Temperature and flow rate effects on the ion-exchange separation of erbium and thulium

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TEMPERATURE AND FLOW RATE EFFECTS ON THE ION-EXCHANGE SEPARATION OF ERBIUM AND THULIUM

By
Irvin Leroy Sellers
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May 1960

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Irvin Leroy Sellers
J. E. Powell

May, 1960

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TEMPERATURE AND FLOW RATE EFFECTS ON THE ION-EXCHANGE SEPARATION OF ERBIUM AND THULIUM*

by

Irvin Leroy Sellers and J. E. Powell

ABSTRACT

The concept of a theoretical plate has been applied as a column operation parameter to evaluate the effects of flow rate and temperature on the separation of erbium and thulium with HEDTA using an ion-exchange technique. It has been shown that for separations made at constant temperatures the overlap between the pure forms is directly proportional to the flow rate at all practical flow rates and temperatures. The changes in the HETP were easily explained in terms of the ion-exchange kinetic theory. We would expect a decrease in the HETP for any other change in the system which would facilitate the diffusion of ions through the resin particle, i.e., resin of small particle size or a resin of low cross-linkage.

*This report is based on an M.S. thesis by Irvin Leroy Sellers submitted May, 1960, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.
I. INTRODUCTION

The rare earths occur in appreciable quantities in the earth's crust and are not really as rare as the name implies. Cerium is estimated to be more abundant than many of the more familiar elements such as zinc, tin, or mercury. They are, however, widely distributed in nature and only a few minerals are sufficiently rich in rare earths to serve as practical sources. They were undoubtedly termed rare because of the extreme difficulty in separating them in appreciable quantities by ordinary chemical means.

Prior to 1947, all separations were based on repeated fractionation processes such as crystallization, precipitation, or decomposition. To obtain a satisfactory degree of purity these operations had to be repeated up to thousands of times over a period covering years of tedious labor. An important development came in the early 1930's when several separation processes were reported that utilized the divalent states of samarium, europium, and ytterbium (1-11). Although the tetravalent state of cerium had been known for years, and was commonly used in the isolation of cerium, the divalent states of the aforementioned elements, being relatively unstable in aqueous solution, were not investigated extensively prior to 1930.

In late 1947, a series of papers was published stating that high purity rare-earth elements could be obtained in a relatively short period of time using the salts of complexing acids on cation-exchange columns (12-20). It appeared, for the first time, that macro quantities of high
purity rare earths could be obtained readily, utilizing this technique, and extensive investigations were undertaken at Iowa State University and many other laboratories. From this work came a vast number of improvements and modifications to the original proposals. These are amply reviewed for both tracer and macro scale separations by Powell and Spedding (21).

Of the many methods that have been described, the use of ethylenediaminetetraacetic acid (EDTA) as the eluant and copper as the retaining ion on commercial grade sulfonated styrene-divinylbenzene copolymers has proven to be the most successful for macro scale separations (22). This process has been developed to the point where ton quantities of ore can be processed rapidly and relatively cheaply (22, 23). This brings us to the purpose of this work. It is only natural that the different factors which affect the separation be investigated quantitatively in order to optimize the process and obtain the best yields of high purity rare earths at the lowest possible cost in the shortest time. The work described in this report is part of the research undertaken in the development of more efficient separation procedures. Some important phases of this research were the determination of the stability constants of rare-earth chelates and the determination of theoretical plate heights for various combinations of resins, chelating agents, temperatures, and flow rates.

The use of EDTA as the chelating eluant gives good separation for the rare earths, in general, except in the case of europium and gadolinium where the separation factor is poor and between lutetium and ytterbium.
where, although the separation factor is fair, the actual resolution is poor under normal conditions (probably due to a slow exchange rate of the strongly chelated ions). In addition, the lutetium-, ytterbium-, and thulium-rich fractions are generally found to be contaminated with lead, thorium, zinc, and cobalt (22). It thus becomes advisable to use an auxiliary chelating agent for the separation of the heavy rare earths, erbium through lutetium. Hydroxyethyl ethylenediaminetriacetic acid (HEDTA) has proven successful for this purpose and is superior to EDTA for resolving erbium-thulium-ytterbium-lutetium mixtures in spite of the fact that separation factors for adjacent elements in the middle of the series, samarium to holmium, are unfavorable (21-23). Thus, HEDTA is used to resolve the heavy elements which concentrate at the front edge of the band initially under the influence of EDTA. The foremost part of the band, partially developed by EDTA, is simply detached from the main portion of the band, which contains yttrium and the lighter rare earths, and is eluted separately with HEDTA on a system of hydrogen-state resin beds.

This dissertation is concerned with the latter-phase of this process, specifically the effects of flow rate and temperature upon the separation of macro quantities of heavy rare earths on ion-exchange beds by elution with HEDTA solutions. The elements erbium and thulium were selected as being representative of the heavy rare-earth elements because:

----they are adjacent in the series

----they were available in ample amounts
an analytical procedure had been worked out for the detection of one in the presence of the other

the separation factor was favorable

differ markedly in color, thulium being colorless and erbium, pink.

The variables studied in this dissertation are obviously kinetic in nature. The approach to the problem has not been that ordinarily used in kinetic investigations, but rather one based on the concept of the height equivalent to a theoretical plate (HETP). Spedding, Powell, and Svec have used this concept to estimate optimum conditions for the separation of nitrogen isotopes (24) and various rare-earth mixtures (23). This method of approach has two obvious advantages—the availability of suitable equipment in the laboratory and the similarity of the proposed experiments to actual operating procedures.
II. PREVIOUS DEVELOPMENTS

In the design of an efficient ion-exchange operation, three different aspects must be taken into account:

1) Techniques employed
2) Equilibrium behavior
3) Column operation characteristics

A. Techniques Employed

Most of the different ion-exchange techniques have been applied to the separation of the rare-earth elements. The techniques for operating ion-exchange systems fall into two general categories, namely, elution chromatography and displacement chromatography. In elution chromatography the sorbed ions are moved gradually down a column system by treatment with an eluant ion which is more weakly sorbed by the resin than the ions being separated. Displacement chromatography, on the other hand, involves sharp, complete displacement of the sorbed ions by a more strongly sorbed eluant ion. The techniques differ greatly in principle and application. Both types are suitable for the separation of solutes, but due to the nature of the process of displacement chromatography, one hundred per cent isolation of the species cannot be obtained.

