

formed was left upstream, as the reaction progressed, where it was thereafter contacted by nothing but fresh neodymium chloride solution.

As a consequence of these conditions, an essentially saturated band of neodymium resin forms at the top of the resin bed. The fraction of the resin bed thus converted to the neodymium state would be the ratio of the number of equivalents of neodymium adsorbed to the total capacity of the bed; consequently, it is possible to predict the position of the front of the adsorbed band before elution is begun. Since the resin shrinks approximately 10% when converted from the hydrogen to the neodymium form, the approximate length of the adsorbed band also can be predicted. After the neodymium is adsorbed, distilled water is poured through the column in order to remove the acid liberated during the adsorption step. This ensures that the only shrinkage which takes place is that which occurs within the neodymium band, and it follows that the exchange capacity of the remaining hydrogen-form bed per unit length does not change. As the ammonium ion is the only cation in the eluant which has an appreciable concentration, and since the ammonium ion and the neodymium break-throughs occur simultaneously, it follows that the rate of movement of a band front down the resin bed should be proportional to the amount of ammonium ion in the eluant at a given flow rate. From these observations, it is clear that the break-through volume, in liters, may be calculated precisely by dividing the number of equivalents of hydrogen-form resin, remaining in the column after the rare earth band is adsorbed, by the number of equivalents of ammonium ion

per liter of eluant. The calculated and observed break-through volumes for a number of experiments are given in Table III. The observed values are generally slightly lower than those calculated, since some evaporation takes place while the eluate is being collected and measured, and because the break-through is usually observed before all the hydrogen ion is replaced, due to channeling which causes irregular band fronts. In view of these considerations, the data of Table III are in excellent agreement.

The rate of travel of the rear edge of the band and the rate at which the band spreads out during the initial development of the band are related, but obscure, and are probably complex functions involving the flow rate and pH of the eluant.

In the companion, theoretical paper it is shown that the mole fraction of the ammonium and rare earth resins in the equilibrium band can be calculated; therefore, if the shrinkage which occurs when the rare earths and ammonium ion are adsorbed is taken into account, the length of the equilibrium band can be calculated.

Acknowledgments.—The authors wish to express their gratitude to Jack Evans, of this Laboratory, for his assistance in performing a number of the experiments described in this paper and to Dr. Toshio Nakai for rechecking the relationships between the concentrations of the constituents in the aqueous and resin phases.

AMES, IOWA

[CONTRIBUTION NO. 299 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]¹

The Separation of Rare Earths by Ion Exchange. VIII. Quantitative Theory of the Mechanism Involved in Elution by Dilute Citrate Solutions

BY F. H. SPEDDING AND J. E. POWELL

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The elution of rare earths from cation-exchange resins by means of dilute citrate solutions in the pH range 5.0 to 8.0 has been explained using only classical thermodynamic relationships and the concepts of electrical neutrality and material balance. The predominant ion species have been discussed in detail and the important constants for the neodymium-ammonium citrate exchange system have been evaluated from experimental data. Theoretical curves have been constructed and compared to the actual experimental points; the agreement is excellent.

I. Introduction

This Laboratory has published a series of papers in which it was demonstrated that individual rare earths could be separated from each other in kilogram quantities. The rare earths obtained at a purity greater than 99.9% amounted to 60–95% of the quantities involved and the remainder consisted of binary mixtures.^{2,3} Recent advances have permitted column operation on a continuous basis. The process can be carried out with a single pass through a series of ion-exchange columns of reasonable number, and under conditions wherein the bulk of the eluant is recycled. The operations involved are so simple that the columns can be run with only occasional attention and a minimum of labor.³ As the work progressed and the basic principles were better understood, it became possible to increase the efficiency, and thereby the yields, many-fold during the past several years.

In the course of these investigations, it became

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) (a) F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, *THIS JOURNAL*, **72**, 2354 (1950); (b) F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951).

(3) F. H. Spedding and J. E. Powell, ISC-349, Iowa State College (1953).

apparent that the behavior of the rare earths on the columns was very reproducible, and that the character of the bands obtained resulted from the attainment of true equilibrium throughout the system. Therefore, it was decided to study the equilibrium thoroughly, using small columns, a single pure rare earth, and changing only one variable at a time. During the past four years, a great many experiments were performed with this aim in view. One typical set of such experiments, wherein the total citrate concentration of the eluants entering the columns was kept constant and the only independent variable was the amount of ammonia added to the eluants to adjust the pH, is described in a companion paper.⁴ The theory developed in this article will be applied to this typical set of data. It should be mentioned that the basic theory applies equally well to other sets of data involving other citrate concentrations and other rare earth species in the range where the theory might be expected to apply.

II. Theory

In the course of our investigations it was established that, when the concentration of ammo-

(4) F. H. Spedding and J. E. Powell, *THIS JOURNAL*, **76**, 2545 (1954).

