as α increases has been observed oscillographically.[1] Convection effects appear to become operable near α = 0.0012 v./sec.

BAYTOWN, TEXAS

[CONTRIBUTION NO. 298 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

The Separation of Rare Earths by Ion Exchange. VII. Quantitative Data for the Elution of Neodymium

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

RECEIVED AUGUST 17, 1953

The elution of neodymium from Nalcite HCR resin beds with 0.1% citric acid–ammonium citrate solutions was investigated and quantitative measurements were made to determine the distribution of constituents between the aqueous and resin phases. The data obtained in the *p*H range 5.0 to 8.0 have led to a much clearer understanding of the fundamental mechanisms involved when rare earths are separated by the ion-exchange method. Several basic correlations of the experimental data have been presented.

I. Introduction

It has been shown, by this Laboratory, that excellent separations of rare earths in high purity and good yields can be obtained by eluting the mixed rare earths from Nalcite HCR beds with 0.1% citric acid in the *p*H range 5.0 to 8.0.[2,3] Since it was clear from this earlier work that the columns could be operated under nearly equilibrium conditions, it was considered desirable to obtain quantitative data for the behavior of individual rare earth bands under equilibrium conditions. It was hoped that such information would lead to a better understanding of the fundamental mechanisms involved when rare earths are separated on ion-exchange columns with citrate solutions. We believe this objective has been fulfilled, since it has been possible to explain in a quantitative fashion all the phenomena which are observed by using only the ordinary laws of chemical thermodynamics.

The theoretical part of this discussion is being presented in a companion article[4]; this paper will deal with the experimental results and empirical relationships which were observed concerning variables of the system (part of the results already have been announced[5]). Since that time much more extensive experiments have been carried out and the *p*H range extended. The almost linear relationships described previously were found to deviate somewhat at higher and lower *p*H values, but the chemical thermodynamic theory accounts for these deviations.

A number of frustrating experimental difficulties were encountered, during this work, which we believe to be worthwhile mentioning, since they may save other experimentalists considerable time in future work of this sort.

While a plot of the ammonia in the eluant *versus* the rare earth in the eluate seemed to reproduce from experiment to experiment, a plot of hydrogen ion in the eluate *versus* the rare earth in the eluate gave different results each time the experiment was performed. The erratic behavior was finally traced to three different origins: (1) The citric acid is an excellent medium for the culture of molds. Since the experiments extend over a period of one or two months, this mold growth can be troublesome. Long before mold can be observed visually it will affect the results by upsetting the *p*H balance in the eluate. It was found, in general, that mold growth could be prevented by the addition of 1 gram of phenol per liter of eluant, and that below a *p*H of 6.5 in the eluate the phenol acted as an inert diluent and did not upset the equilibria. For a narrow range above 6.5 the equilibria could be corrected successfully for the presence of phenol. (2) It is necessary to use considerable quantities of pure water in these experiments and since in this Laboratory, as in many others, such quantities of distilled water are not readily available, it was thought that condensed steam would suffice if it were passed first through cation and anion exchangers in order to deionize the water. However, most condensed steam contains appreciable quantities of iron rust from the plumbing, and while cation and anion exchangers remove from ions fairly efficiently they do not remove colloidal iron. Such iron was present in our condensed steam and could be observed readily when this water was illuminated by a beam of light in a darkened room. The colloidal iron dissolved when citric acid was added, and since ferric iron forms strong citrate complexes, the equilibria under observation were upset. The difficulty was circumvented by first passing the condensed steam through packed columns of Pyrex glass wool, which removed the colloidal iron fairly efficiently. The water was then passed through cation and anion exchangers. (3) Citric acid solutions are also good media for the growth of bacteria and it was found, in one of our runs, that the apparatus had become contaminated with an organism similar to acetic acid bacteria. These bacteria seemed to grow even in 0.1% phenol solution and definitely upset the hydrogen-ion equilibria. While the disturbance was not too serious for ordinary separations, it was serious in experiments designed to determine thermodynamic constants. It was, therefore, necessary to sterilize all the equipment to

---

(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).

