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Quantitative studies of the elution of neodymium from high capacity cation-exchange resin with dilute citric acid-ammonium citrate solutions

Jack Edward Powell
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UMI
QUANTITATIVE STUDIES OF THE ELUTION OF NEOXYMIUM FROM HIGH CAPACITY CATION-EXCHANGE RESIN WITH DILUTE CITRIC ACID-AMMONIUM CITRATE SOLUTIONS

by

Jack Edward Powell

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

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1952
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I. INTRODUCTION

The rare earth elements are highly desirable and in great demand as research tools for fundamental scientific studies. Many of the present-day theories of physics, chemistry and metallurgy could be tested critically using this series of elements, since the rare earth atoms differ from each other structurally only by the number of electrons contained in the shielded 4-f subshell and the number of protons in the nucleus. To date, such studies have not been adequate due to the scarcity of pure rare earth salts, in spite of the fact that these elements occur in moderate abundance in nature. They are generally found in rather low concentrations in minerals; are always associated with each other; and, because of their chemical similarity, are extremely difficult to isolate by the classical methods of fractional crystallization and precipitation.

In recent years, however, more practical methods of separating the rare earths by means of ion-exchange have been developed at Ames (1, 2, 3, 4, 5, 6, 7, 8) and elsewhere (9, 10, 11, 12, 13, 14, 15, 16). Using the Ames procedures, all of the naturally occurring rare earths have been isolated spectrographically pure in appreciable quantities and have become much more
readily available for research purposes. As is frequently the case where the demand is great and the supply limited, the art of separating the rare earths by ion-exchange has advanced more rapidly than has the science of their separation. Consequently, little is known about the true mechanism of the process, although much has been learned regarding the conditions necessary for separation. The investigations described in this thesis were performed in order to obtain fundamental information concerning the mechanism of their separation when dilute ammonium citrate solutions are used in conjunction with a sulfonated styrene-divinylbenzene copolymer.
II. HISTORY AND PRESENT STATUS OF THEORIES
OF ION-EXCHANGE

A. History

The discovery of ion-exchange dates back to the middle of the 19th century when Spence, at the suggestion of Thompson (17), passed a solution of ammonia through a tube filled with ground turf in order to investigate the retention of ammonia by cultivated soil. He observed that a chemical exchange took place and that the ammonia in solution was replaced by calcium.

Way (18, 19, 20), shortly thereafter, verified the findings of Spence and Thompson and showed that:

1. Other bases could displace calcium from soil.
2. Equivalent amounts of cations were taken up and liberated in the process.
3. The concentration of the anion in solution remained unchanged during the reaction.
4. The extent of reaction increased with concentration.
5. The temperature coefficient for the rate of exchange was small.
6. Fusion destroyed the ion-exchange properties of the soil.
7. Aluminum silicates present in the soils were responsible for the exchange.

8. Synthetic base-exchange materials could be prepared from sodium silicate and sodium alums.

Way erroneously assumed that the base-exchange reaction was irreversible and it remained for Eichhorn (21) to demonstrate that the exchange of Ca\(^{++}\) for 2 Na\(^+\) in chabazite was actually a reversible process. Somewhat later, Lemberg (22, 23) showed that it was possible to completely transform the mineral leucite \(K_2O\cdot Al_2O_3\cdot 4SiO_2\) into analcrite \(Na_2O\cdot Al_2O_3\cdot 4SiO_2\cdot 2H_2O\) by leaching leucite with sodium chloride and that the transformation could be reversed.

By fusing together quartz, clay and soda, Gans (24, 25, 26) prepared an aluminum silicate base-exchanger which he called Permutit. This material was the first artificial zeolite to be used on a commercial scale for softening water.

Another major development in the field of ion-exchange was the sulfonation of coal, lignite or peat to form a group of exchangers known as sulfonated coals or carbonaceous zeolites (27, 28). These were the first examples of organic ion-exchange materials. It was the discovery by Adams and Holmes (29), however, that resins
prepared from polyhydric phenols and formaldehyde exhibited cation-exchange properties and that resins prepared from aromatic amines, such as phenylenediamine, and formaldehyde could act as anion-exchangers, which led to the development of the large variety of "tailor-made" ion-exchange resins which are known today. Most of the new types of synthetic ion-exchange products have been described in patents. Myers, Eastes and Myers (30) have prepared an extensive review of the patent literature up to the year 1941 and more recent references are to be found in a book by Kunin and Myers (31), a paper by Kunin (32) and a review by Boyd (33). Since this thesis deals with only a single type of resin, it would be beyond the scope of this review to attempt to describe and evaluate any synthetic ion-exchange resins other than the type actually used in the investigation.

One well-characterized type of base-exchange resin commercially available today is the sulfonated copolymer of styrene and divinylbenzene synthesized by D'Alelio (34). Specific directions for the preparation of such a sulfonated copolymer, consisting of 90% styrene and 10% divinylbenzene, have been given by Hale and Reichenberg (35) and directions for preparing spherical particles of polystyrene resin suitable for sulfonation have been presented by Hohenstein and Mark (36).
B. Present Status of Theories

At the present time, the theory of ion exchange is not in a very satisfactory state, since even the simple exchange of two monovalent ions on Dowex 50 has not been adequately explained. The literature on this subject is rather extensive and attempts have been made to explain the exchange phenomena on the basis of many different and sometimes confusing assumptions. While many experimenters have confirmed or denied certain ideas, there remain others which have neither been proved nor disproved completely. Since many of the theories and conclusions which have appeared in the literature do not apply to the work to be described in this thesis, no attempt will be made to give an extensive critical review at this point. However, in order to acquaint the reader with the present status of the subject, a number of the results and conclusions of various investigators will be reported in this section. Any of these results and conclusions which may have a direct bearing on the experimental work presented in this thesis will be discussed later along with results of said work.

Dowex 50, one of the typical sulfonated styrene-divinylbenzene resins which are commercially available,
has been represented by Bauman and Eichhorn (37) as consisting of a permeable hydrocarbon network with attached aromatic nuclei. The aromatic nuclei are sulfonated to the extent that there exist about 1.1 sulfonate groups per benzene ring. The authors have performed chemical analyses for carbon, hydrogen, sulfur, sodium and water and have made capacity measurements which indicate that some of the sulfur may be in the form of sulfone cross-links. They have presented titration data which show that Dowex 50 behaves as a typical strong acid in its chemical reactions and have suggested that the hydrogen ion, or other cation present, may be considered to be completely dissociated within the resin phase.

Bauman and Eichhorn also suggested that the Donnan (38) theory should apply to a resin of this type. It was pointed out that, while the resin cations were free to migrate and exchange with cations from the outside and that both anions and cations were able to diffuse into the resin phase, the sulfonate groups attached to the resin network were not free to migrate into the external solution. In the course of their investigations with hydrochloric acid solutions they found that their data substantiated the Donnan theory in high concentration ranges, but that the theory failed to explain
the results for dilute solutions of hydrochloric acid in contact with the resin.

Bauman and Eischhorn stated that the ion-exchange reaction which occurs when the hydrogen-form resin is immersed in a sodium chloride solution could be considered to be a heterogeneous reaction between the outside solution phase and the resin-gel phase. According to the Donnan concept, equilibrium would be established when

\[ a_{\text{Na}_R} a_{\text{Cl}_R} = a_{\text{Na}_3} a_{\text{Cl}_3} \] \hspace{1cm} (1)

\[ a_{\text{H}_R} a_{\text{Cl}_R} = a_{\text{H}_3} a_{\text{Cl}_3} \] \hspace{1cm} (2)

or

\[ \frac{a_{\text{Na}_R}}{a_{\text{Na}_3}} = \frac{a_{\text{H}_R}}{a_{\text{H}_3}} \] \hspace{1cm} (3)

and for dilute aqueous solutions in which the ratio of the activity coefficients for the monovalent cations approaches unity

\[ \frac{C_{\text{Na}_R} C_{\text{H}_3}}{C_{\text{H}_R} C_{\text{Na}_3}} = \frac{f_{\text{H}_R}}{f_{\text{Na}_R}} = K_m \] \hspace{1cm} (4)

In the above equations, the subscripts, \( S \) and \( R \), refer to the aqueous and resin phases, respectively; \( a \) is the activity coefficient of the ion in the resin phase; \( C \) is
the molar concentration of a component; and $K_m$ is the "molar equilibrium constant" for the reaction

$$
\text{Na}_3^+ + H_R^+ \rightleftharpoons H_3^+ + \text{Na}_R^+
$$

(5)

Bauman and Eichhorn reported a constant value of 1.20 for the "molar equilibrium constant" in the case of ammonium-hydrogen exchange for solution concentrations below 0.1 N, but stated that the value of $K_m$ diminished as the concentration of the solution was increased further. Values of $K_m$ for the exchange of other monovalent ions with hydrogen ion were also determined. The mass-action law was reported to apply to the calcium-hydrogen exchange at a total concentration of 0.1 N.

Several experiments were performed which showed that the rate of exchange between hydrogen and sodium ions for Dowex 50 and low solution concentrations was controlled by the mass-action reaction rate between the ions at the surface of the resin particle. The reaction rate may be expressed by the following equation;

$$
\text{Reaction rate} = k_1 a_{\text{Na}_3} a_{H_R} - k_2 a_{H_3} a_{\text{Na}_R}
$$

(6)

From flow experiments it was found that the rate constant, $k_1$, was dependent upon both the flow rate of the solution over the particles and the size of the resin particles.
The diffusion rates of hydrochloric acid and sodium chloride in the resin phase were reported to be about one fifth as great as in dilute aqueous solution and it was predicted that this rate would become the controlling factor in the exchange rate at solution concentrations above 0.1 molal.

Boyd, Adamson and Myers (39) employed radioactive-tracer techniques in their studies on the kinetics of exchange adsorption of ions. Although they used a phenol-formaldehyde type of resin, Amberlite IR-1, with methylene sulfonic, carboxylic and phenolic exchange groups instead of a sulfonated styrene-divinylbenzene copolymer, they obtained results which agreed essentially with those of Bauman and Eichhorn (37). From their experimental results and certain theoretical considerations, Boyd, Adamson and Myers concluded that for solutions 0.1 M or greater in total electrolyte the rate of exchange was governed by diffusion of the ions in and through the resin phase. For solutions 0.003 M or less the rate of exchange was limited by diffusion through a liquid film at the surface of the resin particle. It was pointed out that a mass-law mechanism was not the controlling factor in the exchange rate, since the rate was found to be dependent upon particle size and upon the flow rate of the solution past the resin particles.
Boyd, Schubert and Adamson (13) have considered ion-exchange first as a heterogeneous process behaving according to Langmuir's adsorption equation and second as a heterogeneous reaction obeying the law of mass-action. In applying the mass-action principle to ion-exchange equilibria, the authors stated that the apparent failure of the mass-law to explain the experimental data of some investigators may have been due to one or all of the following reasons:

1. The chemical equations used to represent the exchange may have been stoichiometrically incorrect, due to hydrolysis of certain ions or to incomplete dissociation of others.

2. Errors may have been introduced as the result of the frequent assumption that the exchange material contained only one type of active group which was capable of exchanging ions, whereas, the exchanger in reality may have been polybasic.

3. The activity coefficients of the ions in the solution and in the solid phase may have been neglected.

They found that their data for the exchange of alkali metal and hydrogen ions substantiated the mass-law equation, which they postulated on the assumptions
that the activities of the ions in the resin phase could be set equal to their mole fractions and that, if the ionic strength were kept low, the ratio of the activity coefficients of the ions in the aqueous phase could be taken as unity. Fair agreement with the mass law was also obtained for the exchange of barium and sodium ions, but the authors noted a slight hysteresis in the equilibrium as they approached it from opposite directions. They reported a somewhat greater hysteresis in the case of the lanthanum-sodium exchange.

Boyd, Schubert and Adamson also postulated the distance of closest approach, $a^0$, given by the Debye-Hückel theory

$$\log \gamma_i = -\frac{A\sqrt{\mu}}{(1+Ba^0/\sqrt{\mu})}$$

should be chosen as the index of ionic hydration in applying the correlation, first observed by Jenny (40), between the order of adsorption affinity of the ions and their hydrated ionic radii. Qualitatively, at least for ions of equal charge, the affinity of an ion for the resin has been shown to increase as the hydrated ionic radius decreases. It has also been established that, in general, affinity increases with the charge of the ion (41, 42, 43, 44), although some overlapping is observed. Boyd, Schubert and Adamson predicted the
following order of decreasing adsorbability for tri-positive ions on the basis of their activity coefficients: La, Ce, Pr, Nd, Sm, Eu, Y, Sc and Al. For the divalent alkaline earths the order predicted was Ba, Sr, Ca and Mg. For the divalent transition metals Boyd and his coworkers predicted the order of decreasing affinity, based on the $a^0$ determined from activity coefficient data, to be: Zn, Cu, Ni, Co and Fe. As will be pointed out later in the review of a subsequent article, this latter series is incorrect, since such factors as the extent of dissociation of the salt must also be taken into consideration.

Kressman and Kitchener (45) studied the exchange equilibria of monovalent cations with a sulfonated phenol-formaldehyde resin. It was demonstrated that the exchange process was completely reversible for monovalent ions by approaching equilibrium from both directions. When a given concentration ratio of monovalent ions was present in solution, the ratio of the concentrations of the ions in resin phase was independent of the total salt concentration in the range from 0.01 to 0.2 M. For the ammonium-potassium exchange it was found that the equilibrium obtained was independent of the anion used, but that the ammonium-thallium equilibrium was different for nitrates than for sulfates.
In the case of thallium, it was pointed out that the sulfate is not as highly dissociated as the nitrate.

Approximately linear functions were obtained when the mole ratio of the ions in the resin phase was plotted against the mole ratio of the ions in the aqueous phase for the exchange of ammonium ion with the other monovalent ions. The equilibrium constants of the monovalent ions against ammonium ion were correlated with the Debye-Hückel distance of closest approach, \( \bar{a} \), and were found to increase as \( \bar{a} \) decreased, which was in agreement with the findings of Boyd, Schubert and Adamson (13). The order of increasing affinity of the ions for the resin, determined by these measurements was: Li, H, Na, K, NH\(_4\), Rb, Cs, Ag and Tl.

