, experiments in which hydrogen resin was used as the initial exchanger yielding, as in the case of the sodium-hydrogen exchange, slightly lower

Figure VII



values of K_a . The lack of constancy in the values of K must be attributed, as before, to the absence of accurate activity data for the solid phase.

A survey of existing ion-exchange literature fails to reveal any evidence that previous workers have encountered a lack of constancy of the activity quotient for an exchange reaction. On the contrary, single values of the equilibrium constant may be found for a large number of ion-exchange pairs. With the exception of the statement noted in the work by Juda and Carron (21), no mention has been made in the literature of the hydrolytic effect. In fact, one worker (19) has specifically stated that equivalent exchange was observed for the ammonium-hydrogen reaction on Dowex-50 at all salt concentrations.

The major point of difference between the investigation and those reported by other workers, is that the present work (with the exception of the superficial study of hydrolytic effect as a function of ionic strength) has been confined to solutions of unit ionic strength, while the investigations of other workers have in general involved solutions of ionic strengths from 0.001 to 0.1 only. Accordingly, experiments were undertaken to determine whether or not the conflict between the data of present and past work might correctly be ascribed to a difference in the behavior of the resin in two solutions of different ionic strengths. Because of the relative ease of the analyses involved, and

because of the precision of the previous data on this system for solutions of unit ionic strength with which the results to be acquired were to be compared, the ammonium-hydrogen exchange in solutions of total ionic strength approximately 0.1 M was selected for this study.

The pure resins to be used as initial exchangers were prepared as previously described. The methods of analysis were likewise similar, except that a micro-buret was employed in order that the use of 0.1 N standard solutions for titration might be continued. The equilibrium samples were prepared as before, except that the total ionic strength of the solutions was 0.1 M instead of unity.

Table XIV contains the data for pure hydrogen resin as the initial solid phase, while in Table XV are tabulated the data for pure ammonium resin as the starting material. A comparison of the values of $\frac{\Delta H - \Delta NH_4}{\text{eq. res.}}$ in Table XIV with values of the corresponding quantity, $\frac{\Delta NH_4 - \Delta H}{\text{eq. res.}}$, of Table XV is illuminating. In Table XIV, this quantity assumes various positive values, indicating that the hydrolytic effect exists even in these more dilute solutions; the magnitude of this effect, however, is now appreciably smaller. In the study of the ammonium-hydrogen exchange at unit ionic strength, hydrogen resin exhibited an average hydrolytic effect of 0.063 equivalent per equivalent of resin; in the present study at ionic strength 0.1 M, the average hydrolytic effect was only 0.033 equivalent per

Dowex-50 $\mu = 0.1$

Table XIV

Hydrogen Resin ($\text{NH}_4\text{Cl} + \text{HCl}$)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔH^+	ΔNH_4^+	$\frac{\Delta\text{H} - \Delta\text{NH}_4}{\text{eq. res.}}$	$N_{\text{NH}_4\text{Res}}$	K_c	K_a
1.	$\text{H}^+ = 0.1112\text{M}$ $\text{NH}_4^+ = 0.1112\text{M}$	0.4526	0.001610	0.00146	0.00136	0.062	0.900	1.36	1.64
2.	$\text{H}^+ = 0.01000$ $\text{NH}_4^+ = 0.1001$	0.4320	0.001528	0.001306	0.001239	0.044	0.845	1.44	1.74
3.	$\text{H}^+ = 0.02000$ $\text{NH}_4^+ = 0.08897$	0.4704	0.001675	0.001310	0.001251	0.035	0.774	1.48	1.79
4.	$\text{H}^+ = 0.02997$ $\text{NH}_4^+ = 0.07787$	0.4840	0.001724	0.001233	0.001175	0.034	0.712	1.58	1.91
5.	$\text{H}^+ = 0.04998$ $\text{NH}_4^+ = 0.05567$	0.4447	0.001582	0.000933	0.000919	0.009	0.585	1.80	2.17
6.	$\text{H}^+ = 0.05998$ $\text{NH}_4^+ = 0.04447$	0.4507	0.001603	0.000834	0.000801	0.021	0.509	1.95	2.37
7.	$\text{H}^+ = 0.06998$ $\text{NH}_4^+ = 0.03335$	0.4464	0.001589	0.000671	0.000649	0.013	0.414	2.03	2.45
8.	$\text{H}^+ = 0.07995$ $\text{NH}_4^+ = 0.02225$	0.4335	0.001542	0.000532	0.000461	0.046	0.316	2.20	2.66

Dowex-50

 $\mu = 0.1$

Table XV

Ammonium Resin ($\text{NH}_4\text{Cl} + \text{HCl}$)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔNH_4^+	ΔH^+	$\frac{\Delta\text{H} - \Delta\text{NH}_4}{\text{eq. res.}}$	$N_{\text{NH}_4\text{Res}}$	K_c	K_a
1.	$\text{H}^+ = 0.09995\text{M}$ $\text{NH}_4^+ =$	0.4063	0.001520	0.001154	0.001163	-0.006	0.237	2.38	2.87
2.	$\text{H}^+ = 0.08995$ $\text{NH}_4^+ = 0.01113$	0.5036	0.001884	0.001152	0.001155	-0.002	0.388	2.19	2.64
3.	$\text{H}^+ = 0.07995$ $\text{NH}_4^+ = 0.02225$	0.4651	0.001740	0.000907	0.000913	-0.003	0.478	2.06	2.48
4.	$\text{H}^+ = 0.06998$ $\text{NH}_4^+ = 0.03335$	0.4914	0.001838	0.000833	0.000808	0.014	0.554	1.84	2.22
5.	$\text{H}^+ = 0.05998$ $\text{NH}_4^+ = 0.04448$	0.4876	0.001824	0.000653	0.000682	-0.016	0.634	1.80	2.17
6.	$\text{H}^+ = 0.04998$ $\text{NH}_4^+ = 0.05560$	0.4834	0.001808	0.000549	0.000536	0.007	0.700	1.70	2.05
7.	$\text{H}^+ = 0.03997$ $\text{NH}_4^+ = 0.06674$	0.4753	0.001778	0.000431	0.000414	0.010	0.762	1.62	1.96
8.	$\text{H}^+ = 0.02997$ $\text{NH}_4^+ = 0.07787$	0.4334	0.001621	0.000290	0.000280	0.001	0.822	1.55	1.87
9.	$\text{H}^+ = 0.02000$ $\text{NH}_4^+ = 0.08897$	0.4416	0.001652	0.000230	0.000197	0.020	0.870	1.33	1.61
10.	$\text{H}^+ = 0.02000$ $\text{NH}_4^+ = 0.08897$	0.4626	0.001731	0.000154	0.000213	-0.040	0.891	1.61	1.94
11.	$\text{H}^+ = 0.01000$ $\text{NH}_4^+ = 0.1001$	0.4594	0.001719	0.00010	0.000103	0.000	0.940	1.42	1.71

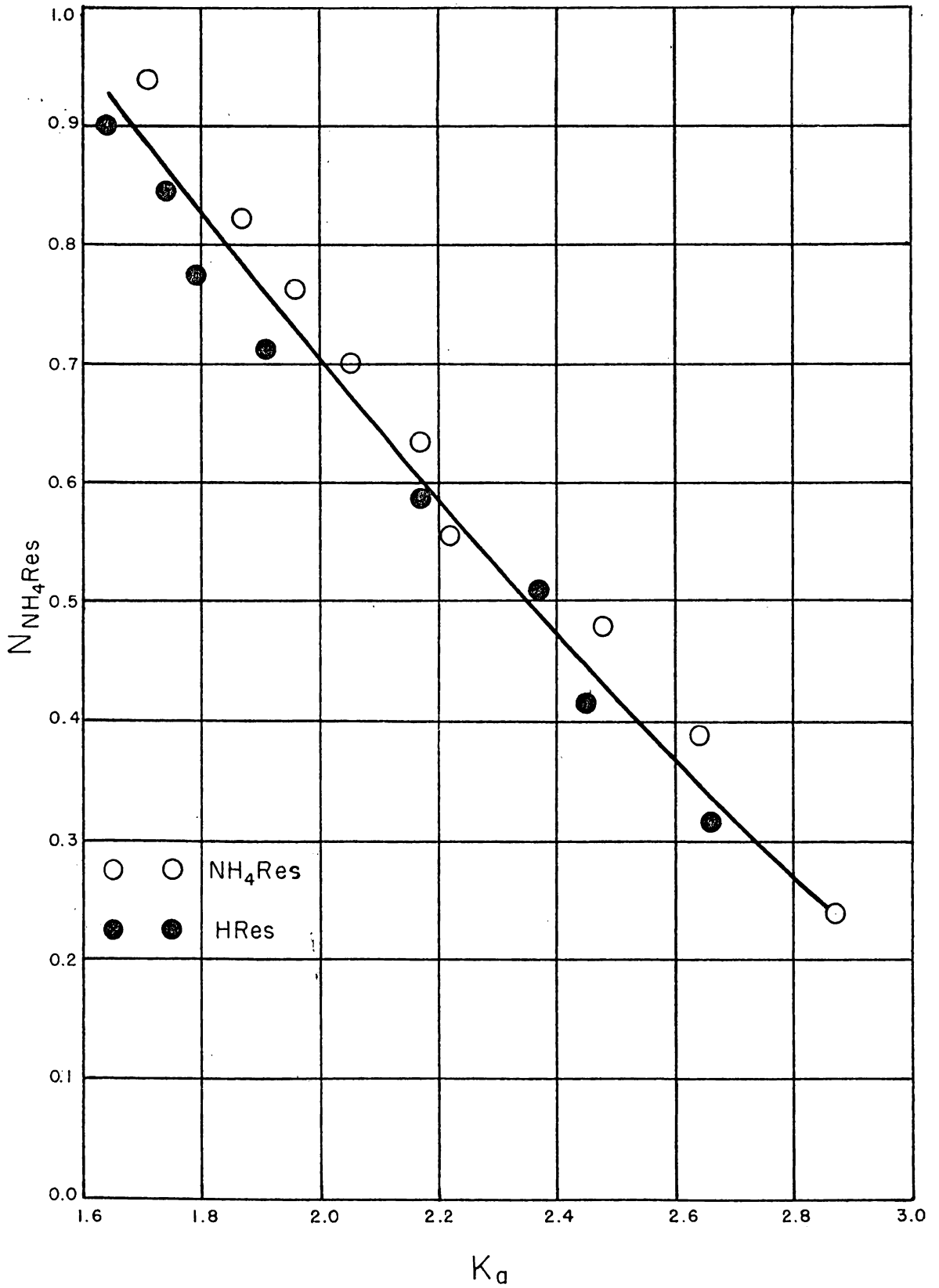
equivalent of resin, or little more than one-half that previously observed. In the study of hydrolytic effect as a function of ionic strength, an average hydrolytic effect of 0.015 was observed when the ionic strength had a value of 0.1 M. As has already been pointed out, however, the latter figure is the average of results on a very small number of samples only, and is therefore probably less reliable than the larger value.