(4) F. H. Spedding and J. E. Powell, THIS JOURNAL, **76**, 2550 (1954).

(5) F. H. Spedding and J. E. Powell, *ibid.*, **74**, 856, 857 (1952).

kill the bacteria and to increase the phenol concentration to 2 grams per liter in order to prevent a recurrence of this difficulty.

II. Experimental

A. **Materials and Apparatus.** 1. **Materials.**—The neodymia used in the following experiments was prepared in a pure state by means of the ion-exchange procedures developed and previously reported by this Laboratory[2,3] and consisted of better than 99.9% Nd_2O_3.

The citric acid used in some preliminary experiments was U.S.P. anhydrous citric acid containing a minimum of 99.5% anhydrous citric acid. In later experiments, performed to yield precise data for the calculation of equilibrium constants, reagent grade citric acid monohydrate was used to minimize the chance that difficulties might arise from the presence of impurities such as tartaric and oxalic acids.

The resin investigated was a sulfonated styrene–divinylbenzene copolymer distributed by the National Aluminate Corporation under the trade name Nalcite HCR. A standard sample of resin was prepared in the following manner. Six kilograms of $-40+50$ mesh-size particles was screened from a large amount of air-dried, commercial grade resin. 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, and the resin bed was carefully backwashed to remove air bubbles and fine particles of resin which were not removed by screening. The resin was converted successively to the ammonium and the hydrogen states, using 5% ammonium citrate solution and 5% by volume hydrochloric acid, respectively, then carefully rinsed with distilled water to remove any unadsorbed acid and allowed to dry in the air at room temperature. After drying for 10 days, the resin was re-screened and stored in a closed reagent bottle until needed.

2. **Apparatus.**—The ion-exchange columns were constructed of Pyrex glass tubing and were 4.5 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 to form a nipple 9 mm. in diameter. The nipple was fitted with a short piece of Tygon tubing, a capillary tip and a screw clamp to control the flow of solution through the column. The columns were calibrated, by adding water from a buret, in order to determine the differences in their diameters. The exchange bed provided for each column consisted of 200 g. of the standard, air-dried, acid-form Nalcite HCR described above. The beds were then backwashed and rinsed with a 5% solution of hydrochloric acid followed by water. The resulting resin beds were approximately 100 cm. long after this treatment.

All *p*H measurements were made with a Beckman, Model G, Laboratory *p*H Meter. The instrument was adjusted to a *p*H of 7.00 with standard *p*H 7.00 buffer solution and rechecked against standard *p*H 4.00 buffer each time it was used.

B. **Procedures and Results.** 1. **Preparation of Standard Citrate Eluant.**—A large stainless steel tank, calibrated to a volume of 2,500 liters and equipped with a motor-driven stainless steel stirrer, was filled to the 2,500 liter mark with distilled water, and 2,500 grams of anhydrous U.S.P. grade citric acid or 2,840 grams of Reagent grade citric acid monohydrate were added. After stirring thoroughly, the total acid concentration was determined by titration of an aliquot with standard base. In some preliminary experiments no phenol was added, but in these experiments it was observed that the *p*H of the eluates which were collected tended to increase upon standing. Microscopic examination of the solutions showed that numerous short rod-shaped bacteria were present, which could readily account for the instability of the unprotected solutions. Consequently, the addition of 12 pounds of phenol per 2,500 liters of solution was adopted as standard procedure in later experiments. The addition of 0.2% phenol had very little effect upon the *p*H of the eluant below a *p*H of 7. After the addition of phenol the *p*H of the citrate solution was adjusted to the lowest *p*H value desired by the addition of concentrated ammonia. After withdrawing sufficient eluant for a proposed experiment the *p*H was increased to the next higher *p*H value desired by the addition of more concentrated ammonia. The ammonia concentration of each batch of eluant was determined by adding excess NaOH, collecting the ammonia evolved by distillation into 4% boric acid, and titrating with standard hydrochloric acid, using methyl purple as an indicator.