Early methods for separating rare earths utilized an elution technique employing citric acid-ammonium citrate eluant on either $H^+$-state or $NH_4^+$-state resin beds. It was soon realized that, for the
process to be economical for separating macro quantities, a technique
must be employed which made more effective use of the eluting agent (25). This realization led to the highly efficient techniques used today, which employ a retaining ion and a displacement fractionation process. The retaining ion serves as a barrier through which the rare-earth complex cannot pass. The complex decomposes at this point and the rare earth is resorbed on the resin bed. The complexing anion forms a more stable chelate species with the retaining ion and flows on through and out of the column. The rare-earth mixture eventually develops into a compact series of head-to-tail bands. The individual bands necessarily overlap as stated above. Consequently, the technique becomes more efficient with increasing length of the individual bands, since the amount of overlap between the pure form of one constituent and the pure form of the adjacent constituent is independent of the quantities present. However, for analysis and separation of micro-quantities, the elution-chromatography technique must be employed in order to completely isolate the individual species.

B. Equilibrium Behavior

The most important factor in the operation of a separation process is the relative movement of a given solute cation with respect to other cations. This depends not only on the distribution ratio (amount of solute cation sorbed to the amount in solution at a given concentration), but also on the concentrations and distribution ratios of other solute
cations present. Usually, however, with the dilute concentrations that are characteristic of elution chromatography, the distribution ratios can be considered to be independent of the concentrations of other species for the purpose of column design. Thus the rate at which a given solute moves down an exchanger in the case of elution chromatography is inversely proportional to its distribution ratio. Two solutes having different distribution ratios will separate, therefore, at a rate which is inversely proportional to the ratio of their distribution ratios. This ratio is referred to as the selectivity coefficient of the resin and is termed the separation factor. Factors which have been shown to influence the selectivity of a resin of given functional type are the degree of cross linking of the exchanger, ionic valence, hydrated ionic radius, and the ionic activity of the solution within the resin, as well as the various functional groups of different type resins (26). Little attention has been paid to the effect of temperature on resin selectivity. Although large temperature effects have been found in ion-exchange processes, these are due primarily to kinetic effects. In general, however, changes in selectivity would be expected as hydration of the ions decreases with temperature. Kraus and Haridon (27) have studied the temperature dependence on the selectivity coefficients for dilute solutions of a number of cations on hydrogen-form and sodium-form resin. Two trivalent rare earths, lanthanum and europium, were studied with hydrogen-form resin. They found that near room temperature lanthanum is more strongly sorbed than europium, while the reverse is the case above 50°C. This would indicate that correlations of ion-exchange selectivities with
temperature must be based on properties of the resin phase. The order of magnitude of the difference reported between the selectivity coefficients is very small being 0.21 at 25°C and 0.31 at 85°C.

It is well known that resin selectivity is almost non-existent in the case of two adjacent rare earths. Although early investigators (28) reported some enrichment of individual rare earths when a mixture was passed through a cation-exchange column, their results were not promising enough to lead to further investigations. Powell and Spedding (23) found the separation factor for erbium and neodymium to be about 1.8 in dilute perchlorate solution. For adjacent pairs then, the separation factor would be less than 1.08. Similar conclusions can be drawn from distribution data of Surls and Choppin (29).

Here the importance of complexing phenomena arises, for the separation factor is governed not only by the resin selectivity, but also by the ability of complex species to ionize in the solution phase. Thus for two adjacent rare earths a reaction of the type:

\[
\text{Tm}^{3+} + \text{Er}^{3+} \rightleftharpoons \text{Tm}^{3+} + \text{Er}^{3+}
\]

(1)

tends only slightly more to the right than to the left in perchlorate solution. However, if the solution phase contains a complexing anion, Ch, which complexes thulium(III) ions to a greater degree than it does erbium(III) ions, the reaction will proceed readily to the right.

\[
\text{Tm}^{3+} + \text{ErCh} \rightleftharpoons \text{TmCh} + \text{Er}^{3+}
\]

(2)

A favorable separation factor then, would be expected in systems of
complexing anions in which a rare earth of higher atomic number is complexed to an appreciably greater extent than its adjacent neighbor of lower atomic number.

Powell and Spedding have used ratios of the stability constants of individual rare-earth chelates of various complexing agents to successfully estimate separation factors for adjacent rare earths (23). From the data of Spedding, Powell, and Wheelwright (30) the separation factor for thulium and erbium for the HETTA system was computed to be 1.6. This type of calculation is applicable provided the elution is performed under conditions which yield compact-band-type elution behavior.

A complete review of the use of chelating agents in the separation of rare earths by ion exchange up to 1959 has been given by Powell and Spedding (22).

Spedding and Powell have shown how to calculate the minimum distance of elution required to separate adjacent pairs of rare-earth solutes once the separation factor has been obtained. These calculations are valid for the displacement fractionation technique provided that the HETP is small and the region of overlap between adjacent solute cations in the fully developed band is small compared to the lengths of the individual bands. When these conditions are satisfied

\[ l_x = l_0 \frac{1 + e N_0}{e} \]  

where \( l_x \) is the minimum elution distance required to resolve the bulk of a binary sorbed mixture, initially \( l_0 \) units in length, into its pure components; \( e \) is the amount that the separation factor differs from one.
i.e., \( e = K_1 \); and \( N_0 \) is the mole fraction of the more strongly complexed solute originally adsorbed on the resin.

C. Column Operation Characteristics

Although an elution system may be selected having a favorable separation factor under equilibrium conditions, the kinetics of the system determine the operation characteristics of the column. A large volume of literature is available containing solutions of partial differential equations that describe ion-exchange processes. A review of both anion-exchange and cation-exchange kinetics is given by Kunin (26). A publication of Selke (31) more adequately reviews the mathematical methods that have been used. It is now generally accepted that the overall rate of exchange in ion-exchange reactions is determined by diffusion rates.