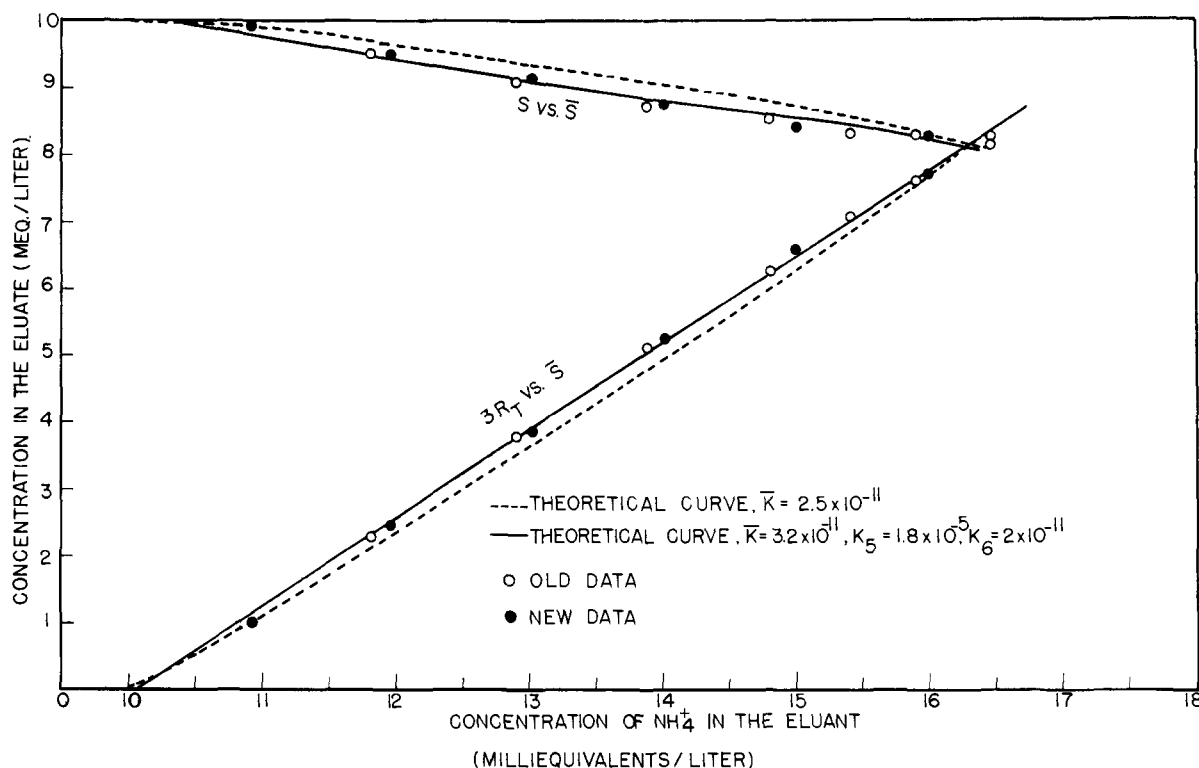


Fig. 1.—Comparison of experimental data for the elution of neodymium with certain theoretical curves; correlations between the concentrations of total neodymium and of ammonium ion in the eluate with the ammonia concentration of the eluant.

mium ion, hydrogen ion or total rare earth in the eluate was plotted against the volume of eluant passed through a column, flat-topped elution curves were obtained over a considerable range of citrate concentrations and over a considerable range of *p*H (the *p*H is, of course, a function of the ammonia added to a given solution of citric acid). The heights of the plateaus in the elution curves remained constant, within experimental error, over a period of many days as the bands progressed off the columns, and depended solely upon the total citrate concentration and the *p*H of the eluant. The plateau values were independent of the rate of flow of the eluant through the resin bed and the amount of rare earth sorbed on a given column, provided the flow rate was sufficiently slow to obtain the flat-topped band and the resin bed was long enough to allow the band to spread out to its equilibrium length. Once the equilibrium condition was attained the band remained constant in length during elution down the remaining portion of the bed.

In order to confirm the establishment of true equilibrium, experiments were performed in which the band initially sorbed upon the resin bed was varied considerably. The bands varied from pure rare earth resin, where the initial solution fed to the column consisted of pure rare earth chloride, to greatly extended hydrogen-rare earth bands produced by strongly acidifying the original rare earth chloride solution. Extended bands have also been produced by adding ammonium ion either in the original solution or by actually inserting a section of ammonium bed between two sections of rare

earth bed. In all cases, after equilibrium was obtained the same plateau concentrations were observed for a given *p*H and citrate concentration of the eluant. Further, when an equilibrium band was deliberately upset by using an excessively rapid flow rate it was found to return to its original state when the flow rate was again reduced below the critical value.

It is the purpose of this paper to deal with the theory underlying the observed phenomena. Since equilibrium conditions are obtained, one would expect the ordinary laws of thermodynamics, electrical neutrality and material balance to apply, and it should be possible to calculate quantitatively what is occurring on the columns. As Figs. 1 and 2 show, this can be done and remarkable agreement can be achieved.

It was found, in theory, that the problem could be solved to any degree of complexity which the data would warrant. One could include all species of simple and complex ions which might be considered important and, if *n* unknown variables are included, *n* independent equations can be written relating them. Therefore, if the composition of the eluant is known, it is possible, in principle, to solve uniquely for the concentrations of all ion species which result on the resin bed and in the eluate which is in equilibrium with the sorbed band. The problem can be simplified by dividing it into the following parts.

