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Divinylbenzene Resin

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CATION-EXCHANGE EQUILIBRIA ON A SULFONATED  
POLYSTYRENE-DIVINYLBENZENE RESIN

by

John Morris Erickson

A Dissertation Submitted to the  
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TABLE OF CONTENTS

INTRODUCTION .....	1
HISTORICAL DEVELOPMENT OF ION EXCHANGERS .....	7
SOME GENERAL ASPECTS OF ION-EXCHANGE EQUILIBRIA .....	10
THEORIES OF ION-EXCHANGE EQUILIBRIA .....	21
EXPERIMENTAL .....	59
DISCUSSION OF RESULTS .....	83
CONCLUSIONS .....	101
BIBLIOGRAPHY .....	103
ACKNOWLEDGEMENTS .....	112

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## INTRODUCTION

The primary application of the ion-exchange process in this laboratory has been the separation of the chemically similar rare earth elements. That it has been extremely successful is shown by the fact that kilogram and larger quantities of most of the individual rare earths are now available in a very high degree of purity. A number of industrial concerns have adopted the process, largely as perfected by this laboratory, for the commercial production of these elements. As a consequence of this availability of pure individual rare earths for research and study, many unique properties have been discovered and the rare earths are taking an increasingly important position among the chemical elements.

As is often the case, during the early work on such a process where the product is in great demand, the technology resulting in the actual separation of the rare earths has advanced more rapidly than the fundamental, basic knowledge of the ion-exchange mechanism. During the past few years a great deal of work has been done in attempting to correct this situation and much of it will be discussed later in this thesis.

Using only classical thermodynamic equations, the concept of electroneutrality, and material balances, Spedding and Powell (134b) have explained the elution of rare earths



from cation-exchange resins. They achieved excellent agreement between theoretical curves and actual experimental points. A number of equations have been taken from their paper to show how the research reported in this thesis fits into the general theory of ion-exchange separation of the rare earths. The equations bear the same numbers assigned to them in the paper but prefixed with the letter "P" to prevent confusion with similarly numbered equations found later in the text. These equations apply when the columns are operated under equilibrium conditions and where sharp bands are obtained, imposed by chemical restraints at the boundaries. Equations (P3), (P6), (P6a), and (P7) refer to the ammonium citrate solution used as the eluate in the column separation procedure while (Pl6) and (Pl7) are concerned with solution-resin equilibria. A subscript "R" refers to the resin phase while no subscript is used for an ionic species in the eluate or solution phase. In equation (P3), the concentration of the rare earth ion,  $R^{+3}$ , in the eluate is so small that it is neglected in this material balance.

$$R_T = RCit_2^{\equiv} + HRCit_2^{\equiv} + RCitOH^- + (R^{+3}) \quad (P3)$$

R = rare earth ion

$R_T$  = total rare earth of all species in the eluate

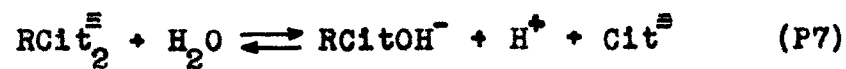


$$K'_5 = \frac{H^+ \cdot RCit_2^{\equiv}}{HRCit_2^{\equiv}}$$

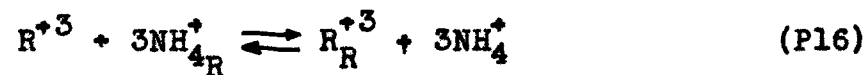
The equilibrium constants are primed because they have the activity coefficients of the different species in them. These activity coefficient ratios do not change during the elution since the solution concentrations do not change appreciably.



$$K'_4 = \frac{R^{+3} \cdot (Cit^{\equiv})^2}{RCit_2^{\equiv}}$$



$$K'_6 = \frac{RCitOH^- \cdot H^+ \cdot Cit^{\equiv}}{RCit_2^{\equiv}}$$



$$K'_9 = \frac{R^{+3}_R \cdot (NH_4^+)^3}{R^{+3} \cdot (NH_4^+_R)^3}$$

$$\frac{R^{+3}_R}{R^{+3}} = \frac{NH_4^+_R}{NH_4^+} = \frac{Q}{S} \quad (P17)$$

Q = total capacity of the resin expressed in

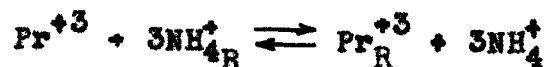
equivalents per kilogram of air-dried resin  
 $\bar{S}$  = total ammonia added to the eluant to adjust  
 pH to the desire value

These equations can be combined to give

$$K = K_9' K_4' Q^2 = \bar{S}^2 (\text{Cit}^{\equiv})^2 \left( 1 + \frac{H^+}{K_5'} + \frac{K_6'}{H^+ \cdot \text{Cit}^{\equiv}} \right) \quad (\text{Pl9})$$

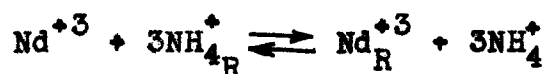
Actually, equation (Pl6) is written just the reverse of the way it is found in Spedding and Powell's paper. It must be written and  $K_9'$  defined as above to get equation (Pl9). They point out that the values of all terms can be obtained from the literature or from ion-exchange data except  $K_9'$  and  $K_4'$ . However, the product of these two terms can be determined from ion-exchange data. Hence, if  $K_9'$  were known,  $K_4'$  could also be determined and, from these facts, more knowledge is obtained of the activity coefficients of the ionic species in these solutions.

Then, too, if  $K_9'$  were known for the exchange of one rare earth, say praseodymium, and the ammonium ion between the solution and resin and again for a second rare earth, say neodymium and the ammonium ion, the ratio of the two values  $K_9'$  would give the selectivity coefficient for the exchange of the two rare earths on this resin. For example,



$$K'_9 = \frac{\text{Pr}_R^{+3} \cdot (\text{NH}_4^+)^3}{\text{Pr}^{+3} \cdot (\text{NH}_{4R}^+)^3}$$

and



$$K'_9 = \frac{\text{Nd}_R^{+3} \cdot (\text{NH}_4^+)^3}{\text{Nd}^{+3} \cdot (\text{NH}_{4R}^+)^3}$$

Dividing the first value of  $K'_9$  by the second,

$$K_D = \frac{\text{Pr}_R^{+3} \cdot \text{Nd}^{+3}}{\text{Pr}^{+3} \cdot \text{Nd}_R^{+3}}$$

which is the apparent equilibrium constant, often called the selectivity coefficient for the reaction



Therefore, a method would be available for checking the values of selectivity coefficients determined by other means.

Furthermore, a knowledge of the manner in which the apparent equilibrium constant varies with the composition of the resin and the composition and concentration of the equilibrating solution may aid in the formulation of a complete theory of ion-exchange equilibria.

The object of this research has been to study the condi-

tions that exist when a cation-exchange resin of the sulfonated polystyrene-divinylbenzene type is in equilibrium with a solution which has a certain ratio of  $\text{NH}_4^+$  to  $\text{Nd}^{+3}$  at a definite total concentration. This has been done using solutions wherein the ratio of equivalents of  $\text{NH}_4^+$  to equivalents of  $\text{Nd}^{+3}$  varied from approximately 999:1 to 70:30 at a total concentration of one equivalent of cation per liter and also wherein this ratio varied from about 9995:5 to 60:40 at a total concentration of 0.1 equivalents per liter. It is hoped that these studies would furnish information to determine how the activity coefficients in the solution phase vary with ionic strength, in the resin phase with composition and water content, and by proper extrapolation of these data, to determine a true equilibrium constant for the exchange reaction.

## HISTORICAL DEVELOPMENT OF ION EXCHANGERS

Credit for recognizing the ion-exchange reaction as such is usually given to Thompson (139) and Way (147, 148) who reported on experiments with soils in 1850 though there have been references to the phenomenon back to the time of Aristotle who noted that the percolation of sea water through sand made it potable. Thompson observed that soils treated with solutions of an ammonium salt would absorb ammonia and release lime. Way verified Thompson's work and also found that;

1. Some ions were more readily exchanged than others.
2. Equivalent amounts of cations were always involved.
3. The exchange of ions differed from true adsorption.
4. Heat treatment destroyed the exchanger's properties.
5. It was the aluminum silicates in the soil that were responsible for the exchange.
6. Exchange materials could be synthesized from soluble silicates and alum.

According to Kressman (89), Way also noted the reversibility of the reaction, a fact that drew much opposition in his day. It should be noted that the law of mass action was not discovered until 1867. Even the great Liebig is supposed to have remarked, "These experiments are very remarkable and should be opposed with might and main."

Whether it was due to the influence of Liebig or to some other cause, the phenomenon was not studied extensively again until the beginning of the twentieth century. The classical studies of Gans (49, 50, 51) were probably the first attempts to use ion exchange for industrial purposes. He used both natural and synthetic aluminum silicates for softening water and treating sugar solutions. The turn of the century brought a virtual flood of contributions as to the nature of ion exchange in clays, soils, and other silicates. However, the limitations of this type of exchanger became more and more apparent as attempts were made to exploit them. Therefore, a definite step forward was made when Liebknecht in 1934 (98) discovered that if certain powdered coals were sulfonated, they developed ion-exchange properties, and were physically and chemically stable over a much wider pH range than were the aluminosilicates.

The next and, from the standpoint of modern ion-exchange processes, the most important development of all came about in 1935 when Adams and Holmes (1) discovered that certain cross-linked synthetic resins with appropriate chemical groups attached were capable of exchanging ions. The first resins prepared were made with phenols and formaldehyde and it soon became clear that the -OH groups were behaving like the Al-OH groups in the aluminosilicates. They further demonstrated that stable cation exchangers of high capacity could be pre-

pared as a sulfonic acid resin. The two investigators then reasoned that if the presence of acid groups in the resin made a cation exchanger, the presence of basic groups ought to exchange anions. So they proceeded to react polyamines with formaldehyde to produce anion exchangers. The versatility of these resins was immediately recognized with the results that a large number of uses of ion exchange were found and many types of resins were developed and improved. In contrast with the early exchanger materials which often had a variety of ion-active groups present in them, the new synthetic resins of the sulfonated polyvinylbenzene and polystyrene types furnished exchangers which had well defined positive or negative centers. Consequently, their properties could be more accurately determined and their exchange reactions more completely described.

Recent developments have been aimed at producing resins with higher and higher capacities, greater stability, and containing active groups of different degrees of acidic and basic strengths. The improved properties of the new synthetic exchangers make it possible to obtain data on the ion-exchange reactions with fewer uncertainties than ever before.

Readers with a greater interest in the historical development of ion exchangers are referred to the works of Kunin and Myers (97), Kressman (89), and Marinsky (100) to list a few.



## SOME GENERAL ASPECTS OF ION-EXCHANGE EQUILIBRIA

The object of the investigations reported in the thesis was to study the equilibrium which exists in cation-exchange reactions. The resin used was a sulfonated polystyrene-divinylbenzene co-polymer. Its sole ion-active groups at any pH were the nuclear sulfonic acid groups. The method used was a dynamic one, a solution of known composition being passed through the resin in a column until equilibrium was attained. The amount of water in the resin phase at equilibrium as well as the amount of each of the species of cation present was determined. The exchanging species were the ammonium and neodymium ions. The ratio of ammonium to neodymium ion in the external or load solution was varied over a wide range and two different concentrations of load solutions were used.

A detailed description of the experimental procedure together with the results obtained will be given in subsequent sections of the thesis. First, however, some of the general aspects of ion exchange will be mentioned, this to be followed by a discussion of the various theories which have been proposed to describe ion-exchange equilibria on resins of sulfonated polystyrene-divinylbenzene type.

Recent literature in the field of ion exchange is very extensive as can be seen from the fact that a book by Osborn

(108), published in 1955, contained a bibliography of nearly 2000 papers that have appeared throughout the world, most of them within the five years just prior to the compilation of this list. Consequently, it was necessary to place definite limitations on the subject matter that could be covered in this thesis.

The resin phase of the cation-exchange system designated above consists of a porous hydrocarbon network of essentially sulfonated benzene nuclei linked and cross-linked by short aliphatic chains. The cross-linking has introduced a steric factor making the resin phase less accessible to ions and molecules as they become larger and larger (65, 66). Solvent and neutral molecules can freely migrate in and through the polymeric network unless the degree of cross-linking is of such magnitude as to offer steric hinderance to the passage of large molecules. Other cations can more or less readily displace the hydrogen ion of the sulfonic acid group. Positive ions from an external solution as well as negative ions can diffuse through the resin as long as electrical neutrality is maintained. Therefore, whenever a cation enters the resin phase it must either be accompanied by an equivalent amount of anion or an equivalent amount of positive ion must move out. The sulfonic acid anions are attached directly to the resin network, hence, cannot migrate into the external solution. The activity of the negative ions in the external

solution is equal to the product of the activity coefficient, which is dependent on the ionic strength of the solution, and the concentration of the ions. Therefore, unless the anion is attached to the cation as a complex species, the ionic strength of the solution will determine the number of negative ions that will diffuse into the resin or gel phase. If low, the high concentration of fixed ions within the resin will effectively prevent solution anions from entering the resin phase.

Comparing the analytically determined amount of sulfur present with the capacity of the resin, Bauman and Eichhorn (8) found approximately 6 per cent of the sulfur was not associated with an exchanging ion suggesting that some of the sulfur may be in the form of sulfone cross-links. Kunin (96), in demonstrating that the exchange of ions takes place throughout the whole gel structure and is not limited to surface effects, compared the total exchange capacities of three Amberlite resins with the equivalents of sulfur present and found they agreed to within one to two per cent. Again, however, the total capacities were always lower than the sulfur content which also hints at the suggestion made by Bauman and Eichhorn. In conjunction with the work reported in this thesis, it was noted that the resin used showed about one-third of a per cent increase in capacity after it had been put through a number of ion exchanges. This could be explained

on the assumption that some of these sulfone-type cross-linkages were ruptured by the expansions the resin was subjected to and so became active ionic sites.

It would seem that any successful theory explaining the ion-exchange process must be concerned, directly or indirectly, with the amount of water in the resin phase at equilibrium and the volume effects that occur in the exchanger as a result. When a resin is first put into water, the polymer network must expand as the ions of resin become hydrated. Further increase in volume takes place due to the uptake of water because of osmotic forces. The extent of the swelling will finally be limited by the elastic forces or bonds between the atoms of the network that hold the polymer together. Considerable work has been done studying the volumes of resins in different conditions (6, 25, 53, 58, 70, 71, 111, 116). In pure water the volumes at maximum swelling depend on the ions present, the exchange capacity of the resin, and the degree of cross-linking. Adamson and Boyd (2) have indicated that water in the swollen resin, referred to as the "water of gelation", is completely mobile judging from the rapid and complete exchange with external heavy water. Glueckauf and Kitt (57) have studied the hydration of cations in polystyrene sulfonates describing the uptake of water with adsorption isotherms. The knowledge of the adsorption isotherms permits the differentiation between water adsorbed

with zero free energy (the swelling water) and the excess adsorbed water (the cation hydration water). The amount of hydration water varies from cation to cation, with water activity, and with temperature. The association of almost all the water molecules is very loose for the cations investigated and is not related to the coordination number of the ions.

Duncan (39) has summarized some experiments of Reichenberg's which are said to have established "beyond doubt" that the water taken up is, within experimental error, identical in density with what it is outside of the exchanger. Working with resins whose divinylbenzene content varied from 2 to 20 per cent, he showed a linear relation between the weight of water taken up and the volume of the swollen exchanger in water extrapolating to a volume just slightly less than the specific volume of the dry resin.