Consider the reaction:

\[
A + B^+ \rightleftharpoons A^+ + B
\]  

where \( A \) represents ion A in the resin phase and \( A^+ \) represents ion A in the solution phase, with analogous symbols for ion B. Making use of the model introduced by Boyd, et al. (32) we can get an idea of the mechanism of exchange. The model consists of an external volume of solution, considered to be perfectly mixed, surrounding the resin bead, considered to be a porous gel-like particle, whose exchange groups are randomly dispersed throughout the particle. The bead and the perfectly mixed solution are separated by a Nernst film of stagnant solution in
which diffusion is the only transport process. The concept of a stagnant film develops since it is never possible to mix a liquid perfectly right up to the surface of the solid phase.

Since the bulk of the solution is considered to be perfectly mixed, the mechanism of exchange can be divided into five steps. As the ion \( B \) in the bulk solution comes to the Nernst film, it must diffuse through this static solution to the resin gel, then diffuse through the resin gel to the exchange site. Here the exchange of the ions takes place and the diffusion of the \( A \) ions through the gel particle and the Nernst film to the bulk of solution completes the mechanism.

Even with this simple model, the mathematical solution is very complicated since the diffusion processes are coupled. Some kinetic data have been fitted to the theory for the special case of isotopic exchange which simplifies the equations since the exchange constant is practically equal to one. These investigations and the investigations of many other workers have shown that, in general, with other factors held constant, a high rate of exchange is favored by the following conditions:

- resin of small particle size
- efficient stirring
- high concentration of solution
- ions of small size
- a resin of low cross-linkage

Column performance can thus be affected by almost any experimental factor. The interplay of these factors is very complex. A universally applicable solution does not exist and, if it did, it would be too complex to be of
use. The alternate solution for design purposes is to characterize the column performance by means of single variables such as "the height equivalent to a theoretical plate" (HETP) used in the more familiar processes of distillation and absorption.

Martin and Synge (33) were the first to realize the similarity of chromatographic elution to the process occurring in distillation columns. The theory was applied to ion-exchange chromatography by Mayer and Tompkins (20) in 1947. Spedding and Powell (24) adopted the concept of the HETP to estimate optimum conditions for the separation of nitrogen isotopes, and later, for the separation of the rare earths by utilizing the mathematics of a counter-current system at steady state in total reflux.

These conditions are satisfied when one separates a mixture into successively following bands by displacement chromatography as long as the bands are kept compact by the use of a retaining ion. The main feature of such a process is that a steady state is approached beyond which no further separation takes place. The boundary between a solute and its neighbor acquires a constant form and all parts of the boundary travel down the column at a constant speed. A plane of reference perpendicular to the resin bed can be envisioned which always maintains a fixed position with respect to the ends of the band as it moves down the bed. When viewed from the plane of reference, the material in the band is being transported upward in the resin phase and downward in the solution phase. At the steady state no net transport of either substance occurs across this reference plane.
A theoretical plate is defined as an increment of the band of such size that the ratios of two components leaving it in the resin phase and solution phase are related by the separation factor. The largest separation possible for the system would be attained if the liquid passing down the column came to full equilibrium with each layer of resin beads and the HETP would be infinitely small. This would require an infinitesimally small rate of flow. At all practical rates of flow, non-equilibrium conditions exist and the HETP increases accordingly. Thus, the HETP is dependent on the rate at which equilibrium is approached, i.e., the kinetics of the system.

In the separation of the rare earths to purities in excess of 99.9%, the overlap fraction between two pure rare earths is given in units of centimeter of band by

\[ L = \frac{6 \text{HETP}}{\log K_{\text{sep}}} \]  

(5)

Thus the impure fraction of the band is dependent on both the separation factor and the HETP. The separation factor for lutetium-ytterbium mixtures in the EDTA systems has been calculated to be 1.8, and in the HEDTA system to be 1.4 (23). However, the resolution of these elements is improved by using the HEDTA system. Although the separation factor may be estimated from stability constant data, the value of HETP must be determined by experiments (23).

A modification of this concept is described by Michaels (34). He defines an "exchange zone" in which the exchange takes place at steady-state conditions and assumes that this zone descends through the bed at a
constant rate. This concept is believed to be completely rigorous only for film-diffusion-controlled cases with favorable equilibria. In the opinion of this worker, the assumption is better than the data for almost all cases with favorable equilibria. The concept is one of the simplest for interpreting kinetic data from fixed-bed ion-exchange experiments and differs from that of the HETP in the fraction of band considered. The "exchange zone" takes in that volume of band in which the concentration of a solute change from 5% to 95% (arbitrary values), whereas the HETP concept considers the volume of band in which the concentration changes by the separation factor.

Glueckauf (35) has refined the theoretical plate treatment of Mayer and Tompkins (20) by replacing the "discontinuous flow" model by a "continuous flow" model. This treatment uses the experimental parameters, volume of elution solution required to obtain break through, and a number of theoretical plates, for the prediction of product purity. The calculations are valid for elution chromatography with favorable kinetics but of little practical value for design purposes. The calculations do not apply to the displacement fractionation technique employed in this dissertation. The purpose of this work is to operate a column under favorable conditions and to use the HETP concept as a parameter to evaluate the overall kinetics of the system.

Selke, et al. (36) proposed a general design procedure for ion-exchange operations based on experimentally determined equilibrium curves, resin diffusion coefficients, and Schmidt numbers. The latter two factors can be obtained by a single shallow bed experiment, but a
programmed computing machine is needed to perform the long and tedious mathematical computations required for the design of larger operations.

Vermeulen and Hiester (37) have made an effort to place the kinetic data available for a vast number of special cases into a form useful to the design engineer. A reference table is presented listing the names of many investigators who have contributed to ion-exchange theory according to the equilibrium and rate conditions studied. Numerous parameters have been introduced to facilitate the use of graphs and tables which present the results of complex mathematical analysis. These figures permit the prediction of column performance over a wide range of conditions when used with some additional experimental data. The treatment is too complex to be of much value in studying the displacement fractionation technique utilized in this dissertation.
III. THEORETICAL CONSIDERATIONS

Powell and Spedding (23) have used ratios of the stability constants of the individual rare-earth chelates with both EDTA and HEDTA to predict satisfactorily the behavior of rare-earth mixtures during elution. Their assumptions have been incorporated into this dissertation. The various equations necessary to describe the erbium-thulium-HEDTA system are developed below.