2. **Determination of Resin Capacity.**—A 5.00-g. sample of the standard, air-dried, Nalcite HCR resin was loaded into each of two short columns, and a total of 500 ml. of 1 *N* NaCl solution was passed through each column over a period of 48 hours. At this time the *p*H's of the influent and effluent solutions were equal, and the amount of acid liberated from each resin bed was determined by titration with standard base. The capacities observed were 4.25 and 4.27 meq. per gram of air-dried resin. Later, a 8.392-g. sample of standard resin was saturated with neodymium ion using 1 liter of 0.5 *N* $NdCl_3$ solution having a *p*H of 4.87 over a period of 24 hours. Aliquots of the effluent solution were titrated with base back to a *p*H of 4.87. The resin bed was washed free of unadsorbed $NdCl_3$, with distilled water, and the adsorbed neodymium was eluted from the bed with 6 liters of 0.1% citrate solution at a *p*H 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. per gram, and the neodymium, recovered upon elution, amounted to 4.26 meq. per gram of air-dried resin. The agreement between the equivalents of hydrogen ion, 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 Beds.**—Samples of Nd_2O_3, ranging from 1.00 to 10.00 g., were dissolved in a slight excess of hydrochloric acid (1.5 ml. of concentrated hydrochloric acid was used per gram of oxide). The chloride solutions were diluted to 4 liters, and adsorbed on prepared acid-form resin beds using a linear flow rate of about 2 cm./min. (approximately 8 cc./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 Nalcite HCR to allow the length of initially adsorbed bands to be measured. When elution of a band is in progress, however, the rear edge of the band is not readily visible under white light. It was found that, if the columns were illuminated with blue light in a darkened room, the neodymium bands could readily be seen as dark areas 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 could be observed visually.

5. **The Elution of Neodymium down a Bed of Nalcite HCR.**—In previous publications,[2] it was reported that an insoluble rare earth complex, identified as $RCit \cdot 2H_2O$, formed at *p*H values above 6.0 with initial loads in excess of about 1.2 g. of Nd_2O_3 per square centimeter cross-section of resin bed. The following preliminary experiment was performed in order to determine how the formation of this precipitate might best be prevented, and to study the movement of neodymium bands on the resin beds.

Four Nalcite HCR resin beds, 22 mm. in diameter and about 100 cm. long, were prepared as previously described. One column was loaded with a sample prepared from 2.8045 g. of Nd_2O_3, dissolved in 4.2 ml. of concentrated hydrochloric acid; two columns were loaded with 5.6090-g. samples of Nd_2O_3, dissolved in 8.3 ml. of acid; and the remaining column was loaded with a 5.6090-g. sample of Nd_2O_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 *p*H of 6.20. All of the columns, except one of those with a load consisting of 5.6090 g. of Nd_2O_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 3.2 liters of eluant had been passed through the bed. The precipitate almost completely blocked the pores of the resin bed at a volume of 7.5 liters, and the column was shut off. A trace of 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 through the column. This precipitate gradually redissolved 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 *p*H values, and with heavy loads, would be to elute the column rapidly during the first stages of development, and then reduce the flow rate in the later stages of elution. This technique has been employed throughout most of the experiments to be described in this paper, and has been used with excellent results in large scale separation of rare earths. Loads consisting of 7–8 kg. of mixed rare earth oxides have been eluted from 6-inch diameter columns without precipitation, at *p*H values as high as 8.0 by using initial linear flow rates of 5–8 cm./min., or approximately 1.0–1.5 liters/min. By such a procedure, a method has been developed by which individual rare earths can be prepared in considerable quantities in a pure state as a result of a single pass through a series of columns. The details of this procedure are of an engineering nature and will not be discussed further in this paper. The authors will furnish this information upon request, and hope to present the details at a later date in a suitable publication.