In Table XV, the quantity under discussion takes on both negative and positive values, none of which deviates very far from zero. The average value for the eleven samples cited in Table XV is only -0.0015 equivalent per equivalent of resin. Thus it may be concluded that the hydrolytic effect has disappeared in the case of ammonium resin in solutions of ionic strength 0.1 M. This absence of hydrolytic effect is especially surprising in view of the fact that in solutions of unit ionic strength ammonium resin exhibited a hydrolytic effect of 0.077 equivalent per equivalent of resin, an even larger value than that found for hydrogen resin in solutions of the same ionic strength.

The values of the equilibrium constant given in Tables XIV and XV are for the reaction as written in the discussion of the study of this exchange pair at unit ionic strength. The equilibrium quotients for the hydrogen resin study were calculated in the manner employed whenever the hydrolytic effect constitutes the only departure from equivalent

exchange. For the ammonium resin study, since no correction for the hydrolytic effect need be applied, calculations were made directly from the mean of the ΔH^+ and ΔNH_4^+ values. The values of K_a range from 1.61 to 2.87; these figures are to be compared with the values of 2.2 to 4.8 obtained at the higher concentration. In Figure VIII, the values of K_a are plotted against the mole fraction of ammonium resin. As in the unit ionic strength study, the hysteretic effect is small. Furthermore, the slopes of the corresponding curves in Figures VII and VIII are almost the same. This fact lends further support to the hypothesis that the lack of constancy of the equilibrium quotient is due solely to the error resulting from the identification of the mole fractions of the components of the solid phase with their activities.

Figure VIII



VIII. THALLOUS-AMMONIUM EXCHANGE ON DOWEX-50

In order to provide further support for the validity of the assumptions made regarding simultaneous adsorption and hydrolytic effects in the silver-hydrogen study, investigations involving thallos ion, the properties of which are similar to those of silver ion, were next undertaken. As in previous studies, equilibrium in the thallos-ammonium exchange was approached from both directions; i.e., pure ammonium resin and pure thallos resin were each treated with aqueous solutions of ammonium and thallos salts.

The ammonium resin used was the same as that prepared for the ammonium-hydrogen exchange. Pure thallos resin was prepared by placing pure hydrogen resin in the column, and passing over it a saturated solution of thallos nitrate.*

*The thallos nitrate was prepared from Eastman thallos formate (90%). The salt as received was dissolved in water and filtered to remove foreign material. Sodium carbonate was added to the clear solution to precipitate thallos carbonate, and this precipitate was washed free of carbonate and sodium ions. The thallos carbonate was then dissolved in dilute nitric acid and the solution was concentrated and cooled, whereupon the thallos nitrate crystallized out.

When the pH of the effluent solution showed only a negligible decrease from that of the influent solution, the conversion was considered to be complete. The resin was then washed until free of thallos ion, as indicated by the absence of a precipitate when potassium iodide solution was added to

the wash water. The resulting product was dried in the usual manner.

The equivalent weight of the thallos resin was determined from the amount of exchangeable cation in the resin. The thallos ion in a weighed quantity of resin was displaced by means of 500 ml. of a saturated sodium nitrate solution. The concentration of thallos ion in the effluent solution was then determined by making the solution 2 N with respect to hydrogen ion, and titrating directly to a potentiometric end point with a standard solution of potassium bromate*, platinum serving as the indicator electrode.

*The potassium bromate solution was standardized against Bureau of Standards arsenious oxide.

A series of samples were treated with aqueous solutions of ammonium nitrate and thallos nitrate, of total ionic strength approximately equal to unity. Thallos nitrate was found to have a somewhat limited solubility, so that when the solutions were adjusted to unit ionic strength with ammonium nitrate, thallos nitrate was precipitated at 30° C. from all solutions above 0.30 M in thallos ion. However, it was found that a 0.30 M influent solution was sufficiently concentrated to yield a solid phase in which the equilibrium mole fraction of thallos resin was approximately 0.6. Consequently, the solutions were so adjusted that neither initially nor at equilibrium was the thallos ion concentration allowed to exceed 0.30 M.

After equilibration of the exchange mixture, a portion was removed and analyzed for ammonium and thallos ions as previously described.

The data for the exchange study with ammonium resin as the initial solid phase may be found in Table XVI, while the data for the study with thallos resin as the initial exchanger are found in Table XVII.

Examination of the values of $\frac{\Delta NH_4 - \Delta Tl}{\text{eq. res.}}$ in Table XVI reveals that for solutions low in thallos ion concentration, this quantity assumes a normal positive value for a hydrolytic effect. As the thallos ion concentration is increased, the quantity decreases and eventually assumes a negative value. Since this behavior is exactly analogous to that observed in exchange studies involving silver ion, the adsorption effect, as well as the hydrolytic effect, must be taken into account in the calculation of the equilibrium constant. Accordingly, the calculations were made in the same manner as for the silver-hydrogen exchange on hydrogen resin; an illustration of this method has already been presented. Inasmuch as it is impossible separately to evaluate the hydrolytic and the adsorption effects, the use of this method requires that a constant hydrolytic effect be assumed. The fixed value chosen in this case was the average of all previously observed hydrolytic effects for this batch of resin, namely 0.077 equivalent per equivalent of resin.

Dowex-50

Table XVI

Ammonium Resin ($\text{NH}_4\text{NO}_3 + \text{TlNO}_3$)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔNH_4^+	ΔTl^+	$\frac{\Delta\text{NH}_4 - \Delta\text{Tl}}{\text{eq. res.}}$	N_{TlRes}	K_c	K_a
1.	$\text{Tl}^+ = 0.05406$ $\text{NH}_4^+ = 0.9165$	4.4346	0.01667	0.00316	0.00195	0.0725	0.125	3.96	7.57
2.	$\text{Tl}^+ = 0.05406$ $\text{NH}_4^+ = 0.9165$	4.3719	0.01643	0.00340	0.00194	0.089	0.130	4.08	7.81
3.	$\text{Tl}^+ = 0.1088$ $\text{NH}_4^+ = 0.8711$	4.6909	0.01763	0.00430	0.00388	0.024	0.181	2.88	5.50
4.	$\text{Tl}^+ = 0.1627$ $\text{NH}_4^+ = 0.8306$	4.8414	0.01819	0.00577	0.00560	0.009	0.260	2.92	5.58
5.	$\text{Tl}^+ = 0.2171$ $\text{NH}_4^+ = 0.7745$	4.7881	0.01799	0.00709	0.00719	-0.006	0.343	3.04	5.81
6.	$\text{Tl}^+ = 0.2774$ $\text{NH}_4^+ = 0.7454$	5.0146	0.01884	0.00845	0.00940	-0.050	0.402	3.04	5.81
7.	$\text{Tl}^+ = 0.3258$ $\text{NH}_4^+ = 0.7103$	4.7627	0.01790	0.00942	0.00971	-0.016	0.485	3.32	6.35
8.	$\text{Tl}^+ = 0.3258$ $\text{NH}_4^+ = 0.7103$	4.2630	0.01602	0.00866	0.00890	-0.015	0.502	3.38	6.46

Dowex-50

Table XVII

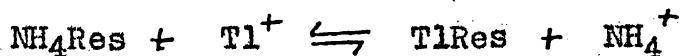
Thallous Resin ($\text{NH}_4\text{NO}_3 + \text{TlNO}_3$)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔTl^+	ΔNH_4^+	$\frac{\Delta\text{Tl} - \Delta\text{NH}_4}{\text{eq. res.}}$	N_{TlRes}	K_c	K_a
1. R	$\text{Tl}^+ = 0.0453\text{M}$ $\text{NH}_4^+ = 0.9302\text{M}$	5.1028	0.01207	0.00667	0.00589	0.063	0.479	4.18	8.00
2.	$\text{Tl}^+ = 0.09080$ $\text{NH}_4^+ = 0.8865$	8.6718	0.02051	0.01039	0.00997	0.022	0.482	3.76	7.18
3.	$\text{Tl}^+ = 0.1364$ $\text{NH}_4^+ = 0.8377$	9.3722	0.02216	0.00965	0.00943	0.010	0.546	3.83	7.33
4.	$\text{Tl}^+ = 0.1862$ $\text{NH}_4^+ = 0.7913$	8.7494	0.02069	0.00754	0.00794	-0.019	0.590	3.93	7.51
5.	$\text{Tl}^+ = 0.2253$ $\text{NH}_4^+ = 0.7435$	7.8753	0.01862	0.00641	0.00647	-0.003	0.629	3.99	7.63
6.	$\text{Tl}^+ = 0.2691$ $\text{NH}_4^+ = 0.6923$	8.0190	0.01896	0.00553	0.00559	-0.003	0.685	4.27	8.15

Examination of the values of $\frac{\Delta Tl - \Delta NH_4}{\text{eq. res.}}$ in Table XVIII shows the same trend from positive to negative as the concentration of thalious ion in the initial solution is increased; the range traversed, however, is not so great as for ammonium resin. This evidence of decreased adsorption may be accounted for in terms of the plausible hypothesis that the thalious resin might already contain some thalious ion which had been adsorbed during its preparation and which could not be washed out with water; if this were true, its adsorptive capacity would be lower than that of ammonium resin which contains no adsorbed ion.