A. Separation Factor

When a trivalent rare earth is eluted down a resin bed in the copper(II) form with the triammonium salt of HEDTA, the formation of a strong rare-earth complex with the HEDTA results in the sharp displacement of the rare-earth ion from the resin and consequently in the ammonium ion being sorbed upon the resin bed. At the front edge of the band the formation of a strong copper-HEDTA complex, combined with the fact that the resin has a greater affinity for a trivalent ion than for a divalent ion, results in the copper ion being sharply displaced from the resin and the rare-earth ion resorbed upon the resin bed. Thus, sharp constraints are imposed at the front and rear boundaries of the rare-earth band that keep it compact as it progresses down the resin bed.

When any two rare earths, thulium and erbium in this case, are present as a mixture in the band the following equilibrium occurs:

\[
\begin{align*}
\text{Er}^{3+} + \text{TmCh} & \rightleftharpoons \text{Tm}^{3+} + \text{ErCh}
\end{align*}
\]
The activity coefficients of rare-earth species of the same type are so nearly identical that they virtually cancel one another and the activities can be replaced with molal concentrations to give:

$$K = \frac{m(Tm^{3+}) \cdot m(ErCh)}{m(Er^{3+}) \cdot m(TmCh)}$$  \hspace{1cm} (8)

When the conditions are such that TmCh and ErCh are the only rare-earth-containing ions present in appreciable amounts in the aqueous phase, then K represents the separation factor.

It has been shown that the resin itself is not highly selective between two adjacent rare earths (23, 28, 29), thus

$$\frac{m(Tm^{3+}) \cdot m(Er^{3+})}{m(Er^{3+}) \cdot m(Tm^{3+})} = K_s = 1$$  \hspace{1cm} (9)

The combination of equation 8 with equation 9 gives a good approximation of the separation factor K, which depends only upon the concentrations of species in the aqueous phase:

$$K = \frac{m(Tm^{3+}) \cdot m(ErCh)}{m(Er^{3+}) \cdot m(TmCh)}$$  \hspace{1cm} (10)

The stability constants of Spedding, Powell, and Wheelwright (38) for the HEDTA complex of the rare earths were defined as follows:
Thus for thulium and erbium,

$$K'_{RCh} = \frac{m(RCh)}{m(R^{+3}) \cdot m(Ch^{3-})} \quad (11)$$

The value for the separation factor of erbium and thulium used in this dissertation was approximated in this manner from the data of Spedding, Powell, and Wheelwright (38).

B. Elution Distance

The minimum distance an adsorbed band must be eluted to attain the steady state can be calculated from the separation factor. If the length of the rare-earth band remains constant as the band is eluted down the resin bed, each time an equivalent of ammonium ion is deposited at the rear edge of the band, it displaces an equivalent of rare-earth ion. The displaced rare-earth ion tends to come to equilibrium with the resin bed as the solution passes over it. When the rare-earth ion in solution reaches the front edge of the band it is redeposited on the resin bed. At all times, the ratio of thulium to erbium on the resin, $R_r$, is less than it is in the solution phase, $R_s$, contacting it. Replacing $K$ with $(1 + e)$, equation 8 becomes,

$$R_r = K R_s = (1 + e) R_s \quad (13)$$
(This assumes that the solution and resin are in equilibrium.) As the band travels down the column, the thulium ions concentrate at the front edge of the band and the erbium ions at the rear edge. Between these regions there exists a plateau region in which the ratio of thulium to erbium in the resin phase and solution phase is not changing, although they differ from each other by the amount \( eR_s \). The thulium to erbium ratio on the resin, \( R_T \), is equal to \( KR_s \) from equation 13; therefore,

\[
R_T - R_s = KR_s - R_s = (K - 1)R_s = eR_s
\]  

Since the solution is flowing past the resin in the plateau region, richer in thulium ions than the resin it contacts, there is a net transfer of thulium ions toward the front edge of the band. It is obvious that the plateau region moves along with the band, but gets smaller and ultimately vanishes as the band progresses down the column. A plane of reference is chosen perpendicular to the moving band at a point within the plateau region. This plane moves with the band. Under these circumstances, each equivalent of rare-earth ion picked up at the rear of the band flows through the reference plane and is redeposited at the front. Simultaneously, an equivalent of rare-earth ion on the resin passes through the plane in the opposite direction, resulting in no net transfer of total rare earth across the plane of reference. Differentiating between the two rare earths, however, there will be a net transfer of \( \Delta n \) moles of thulium ions forward and \( \Delta n \) moles of erbium ions in the opposite direction across the reference plane for each mole.
of rare-earth mixture displaced from the resin by ammonium ion and redeposited. This results from the difference in the thulium to erbium ratios existing in the solution and resin phases.

For one mole of total rare earth transported $\Delta n$ is equal to $N_r - N_s$, where $N_r$ and $N_s$ are the mole fractions of erbium in the resin and solution phases, respectively, in the plateau region. Since $R = N/(1 - N)$ in general, equation 13 becomes

$$\frac{N_r}{1 - N_r} = (1 + e) \frac{N_s}{1 - N_s}$$

(15)

Solving for $N_r$ and $N_s$,

$$N_r = \frac{(1 + e)N_s}{1 + eN_s}$$

(16)

$$N_s = \frac{N_r}{1 + e(1 - N_r)}$$

(17)

Therefore,

$$\Delta n = N_r - N_s = \frac{eN_s(1 - N_s)}{1 + eN_s} = \frac{eN_r(1 - N_r)}{1 + e(1 - N_r)}$$

(18)

For the band initially sorbed on the column and in the plateau region as the band is eluted down the column, $N_s$ is equal to $N_0$, the mole fraction of thulium in the binary mixture. To separate the mixture into its component parts, it is necessary to effect a net transport of $N_0(1 - N_0)$ moles of thulium forward across the plane of reference and a
corresponding amount of erbium in the opposite direction. Since the net number of moles of thulium or erbium transported per mole of band displacement is \( \Delta n \), defined by equation 18, the elution distance, \( l_x \), required to resolve an initially sorbed mixture, \( l_o \) units in length, is

\[
l_x = l_o \frac{N_0(1 - N_o)}{n} = l_o \frac{1 + eN_o}{e}
\]

(19)

C. HETP

Once the band has progressed down the column system a distance about three times its length, the condition of steady state in total reflux is approached very closely. A plane of reference perpendicular to the resin bed can be envisioned which always maintains a fixed position with respect to the ends of the band as it moves down the bed. When viewed from the plane of reference, the material in the band is being transported upward in the resin phase and downward in the solution phase. If one examines the net transport of either thulium or erbium ions across this plane, at any fixed arbitrary distance from the front edge of the band, the net transport is zero. Under these conditions, the mathematics of a counter current system can be utilized, provided the equations used are those which apply to the case in which no product is withdrawn.