A. Ionic Species and Concentrations in the Eluate.—In the series of experiments described in the companion article,⁴ where the citric acid content of the eluant was kept constant at one gram per

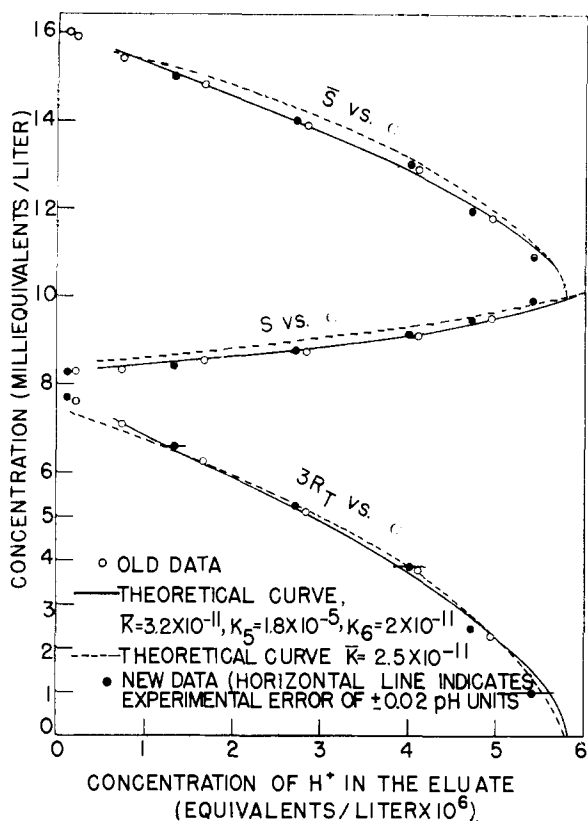


Fig. 2.—Comparison of experimental data for the elution of neodymium with certain theoretical curves; correlations between the concentrations of total neodymium and of ammonium ion in the eluate with the hydrogen ion concentration of the eluate.

TABLE I
INDEPENDENT AND OTHER EQUATIONS RELATING THE VARIABLES IN THE ELUATE^a

1. $C_T = X + Y + Z + 2U + 2V + P$
- 2.^b $H_T = 2X + Y + V - P + [c]$
- 3.^b $R_T = U + V + P + [t]$
also, but not independently
- 3a.^b $S + [3t + c] = X + 2Y + 3Z + 3U + 2V + P$
4. $H_2Cit^- \rightleftharpoons H^+ + HCit^-$
 $K_2 = \frac{a_{H^+} \times a_{HCit^-}}{a_{H_2Cit^-}};$
 $K_2' = \frac{\gamma_{H_2Cit^-}}{\gamma_{H^+} \cdot \gamma_{HCit^-}} K_2 = G_2 K_2 = \frac{cY}{X} = \frac{c^2 Z}{XK_3'}$
5. $HCit^- \rightleftharpoons H^+ + Cit^-$
 $K_3' = G_3 K_3 = \frac{cZ}{Y}$
6. $HRCit^- \rightleftharpoons H^+ + RCit_2^-$
 $K_5' = G_5 K_5 = \frac{cU}{V} = \frac{c^2 Z^2}{VK_4'}$, since
- 6a. $RCit_2^- \rightleftharpoons R^{+3} + 2Cit^-$
 $K_4' = G_4 K_4 = \frac{tZ^2}{U}$
7. $RCit_2^- + H_2O \rightleftharpoons RCitOH^- + H^+ + Cit^-$
 $K_6' = G_6 K_6 = \frac{PcZ}{U}$

^a The symbols used in these and other equations are defined in Table II. ^b Values in brackets are so small that they can be neglected in material balances.

liter and where the ammonia was varied from 10 to 16 meq. per liter, it would be expected that the important ions in the eluate would be NH_4^+ , H^+ , H_2Cit^- , $HCit^-$, Cit^- , $RCit_2^-$, $HRCit_2^-$ and $RCitOH^-$ at the higher pH's. Undoubtedly, minute quantities of R^{+3} , H_3Cit , $RCit$, $H_2RCit_2^-$ and other complex ions also are present, but these species are probably present in such small amounts that they can be neglected in material balance equations. Where these species become important it is possible to write additional equilibrium equations to include them as variables.

There are, accordingly, eight unknown concentrations in the eluate and it is possible to write seven independent equations relating them and, therefore, if any one of these concentrations is determined experimentally the other seven are uniquely determined. The independent equations for the eluate are listed in Table I.

TABLE II
DEFINITION OF SYMBOLS USED IN THE EQUATIONS

(All aqueous concentrations are expressed in moles per liter and all concentrations in the resin phase are given in moles per kilogram of air-dried resin.)

C_T	= total citric acid added to the eluate
S	= total ammonia added to the eluate to adjust the pH to the desired value
H^+	= concn. of H_3Cit in the eluate
X	= concn. of H_2Cit^- in the eluate
Y	= concn. of $HCit^-$ in the eluate
Z	= concn. of Cit^- in the eluate
$C_6H_5O^-$	= concn. of phenolate ion in the eluate
H_T'	= concn. of replaceable hydrogen in the eluate
H_T	= concn. of replaceable hydrogen in the eluate minus the contribution due to ionization of phenol and the hydrolysis of ammonium ion
S	= concn. of ammonium ion in the eluate
W	= concn. of H_3Cit in the eluate
X	= concn. of H_2Cit^- in the eluate
Y	= concn. of $HCit^-$ in the eluate
Z	= concn. of Cit^- in the eluate
H_T	= total concn. of replaceable hydrogen in the eluate
c	= hydrogen ion concn. in the eluate
R_T	= total rare earth concn. of all species in the eluate
U	= concn. of $RCit_2^-$ in the eluate
V	= concn. of $HRCit_2^-$ in the eluate
P	= concn. of $RCitOH^-$ in the eluate
t	= concn. of R^{+3} in the eluate
S_R	= concn. of ammonium ion in the resin phase
R_R	= concn. of rare earth in the resin phase
H_R	= concn. of hydrogen ion in the resin phase
Q	= total capacity of the resin expressed in equiv./kg. of air-dried resin
Σ_R	= total equiv. of cations per kg. of air-dried resin
Σ_S	= total equiv. of exchangeable species in the eluate per liter ($\Sigma_S = c + S + 3R_T$)
K_b	= thermodynamic equilibrium constant
G_n	= activity coefficient ratio
K_n'	= apparent equilibrium constant

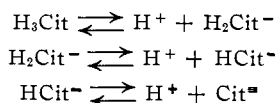
1. **Citrate Balance.**—Under the conditions of our experiments, no citrate is sorbed on the resin. Therefore, the sum of all the citrate species entering the top of the column must equal the sum of all the citrate species (properly weighted) leaving the column (see equation 1).