Figure 1 shows the length of the adsorbed band from the 2.8045-g. 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 movement of the rear edge increased abruptly to the rate the front edge was traveling as the neodymium band reached its fully developed state. The band appeared to be uniform throughout its length when fully extended and both the front and rear boundaries were well defined.

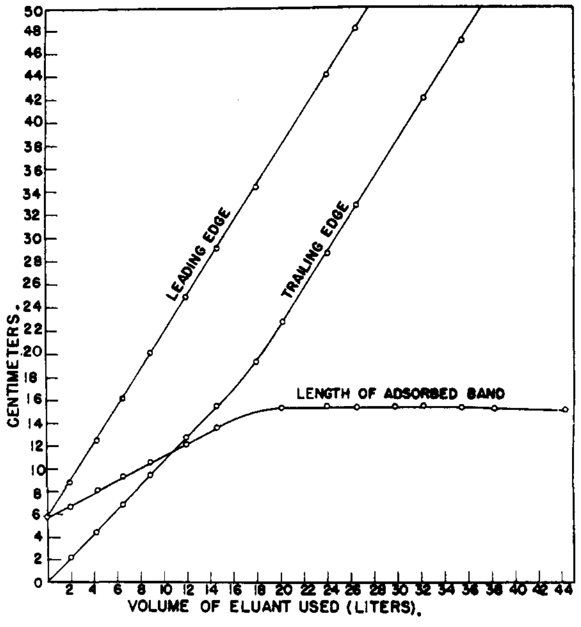

Fig. 1.—The length of the band and the positions of the front and rear edges of an adsorbed neodymium band during elution from a bed of Nalcite HCR with 0.1% citrate solution at a *p*H of 6.2.

Figure 2 illustrates 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 approximately doubled the length of the initially adsorbed band. Upon elution, the length of the band in case (A) increased at a constant rate until it was fully developed. The adsorbed band in case (B) decreased in length when eluted until it became equal to the developing band of case (A), then it increased in length at a constant rate until fully developed. The slight difference in the slopes of curves (A) and (B) in Fig. 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 narrower.

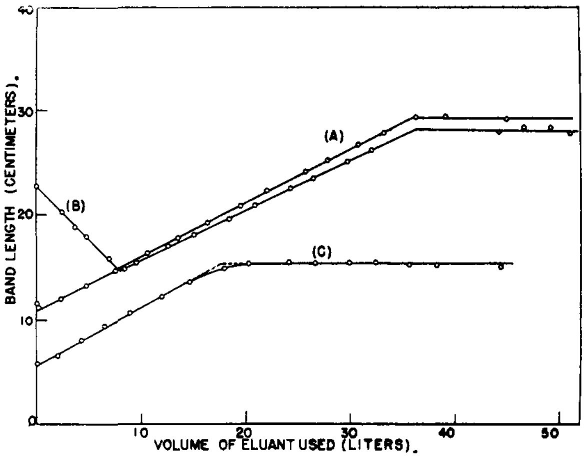

Fig. 2.—The effect of increased load and of excess acid in the original sample upon the initial and final adsorbed bands: A, 5.6090 g. of Nd_2O_3 plus 8.3 ml. of concd. HCl; B, 5.6090 g. of Nd_2O_3 plus 83 ml. of concd. HCl; C, 2.8045 g. of Nd_2O_3 plus 4.2 ml. of concd. HCl.

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-g. load, the lengths of the initial and the developed bands were essentially double those of the 2.8045-g. load. The double load required just twice the volume of eluant and twice the distance down the bed to reach its fully extended state. Again the small discrepancies were due to a slight variation in column diameters.