Kressman and Kitchener also studied the exchange equilibria of multivalent ions with the sulfonated phenol-formaldehyde resin. The order of increasing affinity for the divalent ions in 0.1 \( \text{M} \) chloride solution was reported to be: Hg, Cd, Mn, Mg, Zn, Cu, Ni, Co, Ca, Sr and Ba. The order of increasing affinity for a few sulfates in 0.1 \( \text{M} \) solutions was: Be, Mg and Mn. The affinity for uranyl nitrate was approximately equal to that for manganous chloride, while lead nitrate fell between strontium and barium chlorides in order of affinity in 0.1 \( \text{M} \) solutions. The above order for the
transition elements Zn, Cu, Ni and Co is opposite from that predicted by Boyd, Schubert and Adamson (13). The authors pointed out that the divalent salts of Cd, Co, Ni, Zn, Mn, Cu and Pb exhibit ion association to such an extent that this becomes the major factor determining the apparent affinity of these ions for the resin. The increase of affinity with increased charge of the ion was noted and discussed. Although Th was held tightly by the resin, Zr was not, due to the formation of ZrO$^{++}$ in aqueous solution.

The authors announced that the affinity of certain large organic cations for the resin increased with increasing size of the ion in contrast to the order observed with the simple inorganic cations and suggested that van der Waals forces might be responsible for this effect. For very large organic cations the rate of attaining equilibrium was extremely slow.

Duncan and Lister (46) have attempted to assess the extent to which the mass-action law may be applied to the case of ion-exchange, using sodium and hydrogen ions with Dowex 50 and Amberlite IR-100H resins. Three methods for obtaining the equilibrium constant were used, namely:

1. **The batch equilibration method.** A given weight of exchanger was allowed to come to equilibrium
with solutions containing different proportions of sodium chloride and hydrochloric acid. The amount of sodium ion taken up from the solution was determined.

2. **The resin bed saturation method.** The volume of solution, containing different proportions of sodium chloride and hydrochloric acid, required to saturate a given bed of exchanger was measured. Pure sodium chloride solution alone was used to obtain the total capacity of the bed and the mole fraction of sodium on the bed at equilibrium for the other solutions was obtained very simply in this manner.

3. **By calculation from the rear boundary of a chromatogram.** The chromatographic studies of DeVault (47) and Glueckauf (48, 49, 50) have shown that the adsorption isotherm of a solute on an adsorbent may be derived by calculation from the rear boundary of the curve obtained upon elution of an adsorbed band. The method of calculation used in this paper was given by Glueckauf (51); a complete discussion is beyond the scope of this thesis.

In their experiments, concerned with saturating beds of acid-form Dowex 50 with sodium ion in conjunction
with hydrochloric acid at a very slow flow rate, Duncan and Lister (46) observed that immediately after breakthrough of the sodium ion the concentration of sodium in the eluate rose sharply to its concentration in the solution used to saturate the bed. When sodium chloride solutions were introduced at the top of a bed originally in the hydrogen cycle, it was found that the pH of the eluate, after the sodium ion breakthrough, rose rather slowly to the pH of the solution being introduced, indicating that the last stages of the exchange occurred much more slowly than did the bulk of the reaction. When the adsorbed sodium was eluted with hydrochloric acid solution of the same normality as the total of the salt plus the acid in the saturating solution, it was found that the eluate contained the same ratio of sodium to hydrogen ion as was present in the solution used to load the bed originally. The rear boundaries, obtained upon elution, were in general more diffuse than the front boundaries obtained in the saturating step. This is not surprising since the equilibrium constant for the reaction

$$\text{Na}^+ + \text{H}_2 \text{R}^+ \rightleftharpoons \text{H}_3^+ + \text{Na}_2$$

is greater than unity. It can readily be seen from the equilibrium constant
\[ K_m = k_1/k_2 = C_{H_S} C_{Na_R} / C_{Na_S} C_{H_R} \] (9)

that, since \( K_m \) is greater than 1.0, the forward rate of reaction (8) is more rapid than the rate in the opposite direction and hence the forward reaction should reach completion in a shorter distance of travel down the bed.

It was stated that the sharp front boundary, formed at slow flow rates, became more and more diffuse at flow rates above \( 16 \times 10^{-3} \) centimeters per second (0.96 cm./min.) and that larger volumes of eluant were required to completely remove the sodium from the bed at the more rapid rates.

It was observed in these experiments that the equilibrium constant for the sodium-hydrogen exchange was somewhat dependent upon the mole fraction of sodium in the resin phase. Data from batch, break-through and chromatographic determinations were in good agreement. The value of the equilibrium constant was observed to decrease as the temperature was increased.

Topp and Pepper (52) prepared a number of ion-exchange materials and studied their titration curves. Such curves provide information as to the number and type of functional groups present.

Using a sulfonated coal ion-exchanger, Nachod and Wood (53) showed that monovalent ions exchanged more
rapidly than divalent ions. They showed that the capacity of the exchanger, Zeo-Karb, increased as the hydrated ionic radius increased, for both monovalent and divalent cations, and that the capacity was higher for divalent cations than for monovalent cations. This is a phenomenon which is not generally observed with the sulfonated synthetic exchangers. The sulfonated coal apparently contained functional groups, such as carboxylic and phenolic, which were more weakly ionized than the sulfonic acid group.

Argersinger, Davidson and Bonner (54) developed expressions from the law of mass action and the Gibbs-Duhem (55) equation which they used to determine apparent activity coefficients for ions in the resin phase.

For the reaction

\[ vA^+ + uB^+ \rightleftharpoons uB^+ + vA^+ \] (10)

the thermodynamic equilibrium constant is

\[ K = \frac{N_A f_A \gamma_A u_B \gamma_B u}{N_B f_B \gamma_A u_A \gamma_B u} = K_a \frac{f_A}{f_B} \] (11)

in which \( N \) is the mole fraction of an ion and \( f \) its activity coefficient in the resin phase; \( C \) is the molar concentration of an ion and \( \gamma \) its activity coefficient in the aqueous phase; and \( K_a \) is the apparent equilibrium
constant which gives no credence to the activity coefficients of the ions in the resin phase, but has been corrected for the activity coefficients in the aqueous phase. A and B refer to the ions undergoing exchange.

The logarithm of the last term in equation (11) is

\[ \ln K = \ln K_A + v(\ln f_A) - u(\ln f_B) \] (12)

and upon differentiating the following equation is obtained

\[ -d(\ln K) = v \, d(\ln f_A) - u \, d(\ln f_B) \] (13)

Argersinger, Davidson and Bonner assumed that the system involved only the two ions A and B and applied the Gibbs-Duhem equation

\[ N_A \, d(\ln f_A) + N_B \, d(\ln f_B) = 0 \] (14)

Solving equations (13) and (14) simultaneously

\[ v \, d(\ln f_A) = \frac{-vN_B}{uN_A + vN_B} \, d(\ln K) \] (15)

and

\[ u \, d(\ln f_B) = \frac{uN_A}{uN_A + vN_B} \, d(\ln K) \] (16)

Introducing a new general variable, x, defined as

\[ x = \frac{uN_A}{uN_A + vN_B} \] (17)
then

\[ v \, d(\ln f_A) = -(1-x) \, d(\ln K_a) \quad (18) \]

and

\[ u \, d(\ln f_B) = x \, d(\ln K_a) \quad (19) \]

Integrating by parts

\[ -v \, \ln f_A = (1-x)(\ln K_a) - \int_x^1 (\ln K_a) \, dx \quad (20) \]

\[ u \, \ln f_B = x(\ln K_a) - \int_0^x (\ln K_a) \, dx \quad (21) \]

Substituting (20) and (21) into (12) leads to

\[ \ln K = \int_0^1 (\ln K_a) \, dx \quad (22) \]

For sodium-hydrogen exchange

\[ -\ln f_{Na} = (1-N_{Na})(\ln K_a) - \int_{N_{Na}}^1 (\ln K_a) \, dN_{Na} \quad (23) \]

\[ \ln f_H = N_{Na} (\ln K_a) - \int_0^{N_{Na}} (\ln K_a) \, dN_{Na} \quad (24) \]

and

\[ \ln K = \int_0^{N_{Na}} (\ln K_a) \, dN_{Na} \quad (25) \]

These equations may be readily evaluated using the methods of graphical integration from a plot of \( \ln K_a \) versus \( N_{Na} \).
A number of sulphonated resins containing styrene copolymerized with varying amounts of divinylbenzene were prepared and examined by Reichenberg, Pepper and McCauley (56) in the light of the theory by Gregor (57) that

\[ RT \ln K_D = \Pi (\bar{V}_A - \bar{V}_B) \]  

(26)
in which \( K_D \) is the selectivity ratio; \( \Pi \) is the osmotic pressure within the resin phase; and \( \bar{V}_A \) and \( \bar{V}_B \) are the partial molal volumes of the exchanging ions A and B.

The divinylbenzene content of the styrene-divinylbenzene copolymer was varied from 2 to 33% and it was reported that the amounts of water adsorbed per gram of dry hydrogen-form resin varied from 3.35 grams for the 2% copolymer to 0.55 grams for the 33% copolymer. From Gregor's theory it was deduced that, if \( \bar{V}_A \) was greater than \( \bar{V}_B \), then \( K_D \) was greater than one. Their data showed this to be true (except for resins of high cross-linking at high values of \( N_A \)) in accord with the view that the hydrogen ion in aqueous solution is larger than the sodium ion, due to its higher degree of hydration. Furthermore, they deduced that, if \( \bar{V}_A \) was greater than \( \bar{V}_B \), then, as the mole fraction of B in the resin increased, the resin should contract and \( \Pi \) decrease. If \( \bar{V}_A \) and \( \bar{V}_B \) remained roughly constant and were inde-
dependent of the mole fraction of \( E \) in the resin phase, then it followed that \( K_D \) should decrease as the mole fraction of \( E \) increased. The decrease of \( K_D \) for the sodium-hydrogen exchange with increased mole fraction of sodium in the resin phase was observed with the 17 and 33% resins. It was finally predicted that, at a given ionic composition, \( \Pi \) should depend upon the elastic properties of the resin; hence, the greater the degree of cross-linking, the greater the elastic modulus and the smaller the volume of the swollen resin at equilibrium. The smaller the volume the greater would be the value of \( \Pi \) due to the increased concentration of osmotically active groups. Therefore, if \( (V_A - V_B) \) remained approximately constant for resins of different cross-linking, then the numerical value of \( \ln K_D \) should increase with the amount of divinylbenzene in the copolymer; conversely, a resin having low cross-linking should have a value of \( K_D \) nearly equal to unity for all values of the mole fraction of sodium in the resin phase. This prediction was borne out by the results for the 2% divinylbenzene resin. Since the theory did not predict the drop in \( K_D \) below unity for high sodium content which was observed, Reichenberg, Pepper and McCauley proposed that there could possibly have been some oxidation during the drastic sulphonation required.
by the highly cross-linked resins giving rise to
carboxyl groups as well as sulfonic acid groups on the
resin. It was observed that the 33% resin had a some­
what higher exchange capacity when titrated with base than
that obtained in more acidic solutions. The theory also
failed to account for the portion of the curves, obtained
with 5 and 10% divinylbenzene resins, in which K_D in­
creased with increasing mole fraction of sodium.

Gregor (57, 58) extended the theories of Donnan and
Guggenheim (59) and Donnan (60) to ion-exchange systems.
In particular he considered the pressure-volume free
energy changes which occur when ions in the resin phase
are replaced by others. He considered the internal
volume of the resin, $V_1$, to be the difference between the
total external volume of the resin, $V_2$, and the incom­
pressible portion of the hydrocarbon matrix, $V_3$. He
postulated that the inner phase associated with $V_1$ was
in direct contact with the external solution which was
of infinite volume and at atmospheric pressure.

When the resin was swollen by the internal solution,
a Hooke's law relationship was assumed to apply, namely,

$$ V_1 = m \Pi + b $$

in which $\Pi$ is the osmotic pressure within the resin
phase and $m$ and $b$ are arbitrary constants which depend
upon the system under consideration.

The following assumptions were made by Gregor in the further development of his theory.

1. The hydrated volumes of all ionic and molecular constituents were constant throughout the process.

2. The fixed groups and the movable ions did not interact chemically, but were completely dissociated at all times.

3. The volume of the fixed anionic group was constant.

4. For this ideal system all activity coefficients were unity.

In the notation used by Gregor, $n_1$ moles of cations of molar volume, $v_1$, and $n_0$ moles of water of molar volume, $v_0$, made up the volume, $V$, and the osmotic pressure could be calculated according to the equation

$$
\Pi = \frac{RT}{V_0} \ln \frac{(X_0)^o}{(X_0)^1}
$$

in which $X_0$ is the mole fraction of the water and the subscripts, 1 and 2, refer to the resin and external phases, respectively. It was pointed out that as larger ions assume the exchange positions the volume of the system should increase slightly, but at the same time the
solvent volume $n_0v_0$ should decrease, resulting in a sharp increase in the osmotic pressure. For dilute solutions, the diffusible anions would be almost completely excluded from the resin phase by the Donnan effects. When ions enter or leave the system, a certain amount of solvent also enters or leaves simultaneously and the reaction taking place is

$$A_0^+ + fS_0 + B_1^+ + gS_1 \rightleftharpoons A_1^+ + fS_1 + B_0^+ + gS_0$$

(29)

in which $A$ and $B$ are the exchanging cations; $f$ and $g$ refer to the numbers of moles of solvent $S$ accompanying the ions; exclusive of the solvent of solvation.

The equilibrium constant for this somewhat more complicated process is

$$K = \left( \frac{x_1}{x_2} \right) \left( \frac{x_2}{x_1} \right) \left( \frac{x_0}{x_0} \right) \left( f-g \right)$$

(30)

using $x$ to represent mole fractions and the subscripts 0, 1 and 2 to refer to the solvent, cation $A$ and cation $B$, respectively. Gregor stated that the Donnan equation for the reaction

$$RT \ln \left[ \left( \frac{x_1}{x_2} \right) \left( \frac{x_2}{x_1} \right) \left( \frac{x_0}{x_0} \right) \left( f-g \right) \right] = \Pi [v_2 - v_1(f-g)v_0]$$

(31)

would apply to this ideal system of monovalent ions and derived the following simple expression
On the basis of these equations, Gregor made the following predictions.

1. The volume of an ion-exchange resin should vary directly with the volume of hydrated ions in the exchange positions.

2. The selectivity ratio, \( K_D \), should increase as \( \Pi (v_2 - v_1) \) increases at a constant ion concentration ratio in the external solution.

3. \( K_D \) should increase as the value of \( (n_1/n_2)_o \) decreases.