2. Replaceable Hydrogen Balance.—By replaceable hydrogen is meant that hydrogen which is ionizable. In other words, fixed hydrogen is not considered, *i.e.*, the hydrogen directly connected to the carbon in citric acid or involved in the water molecule when water passes through the column un-ionized. Here again, the replaceable hydrogen leaving the column must equal the replaceable hydrogen entering the column, except for the amount sorbed or desorbed as the solution passes through the resin bed. For all practical purposes, the replaceable hydrogen in the eluate is equal to the replaceable hydrogen in the eluant, because the amount of hydrogen sorbed from the solution by the resin per liter is negligible in comparison to the total replaceable hydrogen present. This fact can be ascertained readily from data presented and arises from the fact that the amount of resin in the equilibrium band is extremely small since it depends upon the ratio of concentrations of hydrogen and ammonium ion in the eluate. Even in the most unfavorable case, the difference between \bar{H}_T and H_T is less than the experimental error (see equation 2). P is introduced here with a minus sign, because, as the RCit_2^{\equiv} hydrolyzes to form RCitOH^- , extra replaceable hydrogen is made available. The hydrogen-ion concentration c itself is so small that it may be neglected in the H_T balance.

3. Rare Earth Balance.—The total rare earth measured in the eluate is the sum of all the species involved (see equation 3). The concentration of rare earth ion t is so low that it may be neglected in the R_T balance.

4. Electrical Neutrality Equations.—Since the solutions must always remain neutral, the sum of the positive charges on the ions must equal the sum of the negative charges (see equation 3a). As t and c are very small compared to S in this equation, they can be neglected within experimental error. Only three of the equations 1, 2, 3 and 3a are independent since 3a may be derived from the other three. For example: $S = 3C_T - 3R_T - H_T$. The charge balance for the eluant shows that $3C_T - \bar{H}_T = \bar{S}$ and, since $\bar{H}_T = H_T$, then $3C_T - H_T = \bar{S}$. These equations combined yield $\bar{S} = S + 3R_T$. This equality is extremely important and states that, whatever the ammonium concentration in the eluant, it is equal to the total number of equivalents of rare earth and ammonium ion in the eluate. This fact has been verified experimentally a number of times under widely varying conditions.⁴ The experimental verification of this equation is strong evidence that the replaceable hydrogen sorbed from solution by the resin is so small that it can be neglected in material balance equations, since, if any appreciable replaceable hydrogen is sorbed or desorbed on the column, \bar{H}_T is not equal to H_T , therefore, \bar{S} would not be equal to S plus $3R_T$.

5. Ionization Equations of Citric Acid.—The three ionization equations for citric acid can be written as



Since the amount of H_3Cit present in the $p\text{H}$ range used was negligible, only the mass action equations for the last two ionizations need be considered. See equations 4 and 5 in Table I. The symbols K_n' denote the apparent equilibrium constants and are equal to the true equilibrium constants K_n times the proper activity coefficient ratios G_n . In our experiments, it can be shown that the equilibrium eluate solutions are buffered automatically to an almost constant ionic strength depending upon the rare earth species involved. The activity coefficient ratios are therefore practically constant and the apparent equilibrium constants can be treated essentially as true constants. In precise calculations, the very slight drift in the apparent equilibrium constants for the citrate ionizations can be corrected for, by the data published by Bates and Pinching⁵ and Bjerrum and Unmach.⁶

6. Ionization Equations for the Rare Earth Complexes.—It has been found that the predominant rare earth complex is RCit_2^{\equiv} . This is a chelate compound in which the R^{+3} ion is completely complexed with two Cit^{\equiv} ions. While the strongest evidence for the predominance of this ion is inherent in the consistency of the quantitative calculations of this paper, there are other indications which confirm its existence. If the rare earth concentration of the eluate is plotted against the ammonium-ion concentration of either the eluate or eluant, there is a change of slope in the region where the rare earth concentration in equivalents is equal to half the equivalents of total citrate present. Similar breaks occur if other variables are plotted. Tevebaugh,⁷ working under Spedding's direction, investigated the absorption spectra of neodymium citrate solutions at various $p\text{H}$ values and found that the absorption bands of only one complex ion were predominant in the $p\text{H}$ range discussed in this paper. The dissociation of the RCit_2^{\equiv} complex into its ions is represented by equation 6a in Table I. Since this complex is undoubtedly a weak acid, it will form a small amount of HRCit_2^{\equiv} at low $p\text{H}$ values (see equation 6). There are probably minute quantities of the neutral RCit molecule also present. This is a relatively insoluble compound, but under the equilibrium conditions of our experiments does not precipitate. Under certain conditions when the concentration of rare earth on the resin is high, and before final equilibrium is established, precipitates of $\text{RCit} \cdot 2\text{H}_2\text{O}$ or $\text{R}_2\text{Cit}_2 \cdot 4\text{H}_2\text{O}$ do form on columns during elution, due to the low solubility of this compound. Therefore, the amount of RCit in the eluate has been assumed to be sufficiently small that it can be neglected. If this proves to be not the case, an ionization equation can be written and solved along with the others.