Following the preliminary experiment just described, a number of experimental runs were made in which series of columns were each loaded with sufficient neodymium to give bands 15–30 cm. long, when fully developed, and eluted with 0.1% citrate solutions at *p*H values ranging from 5.4 to 8.2. Quantitative data, concerning the movement of bands on the columns and the concentrations of constituents in the aqueous and resin phases, were obtained. Figure 3 shows a typical elution curve obtained from one such experiment. In all, more than sixty individual experiments of this type were performed in order to obtain information concerning the movement of the bands and the distribution of ions in the aqueous and resin phases. No attempt will be made to tabulate all of the data obtained from these experiments; instead, just sufficient data will be included to illustrate the significant points of our discussion.

From the typical elution curve shown in Fig. 3 it can be seen that no rare earth or ammonium ion was present in the eluate until a volume of 56 liters was collected, then the *p*H of the eluate, the concentration of the ammonium ion and the total neodymium concentration rose sharply to values which remained constant until the last of the neodymium was eluted from the resin bed. At this point, the *p*H of the eluate and the concentration of the ammonium ion rose to their respective values in the eluant. By observation of the bands under blue light, it was found that nearly all of the slight slant of the front and rear boundaries of the elution curves could be explained by a slight tilting of the adsorbed bands on the columns, due to channeling in the resin beds.

6. The Effect of Flow Rate on the Adsorbed Band.—Typical band progress curves are shown in Fig. 4 for both fast and slow flow rates at two different *p*H values. At the higher *p*H value the effect of increased flow rate was negligible, but at the lower *p*H the adsorbed band spread beyond

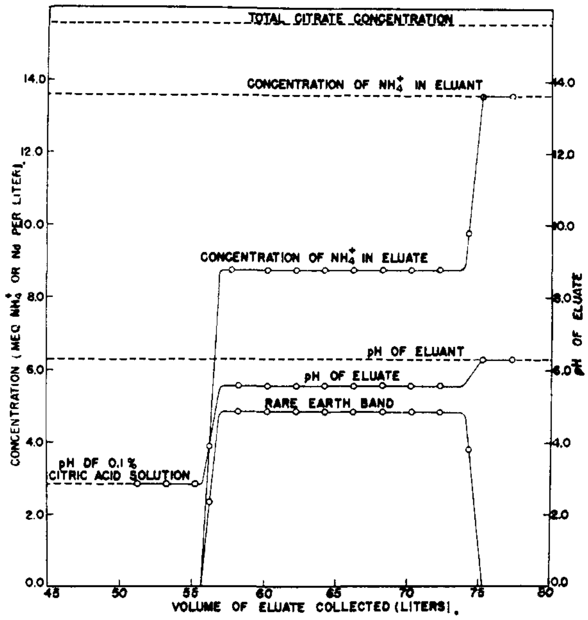

Fig. 3.—Typical elution curve illustrating the break-through of an adsorbed rare earth band and showing the constancy of the total rare earth and ammonium ion concentrations as well as the *p*H of the eluate after equilibrium is attained.