4. \( K_D \) should increase as \( \Pi \) increases for systems which constitute "stiffer springs" and will decrease as \( \Pi \) decreases, as may result from the counter-osmotic pressure developed by a high concentration of ions in the external phase.

These predictions were checked experimentally and the data obtained agreed, at least qualitatively, with the theory.

The counter-osmotic effect of the external electrolyte was also considered by Gregor. For the process

\[
A_o^+ + B_o^- + qS_o \rightleftharpoons A_1^+ + B_1^- + qS_1
\]  

it followed that
\[
RT \ln \frac{(X_1X_2)_1}{(X_1X_2)_0} = -\Pi(v_1 + v_2) \tag{34}
\]

in which the subscripts, 1 and 2, refer to the cation and anion, respectively. Since \( X_1 = n_1/(n_1+n_2) \) and \( X_2 = n_2/(n_1+n_2) \), substituting \( n = n_2 = (n_1-F) \) and \( (n_1+n_2) = (2n_2+F) \), where \( F \) is the number of moles of fixed anionic groups and \( n \) is the number of moles of the mobile anion inside the resin, then

\[
RT \ln \frac{n(F+n)}{(3n+F)^2} \cdot \frac{1}{(X_1X_2)_0} = -\Pi(v_1 + v_2) \tag{35}
\]

Experimentally, Gregor has shown that the deswelling effect of the counter-osmotic pressure was not significant unless the external concentration of electrolyte was an appreciable fraction of the concentration of fixed anionic groups in the resin phase. For external concentrations below 0.1 \( M \) the amount of non-exchange electrolyte in the resin phase was negligible and no appreciable deswelling of the resin was observed.

Gregor also considered the non-ideal case for uni-univalent exchange and suggested methods for evaluating the parameters, \( m \), \( b \) and \( \Pi \). For further information concerning this subject the reader is referred to the original work.

Gregor, Held and Bellin (61) have examined various
methods of determining the specific volume and density of wet resin particles. Their chief problem was the removal of surface water without losing any absorbed water from the sample. The best technique found was to use the solution with which the resin was equilibrated as the pycnometric fluid, then to centrifuge the sample rapidly to remove the surface water, or to plot the wet weight versus the relative humidity and extrapolate to a relative humidity of 100%. Drying by suction or blotting gave low results.

Gregor, Gutoff and Bregman (62) determined the volumes and weights of both wet and dry samples of Dowex 50 in various states. Their values given for the external volume, \( V_e \), the wet weight, \( W_e \), and the dry or matrix volume, \( V_m \), for a given ionic form are those volumes and weights obtained from 1.000-g. samples of dry, hydrogen-form Dowex 50 which have been converted to the desired forms and equilibrated with 0.001 m solutions of the ions. The resinates of the alkali, alkaline earth, hydrogen, ammonium, silver, thallous, magnesium, tetramethylammonium, tetraethylammonium and phenyltrimethylammonium ions with Dowex 50 have been studied, as well as the resinates of potassium, ammonium, lithium, tetramethylammonium, and tetraethylammonium ions with other sulfonated styrene-divinylbenzene resins. The
deswelling of these resins in ammonium chloride solutions was also studied.

It was shown that $v_e$, for a given resin, increased with the hydrated ionic volume of the exchange cation, except where ion-pair formation took place. It was also shown that $v_e$ increased sharply as the degree of cross-linking of the resin decreased. The deswelling of resins in concentrated solutions was described and the mean ionic activity coefficient of the mobile electrolyte within the resin phase was calculated.

Gregor and his associates (63) also studied the exchange capacity of various styrene-divinylbenzene copolymers which they synthesized. The exchange capacities were found to be identical for all monovalent cations studied, but the capacity of a resin for the divalent ions investigated was somewhat greater than its capacity for monovalent ions, especially in the case of Mg$^{2+}$. It was postulated that a complex ion such as MgOH$^+$ or MgCl$^+$ was formed. A study of the rate of uptake of ions showed that large ions reacted much more slowly with the exchanger than small ions and that this effect was more pronounced the more highly cross-linked the polymer.

Lowen and co-workers (64) studied the exchange which takes place when hydrogen-form Dowex 50 is immersed
in a solution of the salt of another ion and vice versa. They also investigated the effect of ionic strength on the equilibrium constant for the ammonium-hydrogen exchange. It was shown that the apparent equilibrium constants, $K_a$, vary with the mole fractions of the ions in the resin phase for sodium-hydrogen, ammonium-hydrogen, silver-hydrogen, thallous-hydrogen, thallous-ammonium, nickel-hydrogen, calcium-hydrogen and nickel-calcium exchange systems. It was also demonstrated that the equilibrium constant, $K_a$, varied with ionic strength in the case of the ammonium-hydrogen exchange and that for low concentrations of external electrolyte the value of $K_a$ decreased and approached unity when the mole fraction of ammonium ion in the resin phase was increased.

Bonner, Argersinger and Davidson (65, 66) have investigated the factors involved in cation-exchange equilibria and calculated the activity coefficients of the ions in the resin phase by the method of graphical integration, developed earlier. It was pointed out that errors in simple computation of equilibrium compositions may arise from the following three factors which are sometimes neglected:

1. The absorption or desorption of water by the resin phase.
2. The uptake of electrolyte by a process other than
ion-exchange.

3. The change in volume of the solution accompanying the exchange of electrolytes of different apparent molar volume.

The authors concluded that only the first of these factors was of any magnitude in the case of dilute solutions, but that the measurement of both solution and resin phase concentrations was necessary in order to prevent errors in the calculation of $K_a$.

It was shown that the value of $K_m$ for the ammonium-hydrogen exchange between solutions of hydrochloric acid and ammonium chloride and Dowex 50 resin approached the value of one as the mole fraction of ammonium ion in the resin phase approached unity. This factor is of great importance in the following investigations concerned with the elution of neodymium from columns of hydrogen-form resin, using dilute solutions of citric acid and ammonium citrate. In this case, the mole fraction of ammonium ion in the resin phase is always large compared to the mole fraction of hydrogen ion, hence, the molar equilibrium constant for the exchange of ammonium and hydrogen ions may be set equal to one.

An exhaustive, critical review of many of the preceding theories has been presented by Marinsky as part of his doctoral thesis. Since the review of theories
and the experimental portion of his thesis has appeared
in a technical report, the reader is referred to this
source for further information regarding these theories
of ion-exchange (67). Marinsky has indicated that his
experimental results, concerned with the ion-exchange
equilibria between hydrogen ion and sodium, calcium,
barium and cerium ions, are contrary to the Donnan
membrane theory and the assumption by Bauman and Eichhorn
(37) and others (57, 58) that there is complete ionization
within the resin phase. He stated that his data was in
better agreement with the concept of Juda and Carron (68),
that any cation in resin phase may be in part sterically
fixed by chemical binding and in part free to migrate.

There have appeared in the literature other theoret­
ical papers, some simple in their basic assumptions (47,
69, 70) and others involving more complex mechanisms
(48, 71, 72). However, since these papers are not needed
in interpreting the experimental results of this thesis,
it was felt that the description of these general theories
would unduly lengthen this review and the reader is re­
ferred to the original articles for further details. The
same statement applies to a number of experimental papers
which are concerned with ion-exchange phenomena, but
which have little or no bearing upon the ion-exchange
equilibria of rare earths with ammonium citrate solutions.
III. RESEARCH

A. Materials and Apparatus

1. Materials

The source of the neodymium was crude neodymium carbonate, code #630, manufactured by the Lindsay Light and Chemical Company, West Chicago, Illinois. After ignition the composition of the oxide mixture was: 76% Nd₂O₃, 11% Sm₂O₃, 9% Pr₆O₁₁ and 4% other rare earth oxides. The carbonate was dissolved in hydrochloric acid and purified by the ion-exchange procedure developed in these laboratories (6).

Aliquots of the acid solutions, each containing the equivalent of 325 grams of R₂O₃, were diluted to 45 liters and passed slowly down -30+40 mesh-size, Nalcite HCR, resin beds which were 6 inches in diameter and 30 inches long and initially in the hydrogen cycle. The acid, liberated during the adsorption step, was then washed out of the resin beds with distilled water and the adsorbed rare earths were eluted down the columns with 0.1% citric acid solution, adjusted to a pH of 6.1 with ammonium hydroxide. A linear flow rate of 0.5 cm./min. was used throughout the elution and the eluate was collected in 45-liter fractions as it drained from the resin beds. The rare earths were recovered by
adding 200 grams of oxalic acid crystals to each 45-liter fraction of the eluate which was collected after break-through of the rare earths occurred. The oxalate precipitate was filtered off and ignited to the oxide at 800°C. The individual fractions of neodymium oxide were analyzed spectrographically for trace impurities by the spectrographic group, directed by Dr. V. A. Fassel, and those samples consisting of greater than 99.9% Nd₂O₃ were combined and used in subsequent experiments.

The citric acid used for purifying the neodymium and in the experiments to be described was U.S.P. purity, anhydrous citric acid manufactured by the Mallinckrodt Chemical Works, St. Louis, Missouri, it contained a minimum of 99.5% anhydrous citric acid.

The resin used in the small ion-exchange columns, described under apparatus, was the sulfonated, styrene-divinylbenzene copolymer manufactured by the National Aluminate Corporation, Chicago, Illinois, and sold under the trade name of Nalcite HCR. A standard sample of resin was prepared in the following manner. Six kilograms of -40+50 mesh-size particles were screened from a large amount of commercial grade Nalcite HCR cation-exchange resin which had been previously air-dried at room temperature for a week. The -40+50 mesh-size spheres of resin, ranging in diameter from
0.42 to 0.30 mm., were poured into a Pyrex glass column filled with distilled water. The resin bed was carefully back-washed with distilled water in order to remove air bubbles and any fine particles which were not removed by the screening process. The resin was then converted successively to the ammonium and the hydrogen cycles, using 5% citric acid, adjusted to a pH of 6 with ammonium hydroxide, and 5% by volume hydrochloric acid solutions, respectively. The resin bed was carefully rinsed with distilled water to remove any unadsorbed acid; then the resin was removed from the column and spread out in a thin layer to dry. After drying for 10 days, the resin was again screened and the particles which passed through a U.S. Standard No. 40 screen and were retained on a U.S. Standard No. 50 screen were stored in a closed reagent bottle to protect them from laboratory fumes and changes in humidity until they were used.

2. Apparatus

The ion-exchange columns, used in the following experiments, were constructed of Pyrex glass tubing and were 4 \(\frac{3}{8}\) feet long with a bore of approximately 22 mm. Each column was closed near the bottom with a fritted glass disc to support the resin bed and drawn down at the bottom to a nipple 9 mm. in diameter. The nipple was fitted with a piece of Tygon tubing, a capillary
tip and a screw clamp to control the flow of solution through the column. The columns were then calibrated by adding water from a burette in order to correct for differences in diameter. The exchanger bed of each column consisted of a 200-gram sample of the standard, air-dried, acid-form, Nalcite HCR described previously. The columns were partly filled with distilled water before the air-dried resin was poured in the top, since the pressure exerted when dry resin absorbs water is sufficient to crack the walls of a column. The beds were then back-washed and rinsed with a 5% solution of hydrochloric acid followed by distilled water. The resulting resin beds were approximately 100 cm. long.

All pH measurements were made with a Beckman, Model G, Laboratory pH Meter. The instrument was adjusted to a pH of 7.00 with standard buffer solution supplied by the National Technical Laboratories, South Pasadena, California. The pH of 7.00 setting was then checked against a standard buffer solution at pH values of 7.00 and 4.00 prepared from certified buffer tablets compounded by Coleman Instruments, Inc., Maywood, Illinois.

B. Procedures and Results

1. Preparation of standard citrate eluant

The large stainless steel tank, calibrated to a
volume of 2500 liters and equipped with a motor-driven, stainless steel stirrer, was filled to the 2500-liter mark with distilled water and 2500 grams of anhydrous, U.S.P. grade, citric acid were added. After thorough stirring, a 2-liter portion of the citric acid solution was withdrawn to check the citric acid content and sufficient concentrated ammonium hydroxide was added to the tank to give the lowest pH value desired for a particular experiment. Enough of this citrate solution to provide all the eluant needed for the complete elution of a column was pumped into covered, 45-liter Pyrex carboys for storage, then the pH of the solution in the tank was increased to the next higher pH value by the addition of another small portion of concentrated ammonium hydroxide. This procedure was repeated until eluant was provided for all of the columns to be operated. For pH values from 5.5 to 7.5, the amount of ammonium hydroxide required to adjust 2500 liters of 0.1% citric acid solution ranged from about 2.0 to 2.5 liters. The addition of this quantity of liquid to the tank caused a dilution of less than 0.1% and was considered to be negligible.

The concentration of ammonium ion in each batch of eluant was determined by adding excess sodium hydroxide to an aliquot of the solution, distilling the liberated
ammonia into a receiver of 4% boric acid solution and titrating the ammonium borate with standard hydrochloric acid solution, using methyl purple as an indicator.

The amounts of ammonia found at various pH values for 0.1% citrate solutions are given in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Total citrate (meq. per liter)</th>
<th>pH</th>
<th>NH₄⁺ concentration (meq. per liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.60±.02</td>
<td>7.30±.02</td>
<td>15.59±.03</td>
</tr>
<tr>
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</tr>
<tr>
<td>15.56</td>
<td>5.60</td>
<td>11.17</td>
</tr>
</tbody>
</table>

2. **Determination of resin capacity**

A 5.00-gram sample of the standard air-dried, Nalcite HCR resin was loaded into each of two short columns, treated with dilute acid to ensure their being completely
in the hydrogen cycle and then rinsed with distilled water until the washings were neutral. A total of 500 ml. of 1 M NaCl solution was passed through each bed over a period of 48 hours. At this time the pH of the effluent was equal to the pH of the influent solution for both columns. The liberated acid was titrated with standard base using phenolphthalein as an indicator. The capacities observed were 4.25 and 4.27 meq./gram of air-dried resin giving an average value of 4.26 meq./gram. Later, a 8.392-gram sample of the standard air-dried resin was placed in a small column, treated with acid and washed. A total of 1 liter of 0.05 M NdCl₃ solution, having a pH of 4.87, was passed through the resin over a period of 24 hours at which time the pH of the effluent solution was 4.87. Aliquots of the effluent solution were titrated with standard sodium hydroxide back to a pH of 4.87. After rinsing out any unadsorbed neodymium chloride with distilled water, the adsorbed neodymium was eluted from the resin with 6 liters of 0.1% citrate solution at a pH of 7.4, recovered as the oxalate and ignited to the oxide for weighing. The acid liberated by the neodymium chloride solution amounted to 4.26 meq./gram and amount of neodymium recovered upon elution amounted to 4.26 meq./gram of air-dried resin. The agreement between the equivalents of acid liberated by either
sodium or neodymium ion and the amount of neodymium adsorbed constituted an excellent check on the equivalence of exchange and showed that no neodymium was adsorbed as a complex ion under these conditions.