The concentrations of the exchanging ions considered to be dissolved in the water of gelation can be relatively high. For example, one gram of the hydrogen form of a sulfonated polystyrene-divinylbenzene resin made with 8 per cent divinylbenzene will contain approximately 40 per cent water and have an exchange capacity of about three milliequivalents per gram of wet swollen resin. This composition gives a stoichiometric molality of 7.5 for the gel solution. Concentrations of 20 normal and up have been mentioned for other systems

(56, 132). In spite of this high concentration, the gel electrolyte appears to be highly dissociated. Boyd and co-workers (19) have revealed the rapid self-exchange of ions in the exchanger with ions in an external solution using radioactive tracer techniques to be consistent with the idea of much dissociation and that the polymer network must be a fairly open one. Conductometric titration by Kanamaru et al. (86) of Amberlite IR-120 ( $-\text{SO}_3\text{H}$  type resin) indicated practically complete dissociation. This was not true with an Amberlite IRC-50 ( $-\text{COOH}$  type) resin. They reported a dissociation constant of  $10^{-3}$  for it. The data of Davies and Yeoman (29) and Duncan (37, 40) also indicates that there is practically complete dissociation in the resin phase. Their experiments were also done on the sulfonic acid type resin. Glueckauf (39, 55) implies that the cations in a wet exchanger are in a state of mobility somewhere between that of nitrates and chlorides of similar ionic strengths. However, the idea of ion-pair formation in the resin has been used by both Gregor (61), Glueckauf (54, 39), and Kielland (88) to explain certain results. The concentrated ion-exchange gel electrolyte is a special type since it contains a non-diffusible, structurally bound anion and therefore, even if the exchanging cations are highly dissociated, they still are not free to migrate even into external pure water.

Some more aspects of the distribution of ions between

the resin phase and the external aqueous solution can be seen by considering a given example. Consider immersing a wet, swollen pure hydrogen form strong acid resin in a solution of hydrochloric acid. Two effects will be noted. First, the resin will deswell and, second, the chloride ion and an equivalent amount of hydrogen ion will be taken up by the exchanger. The deswelling has been found to be dependent on the external ionic strength and the degree of cross-linking (8, 125). It will be accompanied by a decrease in the volume and moisture content of the resin. At the same time, the total ionic strength of the gel electrolyte will increase in part because of the lowered water content and in part due to the adsorption of the chloride and hydrogen ions. The amount of diffusible anion, in this case the chloride ion, and hence additional cation taken up by the exchanger, depends on the nature of the cation in the resin phase (65) and the degree of cross-linking (8, 125) as well as the external ionic strength (8).

If, instead of immersing the wet swollen hydrogen form resin in an external solution containing a common ion (hydrochloric acid in the above illustration), it were immersed in a solution containing an electrolyte such as sodium chloride, the same general effects would have been noted. In addition, one highly important reaction would take place in that an ion exchange would occur with hydrogen ion being displaced from

the exchanger by an equivalent amount of sodium ion. This demonstrates the most useful property exhibited by these high molecular weight polymers. Hence, all ionic species and neutral molecules are to be found in all parts of the system except the structurally bound resin anions. A simple metathetical reaction can be written for the cations at the exchange equilibrium,



where the subscripts "o" and "i" refer to the ions being outside or inside the resin phase. Two important facts can be pointed out at this time. One is that equivalent amounts of ions are involved in the exchange reaction. The other, that selectivity is shown in nearly all reactions, i.e., one ion is preferred by the resin over the other. A selectivity coefficient,  $K_D$ , has been defined as

$$K_D = \frac{\left( \text{Na}^+ / \text{H}^+ \right)_i}{\left( \text{Na}^+ / \text{H}^+ \right)_o} \quad (2)$$

where the quantities are the appropriate stoichiometric concentrations of the ions in the two equilibrium phases. This is really the mass action equilibrium constant written with concentrations instead of activities, and selectivity is implied by stating that the equilibrium constant has a value other than unity.



A number of facts concerning the selectivity of ions are listed below:

1. Generally, the more highly charged ions are preferred over those of lesser charge and for two ions of the same charge, those with the smaller hydrated radius are preferentially concentrated on the resin (20, 68, 90, 116, 126).
2. The selectivity of the exchanger is dependent on the degree of cross-linking in the resin (6, 10, 22, 64, 65, 115, 116, 126). At very high degrees of cross-linking the order of selectivity may actually be reversed (64).
3. Other factors remaining constant, the selectivity coefficient diminishes slightly with the ionic strength of the external solution (22, 64, 65), though there have been reports of actual reversal of selectivity at very high concentrations of the solution (33).
4. There is general agreement that the dependence of the selectivity coefficient on temperature is small (20, 22, 41, 64, 73, 90).
5. The selectivity coefficient, as defined, varies with the fraction of the resin occupied by a given ion and has little meaning unless accompanied by a statement as to the corresponding state of the resin (10, 16, 17, 22, 41, 42, 65, 81, 99, 100, 116, 122, 123,

124, 129, 136).

6. Usually, equilibrium can be approached from either side and  $K_D$  determined to agree within experimental accuracy (81) although others (5, 99) have reported adsorption or complexing effects with ions that can form covalent bonds which interfere with the symmetry of the equilibrium process. (It may be that with exchanging ions of this type, final equilibrium is approached so slowly that it was not reached in the time allowed in these experiments.)

Selectivity coefficients have been studied for a number of uni-univalent exchange systems (20, 26, 42, 64, 81, 85, 90, 99, 100, 116), uni-divalent systems (20, 42, 80, 91, 99, 100), uni-trivalent systems (20, 26, 91, 100), and two uni-tetravalent ones (91).

Occasionally the selectivity coefficient is written  $K_{B/A}$  where A is the ion in solution exchanging with B ion in the resin in writing the forward reaction. Sometimes the activities of the ions in solution are used when known instead of concentrations in calculating the selectivity coefficient. There is often a great deal of discrepancy among the data presented for any one system. However, the order of magnitude of  $K_{B/A^{++}}$ , that is, the exchange of a divalent ion for a univalent one on the resin, appears to be at least 10 to 20 times that of  $K_{H/K^+}$  at a total concentration of about 0.1 N.

While the total ionic strength was a minor variable with the uni-univalent systems (8), it is a major one when dealing with exchanges involving ions of different valences. For a uni-divalent system,  $K_B A^{++}$  increases as the concentration decreases (8). The usefulness of such equilibrium data both in theoretical work and in industrial applications would warrant further extensive investigations of the selectivity coefficients of the multivalent system.

## THEORIES OF ION-EXCHANGE EQUILIBRIA

Not many physico-chemical processes have been blessed with as great a number and as wide a variety of theories to explain their behavior as has that of ion-exchange equilibria. As a result, the present status of the theory of ion exchange is one of considerable confusion. There is a great deal of contradictory data in the literature and the disagreements are probably more numerous than the agreements. This is not too surprising in view of the exchange materials used by early investigators in the field. The uncertainties, due to the chemical instability and the dubious structure of the complex substances worked with, resulted in information of doubtful value. Much is expected of the investigations which have been made and which are underway with the "tailor-made" resins now available.

The different attempts to give theoretical interpretations to ion-exchange equilibria can be roughly classified as follows:

1. Treat the phenomenon as an ionic adsorption process to be described by some sort of adsorption isotherm.
2. Regard the exchange as a reversible, double decomposition reaction and apply the law of mass action.
3. Consider the resin matrix as a membrane, which prevents the resin anion (or cation) from diffusing

through thereby resulting in unequal distribution of ions on the sides of the membrane, and apply Donnan membrane theory. This approach has been used in two, slightly different ways:

- a. Represent the ion-exchange behavior by a model wherein the outward swelling pressure due to the osmotic activity of the exchanging ions and an inward counter pressure due to the elastic forces of the cross-linked network oppose each other. At equilibrium, the two forces are balanced.
- b. Apply solution physical chemistry to the ion-exchange system treating the resin phase as a concentrated aqueous solution, the resinate dissolved in the swelling water which the exchanger absorbs.

As mentioned earlier, this discussion will be more or less limited to material directly concerned with cation-exchange equilibria in a sulfonated polystyrene-divinylbenzene resin. This type of resin has been used for the bulk of the recent fundamental studies for the following reason; (a) monofunctionality, (b) reproducible dry weight capacity, (c) essential uniformity throughout its structure, (d) rapid exchange rates, (e) relatively simple structure, and (f) availability. However, much work has been done with other

materials, such as the early work with clays and zeolites, and parts of it will be briefly covered since some of the theories which originated therein are still being considered in present day investigations. The various theories will be discussed in some detail in the order they were classified above.

### Adsorption Theories

Since the first experiments with cation-exchange reactions were performed with natural inorganic materials of uncertain composition, it is not surprising that the data obtained did not obey the simple mass action law for a reaction of the type,



where  $A^+$  and  $B^+$  are the exchanging ions and R represents one equivalent of the exchanger. Consequently simple empirical adsorption relations were tried. Kunin (97) lists the five following attempts to explain the exchange. For example, soon after Way (147, 148) reported his experiments, Boedeker attempted to describe the exchange with the equation

$$X = ka^n \quad (4)$$

In this and subsequent equations in this section, the terms are loosely defined thus:

$X$  = the quantity adsorbed

$a$  = initial quantity of electrolyte added

$C$  = equilibrium concentration of added electrolyte

$c$  = amount of added electrolyte present in solution at equilibrium

$m$  = absorbent mass

$x$  = amount exchanged

$(x)_A, (y)_B$  = equivalents of ions A and B adsorbed per unit of exchanger

$k, k_1, k_2, k_3, n, p, S, b$  = constants

At about the same time, Wolff considered the following:

$$X = k_1 = \frac{k_2 C}{C + k_3} \quad (5)$$

In 1892, Kroeker suggested using

$$\log \frac{a}{c} = km \quad (6)$$

Wiegner first used the Freundlich adsorption isotherm in the form

$$\frac{X}{m} = kc^{1/p} \quad (7)$$

Later this equation was modified by Wiegner and Jenny as follows

$$\frac{X}{m} = k \left( \frac{c}{a-c} \right)^{1/p} \quad (8)$$

so as to indicate a finite capacity.

Probably the best of the empirical equations for collating ion-exchange data, especially for cation exchangers containing a constant amount of exchangeable ion, has been the Rothmund-Kornfeld (118, 119) equation that

$$\frac{(x)_A}{(y)_B} \cdot \left( \frac{C_B}{C_A} \right)^p = k \quad (9)$$

According to Walton (143, 144, 145) almost all the data in the literature on the distribution of ions in ion-exchange resins fit this equation. Hogfeldt (76) tested a number of empirical equations with data from the Ag-H exchange on Dowex-50 and Wofatit KS resins and found the Freundlich equation represented the best way of presenting the data, but the Rothmund-Kornfeld equation was the most useful.

One other equation that relates degree of exchange and concentration is that of Vaegler,

$$x = \frac{S \cdot a}{a + b} \quad (10)$$

which is identical in form to Langmuir's adsorption isotherm.

Another form of the Langmuir equation, for the adsorption of a gas on a surface, is as shown:

$$v = \frac{v_m b p}{1 + b p} \quad (11)$$



where  $v$  = volume of gas added

$p$  = equilibrium pressure

$v_m$  = volume of gas needed to form a monolayer

$b$  = constant

Boyd et al. (20), by formal analogy with the Langmuir equation for adsorption from a binary gaseous mixture, derived the following equation for the adsorption by an exchanger of one ion,  $A^+$ , from a dilute binary electrolyte solution:

$$\left(\frac{X}{m}\right)_{A^+} = \frac{k b_1 C_{A^+}}{1 + b_1 C_{A^+} + b_2 C_{B^+}} \quad (12)$$

where, using their terminology,  $(X/m)_{A^+}$  = amount of  $A^+$  adsorbed per unit weight of exchanger;  $C_{A^+}$ ,  $C_{B^+}$  = activities of cations in the equilibrium solution;  $k, b_1, b_2$  = constants. By a simple assumption and rearranging, they put the equation in a linear form easily plotted to permit evaluation of the constant terms, i.e.,

$$\frac{C_{A^+}/C_{B^+}}{\left(\frac{X}{m}\right)_{A^+}} = \frac{b_2}{b_1 k} + \frac{1}{k} \frac{C_{A^+}}{C_{B^+}} \quad (13)$$

For exchange involving ions of unequal charge the equations become somewhat more complicated.

A very important point to bear in mind in discussing the various theories of ion exchange might well be brought up here. There are a number of instances in the literature where

an equation derived according to the principles imposed by one theory will be identical or similar in form to an equation arrived at independently using the concepts of a second theory. Consequently, the fact that a given set of data fits this equation cannot be taken as proof that either one of the theories are correct. Two examples can be shown from the equations already presented. Actually, equation (10) was derived, according to Marshall and Gupta (101), by a "subtle application of mass action principles". It was included above because it is identical to the Langmuir equation. Also, Boyd et al. (20) state that equations of the same form as (12) and (13) can be derived from the law of mass action when applied to the exchange of equally charged ions. Therefore, agreement of experimental data with equation (13) "cannot be taken as evidence that base-exchange is an 'adsorption' phenomenon in any special sense".

Other instances of this type were noted while reviewing the various theories.

The idea that the exchange reaction could be represented as an adsorption phenomenon led some workers to apply a statistical treatment to the problem. One of the first was Jenny (83) in 1936. He proposed a simple model of the exchange mechanism and then theoretically deduced an adsorption isotherm which permitted a quantitative understanding of most of the facts of ion exchange. He also showed where his

relationship involving the exchange of two ions of equal valency would reduce to the same form as Vaegler's equation (13) if the exchange properties of the two ions were similar. Davis and coworkers (31, 32, 92, 93, 94, 95) have advanced a theoretical approach based on statistical thermodynamics and mechanics treating the exchanger surface as a system of identical discrete sites, each consisting of one unit of electrical charge. The exchanging ions constitute a monolayer in the important sense that the total number of ionic unit charges is not different than the total number of oppositely charged sites. There are no empty sites as electroneutrality is maintained and in this sense the exchanger surface is different than ordinary absorbers treated by Langmuir, Freundlich, and others. The method of Fowler and Guggenheim for adsorption of gases on a surface was applied with some modifications and the conditions of exchange equilibria derived. The equations are of the mass action type. Davis et al. found their relationships to fit both resin and clay exchanger systems for all pairs of ions except those involving hydrogen.

In line with Davis, Sakai and Seiyama (120, 121) derived a new chemical equilibrium equation based on statistical thermodynamics. Their generalized equation is a function of the equivalent fraction of exchangeable ions and contains terms resulting from interionic attractions in the resin and

from the configurational partition of exchangeable ions over the sites. Experimental verification shows that the term representing the interionic action is the important one. For specialized cases, their equation reduces to the Davis formula.

### Mass Action Law Theories

Of the various theories put forth to describe the ion-exchange equilibria, the application of the law of mass action has been attempted by the greatest number of investigators. The fact that the exchange reaction was generally found to be reversible and that equivalent amounts of ions were observed in the exchange induced many to try this approach.

As an aid in the discussion to follow, a number of terms are defined below. Others may be brought in and defined at a more convenient time. Occasionally, for ease in following a certain paper, the author's symbols may be used and, if so, they will be clearly defined.

The cation-exchange reaction involving a resin exchanger can be written as follows for a uni-univalent exchange and with appropriate coefficients and charges can be extended to include multivalent ions:



where  $A^+$ ,  $B^+$  = exchanging cations in the external (solution)

phase or, when used in mathematical equations, represent the concentration of the respective ion in the solution phase.

$R$  = one equivalent of the exchanger.

$AR, BR$  = resin form, in mathematical equations refers to the concentration of the respective cation in the resin phase.

$a_X, a_{XR}$  = activity of species  $X$  in solution and in the exchanger phase, respectively.

$m$  = molality.

$\gamma_X$  = activity coefficient of species  $X$  in solution.

$f_{XR}$  = activity coefficient of species  $X$  in the exchanger.

$N_X, N_{XR}$  = equivalent fraction of  $X$  in solution and in the exchanger, respectively.

$X_X, X_{XR}$  = mole fraction of  $X$  in solution and in the exchanger, respectively.

One of the earliest examples of the application of the mass action law is found in the work of Ganssen (97) in 1908. From that time until about 1943 there were occasional reports of experimental data from different kinds of exchangers such as clays, soils, and zeolites (3, 100, 104, 149), sulfite cellulose (44), and resins (26) that gave near constant values for the mass action equilibrium quotient. Walton (144) showed that the law of mass action was nearly obeyed for the exchange

of ions of the pairs of metals Na-K, Na-Ca, and Ca-Ba, but not for Na-H or Ca-H. He attributed the results for the systems involving hydrogen ion to the fact that the carbonaceous exchanger used, a sulfonated coal, might consist of two or more solid acids with different dissociation constants. In general, agreement with the mass action law was not good.