7. Hydrolysis of the RCit_2^{\equiv} Ion.—In high $p\text{H}$ solutions the RCit_2^{\equiv} ion will hydrolyze to give RCitOH^- (see equation 7). Probably in solutions of very high $p\text{H}$ other hydrolysis products are

(5) R. G. Bates and G. D. Pinching, *THIS JOURNAL*, **71**, 1275 (1949).

(6) N. Bjerrum and A. Unmach, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **21**, No. 4, 1 (1944).

(7) A. D. Tevebaugh, Ph.D. Thesis, AEC-D-2949, Iowa State College (1947).

formed, but in the range of our experiments they appear to be unimportant.

Fortunately, the equations for the eluate, 1 through 7, can be solved simultaneously to give a number of convenient relationships between the variables, and can be reduced to a single equation involving only two independent variables. If equations 4, 5, 6 and 7 are substituted into equation 1, one obtains the relationship

$$C_T = \left[\frac{c^2}{K_2'K_3'} + \frac{c}{K_3'} + 1 \right] Z + \left[2 + 2 \frac{c}{K_5'} + \frac{K_6'}{cZ} \right] U \quad (8)$$

By substituting equations 3, 4 and 5 in equation 1 one obtains

$$C_T - 2R_T = \left[\frac{c^2}{K_2'K_3'} + \frac{c}{K_3'} + 1 \right] Z - P \quad (9)$$

Similar substitutions yield

$$H_T = \left[\frac{2c^2}{K_2'K_3'} + \frac{c}{K_3'} \right] Z + \left[\frac{c}{K_5'} + \frac{K_6'}{cZ} \right] U = \left[\frac{2c^2}{K_2'K_3'} + \frac{c}{K_3'} \right] Z + V - P \quad (10)$$

and

$$S = 3C_T - H_T = \left[\frac{c^2}{K_2'K_3'} + 2 \frac{c}{K_3'} + 3 \right] Z + \left[6 + 5 \frac{c}{K_5'} + 4 \frac{K_6'}{cZ} \right] U \quad (11)$$

Finally, by rearranging equations 8 and 11 and dividing one by the other, one obtains

$$\frac{\bar{S} - \left[\frac{c^2}{K_2'K_3'} + 2 \frac{c}{K_3'} + 3 \right] Z}{C_T - \left[\frac{c^2}{K_2'K_3'} + \frac{c}{K_3'} + 1 \right] Z} = \frac{\left[6 + 5 \frac{c}{K_5'} + 4 \frac{K_6'}{cZ} \right]}{\left[2 + 2 \frac{c}{K_5'} + \frac{K_6'}{cZ} \right]} \quad (12)$$

Equation 12 contains only two independent variables c and Z . \bar{S} and C_T are determined by the composition of the eluant fed to the column. Unfortunately, the constants K_5 and K_6 have not yet been determined by independent means, nor have the activity coefficient ratios G_5 and G_6 of the ions involved been established. However, these activity coefficient ratios should remain constant, since the ionic strength of the solutions does not change appreciably throughout the range being discussed here. If the K_n' values were known independently, then, if any one of the variables in the eluate was determined experimentally, all the other ionic concentrations could be calculated uniquely and precisely. Since it is possible to determine three of the unknown variables experimentally for any eluate, namely, S , R_T and c , both K_5' and K_6' could be evaluated for each experiment. Taking the best average values of K_5' and K_6' determined in this manner, it was found that, if the measured values of one variable—say hydrogen-ion concentration—were substituted in the above equations, excellent agreement between the calculated and observed values of the other measurable variables resulted. The solutions of these equations clearly showed that $\text{RCit}_2^=$ was indeed the dominant rare earth species present.

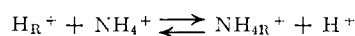
B. Ionic Species and Concentrations in the Resin Phase.—There are three arbitrary variables

connected with the resin phase, namely, the concentrations of rare earth, ammonium ion and hydrogen ion within that phase. One equation can be written involving only these concentrations, that is, the material balance or electrical neutrality equation for the resin phase.

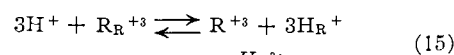
$$Q = 3R_R + S_R + [H_R] \quad (13)$$

The amount of hydrogen ion in the resin phase is negligible compared to either the rare earth or ammonium-ion concentrations.

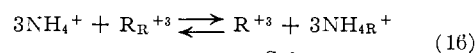
C. The Solution-Resin Equilibria.—Three independent equations can be written involving both the resin and aqueous phases. Whenever a rare earth ion is sorbed in the resin phase, it replaces three ammonium or hydrogen ions or a combination thereof. Therefore, three equilibria must be considered.