3. Adsorption of neodymium on the resin bed

Samples of Nd$_2$O$_3$ ranging from 1.00 to 10.00 grams were dissolved in a slight excess of hydrochloric acid (1.5 ml. of concentrated hydrochloric acid were used per gram of oxide). The chloride solutions were diluted to 4 liters each with distilled water and adsorbed on prepared resin beds using a flow rate of about 2 cm./min. The last bits of these solutions were rinsed through the columns with distilled water in order to remove the acid formed in the adsorption step.

4. Observation and measurement of adsorbed neodymium bands

There is sufficient difference in color between hydrogen-form and neodymium-form Malcite HCR to allow the length of the initially adsorbed band to be measured. When elution of the band is in progress, however, the rear edge of the band is not visible under white light. During the course of experiments to determine the optimum condition for the separation of rare earth mixtures by ion-exchange, it became desirable to be able to determine the positions of the bands visually. Since certain
of the rare earth ions are colored in solution, it was thought that it should be possible to observe the concentrated bands on the resin bed if the columns were illuminated properly. It was subsequently found that, if the columns were illuminated with blue light in a darkened room, the neodymium bands could readily be seen as dark bands which contrasted sharply with the rest of the resin bed. The neodymium bands were sufficiently distinct under these conditions to be photographed, if desired, and many of the fine details of channeling in the resin bed could be observed visually. For this reason neodymium was used in all experiments which were performed to study the movement of rare earth bands on resin beds. It was found that neodymium bands on the resin bed could be photographed readily using filtered blue light with Eastman Kodak, Contrast Process Ortho Film. Figures 1 and 2 illustrate these techniques.

5. The elution of neodymium down a bed of Nalcite HCR

In previous publications (6, 8) it was reported that an insoluble rare earth complex, identified by Tevebaugh (73) as RCit·2H₂O, formed at pH values above six with initial loads in excess of about 1.2 grams of Nd₂O₃ per square centimeter cross-section of resin bed. The following preliminary experiment was performed in
Fig. 1. Fully Developed Narrow Neodymium Bands on Ion-Exchange Columns

Photographed Under Blue Light
Fig. 2. A Fully Developed Narrow Neodymium Band
          Showing Extreme Channeling
order to determine how the formation of this precipitate might be prevented and to study the movement of the neodymium bands on the resin bed.

Four Nalcite HCR resin beds, 22 mm. in diameter and about 100 cm. long, were prepared as previously described. One of the columns was loaded with a sample prepared from 2.8045 grams of Nd$_2$O$_3$ dissolved in 4.2 ml. of concentrated hydrochloric acid; two columns were loaded with 5.6090-gram samples of Nd$_2$O$_3$ dissolved in 8.3 ml. of acid; and the remaining column was loaded with a 5.6090-gram sample of Nd$_2$O$_3$ dissolved in 83 ml. of acid. The details of loading the columns have been described above. The columns were eluted with 0.1% citrate at a pH of 6.20. All of the columns, except one of those with a load consisting of 5.6090 grams of Nd$_2$O$_3$ in 8.3 ml. of acid, were eluted at a flow rate of 0.5 cm./min.; this one column was eluted at half the flow rate of the others. A precipitate of considerable magnitude was observed in the latter column after about 3.2 liters of eluant had been passed into the column. This precipitate almost completely blocked the pores of the bed at a volume of 7.5 liters and the column was shut off. A very slight precipitate was observed in the other column, which was loaded identically but operated at the 0.5 cm./min. flow rate, when 6.3 liters of eluant had been passed into the
column. The precipitate redissolved gradually and was no longer visible at a volume of 16.3 liters. Neither of the other two columns showed any traces of precipitation. From this evidence it was concluded that a fast flow rate, a smaller initial sample and the addition of excess acid to the initial sample all tended to prevent the formation of the precipitate. It was apparent, from the fact that the precipitate redissolved as the neodymium band moved down the column and spread out, that a simple way to avoid precipitation at high pH values and with heavy loads would be to elute the column rapidly in the first stages of the development and then reduce the flow rate in the later stages. This technique has been employed throughout most of the experiments to be described in this paper.

Figure 3 shows the length of the adsorbed band from the 2.8045-gram load as well as the positions of the leading and trailing edges of the band, measured from the top of the bed at the time elution was begun. The band length increased steadily until a length of 15.4 cm. was reached and then remained constant. The front edge of the band progressed at a constant rate throughout the elution. The rear boundary of the band advanced steadily, but more slowly than the front boundary, during the first part of the experiment; subsequently, the rate of move-
Fig. 3. The Development of an Adsorbed Neodymium Band During Elution
ment of the rear edge increased abruptly to the rate the front edge was traveling as the neodymium band reached its fully developed state.

Figure 4 shows the effect of excess acid on the adsorbed sample. The amount of acid used in case (A) was just sufficient to dissolve the neodymium sample; in case (B) ten times as much acid was used for the same size sample. The excess acid doubled the length of the initially adsorbed band. Upon elution, the length of the band formed in case (A) increased at a constant rate until it was developed. The adsorbed band in case (B) decreased in length until it became equal to the developing band from the former sample, then it increased at a constant rate until the band was fully developed. The slight difference in the slopes of curves (A) and (B) in Figure 4 was due to a small difference in the diameters of the two columns. Column (B) was slightly larger in diameter, hence the fully developed band was somewhat narrower.

By comparing curves (A) and (C), it can be seen that the rate of increase in band length was independent of the amount of sample originally adsorbed. With the 5.6090-gram load the lengths of the initial and the developed bands were essentially double those of the
Fig. 4. The Effects of Excess Acid and Size of Sample on the Subsequent Elution

(A) 5.6090 g. Nd$_2$O$_3$ dissolved in 8.3 ml. of hydrochloric acid
(B) 5.6090 g. Nd$_2$O$_3$ dissolved in 83 ml. of hydrochloric acid
(C) 2.8045 g. Nd$_2$O$_3$ dissolved in 4.2 ml. of hydrochloric acid
2.8045-gram load. Again the small discrepancies were due to a slight variation in the diameters of the columns.

Following the preliminary experiment just described, a number of experimental runs were made in which series of columns were loaded with sufficient neodymium ion to give bands 15-30 cm. long when fully developed and eluted with 0.1% citrate solution at pH values ranging from 5.4 to 7.4. Quantitative data, concerning the movement of bands on the column and the concentration of ions in the aqueous and resin phases, were obtained.

(a) First experimental run. In the first run a series of seven columns were prepared as previously described. Five of the columns were loaded with samples prepared from 5.00-gram samples of Nd$_2$O$_3$, one was loaded with 3.00 grams of the oxide and one with 1.50 grams. The samples were eluted at a flow rate that was controlled at 0.5 - 0.6 cm./min. throughout the run with 0.1% citrate solutions at pH values of 7.4, 7.1, 6.8, 6.5, 6.2, 5.9, and 5.6, respectively. A dense precipitate formed in the column operated at a pH of 5.8 shortly after the experiment was started and blocked the pores of the resin bed to such an extent that the elution of this column had to be discontinued.

The positions and lengths of the bands were measured periodically and, as the fronts of the bands reached a
point about 25 cm. from the bottoms of the resin beds, a number of appendages, containing weighed samples of standard resin, were attached to the outlets of the columns. The bands were then allowed to move onto the appendages.

Some of the resin samples were placed in a distillation apparatus where the adsorbed ammonia was evolved by means of sodium hydroxide, distilled into a receiver of boric acid solution, and titrated with acid. The adsorbed neodymium in the remaining resin samples was recovered by ashing the resin, dissolving in hydrochloric acid, precipitating as the oxalate, and igniting to the oxide for weighing.

The ammonium ion in the eluate in contact with the developed band was determined by the evolution method described above and the neodymium in the aqueous phase was determined by simply precipitating it as the oxalate and igniting the oxalate to the oxide for weighing. Analytical data for this experiment are given in Table 2.

The distribution ratios of the ammonium ion and of the neodymium between the resin-gel and the aqueous phase have been compared, in Table 2, to the ratio of the resin capacity to the concentration of the ammonium ion in the eluant, that is \( Q/\text{NH}_4^+ \). The reason for this correlation will be discussed later.
### Table 2

Analytical Data from the First Experimental Run

#### The Aqueous Phase

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>$\text{NH}_4^+$ in eluant (meq. per liter)</th>
<th>$\text{NH}_4^+$ in eluate (meq. per liter)</th>
<th>Nd in eluate (meq. per liter)</th>
<th>pH of eluate (meq. per liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>15.39 ± 0.03</td>
<td>8.16 ± 0.03</td>
<td>7.42 ± 0.02</td>
<td>6.79 ± 0.01</td>
</tr>
<tr>
<td>7.1</td>
<td>15.19</td>
<td>8.21</td>
<td>7.16</td>
<td>6.40</td>
</tr>
<tr>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>14.10</td>
<td>8.45</td>
<td>5.70</td>
<td>5.70</td>
</tr>
<tr>
<td>6.2</td>
<td>13.04</td>
<td>8.80</td>
<td>4.36</td>
<td>5.52</td>
</tr>
<tr>
<td>5.9</td>
<td>11.92</td>
<td>9.21</td>
<td>2.85</td>
<td>5.40</td>
</tr>
<tr>
<td>5.6</td>
<td>10.94</td>
<td>9.66</td>
<td>1.51</td>
<td>5.34</td>
</tr>
</tbody>
</table>

#### The Resin Phase

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>$\text{NH}_4^+$ in resin (meq. per gram)</th>
<th>Nd in resin (meq. per gram)</th>
<th>$\text{Nd}_R^+$/Nd$_3$</th>
<th>$\text{Nd}_R^+$/Nd$_3$</th>
<th>$\text{Q}/\text{NH}_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>2.25 ± 0.01</td>
<td>2.01 ± 0.01</td>
<td>0.271</td>
<td>0.275</td>
<td>0.277</td>
</tr>
<tr>
<td>7.1</td>
<td>2.27</td>
<td>1.98</td>
<td>0.277</td>
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<td>0.281</td>
</tr>
<tr>
<td>6.8</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>2.54</td>
<td>1.66</td>
<td>0.291</td>
<td>0.301</td>
<td>0.302</td>
</tr>
<tr>
<td>6.2</td>
<td>2.79</td>
<td>1.41</td>
<td>0.323</td>
<td>0.317</td>
<td>0.327</td>
</tr>
<tr>
<td>5.9</td>
<td>3.15</td>
<td>1.01</td>
<td>0.355</td>
<td>0.342</td>
<td>0.357</td>
</tr>
<tr>
<td>5.6</td>
<td>3.65</td>
<td>0.53</td>
<td>0.350</td>
<td>0.378</td>
<td>0.389</td>
</tr>
</tbody>
</table>
(b) **Second experimental run.** In the second experiment, 7.00, 6.50, 6.00, 5.00, 3.00 and 1.50-gram samples of Nd$_2$O$_3$ were eluted at pH values of 7.3, 6.9, 6.6, 6.3, 6.0 and 5.7, respectively. The flow rates were 1.0 - 1.2 cm./min., initially, and were reduced gradually to about 0.33 cm./min. before the breakthrough occurred.

A heavy precipitate formed in the column at a pH of 6.6 when the flow rate was reduced to 0.5 cm./min. and it was necessary to discontinue the elution of this column. The neodymium was eluted from the other five columns of the series. The concentrations of ammonium ion and of total neodymium in the eluate were determined and the pH values of the solutions were read. The analytical data and the pH values for this experiment are given in Table 3 and a typical elution curve showing the ammonium-ion concentration, the neodymium concentration and the pH of the eluate as functions of the volume of eluate collected is given in Figure 5.

(c) **Third experimental run.** In the third experiment, 6.50, 6.00, 5.00, 4.00, 2.50 and 1.00-gram samples of Nd$_2$O$_3$ were eluted at pH values of 7.20, 6.76, 6.52, 6.17, 5.87 and 5.40, respectively. The flow rate used initially was 2.0 cm./min. When the band front reached the middle of the resin bed, the flow rate was reduced
Table 3

Analytical Data from the Second Experimental Run

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>NH₄⁺ in eluant (meq. per liter)</th>
<th>NH₄⁺ in eluate (meq. per liter)</th>
<th>Nd in eluate (meq. per liter)</th>
<th>pH of eluate</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.30 ± 0.01</td>
<td>15.59 ± 0.03</td>
<td>8.20 ± 0.03</td>
<td>7.40 ± 0.02</td>
<td>6.58 ± 0.01</td>
</tr>
<tr>
<td>6.90</td>
<td>14.98</td>
<td>8.33</td>
<td>6.68</td>
<td>6.00</td>
</tr>
<tr>
<td>6.60</td>
<td>14.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.30</td>
<td>13.57</td>
<td>8.75</td>
<td>4.84</td>
<td>5.55</td>
</tr>
<tr>
<td>6.00</td>
<td>12.56</td>
<td>9.06</td>
<td>3.56</td>
<td>5.41</td>
</tr>
<tr>
<td>5.70</td>
<td>11.53</td>
<td>9.54</td>
<td>2.10</td>
<td>5.34</td>
</tr>
</tbody>
</table>
Fig. 5. A Typical Elution Curve
to 1.0 cm./min. At the three-quarter mark the flow rate was reduced to 0.33 cm./min.

(d) Fourth experimental run. This experiment was identical to the third run, except that exactly half the flow rate used in run three was used throughout the run.

Band progress curves at two widely different pH values for the fast and slow rates are compared in Figure 6. It was noted that similar curves were obtained for both flow rates at the higher pH value, but that at the lower pH value the band spread out past the equilibrium length at the fast flow rate. For intermediate pH values the bands also increased beyond the equilibrium length when the faster flow rate was used. It was generally observed that a band, which initially spread out too far at the fast flow rate, contracted when the flow rate was decreased and approached the length obtained with the slower flow rate for the same pH of eluant. It appears unwise to use flow rates in excess of 1.0 cm./min. in experiments of this type.