Kerr (87) is credited with the first true analysis of the applicability of the mass action principle to ion-exchange systems. Looking at equation (14), the BR and AR might be considered as pure independent solids and assigned activities of unity. Then

$$K = \frac{B^+}{A^+}$$

might be written as expressing the equilibrium constant. Kerr demonstrated that this could not be done for ion-exchange systems. He assumed the solid phase acted like it was dissolved in the solution and so had similar activities for both the soluble and the insoluble species. Then

$$K = \frac{B^+ \cdot AR}{A^+ \cdot BR}$$

Vanselow (142) assumed the two solids formed a series of ideal continuous solid solutions and that their activities were not unity but equal to their respective mole fractions in the solid. For the exchange of ions of the same valence, Kerr and Vanselow would write the same equation, but for ions of un-

equal valence they would differ considerably. Later, Strocchi (136) reported data for the Ba-Na and Ba-H systems that claimed to invalidate Vanselow's assumption of ideal solution. In 1933, Marshall and Gupta (101) showed with a sodium clay-calcium chloride exchange system that when a sufficiently wide range of concentrations was covered, none of the base-exchange equations so far suggested were satisfactory.

In general, when data did seem to fit the law of mass action, it was usually with ions of similar properties as, for example, the potassium and ammonium ions where the value of the equilibrium constant was approximately unity and also with solutions of relatively low ionic strength. The early failures are often attributed to one or more of the following:

1. The exchangers employed possessed few of the characteristics necessary for accurate quantitative study. The structure and composition was often uncertain. They sometimes contained more than one functional group, making it difficult to write an accurate chemical equation to represent the reaction. The exchangers were often unstable at pH ranges necessary to prevent hydrolysis of cations in the solution.
2. Direct analysis of the exchanger phase was impossible in most cases and concentrations in the solid had to be determined by small variations in concentration of

the solution.

3. Activity coefficients of the ions in the solution were usually neglected, and no methods were available for determining them in the resin phase.

With the advent of the stable, synthetic, monofunctional cation-exchange resins, many of these early difficulties can be overcome. Work can be done at pH values suitable to prevent hydrolysis. Direct analysis of the exchanger at equilibrium is possible. A great deal is being done in attempting to evaluate the activity coefficient of species in the resin. It is a difficult problem since the work involves concentration ranges about which little is known even in pure electrolyte solutions.

Kielland (88), in 1935, realized that the assumption of ideal solid solution in the resin phase was probably not valid and suggested that the activity coefficient of each resin component might vary according to a single term Margules equation. This has been found to be applicable to cases involving the exchange of univalent ions (20) but not in the exchange of more highly charged cations, for example, lanthanum and hydrogen (18). From free energy changes for the reaction and the Margules equation, Kielland derived the expression

$$\ln K = \ln \frac{a_{B^+} \cdot X_{AR}}{a_{A^+} \cdot X_{BR}} + C(X_{BR}^2 - X_{AR}^2)$$



$$= \ln K_a + C(X_{BR}^2 - X_{AR}^2)$$

where

$$\ln K_a = \ln \frac{a_{B^+} \cdot X_{AR}}{a_{A^+} \cdot X_{BR}}$$

Writing the equation  $\ln K_a = \ln K - C(X_{BR}^2 - X_{AR}^2)$ , it is obvious that a plot of  $\ln K_a$  versus  $X_{BR}^2 - X_{AR}^2$  will permit evaluation of  $C$  and from the form of the Margules equation used that

$$\ln f_{AR} = C X_{BR}^2$$

the activities in the resin phase can be calculated. Applying his equations, Kielland concluded that in many cases there is interaction between components in the solid phase resulting in compound formation and, from the reanalysis of some of the Marshall and Gupta data, showed that their results do obey the mass action law if compound formation is assumed. Boyd, Schubert, and Adamson (20) made a somewhat similar approach to the problem when they developed equivalent equations from both adsorption and mass action law concepts.

Juda and Carron (84) in 1948 ascribed an ionic character to exchange systems citing the work of Möller (104) and others. However, they do not insist on complete dissociation believing instead that a dissociation equilibrium exists in the exchanger phase. Their mass action expression then involves the activities of the dissociated cations in the exchanger as

well as in the solution

$$K = \frac{a_{B^+} \bar{a}_{A^+}}{a_{A^+} \bar{a}_{B^+}} = \frac{\gamma_{B^+} m_{B^+} f_{A^+} \bar{m}_{A^+}}{\gamma_{A^+} m_{A^+} f_{B^+} \bar{m}_{B^+}} = K_a \frac{f_{A^+}}{f_{B^+}} \quad (15)$$

The bar ( — ) over a term refers to the exchanger phase. Juda and Carron studied the exchange of Na-H on four exchangers varying the ionic strengths of their solution a thousand-fold and reported that  $K_a$  was substantially "constant", (actually they found a 20% change in  $K_a$  over the concentration range investigated) therefore directly proportional to  $K$ . They indicated that this means the ratio of the activity coefficients in the exchanger phase was a "constant" in this case. This treatment cannot be accepted as conclusive proof that the exchanger can be treated as an ionic solution since the expression for the equilibrium constant was the same as the one written earlier for the solid solution concept. It does further substantiate the view that the exchange reaction equilibrium can be described by the law of mass action.

Kressman and Kitchener (90, 91) claimed agreement with the mass action law expressed in concentrations for a number of systems involving a synthetic phenolsulfonate resin. They included some di-, tri-, and tetravalent ions but at concentrations of only about 0.1 normal.

Others (20, 41, 42, 100, 124, 155) have shown that the mass action equations are sometimes approximately obeyed over small concentration ranges, though some of these workers (41,

42, 100, 124, 155) point out that the mass action equilibrium "constant" does vary usually with the fraction of given ionic species on the resin. Cosgrove and Strickland (26), however, in testing the practical importance of the mass law, found considerable variation for the exchange of hydrogen ion with a number of other ions on synthetic resins. Gregor (59) predicts such variability as a necessary outcome of most exchange processes.

Mayer (103) suggests the application of the empirical Harned rule (74), relating activity coefficients to mixtures of electrolytes, to the mixed gel electrolyte and has demonstrated an improvement in the constancy of the mass action law constant on a set of data from the literature of Boyd, Schubert, and Adamson.

Probably the most extensive of the recent work on the application of mass action principles to the exchange reaction has been done following the approach suggested by Argersinger, Davidson, and Bonner (5) and coworkers (28) in 1950, and independently by Ekedahl, Högföldt, and Sillén (45, 79) about the same time. Argersinger et al. have felt that other investigators had overlooked the fact that for the ion-exchange reaction, the constancy of the true equilibrium constant,  $K$ , is a thermodynamic necessity as a consequence of the definition of activity and formulation of the process and is independent of the mechanism or the nature of the solid

phase. Therefore, the application of the law of mass action combined with the Gibbs-Duhem equation affords a method of determining the true  $K$  and the activity coefficients of the species in the resin from experimental data.

Briefly, their approach (5) was as follows. For equation (14)

$$K = \frac{a_B + a_{AR}}{a_A + a_{BR}} = \frac{\gamma_B + m_B + f_{AR} m_{AR}}{\gamma_A + m_A + f_{BR} m_{BR}} \quad (16)$$

$$= K_a \frac{f_{AR}}{f_{BR}} \quad (17)$$

$K_a$  is called the apparent equilibrium constant. Taking the logarithm of both sides, the following equation results

$$\ln K = \ln K_a + \ln f_{AR} - \ln f_{BR} \quad (18)$$

If the derivative is taken next, realizing that  $K$  is a constant,

$$0 = d \ln K_a + d \ln f_{AR} - d \ln f_{BR} \quad (19)$$

Now the Gibbs-Duhem equation for the exchanger phase can be written for two components thus:

$$N_A d \ln f_{AR} + N_B d \ln f_{BR} = 0 \quad (20)$$

Solving the two equations (19) and (20) simultaneously:

$$d \ln f_{AR} = -N_{BR} d \ln K_a \text{ and}$$

$$d \ln f_{BR} = N_{AR} d \ln K_a$$

Integrating these two equations by parts yields

$$\ln f_{AR} = -(1-N_{AR}) \ln K_a + \int_{N_{AR}}^1 \ln K_a dN_{AR} \quad (21)$$

$$\ln f_{BR} = N_{AR} \ln K_a - \int_0^{N_{AR}} \ln K_a dN_{AR} \quad (22)$$

Substituting these into equation (18) gives the final desired form

$$\ln K = \int_0^1 \ln K_a dN_{AR} \quad (23)$$

These equations can be readily evaluated by graphical integration from a plot of  $\ln K_a$  versus  $N_{AR}$ . Argersinger et al. (5) develop the equations for a perfectly general exchange reaction as well as the simple univalent exchange given here (27) but the procedure is identical. This group of workers have since been busy making refinements and corrections to their theory and adding to their store of data concerning the exchange reaction. As a result of their early investigations (99), they found that a more accurate determination of the

concentration of the two cations in the solution and in the resin at equilibrium was necessary (4). Therefore, the first refinement to the procedure was to analyze both phases directly.

The second refinement had to do with evaluating the activity coefficients of the individual species of the mixed electrolyte solution. Their first approximation had been to assign an activity coefficient of, say, component AX in the mixed electrolyte of total concentration,  $m$ , the value it would have in a pure solution of AX at concentration,  $m$ . This principle is satisfactory at ionic strengths of 0.1 molal or less but not in more concentrated solutions. Instead, Harned's rule was applied as

$$\ln \gamma_{AX} = \ln \gamma_{AX}^{\circ} - \alpha_{AB} m_{B^{+}} \quad (24)$$

where  $\gamma_{AX}$  is the mean activity coefficient of AX in the mixed solution of total molality,  $m$ , in which the individual molalities are  $m_{A^{+}}$  and  $m_{B^{+}}$  ( $m_{A^{+}} + m_{B^{+}} = m$ ) and  $\gamma_{AX}^{\circ}$  denotes the activity coefficient of AX in a pure solution of AX at concentration,  $m$ .  $\alpha_{AB}$  is a constant. The activity coefficients for some mixed solutions were actually determined and the values obtained were used to calculate  $K$  for some systems (13).

An important correction was made to their theory when Davidson and Argersinger (27) considered the effect that a

transfer of water between solution and resin during the exchange reaction has on the equilibrium constant. They realized that the water in the resin made the exchanger phase a three component system and must be considered as well when applying the Gibbs-Duhem equation.

Recently the influence of the electrolyte taken up by the resin on the equilibrium was reported by Baumann and Argersinger (9). They found the effect was negligible when ions of similar sorption tendencies were involved but could be significant in the case of ions whose behavior towards the resin was quite different.

A number of exchange systems were studied by these investigators (10, 11, 16, 17, 152).

Bonner and coworkers (14, 15) have been investigating the properties of p-toluenesulfonic acid and some of its salts with an eye towards a possible relationship to ion-exchange equilibria.

It was mentioned that Ekedahl, Högf<sup>n</sup>feldt, and Sillén (45, 79) had independently presented the same approach for determining the true equilibrium constant and activity coefficients in the resin phase as given above. They (77, 80) applied their method to two sets of data on the same system, i.e., Ba-H exchange on Dowex-50 (41, 100), and got serious disagreement indicating further research is essential to clear up these contradictory findings. Högf<sup>n</sup>feldt (75, 78) has additional

information on the Ag-H exchange.

### Donnan Membrane Theories

A number of early investigators (8, 44, 82, 102, 124, 125, 144, 151) appeared to recognize the possibility that ionic distribution between an ion exchanger and an aqueous electrolyte solution might be governed by a Donnan equilibrium. Three important items of experimental evidence that lend support to this idea are:

1. The swelling and deswelling of the cross-linked ion-exchange polymers with varying concentration of the external electrolyte solution (8, 125).
2. The presence of diffusible anions in the cation exchanger and of diffusible cations in the anion exchanger (8).
3. The fact that satisfactory agreement between experimental data and the Donnan equation has been obtained for the effect of dilution on the exchangers of the sulfonic acid type (82, 124, 151).

However, some of the early attempts were based on oversimplified versions of the Gibbs-Donnan theory and could only be successful for very weakly cross-linked exchangers.

Starting with the principles of heterogeneous equilibrium formulated by Gibbs (52), Donnan and Guggenheim (36) and



Donnan (35) have given exact thermodynamical treatment for a number of types of membrane equilibria, some of which have been shown to apply to ion-exchange systems. Donnan (34) has pointed out that the theory of membrane equilibria is based on two assumptions:

1. The existence of an equilibrium.
2. The existence of certain constraints which restrict the free diffusion of one or more electrically charged or ionized constituents.

These assumptions apply directly to the ion-exchange systems since equilibrium surely exists, and the fact that the resin anions (or cations, if an anion exchanger) are directly attached to the resin network satisfies the condition that diffusion of these ions is restricted. Then, if complete ionization occurs throughout and diffusible cations and anions are present as well as diffusible solvent molecules, the following relationship can be written for an exchange equilibrium between two univalent ions:

$$RT \ln K = \pi (\bar{V}_{B^+} - \bar{V}_{A^+}) \quad (25)$$

where

$K$  = the thermodynamic activity product ratio.

$\pi$  = swelling pressure.

$\bar{V}_{B^+}$ ,  $\bar{V}_{A^+}$  = partial molar volumes of the exchanging ions  $B^+$  and  $A^+$ .

Considerable impetus has been given to the Donnan membrane equilibrium approach by the theory of Gregor (59, 60). He considers the exchange resin to be a swelling gel wherein equilibrium is set up between the outward swelling (osmotic) pressure and the elastic forces of the resin network. If conditions are changed, this equilibrium will shift to some new point. For example, if a fully swollen (with water) sodium form resin is converted to the hydrogen form by contacting it with an external solution such as hydrochloric acid, it expands to some extent because the hydrated hydrogen ion has a greater volume than the hydrated sodium ion. (Two of the assumptions upon which Gregor has based his theory are that the "hydrated volumes" of all molecular and ionic species are constant and that there is complete dissociation.) The total increase in volume is less than the difference between the volume occupied by all of the hydrated sodium ions that move out and the volume required by all the hydrogen ions that come into the exchanger, that is,

$$\Delta V_{\text{resin}} < (V_{\text{hydrated H}^+} - V_{\text{hydrated Na}^+})$$

The following explanation was given. As the hydrogen ions replace the sodium ions the resin swells. However, this causes an increase in the elastic forces in the resin, which in turn, causes a back-pressure on the mobile particles in the phase. This squeezes some of the "free" water --- water not bound as water of hydration --- out of the resin. The greater

the degree of cross-linking, the greater will be the elastic forces for a given volume increase and the more "free" water will be squeezed out. This overall process tends to increase the ionic strength in the resin phase. This results from the presence in the resin of some of the diffusible chloride ions (and enough cations to maintain electroneutrality) from the external phase, due to the greater ionic strength of the hydrochloric acid solution, and from the "squeezing out" of some of the water molecules. Hence, more ions in less water in the exchanger and a resultant increase in ionic strength.

Data such as a plot of the  $\Delta V$  as one ion displaces another in the resin versus the degree of cross-linking, extrapolated to zero cross-linking, can furnish information on the lower limit of the "hydration number" of the ions involved. The agreement between the "hydration number" determined this way and that from other methods is reasonable (108) in view of the crudeness of the assumptions. The idea of "free" and bound water (water of hydration) is sound but the assumption that the "hydration number" of an ion remains the same regardless of the degree of cross-linking is probably invalid. The more cross-linking in a resin, the less the volume change, the closer the mobile ions will be to the fixed ions in the resin matrix, and the greater will be the interaction between them. This increased interaction will tend to displace water molecules around the ions so that a smaller

"hydration number" for the same ion would be expected in a resin with high degree of cross-linking than in one weakly cross-linked.

Experimental evidence shows that in general, for ions of the same charge, the larger the ion in its normal hydration state, the less is its affinity for the resin. Gregor attempts to explain this relative affinity on the basis of his swelling theory, attributing this correlation primarily to the fact that the larger ion tends to make the resin expand more, thereby increasing the swelling pressure. He writes a sort of equation of state for the resin which shows the basis of his theory, the Hookes law type of linear relationship between the swelling pressure,  $\pi$ , and the internal resin volume thus:

$$V_1 = m \pi + b \quad (26)$$

$V_1$  is the difference between the total external volume of the resin,  $V_e$ , and the volume,  $V_m$ , of the incompressible hydrocarbon matrix including the attached hydrated anionic groups (in the case of a cation exchanger). The constants  $m$  and  $b$  are unique for a given system.

The assumptions that Gregor makes in developing his theory for the case of a resin with a single species of ion in the exchange position immersed in pure water are summarized below.