A theoretical plate is defined as an increment of the band of such size that the ratios of two components leaving it in the resin phase and solution phase are related by the separation factor. If two points
on the resin are chosen a distance, L, apart, the ratios of erbium to thulium at the two points will differ by the factor $K^m$ where $m$ is the number of theoretical plates between the points.

$$R_m = K^m R$$  \hspace{1cm} (20)

or

$$\log \frac{R_m}{R} = m \log K$$  \hspace{1cm} (21)

If, under the conditions of steady state and total reflux, the HETP is assumed constant across the band, then the plate height can be calculated; since,

$$m = \frac{L}{\text{HETP}}$$  \hspace{1cm} (22)

giving

$$\log \frac{R_m}{R} = \frac{\log K}{\text{HETP}} L$$  \hspace{1cm} (23)

Using the value for $K$ determined independently, the HETP can be found. A plot of $\log R_m/R$ versus $L$ is linear and the slope is equal to $\log K$ divided by HETP.
IV. MATERIALS AND APPARATUS

A. Chemicals

1. HEDTA

Chaberek and Bersworth (39) were the first to prepare HEDTA.

It has the structure

\[
\text{HOOC-CH}_2\text{N-CH}_2\text{CH}_2\text{N-CH}_2\text{-OH} \\
\text{HOOC-CH}_2\text{N-CH}_2\text{COOH}
\]

The material used in this research was purchased under the trade name of Chel DM Acid from Geigy Industrial Chemicals, a division of Geigy Chemical Company, Cranston, Rhode Island. It was obtained at a purity of greater than 98 per cent. The material contained an insoluble dirty residue of undetermined origin, so that it was necessary to prepare a very concentrated solution and filter this through Pyrex glass wool before use.

2. Thulium and erbium oxides

Thulium and erbium oxides were available as the result of the ion-exchange separations of rare earths performed in this laboratory by Dr. Powell's group (22, 23). The material was received as thulium and erbium oxide mixture and contained only trace amounts of holmium and ytterbium impurities.

3. Resin

The resin used was a sulfonated copolymer of styrene and divinylbenzene obtained from Rohm and Haas, Resinous Products
Division, Philadelphia, Pennsylvania, under the trade name of Amberlite IR-120. It was specified to be eight per cent cross linked and to be of \(-40 +50\) mesh size. Prior to its use, however, it was necessary to backwash the columns many times to remove fines. In this operation the resin was forced up into an auxiliary length of column by means of a current of deionized water. The resin was then allowed to settle by gravity back into the original column. The finest particles concentrated at the very top of the beds and were easily removed. These particles made up less than one-half of one per cent of the volume of the bed. No attempt was made to remove any heavy particles that might have concentrated at the bottom of the column, since it was assumed that previous screening had removed these effectively.

4. Oxalic acid

The oxalic acid used was the C. P. crystalline grade obtained from Fisher Scientific Company, Fair Lawn, New Jersey. The material was reported to be 99.8 per cent pure with 0.03 per cent ash.

5. Miscellaneous chemicals

The hydrochloric acid, sulfuric acid, and ammonium hydroxide used in this work were all Baker and Adamson C. P. grade and were obtained from the General Chemical Division of Allied Chemical and Dye Corporation, New York, New York.

The copper sulfate was technical grade material obtained from Warren Douglas Company, Des Moines, Iowa. It was necessary to filter the copper sulfate solutions through Pyrex glass wool prior to their use.

The water used was condensed steam which was further demineralized in
the commercial mixed-bed demineralizer obtained by this laboratory from Illinois Water Treatment Company, Rockford, Illinois.

B. Apparatus

1. Column assembly

All the columns described below were obtained from Corning Glass Works. They were made of double duty Pyrex glass and flanged at both ends.

The inside diameter of the columns which contained the resin beds was 1.0 inches. The apparatus consisted of three columns so constructed that the ion-exchange process could be performed at various controlled temperatures. Two of the columns were five feet in length and the third column was only one foot long. The one-foot column was fitted with a soft-glass water jacket by the Laboratory Glass Shop. The bottom-most section of the column used to retain the resin in the column (which is described below) was heavily insulated.

The end plates were machined from three-fourths inch Plexiglas plastic sheets. Grooves three-eighths inch deep were countersunk for the column fittings. A conical cavity exactly one inch in diameter at the top was machined into the center of the bottom end plate to allow uniform exit of solution from the resin bed.

The assembly of the columns was the most critical part of the experiments, since channeling in the columns would increase the column operation parameter, the HETP. The resin was retained in each column by
a Saran cloth screen. Water-tight seals were obtained between the glass columns and the plastic end-plates with the aid of neoprene gaskets and a small amount of Sanford's Rubber Cement. Care was exercised not to permit excess cement to enter the area of the Saran cloth directly beneath the resin bed. The one-inch column was connected to its bottom end-plate with three stainless steel bolts and a plastic flange. The four-inch column was connected, so as to surround all the one-inch column fittings, to a permanent base and the common bottom plate with a six-bolt metal flange. The bolts were adjusted until the four-inch column was exactly perpendicular. The upper end-plate and gasket arrangement sealed both columns simultaneously and was secured by means of a six-bolt metal flange around the four-inch column. The inner chamber was tapped and threaded for one-eighth-inch pipe fittings, the outer chamber for one-quarter-inch pipe fittings.

Prior to attaching the upper end-plate, the resin was introduced into the inner chamber. The procedure for this follows.

A Saran tube of one-eighth-inch inside diameter was connected with Saran fittings between the bottom of the inner chamber to the demineralized water tap. Enough water was passed upward into the column to flush out all the air bubbles from the tubing and lower collection section of the column. The excess water was siphoned from the top of the column until a water depth of approximately six inches remained in the resin chamber. A water slurry of the resin in the hydrogen form, sufficient to almost fill the column with loosely packed resin, was poured into the column.
At this point an auxiliary column of equal length was attached to the top of the resin column, with a neoprene washer as a seal. The water tap was opened until the resin was forced to the top of the auxiliary column. The resin then was allowed to settle slowly into the resin chamber. The water above the resin bed was siphoned off and the fine particles which concentrated at the top of the bed were also removed. The fine particles could easily be seen due to their lighter color. The backwash operation was repeated until all air bubbles and fine particles were removed from the bed. Generally, one or two operations were sufficient to remove the air in the bed, but numerous repetitions were necessary before the fine resin particles were completely eliminated.