The ammonium-thalious exchange on thalious resin is similar to the silver-hydrogen exchange on silver resin; correspondingly, the calculation of the equilibrium constant was carried out in the manner described for the analogous case. The constant hydrolytic effect was obtained from sample IR by assuming that in this solution, dilute in thalious ion, no adsorption occurred, so that the whole of the difference in increments $\frac{\Delta Tl - \Delta NH_4}{\text{eq. res.}}$ might properly be ascribed to the hydrolytic effect.

The values of the equilibrium constant recorded in Tables XVI and XVII are for the reaction



that is,

$$K = \frac{(NH_4^+)(Tl\text{Res})}{(Tl^+)(NH_4\text{Res})}$$

where the quantities in parentheses have the usual

significance. In order to convert K_c values to K_a , K_c must be multiplied by the square of the ratio of the activity coefficients of NH_4NO_3 and TlNO_3 in solutions of unit ionic strength; i.e.,

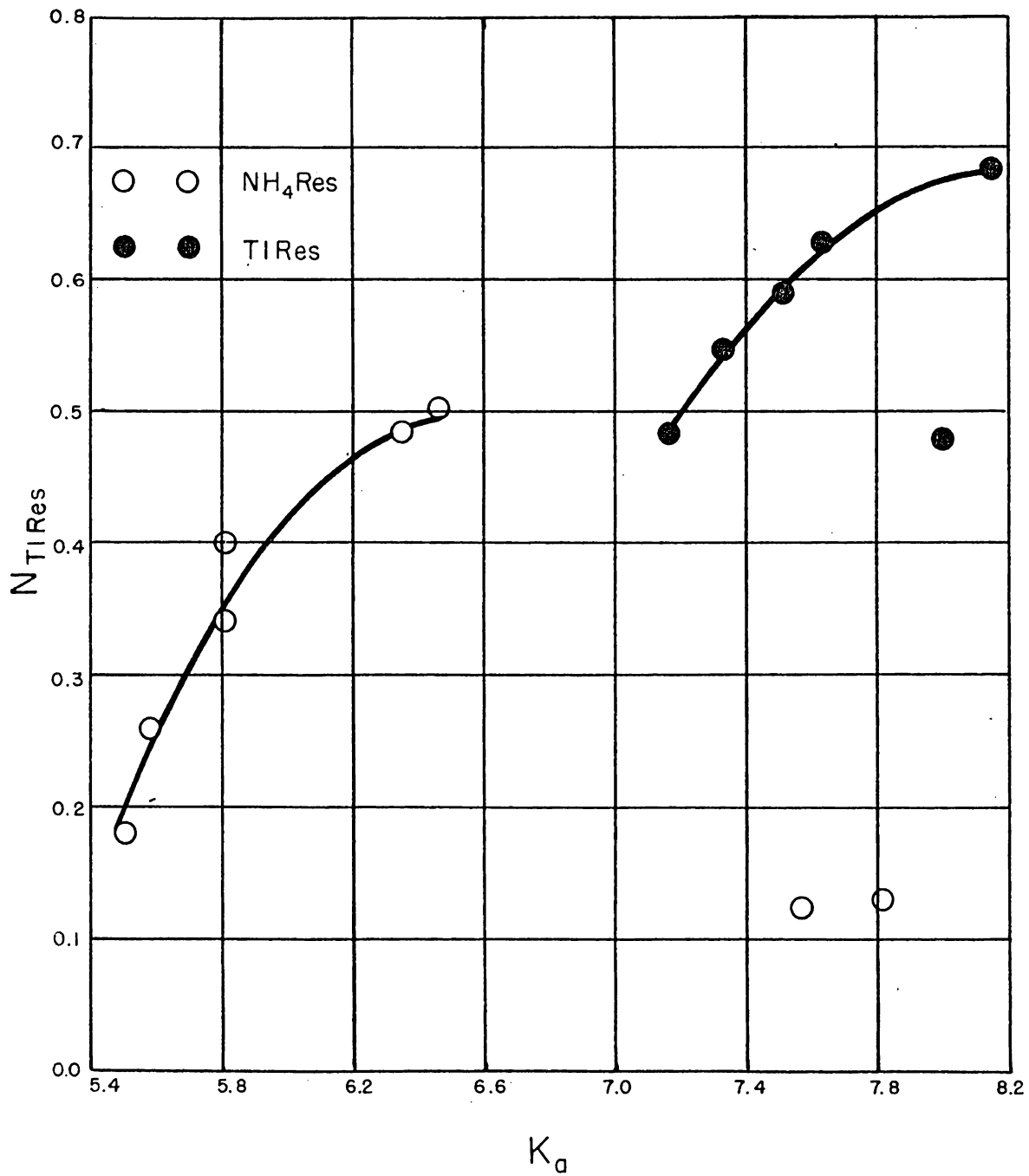
$$K_a = K_c \cdot \frac{(\gamma_{\pm} \text{NH}_4\text{NO}_3)^2}{(\gamma_{\pm} \text{TlNO}_3)^2}.$$

Since thalious nitrate is soluble only to the extent of ~ 0.3 M, the value of the mean activity coefficient of this salt in 1 M solution is unavailable. In order to arrive at an approximation, existing data for solutions up to 0.3 M were extrapolated, by comparison with the mean activity coefficients of other similar salts, on a plot of $\log \gamma_{\pm}$ vs. \sqrt{m} . The approximate value so obtained,

$\gamma_{\pm} \text{TlNO}_3 = 0.34$ when $\mu = 1$, is believed to be fairly accurate.

A plot of the equilibrium activity quotient against the equilibrium mole fraction of thalious resin is presented in Figure IX. Because of the magnitude of the constant, and the limited solubility of thalious nitrate, no direct comparison between ammonium resin and thalious resin as initial exchangers can be made. The points of the curve for the thalious resin appear on a slightly displaced continuation of that for the ammonium resin. Extrapolation of either curve indicates the existence of approximately the same degree of hysteresis as has been encountered in other systems. Over the range of concentrations studied, the values of K_a range from 5.5 to 8.1, with an average of 6.91.

Figure IX



IX. THALLOUS-HYDROGEN EXCHANGE ON DOWEX-50

As in all the previous investigations, equilibrium in the thallos-hydrogen exchange was approached from both directions, i. e., pure hydrogen resin and pure thallos resin were each treated with aqueous solutions of hydrogen and thallos ions. Both resins employed were from batches which had been used in previous exchange studies. The mixture was allowed to come to equilibrium, and aliquot portions of the solution were removed and analyzed for thallos and hydrogen ions as already described. As previously stated, the low solubility of thallos nitrate limited the initial thallos ion concentration to 0.30 M. The equilibrium studies were carried out at 30° C. in the same manner as has been described for previous investigations involving thallos ions. The data and results of this exchange are presented in Tables XVIII and XIX.

An examination of the values of $\frac{\Delta H - \Delta T1}{\text{eq. res.}}$ in Table XVIII again reveals the occurrence not only of true exchange, but also of the hydrolytic effect and of physical adsorption of thallos ion on the equilibrium resin. Consequently, the method employed in the calculation of the equilibrium constant was that illustrated for the silver-hydrogen exchange on hydrogen resin. Throughout this series of samples, the hydrolytic effect was assumed to be constant at the average value for this batch of hydrogen resin as found in other exchanges.

Dowex-50

Table XVIII

HRes (HNO₃ + TlNO₃)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔH^+	ΔTl^+	$\frac{\Delta H - \Delta Tl}{\text{eq. res.}}$	N_{TlRes}	K_c	K_a
1.	H ⁺ = 0.9675M Tl ⁺ = 0.0500M	4.3589	0.01554	0.00344	0.00219	+0.0675	0.151	6.35	28.5
2.	H ⁺ = 0.9675 Tl ⁺ = 0.0500	4.9449	0.01759	0.00324	0.00238	+0.049	0.142	6.35	28.5
3.	H ⁺ = 0.9612 Tl ⁺ = 0.0482	3.2135	0.01143	0.00223	0.00157	+0.058	0.146	6.18	27.7
4.	H ⁺ = 0.9109 Tl ⁺ = 0.1081	4.4475	0.01583	0.00501	0.00437	+0.040	0.272	5.56	24.9
5.	H ⁺ = 0.8615 Tl ⁺ = 0.1498	3.8710	0.01379	0.00558	0.00529	+0.021	0.368	5.50	24.6
6.	H ⁺ = 0.8108 Tl ⁺ = 0.1997	4.4860	0.01599	0.00744	0.00731	+0.008	0.432	5.32	23.8
7.	H ⁺ = 0.7621 Tl ⁺ = 0.2495	4.4185	0.01576	0.00842	0.00847	-0.003	0.506	5.26	23.6
8.	H ⁺ = 0.7160 Tl ⁺ = 0.2754	4.2323	0.01508	0.00869	0.00869	0.000	0.551	5.22	23.4
9.	H ⁺ = 0.7097 Tl ⁺ = 0.2993	4.3393	0.01544	0.00930	0.00948	-0.012	0.577	5.36	24.0