$$K_7 = \frac{a_{NH_{4R}^+} a_{H^+}}{a_{NH_4^+} a_{H_R^+}}; \quad K_7' = \frac{f_{NH_{4R}^+} \times \gamma_{H^+}}{\gamma_{NH_4^+} \times f_{H_R^+}} \quad K_7 = G_7 K_7' = \frac{S_R c}{S H_R} \quad (14)$$



$$K_8' = G_8 K_8 = \frac{H_R^3}{c^3 R_R}$$



$$K_9' = G_9 K_9 = \frac{S_R^3}{S^3 R_R}$$

Only two of these equations are independent, since the third can be derived from the other two. Here again the activity coefficient ratios have been included in the K_n' values. The activity coefficients of the ions in the eluate are approximately constant for the citrate concentrations used in our experiments, because the solutions of neodymium eluate automatically adjust themselves to an ionic strength of about $15.8 \pm 0.2 \times 10^{-3}$. The behavior of the activity coefficients of ions within the resin phase is not too well established. However, if one derives the above equations by the Donnan Equilibrium Mechanism, one would conclude that, under the conditions of our experiments where the eluting solutions are very dilute, the concentrations of anions from the eluate which enter the resin phase would be inappreciable. Also, if one assumes that the ions are sorbed within the resin phase by charge only, so that they are free to adjust themselves in the water phase within the resin to satisfy the charge relationships, then the thermodynamic constants (involving activities) should be unity for the exchange equations. Since the sorbing resin is a cross-linked polymer having its negative charges in fixed positions, the negative ionic atmosphere about any point should be virtually independent of the mole fractions of various cations sorbed. Therefore, when positive ions are sorbed in the resin, they should come to equilibrium with the negative charges so that the positive atmosphere would be determined by the fixed negative atmosphere. Accordingly, the resultant ionic atmosphere around a given ion would be fixed regardless of the mole fractions of cations present in the resin. Since the activity coefficient ratios depend upon the ionic at-

mospheres, these ratios should also be constant. Of course, if the resin expands or contracts as the mole fractions of the cation species vary, due either to the localization of positive charges on polyvalent ions or to the sorption or desorption of water, the activity coefficient ratios would shift somewhat with mole fraction and result in a drift of the apparent equilibrium constants. This drift would be a second-order effect, and it might be expected to be small. Whether or not these speculations are valid will be indicated from our experiments by how constant \bar{K} (equation 19) remains as the mole fractions of cations in the resin phase are changed.

It should be pointed out that in most of the experiments described in the literature the apparent constants for resin equilibria vary, frequently showing a steep slope when plotted against the mole fraction of one of the cations sorbed on the resin. However, in most cases the scientists, for experimental convenience, have buffered their aqueous phases at rather high ionic strengths. Under these conditions an appreciable amount of negative ions enter the lattice, and the positive ions would then be likely to readjust so as to result in a considerable change in ionic atmosphere within the resin phase. It would be interesting to repeat a number of these experiments wherein the solution phase was buffered at extremely low ionic strengths.

If polyvalent ions in addition to their charge attraction also exhibit some association with the resin anions, the apparent equilibrium constants might be considerably different from unity. However, the equivalence of the resin for most valency species indicates that the binding cannot generally be highly localized, and that the polyvalent ions must be free to adjust themselves to equilibrium conditions as determined by the negative atmosphere within the resin.

D. Equivalent Equilibrium between the Solution and Resin Phases.—It is noted experimentally that, as a sorbed rare earth band is eluted down a column, it spreads out or shrinks until it reaches an equilibrium length and that from there on, as the band progresses down the column, the length of the band remains constant. This means that the eluant, as it encounters the rear edge of the band, continually picks up rare earth ions, ammonium ions and hydrogen ions in a fixed ratio and deposits them in exactly the same ratio when it reaches the bottom of the sorbed rare earth band where the liberation of hydrogen ion from the acid resin competes for the Cit^{\ominus} ion and permits the redeposition of the rare earth on the resin. In other words, the equivalent fractions of hydrogen ion, ammonium ion and rare earth on the resin within the equilibrium band are equal, respectively, to the equivalent fractions of the hydrogen ion, ammonium ion and total rare earth in the associated eluate. This conclusion has been verified experimentally a number of times by analyzing both the resin and solution phases to determine the equivalent ratio of ammonia to rare earth in each phase.⁴ Good agreement, within experimental error, was found between these ratios for all measurements made. These ratios can be rearranged and expressed as shown in equation 17

$$\frac{R_R}{R_T} = \frac{S_R}{S} = \frac{H_R}{c} = \alpha = \frac{\Sigma_R}{\Sigma_S} = \frac{Q}{S} \quad (17)$$

The first equality results from the establishment of the equilibrium band; the second equality also results from the establishing of this band, but it should be noted that it is also equivalent to setting K_7' in equation 14 equal to unity.⁸ Since $R_R = \alpha R_T$, $S_R = \alpha S$ and $H_R = \alpha c$, then

$$3R_R + S_R + H_R = \Sigma_R = Q = \alpha(c + S + 3R_T) = \alpha \Sigma_S = \alpha S \quad (18)$$

Therefore

$$\alpha = \frac{\Sigma_R}{\Sigma_S} = \frac{Q}{S}$$

We now note that for the entire system there exist eleven unknowns and eleven independent equations. A second important equation involving only c and Z can be obtained by combining equations 3, 6a, 6, 7, 16 and 17.

$$\bar{K} = K_9' K_4' Q^2 = S^2 Z^2 \left(1 + \frac{c}{K_5'} + \frac{K_6'}{cZ} \right) \quad (19)$$

Equations 12 and 19 can be solved simultaneously to obtain c and Z . This can perhaps best be done graphically.