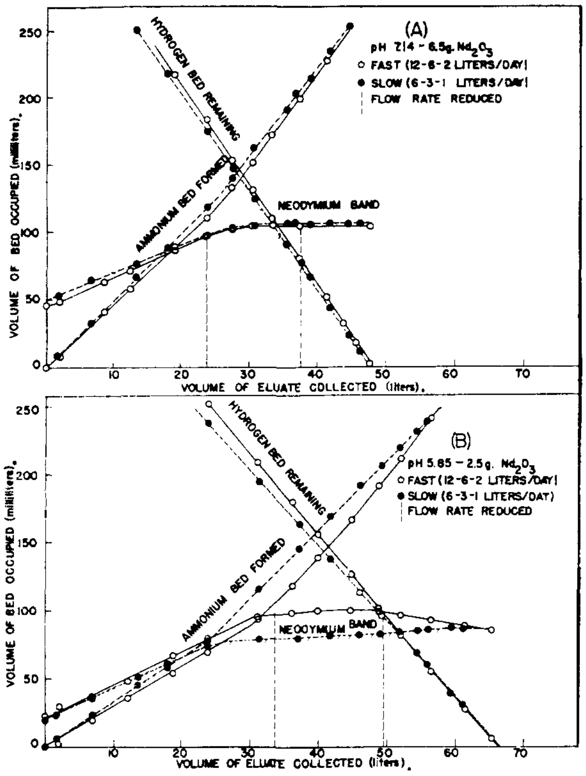

Fig. 4.—The effect of increased flow rate on the elution of neodymium from a Nalcite HCR bed with 0.1% citrate solution at different *p*H values.

its equilibrium length at the more rapid flow rate. When the rate was reduced, the adsorbed band became shorter and approached the equilibrium length obtained at the slower flow rate. This latter effect was due primarily to the re-sharpening of the front and rear boundaries of the adsorbed band. From the experiments just described, it was concluded that an initial fast flow rate to avoid the formation of insoluble NdCit·2H$_2$O (Nd$_2$Cit$_2$·4H$_2$O) had no permanent effect, provided the flow rate was reduced before the band reached the bottom of the column. However, it was deemed neither necessary nor advisable to exceed a linear flow rate of 1.0 cm. per minute in experiments of this type (this flow rate was calculated for a portion of the column not obstructed by the resin bed).

7. **Distribution between the Aqueous and Resin Phases.**—In one series of experiments, weighed samples of hydrogen-form resin were appended to the bottoms of the columns after the bands were developed on the main resin beds, and the adsorbed bands were allowed to move onto the appendages. The resin appendages were analyzed for ammonia and neodymium, and the concentrations of these constituents in the resin phase were compared to their concentrations in the aqueous phase in contact with the resin. Table I shows that the sum of the equivalents of neodymium and ammonium in the resin ($3R_R + S_R = \Sigma_R$) is essentially equal to Q, the capacity of the resin; that the sum of the neodymium and ammonium concentrations in the aqueous phase ($3R_T + S = \Sigma_S$) is essentially equal to $\bar{S}$, the concentration of ammonium ion in the eluant; and that the ratio of neodymium in the resin phase to neodymium in the aqueous phase is equal to the ratio of the ammonium ion in the resin phase to the ammonium ion in the eluate. Both ratios are in turn always equal to the ratio $Q/\bar{S}$. The significance of this important observation is discussed in the companion paper which deals with theory. It should be pointed out that ammonium and hydrogen ions are the only ions present in the eluant which are capable of replacing neodymium in the resin phase. Since the ammonium-ion concentration in the eluant is always greater than 10^3 times the hydrogen-ion concentration, under the conditions of our experiments, no appreciable exchange between hydrogen and neodymium ions can take place. Consequently, the concentration of total neodymium which appears in the eluate must just equal the difference between the ammonium-ion concentrations in the eluant and the eluate.

8. **Nearly Linear Relationships between the Ammonium Ion in the Eluant and the Ammonium Ion and the Total Neodymium in the Eluate.**—Data from two recent, carefully controlled, experimental runs are given in Table II. These data are consistent throughout and have been used as an experimental check on the theoretical thermodynamic calculations. Figure 5 shows the concentrations of ammonium ion and total neodymium in the eluate as functions