Dowex-50

Table XIX

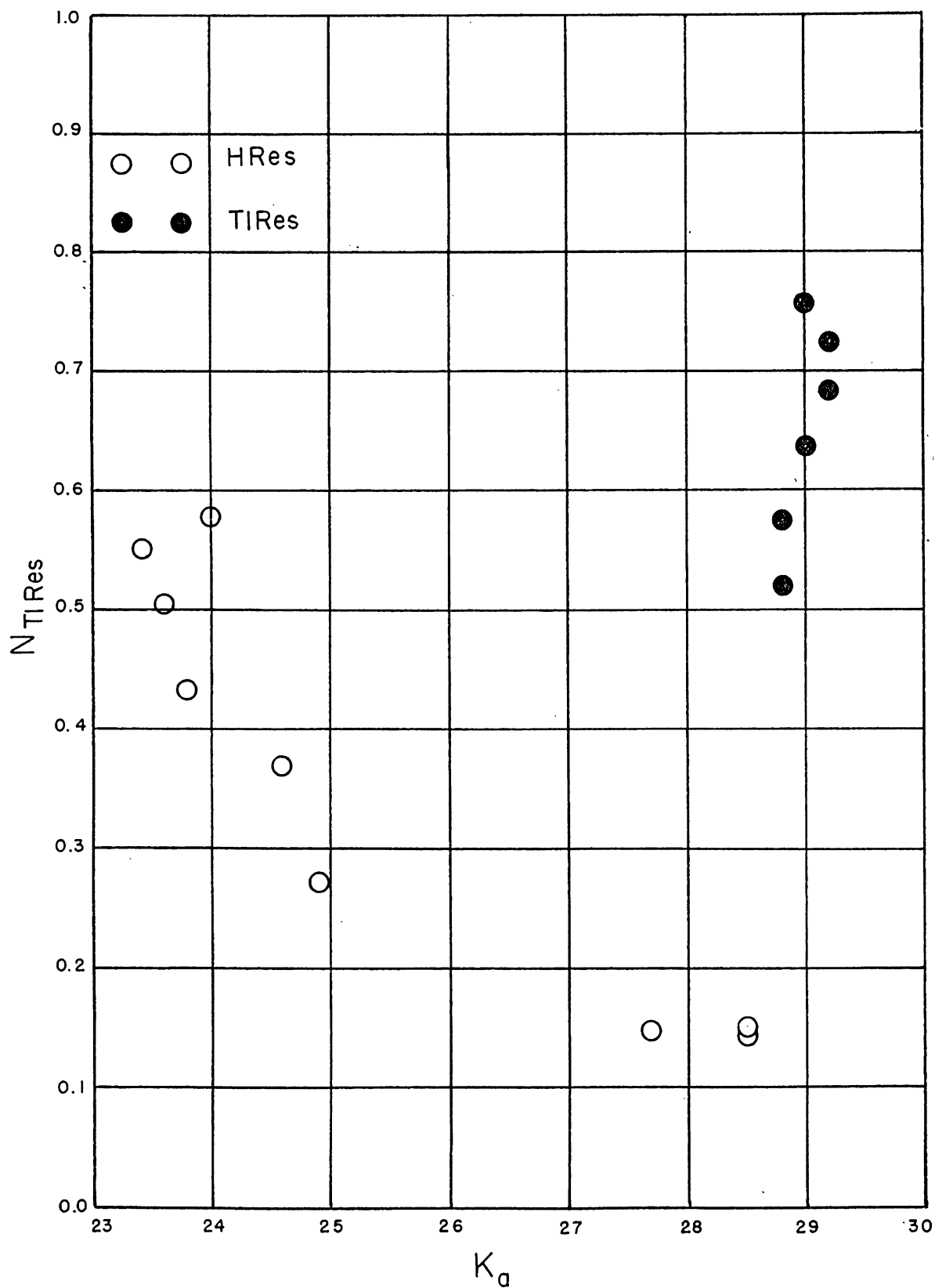
TlRes (TlNO₃ + HNO₃)

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔTl^+	ΔH^+	$\frac{\Delta Tl - \Delta H}{eq. res.}$	N_{TlRes}	K_c	K_a
1.	H ⁺ = 0.9612M Tl ⁺ = 0.0482M	8.0898	0.01908	0.00982	0.00867	+0.0602	0.518	6.44	28.8
2.	H ⁺ = 0.9120 Tl ⁺ = 0.0961	7.5676	0.01786	0.00807	0.00718	+0.0495	0.574	6.42	28.8
3.	H ⁺ = 0.8632 Tl ⁺ = 0.1437	7.7981	0.01840	0.00715	0.00633	+0.0444	0.636	6.49	29.0
4.	H ⁺ = 0.8112 Tl ⁺ = 0.1901	7.7558	0.01831	0.00621	0.00547	+0.0406	0.684	6.51	29.2
5.	H ⁺ = 0.7616 Tl ⁺ = 0.2324	8.2098	0.01939	0.00569	0.00501	+0.0350	0.725	6.52	29.2
6.	H ⁺ = 0.7160 Tl ⁺ = 0.2754	7.8031	0.01840	0.00455	0.00426	+0.0157	0.756	6.48	29.0

Examination of the values of $\frac{\Delta Tl - \Delta H}{\text{eq. res.}}$ in Table XIX shows a trend from positive to negative values, once again indicating that physical adsorption of thalious ion is involved in the over-all exchange reaction. The constant hydrolytic effect for this batch of thalious resin was taken as the average value for three samples in which the initial concentration of thalious ion was 0.05 M, at which low concentration little adsorption is to be expected. This average value was 0.058 equivalent per equivalent of resin.

In order to convert K_c to K_a , the value of γ_{\pm} for thalious nitrate at a total ionic strength of unity was required. As pointed out previously, solubility limitations necessitate an approximation, the details of which have already been explained; the value $\gamma_{\pm} = 0.34$ was again used in these calculations. A plot of the values of K_a vs. equilibrium mole fractions of thalious resin is presented in Figure X. As in the previously reported ammonium-thalious system, a hysteretic effect is observed in this study. However, the displacement of the curve is accompanied in this case by a change in shape, and for the first time the values of K_a are found to be constant over a considerable range of compositions at constant ionic strength. No explanation is offered at this time either for the hysteresis or for this unexpected constancy. The range of K_a for the thalious-hydrogen exchange is from 23.4 to

Figure X.



29.2, the quotient being formulated with the equilibrium concentration of thallos resin in the numerator. The over-all average for this equilibrium constant is the largest so far reported, 26.9. Once again, the lack of absolute constancy is attributable to the absence of activity data for the two components of the solid phase, as well as to the assumption that the activity coefficient of a salt in a mixed solution at an ionic strength as high as unity is a function of total ionic strength only.

X. LOGARITHMIC ADDITIVITY OF EQUILIBRIUM CONSTANTS

If the ion exchange process results in a true equilibrium, thus behaving in the manner described by the Law of Mass Action, then it should be possible to calculate the equilibrium constant for a given exchange reaction from those of two other reactions, as in the case of other chemical changes. Thus, let us consider the three exchanges represented by the equations



For convenience, we shall refer to a trio of three exchange reactions so related as a "triangular" system of exchanges. Now if K_C , K_A and K_B are the respective equilibrium constants, the following relationships should be valid:

$$\log K_C = \log K_A + \log K_B$$

$$K_C = K_A \times K_B.$$

With the completion of the exchange studies of ammonium ion with hydrogen ion, and of thallos ion with ammonium ion and hydrogen ion, data are available which permits an experimental test of the validity of this relationship for a "triangular" system. The system of exchanges involving ammonium, thallos, and hydrogen ions and the corresponding resins is, in fact, especially suitable because the constants for each pair are different at least by a factor of two. Agreement between the observed value of the

equilibrium constant for one of the exchanges and the calculated value (the product of the other two equilibrium constants), would provide strong additional support for our hypotheses of hydrolytic and adsorption effects, and for the correctness of our method of application of these hypotheses in the calculation of the equilibrium constants. Mean values of K_a were used in this "triangular" comparison, but since the data for the thallos ion systems were limited by the solubility of thallos nitrate to equilibrium mole fractions of 0.7 in the heavier ion resin, the average value of K_a for the ammonium-hydrogen system was based only upon values of K_a corresponding to equilibrium mole fractions of ammonium (the heavier ion) resin up to 0.7. Calculations were made as shown below.

$$K_{aA} = \frac{(\text{NH}_4\text{Res})(\text{H}^+)}{(\text{HRes})(\text{NH}_4^+)} = 3.54$$

$$K_{aB} = \frac{(\text{TlRes})(\text{NH}_4^+)}{(\text{NH}_4\text{Res})(\text{Tl}^+)} = 6.91$$

$$K_{aC} = \frac{(\text{TlRes})(\text{H}^+)}{(\text{HRes})(\text{Tl}^+)} = 26.9 \text{ (observed)}$$

$$K_{aA} \times K_{aB} = K_{aC} = 24.4 \text{ (calculated)}$$

The fact that the deviation between the observed and calculated values of K_a is less than 10% of the observed value, may be considered as additional confirmation of the validity of the several new concepts and assumptions which are involved in the determination of the individual values of K_a

for the three systems.

XI. NICKEL-HYDROGEN EXCHANGE ON DOWEX-50

The study of exchange reactions between representative univalent ions having been completed, our attention was turned to exchange reactions involving one univalent and one bivalent ion. Nickel, a typical member of the first transition series of elements, was selected as the bivalent ion because it lends itself readily to accurate analytical determination.

As in previous exchange studies, equilibrium in the nickel-hydrogen exchange reaction was approached from both directions; i.e., both pure nickel and pure hydrogen resin were used as the initial exchangers. The nickel resin was prepared by passing a concentrated solution of nickel chloride through a quantity of pure hydrogen resin contained in a column. The pH of the effluent solution was brought back to a value of 7 by the addition of solid nickel carbonate, and after filtration the solution was recirculated through the column. The conversion was considered to be complete when there was no more than a negligible difference between the pH values of the influent and effluent solutions. The resin was washed and dried as before.

Because of the prohibitive amounts of salt solution required to achieve complete replacement of nickel ion, attempts to determine the equivalent weight of the resin by removal of replaceable cation with a saturated solution of

sodium nitrate or a concentrated solution of calcium chloride were unsuccessful. Instead, weighed quantities of the resin were decomposed by means of a sulfuric acid digestion, with powdered selenium as catalyst. The nickel content of each sample was then determined by the usual gravimetric method with dimethylglyoxime as the precipitating reagent.

Inasmuch as the ionic strength of an exchange solution containing a bivalent cation with a univalent cation does not remain constant, but changes as the exchange reaction proceeds, it was necessary to fix the initial concentrations of the exchange solutions in such a manner that the effluent solution at equilibrium would have an ionic strength approximately equal to unity. This was desirable in order that a comparison might be made between univalent-bivalent exchanges and the previous univalent-univalent exchanges.