It is seen from the equations that, for any arbitrary value of citric acid and ammonia entering the top of the column, the concentrations of all the ions in the eluate and on the resin under equilibrium conditions can be calculated for any rare earth, if the proper values of \bar{K} , K_5' and K_6' are known. These constants have not been determined by independent means; nevertheless, by substituting experimental values in the equations, the apparent equilibrium constants can be evaluated and are found to be relatively constant. Fortunately, RCitOH^- is not present in any appreciable quantity at the lower pH values, so that K_5' and \bar{K} can be determined very closely in this range, then K_6' can be evaluated in the high pH range and, by substituting this approximate value of K_6' in the lower range, better values of the other constants can be found.

The best values of the three fundamental constants for neodymium have been determined by substituting experimental data in the equations; then, starting with fixed citric acid and ammonia values in the eluants and the three constants, theoretical curves (Figs. 1 and 2) have been constructed and compared with experimental data. The agreement is remarkable, showing that \bar{K} , K_5' and K_6' are nearly constant. Actually, it will be noted that there is a slight drift in the experimental rare earth values when they are plotted against the ammonia in the eluant. This drift is small, but might be anticipated since it is known that the resins do shrink somewhat as the mole fraction of neodymium on the resin increases. This would cause a slight change in \bar{K} , since the activity coefficient ratios for the ions in the resin phase would change as the resin contracted. The surprising conclusion is that the drift is as small as it is.

(8) Bonner and co-workers have shown the apparent equilibrium constant for the ammonium-hydrogen exchange, even for one molar solutions in contact with the resin, decreased and approached unity as the mole fraction of ammonium ion in the resin phase was increased (THIS JOURNAL, **74**, 1044 (1952)).

E. Hydrolysis at High pH Values Which May Occur in the Eluate or Eluant.—When the pH of either the eluant or eluate is greater than approximately 6.5, the ammonium ion in solution hydrolyzes appreciably. In many of the eluants used in the experiments, 0.2% phenol was added as an inert diluent to prevent the growth of molds and bacteria. To establish that the phenol acted only as an inert diluent, the pH's of the eluants were calculated from the citrate concentration and the amounts of ammonia added, using the ionization constants of citric acid (corrected for ionic strength) which are given in the literature.^{5,6} Excellent agreement was found between the measured and calculated values. Above a pH of 6.5, phenol begins to ionize to some extent, and to obtain agreement above this pH small corrections had to be made for both the hydrolysis of ammonium ion and the ionization of phenol. Close consideration of electrical neutrality and hydrogen balance equations shows that

$$\bar{S} - [C_6H_5O^-] - [NH_4OH] = \bar{X} + 2\bar{Y} + 3\bar{Z} \quad (20)$$

and

$$\bar{H}_T' = \bar{H}_T + [C_6H_5O^-] + [NH_4OH] = 2\bar{X} + \bar{Y} \quad (21)$$

Therefore, it follows that

$$\bar{S} + \bar{H}_T = 3\bar{X} + 3\bar{Y} + 3\bar{Z} = 3C_T \quad (22)$$

and, upon rearranging

$$3C_T - \bar{S} = \bar{H}_T = H_T$$

Thus, it is seen that, even if the eluant is in the pH range where the ammonium hydroxide concentration is appreciable and the phenol appreciably ionized, a correction is unnecessary as long as the resulting equilibrium eluate is below a pH of 6.5. The correction is taken into account when the measured ammonia value \bar{S} is used to calculate the H_T of the eluate instead of the actual value of the ammonium ion in the eluant. This results in a negative \bar{H}_T at high pH values, and means that the $RCit_2^=$ must hydrolyze sufficiently in the resulting eluate to correct the deficiency and to supply the hydrogen associated with the citrate species in the eluate. It is evident that, as long as the resulting eluate has a pH below 6.5, any extra replaceable hydrogen formed in the eluant, due to the hydrolysis of ammonium ion or the ionization of phenol, will be recombined when the ammonium ion and the phenol in the eluate are no longer hydrolyzed or ionized. On the other hand, if the pH of the eluate is above 6.5, a correction term must be added to H_T to account for the extra replaceable hydrogen which is made available by ionization and hydrolysis. The correction can be calculated simply from the ionization constants of phenol and ammonium hydroxide.

III. Discussion of Results

From the remarkable agreement between calculated and observed variables for such a complicated system as that existing on ion-exchange columns when rare earths are separated, it is obvious that it is possible to approach equilibrium conditions very closely and, under such conditions, the ordinary laws of chemical thermodynamics can be applied. These conditions are unique in that they minimize the complexities arising from rapidly varying ionic

atmospheres and rapidly changing activity coefficients. Furthermore, the equations are of such a nature that, if the experimental range is extended and other complex ions become important, for each unknown added a corresponding equation is available and the problem should still be solvable. While the equilibrium constants involved in the equations can be determined from the data, the actual numerical values cannot be determined precisely; however, the first figure and the exponential are probably correct, although the second digit may be open to some question. This uncertainty arises because only two-figure accuracy is obtained in the pH measurements and, further, there is an interplay between constants so that if one constant is varied slightly, in one direction, another constant can be varied so as to partially compensate for the change. Preliminary observations of data now being obtained for erbium ion-exchange systems indicate that the same set of equations apply very well, and that the constants shift in just the manner one would predict as the rare earth involved is changed.

The broken line curves in Figs. 1 and 2 are obtained by assuming that the rare earth in solution consists of $NdCit_2^=$ entirely. In combining equations to obtain the expression for $\bar{K} = K_3'K_4'Q^2$, the tripositive rare earth ion concentration, t , was eliminated and the variable U was introduced. If the rare earth in the aqueous phase is assumed to consist entirely of the single species $RCit_2^=$, the value of t thus introduced would be too large, and the value for \bar{K} obtained would be lower than if the proper value of t had been used.