TABLE I

THE DISTRIBUTION OF CONSTITUENTS BETWEEN THE AQUEOUS AND RESIN PHASES UNDER EQUILIBRIUM CONDITIONS

$\bar{S}$, meq./l.	$3R_T$, meq./l.	S, meq./l.	Q, meq./g.	$3R_R$, meq./g.	S_R, meq./g.	Σ_S, meq./l.	Σ_R, meq./g.	R_R/R_T	S_R/S	$\frac{\Sigma_R}{\Sigma_S}$	$Q/\bar{S}$
10.72	0.78	9.92	4.08[a]	0.30	3.78	10.70	4.08	0.385	0.381	0.381	0.380
11.85	2.42	9.45	4.08	0.84	3.26	11.87	4.10	.347	.345	.345	.344
13.03	3.96	9.06	4.08	1.25	2.86	13.02	4.11	.316	.316	.316	.313
14.91	6.53	8.39	4.08	1.79	2.28	14.92	4.07	.274	.272	.273	.274
15.29	6.99	8.33	4.08	1.88	2.20	15.32	4.08	.269	.264	.266	.266
15.93	7.29	8.27	4.08	1.99	2.10	15.96	4.10	.259	.255	.257	.256
16.78	8.68	8.15	4.08	2.12	2.00	16.83	4.12	.244	.245	.245	.243

[a] The resin used in the appendages was not quite as dry as that used in the original determination of the resin capacity due to a difference in the relative humidity of the air at the time it was weighed; hence, the capacity given here per gram is slightly lower. This value is the average of fourteen separate determinations.

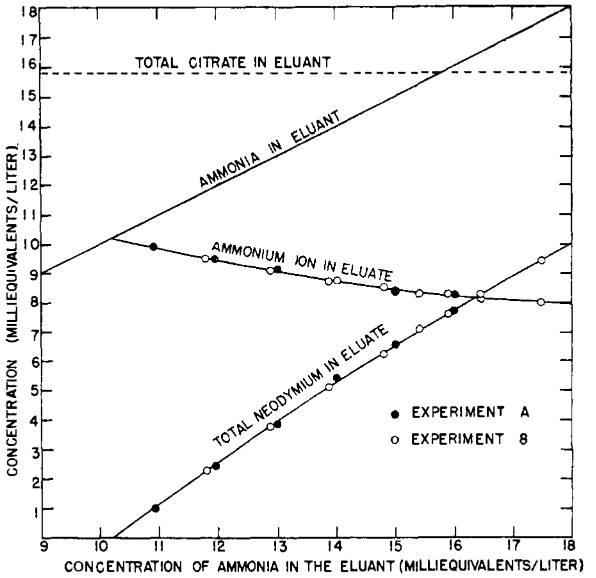

Fig. 5.—The concentrations of ammonium ion and total neodymium in the eluate under equilibrium conditions as functions of the concentration of ammonia in the eluant.

of the concentration of ammonium ion in the eluant. Figure 6 shows the concentrations of ammonium ion and of total neodymium in the eluate as functions of the hydrogen ion concentration of the eluate as determined by *p*H measurements.

TABLE II

EXPERIMENTAL DATA FOR THE ELUTION OF NEODYMIUM FROM NALCITE HCR WITH AMMONIUM CITRATE[a]

	*p*H						
Expt.	Eluant	Eluate	H^+ concn. (γ = 0.88)	$3R_T$, meq./l.	S, meq./l.	Σ_S, meq./l.	$\bar{S}$[b] meq./l.
A	5.53	5.32	5.42 × 10^{-6}	1.01	9.92	10.93	10.93
	5.81	5.38	4.72	2.46	9.50	11.96	11.96
	6.10	5.45	4.02	3.87	9.15	13.02	12.98
	6.41	5.62	2.72	5.25	8.77	14.02	14.00
	6.81	5.93	1.34	6.59	8.42	15.01	15.02
	7.46	6.90	0.143	7.72	8.28	16.00	15.99
	8.00	7.51	0.035	8.45(?)	8.43(?)	16.88	16.86
B	5.79	5.36	4.95	2.29	9.52	11.81	...
	6.08	5.44	4.11	3.79	9.11	12.90	...
	6.38	5.63	2.84	5.12	8.75	13.89	...
	6.70	5.83	1.68	6.26	8.55	14.81	...
	7.01	6.18	0.75	7.09	8.33	15.42	...
	7.38	6.70	0.23	7.61	8.30	15.91	...
	7.74	7.33	0.053	8.20	8.27	16.47	...
	8.19	7.73	0.021	9.46	8.03	17.49	...