Table XX contains the data for the exchanges involving pure hydrogen resin as the initial solid phase, while in Table XXI are tabulated data for the study based on pure nickel resin as the original exchanger. Since the values of $\frac{\Delta H - \Delta Ni}{\text{eq. res.}}$ in Table XX and the corresponding quantity $\frac{\Delta Ni - \Delta H}{\text{eq. res.}}$ of Table XXI are all positive with no obvious trend, only the hydrolytic effect need be considered in the calculation of the equilibrium constant. Despite the presence of a bivalent ion, the hydrolytic effect is expressed, as before, as the number of equivalents per equivalent of

Dowex-50

Table XX

Hydrogen Resin ($\text{NiCl}_2 + \text{HCl}$)

NO.	Original Solution	Wt. of Resin	Eq. of Resin	ΔH^+	ΔNi^{++}	$\frac{\Delta\text{H}-\Delta\text{Ni}}{\text{eq.res.}}$	N_{NiRes}	μ equilibrium	K_c	K_a
1.	$\text{H}^+ = 0.0$ $\text{Ni}^{++} = 0.3434\text{M}$	4.6987	0.01674	0.01529	0.01490	0.023	0.912	0.9596	2.73	11.5
2.	$\text{H}^+ = 0.1301$ $\text{Ni}^{++} = 0.3011$	5.0667	0.01805	0.01520	0.01438	0.045	0.834	0.9697	3.09	13.0
3.	$\text{H}^+ = 0.2813$ $\text{Ni}^{++} = 0.2524$	4.5984	0.01638	0.01257	0.01192	0.040	0.757	0.9854	3.44	14.5
4.	$\text{H}^+ = 0.4188$ $\text{Ni}^{++} = 0.2015$	4.5256	0.01612	0.01102	0.01048	0.034	0.673	0.9763	3.92	16.5
5.	$\text{H}^+ = 0.5706$ $\text{Ni}^{++} = 0.1504$	4.4425	0.01583	0.00930	0.00854	0.048	0.567	0.9867	4.42	18.6
6.	$\text{H}^+ = 0.7166$ $\text{Ni}^{++} = 0.1004$	4.6388	0.01653	0.00765	0.00680	0.051	0.433	0.9923	5.02	21.1
7.	$\text{H}^+ = 0.7166$ $\text{Ni}^{++} = 0.1004$	4.5695	0.01628	0.00763	0.00674	0.055	0.435	0.9936	5.07	21.3
8.	$\text{H}^+ = 0.8593$ $\text{Ni}^{++} = 0.05181$	4.6362	0.01652	0.00490	0.00427	0.038	0.269	0.9997	5.90	24.8

Dowex-50

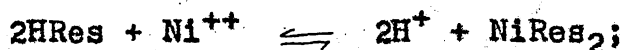
Table XXI

NiRes (NiCl₂ + HCl)

No.	Original Solution	Wt. of Resin	Eq. or Resin	ΔNi^{++}	ΔH^+	$\frac{\Delta Ni - \Delta H}{eq. res.}$	N_{NiRes}	μ equilibrium	K_c	K_a
1.	H ⁺ = 0.1014M Ni ⁺⁺ = 0.2911M	5.8277	0.01863	0.00216	0.00163	0.028	0.909	0.9908	0.73	3.08
2.	H ⁺ = 0.2013 Ni ⁺⁺ = 0.2573	5.6417	0.01804	0.00292	0.00251	0.023	0.858	0.9919	1.38	5.81
3.	H ⁺ = 0.3519 Ni ⁺⁺ = 0.2068	5.4681	0.01748	0.00422	0.00368	0.031	0.783	0.9988	2.24	9.41
4.	H ⁺ = 0.5008 Ni ⁺⁺ = 0.1559	5.4480	0.01742	0.00566	0.00510	0.032	0.698	1.0024	2.71	11.4
5.	H ⁺ = 0.6499 Ni ⁺⁺ = 0.1036	5.8551	0.01872	0.00774	0.00683	0.049	0.617	1.0085	3.44	14.5
6.	H ⁺ = 0.8026 Ni ⁺⁺ = 0.05076	5.8179	0.01860	0.00954	0.00907	0.025	0.499	1.0073	3.85	16.2
7.	H ⁺ = 0.9489 Ni ⁺⁺ = -----	5.5544	0.01776	0.01158	0.01067	0.051	0.367	1.0159	4.58	19.3

resin. The average value of the hydrolytic effect for the hydrogen resin study is 0.042. This figure is appreciably lower than those previously encountered in hydrogen resin investigations, possibly because the previous history of this batch of resin was different from that of the hydrogen resin used in other exchange studies. The average hydrolytic effect for the nickel resin study is 0.034 equivalent per equivalent of resin.

The values of K_a listed in Tables XX and XXI are for the reaction



that is,

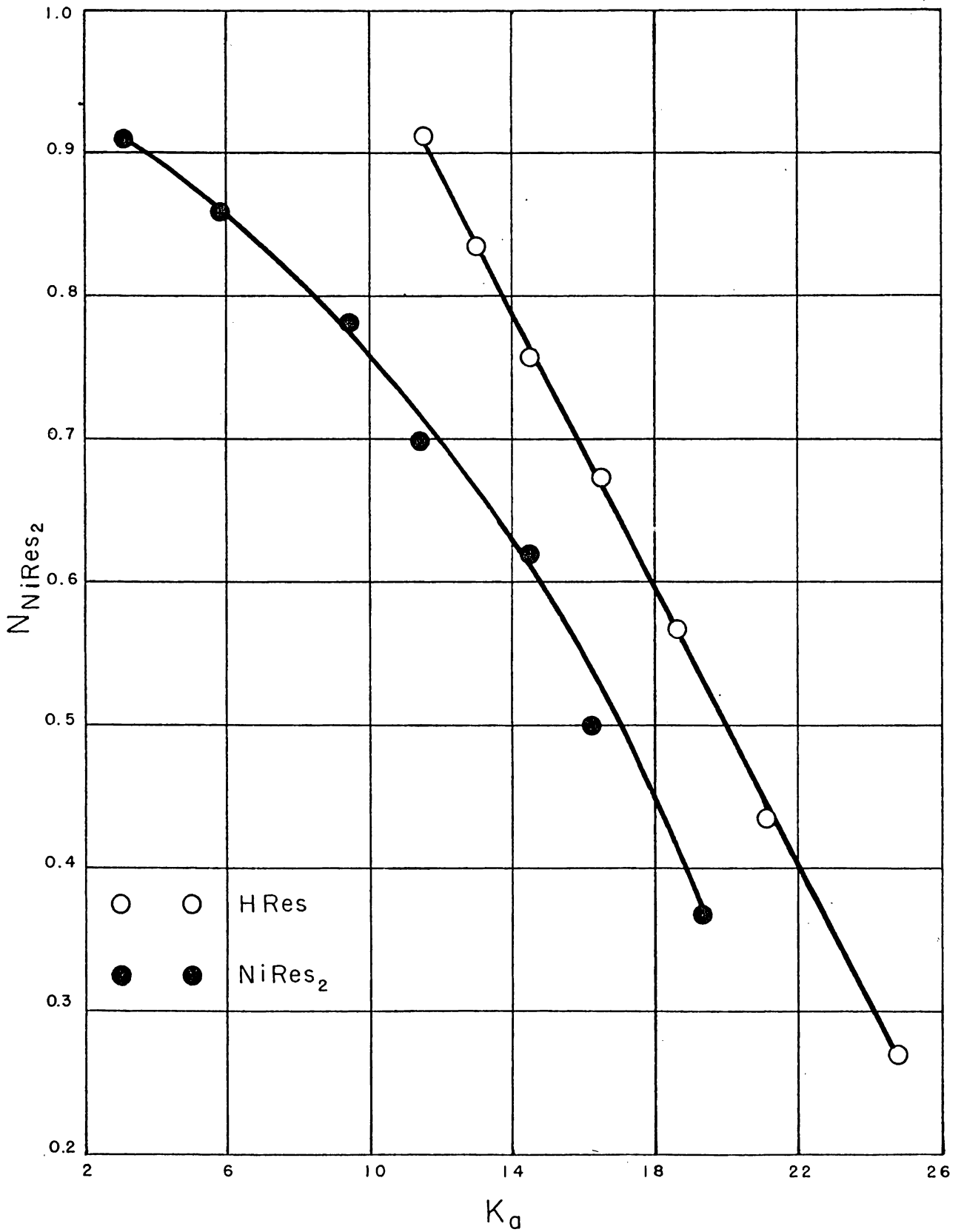
$$K_0 = \frac{(\text{H}^+)^2 (\text{NiRes}_2)}{(\text{Ni}^{++}) (\text{HRes})^2},$$

where the quantities in parentheses have their usual significance. K_a values are derived as the product of K_0 and the ratio, $\frac{\gamma_{\text{H}^+}^2 \gamma_{\text{HCl}}}{\gamma_{\text{Ni}^{++}} \gamma_{\text{NiCl}_2}^2}$, i.e.,

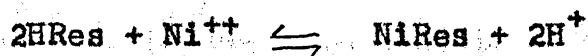
$$K_a = K_0 \cdot \frac{\gamma_{\text{H}^+}^2 \gamma_{\text{HCl}}}{\gamma_{\text{Ni}^{++}} \gamma_{\text{NiCl}_2}^2}$$

Values of K_a in Tables XX and XXI are represented graphically in Figure XI as a function of the equilibrium mole fraction of nickel resin. It may be noted that the range of values is much wider than in any exchange previously studied. In the nickel-hydrogen exchange, also, there is encountered for the first time a system showing marked hysteresis. No explanation for this phenomenon can be offered at present.