1. The hydrated volumes of all molecular and ionic

species are constant.

2. The fixed groups and the movable ions do not interact but are completely dissociated at all times.
3. The volume of the fixed ionic groups is constant.
4. The activity coefficients of all species involved are unity.

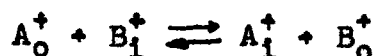
Then,  $n_1$  moles of exchange ions of molar volume  $v_1$  and  $n_0$  moles of water of volume  $v_0$  make up the volume  $v_1$ .

The thermodynamic osmotic pressure for this system is given by the equation

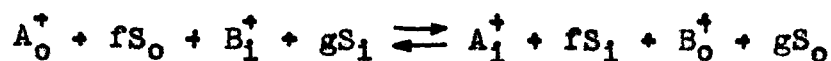
$$\pi = \frac{RT}{v_0} \ln \frac{(X_0)_0}{(X_0)_1} \quad (27)$$

in which  $X_0$  is the mole fraction of water and the subscripts 1 and 0 refer to the resin and external phases, respectively.

Using Gregor's notation, consider an exchange reaction occurring under the above ideal conditions.



Due to osmotic pressure effects, as ions move in and out of the system a certain amount of solvent (other than hydration solvent) enters and leaves. Thus,  $f$  moles of solvent  $S$  accompany each mole of  $A$  moving from outside to inside. Likewise,  $g$  moles of  $S$  with each mole of  $B$  from inside to out. The total process then is



If subscripts 0, 1, and 2 refer to solvent,  $A^+$  and  $B^+$ , respectively, the equilibrium constant for this process can be written

$$K_x = \left( \frac{X_1}{X_2} \right)_1 \left( \frac{X_2}{X_1} \right)_0 \left( \frac{\left( \frac{X_0}{X_0} \right)_1}{\left( \frac{X_0}{X_0} \right)_0} \right)^{f-g} \quad (28)$$

where  $X$  represents mole fraction. The Donnan equation (35) which applies to this system is

$$RT \ln \left[ \left( \frac{X_1}{X_2} \right)_1 \left( \frac{X_2}{X_1} \right)_0 \left( \frac{\left( \frac{X_0}{X_0} \right)_1}{\left( \frac{X_0}{X_0} \right)_0} \right)^{f-g} \right] = \pi [v_2 - v_1 - (f-g)v_0] \quad (29)$$

Using equation (27), Gregor simplifies this equation to

$$RT \ln \left[ \left( \frac{n_1}{n_2} \right)_1 \left( \frac{n_2}{n_1} \right)_0 \right] = \pi (v_2 - v_1) \quad (30)$$

where  $n$  refers to the number of moles of the species. From these equations, Gregor made a number of predictions concerning resin volumes and selectivity coefficients which have been borne out, at least qualitatively, by experimental data (60).

Gregor also considered the counter osmotic effect, and the resulting deswelling as free solvent is squeezed out of the resin, and showed that it was not significant until the external concentration of the electrolyte is an appreciable

fraction of the concentration of the fixed groups within the resin. He also considers the non-ideal system of exchange between univalent ions and suggests methods of evaluating  $m$ ,  $b$ , and  $\pi$ .

Extensive experimentation is necessary to get the data for the quantitative verification of Gregor's theory. This work is underway. Gregor and others are reporting the type of data necessary to test this and other theories. A number of papers (25, 58, 70, 71) have appeared describing techniques for measuring the necessary resin volume terms and reporting results obtained. Gregor and Bregman (64) rewrite equation (30) as follows:

$$RT \ln \left[ K_D \left( \frac{\gamma_1}{\gamma_2} \right)_1 \right] = \pi (v_2 - v_1) \quad (31)$$

or

$$RT \ln K_D = RT \ln \left( \frac{\gamma_1}{\gamma_2} \right)_1 + \pi (v_2 - v_1) \quad (32)$$

and note that the selectivity coefficient,  $K_D$ , is a function of the ratio of the activity coefficients in the resin phase (which Gregor assumes to be unity), the thermodynamic osmotic pressure, and the difference in the ionic volumes. They also show that the variation of  $K_D$  with ionic composition of the resin and the effects of temperature and ionic strength are all consistent with the pressure-volume term of Gregor's theory. Gregor (61) contributes failure of the mass action type of

selectivity coefficient to ion-pair formation. Gregor and co-workers have made some fundamental studies of the sorption of water by some different resins (72), by linear polystyrenesulfonic acid (146), and cross-linked polystyrenesulfonic acid resins (137) to establish relationships between structure, physical properties, and exchange properties. They show that the fixed sulfonic groups in a cation exchange resin are osmotically inactive. Also, the linear polystyrenesulfonic acids sorb considerably less water at the same relative humidity than do their cross-linked analogs and sulfuric acid. This is interpreted as due to polymer-polymer interactions where van der Waal's and other attractive forces act to prevent swelling and solution of the polymer chains. Properties of the linear polystyrenesulfonic acids are of interest for comparison when some property of a given polystyrenesulfonic acid resin is studied versus degree of cross-linking and the results extrapolated to zero cross-linking. Pepper, Reichenberg, and Hale (112) have also reported water-vapor sorption studies on exchange resins. Gregor and Gottlieb (69) determined the activity coefficients of a number of electrolytes in a polystyrenesulfonic type resin from the activities in the external phase and the composition of the resin, neglecting the P-V correction term. The resins used contained from 0.4% to 26% divinylbenzene. The activity coefficients were much lower inside the resin than outside when the external solution was dilute. They found that the ratio



of the two coefficients tended to approach one as the concentration of the external solution approached 10 molar, since at this concentration the electrolyte outside the resin is in an environment similar to that inside the resin phase.

Gregor, Abolafia, and Gottlieb (62) studied the Mg-K exchange on a polystyrenesulfonic acid cation exchanger and found the selectivity coefficient, which usually varies with the composition of the resin, was remarkably constant over a wide range of solution phase normalities (0.001 - 1.0) and resin compositions ( $X_K = 0.01 - 0.78$ ). They concluded this could only be so if the selectivity coefficient was unity, i.e., neither ion being preferred by the resin, hence,  $K_D$  does not vary with  $X_K$  on the resin. Reichenberg and McCauley (115) conclude that the simplified form of Gregor's theory does not account for all the results, that the theory must be modified to take into account the statistical variation of the cross-linking in the resin and the relative ease with which hydrated ions may lose some of their water of hydration.

Other workers have also used Donnan membrane theory (85, 150). Davies and Yeoman (29, 30) determined the activity coefficients of the diffusible electrolyte in the resin phase applying Donnan equilibrium equation and Gregor's P-V energy term whenever it was significant. Their results did not agree with those predicted from solution physical chemistry until they recalculated their data, assuming 5% of the water taken up by the resin is in the form of occluded external solution

caused by the statistical variations in the cross-linking. They then obtained reasonably good agreement with activity coefficients calculated from the data for aqueous solutions of mixed electrolytes using Harned's rule. However, Gregor and Gottlieb (69) dismiss this possibility of occluded solution by noting that the aggregate volume of such cavities would have to be in the range of 20-70% of the resin solution volume to account for the results observed.

Probably the most severe limitation imposed by Gregor's theory of ion-exchange equilibria is the neglect of the activity coefficients in the resin phase or rather the assumption that their values are unity. In some special cases with certain univalent exchanging ions in lightly cross-linked resins perhaps this assumption is valid but, in general, it would seem that the internal interactions would have more effect on the selectivity than the mechanical factors. The swelling behavior of resins might fairly well be described by the expansion model over certain ranges of conditions. The linear relationship between volume and swelling pressure may be valid over certain regions, but surely the swelling pressure must rise very rapidly, perhaps exponentially, with volume increase in regions of maximum extension of the resin network. There have been instances where a resin, which had been excessively extended and then deswelled, showed a lesser degree of cross-linking after the experiment than before indicating some actual bond rupture. It would hardly be expected that the

same linear volume-pressure relation would hold near these upper limits.

Gregor's theory and Donnan membrane equilibria have played an important part in recent new developments. Only a more complete understanding of ion exchangers can determine which suggestions will or will not survive.

Somewhat later than Gregor, Glueckauf (54) independently applied the Gibbs-Donnan equation to ion-exchange equilibria in a slightly different manner. He treats the ion-exchange resin as a concentrated aqueous electrolyte solution, subject to internal forces equivalent to a swelling pressure due to the cross-linking network, and applies ordinary solution physical chemistry to the system. The first term on the right side of equation (32) is considered to outweigh the second. Using activity and osmotic coefficients and Harned's rule for getting these coefficients in mixtures, Glueckauf obtained equations from which he drew the following conclusions:

1. The swelling pressure turns out to be a mildly curving function of the equivalental volume of the resinate.
2. While the swelling pressure term influences the water-uptake of the resin and thus the resin phase concentration, it does not greatly affect the electrolyte activity in the resin which, therefore, for resins of moderate cross-linking, can be expressed almost equally well without considering the swelling pressures but not without considering activity coefficients

in the resin phase.

3. Increased cross-linking should improve discrimination between different ions.
4. For a given resin and ions of equal charge, ions that swell the resin least should be more strongly absorbed.
5. Mean molal activity coefficients can be assigned the various metal resins and in the case of Dowex-50, these are approximately one-half those of the corresponding nitrates suggesting considerable ion-pair formation.

Points 3 and 4 are not new, coming directly out of equation (32). Point 1 contradicts Gregor's linear P-V "equation of state" for the resin, though for small expansions it may be sufficiently accurate. Items 2 and 5 negate Gregor's assumption that activity coefficients in the resin can be assumed equal to unity in determining selectivity properties of exchangers.

Glueckauf (53) in 1951 and again in 1952 in a report summarized by Duncan (39) reviewed ion-exchange theory, and later (55) presented a theoretical treatment of the prediction of ion-exchange equilibria from osmotic data. He showed that the water content of resins at known water activities,  $a_w$ , determined isopiastically by Kitt (56, 57), permit the calculation of the osmotic coefficient,  $\phi$ , using

$$\phi = \frac{\ln a_w}{.018 m} \quad (33)$$

The trend of the data shows that  $\nu$ , the number of mobile ions, is unity, meaning the fixed ionic groups of the resin do not contribute to the ideal statistical entropy terms of the free energy. By comparing the water-vapor pressure ( $a_w$  and  $a_w^i$ , respectively) of two exchangers at the same concentration (in moles per 1000 grams of swelling water) one at high cross-linking and the other at effectively zero cross-linking, it is possible to calculate the swelling pressure,  $\pi$ , of the highly cross-linked resin from the thermodynamically derived equation

$$\ln \frac{a_w}{a_w^i} = \frac{0.018 \pi}{RT} \quad (34)$$

Within experimental error,  $\pi$  was found to be a linear function of the resin extension (Hookes law). This seems to be a contradiction to one of his conclusions stated earlier (54). He also demonstrated that with the resins of hydrogen, lithium, sodium, and potassium (but not silver), it is possible to use the Harned rule for activity coefficients of mixtures and also that a knowledge of  $\nu\phi$  for different resins permit a good estimation of the ratio of activity coefficients of these resins. With this ratio and  $\pi$ , it is possible to determine separation factors with an equation of the general form of equation (32) under varying conditions of external solutions and of the internal resin structure. Glueckauf also indicated how the absolute value of the thermodynamic activity of the resin could be determined from information concern-

ing electrolyte uptake and water loss when a given exchanger was contacted with a solution containing a common ion. Using experimental data, he showed that in sulfonated polystyrene resins of different cross-linking in contact with hydrochloric acid, there is a surprisingly high dissociation of hydrogen resin at 20 molal concentration, comparable to perchloric acid. Duncan (40) finds this to be true, stating that at high concentrations there is less ion-pair formation in this type of resinate than in aqueous solutions of nitrates at the same ionic strength.

In essence, both Glueckauf's and Gregor's treatment emphasize the importance of the elastic properties of the resin network on the exchange properties. Gregor does so directly by considering the influence of these forces on the osmotic term of equation (32). Glueckauf holds to the importance of the ionic interaction term which is dependent on the effective concentration of ions within the resin, i.e., on the water absorption which in itself is dependent on the elastic properties of the cross-linked network and the osmotic pressure set up.

Duncan (37, 38, 39, 40) has been active as a contributor to the fund of data on ion exchangers and to the theory that treats the resin phase as concentrated aqueous electrolyte solutions. He (40) has derived an equation which is analogous to, but not identical with, the Harned rule for calculating activity coefficients for the resins in mixtures. He (38)

also shows how to calculate activity and osmotic coefficients from several independent experimental data. For example, he demonstrates how to calculate osmotic coefficients from: (a) isopiestic data, (b) isopiestic data on exchangers of high cross-linking, (c) the water content of an exchanger immersed in water, and (d) the change in volume of an exchanger in dilute salt solution. Similarly, he demonstrates the calculation of activity coefficients from: (a) osmotic coefficients using Harned's rule, (b) osmotic coefficients using empirical  $\phi$ - $\gamma$  relations, (c) other activity coefficients using the Gibbs-Duhem relation and a single value of activity coefficient in the resin, (d) ion-exchange equilibria by use of the Gibbs-Duhem relation, and (e) ion-exchange equilibria by application of the Donnan equation. Examples are given and activity coefficients of a number of uni- and divalent resins show trends similar to those of aqueous electrolytes.

Boyd and Soldano (21) have carefully examined the terms in equation (32) and point out the arbitrariness in the choice of definitions for the different quantities involved. However, for a given discussion, it makes no difference how the terms are used, provided the treatment is consistent throughout. Soldano and coworkers (131, 132, 133) have followed up this osmotic approach to ion-exchange equilibria. They find that the osmotic coefficient can be defined by an equation with two independent parameters over a range of concentrations from 2 to 30 molal in anion exchangers and 2 to 15 molal in cation

exchangers. They found agreement between values of the selectivities measured as a function of resin composition and structure and calculated from osmotic coefficients.

There have been other approaches to the problem of expressing ion-exchange equilibria. Pauley (109) predicts equilibria based on a consideration of coulombic forces acting within the system. He considers the resin to be a series of point charges randomly distributed, and the exchange ions are held at the distance of closest approach (the sum of the radii of the hydrated mobile ion and the fixed resin ion). The free-energy change, hence equilibrium constant, can be determined from work necessary to move each of the two types of ions involved in the exchange from the distance of closest approach to infinity against the coulombic attractive forces. He cites several instances of agreement with experiment. Gaines and Thomas (48) with a special formulation of exchange equilibria suitable for application to clays, Rice and Harris (117) with their treatment of ion-exchange resins as polyelectrolyte gels, and Sakai *et al.* (122, 123) with their lattice model for exchanging ions offer other theories which will not be discussed here in detail.

It can be seen from the foregoing discussion that the theory of ion-exchange equilibria is in a somewhat unsatisfactory state. The theories are all similar in that exchanging ions must satisfy the law of electroneutrality. The ion



exchangers have a certain number of sites, generally ionic groups attached to a resin network, which can form an electrostatic, perhaps sometimes a partially covalent bond, with ions of opposite charge. The position and manner of occupancy of these sites may vary from theory to theory. The exchange of ions in the resin will be concerned with the relative ease of making and breaking these bonds, much like the dissociation of electrolyte. The laws governing the exchange of ions in this heterogeneous system are probably quite analogous to those governing solutions of electrolytes. Many of the problems in ion-exchange equilibria are related to those that exist in the present state of the general theory of solutions. For example, attempts are being made to calculate activity coefficients in resins where the mixed electrolytes may be 10-20 molal and up, when the explanation of the behavior of activity coefficients of electrolytes in solutions much less concentrated is unsatisfactory. It may be that resins will help formulate laws governing solutions by furnishing a media that can support such high concentrations without precipitation, crystallization, etc.

This survey must of necessity be brief and somewhat incomplete. An attempt has been made to include the major contributions in this field. If further interest dictates, the reader is referred to a few of the many fine reviews on the subject of ion exchange (7, 18, 23, 43, 97, 105, 106, 107, 108, 114, 126, 127, 128, 138, 153).

## EXPERIMENTAL

### Materials

The resin used in these experiments was of the sulfonated polystyrene-divinylbenzene type purchased from the Bio-Rad Laboratories of Berkeley, California. It was labeled as Ag 50-X8 and was actually Dowex-50 reprocessed by the Bio-Rad Laboratories to an analytical grade product. It was a medium porosity resin, was received in the hydrogen form, and was from 60 to 80 mesh.