Analytical data from the third and fourth experiments are compared in Table 4. It was observed that the data for these runs were in close agreement in spite of the difference in flow rates. Apparently equilibrium was re-established in the case of the faster flow rates
FIG. 6. Band Progress Curves for Fast and Slow Flow Rates at Two Different pH Values
Table 4

Analytical Data from the Third and Fourth Experimental Runs

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>NH₄⁺ in eluant (meq. per liter)</th>
<th>NH₄⁺ in eluate (meq. per liter)</th>
<th>Nd in eluate (meq. per liter)</th>
<th>pH of eluate</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.20 ± 0.01</td>
<td>15.34 ± 0.03</td>
<td>8.18 ± 0.03</td>
<td>7.22 ± 0.02</td>
<td>6.45 ± 0.01</td>
</tr>
<tr>
<td>6.76</td>
<td>14.67</td>
<td>8.35</td>
<td>6.36</td>
<td>5.90</td>
</tr>
<tr>
<td>6.52</td>
<td>14.22</td>
<td>8.48</td>
<td>5.79</td>
<td>5.72</td>
</tr>
<tr>
<td>6.18</td>
<td>13.07</td>
<td>8.87</td>
<td>4.22</td>
<td>5.51</td>
</tr>
<tr>
<td>5.87</td>
<td>11.99</td>
<td>9.26</td>
<td>2.69</td>
<td>5.40</td>
</tr>
<tr>
<td>5.40</td>
<td>10.42</td>
<td>9.92</td>
<td>0.54</td>
<td>5.31</td>
</tr>
<tr>
<td>slow rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.20</td>
<td>15.34</td>
<td>8.25</td>
<td>7.12</td>
<td>6.49</td>
</tr>
<tr>
<td>6.76</td>
<td>14.67</td>
<td>8.41</td>
<td>6.30</td>
<td>5.93</td>
</tr>
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<td>6.52</td>
<td>14.22</td>
<td>8.47</td>
<td>5.73</td>
<td>5.75</td>
</tr>
<tr>
<td>6.18</td>
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<td>8.87</td>
<td>4.22</td>
<td>5.52</td>
</tr>
<tr>
<td>5.87</td>
<td>11.99</td>
<td>9.28</td>
<td>2.68</td>
<td>5.41</td>
</tr>
<tr>
<td>5.40</td>
<td>10.42</td>
<td>10.01</td>
<td>0.45</td>
<td>5.32</td>
</tr>
</tbody>
</table>
after the rate was reduced and before break-through occurred. Comparison of the analytical data from these and previous runs with the hydrogen ion concentration, as determined by pH measurements, showed deviations which could not be accounted for by the experimental error in determining the pH or the concentrations of the ammonium ion and the total neodymium in the eluate. As a check, the pH values of solutions from the second run were redetermined after they had been standing in Pyrex glass-stoppered volumetric flasks for a period of about two months. A considerable shift in the pH of the solutions was observed as can be seen in Table 5.

Table 5

The Change in pH of Solutions of Eluate from the Second Run upon Standing

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>pH of eluate fresh</th>
<th>pH of eluate 2 months later</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.30</td>
<td>6.58</td>
<td>6.84</td>
</tr>
<tr>
<td>6.90</td>
<td>6.00</td>
<td>6.19</td>
</tr>
<tr>
<td>6.30</td>
<td>5.56</td>
<td>5.68</td>
</tr>
<tr>
<td>6.00</td>
<td>5.43</td>
<td>5.50</td>
</tr>
<tr>
<td>5.70</td>
<td>5.34</td>
<td>5.82*</td>
</tr>
</tbody>
</table>

* This solution had become noticeably cloudy.
It was also discovered that the pH of the solution from the third and fourth runs changed upon standing in the same manner. This discovery suggested that the solutions were unstable, probably due to the presence of some micro-organism which was slowly destroying the citric acid. Subsequently, samples of the solution were tested by Dr. L. A. Underkofler, who reported that bacteria, in the form of short rods, were present in the solutions. At this point it was concluded that further experiments were necessary before any calculations which depended upon the hydrogen-ion concentration could be made.

(e) Fifth experimental run. In this run, precautions were taken to minimize the chance of errors due to the presence and growth of micro-organisms. The resin beds, the siphon tubes, the make-up tank and the carboys, used for storing solutions, were rinsed with hot water and with 1% phenol solution. As an added precaution 0.2% phenol was added to the eluant for one series of columns to inhibit the growth of microorganisms while a second series of columns was eluted containing no preservative. When the bands on both series of columns were nearly spread out to their equilibrium lengths and the front boundaries of the bands had moved about half-way down the resin beds,
the original batches of eluant were discarded and were replaced by fresh citrate solutions in order to further reduce the chance of spoilage by bacterial action.

Each series in this experiment consisted of seven columns which were loaded with 6.50, 6.25, 6.00, 5.00, 4.00, 2.50 and 1.00-gram samples of Nd₂O₃, to provide bands about 25 cm. long when fully developed, and eluted with 0.1% citrate at pH values of 7.4, 7.1, 6.8, 6.5, 6.2, 5.9 and 5.6, respectively. The flow rate during the first half of the elution was 1.0 cm./min. and was reduced to 0.33 cm./min. during the last half of the elution.

The eluate from each column was collected in covered, 2-liter, Pyrex, volumetric flasks at the latter flow rate and was analyzed for ammonium ion and neodymium by the methods described above. The analytical data and the pH values of the eluates from both series of columns are given in Table 6. The pH of the eluate from each column was measured immediately after it was collected and periodically thereafter.

It was observed that the pH values of the eluates with no preservative increased markedly upon standing a short time, but that the pH values of the eluates with phenol added did not change appreciably until they had stood for a considerably longer period of time. A
Table 6

Analytical Data Obtained from the Elution of Neodymium with 0.1% Citrate

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>NH$_4^+$ in eluant (meg./l.)</th>
<th>NH$_4^+$ in eluate (meg./l.)</th>
<th>Nd in eluate (meg./l.)</th>
<th>pH of eluate</th>
<th>H$^+$ in eluate (meg./l. x10$^{-3}$)</th>
<th>NH$_4^+$ + Nd (meg./l.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without phenol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.42 ± 0.01</td>
<td>15.52 ± 0.03</td>
<td>8.15 ± 0.03</td>
<td>7.45 ± 0.02</td>
<td>6.87 ± 0.01</td>
<td>0.14 ± 0.01</td>
<td>15.60 ± 0.05</td>
</tr>
<tr>
<td>7.07</td>
<td>15.15</td>
<td>8.18</td>
<td>6.96</td>
<td>6.30</td>
<td>0.50 ± 0.02</td>
<td>15.14</td>
</tr>
<tr>
<td>6.78</td>
<td>14.61</td>
<td>8.38</td>
<td>6.32</td>
<td>5.95</td>
<td>1.12 ± 0.03</td>
<td>14.70</td>
</tr>
<tr>
<td>6.49</td>
<td>13.89</td>
<td>8.58</td>
<td>5.42</td>
<td>5.71</td>
<td>1.95 ± 0.05</td>
<td>14.00</td>
</tr>
<tr>
<td>6.19</td>
<td>12.96</td>
<td>8.89</td>
<td>4.12</td>
<td>5.52</td>
<td>3.02 ± 0.07</td>
<td>13.01</td>
</tr>
<tr>
<td>5.90</td>
<td>11.90</td>
<td>9.27</td>
<td>2.65</td>
<td>5.42</td>
<td>3.80 ± 0.09</td>
<td>11.92</td>
</tr>
<tr>
<td>5.60</td>
<td>10.90</td>
<td>9.68</td>
<td>1.23</td>
<td>5.36</td>
<td>4.37 ± 11</td>
<td>10.91</td>
</tr>
<tr>
<td>as above, but phenol added</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.40</td>
<td>15.49</td>
<td>8.17</td>
<td>7.43</td>
<td>6.70</td>
<td>0.20 ± 0.01</td>
<td>15.60</td>
</tr>
<tr>
<td>7.05</td>
<td>15.05</td>
<td>8.17</td>
<td>6.96</td>
<td>6.19</td>
<td>0.65 ± 0.02</td>
<td>15.13</td>
</tr>
<tr>
<td>6.77</td>
<td>14.54</td>
<td>8.38</td>
<td>6.29</td>
<td>5.90</td>
<td>1.26 ± 0.03</td>
<td>14.67</td>
</tr>
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<td>6.49</td>
<td>13.88</td>
<td>8.56</td>
<td>5.39</td>
<td>5.70</td>
<td>2.00 ± 0.05</td>
<td>13.95</td>
</tr>
<tr>
<td>6.19</td>
<td>12.95</td>
<td>8.87</td>
<td>4.08</td>
<td>5.51</td>
<td>3.09 ± 0.07</td>
<td>12.95</td>
</tr>
<tr>
<td>5.88</td>
<td>11.83</td>
<td>9.32</td>
<td>2.57</td>
<td>5.40</td>
<td>3.98 ± 0.09</td>
<td>11.89</td>
</tr>
<tr>
<td>5.60</td>
<td>10.89</td>
<td>9.62</td>
<td>1.26</td>
<td>5.33</td>
<td>4.68 ± 11</td>
<td>10.88</td>
</tr>
</tbody>
</table>
slight drift in the pH was noted even in the phenolic solutions after several weeks. The changes in pH with time are shown in Table 7.

Table 7

The Change of pH with Time in Neodymium Ammonium Citrate Solutions with and without Preservative

<table>
<thead>
<tr>
<th>pH of eluant</th>
<th>pH of eluate after 1 week</th>
<th>pH of eluate after 2 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh</td>
<td></td>
</tr>
<tr>
<td>no phenol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.42</td>
<td>6.88</td>
<td>6.91</td>
</tr>
<tr>
<td>7.07</td>
<td>6.30</td>
<td>6.47</td>
</tr>
<tr>
<td>6.78</td>
<td>5.95</td>
<td>6.05</td>
</tr>
<tr>
<td>6.49</td>
<td>5.71</td>
<td>5.77</td>
</tr>
<tr>
<td>6.19</td>
<td>5.52</td>
<td>5.59</td>
</tr>
<tr>
<td>5.90</td>
<td>5.42</td>
<td>5.50</td>
</tr>
<tr>
<td>5.60</td>
<td>5.36</td>
<td>5.40</td>
</tr>
<tr>
<td>with phenol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.40</td>
<td>6.69</td>
<td>6.71</td>
</tr>
<tr>
<td>7.05</td>
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<tr>
<td>6.77</td>
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<tr>
<td>6.49</td>
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<tr>
<td>6.19</td>
<td>5.51</td>
<td>5.51</td>
</tr>
<tr>
<td>5.88</td>
<td>5.40</td>
<td>5.40</td>
</tr>
<tr>
<td>5.60</td>
<td>5.33</td>
<td>5.33</td>
</tr>
</tbody>
</table>

From the data in Table 6, it was apparent that the addition of 0.2% phenol to the eluant did not greatly change its pH. Consequently, little or no difference should have been noted in the pH of the eluates unless the phenol complexed with the neodymium or some micro-
organism was active. At the higher pH values, some differences were observed in pH's of corresponding eluates, although the differences in neodymium and ammonium-ion concentrations were within the limits of experimental error. These differences in pH at the higher pH values were probably due to bacterial action in the unprotected solutions. Consequently, in this thesis, for calculations which involved the hydrogen-ion concentration it was assumed that the correct pH values were those initially observed in the solutions which were stabilized by the addition of phenol.
IV. DISCUSSION OF RESULTS

A. Material Balance

1. Conservation of electrical charge in the aqueous phase

It is obvious that, if large space charges are not to be built up, a solution flowing past an ion-exchange resin must remain neutral at all times. In the elution of rare earths with solutions containing citric acid and ammonium citrate, the only negative ions present in concentrations greater than $10^{-6}$ are those which contain the citrate radical. Since there are no anions present except the trinegative citrate ion and its complex ions formed with either hydrogen or neodymium ion or both, it follows that the sum of the equivalents of ammonium ion, total hydrogen and total rare earth present must be equal to the number of equivalents of total citrate. Expressed mathematically,

$$\text{Cit}^T = H^T + R^T + \text{NH}_4^+$$  (36)

in which all concentrations are expressed in equivalents. In the above formulation $\text{Cit}^T$ represents the total citrate concentration, whether it be present as $\text{Cit}^-$, $\text{HCit}^-$, $\text{H}_2\text{Cit}^-$, $\text{RCit}_2^-$, $\text{HRCit}_2^-$, or any other negative citrate complex; $H^T$ is the total concentration of available
hydrogen, whether present as $\text{HCit}^-$, $\text{H}_2\text{Cit}^-$, $\text{H}_3\text{Cit}$, $H^+$, or any acid rare-earth-citrate complex, such as $\text{HRCit}_2^-$, but does not include hydrogen bound in water molecules or in the structure of the trinegative citrate radical; $R^T$ is the total rare earth concentration, whether present as $\text{RCit}_2^-$, $R^{+++}$, or any acidic rare earth complex, such as $\text{HRCit}_2^-$; $\text{NH}_4^+$ is the total ammonium-ion concentration present. It is assumed in the dilute solutions used that all ammonium salts are completely ionized.

No evidence was found that any form of citrate ion, either free or complexed, is adsorbed on the resin when the bands are at equilibrium, therefore, the $\text{Cit}^T$ of the eluate must always equal the $\text{Cit}^T$ of the eluant. Since all the described experiments, for eluants of various pH values employed, used the same concentration of total citrate, this concentration is a true constant for all solutions involved, whether eluates or eluants. Therefore, $(H^T + \text{NH}_4^+)$ must be equal for all eluants when expressed in equivalents and, in turn, must also be equal to $(H^T + R^T + \text{NH}_4^+)$ for all eluates. It has been shown in the literature (37, 64, 65), for the ammonium-hydrogen exchange on a resin identical with Nalcite $\text{HCR}$, that

$$\text{NH}_4^+ + R^+ \rightleftharpoons \text{NH}_4^+_R + H^+_R$$  \hspace{1cm} (37)$$

and the value of the molar equilibrium constant;
\[ k_m = \frac{C_{H_3C\text{NH}_4 R}}{C_{H\text{R}C\text{NH}_4 S}} \]

is approximately one, when the mole fractions of hydrogen on the resin and in solution are very small.