Generally, this operation gives a uniformly packed bed that can be operated with only slight channeling effects. However, the above treatment was not entirely adequate for this work and apparatus. Possibly this was due to the design of the equipment. To position the resin column exactly vertical, the outer column is adjusted. This insures that the inner column is exactly upright only when the top end-plate is in place. During the backwashing operation the end-plate is not in place and there is no assurance the resin column is vertical except by measurement. The difficulties in measuring the one-inch resin column which is inside the four-inch column are obvious, although it is possible to adjust the position so that the column is very close to the vertical position. However, even after the resin column was thought to be positioned correctly and was repeatedly backwashed, channeling effects
were still observed.

When observing the settling of the resin from the backwash operation, it was noted that, after a small amount of the resin had settled into the lower column, currents were set up in the column so that some resin was transported downward on one side of the column and upward on the opposite side. This resulted in the resin being deposited in an uneven manner, sloping upward toward the upward current. This effect was overcome by backwashing the resin only about four inches, several times, after the previously reported treatment. Under these conditions no currents could be observed and channeling effects were lessened.

The two five-foot-long columns were assembled and backwashed in this manner. The water-jacketed one-foot column was added to the system to help correct the channeling effect which increased with column length.

It was observed that, as a copper-HEDTA boundary traveled down a four-foot bed length, the boundary remained level until it was almost one-half the way down the column. It then would develop channeling effects which were visible to the eye. Thus it appears that small channeling effects develop into larger ones as the band traverses the column. By using a final short bed these effects did not have as much opportunity to become magnified. It may appear to the reader that a short, final stage, would not provide adequate elution distance for the HETP to readjust to the conditions of the experiment since the solution in the system between resin beds is not in contact with resin. An inspection of the data will convince the reader that the kinetics are rapid and the HETP adjusts quickly to any minor change in experimental conditions. The controlling factor is the
transport of sufficient moles of solute to satisfy the equilibrium. One band length is much more than sufficient to readjust any disturbance in equilibrium between columns.

2. **Temperature control assembly**

A constant temperature was maintained in the resin columns by water circulating from a controlled temperature bath. The constant temperature bath was constructed from an insulated thirty-gallon stainless-steel barrel. A Bakelite top was fitted to the barrel and the bath was equipped with a mercury thermoregulator, two cal-rod heaters of 1500 watts total capacity, and a cooling coil connected to a refrigeration unit for maintaining temperatures below 20°C. This arrangement made it easy to regulate the constant temperature bath at any temperature between zero and 80°C. For the runs made at the two extreme temperatures it was necessary to insulate the columns as well to obtain short on-off cycling of the heating or cooling source.

3. **Flow rate control assembly**

Since the column parameter, HETP, is directly proportional to the flow rate, its control and measurement is very important. A rotameter was installed into the eluate line to facilitate checking for constant flow after the rate had been set and measured. The calibration of the rotameter so as to read flow rate directly was too complex to be of use for this work, since the density of the solution changes with each solute in the eluate and with temperature. The flow rate was measured by simply collecting an aliquot of solution during a measured time interval.

The control of the flow rate was accomplished by two different
methods. Fair success was obtained by adjusting the flow with a screw clamp on a small polyethylene tube in the eluate line when the eluant was fed into the system from an overhead tank. Frequent adjustments were required, however, due to resistance changes in the system. These changes became less significant when the eluant was fed into the system by a centrifugal pump. A capillary tube was introduced into the eluant line to provide a high total pressure drop over the system. This large pressure on the resin beds also served to minimize degassing of eluant in the resin voids at elevated temperature. However, line voltage fluctuations still resulted in unpredictable changes in the flow rate. Best results were obtained with a constant displacement pump.

Considering the cost and pulsation of flow, a low priced finger pump was selected and installed. The flow pulsation in the columns was minimized and could not be detected on the rotameter after connecting the columns and pump with a forty-foot polyethylene line and inserting a capillary tube in the eluate line. The flow could be maintained to within one-tenth milliliter per minute at a flow rate of nine milliliters per minute. The high pressure again served to minimize degassing at elevated temperatures. The chief disadvantage of this assembly lay in the difficulty of adjusting the flow rate to a set value as the response of flow to a change in pumping speed was slow.

4. *Aliquot collection assembly*

For the calculation of the HETP it is necessary to divide the overlap region between bands into aliquots and to measure the total volume of the aliquots. Two different techniques were used. Automatic sample collectors
based on both volume and time intervals were tried. The volume-interval bottle changer was used with volumetric flasks, but the most satisfactory results were obtained with a time-interval changer. The volume of the aliquots collected in a given time was measured to the closest five milliliter mark in a graduated cylinder. This method served to provide a continual check on the flow rate as the eluate issued from the column.
V. EXPERIMENTAL

A. Solutions

1. Preparation of erbium chloride-thulium chloride mixture

An excess of erbium and thulium oxides were dissolved in hydrochloric acid. The solution phase was filtered into a twenty-one-liter bottle and diluted with demineralized water. The resultant solution was approximately 0.5 normal in rare earths. An arithmetic weight analysis of the original oxides showed that the solution contained about fifty-six per cent thulium and forty-four per cent erbium.