The neodymium was supplied as the oxide by the rare earth separation group at the Ames Laboratory of the Atomic Energy Commission. Its purity was greater than 99.9%. The methods by which the rare earths are separated and purified are described elsewhere (134b, 134c, 134d).

Baker and Adamson C.P. reagent hydrochloric acid was used for dissolving the neodymium oxide and for stripping the resin after equilibration. All other chemicals used, such as the ammonium chloride, sodium hydroxide, silver nitrate, and oxalic acid, were "Baker Analyzed" reagent grade. The oxalic acid was recrystallized, the others used as supplied.

The water used was regular laboratory distilled water which had been passed through glass wool filters and a mixed anion and cation exchange demineralizer.

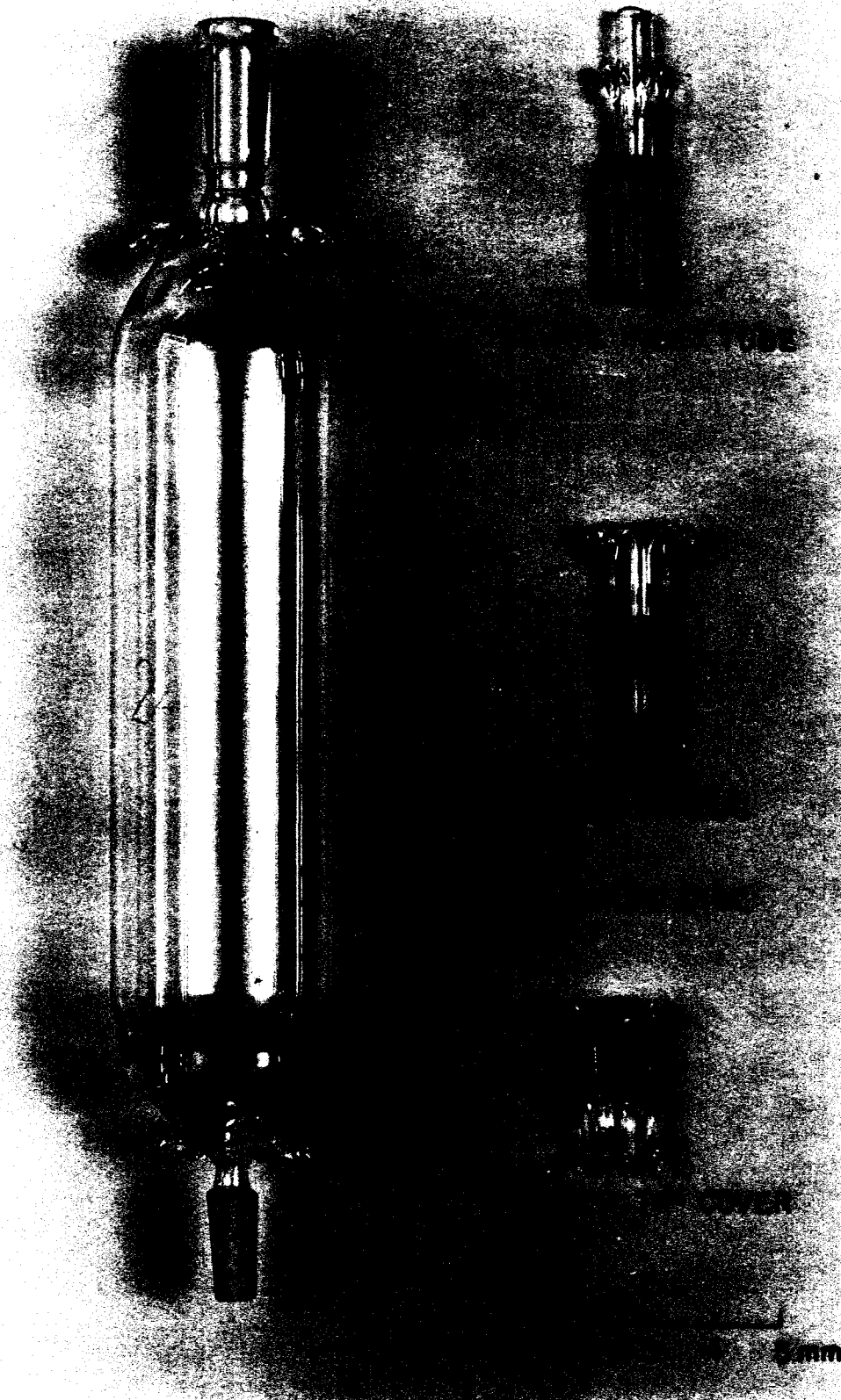
### Apparatus

The apparatus used for the actual experimental work was quite simple consisting of some relatively small columns and the necessary Tygon tubing and flasks to bring the load solution to and collect the solution from the columns. All volumetric glassware used throughout the experiment was "Normax" or "Class A" pyrex.

The columns are pictured in Figure 1 drawn to scale. They were made from pyrex tubing, the fritted glass disc welded in to support the resin. The top and bottom of the tubing was drawn in so that the 7/25 mm standard taper ground glass joints could be attached as shown. The inlet tube, plug, and tip cover were fitted with these same type joints. The columns were cleaned, thoroughly dried at 110°C, cooled, allowed to come to equilibrium with the atmosphere in the laboratory, and then weighed with only the lower tip cover in place. This weight is designated  $W_{EC}$  (weight of empty column) in later discussions. When in use, the inlet tube was inserted in the top of the column and a Tygon tube attached to bring solution to the column. The lower tip was fitted with a short piece of Tygon tubing, a glass capillary tip, and a screw clamp to control the rate of flow of solution through the column. Whenever it was necessary to weigh the column, the inlet tube was replaced by the glass plug, the lower joint

Figure 1. Column assembly used for the ion-exchange equilibria studies

61b



covered by tip cover, and the entire assembly weighed on a 200 gram capacity analytical balance. The column assembly and resin plus enough solution to just cover the resin bed weighed less than 150 grams in all cases.

The following procedure was used in preparing the columns. The resin was spread out in a thin layer on a large sheet of filter paper on a table top, covered with another large sheet of filter paper, and left for about three weeks with occasional stirring to air-dry it. On the day it was weighed into the columns, it was transferred to a wide mouth bottle which was kept tightly closed except when samples were removed for weighing. A 30-gram sample of resin was accurately weighed into a small beaker for each column prepared. The resin was immediately covered with water to prevent any of the small particles from being carried out of the beaker by stray air currents. Three samples, about five grams each, were removed for drying experiments while weighing out the 30-gram samples. One of these three was taken at the start of the weighings, one after half of the 30-gram samples had been weighed out, and one at the end of the weighings. These three samples were kept in weighing bottles in a desiccator over fresh phosphorus pentoxide until they came to a constant weight at which they were labeled "bone-dry" hydrogen resin. The amount of moisture in the original air-dried resin could then be determined.

A glass funnel was made up and fitted with a male 7/25 mm

standard taper so that the 30-gram samples could be transferred to the columns without danger of loss. The funnel was inserted into the top of the column, a gentle vacuum pulled on the column through the lower tip, and the resin slurry sucked into the column. Enough space remained in the column to permit backwashing. This technique worked very well for getting the resin into the columns through the relatively small bore of the 7/25 mm standard taper joints.

#### Preparation of Solutions

The various load solutions were designated by the approximate ratio of equivalents of ammonium ion to equivalents of neodymium ion in the solution and by the normality of the solution based on the total number of equivalents of cation per liter. For example, the load solution labeled "99:1, 1.0 N" has a ratio of ammonium ion to neodymium ion of 99:1 (the actual analytically determined ratio will be given later) and a total concentration of one equivalent of cation per liter. One set of experiments was run with load solutions that were 1.0 N and another set with solutions that were 0.1 N.

A concentrated neodymium chloride stock solution was prepared by dissolving the neodymium oxide in slightly less than the theoretical amount of hydrochloric acid. The slight excess of neodymium oxide was filtered off and the solution heated to boiling and allowed to slowly cool to room temperature. The

pH was between 4.6 and 5.0 at this point and the solution between five and six normal. An aliquot was removed and titrated with dilute hydrochloric acid using a Beckman Model G pH meter. A normal acid-base titration curve resulted. The equivalence point was determined as at a pH of 3.68 and the bulk of the solution brought to this value by adding more acid. The solution was brought to boiling, slowly cooled to room temperature, diluted to its original volume and the pH determined. At first, the pH was back near its original value. The cycle of adding acid, boiling, cooling, diluting, and reading pH was repeated until the pH remained constant at the equivalence point. The solution was then analyzed.

This concentrated neodymium chloride stock solution was used directly when preparing the 1.0 N load solution. However, a second stock solution of about 0.5 N was made up from this concentrated solution for preparing the 0.1 N load solutions. This 0.5 N stock solution was carefully analyzed also.

An ammonium chloride stock solution was prepared by weighing out the desired amount of the salt which had been dried overnight at 110°C and cooled in a desiccator and dissolving it in the demineralized water. It was diluted to near volume and allowed to come to room temperature, then diluted to the desired volume. It was analyzed for both ammonium and chloride ion and these analyses checked against the weight of salt used.

Eight different 1.0 N load solutions were prepared having



the following ratios of equivalents of ammonium ion to equivalents of neodymium ion: 999:1, 995:5, 99:1, 98:2, 95:5, 90:10, 80:20, and 70:30. All of these except the 999:1 and 995:5 were prepared by weighing out the calculated amount of the concentrated neodymium chloride stock solution and dry ammonium chloride crystals. These solutions were all analyzed individually for neodymium and ammonium ions and the results will be tabulated later. Because of the small amounts of neodymium in the 999:1 and 995:5 solutions (only one and five milliequivalents per liter, respectively), the neodymium for these was obtained by measuring out aliquots of the carefully analyzed 90:10 solution and no further analysis made for neodymium. Extra ammonium chloride had to be added and ammonium analyses were made on these solutions.

Five 0.1 N load solutions were used. The ratios of ammonium to neodymium ions were: 9995:5, 999:1, 99:1, 95:5, and 60:40. The final load solution through each column used in this part of the experiment was prepared by weighing out the required amount of the analyzed 0.5 N neodymium chloride stock solution, and of the ammonium chloride stock solution, and making up to volume in calibrated bottles. The solutions were not analyzed afterward.

Some of the first of the 9995:5 and 999:1 load solutions put through the respective columns were made up using carefully dried ammonium chloride crystals instead of the stock solution. The neodymium came from the same 0.5 N stock solution mentioned

above. Near equilibrium conditions were attained with solution prepared thus, but the final solution through each column was prepared as indicated in the above paragraph.

### Analytical Methods

The neodymium analysis consisted of precipitating the neodymium ion from a solution near boiling by adding an excess of a saturated (at room temperature) solution of oxalic acid. The excess added was equivalent to from 5.0 to 7.5 grams of the oxalic acid dihydrate crystals per liter of solution from which the neodymium was precipitated. The precipitated sample was allowed to cool slowly and set overnight. It was filtered using Schleicher and Schuell No. 589 White Ribbon filter paper, the precipitate washed with dilute oxalic acid, and transferred to tared porcelain crucibles. They were dried under an infra-red lamp and ignited in a muffle furnace overnight at approximately 850°C. The samples were removed from the oven at about 400°C, cooled for three hours in a desiccator, and weighed. The ignition, cooling, and weighing was repeated to make sure the samples were to constant weight. From the difference in weight between crucible plus sample and the empty crucible the weight of neodymium oxide was obtained.

When the neodymium ion was eluted off the column after equilibration, it ended up in a strong hydrochloric acid solution. When analyzing such a sample, it was first evaporated

to dryness to get rid of the acid. The final stage of the evaporation was accomplished using an infra-red heat source so none of the sample would be lost by spattering. The residue was taken up with water to which a few drops of hydrochloric acid had been added and the sample was analyzed as outlined above.

The ammonium ion was determined by the Kjeldahl procedure. The samples were placed in a distillation apparatus and the ammonia driven off by adding concentrated sodium hydroxide and boiling. The ammonia was collected into a receiver containing an indicator-boric acid solution and titrated with standard hydrochloric acid. The indicator-boric acid solution was prepared by adding 10 ml of the concentrated methyl purple indicator solution, supplied by Fleischer Chemical Company, and 30 grams of boric acid crystals to a liter volumetric flask and making up to volume with water. About 20 ml of this solution was added to the flask used to collect the ammonia as it was distilled over. The size of the sample taken was such that would require from 20 to 45 ml of standard 0.1 N hydrochloric acid to titrate.

The gravimetric procedure was followed to analyze for the chloride ion when necessary. The beakers and covers used were painted black and covered with aluminum foil. Samples were measured into these beakers, 0.5 ml of concentrated nitric acid added to each, and the solution brought to near boiling. An approximately 20% excess of 0.25 N silver nitrate solution

was added in subdued light and with stirring, the beaker covered and placed in a dark cabinet to cool to room temperature. The precipitate was filtered off into tared porcelain filter crucibles, wrapped in aluminum foil, and dried overnight at  $115^{\circ}\text{C}$ . The filtering was always done at night with a minimum of light. The crucible was removed from the oven, cooled for one hour in a desiccator, and weighed without removing the foil. It was returned to the oven and heated for the rest of the day. After cooling again for an hour, it was weighed and if the morning and evening weights were reasonably close (they always checked within 0.3 mg) the foil was removed and the crucible plus sample weighed. This value minus that of the empty crucible gives the amount of silver chloride.

The capacity of the air-dried resin was determined using some of the columns prepared for this experiment. A large excess of acid was sent through the columns picked for capacity determinations to make sure all the resin was in the hydrogen form. They were then washed with water and the hydrogen ion eluted off with two liters of 0.9 N sodium chloride. The eluate was diluted to exactly two liters and aliquots titrated with standard 0.1 N sodium hydroxide to a phenolphthalein endpoint to determine the amount of hydrogen ion. The first capacity determinations made gave an average value of 4.172 meg (milliequivalents) per gram of air-dried hydrogen resin. After the columns had been subjected to a number of exchange experiments, the capacity was redetermined using some of the

same columns and showed an increase to 4.186 meq per gram. This final figure will be used for any calculations to follow.

Appropriate blanks were determined and corrections applied to all titrations done in connection with these experiments.

### Procedure

Briefly, the procedure for each load solution consisted of passing a large excess of the solution of known composition through a pair of columns arranged in parallel. The resin in one of the columns was initially on the ammonium side of equilibrium and the other on the neodymium side. Therefore, equilibrium was approached from two directions. After equilibrium had been attained, the solution was carefully washed from the column, the cations eluted off with hydrochloric acid, and the amount of ammonium and neodymium ion in the eluate determined by analysis. The composition of the solution and resin at equilibrium was then known. The procedure for a specific example is given below in greater detail.

The first set of experiments run was made with the 99:1, 1.0 N load solution. Two pairs of columns were used in this run, one column of each pair contained resin in the ammonium form and the other, in the neodymium form. Ten liters of the load solution were passed through each column of the first pair while 20 liters were passed through each column of the

second pair to see how much solution was necessary to reach equilibrium. The flow of solution was controlled at about two liters per 24 hours. Occasionally the flow was stepped up for a few minutes to create some additional turbulence in the solution in the resin bed but not to the point where the resin particles themselves were disturbed.

After the desired amount of load solution had passed through a given column, the top and bottom connections to the column were removed and the solution permitted to drain out of the column until just enough remained to cover the resin. The exact amount left in the column was not critical. The lowering of the solution level was accomplished using the glass plug in the top joint. Inserting the plug would prevent air from entering the column and so hold the solution at any desired level. The lower tip was wiped dry and the tip cover put in place. By warming the column with the palm of the hand or cooling it with a cloth wet with acetone, the pressure inside the column could be controlled so that no solution need ever be lost or even wet the inside of the tip cover. The column was removed from the rack and weighed on an analytical balance. This weight minus the weight of the glass plug and rubber band used to suspend column in the balance was designated  $W_T$  (weight total). After again mounting the column in place in the laboratory, the lower tip cover was removed and the washed capillary tip, Tygon tube, and screw clamp put back on the column. The glass plug was removed and the column carefully

filled with water using a wash bottle with a small plastic delivery tube that could reach into the column and deliver the water against the walls of the column. When filled, the inlet tube and Tygon tubing was attached to the top of the column and the load solution electrolyte washed from the column with two liters of water. The washings from the column were collected in a two liter volumetric flask and analyzed for chloride ion. With this information the weight of 1.0 N load solution equivalent to the weight of chloride ion included in  $W_T$  was calculated. This data was necessary to determine the water present in the resin over and above that associated with the 1.0 N load solution as will be shown later.