In the solutions employed, the concentration of the ammonium ion in the eluate varied from \(8 \times 10^{-3}\) to \(1 \times 10^{-2}\) N, while the hydrogen-ion concentration varied between \(2 \times 10^{-7}\) and \(5 \times 10^{-6}\) N. That is, the ratio of the hydrogen resin to the ammonium resin varied from 1:40,000 to 1:2,000 in the experiments.

One liter of eluant under equilibrium conditions on a column will saturate from

\[ \frac{15.6 \times 10^{-3}}{4.26 \times 10^{-3}} = 3.66 \]

to

\[ \frac{10.0 \times 10^{-3}}{4.26 \times 10^{-3}} = 2.35 \]

grams of resin with ammonium ion. This amount of resin, when in contact with the equilibrium eluate, contained from \(2 \times 10^{-7}\) to \(5 \times 10^{-6}\) equivalents of hydrogen ion.

The amount of hydrogen ion taken up from the resin by each liter of solution which flows past is actually somewhat less than this amount, because a certain amount
of hydrogen resin remains behind in equilibrium with ammonium resin after the rare-earth band has moved on. In fact, when the pH of the eluant is decreased to about 5.3, the concentration of the ammonium ion in the eluate equals the concentration of the ammonium ion in the eluant and the net change in hydrogen-ion concentration in the resin phase will be zero. Therefore, the maximum net transfer of hydrogen ion from the resin to solution will be less than 2x10^-7 equivalents per liter of eluate.

The value of $H^T$ in the eluant varies from 1x10^-4 to 5.6x10^-3 equivalents per liter; therefore, the addition of 2x10^-7 equivalents of hydrogen will only change the value of $H^T$ one part in five hundred; this variation can be neglected since it is within experimental error. Therefore, the value of $H^T$ for any eluate can be assumed equal to the $H^T$ of the original eluant. It should be cautioned that, while $H^T$ may be considered constant from eluant to eluate, the concentration of hydrogen ion varies appreciably.

Accordingly, equation (36) reduces to

$$NH_4^+ = NH_4^+ + R^T = C_{it}^T - H^T$$

(39)

in which $NH_4^+$ is the concentration of ammonia in the eluant and $NH_4^+$ is the concentration of ammonium ion in the eluate. That this relationship holds can be seen from the experi-
mental data given in Tables 2, 3, 4 and 6.

2. The formation and development of the bands and the prediction of break-through volumes

In all the preceding experiments, each column contained exactly 200 grams of air-dried, hydrogen-form, Nalcite HCR resin. This standard resin was found to have a capacity of 4.26 milliequivalents per gram for either monovalent ions or for trivalent neodymium ion. Consequently, all resin beds used had a total capacity of 852 milliequivalents.

For the adsorption of neodymium on the hydrogen-form resin, a dilute solution of neodymium chloride, containing only a slight excess hydrochloric acid was passed slowly down the resin bed. Since neodymium was by far the most predominant cation in the solution entering the column and the resin bed was completely saturated with hydrogen ion at all points below the reaction zone, the reaction represented by equation (40) proceeded irreversibly toward the right.

$$\text{Nd}^{3+} + 3H^+_{\text{R}} \rightleftharpoons \text{Nd}^{3+}_{\text{R}} + 3H^+$$  \hspace{0.1cm} (40)

Only the reactants, neodymium chloride and hydrogen-form resin, were brought into contact with each other, due to the fact that the hydrochloric acid, formed during
the reaction, was swept downstream and out of the reaction zone by the flowing solution; furthermore, the neodymium resin formed during the reaction was left upstream where it was contacted by nothing but fresh neodymium chloride solution.

As a consequence of the above arguments, it can be seen that a saturated band of neodymium resin would form at the top of the resin bed. The fraction of the resin bed converted to the neodymium form was equal to the number of equivalents of neodymium ion adsorbed divided by the total capacity of the bed, consequently, it was possible to predict the approximate length of an initial adsorbed rare-earth band. Since Nalcite HCR resin shrinks considerably when it is converted from the hydrogen to the neodymium form, it is necessary to know the shrinkage factor if the band length is to be calculated precisely. The portion of the bed below the adsorbed rare earth band remained in the hydrogen cycle throughout the adsorption process. After the neodymium was adsorbed, distilled water was passed through the column in order to remove the excess free acid. This insured that the only shrinkage which took place was that which occurred in the neodymium band and it followed that the exchange capacity of the remaining hydrogen-form bed per unit length did not change. The concentration
of the hydrogen ion in the eluant was much less than the concentration of ammonium ion in the experiments described above. Since the affinities of hydrogen and ammonium ions for the resin are nearly equal, the amount of hydrogen ion adsorbed from the eluant was negligible compared to the amount of ammonium ion adsorbed when the neodymium bands were eluted. Since the ammonium and neodymium break-throughs occurred simultaneously, it follows that the rate of movement of a band front down the resin bed should be proportional to amount of ammonium ion in the eluant. From these observations it is clear that the break-through volume, in liters, may be calculated by dividing the number of equivalents of hydrogen-form resin remaining after the rare-earth band was adsorbed, by the number of equivalents of ammonium ion per liter of eluant. The calculated and observed break-through volumes for the first four experimental runs are given in Table 8. The observed values are generally slightly lower than the calculated values since some evaporation took place while the eluate was being collected and measured and because the break-through was usually observed before all of the hydrogen ion on the column was replaced, due to channeling which caused uneven band fronts. In view of these facts the data of Table 8 are in excellent agreement.
Table 8

Calculated and Observed Break-Through Volumes in the Elution of Neodymium

<table>
<thead>
<tr>
<th>Capacity of bed (meq.)</th>
<th>Neodymium adsorbed (meq.)</th>
<th>Hydrogen remaining (meq.)</th>
<th>Ammonium ion concentration (meq./liter)</th>
<th>Break-through volume predicted (liters)</th>
<th>Break-through volume observed (liters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>852</td>
<td>116</td>
<td>736</td>
<td>15.34</td>
<td>48.0</td>
<td>48.0</td>
</tr>
<tr>
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<td>116</td>
<td>736</td>
<td>15.34</td>
<td>48.0</td>
<td>48.4</td>
</tr>
<tr>
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<td>107</td>
<td>745</td>
<td>14.67</td>
<td>50.8</td>
<td>50.5</td>
</tr>
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<td>852</td>
<td>107</td>
<td>745</td>
<td>14.67</td>
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<tr>
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<td>89</td>
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<td>14.22</td>
<td>53.6</td>
<td>53.4</td>
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<td>13.07</td>
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<td>59.1</td>
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<tr>
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<td>834</td>
<td>10.42</td>
<td>80.0</td>
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<tr>
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<td>80.0</td>
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<td>46.6</td>
<td>46.5</td>
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<td>49.2</td>
<td>49.1</td>
</tr>
<tr>
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<td>763</td>
<td>13.57</td>
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<td>56.3</td>
</tr>
<tr>
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<td>12.56</td>
<td>63.6</td>
<td>63.0</td>
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<tr>
<td>852</td>
<td>27</td>
<td>825</td>
<td>11.53</td>
<td>71.5</td>
<td>70.6</td>
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<td>763</td>
<td>15.58</td>
<td>48.0</td>
<td>48.4</td>
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<tr>
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<td>763</td>
<td>15.58</td>
<td>48.0</td>
<td>48.4</td>
</tr>
<tr>
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<td>89</td>
<td>763</td>
<td>14.15</td>
<td>53.9</td>
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<tr>
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<td>763</td>
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<td>12.06</td>
<td>66.2</td>
<td>65.8</td>
</tr>
<tr>
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<td>27</td>
<td>825</td>
<td>11.17</td>
<td>73.9</td>
<td>73.2</td>
</tr>
</tbody>
</table>
It can be seen from the data in Figures 3 and 6 that the rear edge of each band, as well as the front edge, traveled at a constant rate while the equilibrium band was developing, but that this rate was slower than the rate at which the front edge traveled. When the adsorbed band reached its fully developed state as indicated by a fully developed elution curve such as is shown in Figure 5, the rate of movement of the rear edge of the band increased abruptly to the same rate at which the front edge was traveling. Beyond this point there was no further change in the length of the adsorbed band or in the shape of the elution curves obtained as elution was continued; this has been reported in a previous paper (6).

The rear edge of the band traveled down the column as a linear function of the volume of the eluant introduced, at a given flow rate, until the band spread out to its equilibrium length. It should be noted that solution, passing through the column, had to travel through a portion of the resin which contained a high mole fraction of neodymium. Under these conditions it is possible that other neodymium-citrate complexes may form than those which are normally present in contact with the equilibrium band. For example it has been noted that an insoluble citrate complex forms occasionally in this phase of the elution. In view of these facts it
is evident that sufficient experimental data are not yet available which would enable the prediction of the rate of travel of the rear edge of the band.

3. **The distribution of hydrogen ion, ammonium ion and neodymium between the aqueous resin phases**

   It has been stated previously that neodymium adsorption bands reach an equilibrium state in which the elution curves obtained have flat tops and steep front and rear boundaries, and that the shapes of the curves and the plateau concentrations do not change as the column length is increased, as long as all the other conditions of elution remain constant. Figure 7 shows the elution curves for a number of neodymium samples which were eluted at various pH values in the experiments described above. The flatness of the plateaus indicates that the adsorbed bands were uniform after equilibrium was attained except for a small portion at each end of the bands. Most of the slope of the front and rear portions of the curves can be accounted for by the tilt of the adsorbed bands, which was actually observed when the bands were examined under blue light, due to channeling in the resin beds.

   In Figures 1 and 2 it can be seen that tilting of the bands is a factor which becomes very important in
Fig. 7. Elution Curves for Neodymium Samples at Various pH Values
the elution of narrow rare-earth bands; this will be discussed at length in a later section. In the present experiments relatively wide bands were used and the end effects were relatively unimportant.

When the bands are in a fully developed state, the ammonium ion and the neodymium in the solution flowing over the uniform region of the band must be adsorbed upon the resin in the same ratio as they exist in solution when they reach the bottom end of the adsorbed band, since it would be impossible for the neodymium and ammonium fronts to travel at the same rate and to break-through simultaneously under any other conditions. It has therefore been concluded that the ratios of the constituents in the resin phase must be equal to their ratios in the aqueous phase at equilibrium with it, that is

\[
\left( \frac{\text{NH}_4^+}{\text{Nd}^+} \right)_S = \left( \frac{\text{NH}_4^+}{\text{Nd}^+} \right)_R
\]

(41)

and

\[
\left( \frac{\text{H}^+}{\text{NH}_4^+} \right)_S = \left( \frac{\text{H}^+}{\text{NH}_4^+} \right)_R
\]

(42)

Equation (41) is also a direct consequence of setting the molar equilibrium constant for the ammonium-hydrogen
exchange equal to unity. Bonner, Argersinger and Davidson (65) have shown that this is true for such a system in which the mole fraction of hydrogen ion on the resin is low. Combining equations (41) and (42)

\[
\frac{H_R^+}{H_S^+} \frac{NH_R^+}{NH_S^+} = \frac{Nd_R^T}{Nd_S^T}
\]

(43)

As was shown in an earlier section, when the hydrogen-ion concentration in both phases is negligible compared to the concentrations of ammonium ion and total neodymium, two conservation conditions hold, namely

\[
NH_S^+ + Nd_S^T = NH_S^E
\]

(44)

\[
NH_R^+ + Nd_R^T = Q
\]

(45)

In the preceding equations:

\[
NH_S^+ = \text{the concentration of ammonium ion in the eluate;}
\]

\[
NH_R^+ = \text{the concentration of ammonium ion in the resin;}
\]

\[
Nd_S^T = \text{the total concentration of neodymium in the eluate;}
\]

\[
Nd_R^T = \text{the total concentration of neodymium in the resin;}
\]

\[
NH_S^E = \text{the concentration of ammonium ion in the eluant;}
\]

\[
Q = \text{the capacity of the resin.}
\]
For convenience $\text{NH}_4^*$ and the symbols with the subscript, $\text{Q}$, are generally expressed in milliequivalents per liter of solution; $\text{Q}$ and the symbols with the subscript, $\text{R}$, are expressed in milliequivalents per gram of resin in the standard, air-dried, hydrogen form.

From the above equations it follows that

$$\frac{\text{Nd}^T_R}{\text{Nd}^T_S} = \frac{\text{Q}}{\text{NH}_4^*} = \frac{\text{NH}_4^+}{\text{NH}_4^+} = \frac{\text{H}_R^+}{\text{H}_S^+}$$  \hspace{1cm} (46)

That this condition is true may be established by comparing the concentration ratios given in Table 2. In the first experimental run the resin appendages were attached late in the experiment and probably upset the equilibrium somewhat causing erratic results; however, the data agree fairly well with the assumption that the concentration ratios are equal for a fully developed band.

4. **Linear relationships between the ammonium ion in the eluant and the ammonium ion and the total neodymium in the eluate.**

The concentration of the ammonium ion and of the total neodymium in the eluate at equilibrium have been plotted as functions of the ammonium-ion concentration of the eluant in Figure 8. Data from all five exper-
Fig. 8. The Concentration of Total Neodymium and Ammonium Ion in the Eluate for Various Concentrations of Ammonium Ion in the Eluant
imental runs were included and the curves obtained were very nearly linear functions. Experimentally it was found that the rare earth content of the eluate approached zero as the ammonium-ion concentration was reduced to 10 meq. per liter. While it is possible to elute neodymium from Nalcite HCR with 0.1% citric acid solutions containing less than this concentration of ammonium ion, the rate of elution is slow, the elution curves are bell-shaped and the band continues to spread out.

For eluants in the pH range 5.3 - 7.4, which corresponds to 10.0 - 15.6 milliequivalents of ammonium ion per liter of 0.1% citric acid solution, the concentration of neodymium ion in the eluate was found to increase linearly with increased ammonium-ion content of the eluant until it reached a value approximately one-half the number of equivalents of total citrate present. At this point the ammonium-ion concentration in the eluant was equal to the total concentration of citrate. Expressed mathematically,

\[ Nd_3^T = \frac{1}{2} (\text{NH}_4^+ - 10.0) \]  

(47)

Nd_3^T and NH_4^+ are expressed in milliequivalents per liter. Since

\[ R_3^T + \text{NH}_4^+ = \text{NH}_4^+ \]  

(48)
if $R_T^S$ is a linear function of $NH_4^+$, it follows that $NH_4^+$ vs. $NH_4^+$ and the $NH_4^+$ vs. $R_T^S$ must also be linear. Furthermore, if the slope of any one of these straight lines is known experimentally, then by differentiating (48) the slopes of the others can be calculated, for example

$$\frac{dNH_4^+}{dNH_4^+} = 1 = \frac{dNH_4^+}{dNH_4^+} \quad \frac{dNa_T^3}{dNH_4^+} \quad (49)$$

or

$$\frac{dNH_4^+}{dNH_4^+} = 1 - \frac{4}{3} = -\frac{1}{3} \quad (50)$$

The equation for the $NH_4^+$ vs. $NH_4^+$ relationship has been found experimentally to be

$$NH_4^+ = -\frac{1}{3} \quad NH_4^+ + 13.3 \quad (51)$$

in agreement with equation (50).