By taking into account the small amounts of $HRCit_2^=$ and $RCitOH^-$ ions actually present, it is possible to more correctly express t , so that it can be properly eliminated, and to obtain a substantially better fit of the experimental data. The solid curves in Figs. 1 and 2 are the result of considering $HRCit_2^=$ and $RCitOH^-$. The curves are actually not very sensitive to V and P , the respective concentrations of $HRCit_2^=$ and $RCitOH^-$; therefore, it is not possible to calculate the numerical values of \bar{K} , K_3' and K_4' to much better than one-figure accuracy from the experimental data. If it were possible to calculate one of the constants independently, the others could be determined with greater precision, because the fixing of one constant reduces the interplay between constants which experimental errors in the data permit. The curves are most sensitive to V in the central portions and to P in the hydrogen-ion plots at high pH values. While P does not play a very important role in the experimental range of the data for neodymium, it becomes increasingly important with the heavier rare earths as does V .

We have chosen to neglect the presence of the $RCit$ species in the eluate. If its presence is considered in the equations, it is found that it causes a shift in the curves over a considerable range of \bar{S} in much the same manner as V . It may later be shown that a small amount of $RCit$ is actually present, in which case K_5' for the $HRCit_2^=$ would be decreased slightly, and K_6' for the $RCitOH^-$ species would also be affected.

One conclusion derived from these equations is extremely important and accounts for the unique success of the ion-exchange method in separating rare earths. It will be noted that once the ammonia in the eluant is fixed, all variables in the equilibrium eluate and on the column are determined for each individual rare earth present. As the equilibrium constants of the complexes change from rare earth to rare earth, the Cit^{\equiv} concentration in the eluate changes. This means that the rare earths must separate into bands on the resin bed, each band having a specific citrate concentration, hydrogen-ion concentration and ionic strength associated with it. As a result of this, the bands develop autosharpening boundaries, and one band rides immediately on the tail of the preceding band. If an ion of a given rare earth species gets ahead of or behind its own band for any reason, it will be subjected to an adverse citrate concentration and will either be accelerated or retarded in its movement down the column, so that it returns to its own band.

It will be seen, while in theory it is possible to separate tracer quantities of rare earth ions on ion-exchange columns, that in practice, under equilibrium conditions as carried out in *these experiments*, it is impossible to do so. There is always a slight tilting of the band and a small amount of channeling so that when the band front leaves the column one part of the front will have passed the boundary while the other part still remains on the resin bed. For an infinitely thin band, there will always be found a mixture of rare earths, at least binary in composition, in the eluate. The requirement for good separation of rare earths is that the band be long compared with its diameter, so that any tilting of the band is small compared with the length of the band. If tracer quantities are to be separated under these conditions, very small diameter col-

umns should be used and carriers should be present to give the proper type of bands. Of course, carrier-free tracers may be separated if non-equilibrium conditions are used in other citrate ranges, but it is our conclusion that they cannot be separated under the conditions of *these particular experiments*.

Under equilibrium conditions, the equations indicate that flat-topped elution curves should be obtained. However, it is interesting that, if the bands are narrow due to only a small amount of a rare earth species being present, a bell-shaped elution curve may be observed. This results from the fact that the columns are circular in cross-section and that, if a narrow band is tilted, the concentration of a particular rare earth in the eluate is proportional to the area of the band front crossing the boundary at a given moment. This area will vary from zero, at the edge, to a maximum corresponding to the diameter of the column, and then decrease to zero again. The bell-shaped curve observed is really the envelope of a series of equilibrium increments weighted according to the geometry of the sorbed band.

Under non-equilibrium conditions, where the bands are continually spreading out as they progress down the column, true bell-shaped curves are obtained, but the height of these curves continually diminishes as the length of the column is increased, and there is always a certain amount of overlap of one rare earth with the other. Under these conditions, equation 17 is no longer controlling. Instantaneously, at any point in the column, the solution adjusts itself, according to the other ten equations, to the concentrations of the components on the resin at that point, or *vice versa*, but the adjustment is different at each succeeding point, and the concentrations constantly change as the band spreads out.

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The Use of Copper as the Retaining Ion in the Elution of Rare Earths with Ammonium Ethylenediamine Tetraacetate Solutions

By F. H. SPEDDING, J. E. POWELL AND E. J. WHEELWRIGHT

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A rapid method for separating mixtures of rare earths into the pure components is described. The method consists of eluting a band of mixed rare earths adsorbed on a cation-exchange resin through a second cation-exchange bed in the copper^{II} state. The eluant consists of an ammonia-buffered solution of ethylenediaminetetraacetic acid. It was found that gram quantities of pure heavy rare earths could be obtained in a few days by this method.

Introduction

In a preliminary note,² the possibility of using ethylenediamine tetraacetic acid as an eluting agent for the separation of adjacent rare earths on cation-exchange resins was discussed. This earlier publication described an experiment in which a mixture of neodymium and praseodymium was

eluted through a cation-exchange bed in the iron^{III} state with a solution of ammonium ethylenediamine tetraacetate. The iron^{III} resin bed served as a barrier through which a solution of rare earth-ethylenediamine tetraacetate complex could not pass without decomposition, since the iron^{III} ion forms a more stable complex with EDTA than does any trivalent rare earth ion. In this preliminary experiment, only short sections of resin bed were used and a moderate degree of separation was attained. Subsequent experiments with longer resin beds,

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *THIS JOURNAL*, **76**, 612 (1954).