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COUNTERCURRENT ION EXCHANGE WITH GROSS
COMPONENTS. PART I IN AN EQUILIBRIUM
STAGE CONTACTOR. PART II IN A CONTINUOUS
COUNTERCURRENT COLUMN

Technical Report Number 6

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PREFACE

The attached report, in two parts, covers one completed phase of the countercurrent ion exchange program carried out by Stanford Research Institute for the Atomic Energy Commission. It is concerned mainly with proposed calculation methods for countercurrent ion exchange under gross conditions, i.e., with mixtures in which the ion of interest is a major component.

Many of the potential applications for ion exchange involve the recovery or separation of components in multicomponent gross ion systems. The calculation procedures discussed in this report should make possible engineering studies of these applications and thus advance their technical development. Water softening, demineralization, and the removal of inorganic contaminants from organic products are typical processes which involve ion exchange of gross components.

In Part I, a theory is proposed for multicomponent gross ion exchange in an equilibrium stage contactor. From the theory, a graphical calculation procedure, much like plate-to-plate distillation design, is developed; it is applied to the evaluation of gross runs made in the intermittent mixture-settler contactor. This apparatus is described in Technical Report III, "Ion Exchange of Trace Components in a Countercurrent Equilibrium Stage Contactor."

In Part II, the theory is extended to apply to gross exchange in a continuous countercurrent column. Several moving bed runs were made, under gross conditions, in the equipment described in Technical Report V, "Continuous Countercurrent Ion Exchange with Trace Components." The fundamental theory, together with the ion exchange correlation reported in Technical Report V, allowed the graphical evaluation of the data.

The analytical techniques used in obtaining the resin and solution compositions were detailed in Technical Report IV, "Analytical Methods Used in the Studies on Continuous Separation of Ions by Countercurrent Ion Exchange."

The principal conclusions of the present study are:

1. The performance of an equilibrium stage contactor can be predicted quite accurately by the proposed calculation method, i.e., given the degree of exchange desired, the number of equilibrium contacts needed between resin and solution phases can be calculated, as well as the necessary effective flowrate of each phase.

2. The evaluation of the continuous column data gave transfer heights (Ht's) that were, on the average, comparable to those obtained in the trace exchange experiments, although they showed a greater spread from the mean. While these results do not compare in accuracy with those for the equilibrium stage contactor, the method may be suitable for engineering purposes. Further work is required to refine the procedure.

This report will be submitted to "Chemical Engineering Progress" for publication, and Part I will be presented at the San Francisco meeting of the American Institute of Chemical Engineers, September, 1953.

The data from which the experimental results were derived are contained in Stanford Research Institute Notebook numbers 1225, 1245, 1259, and 1266.

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**COUNTERCURRENT ION EXCHANGE WITH GROSS COMPONENTS
IN AN EQUILIBRIUM STAGE CONTACTOR**

ABSTRACT

The use of countercurrent ion exchange for the separation of trace components has been discussed previously. The present paper covers ion exchange separations under gross conditions, i.e., where non-linear equilibrium isotherms govern.

The variables affecting the separation of two or more ionic components in such a multicomponent system were considered in the development of a semi-graphical design procedure. This method permits the design of equilibrium stage units involving countercurrent contact between resin and solution, making it possible to predict the behavior of the contactor from the operational variables and the equilibrium relations for the system. The design procedure, involving step-by-step calculations, was suggested by the Lewis and Cope method for multicomponent distillation.

The method was applied to the evaluation of experimental data, which were obtained, under gross conditions, with a countercurrent mixer-settler contactor. Comparisons of the ion separations obtained with this apparatus, on a $\text{Li}^+ - \text{K}^+ - \text{H}^+$ -Chempro C-20 resin system, and the values predicted by the design procedure showed good agreement.

INTRODUCTION

In a previous paper³ the present authors described an intermittent mixer-settler ion exchange unit in which the separation of trace ions was achieved by countercurrent and stagewise contact between resin and solution aliquots. The fundamental theory governing the separation of trace ions and the design relations derived for an equilibrium stage contactor were presented. The performance obtained with the apparatus was in agreement with that predicted from the design relations.