Figure XI



In the case of a bivalent-univalent exchange, the equilibrium expression developed by Krishnamoorthy and co-workers (25) is not equivalent to the Mass Action expression; hence the nickel-hydrogen exchange system affords the first opportunity in this work for an experimental test of their equation. A brief discussion of the equation presented by Krishnamoorthy may be found in the introductory section of this dissertation. As applied to the nickel-hydrogen exchange, the expression for the equilibrium constant for the reaction



reduces to the following

$$K_a = \frac{[\text{NiRes}]}{[\text{HRes}]^2} \cdot \left\{ 3/2[\text{NiRes}] + [\text{HRes}] \right\} \cdot \frac{(\text{H}^+)^2}{(\text{Ni}^{++})} \cdot \frac{\gamma_{\text{HCl}}^4}{\gamma_{\text{NiCl}_2}^3}$$

or

$$K_a = \left\{ 3/2 \frac{[\text{NiRes}]^2}{[\text{HRes}]^2} + \frac{[\text{NiRes}]}{[\text{HRes}]} \right\} \frac{(\text{H}^+)^2}{(\text{Ni}^{++})} \cdot 4.21$$

where the terms in brackets represent numbers of moles of replaceable ions in the solid phase. Terms in parentheses are the equilibrium concentrations of the two exchanging cations in the solution phase. When this equation is applied to the data of the nickel-hydrogen exchange the results are those given in Table XXII. It may be observed that the values of the quotient (last column) exhibit exactly the same trend as when calculated by the Mass Action expression; moreover, the range of values is greater than the range of the conventional quotients, as previously presented. The

Table XXII

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HRes + NiCl₂ + HCl

No.	N _{NiRes₂}	K _a (equiv.)	K _a (mols)
1.	0.912	61.7	16.3
2R	0.834	63.0	17.6
3.	0.757	64.5	18.9
4R	0.673	66.3	20.6
5.	0.567	66.5	22.3
6.	0.435	67.0	24.5
7.	0.269	64.8	26.7

NiRes₂ + NiCl₂ + HCl

No.	N _{NiRes₂}	K _a (equiv.)	K _a (mols)
1.	0.909	16.5	4.38
2.	0.858	55.2	7.98
3.	0.783	42.1	12.2
4.	0.698	47.3	14.5
5.	0.617	54.9	17.8
6.	0.499	49.8	19.3
7.	0.367	55.9	21.4

apparent hysteretic behavior of this exchange pair, likewise, is not diminished by this method of calculation. From this evidence it was concluded that no advantage was to be gained by the use of this more complicated expression in place of the Mass Action equation.

The values of $K_a(\text{eq})$ contained in the third column of Table XXII were also obtained from the Krishnamoorthy expression, but the number of equivalents of exchangeable cation in the solid phase was substituted for the number of moles. This deviation from the equation as developed by Krishnamoorthy is difficult to justify in view of the relationship between mole quantities and activities. However, one might consider the resin matrix as being composed of inactive areas and active exchange sites. The number of equivalents, rather than the number of moles, of nickel in the resin would then be a direct measure of the number of exchange sites occupied by the nickel ion in the solid phase, and thus would be a measure of the activity of the nickel resin component, corresponding to that of the other component, hydrogen resin.

As may be seen from Table XXII, the equilibrium constant for the nickel-hydrogen exchange on hydrogen resin, calculated in this manner, has an average value of 64.8 with an average deviation of only 2.3%. The equilibrium quotient for the same exchange on nickel resin, however, does not exhibit the same degree of constancy. Sample I

being omitted, the average value is 50.9 with an average deviation of 8.8%. Very little diminution is noted in the apparent hysteretic behavior when the constants are calculated in this manner.

Although the interpretation of the data according to this modification of the Krishnamoorthy expression yields a more nearly constant value of the equilibrium quotient, further experimental evidence seems necessary before it is postulated as the expression best suited to describe the base exchange reaction.

XII. CALCIUM-HYDROGEN EXCHANGE ON DOWEX-50

Since the study of the nickel-hydrogen exchange showed this exchange pair to exhibit marked hysteretic behavior, it seemed of interest to investigate the exchange of hydrogen ion with another bivalent ion, and particularly with one of approximately the same size but of less complex electron configuration than the transition element. With this consideration in mind, as well as the ease and accuracy of the analysis involved, calcium ion was selected for the second investigation of a bivalent-univalent ion exchange.

As in previous studies, equilibrium was approached from both directions; i.e., both pure hydrogen resin and pure calcium resin were employed as the initial solid phase. Pure calcium resin was prepared by placing pure hydrogen resin in a column, and passing through it a concentrated solution of calcium chloride. The effluent solution was neutralized with solid calcium carbonate, filtered, and recirculated through the column. When the effluent solution showed only a negligible decrease in pH after passage through the column, the conversion was considered to be complete. The resin was then washed free of chloride ion and dried in the usual manner.

Calcium ion concentrations were determined by the standard gravimetric method; the calcium was precipitated with ammonium oxalate, filtered in a porcelain filter,

ignited at 600° C. in an atmosphere of carbon dioxide, and weighed as calcium carbonate.

Because of the difficulties of manipulation resulting from the insolubility of calcium sulfate, the sulfuric acid digestion method could not be used for the determination of the equivalent weight of the calcium resin. Instead, weighed quantities of resin were treated with 10 ml. portions of 72% perchloric acid, and allowed to stand for 24 hours at a temperature of about 50°.* After this period,

*The use of a relatively low temperature was necessitated by the excessive "bumping" which took place at normal fuming or evaporation temperatures.

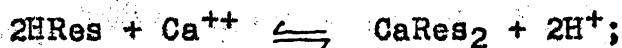
the decomposition was sufficiently complete so that the excess perchloric acid could be evaporated, leaving calcium perchlorate as the residue. This salt was dissolved in water, and the determination of calcium was then carried out in the manner previously described.

As mentioned in connection with the nickel-hydrogen exchange, the ionic strength of an exchange solution containing a bivalent and a univalent ion does not remain constant, but changes with the progress of the exchange reaction. Consequently, it was necessary to adjust the initial concentrations of the exchange solutions in such a manner that the effluent solution at equilibrium would have an ionic strength approximately equal to unity.

The data for the exchanges involving pure hydrogen

resin are contained in Table XXIII, while the data for the study in which pure calcium resin was employed as the initial exchanger are tabulated in Table XXIV. Examination of the values of $\frac{\Delta H - \Delta Ca}{\text{eq. res.}}$ in Table XXIII and the corresponding values of $\frac{\Delta Ca - \Delta H}{\text{eq. res.}}$ in Table XXIV reveals that they are all positive with no apparent trend; hence only the hydrolytic effect need be considered in the calculation of the equilibrium constant. The average value of the hydrolytic effect for the hydrogen resin is 0.036 equivalent per equivalent of resin. As in the case of the nickel-hydrogen exchange, this figure is somewhat lower than that expected for hydrogen resin in solutions of unit ionic strength. The average hydrolytic effect for calcium resin is 0.078 equivalent per equivalent of resin.

The values of K_a contained in Tables XXIII and XXIV are for the reaction



that is,

$$K_c = \frac{(\text{H}^+)^2 (\text{CaRes}_2)}{(\text{Ca}^{++}) (\text{HRes})^2}$$

and

$$K_a = K_c \cdot \frac{\gamma_{\pm}^4 \pm \text{HCl}}{\gamma_{\pm}^3 \pm \text{CaCl}_2^2},$$

where the quantities in parentheses have their usual significance. In Figure XII, values of K_a are presented graphically as a function of the equilibrium mole fraction of calcium resin. It may be seen that the K_a values obtained from the studies involving the two different pure resins, as

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Table XXIII

HRes + CaCl₂ + HCl

No.	Original Solution	Wt. of Resin	Eq. of Resin	ΔH^+	ΔCa^{++} (eq.)	$\frac{\Delta H - \Delta Ca}{eq. res.}$	μ Equi- librium	N_{CaRes}	K_c	K_a
1.	Ca ⁺⁺ =0.3504M H ⁺ =	4.4951	0.01601	0.01508	0.01480	0.017	0.9800	0.888	5.86	25.8
2.	Ca ⁺⁺ =0.3000 H ⁺ =0.1504	4.5633	0.01626	0.01447	0.01406	0.025	0.9842	0.798	7.33	32.2
2R	Ca ⁺⁺ =0.3000 H ⁺ =0.1504	4.4300	0.01578	0.01414	0.01342	0.046	0.9905	0.803	7.61	33.5
3.	Ca ⁺⁺ =0.2505 H ⁺ =0.2908	4.5471	0.01620	0.01357	0.01318	0.024	0.9803	0.716	8.65	28.0
3R	Ca ⁺⁺ =0.2505 H ⁺ =0.2908	4.8312	0.01721	0.01425	0.01398	0.016	0.9751	0.703	8.25	36.3
4.	Ca ⁺⁺ =0.2001 H ⁺ =0.4398	4.4438	0.01583	0.01230	0.01166	0.040	0.9882	0.623	9.80	43.1
4R	Ca ⁺⁺ =0.2001 H ⁺ =0.4398	4.6185	0.01645	0.01275	0.01200	0.046	0.9873	0.618	9.75	42.9
5.	Ca ⁺⁺ =0.1521 H ⁺ =0.5830	4.5399	0.01617	0.01116	0.01073	0.027	0.9900	0.518	10.85	47.7
5R	Ca ⁺⁺ =0.1521 H ⁺ =0.5830	4.2983	0.01531	0.01067	0.01022	0.031	0.9927	0.525	11.00	48.4
6R	Ca ⁺⁺ =0.09981 H ⁺ =0.7265	5.0078	0.01784	0.01039	0.00932	0.060	0.9911	0.383	12.9	56.8
7.	Ca ⁺⁺ =0.05031 H ⁺ =0.8676	4.4269	0.01577	0.00643	0.00546	0.061	1.006	0.226	14.2	62.5