2. HEDTA solutions

It was desired to make all the experimental runs at a constant concentration of eluant. The HEDTA eluant solutions for the individual runs were made up by dilution of a stock solution with demineralized water. Three different stock solutions were used. The preparation of each is given below.

   a. Eluant C. Three kilograms of HEDTA were stirred with forty-two liters of demineralized water. The solution was filtered to remove suspended dirt and undissolved HEDTA. The solution was then adjusted to a pH of 7.7 with concentrated ammonium hydroxide. Fifty milliliters of phenol were added to the solution to prevent the growth of mold. The eluant solutions were prepared by dilution of 4.200 liters of the stock to 45.00 liters with demineralized water. The final eluant solutions contained 5.78 grams per liter of HEDTA and had a pH of 7.5.
b. **Eluant F.** Twelve kilograms of HEDTA were dissolved in forty-one liters of demineralized water by slowly adding concentrated ammonium hydroxide with stirring. The solution was filtered and adjusted to a pH of 8.2 with ammonium hydroxide. Fifty milliliters of phenol were added to the stock solution to prevent the growth of mold. The eluant solutions were made up by diluting a 1.034 liter aliquot to a total volume of 45.00 liters with demineralized water. The eluant solutions contained 5.41 grams of HEDTA per liter and had a pH of 7.6.

c. **Eluant G.** When a fifty-gallon overhead tank became available, the eluant was made up at the concentration at which it was to be used. Two and one-half kilograms were added to approximately forty-five gallons of demineralized water. The pH was adjusted to 7.5 with concentrated ammonium hydroxide. Analysis of the eluant showed the solutions contained 6.31 grams of HEDTA per liter.

**B. Procedure**

1. **General procedure**

The three water-jacketed columns were connected in series with Saran tubing. The columns were rinsed with demineralized water to flush out the HEDTA solution from the previous run. This left the resin in the ammonium form. The resin was converted to the copper(II) cycle by passing an excess of a saturated copper-sulfate solution through the columns. The copper(II) ion was preferentially sorbed on the resin and only a small excess was necessary after the blue color appeared in the
eluate to insure that all the resin sites were occupied by copper(II) ions. The excess copper sulfate was washed from the column system with demineralized water.

A 500-milliliter aliquot of the erbium-thulium solution was passed through the columns. The rare-earth ions displaced the copper(II) ions from the resin and formed a visible band, about thirty centimeters long at the top of the first column. The displaced copper(II) ions were washed out of the system with demineralized water.

The water in the constant temperature bath was circulated through the water jackets of the columns and the thermoregulator was set to maintain the appropriate temperature. When the temperature of the bath was near the selected value, the eluant was connected to the top of the first column. The flow rate was then set by means of a screw clamp (or glass stopcock) in the eluate line and was checked periodically thereafter by reading the rotameter and measuring directly by means of a stop watch and graduated cylinder. It was generally necessary to adjust the flow rate two or more times a day depending on the flow rate and the control method used.

The copper-HEDTA eluate was discarded, except for special measurements (see below), until the front edge of the rare-earth band had progressed onto the third column. From this point on, the eluate was collected in aliquots with the aid of a bottle changer. When the blue color faded in the eluate, the aliquots were numbered in the order taken from the column and their volumes recorded. The flow rate was measured again at this point, recorded, and adjusted frequently thereafter to
maintain it constant as the band came off the column. In those cases where the time-interval bottle changer was used, the average flow rate was recorded from each aliquot.

The rare earths were precipitated from the individual aliquots by addition of oxalic acid. The oxalate precipitate was filtered out, placed in a porcelain crucible, dried under an infrared heat lamp, and ignited to the oxide in an electric muffle at approximately 850°C. The oxides were stored in desiccators. Each mixture was analyzed for its thulium and erbium contents.

2. Special precautions

a. Elevated temperature. In runs made at temperatures above 40°C., degassing of the solution occurred unless preliminary measures were taken to prevent it. It was necessary to avoid degassing of the solution even when the rare-earth band was not on the column, because bubble formation would require that the column be backwashed before the next run was made. The gas formed in the column disturbs the carefully packed resin and promotes channeling.

When degassing occurred during a run, the bubbles always formed in the top half of the first column and sometimes in the top of the second column. However, bubble formation was never observed in the third column and it was not necessary to disturb this section of the resin bed by backwashing. Since this was the last section of resin the band came down, it was expected that the degree of channeling for all the runs was about the same, even though the channeling in the other sections of resin may have been altered by backwashing.
Degassing was minimized by keeping a pressure on the columns when the temperature was above 40°C. Very good results were obtained when the demineralized water used to make up the various eluant solutions was boiled for several hours before use and allowed to cool under a slight vacuum.

b. Constant flow rate. Only with a constant displacement pump could the flow rate be kept reasonably constant. When the eluant was fed into the system by either a centrifugal pump or by gravity, appreciable changes in the flow rate were detected with

--- changes in feed level
--- changes in resin size
--- line voltage fluctuation
--- elasticity of tubing

3. Relation of band length to volume

The relationship between the distance the rare-earth band moves per liter of eluate was established in the following manner. The edge of the copper-H_5O_2+ boundary was observed as it came down the first column. When the blue color disappeared from the resin, the tube between the first and second columns was disconnected. The solution level in the second column was lowered to the top of the resin and turned off. The column was refilled with a measured volume of demineralized water. The eluate stream from the first column was tested for the rare-earth breakthrough. As the rare earths started off the first column the column was again connected into the series. The flow rate was adjusted to the selected
value and the eluate volume measured from this point until the rare-earth breakthrough from the third column. The lengths of the two resin beds were measured in the ammonium cycle and the distance moved per unit volume was calculated in the units, centimeters per liter. Several such measurements were made for runs using eluant C. The values for runs made with eluants F and G were calculated from this information, since the rate at which the band moves is directly proportional to the concentration. The kinetics of the system are also dependent on the concentration; but since the changes in concentration are small and, in most cases reported here, are particle-diffusion controlled, this is not detected in the data.

4. Conditions for the experimental runs

The concentration of the HEDTA and the pH of the eluant was maintained constant for all runs within the accuracy stated above. The type of resin, resin bead size in the hydrogen cycle, and the diameter of the resin beds were maintained constant at the values reported above. All thulium and erbium bands were eluted down a length of resin bed at least four times its original size to insure the steady state was obtained.

a. Constant temperature. Seven runs were made at a constant temperature of 60°C. at various flow rates.

b. Constant flow rate. Runs were made at different temperatures between zero and 80°C. at constant flow rates. The actual values for the low rate varied from 8.3 to 9.1 milliliters per minute for the different runs. The value for the HETP at 8.5 milliliters per minute was obtained by plotting all the data available at any one temperature as flow rate
versus HETP. A straight line was drawn through the data and the origin. The value of the HETP at 8.5 milliliters per minute was read from the graph.