Others, and notably Amundson,¹ Selke,⁵ and Dickel,² have presented relations applying to ion exchange between two components under gross conditions. However, the need remained for an explicit calculation procedure covering countercurrent exchange with multicomponent gross ion systems.

Thus, the trace work was extended in the present paper to the development of design relations for the separation of gross components, and the calculation methods were evaluated by the experimental separation of gross ions in the intermittent mixer-settler. Since the operation and performance of the equipment was given in some detail in the earlier paper, the principal emphasis will be on the development of the calculation method and its application to the evaluation of experimental results.

It would be well to review the distinction between trace and gross conditions. The differentiation is not based on the absolute concentration of the ion concerned but on the concentration relative to the total ionic concentration of the solution. A trace ion is dilute with respect to the total ionic level, whereas the concentration of a gross ion is of

the same order of magnitude as, or is identical with, the total ionic concentration. The exchange conditions under which an ion can be considered as trace or gross have been defined mathematically.⁶

THEORETICAL CONSIDERATIONS

Basic Relations. In countercurrent ion exchange the resin and solution streams move in opposite directions with the ions concerned continuously distributing themselves between the two phases. If the ions to be separated, say ions A and B, have different partition ratios, the ion most strongly held by the resin, say ion B, will be enriched in that moving phase, while ion A will be enriched in the solution stream. In order then to transfer ion B back to a solution, it is necessary to elute the resin with a third component, say ion G.

Thus, in the simplest ion exchange separation system, three components (ions A, B, and G) and two phases (resin and solution) are involved. The exchange reactions for this case may be represented in the normal mass action manner as:

with the equilibrium constants being defined as

$$K_{AG} = \frac{(G^+)(A \cdot \text{Resin})}{(G \cdot \text{Resin})(A^+)} \quad (2A)$$

$$K_{BG} = \frac{(G^+)(B \cdot \text{Resin})}{(G \cdot \text{Resin})(B^+)} \quad (2B)$$

* Note: Equations are designated A and B to indicate their application to ions A and B.

Here the terms in parentheses denote either solution or resin concentrations rather than activities and therefore K_{AG} and K_{BG} are not true constants. For engineering purposes, however, the use of concentrations, and constant values of K , may be assumed to be sufficiently accurate.

It is more convenient, however, to handle these quantities in terms of their equivalent fractions. This is easily done, since ion exchange takes place on an equivalent basis. Thus, if C_x is the initial total ionic concentration of the solution (in meq/ml of fluid), and if Q is the total or ultimate exchange capacity of the resin (in meq/g of bone dry resin), the following relations must be satisfied.

$$(A^+) + (B^+) + (G^+) = C_x \quad (3)$$

$$(A \cdot \text{Resin}) + (B \cdot \text{Resin}) + (G \cdot \text{Resin}) = Q \quad (3')$$

with C_x and Q remaining constant. The equivalent fraction of a component in the solution will be designated by x and in the resin by y , so that

$$x_A = \frac{(A^+)}{C_x} \quad (4)$$

and

$$y_A = \frac{(A \cdot \text{Resin})}{Q} \quad (4')$$

The mass action equilibrium relation, Equation (2), then becomes

$$K_{AG} = \frac{x_G y_A}{y_G x_A} \quad (5A)$$

$$K_{BG} = \frac{x_G y_B}{y_G x_B} \quad (5B)$$

The countercurrent contactor may be considered as being composed of a finite number of equilibrium plates or contacts, as represented

diagrammatically in Figure 1. Here a stream of ion exchange resin of constant composition, $(y_A)_{entr}$, is fed into the top of a countercurrent contacting section at a constant weight rate of flow, $R_p \rho_p$, and is removed from the bottom of the section at the same rate. Simultaneously, a solution stream of constant composition, $(x_A)_{entr}$, is introduced into the bottom of the section at a constant volumetric rate of flow, R_F , and passes up through the column countercurrent to the resin and leaves the top at this same rate. The composition of the effluent solution is $(x_A)_{exit}$, and that of the effluent resin is $(y_A)_{exit}$. Similar considerations hold for components B and G.