By means of equations (47) and (51) it is possible to calculate fairly accurately the rare-earth and the ammonium concentrations in the eluate for any concentration of ammonium ion in the eluant between 10.0 and 15.6 meq. per liter.

5. **Calculation of the equilibrium band length**
After establishing that the ratio of neodymium to ammonium ion in the resin phase was equal to the ratio of neodymium to ammonium ion in solution and that the concentration of hydrogen ion in the resin phase was negligible, it was a simple matter to calculate the length of the equilibrium band from a knowledge of the neodymium and ammonium-ion concentrations in the equilibrium eluate. If the number of equivalents of neodymium originally adsorbed be multiplied by the concentration of ammonium ion in the eluant divided by the concentration of neodymium in the eluate at equilibrium, the total number of equivalents of all cations in the equilibrium band can be determined. From this result and a knowledge of the exchange capacity per unit length of hydrogen-form resin bed the length of the adsorbed band at equilibrium may be calculated. For more precise calculations it is necessary to take into account the differences in the equivalent volumes of the hydrogen, ammonium and neodymium-form resins.

6. The composition of the predominant neodymium-citrate complex

It was observed, in data from experiments which were performed at pH values greater than 7.4, that a break occurred at a point where the neodymium concentration was equal to half the total citrate concentration.
This break was considered as strong evidence that the predominant rare-earth complex ion in this pH range was $\text{RCit}_2^-$; this conclusion has been further substantiated by the spectrographic results reported by Spedding and Tevebaugh (73). They photographed the absorption spectra of the neodymium-citrate solutions at various pH values and found that the absorption bands of only one complex ion were observed in the pH range discussed in this thesis. In addition to the above evidence, Ryabchikov and Terent'eva (74) have recently shown that the water-soluble complexes formed by adding $\text{K}_3\text{Cit}$, $\text{Na}_3\text{Cit}$ and $(\text{NH}_4)_3\text{Cit}$ to insoluble $\text{NdCit}_2\cdot2\text{H}_2\text{O}$ can be precipitated by the addition of alcohol and have the compositions: $\text{K}_3(\text{NdCit}_2)$, $\text{Na}_3(\text{NdCit}_2)\cdot3\text{H}_2\text{O}$ and $(\text{NH}_4)_3(\text{NdCit}_2)\cdot3\text{H}_2\text{O}$, respectively. Consequently, $(\text{NdCit}_2)^-$ was assumed to be the predominant complex ion of neodymium which was present in the eluates obtained from experiments (a) through (e).

Since the ionization constants of citric acid are known (75, 76), it was a relatively simple task to calculate the number of equivalents of anions present in the equilibrium eluate and to check the assumption that the predominant citrate complex present was $\text{NdCit}_2^-$; this was accomplished by comparing the calculated number of equivalents of negative ions to the analytically
determined concentration of ammonium ions.

For the ionization reactions

\[ \text{H}_3\text{Cit} \rightleftharpoons \text{H}_2\text{Cit}^- + \text{H}^+ \]  
\[ \text{H}_2\text{Cit}^- \rightleftharpoons \text{HCit}^= + \text{H}^+ \]  
\[ \text{HCit}^- \rightleftharpoons \text{Cit}^= + \text{H}^+ \]

the respective ionization constants are

\[ K_1 = \frac{(\text{H}_2\text{Cit}^-)(\text{H}^+)}{(\text{H}_3\text{Cit})} \]  
\[ K_2 = \frac{(\text{HCit}^=)(\text{H}^+)}{(\text{H}_2\text{Cit}^-)} \]  
\[ K_3 = \frac{(\text{Cit}^=)(\text{H}^+)}{(\text{HCit}^-)} \]

The numerical values of the ionization constants of citric acid which were used to calculate the various ionic species present in solutions of eluate were those derived from the following relationships reported by Bjerrum and Unmack (75) for citrate solutions at 25°:

\[ p\text{K}_1 = 3.057 - 0.504\sqrt{\mu} + 0.41\mu \]  
\[ p\text{K}_2 = 4.759 - 1.512\sqrt{\mu} + 1.25\mu \]  
\[ p\text{K}_3 = 6.400 - 2.520\sqrt{\mu} + 2.23\mu \]

in which the ionic strength, \( \mu \), is given by the relation,
\[ \mu = \frac{1}{2} \sum_{i=1}^{m} z_i^2 \]  

The following expressions were used to calculate the fractions of each citrate ion present:

\[
\frac{[H_2\text{Cit}^-]}{M^i} = \frac{K_1}{(H^+)+K_1+K_1K_2/(H^+)+K_1K_2K_3/(H^+)^2} \tag{62}
\]

\[
\frac{[HCit^-]}{M^i} = \frac{(H_2\text{Cit}^-)K_2}{(H^+)} \tag{63}
\]

\[
[Cit^-]^i = \frac{(H_2\text{Cit}^-)K_2K_3}{(H^+)^2} \tag{64}
\]

in which \( [H_2\text{Cit}^-] \), \( [HCit^-] \) and \( [Cit^-] \) represent the molar concentrations of the respective citrate ions; \( [H^+] \) is the hydrogen-ion concentration; \( M^i \) is the total molar concentration of citrate exclusive of that complexed with neodymium; and \( K_1, K_2 \) and \( K_3 \) are the ionization constants of the mono-, di- and trinegative citrate ions.

By means of equations (58) through (64), it is possible to calculate the amount of ammonium ion present in a citrate solution if the pH is known, or vice versa.

The value of \( M^i \) in the eluate was calculated by subtracting twice the concentration of neodymium, in moles per liter, from the total molar concentration of citrate, \( \text{Cit}^T \), present in the solution. This was
done under the assumption that the amount of Nd\(^{++}\) present was negligible and that the only complex neodymium ion present was associated with two citrate radicals.

As a first approximation, prior to making corrections for the actual ionic strength of each solution of eluate, the concentrations of the individual citrate ions were estimated using the mole ratios of the ions calculated for 0.1\% citric acid solutions at the same pH value. The mole fractions of the citrate ions in 0.1\% citric acid solution in the pH range 5.0-7.4 have been calculated and appear in Table 9. These data have also been plotted in Figure 9.

The number of moles of each individual citrate ion was then calculated according to the preceding equations in which the values of \(K_1\), \(K_2\) and \(K_3\) were those corrected for ionic strength; the hydrogen-ion concentration used was that determined by pH measurements. Finally, the total concentration of anionic charges was evaluated by multiplying the molar concentration of each negative ion by its charge and adding these values.

The addition of phenol in small quantities to the eluant did not change the pH appreciably in the pH range of these experiments, nor did it change the ammonium or rare earth concentration of the eluate. It did stabilize the pH of the solutions which, in the absence of phenol,
Table 9

Mole Fractions of Citrate Ions Present in 0.1% Citric Acid

<table>
<thead>
<tr>
<th>pH</th>
<th>Hydrogen ion Concentration (moles per liter)</th>
<th>((\text{H}_2\text{Cit}^-)/\text{M}^1)</th>
<th>((\text{HCit}^\equiv)/\text{M}^1)</th>
<th>((\text{Cit}^\equiv)/\text{M}^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>1.00x10^{-5}</td>
<td>0.270</td>
<td>0.680</td>
<td>0.049</td>
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<tr>
<td>5.2</td>
<td>6.32x10^{-6}</td>
<td>0.181</td>
<td>0.731</td>
<td>0.088</td>
</tr>
<tr>
<td>5.4</td>
<td>3.98x10^{-6}</td>
<td>0.114</td>
<td>0.742</td>
<td>0.144</td>
</tr>
<tr>
<td>5.6</td>
<td>2.51x10^{-6}</td>
<td>0.067</td>
<td>0.708</td>
<td>0.225</td>
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<tr>
<td>5.8</td>
<td>1.59x10^{-6}</td>
<td>0.0374</td>
<td>0.635</td>
<td>0.327</td>
</tr>
<tr>
<td>6.0</td>
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<td>0.0194</td>
<td>0.532</td>
<td>0.449</td>
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<tr>
<td>6.2</td>
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<td>0.417</td>
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<tr>
<td>6.4</td>
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<td>6.6</td>
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<tr>
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<tr>
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<td>3.98x10^{-8}</td>
<td>0.00005</td>
<td>0.040</td>
<td>0.053</td>
</tr>
</tbody>
</table>
Fig. 9. The mole fractions of citrate ions present in 0.1M citric acid solutions as a function of pH.
tended to increase due to the action of micro-organisms. Since the experiments covered a period of a month, the pH values of the eluate in which phenol was present were considered to be the most reliable.

The total concentrations of anionic charges in the solution from the fifth experimental run, in which phenol was used as a preservative, have been calculated and have been compared to the analytically determined ammonium-ion concentrations in Table 10. From the results of these calculations it was apparent that the assumed composition, NdCit$_2$$\equiv$, was the most probable composition of the complex.

The differences between calculated and observed ammonium ion concentrations are greater than the experimental error, but these differences are reasonable in view of the oversimplified theoretical calculations. In these calculations no account was taken of the ionization of NdCit$_2$$\equiv$ which must occur to some extent; all other rare earth complexes have been assumed to be negligible over the entire pH range studied. It is highly probable that at least the complex ion HNdCit$_2$$\equiv$ will have to be given serious consideration in the more acidic ranges. Another possible source of these deviations, which has not yet been ruled out from consideration, is the possibility of small amounts of
Table 10
Comparison of the Calculated and Observed Concentration of Ammonium Ion in the Eluate

<table>
<thead>
<tr>
<th>H⁺ conc. (meg./liter x 10³)</th>
<th>Nd conc. (meg./liter)</th>
<th>Ammonium-ion concentration</th>
<th>Difference Actual-Calc'd (meg./liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Actual (meg./liter)</td>
<td>Calculated (meg./liter)</td>
</tr>
<tr>
<td>0.20</td>
<td>7.13</td>
<td>8.17</td>
<td>8.05</td>
</tr>
<tr>
<td>0.65</td>
<td>6.96</td>
<td>8.17</td>
<td>8.33</td>
</tr>
<tr>
<td>1.20</td>
<td>6.29</td>
<td>8.38</td>
<td>8.61</td>
</tr>
<tr>
<td>2.00</td>
<td>5.39</td>
<td>8.56</td>
<td>8.90</td>
</tr>
<tr>
<td>3.09</td>
<td>4.08</td>
<td>8.87</td>
<td>9.23</td>
</tr>
<tr>
<td>3.98</td>
<td>2.57</td>
<td>9.32</td>
<td>9.60</td>
</tr>
<tr>
<td>4.68</td>
<td>1.26</td>
<td>9.62</td>
<td>9.85</td>
</tr>
</tbody>
</table>
impurities in the U.S.P. citric acid used. While tartaric acid and other organic impurities in the citric acid are stated by the manufacturers to be negligible in quantity, it is possible that even these small amounts may have had some influence on the experimental results. For example, since citric acid is largely tied up as a complex ion in the eluate, it is possible that any uncomplexed acidic impurity might ultimately alter the pH of the eluate.
B. Conclusions

1. Fundamental relationships

From the experimental results and the subsequent discussions it was evident that the behavior of the neodymium bands on ion-exchange columns, when eluted with solutions of ammonium citrate under equilibrium conditions, could be accounted for quantitatively on the assumptions of electrical neutrality of the solution and resin, material balances of the chemicals involved and the thermodynamic relations which concern these materials in equilibrium with each other. It was shown that if the total citrate and the ammonium-ion concentrations of the eluant were known the pH of the eluant, the concentration of the total neodymium, the ammonium ion and the pH of the eluate could be calculated to a reasonable degree of accuracy, in most cases to better than two per cent. This was also true for the rate of travel of the front edge of the adsorbed band down the column and for the volume of eluant required to obtain break-through of the neodymium at the bottom of the column. Furthermore, if the number of equivalents of rare earth adsorbed on the column were known, then the length of the band at equilibrium could also be calculated.
The experimental results indicated that NdCit$_2^{\equiv}$ was the predominant neodymium-citrate complex in the eluate. If this complex is assumed to be the only rare earth complex present in the solution, the hydrogen-ion concentration of the eluate could be calculated to within a few per cent of that observed. This assumption also fixes the extrapolated rare earth concentration in the eluate when the pH of the eluate approaches 7. Unless the value of the equilibrium constants of the rare-earth complexes formed and the activity coefficients of the various ions in solution and on the resin are known, it is necessary to obtain the ammonium-ion concentration of the eluate or eluant when the rare earth content of the eluate goes to zero; in addition, use has to be made of the observed fact that the neodymium-ammonium ion relationships are linear. This is necessary because the linearity and slope of these relationships are determined by the equilibrium constants.

Since further work is in progress, in the Ames Laboratory, to evaluate these constants and activity coefficients, it would be premature at this time to attempt to refine these calculations beyond those which are in this thesis. It is interesting to note, however, that it is possible to list the unknowns in the solution and in the resin phase and to set up the same number of
independent equations from which it is possible to solve uniquely for the unknown variables. The variables are ammonium, neodymium and hydrogen ions in the resin phase; hydrogen, neodymium and ammonium ions in the eluate; the four citrate species; and \( \text{NdCit}_2^\equiv \) and any other neodymium-citrate complexes such as \( \text{HNdCit}_2^\equiv \). The known constants include the total citrate concentration; the total hydrogen or the ammonium-ion concentration of the eluant; and the capacity of the resin, \( Q \). The equation relating the components of the aqueous phase involve

1. Citrate balance
2. Total hydrogen balance
3. Neodymium balance
4. Balance of positive and negative charges in solution
5. The first ionization of citric acid
6. The second ionization of citric acid
7. The third ionization of citric acid
8. Ionization of \( \text{NdCit}_2^\equiv \)
9. Ionization of any other citrate complexes

It will be noted that there are nine equations and nine unknowns in the aqueous phase. However, the total neodymium concentration in the eluate which is required for the neodymium balance must be known experimentally, as well as the equilibrium constants and ionic activity...
coefficients required for the above equations, before the equations can be solved. The activity coefficients of the ions can be determined by independent experiments and in fact most of them are already available in the literature.