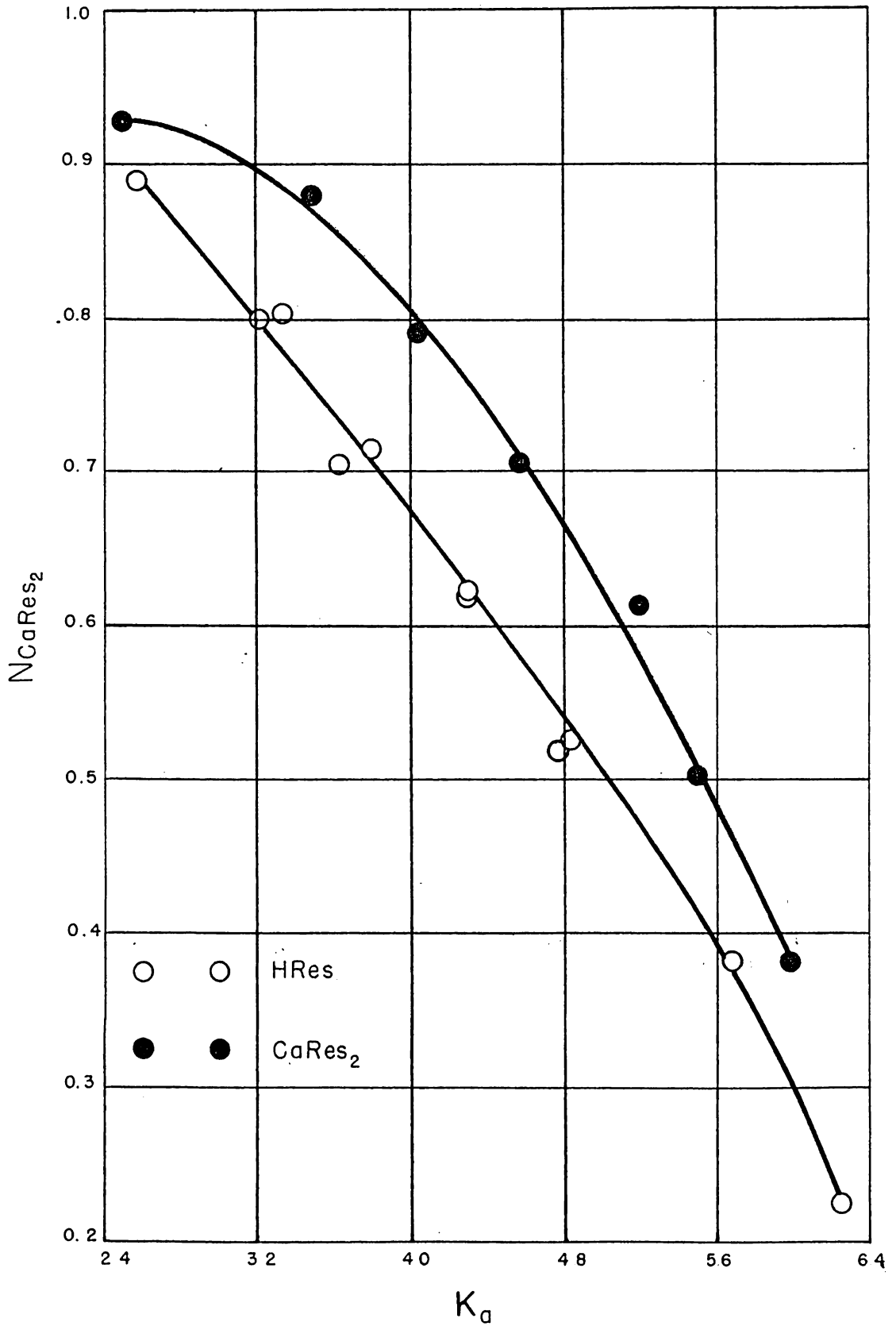
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Table XXIV

CaRes₂ + HCl + CaCl₂

No.	Original Solution	Wt. of Resin	Eq. of Resin	ΔCa^{++} (eq.)	ΔH^+	$\frac{\Delta\text{H}-\Delta\text{Ca}}{\text{eq.res.}}$	μ Equilibrium	N_{CaRes_2}	K_c	K_a
1.	Ca ⁺⁺ =0.2924M H ⁺ =0.1028M	5.0794	0.01967	0.00182	0.00068	0.058	1.0005	0.929	5.68	25.0
2.	Ca ⁺⁺ =0.2571 H ⁺ =0.2042	5.8878	0.02280	0.00284	0.00138	0.064	1.004	0.879	7.95	35.0
3.	Ca ⁺⁺ =0.2021 H ⁺ =0.3569	5.4732	0.02119	0.00388	0.00228	0.079	0.9986	0.791	9.20	40.4
4.	Ca ⁺⁺ =0.1528 H ⁺ =0.5137	5.5855	0.02163	0.00504	0.00349	0.072	1.0128	0.705	10.4	45.8
5R	Ca ⁺⁺ =0.1027 H ⁺ =0.6650	5.3389	0.02068	0.00624	0.00453	0.083	1.0214	0.614	11.8	51.9
6.	Ca ⁺⁺ =0.04927 H ⁺ =0.8168	5.5772	0.02160	0.00857	0.00645	0.099	1.0287	0.503	12.5	55.0
7.	Ca ⁺⁺ =----- H ⁺ =0.9737	5.8218	0.02255	0.01134	0.00912	0.098	1.0526	0.381	13.6	59.8

Figure XII



starting materials lie on two nearly parallel lines separated by but a small distance from each other. The hysteresis exhibited in the first bivalent-univalent study, nickel-hydrogen exchange, has all but disappeared in the calcium-hydrogen exchange.

It is of interest to classify the exchange pairs thus far studied, according to whether or not they exhibit the phenomenon of hysteresis.

<u>Hysteretic</u>	<u>Non-hysteretic</u>
Thalious-hydrogen	sodium-hydrogen
Thalious-ammonium	ammonium-hydrogen
Nickel-hydrogen	silver-hydrogen
	calcium-hydrogen

There is some question as to the proper classification of the silver-hydrogen exchange. Over most of the range studied, this system exhibited little hysteresis; however, when the equilibrium solid phase was composed largely of silver resin, the K_a values derived from the two pure resins as initial exchangers were appreciably different. With this exception, it may be seen that the exchange pairs exhibiting no hysteresis consist entirely of those ions which form electrovalent bonds only, and which have little or no tendency to form coordinate bonds. On the other hand, one ion of each exchange pair exhibiting hysteresis forms coordinate bonds very readily. Of the ions listed, nickel ion has the greatest tendency to form coordinate bonds, and

the nickel-hydrogen exchange system was found to exhibit hysteresis to the greatest degree. Thus it would seem that the phenomenon of hysteresis is in some manner related to the types of linkage which the ions of the exchange pair are capable of forming.

XIII. NICKEL-CALCIUM EXCHANGE ON DOWEX-50

As a final study, an investigation of a bivalent-bivalent exchange was undertaken, with nickel and calcium as the exchange pair. As in previous exchanges, the equilibrium was approached from both sides, i.e., both pure calcium resin and pure nickel resin were employed as the initial solid exchangers. In both cases, the pure resins were those which had been used in previous studies.

Because of the error introduced by coprecipitation, the separation of these two ions proved very difficult. In the determination of calcium, attempts were made to hold the nickel ion in solution by the addition of complexing agents, while the calcium ion was precipitated with ammonium oxalate. Experiments made with ammonia and with sodium cyanide as complexing agents were unsuccessful. The procedure finally adopted consisted of the addition of an excess of ammonium hydroxide to the sample to be analyzed for calcium. After precipitation of the calcium oxalate, the supernatant liquid, which contained most of the nickel, was decanted through a porcelain filter. The remaining precipitate was dissolved with a few milliliters of hydrochloric acid, and reprecipitated by the addition of an excess of ammonium hydroxide. The filtration and ignition of the precipitate were then carried out as before.

Since the nickel dimethylglyoxime precipitate undergoes decomposition when dissolved in hydrochloric acid,

some scheme other than reprecipitation had to be employed for the determination of nickel. This was accomplished by the electrolytic deposition of nickel metal on a platinum cathode, from an ammoniacal solution to which had been added ammonium chloride to reduce the internal resistance of the electrolytic cell.

A series of samples were treated with aqueous solutions of calcium chloride and nickel chloride of total ionic strength approximately equal to unity. Inasmuch as there was an appreciable decrease in volume upon mixing solutions of these two salts, it was found necessary to prepare and analyze each exchange solution individually, before it was placed in contact with the resin. After the mixture had been allowed to come to equilibrium, portions of the effluent were removed and analyzed for calcium and nickel ions.

The data for the exchange study on pure calcium resin are to be found in Table XXV, while the data based on the study involving pure nickel resin are contained in Table XXVI. Examination of the values of $\frac{\Delta Ca - \Delta Ni}{eq. res.}$ in Table XXV reveals that they are all positive with no apparent trend, thus indicating that the hydrolytic effect is the only departure from equivalent exchange that need be considered in the calculation of K_a . The average value of the hydrolytic effect for the study on calcium resin is 0.059 equivalent per equivalent of resin. This figure may

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Table XXV

NiRes₂ + CaCl₂ + NiCl₂

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔNi^{++} (mol)	ΔCa^{++} (mol)	$\frac{\Delta Ni - \Delta Ca}{eq. res.}$	N_{CaRes_2}	K_c	K_a
7R	Ni ⁺⁺ =----- Ca ⁺⁺ =0.3306M	5.5400	0.01782	0.00769	0.00723	0.052	0.856	1.77	1.85
6R	Ni ⁺⁺ =0.4976 Ca ⁺⁺ =0.2756	5.2077	0.01675	0.00657	0.00611	0.055	0.772	1.82	1.90
5.	Ni ⁺⁺ =0.1008 Ca ⁺⁺ =0.2290	6.1380	0.01974	0.00665	0.00651	0.014	0.669	2.06	2.15
4.	Ni ⁺⁺ =0.1516 Ca ⁺⁺ =0.1801	5.4541	0.01754	0.00513	0.00510	0.004	0.584	2.20	2.30
3.	Ni ⁺⁺ =0.1988 Ca ⁺⁺ =0.1314	5.2131	0.01677	0.00401	0.00403	-0.004	0.481	2.43	2.54
2.	Ni ⁺⁺ =0.2478 Ca ⁺⁺ =0.08157	5.5357	0.01781	0.00311	0.00291	0.022	0.334	2.67	2.79