Next, the cations were eluted off the resin. First, two liters of one normal hydrochloric acid were sent through the column, the eluate collected in a two liter volumetric flask. This eluant stripped off all the ammonium ion and some of the neodymium ion. The collected solution was labeled "1 N eluate". The one normal acid was followed by two liters of four normal acid which took off the rest of the neodymium. The two liters collected from this operation were labeled "4 N eluate".

The 1 N eluate was analyzed for ammonium ion. In some instances, the 1 N and the 4 N eluates were analyzed separately for neodymium but usually aliquots of each were combined, evaporated to dryness, redissolved, and analyzed. The results from these analyses furnished the data for calculating the

amount of ammonium and neodymium in the resin when in equilibrium with the load solution.

The column was flushed out with water and was then ready for the next phase of the experiment.

This procedure was repeated for each of the load solutions with but two changes. Only two columns were used for each of the load solutions except the 99:1, 1.0 N discussed above. Also, after some information was obtained from early runs, solutions could be made up about one normal that contained the right ratio of ammonium to neodymium to put the resin in a column near, but yet on the desired side of, equilibrium prior to the start of a run with a given load solution. Consequently, the load solution did not have to make such drastic changes in the amounts of ions in the resin as it would if the resin was all in the neodymium or ammonium form at the start of the experiment. This was especially important in the case of the runs with the 0.1 N load solutions since most of these contained a very small amount of neodymium ion per liter and very large volumes of solution would be required to make rather small changes in the amounts of neodymium in the resin.

#### Data and Results

Table 1 contains the data on the columns used in these experiments. The meaning of the column headings are defined



below. All weights are given in grams.

$W_{EC}$  = Weight of empty column plus lower tip cover (see under "Apparatus", page 60).

Weight air-dried H-resin = actual weight of resin weighed into each column.

Weight Bone-dry H-resin =  $79\% \times \text{column (C)}$ . The samples of H-resin set aside for moisture determination have been in a desiccator over  $P_2O_5$  for about 20 months and the drying curves are asymptotically approaching a value of 21% moisture in the original resin sample.

Meq.  $H^+$  on resin = column (C)  $\times$  the capacity of the resin determined to be  $4.186^1$  milliequivalents (meq.) per gram of air-dried H-resin.

Grams of  $H^+$  on resin = column (E)  $\times$  the weight of one meq. of  $H^+$ .

Weight bone-dry resin anion = column (D) - column (F).

The data concerning the load solutions used are summarized in Table 2. The preparation of the solutions has been described. For the 1.0 N solutions, the molalities were calculated from direct analyses for the neodymium, ammonium, and chloride ions. The chloride analysis was made from a weighed sample of the solution which made it possible to calculate the amount of water in the solution. It also furnished the information for column (E) which was used in determining the amount of water in the resin. The 1.0 N load

Table 1. Data on the columns and resin used in these experiments

(A) Column no.	(B) W <sub>EC</sub>	(C) Weight air-dried H-resin	(D) Weight bone-dry H-resin	(E) Meq. H <sup>+</sup> on resin	(F) Grams H <sup>+</sup> on resin	(G) Weight bone-dry resin anion
11	52.3265	30.0273	23.7216	125.697	.1267	23.5949
12	54.3078	30.0128	23.7101	125.637	.1266	23.5835
13	59.2760	30.0007	23.7006	125.586	.1266	23.5740
14	54.8864	30.0058	23.7046	125.607	.1266	23.5780
15	54.3320	30.0120	23.7095	125.633	.1266	23.5829
17	52.9567	30.0041	23.7032	125.600	.1266	23.5766
18	54.0222	30.0102	23.7081	125.626	.1266	23.5816
19	55.2228	30.0192	23.7152	125.663	.1267	23.5886
20	54.1170	30.0036	23.7028	125.598	.1266	23.5762
21	55.2697	30.0033	23.7026	125.597	.1266	23.5760

Table 2. Load solution data

(A)	(B)	(C)		(D)		(E)	(F)
Column no.	Load solution	Equivalent/liter of		Moles/1000g water		Wt. solution equivalent 1.0g AgCl	Ionic strength
		NH <sub>4</sub> Cl	NdCl <sub>3</sub>	NH <sub>4</sub> Cl	NdCl <sub>3</sub>		
For 1.0 N load solutions							
18, 19	999:1	.99960	.001000	1.0424	.000348	7.0592	1.0445
20, 21	995:5	.99862	.005000	1.0385	.001734	7.0586	1.0490
11, 12,							
13, 14	99:1	.99465	.00852	1.0361	.002958	7.0625	1.0538
11, 12	98:2	.97736	.01993	1.0179	.006920	7.0943	1.0594
13, 14	95:5	.94766	.04979	.98559	.01726	7.1089	1.0892
15, 17	90:10	.89328	.09941	.93137	.03455	7.1348	1.1387
11, 12	80:20	.80310	.19982	.82985	.06883	7.1470	1.2428
13, 14	70:30	.70167	.29986	.72364	.10308	7.1904	1.3421
For 0.1 N load solutions							
15, 17	9995:5	.09995	.00005	.10062	.000017	69.6735	.10072
13, 14	999:1	.09990	.00010	.10057	.000034	69.6756	.10077
13, 14	99:1	.09900	.00100	.09966	.000336	69.6784	.10167
11, 12	95:1	.09500	.00500	.09561	.001677	69.7014	.10567
11, 12	60:40	.06000	.04000	.06032	.013405	69.8465	.14075

solutions were made up by weighing aliquots of stock solutions or dry salt into calibrated flasks and adding water to the desired volume. The densities of these solutions were measured and the molarities converted to molalities. Column (F) lists the ionic strength of the solutions calculated from the molalities of the ions present.

Table 3 gives, for each column, the conditions in the resin when it is in equilibrium with the corresponding 1.0 N load solution. The same information for the 0.1 N load solutions is given in Table 4. The weight,  $W_T$ , has been referred to previously and is the total weight of the column, tip cover, resin and enough load solution to just cover the resin. The values in columns (D) and (E) in both tables were determined analytically. The terms,  $N_{NH_4^+}$  and  $N_{Nd^{+3}}$ , are defined as the equivalent fraction of the respective species present in the resin at equilibrium and are calculated directly from columns (D) and (E).

The term,  $W_T$ , warrants further attention since it is used to determine the moles of water in the resin per equivalent of resin. It is made up of the following quantities:

$$W_T = W_{EC} + W_{BR} + W_{LS} + W_{WR} \quad (35)$$

where  $W_{EC}$  = weight of the empty dry column plus the lower tip cover, column (B), Table 1.

$W_{BR}$  = column (G), Table 1, plus the weight of ammonium ion and neodymium ion found in the resin by

Table 3. Data on the resin in the columns in equilibrium with 1.0 N load solutions

(A) Column no.	(B) Load solution	(C) $W_T$	(D) Meq. $\text{NH}_4^+$ on resin	(E) Meq. $\text{Nd}^{+3}$ on resin	(F) $N_{\text{NH}_4^+}$	(G) $N_{\text{Nd}^{+3}}$	(H) Moles water per equiv. resin
18	999:1	124.1799	118.998	6.671	.94692	.05308	6.828
19	999:1	125.3662	118.803	6.632	.94713	.05287	6.800
20	995:5	125.4043	103.992	21.694	.82740	.17260	6.783
21	995:5	125.9733	103.772	21.801	.82639	.17361	6.776
11	99:1	122.1833	96.550	29.353	.76686	.23314	6.769
12	99:1	126.2889	96.580	29.296	.76726	.23274	6.782
13	99:1	131.9740	96.344	29.438	.76596	.23404	6.761
14	99:1	125.5267	96.472	29.324	.76689	.23311	6.763
11	98:2	122.4062	82.216	43.587	.65353	.34647	6.763
12	98:2	126.9304	82.241	43.676	.65314	.34686	6.760
13	95:5	131.8761	65.670	60.139	.52198	.47802	6.707
14	95:5	126.1961	65.792	60.178	.52228	.47772	6.697
15	90:10	127.4616	53.010	72.972	.42077	.57923	6.689
17	90:10	124.0728	52.961	73.029	.42036	.57964	6.681
11	80:20	124.8936	39.972	86.005	.31730	.68270	6.651
12	80:20	128.9710	39.911	86.037	.31689	.68311	6.649
13	70:30	137.0323	31.576	94.245	.25096	.74904	6.670
14	70:30	129.8295	31.589	94.231	.25106	.74894	6.675

Table 4. Data on the resin in the columns in equilibrium with 0.1 N load solutions

(A) Column no.	(B) Load solution	(C) $W_T$	(D) Meq. $\text{NH}_4^+$ on resin	(E) Meq. $\text{Nd}^{+3}$ on resin	(F) $N_{\text{NH}_4^+}$	(G) $N_{\text{Nd}^{+3}}$	(H) Moles water per equiv. resin
15	9995:5	128.3463	61.009	64.557	.48587	.51413	8.470
17	9995:5	126.3136	60.985	64.646	.48543	.51457	8.470
13	999:1	134.5956	51.141	74.691	.40642	.59358	8.440
14	999:1	128.5131	51.117	74.498	.40693	.59307	8.423
13	99:1	136.3015	27.275	98.467	.21691	.78309	8.241
14	99:1	130.7932	27.239	98.520	.21660	.78340	8.229
11	95:5	127.2530	16.351	109.606	.12982	.87018	8.033
12	95:5	130.9710	16.315	109.610	.12956	.87044	8.043
11	60:40	126.3641	5.282	120.856	.04188	.95812	7.495
12	60:40	130.9761	5.167	120.884	.04099	.95901	7.516

analysis, the latter being calculated from columns (D) and (E) in Tables 3 and 4.

$W_{LS}$  = the weight of load solution which would contain the amount of chloride ion included in  $W_T$ . The chloride ion was washed from the column and analyzed for by precipitating as silver chloride.  $W_{LS}$  was calculated from the weight of silver chloride obtained and column (E) of Table 2. This calculation has assumed that all of the chloride ion is in the outer solution phase. Actually, and this is especially true of the 1.0 N load solutions, a small amount of chloride ion will have diffused into the resin due to Donnan behavior and, perhaps, come in as complex ions of the type,  $NdCl^{++}$ , which may exist in the solution. The values of  $W_{WR}$  calculated here will be low to the extent to which these effects take place. This point will be discussed later.

$W_{WR}$  = weight of water in the resin included in  $W_T$  over and above that associated with  $W_{LS}$ . This weight, converted to moles of water and divided by the capacity of the column in equivalents, is equal to the moles of water per equivalent of resin and is given in column (H) of Tables 3 and 4.

Since 1000 grams of water is equal to 55.5 moles, dividing this figure by the number of moles of water per equivalent of resin

will give the equivalents of resin per 1000 grams of water.

The sum of corresponding values in columns (D) and (E), Tables 3 and 4, gives the capacity of the resin in a given column for one experiment. If the value in column (D) of the table for this experiment is changed to moles of ammonium ion and divided by the capacity, the quotient obtained is the number of moles of ammonium ion per equivalent of resin. This latter term, multiplied by the number of equivalents of resin per 1000 grams of water, results in the number of moles of ammonium ion per 1000 grams of water, i.e., the molality of the ammonium ion in the resin phase. Following the same scheme for the corresponding terms in column (E) gives the molality of the neodymium ion in the resin. Table 5 summarizes the results of these calculations.

The mean molal activity coefficients of the ammonium chloride and the neodymium chloride in the various load solutions were also necessary for the calculations to be made later. They had to be estimated since no work has been done in measuring them in these mixed electrolyte solutions. The Harned rule (74) could not be used because there was not enough information to determine the constants involved. Consequently, the activity coefficients of ammonium chloride in pure ammonium chloride solutions (154) were plotted against the ionic strength of the solutions. This was also done for pure neodymium chloride solutions (74, 134a). The value used for the activity coefficient of the ammonium chloride in a



Table 5. Concentrations in the resin phase at equilibrium

(A) Column no.	(B) Load solution	(C) Equivalents of resin per 1000g water	(D) Moles $\text{NH}_4^+$ per 1000g of water	(E) Moles $\text{Nd}^{+3}$ per 1000g of water
For 1.0 N load solutions				
18	999:1	8.129	7.6977	.14385
19	999:1	8.162	7.7311	.14386
20	995:5	8.183	6.7707	.47081
21	995:5	8.192	6.7694	.47406
11	99:1	8.200	6.2883	.63725
12	99:1	8.184	6.2795	.63493
13	99:1	8.210	6.2884	.64048
14	99:1	8.207	6.2941	.63773
11	98:2	8.207	5.3637	.94786
12	98:2	8.211	5.3629	.94936
13	95:5	8.276	4.3199	1.3187
14	95:5	8.288	4.3288	1.3198
15	90:10	8.298	3.4916	1.6022
17	90:10	8.308	3.4924	1.6052
11	80:20	8.345	2.6477	1.8990
12	80:20	8.348	2.6454	1.9009
13	70:30	8.322	2.0884	2.0778
14	70:30	8.316	2.0877	2.0759
For 0.1 N load solutions				
15	9995:5	6.553	3.1840	1.1231
17	9995:5	6.553	3.1811	1.1240
13	999:1	6.577	2.6728	1.3012
14	999:1	6.590	2.6816	1.3027
13	99:1	6.735	1.4610	1.7581
14	99:1	6.745	1.4610	1.7614
11	95:5	6.910	.8970	2.0042
12	95:5	6.901	.8941	2.0024
11	60:40	7.406	.3101	2.3652
12	60:40	7.385	.3027	2.3608

given load solution was the value read from the plot for pure ammonium chloride but at an ionic strength equal to the total ionic strength of this load solution. The same procedure was followed to get the activity coefficient of the neodymium chloride in the same load solution. It is realized that the values obtained are approximate but they are the best available until more is known of these mixed electrolyte solutions.

## DISCUSSION OF RESULTS

Most of the recent attempts made to explain ion-exchange equilibria have been based either on the application of the mass action law or on the treatment of the resin as a semi-permeable membrane and using Donnan membrane theory. Neither of these approaches are entirely satisfactory. It can be assumed that the system consists of a dilute solution of electrolytes outside the resin in equilibrium with a concentrated solution of ions inside. However, this system differs from the normal liquid-liquid equilibrium in that the anions in the resin phase are bound to the resin network and, hence, are not free to migrate. Furthermore, they are bound fairly close together so that the charged ionic atmosphere around the cations is always high and this proposes serious difficulties in determining the activity coefficients of the species within the resin. The elastic forces resulting from the bonds holding the atoms together in the resin network are always present. Therefore, irrespective of how much the external solution is diluted, the concentration of the ions inside the resin remains large and this introduces an osmotic pressure factor between the inside and the outside solutions of the system.

If the ion-exchange reaction investigated is written according to the mass action law, at the same time recognizing its limitations since the pressure inside will not remain

constant as the equivalent fraction of the cations inside the resin changes, it can be represented by the equation



where the subscript R refers to the resin phase while no subscript means solution phase. The true thermodynamic equilibrium constant is written

$$K = \frac{a_{\text{Nd}^{+3}_{\text{R}}} a_{\text{NH}_4^+}^3}{a_{\text{NH}_4^+_{\text{R}}}^3 a_{\text{Nd}^{+3}}}$$

$$= \frac{f_{\text{Nd}^{+3}_{\text{R}}} m_{\text{Nd}^{+3}_{\text{R}}} \gamma_{\text{NH}_4^+}^3 m_{\text{NH}_4^+}^3}{f_{\text{NH}_4^+_{\text{R}}}^3 m_{\text{NH}_4^+_{\text{R}}}^3 \gamma_{\text{Nd}^{+3}} m_{\text{Nd}^{+3}}}$$
(36)

and here the effects of the changing pressure inside has been lumped into the activity coefficients of species in the resin phase. Since the activity coefficients in the resin phase are not known, these terms were transferred to the left side of the equation and a new quantity,  $K''$ , defined as

$$K'' = K \frac{f_{\text{NH}_4^+_{\text{R}}}^3}{f_{\text{Nd}^{+3}_{\text{R}}}} = \frac{\gamma_{\text{NH}_4^+}^3 m_{\text{Nd}^{+3}_{\text{R}}} m_{\text{NH}_4^+}^3}{\gamma_{\text{Nd}^{+3}} m_{\text{NH}_4^+_{\text{R}}}^3 m_{\text{Nd}^{+3}}} \quad (37)$$

$K''$  will not remain constant as the composition of the resin changes and this research has determined experimentally how

$K''$  varies with the equivalent fraction of neodymium in the resin.