[a] The total citrate concentration was 5.27 × 10^{-3} molar after correcting for evaporation. The solutions were stabilized by the addition of 0.2% by weight phenol. [b] The ammonia in the eluate should be measured at the time breakthrough occurs as well as at the time the solutions were prepared so that any evaporation can be accounted for. The values of $\bar{S}$ in this table are the final values for the ammonia concentration which compare most favorably to the values of Σ_S with respect to the time element.

9. Formation and Development of the Bands and the Prediction of Break-through Volumes.—In all experiments described, each column contained 200 g. (852 meq.) of air-dried hydrogen-form resin. For the adsorption of neodymium on the resin beds, a dilute solution of neodymium chloride containing only a slight excess of hydrochloric acid was passed slowly down the resin bed. The amount of hydrochloric acid in the neodymium solution was so low that the amount of hydrogen resin in equilibrium with it could be neglected in comparison to the neodymium resin present. 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 1 proceeded almost completely to the right.

$$\mathrm{Nd_S}^{+3} + 3\mathrm{H_R}^+ \rightleftarrows \mathrm{Nd_R}^{+3} + 3\mathrm{H_S}^+ \qquad (1)$$

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

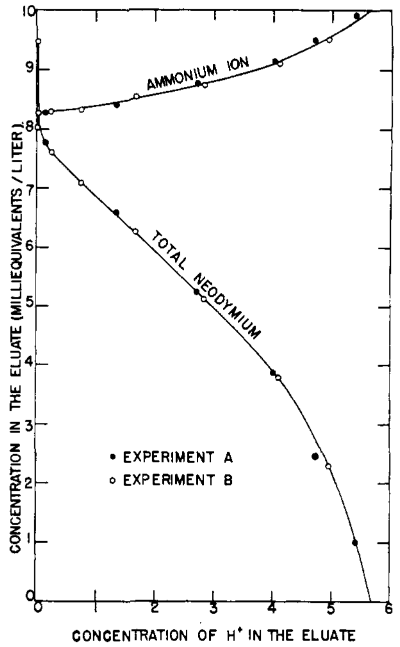

Fig. 6.—The concentration of ammonium ion and of total neodymium in the eluate under equilibrium conditions as functions of the hydrogen ion concentration of the eluate.

TABLE III

CALCULATED AND OBSERVED BREAK-THROUGH VOLUMES IN THE ELUTION OF NEODYMIUM

Capacity of bed, meq.	Neodymium adsorbed, meq.	Hydrogen remaining, meq.	Ammonium-ion concn., meq./l.	Break-through predicted, l.	Vol. obsd., l.
852	116	736	15.34	48.0	48.0
852	116	736	15.34	48.0	48.4
852	107	745	14.67	50.8	50.5
852	107	745	14.67	50.8	51.3
852	89	763	14.22	53.6	53.2
852	89	763	14.22	53.6	53.4
852	71	781	13.07	59.8	59.1
852	71	781	13.07	59.8	59.2
852	45	807	11.99	67.4	66.8
852	45	807	11.99	67.4	67.0
852	18	834	10.42	80.0	79.8
852	18	834	10.42	80.0	79.7
852	125	727	15.59	46.6	46.5
852	116	736	14.98	49.2	49.1
852	89	763	13.57	56.2	56.3
852	53	799	12.56	63.6	63.0
852	27	825	11.53	71.5	70.6
852	89	763	15.58	48.0	48.4
852	89	763	15.37	49.6	49.2
852	89	763	14.15	53.9	52.5
852	89	763	13.16	58.0	57.3
852	53	799	12.06	66.2	65.8
852	27	825	11.17	73.9	73.2

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

RECEIVED AUGUST 17, 1953

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 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-

---

(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).

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