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Table XXVI

CaRes₂ + NiCl₂ + CaCl₂

No.	Original Solution	Wt. of Resin	Equivalents of Resin	ΔCa^{++} (mols)	ΔNi^{++} (mols)	$\frac{\Delta\text{Ca} - \Delta\text{Ni}}{\text{eq.res.}}$	N _{CaRes₂}	K _c	K _a
1.	Ni ⁺⁺ =0.3330M Ca ⁺⁺ =-----	5.1922	0.02011	0.00648	0.00573	0.075	0.387	2.69	2.81
2R	Ni ⁺⁺ =0.2509 Ca ⁺⁺ =0.0800	5.4745	0.02120	0.00454	0.00367	0.082	0.624	2.82	2.95
3R	Ni ⁺⁺ =0.2028 Ca ⁺⁺ =0.1310	3.9010	0.01511	0.00241	0.00222	0.026	0.699	2.46	2.57
4.	Ni ⁺⁺ =0.1516 Ca ⁺⁺ =0.1801	5.5869	0.02153	0.00265	0.00215	0.046	0.791	2.38	2.49
5.	Ni ⁺⁺ =0.1008 Ca ⁺⁺ =0.2290	5.6477	0.02187	0.00184	0.00130	0.050	0.875	2.49	2.61
6.	Ni ⁺⁺ =0.0505 Ca ⁺⁺ =0.2792	5.5398	0.02145	0.00132	0.00055	0.072	0.944	2.64	2.76

be compared to that of 0.078 equivalent per equivalent of resin, as obtained from the calcium-hydrogen exchange study on the same calcium resin. The corresponding values of $\frac{\Delta \text{Ni} - \Delta \text{Ca}}{\text{eq. res.}}$ contained in Table XXVI are, with one exception, likewise all positive with no obvious trend. The exceptional figure is believed to be due to analytical errors. In the calculation of the equilibrium constant, this negative value was disregarded, and the data were treated according to the supposition that the hydrolytic effect is the only deviation from equivalent exchange.

The values of K_a contained in Tables XXV and XXVI are for the reaction



that is,

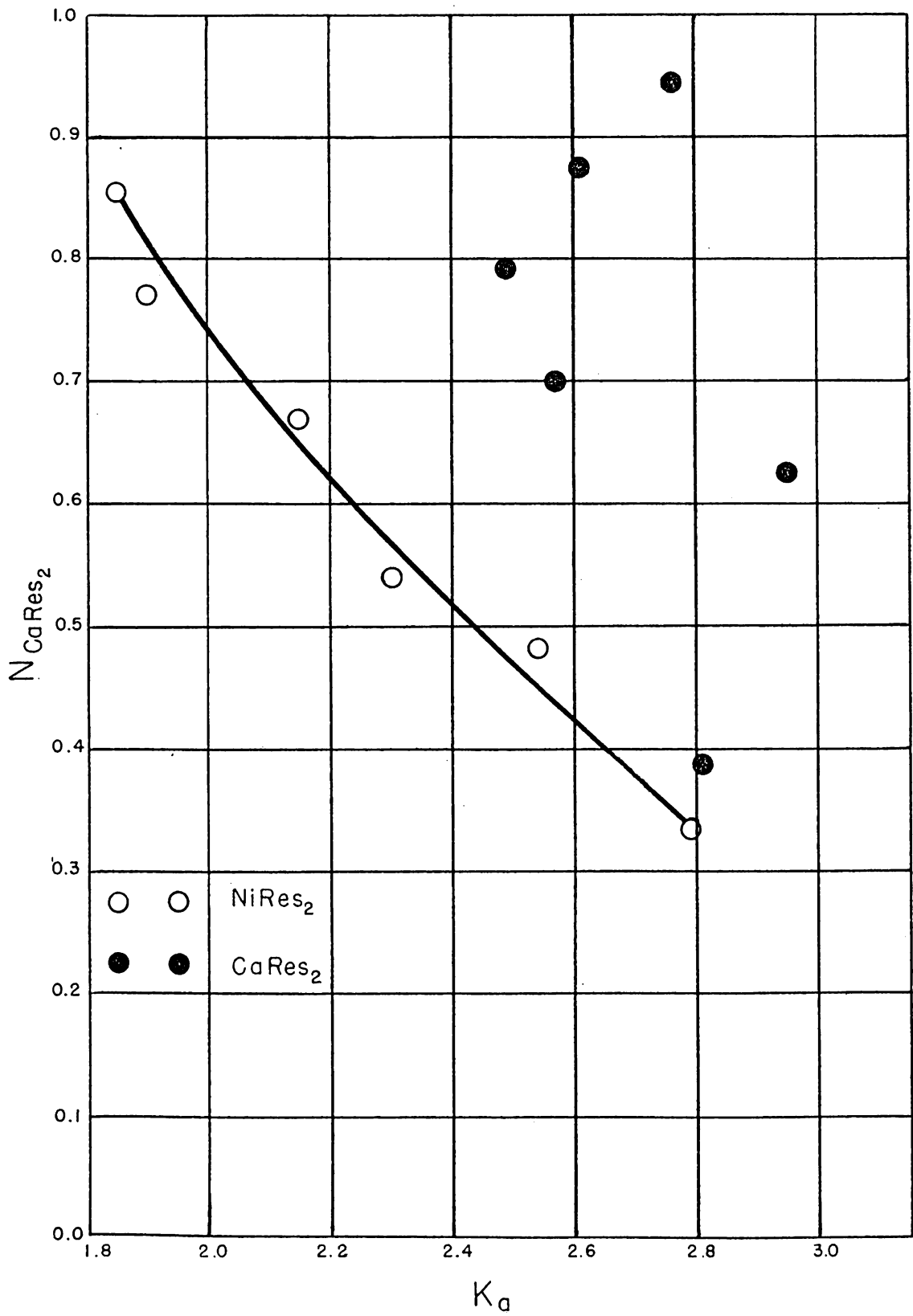
$$K_c = \frac{(\text{Ni}^{++})(\text{CaRes}_2)}{(\text{Ca}^{++})(\text{NiRes}_2)}$$

and

$$K_a = K_c \cdot \frac{\gamma_{\pm}^3 \text{NiCl}_2}{\gamma_{\pm}^2 \text{CaCl}_2}$$

In Figure XIII, the values of K_a are presented graphically as a function of the equilibrium mole fraction of calcium resin. The points lying on the smooth curve are the values of K_a for the exchange on nickel resin. K_a values for the exchange on calcium resin appear randomly distributed above the smooth curve. Undoubtedly, with a larger number of experiments, these values could be so refined as to place them on a curve parallel to that shown in the figure, but limitations of time did not permit such further investigations.

Figure XIII



Because of the inadequacy of the data for the calcium-nickel exchange on calcium resin, it is difficult to decide whether or not this exchange pair exhibits the phenomenon of hysteresis. The fact that each value of K_a for the exchange on calcium resin is greater than the corresponding value of K_a for the exchange on nickel resin would appear to indicate that there is some degree of hysteresis in this system. Such behavior would be expected, also, on the basis of the respective capacities of the ions to form coordinate linkages.

XIV. SUMMARY AND CONCLUSIONS

The exchange reactions between a synthetic ion exchange resin and a series of cation pairs in solutions of total ionic strength approximately equal to unity have been investigated. The Law of Mass Action has been applied to describe their behavior under equilibrium conditions. Two causes of departure from simple equivalent exchange, which have been designated as hydrolytic and adsorption effects, respectively, have been defined, and appropriate corrections for these effects have been made in the calculation of the equilibrium constant. The list of cation pairs studied, with the range of the respective equilibrium quotients is given below. In each case, the quotients are calculated for the reaction between a resin containing the first named ion and a solution containing the second.

Univalent-univalent

Hydrogen-sodium	1.3-2.5
Hydrogen-ammonium	2.2-4.8
Hydrogen-silver	16-28
Hydrogen-thallos	23-29
Ammonium-thallos	5.5-8.2

Univalent-bivalent

Hydrogen-nickel	3-25
Hydrogen-calcium	24-60

Bivalent-bivalent

Nickel-calcium	1.8-3.0
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The ammonium-hydrogen exchange on hydrogen resin has been investigated at a series of ionic strengths varying from 0.1 to 1. The hydrolytic effect was found to increase with increasing ionic strength. Contrary to the reports of previous investigations, the equilibrium constant was found to increase with increasing ionic strength.

The Kielland formulation, which is derived from the Duhem-Margules equation, has been applied to a portion of the data for the sodium-hydrogen exchange system, resulting, however, in no improvement in the constancy of K_a .

The Krishnamoorthy expression was applied to the data of the hydrogen-nickel exchange study. No improvement over the conventional expression derived from the Law of Mass Action is achieved when the composition of the solid phase is expressed in terms of mole fractions of the two components; however, if the composition of the solid phase is expressed in terms of equivalent fractions of the two components, the data yield values of K_a with a surprising degree of constancy.

In certain cases there was observed a marked divergence in equilibrium conditions, according to which of the two pure resins was used as the initial exchanger. A suggestion as to a possible explanation of this phenomenon, which has been designated as hysteresis, has been advanced.

It may be concluded that the ion exchange process on synthetic ion exchange resins cannot be expressed by a single

stoichiometric equation. Depending upon the ionic strength of the solution and the nature of the initial resin, the exchange reaction may be accompanied by a hydrolytic reaction or by physical adsorption of one of the ions on the resin surface, or both of these anomalies may occur simultaneously along with the exchange reaction. In previous investigations, however, these effects were frequently overlooked because the equilibrium conditions were deduced from the observed changes in concentration of a single cation. It is believed that the present investigation, in which concentrations of both exchanging cations in the equilibrium effluent were determined, has afforded the best data so far available for the analysis of the hydrolytic and adsorption effects.

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