5. Analysis of aliquots

   a. Spectrographically. Analyses of aliquots containing less than one per cent of the minor constituent were performed by the spectrographic department of this laboratory headed by Dr. V. A. Fassel.

   b. Spectrophotometrically. Analyses of aliquots containing both constituents in quantities greater than one per cent were performed by Floy Sealock, a member of the analytical group of this laboratory which is headed by Dr. C. V. Banks. For a discussion of the method used the reader is referred to a publication by Banks (40).
VI. RESULTS AND CONCLUSIONS

A. Data

Analytical data for several runs made at 60°C and various constant flow rates are plotted versus distance along the band in Figure 1 to illustrate the calculation of the change in HETP with the change in flow rate. The HETP values calculated for all runs are tabulated with the conditions for the runs in Table 1.

B. Discussion

1. HETP versus flow rate

A theoretical plate is defined as an increment of the band of such size that the ratios of two components leaving it in the resin phase and solution phase are related by the separation factor. If each layer of resin were in full equilibrium with the solution surrounding it, this increment of band would be infinitely small in length. This would require an infinitesimally small rate of flow. At all finite rates of flow non-equilibrium conditions must exist, since there is a finite time interval before equilibrium can be established. The HETP is a measure of this time interval by its definition, i.e., it measures the length of resin bed necessary for the ratios of the components to attain the value that would be obtained at equilibrium. From this we would expect a plot of flow rate versus HETP to show an infinitesimally small HETP at infinitely
Figure 1. Plot of the ratio of erbium to thulium versus the distance along the band.
Table 1. HETP data obtained on one-inch columns for runs made at constant concentrations and various flow rates and temperatures

<table>
<thead>
<tr>
<th>Run number</th>
<th>Temperature (degrees centigrade)</th>
<th>Flow rate (milliliters per minute)</th>
<th>HETP (centimeters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCB</td>
<td>0</td>
<td>8.3</td>
<td>7.64</td>
</tr>
<tr>
<td>KFA</td>
<td>10.0</td>
<td>8.2</td>
<td>6.19</td>
</tr>
<tr>
<td>KFB</td>
<td>10.0</td>
<td>8.4</td>
<td>5.41</td>
</tr>
<tr>
<td>TGA</td>
<td>20.0</td>
<td>8.5</td>
<td>5.26</td>
</tr>
<tr>
<td>JFA</td>
<td>30.0</td>
<td>8.6</td>
<td>2.03</td>
</tr>
<tr>
<td>LFA</td>
<td>35.0</td>
<td>8.4</td>
<td>1.72</td>
</tr>
<tr>
<td>FGA</td>
<td>40.0</td>
<td>9.0</td>
<td>1.38</td>
</tr>
<tr>
<td>FCB</td>
<td>40.0</td>
<td>8.3</td>
<td>1.28</td>
</tr>
<tr>
<td>IFB</td>
<td>50.0</td>
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<td>1.01</td>
</tr>
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<td>5.5</td>
<td>0.50</td>
</tr>
<tr>
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<td>1.1</td>
<td>0.27</td>
</tr>
<tr>
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<td>15.0</td>
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</tr>
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</tr>
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</tr>
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</tr>
<tr>
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<tr>
<td>EFG</td>
<td>80.0</td>
<td>8.4</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Small flow rates and the HETP to increase linearly with increasing flow rate. This would be true only if the kinetics of the system were unaltered.

Powell and Karraker* have conducted experiments on the separation of erbium and thulium with HEDTA in four-inch columns at room temperature. A plot of their data—HETP versus flow rate—gives a straight line.

line with the slope passing through the origin at flow rates greater than fifty milliliters per minute on four-inch columns. (This corresponds to a flow rate of three milliliters per minute on a one-inch column.) At a slower flow rate the experimental point lies above the line indicating a change in the kinetics of the system. It is obvious that, with the flow rates greater than fifty milliliters per minute on the four-inch columns, the time necessary to obtain equilibrium is constant; and the influence of more efficient stirring from the faster rate of flow of the solution has no effect on the kinetics. In terms of the model of Boyd, et al. (32), this means that the kinetics must be controlled by particle rather than film diffusion.

The deviation of the point from the straight line at slow flow rates can then be attributed to the inefficient stirring of the aqueous phase. Here film diffusion also becomes important and the kinetics for the system become slower since the time for attaining equilibrium would be the sum of the time required for each diffusion step when they occurred independently.

Thus, at room temperature, the kinetics of the system improve with an increase of flow rate until the thickness of the stagnant layer of solution surrounding the resin bead (Nernst film) is reduced to the point where transport of the ions through the solution phase is not important to the kinetics. The kinetics then remain constant as the flow rate is increased further and the increase in HETP is due only to the increase in volume of solution passing through the theoretical plate in the constant interval of time necessary to attain equilibrium.
A plot of HETP versus flow rate (Figure 2) for runs made at 60°C gives a straight line which passes near the origin. From the data it appears that the film diffusion step does not become important even at the slow flow rates used. The increase in temperature apparently increases the transport of ions in the solution phase sufficiently. The fact that the line does not pass through the origin is apparently due to tilting of the bands and other systematic errors in the data.

2. HETP versus temperature

A plot of HETP versus temperature (Figure 3) at a constant flow rate of 8.5 milliliters per minute on a one-inch column gives an exponential curve with the HETP decreasing with increasing temperature. The values of HETP for this flow rate were obtained from the data by plotting the HETP data available at each temperature versus flow rate. A straight line was drawn through the points and the origin. The value of the HETP at 8.5 milliliters per minute was estimated from the graph. Since all the temperatures had at least one run made between 8.3 and 9.1 milliliters per minute, the error, introduced due to the fact that the line does not necessarily pass through the origin as illustrated by Figure 2, is small.

The separation factor enters into the value of the HETP and, of course, changes with temperature. However, the magnitude of the changes observed in the HETP could not be explained by the change in the separation factor since it enters the equation as a logarithmic function.
Figure 2. Plot of HETP versus flow rate for runs made at a constant temperature of 60°C.
Figure 3. Plot of HETP versus temperature at a constant flow rate of 8.5 milliliters per minute.
The decrease in HETP then must be due to the improved kinetics of the system at higher temperatures. An increase in temperature would, of course, increase the rate of diffusion of the ions through the resin particle.
VII. LITERATURE CITED