In the equilibrium involving the resin phase, four equations can be written for the remaining variables, namely

1. Balance of positive and negative charges in the resin phase
2. Equilibrium constant for ammonium-hydrogen exchange
3. Equilibrium constant for ammonium-neodymium exchange
4. Equal ratios of ammonium ion, hydrogen ion and total neodymium exist in the aqueous and resin phases

or the equivalent equations for 2, 3 and 4

\[
\frac{\text{NH}_3^+}{\text{NH}_4^+} = \frac{\text{H}_2^+}{\text{H}_3^+} = \frac{\text{Nd}_2^+}{\text{Nd}_3^+} = \frac{\text{Q}}{\text{NH}_4^+}
\]

In this case it is also necessary to determine independently the activity coefficients of the ions in the resin phase or to use the experimental fact that the beds have an equilibrium length and therefore that the ratio
of the ammonium-ion concentration in the resin to the ammonium-ion concentration in the eluate is equal to the ratio of the total concentrations of neodymium in the resin and in the aqueous phase, which is in turn equal to the ratio of the hydrogen-ion concentration in the resin phase to the concentration of the hydrogen ion in the eluate.

Since it is difficult to determine the activity coefficients of the ion in the resin experimentally it is perhaps better to use the analytically determined ion concentrations to find the activity coefficient ratio of the ions.

2. Self-sharpening of bands

If one examines the dissociation constant equation of the neodymium citrate complex

$$K = \frac{(\text{NdCit}_2^\equiv)}{(\text{Nd}^{+3})(\text{Cit}^\equiv)^2}$$

it will be noted that the value of $K$ for each rare earth would be different. Although several rare earths may be present at the same time in solution there can only be one concentration for the Cit$^\equiv$ ion. Therefore, the ratio RCit$^\equiv$/R$^{+3}$ for each rare earth will have to be different. This fact will cause some of the rare earth ions to be out balance with the resin phase and the rare earths
will separate into bands with each ion seeking the proper citrate ion concentration. Once they have separated, the citrate-ion concentration will adjust itself so that each band travels at the same rate. Under these conditions, if a rare earth ion from one band either gets ahead into a preceding band or falls behind into a following band, it will meet an unfavorable citrate ion concentration and its progress will either be retarded or speeded up so that it returns to its own band. Therefore, one would expect the band fronts to be extremely sharp under equilibrium conditions.

C. Narrow Bands

It will be noted from the above discussion that if trace amounts of rare earths are adsorbed on the columns and eluted with citric acid, in the pH and concentration ranges given above, that the individual rare earth bands will be extremely narrow after development; they will ride one upon the other and in no circumstances will they spread apart under equilibrium conditions. If the band fronts could be maintained perfectly flat, each elution band would be rectangular in shape with an extremely narrow abscissa. If the band fronts become tilted or channeled, as practically always happens in practice, then as the solution moves across a given cross-section
of the column one rare-earth will be exchanging in one area while a different rare earth will be exchanging elsewhere in the same plane. The eluate will be made up of a composite as it flows from the column and the separation will be very poor. Therefore, it is desirable when separating rare earths under these conditions of pH and concentration to choose column diameters so as to make the rare earth bands as long as practical and to load the columns with as heavy loads as the experimental conditions will permit.

It will also be observed that if a single rare earth is adsorbed in trace amounts, and if the bands become tilted upon elution, pseudo bell-shaped elution curves will result. This effect results from the fact that the quantity of rare earth being removed at the bottom of the column does not come from a complete laminar cross-section of the adsorbed band, but rather from rectangular increments of an inclined ellipse which progresses across the bottom boundary of the resin bed. Accordingly, the bell-shaped curve is in reality made up of an envelope of narrow rectangular increments which first increase in height and then decrease as successive chords of the tilted ellipse are eluted from the column.
V. SUMMARY

1. Investigations were made on the adsorption of neodymium on Nalcite HCR resin beds and subsequent elution with citric acid-ammonium citrate solutions at a number of pH values. Quantitative measurements were made to determine the distribution of the ions between the aqueous and resin phases under equilibrium conditions.

2. It was found that neodymium adsorbed on the resin could be observed as a dark band when viewed under blue light and several photographs of bands were presented which showed the effects of channeling in the bed.

3. Methods for preventing the formation of the insoluble precipitate, \( \text{RCit} \cdot 2\text{H}_2\text{O} \), were studied. It was found that a small initial sample, a fast flow rate in the early stages of elution and the introduction of excess acid to the sample being adsorbed each tended to prevent the formation of this insoluble compound.

4. The rate of movement of the front edge of the adsorption band was measured and found to be proportional to the rate at which the ammonium ion was being added from the eluant. It was found that the break-through volumes, in liters, could be calculated precisely by dividing the number of equivalents of hydrogen-form resin remaining in the column after the neodymium band
was adsorbed by the number of equivalents of ammonium ion per liter of eluant.

5. The capacity of the resin for both monovalent and trivalent ions was measured. In both cases a capacity of 4.26 meq. per gram of air-dried hydrogen-form resin was observed; from this it was concluded that neodymium was adsorbed only as the tripositive ion.

6. From theoretical considerations and the behavior of the adsorbed bands the following relationships were formulated.

\[
\frac{R_T}{R_S} = \frac{\text{NH}_4^+}{\text{H}_3^+} = \frac{H_2^+}{Q} = \frac{Q}{\text{NH}_4^+}
\]

Experiments showed that these relationships were valid for the pH range investigated.

7. Analytical data from five experimental runs were plotted and it was found that the concentration of ammonium ion in the eluate, the concentration of total neodymium in the eluate and the concentration of ammonium ion in the eluant were linear functions of one another. Equations were derived which related the slopes of the above curves to each other.

8. It was shown that the concentration of the hydrogen ion in the resin phase was so low, compared to the concentrations of the ammonium and the neodymium ions
in the equilibrium band, that it could be neglected in the material balance equation. Knowing the concentrations of the total neodymium and ammonium ion in the eluate as functions of the ammonium ion concentration in the eluant and also the amount of neodymium on the resin bed, it was possible to calculate the length of the adsorbed band under equilibrium conditions.

9. From the material balance equations it was shown that the sum of the concentration of the ammonium ion plus the concentration of the total neodymium in the eluate was always equal, within the experimental error, to the concentration of the ammonium ion in the eluant.

10. Evidence was presented to show that the predominant complex neodymium ion was \( \text{NdCit}_2^= \).

11. Making the oversimplified assumption that \( \text{NdCit}_2^= \) was the only neodymium-citrate complex present in the eluate, the pH values of the eluates could be calculated with a fair degree of accuracy.

12. It was shown that, if the equilibrium constants were known and the activity coefficients of the ions in the aqueous and resin phases were determined independently, all pertinent data could be calculated on the assumptions that equilibrium was attained and that electrical neutrality was maintained both in the aqueous phase and in the resin. Even without knowing the values
of the equilibrium constants and the activity coefficients, it was possible to describe the behavior of the system quantitatively, since the ammonium-ion intercept and the slope of the linear relationship between total neodymium in the eluate and ammonium ion in the eluant were known experimentally for 0.1% citrate solutions.

13. In setting up the necessary equations to calculate the variables, to an accuracy of one or two per cent, it may be necessary to make a correction by including the possibility of formation and, therefore, the equations which involve the HNdCit$_2^-$ complex.

14. The mechanism of self-sharpening of rare-earth bands upon elution was discussed.

15. The effect of channeling on narrow bands was considered in detail. Several photographs of narrow bands were presented.
VI. LITERATURE CITED

   *J. Am. Chem. Soc.*, 69, 2777 (1947)

   *ibid.*, 69, 2786 (1947)

   *ibid.*, 69, 2812 (1947)

   *ibid.*, 70, 1671 (1948)

5. Spedding, F. H., E. I. Fulmer, T. A. Butler and J. E. Powell
   *ibid.*, 72, 2349 (1950)

6. Spedding, F. H., E. I. Fulmer, J. E. Powell and T. A. Butler
   *ibid.*, 72, 2354 (1950)

7. Spedding, F. H., and J. L. Dye
   *ibid.*, 72, 5350 (1950)

8. Spedding, F. H., E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe
   *ibid.*, 73, 4840 (1951)

   *ibid.*, 69, 2769 (1947)

    *ibid.*, 69, 2781 (1947)

    *ibid.*, 69, 2792 (1947)

    *ibid.*, 69, 2800 (1947)
   *ibid.*, 62, 2818 (1947)

   *ibid.*, 62, 2859 (1947)

15. Mayer, S. W., and E. R. Tompkins
   *ibid.*, 62, 2866 (1947)

   *ibid.*, 71, 2504 (1949)

17. Thompson, H. S.

18. Way, J. T.
   *ibid.*, 11, 313 (1850)

19. Way, J. T.
   *ibid.*, 12, 123 (1852)

20. Way, J. T.
   *ibid.*, 15, 491 (1855)

21. Eichhorn, H.

22. Lemberg, E.
   *Z. deut. geol. Ges.*, 22, 335 (1870)

23. Lemberg, E.
   *ibid.*, 28, 519 (1876)

24. Gans, R.
   *Jahrb. preuss. geol. Landesanstalt.*, 26, 179 (1905)

25. Gans, R.
   *ibid.*, 27, 63 (1906)

26. Gans, R.
   German Patent 197,111 (1906)

27. Broderick, S. J., and D. Bogard
   *U. S. Bureau of Mines Report of Investigation No. 3559* (1941)

28. Liebknecht, O.
   *U. S. Patent 2,206,007* (June 23, 1940)
29. Adams, B. A. and E. L. Holmes
   J. Soc. Chem. Ind., 54, 1-6T (1935)

30. Myers, R. J., J. W. Eastes and F. J. Myers
   Ind. Eng. Chem., 33, 697 (1941)

31. Kunin, R. and R. J. Myers
   "Ion Exchange Resins," John Wiley and Sons, Inc.,
   New York (1950)

32. Kunin, R.
   Ind. Eng. Chem., 44, 79 (1952)

33. Boyd, G. E.

34. D'Alelio, G. F.

35. Hale, D. K. and D. Reichenberg

36. Hohenstein, W. P. and H. Mark
   J. Polymer Sci., 1, 127 (1946)

37. Bauman, W. C. and J. Eichhorn
   J. Am. Chem. Soc., 69, 2830 (1947)

38. Donnan, F. G., Z. Elektrochem., 17, 572 (1911)

   ibid., 69, 2836 (1947)

40. Jenny, H.
   J. Phya. Chem., 36, 2217 (1932)

41. Walton, H. F.
   J. Franklin Inst. 232, 305, 318 (1941)

42. Walton, H. F.
   J. Phya. Chem., 47, 371 (1943)

43. Walton, H. F.
   ibid., 49, 471 (1945)

44. Walton, H. F.

46. Duncan, J. F., and B. A. J. Lister  
   Ibid., 1949, 3285

47. De Vault, D.  
   J. Am. Chem. Soc. 65, 532 (1943)

48. Glueckauf, E.  

49. Glueckauf, E.  
   Nature, 156, 748 (1945)

50. Glueckauf, E.  

51. Glueckauf, E.  
   Ibid., 1949, 2280

52. Topp, N. E., and K. W. Pepper  
   J. Chem. Soc., 1949, 3299

53. Naehod, P. O., and W. Wood  

54. Argersinger, W. J., Jr., A. W. Davidson and O. D. Bonner  
   Trans. Kansas Acad. Sci., 52, 404 (1950)

55. Glasstone, S., "Text-Book of Physical Chemistry,"  
   D. van Nostrand Co., Inc., New York (1940)  
   pp. 231 and 678

56. Reichenberg, D., K. Pepper and D. McCauley  

57. Gregor, H. P.  
   J. Am. Chem. Soc., 70, 1293 (1948)

58. Gregor, H. P.  
   Ibid., 73, 642 (1951)

59. Donnan, F. G., and E. A. Guggenheim  
   Z. physik. Chem., 162A, 346 (1932)
60. Donnan, F. G.

61. Gregor, H. P., K. M. Held and J. Bellin,
    *Anal. Chem.*, 22, 620 (1951)

62. Gregor, H. P., F. Gutoff and J. I. Bregman
    *J. Colloid Sci.*, 6, 245 (1951)

63. Gregor, H. P., J. I. Bregman, F. Gutoff, R. D.
    Broadly, D. E. Baldwin and C. G. Overberger
    *Ibid.*, 6, 20 (1951)

64. Lowen, W. K., R. W. Stoener, W. J. Argersinger,
    Jr., A. W. Davidson and D. N. Hume
    *J. Am. Chem. Soc.*, 73, 2666 (1951)

65. Bonner, O. D., W. J. Argersinger, Jr., and A. W.
    Davidson
    *Ibid.*, 74, 1044 (1952)

66. Bonner, O. D., A. W. Davidson and W. J. Argersinger,
    Jr.
    *Ibid.*, 74, 1047 (1952)

67. Marinsky, J. A.
    "A Study of the Ion-Exchange Equilibria Between
    Hydrogen Ion and Sodium, Calcium, Barium, and
    No. 34, Laboratory for Nuclear Science and Engineer-
    ing, Massachusetts Institute of Technology, Cam-
    bridge, Massachusetts (1949)

68. Juda, W., and M. Carron
    *J. Am. Chem. Soc.*, 70, 3295 (1948)

69. Wilson, J. N.
    *Ibid.*, 62, 1583 (1940)

70. Weiss, J.
    *J. Chem. Soc.*, 1943, 297

71. Thomas, H. C.,
    *Ann. N. Y. Acad. Sci.*, 42, 161 (1943)

72. Walter, J. E.,
    *J. Chem. Phys.*, 12, 229 (1945)
73. Tevebaugh, A. D.

74. Ryabchikov, D. I., and E. A. Terent'eva


VII. ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. F. H. Spedding for his helpful advice and encouragement during the course of these investigations and in the preparation of this thesis. During the months this research was in progress Dr. Spedding showed a keen interest and actually devoted much valuable time to the theoretical aspects of the problem.

The author also wishes to thank Dr. E. I. Pulmer for helpful consultation on problems connected with mold growth and bacterial action and for his editorial suggestions relating to this thesis. In addition, he would like to thank his wife, Darlene, for her assistance in preparing the manuscript and Mr. J. L. Evans for his assistance in carrying out many of the experiments.