The values of the molalities of the various species in both resin and solution for the different experiments have been listed in Tables 2 and 5. The activity coefficients in the right side of equation (37) are those of the positive ammonium and neodymium ions. However, they can be evaluated from the mean molal activity coefficients of the ammonium chloride and neodymium chloride by the following schemes:

$$\gamma_{\pm \text{NH}_4\text{Cl}}^2 = \gamma_{\text{NH}_4^+} \gamma_{\text{Cl}^-} \quad (38)$$

$$\gamma_{\pm \text{NdCl}_3}^4 = \gamma_{\text{Nd}^{+3}} \gamma_{\text{Cl}^-}^3 \quad (39)$$

If both side of equation (38) are cubed and then divided by equation (39), the result is

$$\frac{\gamma_{\pm \text{NH}_4\text{Cl}}^6}{\gamma_{\pm \text{NdCl}_3}^4} = \frac{\gamma_{\text{NH}_4^+}^3 \gamma_{\text{Cl}^-}^3}{\gamma_{\text{Nd}^{+3}} \gamma_{\text{Cl}^-}^3}$$

The activity coefficient of the chloride ion cancels, leaving

$$\frac{\gamma_{\text{NH}_4^+}^3}{\gamma_{\text{Nd}^{+3}} \gamma_{\pm \text{NdCl}_3}^4} = \frac{\gamma_{\pm \text{NH}_4\text{Cl}}^6}{\gamma_{\pm \text{NdCl}_3}^3} \quad (40)$$

The values in the right side of this equation can be estimated

as described previously so  $K''$  can be evaluated. Table 6 contains the values of the mean activity coefficients used in these calculations.

The values of  $K''$ , calculated using equation (37), are

Table 6. Activity coefficients of  $\text{NH}_4\text{Cl}$  and  $\text{NdCl}_3$  in solution

Load solution	$\gamma_{\pm\text{NH}_4\text{Cl}}$	$\gamma_{\pm\text{NdCl}_3}$	$\frac{\gamma_{\pm\text{NH}_4\text{Cl}}^6}{\gamma_{\pm\text{NdCl}_3}^4}$
For 1.0 N load solutions			
999:1	.6001	.2980	5.922
995:5	.5998	.2976	5.936
99:1	.5995	.2974	5.934
98:2	.5993	.2970	5.955
95:5	.5978	.2958	5.961
90:10	.5950	.2936	5.972
80:20	.5900	.2895	6.005
70:30	.5860	.2862	6.035
For 0.1 N load solutions			
9995:5	.7700	.4938	3.506
999:1	.7699	.4937	3.506
99:1	.7695	.4928	3.520
95:5	.7670	.4884	3.578
60:40	.7430	.4552	3.918

plotted against equivalent fraction of neodymium in the resin in Figure 2.

If, in equation (37), the activity coefficients of the ions in the external solution were also taken over to the left side and lumped together with the true equilibrium constant

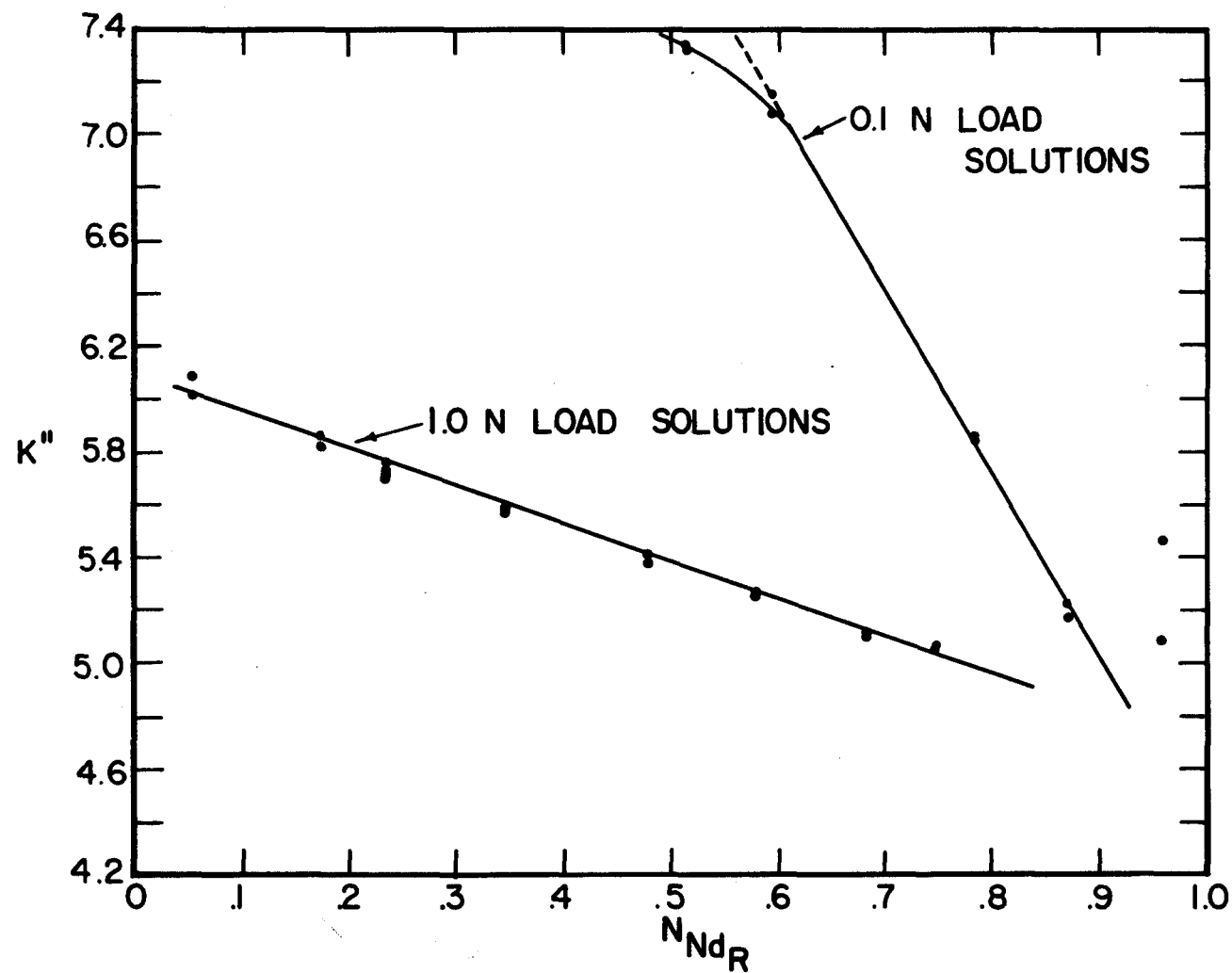


Figure 2. Variation of  $K''$  with equivalent fraction of  $Nd^{+3}$  in the resin

and the resin phase coefficients, a new term,  $K'$ , is defined as

$$K' = K'' \frac{\gamma_{\text{Nd}^{+3}}}{\gamma_{\text{NH}_4^+}^3} = \frac{m_{\text{Nd}^{+3}\text{R}}^3 m_{\text{NH}_4^+}^3}{m_{\text{NH}_4^+\text{R}}^3 m_{\text{Nd}^{+3}}^3} \quad (41)$$

Figure 3 shows the manner in which  $K'$  varies with the equivalent fraction of neodymium in the resin

It is very easy to give the concentration of a cation in the resin as the equivalent fraction of the resin occupied by that cation. An equation of the same type as equation (37) can be readily derived using equivalent fractions of the species in the resin instead of molalities by proceeding as follows: the numerical value of the right side of equation (37) is unchanged if the manipulations shown below are made,

$$K'' = \frac{\gamma_{\text{NH}_4^+}^3 \frac{Q}{3} \cdot \frac{3m_{\text{Nd}^{+3}\text{R}}}{Q} \cdot m_{\text{NH}_4^+}^3}{\gamma_{\text{Nd}^{+3}} Q^3 \left( \frac{m_{\text{NH}_4^+\text{R}}}{Q} \right)^3 \cdot m_{\text{Nd}^{+3}}} \quad (42)$$

where  $Q = 3 m_{\text{Nd}^{+3}\text{R}} + m_{\text{NH}_4^+\text{R}}$ . However,

$$\frac{3m_{\text{Nd}^{+3}\text{R}}}{Q} = N_{\text{Nd}^{+3}\text{R}}, \text{ the equivalent fraction of } \text{Nd}^{+3} \text{ in}$$

the resin and



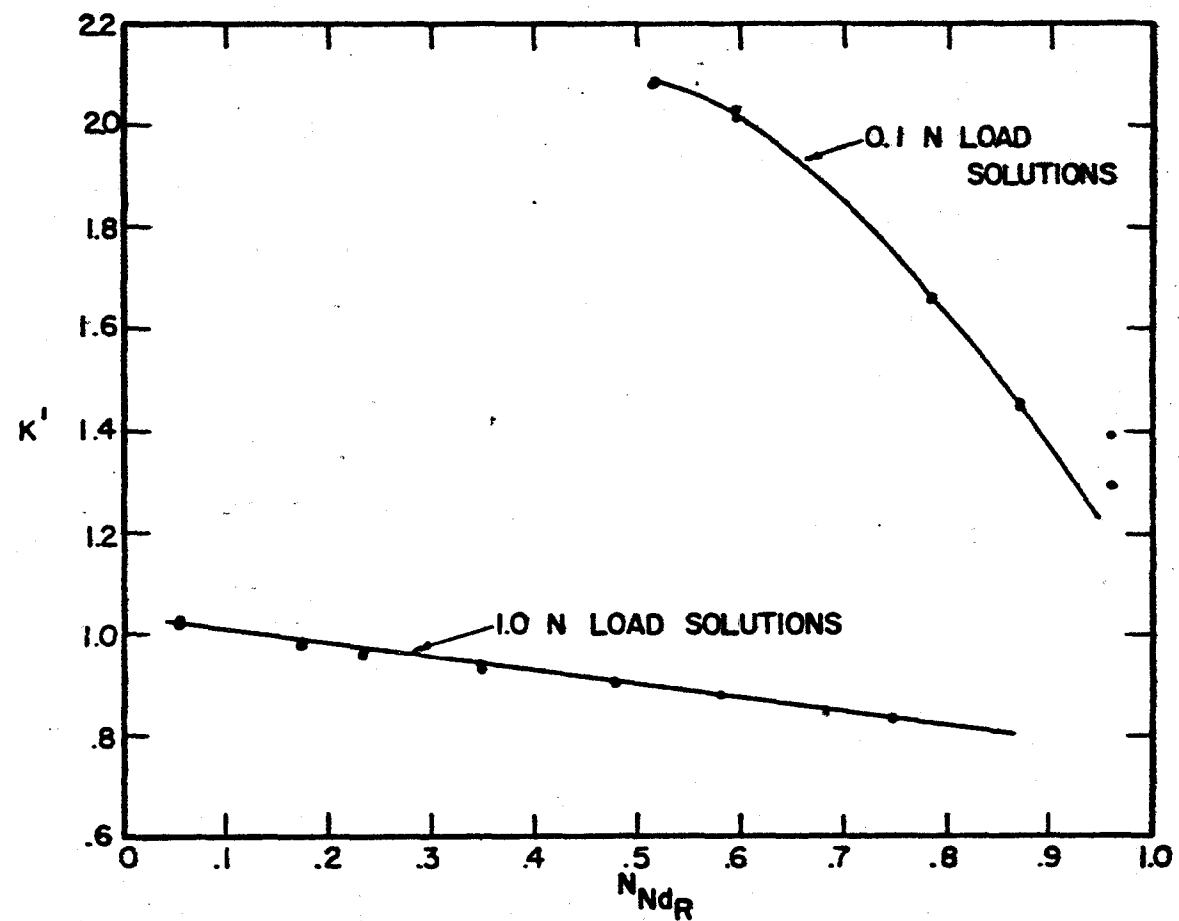


Figure 3. Variation of  $K'$  with equivalent fraction of  $Nd^{+3}$  in the resin

$$\frac{m_{\text{NH}_4^+ \text{R}}}{Q} = N_{\text{NH}_4^+ \text{R}}, \text{ the equivalent fraction of } \text{NH}_4^+ \text{ in the resin}$$

Therefore, equation (42) can be written

$$K_{(N,m)}'' = \frac{\gamma_{\text{NH}_4^+}^3 N_{\text{Nd}^{+3} \text{R}} m_{\text{NH}_4^+}^3}{3Q^2 \gamma_{\text{Nd}^{+3}}^3 N_{\text{NH}_4^+ \text{R}}^3 m_{\text{Nd}^{+3}}^3} \quad (43)$$

The subscript (N,m) is used to distinguish the  $K''$  calculated from equivalent fractions and molalities from the  $K''$  calculated using molalities throughout. This latter  $K''$  is left without a subscript. If  $Q$  is equal to the number of equivalents of resin per 1000 grams of water in the resin,  $K_{(N,m)}''$  will equal  $K''$ . However, since the equivalent fraction of a species of ion in a resin will remain the same irregardless of the amount of resin considered,  $Q$  may be defined in any number of different ways and, while the value of  $K_{(N,m)}''$  will change, equation (43) is still valid throughout any discussion. For example, it is interesting to see how  $K''$  compares with  $K_{(N,m)}''$  if  $Q$  is defined as the capacity, in equivalents, of 1000 grams of air-dried hydrogen-form resin as originally weighed into the columns. Figure 4 shows how  $K_{(N,m)}''$  varies with the equivalent fraction of neodymium in the resin.

Before discussing these different plots, the actual calculated values of  $K''$ ,  $K'$ , and  $K_{(N,m)}''$  will be summarized in

Figure 4. Variation of  $K''$  (mm) with equivalent fraction of  $Nd^{+3}$  in the resin

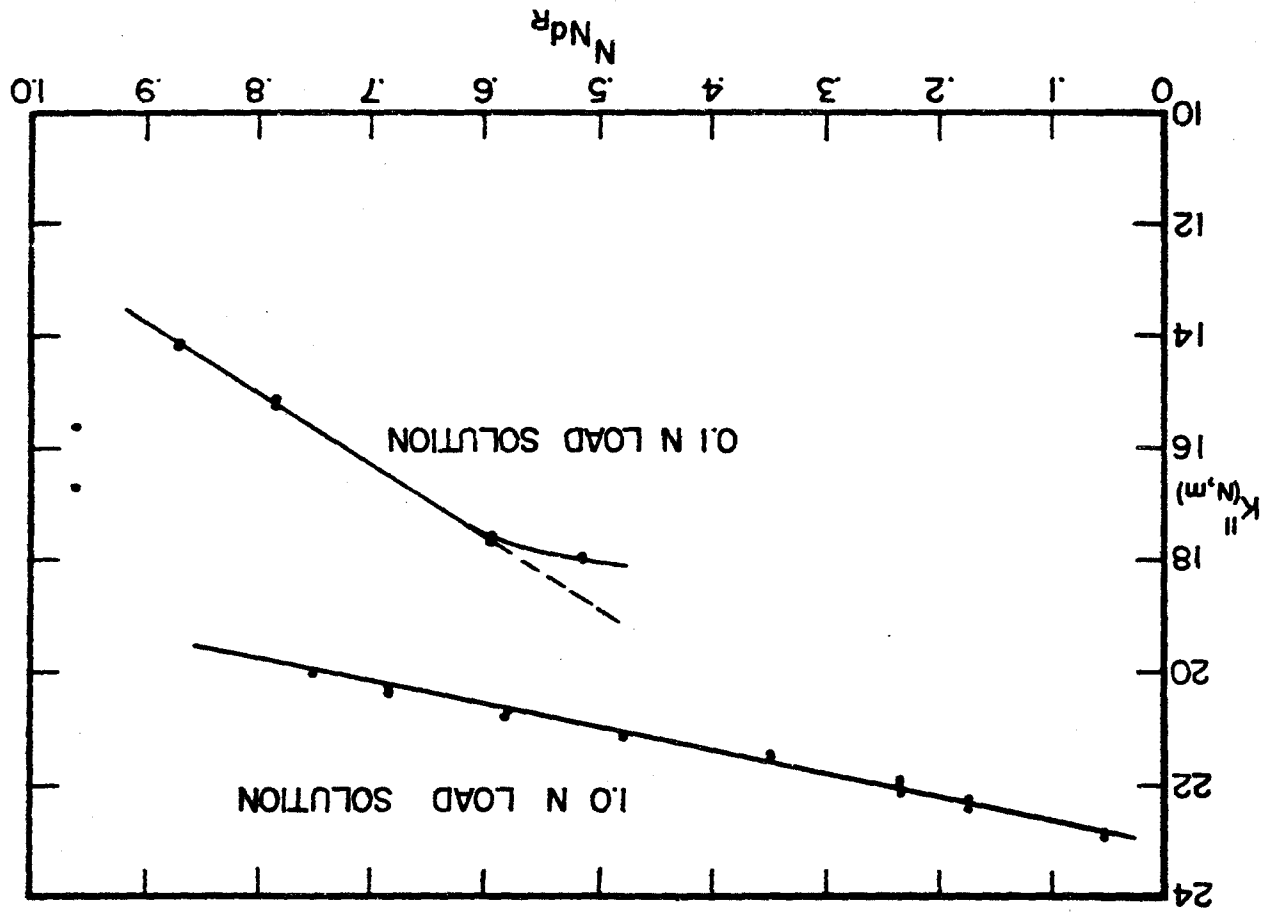


Table 7.

Table 7 shows that there are two values (actually four for the 99:1 1.0 N solution) for each of the various equilibrium "constants" for each load solution, since at least two columns were equilibrated in each case. This fact is not evident in Figures 2, 3, and 4 because in some instances the two or more points fall one on top of the other. The first column number (first two for the 99:1 1.0 N solution) listed for each different load solution in Table 7 refers to that column which, at the start of the experiment, contained resin on the ammonium ion side of the equilibrium. The last column (last two in the special case) listed for each solution was initially on the neodymium side of equilibrium. An examination of the values of the equilibrium "constants" shows that the columns initially on the ammonium side give results which are neither consistently higher nor consistently lower than values obtained from columns originally on the neodymium side. This demonstrates the reversibility of the exchange reaction studied.

When the sum of the number of milliequivalents of ammonium and neodymium ions found in the resin in a column by analysis is compared to the determined hydrogen ion capacity of the column (Table 1), it can be seen that equivalence of exchange takes place. The average deviation for the 28 individual column experiments, calculated by the formula

Table 7. The calculated values of  $K''$ ,  $K'$ , and  $K''_{(N,m)}$ 

Column no.	Load solution	$K''$	$K'$	$K''_{(N,m)}$
For 1.0 N load solutions				
18	999:1	6.083	1.027	22.92
19	999:1	6.005	1.014	22.82
20	995:5	5.815	.980	22.22
21	995:5	5.858	.987	22.44
11	99:1	5.718	.964	21.94
12	99:1	5.722	.964	21.87
13	99:1	5.747	.969	22.11
14	99:1	5.706	.962	21.94
11	98:2	5.575	.936	21.43
12	98:2	5.585	.938	21.49
13	95:5	5.411	.908	21.14
14	95:5	5.379	.902	21.09
15	90:10	5.256	.880	20.65
17	90:10	5.263	.881	20.73
11	80:20	5.101	.850	20.27
12	80:20	5.120	.853	20.36
13	70:30	5.061	.839	20.00
14	70:30	5.061	.839	19.98
For 0.1 N load solutions				
15	9995:5	7.318	2.088	17.92
17	9995:5	7.324	2.089	17.98
13	999:1	7.151	2.040	17.64
14	999:1	7.078	2.019	17.56
13	99:1	5.846	1.661	15.13
14	99:1	5.857	1.664	15.21
11	95:5	5.179	1.447	14.11
12	95:5	5.225	1.460	14.20
11	60:40	5.089	1.299	15.65
12	60:40	5.461	1.394	16.71

$$\% \text{ deviation} = \frac{(\text{Meq. NH}_4^+ + \text{Meq. Nd}^{+3}) - \text{H}^+ \text{ capacity}}{\text{H}^+ \text{ capacity}} \times 100$$

is +0.15%. The extremes of the deviations were +0.330% and -0.181%. These deviations could be attributed to experimental error though it may be significant that there were only three negative deviations, one each with columns equilibrated with the 999:1 and 995:5 1.0 N load solutions and with the 9995:5 0.1 N solutions. These are the solutions for each concentration that leave the greatest number of equivalents of ammonium ion in the resin. Conversely, the larger deviations occurred in columns equilibrated with solutions that left the smaller number of equivalents of ammonium ion in the resin. The worst deviation, that of +0.330%, was for column number 12, initially on the neodymium side of equilibrium, equilibrated with the 60:40 0.1 N load solution. The other column (No. 11) equilibrated with this same solution showed a deviation of +0.278%. There is considerable scattering of these percent deviations but the trends are as indicated. There is the possibility that the hydrogen ion capacity is slightly low because of the difficulty of getting the very last of it off when eluting with sodium ion, but this effect will be constant and will not change the relative amounts of the deviations cited.

There has been evidence in connection with nitrogen isotope separation in this laboratory that small amounts of the

ammonium ion forms a very stable complex or compound with the resin. Columns thought to have been completely stripped of ammonium ion by commonly used eluants showed small quantities of ammonium ion in the eluate when eight normal sodium hydroxide was passed through the resin. If some of this effect was present in these equilibria studies perhaps not all of the ammonium ion was eluted off with the hydrochloric acid solution used, tending to make the ammonium-neodymium capacity of the column low. This effect would be most noticeable in experiments where the equilibrium concentration of ammonium ion in the resin is high.

There is also the possibility that the load solution contains complex ions of the type  $\text{NdCl}^{++}$  and  $\text{NdCl}_2^+$ . If the resin in equilibrium with the load solution would have some of these ions in it, and if they survived the washing process and be eluted off with the hydrochloric acid solutions, the neodymium-ammonium capacity would tend to be too high. This effect would be most appreciable with load solutions containing the larger amounts of neodymium chloride.

These two effects could explain the trends of the capacity deviations given above.

Consider now Figures 2, 3, and 4. The calculation of  $K'$  effectively assumes that the activity coefficients of the different ions are the same inside the resin as they are in the outer solution, a rather poor assumption. The plot of  $K'$  in Figure 3 for the 0.1 N load solution is a definite smooth curve

while the 1.0 N solution data gives a straight line. Introducing the activity coefficients as estimated for the mixed electrolytes in the outer solution as is done in calculating  $K''$  has a beneficial effect. The central portion of the 0.1 N solution plot, Figure 2, now is a straight line and the relative slopes of the 0.1 N and 1.0 N plots are more nearly the same by a factor of two of what they were in Figure 3. The effect of the activity coefficients should be more noticeable on the 0.1 N data since the concentration inside the resin compared to that in the outside solution is of the order of 100-fold greater in this case while it is some 10-fold greater for the 1.0 N solutions.

The values of  $K''_{(N,m)}$  in Figure 4 are relatively insensitive to the differences in the amount of water calculated to be in the resin phase. The slopes of the two lines are a little closer together than those in Figure 2. The relative positions of the two plots have been reversed.

$K''$  and  $K'$  would be quite sensitive to the effects resulting from the presence of chloride ions (and attendant cations) inside the resin phase. If, for example, some of the chloride ion, previously assumed all in the external solution in calculating the amount of water in the resin, were actually in the resin phase instead, it should be subtracted from the total chloride washed out of the column. Hence,  $W_{LS}$ , the weight of external solution would be less and,  $W_{WR}$ , the water in the resin, would be greater. Even though the chloride ion



brought into the resin with it an equivalent amount of cation, the net effect would be to decrease the molalities of the ions in the resin. At equilibrium, the activities of each salt should be the same inside the resin as in the external solution according to Donnan membrane theory. If the activity coefficients of the salts in the mixed electrolyte inside the resin were known, and those outside were known more accurately, the amount of chloride inside could be approximated. The amount of water in the resin could then be corrected and the molalities of the different species redetermined. Since, this Donnan effect may be appreciable in the case of the 1.0 N load solutions, this correction should help to bring these curves together.

The last pair of points on the lower end ( $N_{Nd_R} = .96$ ) of the 0.1 N load solution curves appears to be far in error on all plots. This may be, in part, legitimate and, in part, due to faulty technique and to errors in analysis. These points came from data of the 60-40 load solution experiments. The fact that the total variation in ionic strength for the other four solutions used was less than 5% while that of the 60-40 solution suddenly increased by about 40%, must have a definite effect on  $K''$  and  $K''_{(N,m)}$ . The manner in which the mean activity coefficient ratio term used in equations (37) and (43) varies reflects this. The values for the number of moles of water per equivalent of resin also shows this abrupt change. Since the

curves for  $K''$  and  $K'$ , which are dependent on the amount of water in the resin, show these two points in a much better position relative to the rest of the curve than does the curve for  $K''_{(N,m)}$ , it is felt that, perhaps, some of this deviation was genuine.

However, the two points themselves do not coincide. This indicates either that equilibrium was not obtained in both columns (perhaps in neither one) or that in handling the columns equilibrium was disturbed in one or disturbed more in one than in the other. This is quite possible. The resin shows a much greater preference for the highly charged ion in dilute solutions than in concentrated. When washing the chloride ion out of the column after getting  $W_T$ , there could very well be a region near the top of the resin where dilution of the load solution would take place. In the case of the other 0.1 N solutions, the amount of neodymium in the external solution included in  $W_T$  is so small that if part of it did go into the resin due to this dilution the effect would be negligible. However, in the case of the 60-40 solution, there is about one milliequivalent of neodymium in the external solution present. If 10% of this or 0.1 meq. went into the resin and displaced 0.1 meq. of ammonium ion from the true equilibrium amount, it would be enough to put the lower of the points on the  $K''$  curve. Of course, it would lower the other point by the same amount.

The densities of the 0.1 N solutions are about that of

water and so the dilution would be more likely with these solutions than with the 1.0 N solutions which are considerably heavier than water.

This effect must be considered when further work is done.

Examination of equation (36) shows that the calculation of the equilibrium constant is very sensitive to analytical results, especially the ammonia determinations since they are cubed in the equation. This is particularly true in the region of the 60-40 0.1 N points where the equivalent fraction of ammonium ion in the resin is small. In this instance, though, calculations show that the errors in analysis must be somewhat larger than it is believed they actually could be to account entirely for the position of the points. However, analytical errors could contribute in part.

In the section of the thesis describing the experimental procedure, it was noted that the information obtained from the studies with the 1.0 N load solutions could be very helpful in preparing the resin for experiments with more dilute load solutions. Near equilibrium conditions could be reached with a small amount of 1.0 N solution of the right composition and final equilibrium attained with the proper dilute solution. Much smaller amounts of dilute solution would be required than if the resin was entirely in one form or another before starting load solution through the column. Figure 5 shows the amount of neodymium ion required per liter of 1.0 N

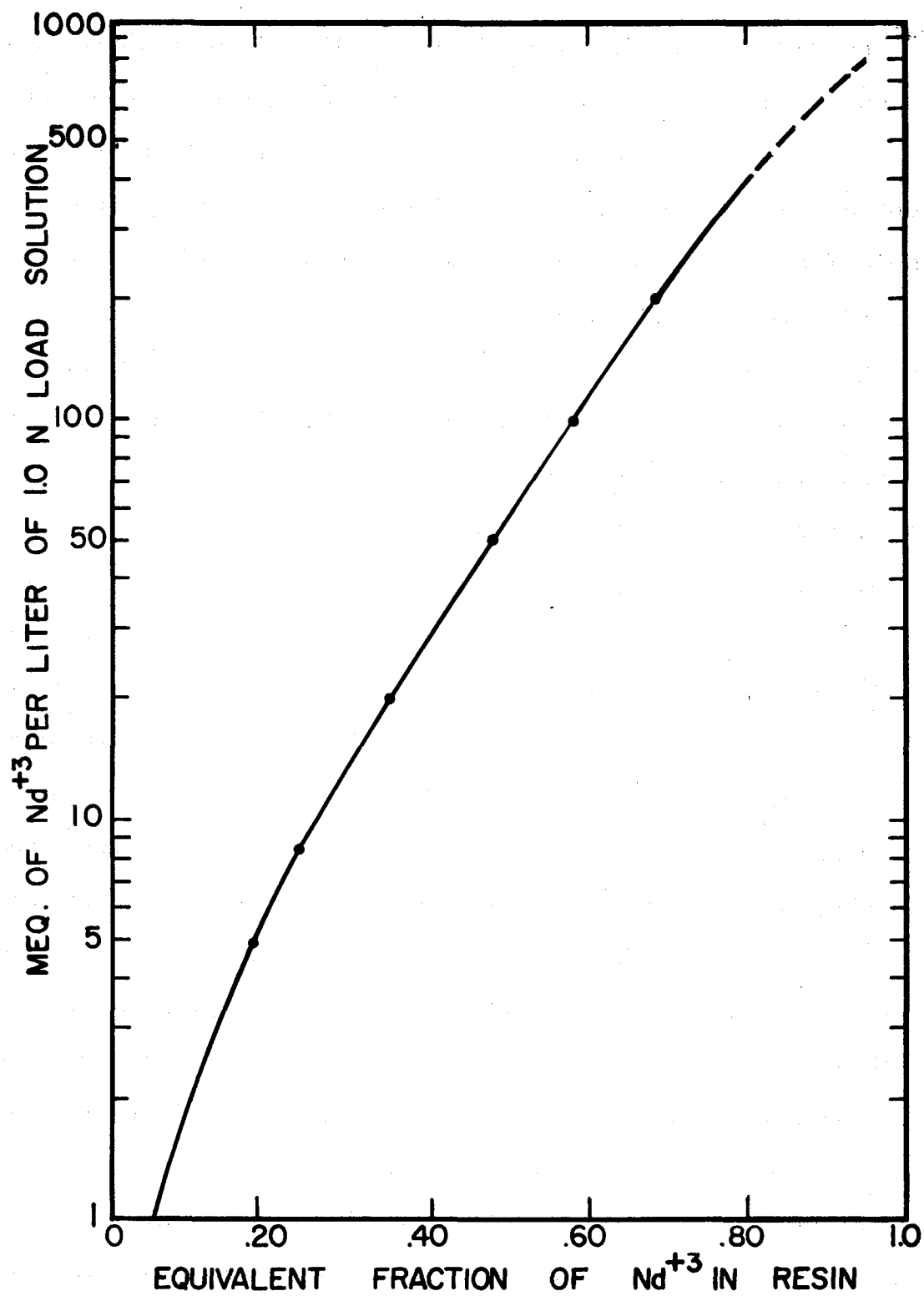


Figure 5. Composition of resin in equilibrium with 1.0 N load solutions of varying  $\text{Nd}^{+3}$  content

solution to give any desired resin composition. When the number of milliequivalents of neodymium per liter of 1.0 N solution has been determined for a proposed experiment, the proper number of milliequivalents of ammonium ion must be added to give the solution its total of one equivalent of cation per liter.

## CONCLUSIONS

As pointed out in the section discussing the various theories of ion-exchange equilibria, it is obvious that considerable accurate experimental data must be obtained before a complete theory can be developed. This became increasingly more apparent as attempts were made, with little success, to use the existing theories to explain the data obtained from the investigations reported in this thesis. It will be necessary to determine experimentally what the really important factors are that will have to be taken into account in a satisfactory theory and, so far, there does not seem to be sufficient available data to adequately evaluate these factors.

In this work, methods for getting exact data have been developed and some precise values have been obtained for a uni-trivalent exchange system, a system wherein these various effects should be most noticeable. However, considerable more data must be had before unique answers can be reached. Additional information needs to be gotten with external solutions more dilute than those studied here and perhaps with a load solution of a concentration between 1.0 and 0.1 normal. The relationships existing between the swelling of the resin and the equivalent fraction of an ionic species in the resin must be determined. The various complex ions that conceivably

exist must be considered. It is felt that by lumping the effects of the free energy change when the resin swells and the energy of association (other than electrostatic) of the cations with the resin into the activity coefficients, that these coefficients can be defined and determined in a manner that will permit the prediction of behavior within the resin. Furthermore, it is hoped that by accurately measuring volume changes, vapor pressures, and other observables, relationships between these quantities and the activity coefficients can be established.

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