At the steady state, a material balance may be written around the entire contactor as

$$R_p \rho_p Q(y_A)_{entr} + R_F C_{\Sigma}(x_A)_{entr} = R_p \rho_p Q(y_A)_{exit} + R_F C_{\Sigma}(x_A)_{exit} \quad (6A)$$

where $R_p \rho_p Q$ and $R_F C_{\Sigma}$ are the equivalent flow rates of the resin and solution phases in meq/sec. If written around the left end of the contactor and the $n-1$ 'th equilibrium contact, the relation is

$$R_p \rho_p Q(x_A)_n + R_F C_{\Sigma}(x_A)_0 = R_p \rho_p Q(y_A)_1 + R_F C_{\Sigma}(x_A)_{n-1} \quad (7A)$$

This conservation equation, and a similar one for component B, plus the equilibrium relations [Equation (5)], and the necessity that the equivalent fractions of the three components add to unity, completely define the operation of a countercurrent equilibrium stage contactor.

Application of Relations to an Equilibrium Stage Contactor. In order to simplify the calculation procedure, it is convenient to redefine some of the terms in the above basic relations.

$$\beta = \frac{y_G}{x_G} \quad (8)$$

$$E'_A = \frac{K_{AG} R_P \rho_P Q}{R_F c_{\Sigma}} \quad (9A)$$

and

$$\Delta'_A = R_P \rho_P Q (y_A)_n - R_F c_{\Sigma} (x_A)_{n-1} \quad (10A)$$

where Δ'_A is the net transfer of component A across any plane in the contactor, i.e., it is the difference between the amount of component A being carried through a given cross-section in the resin phase and that being carried in the opposite direction at the same point by the solution phase.* At the steady state Δ'_A is obviously a constant, so that

$$\Delta'_A = R_P \rho_P Q (y_A)_{entr} - R_F c_{\Sigma} (x_A)_{exit} = \quad (11A)$$

$$= R_P \rho_P Q (y_A)_{exit} - R_F c_{\Sigma} (x_A)_{entr} \quad (11B)$$

The basic relations can now be rewritten. First, from the equilibrium relation, Equation (5A),

$$y_A = \frac{y_G}{x_G} K_{AG} x_A$$

or at the n'th equilibrium contact

$$(y_A)_n = \beta_n K_{AG} (x_A)_n \quad (12A)$$

and for component B

$$(y_B)_n = \beta_n K_{BG} (x_B)_n \quad (12B)$$

* In a previous paper (6), E_A was defined as

$$E_A = \frac{M_A R_P \rho_P Q}{R_F c_{\Sigma}} = \frac{y_G K_{AG} R_P \rho_P Q}{x_G R_F c_{\Sigma}}$$

so that $E_A = \beta E'_A$.

The conservation relation, Equation (7A), gives, in terms of contact numbers,

$$(y_A)_n = \frac{R_F C_{\Sigma}}{R_P \rho_P Q} (x_A)_{n-1} + \frac{R_P \rho_P Q (y_A)_1 - R_F C_{\Sigma} (x_A)_0}{R_P \rho_P Q} \quad (13A)$$

or

$$(y_A)_n = \frac{K_{AG}}{E'_A} (x_A)_{n-1} + \frac{\Delta'_A}{R_P \rho_P Q} \quad (14A)$$

and for component B

$$(y_B)_n = \frac{K_{BG}}{E'_B} (x_B)_{n-1} + \frac{\Delta'_B}{R_P \rho_P Q} \quad (14B)$$

From Equation (8), and the necessity that the equivalent fractions add to unity,

$$\beta_n = \frac{(y_G)_n}{(x_G)_n} = \frac{1 - (y_A)_n - (y_B)_n}{1 - (x_A)_n - (x_B)_n} \quad (15)$$

Replacement of the solution equivalent fractions, through Equations (12A) and (12B), lead to

$$\beta_n = \frac{1 - (y_A)_n - (y_B)_n}{1 - [(y_A)_n / \beta_n K_{AG}] - [(y_B)_n / \beta_n K_{BG}]} \quad (16)$$

and clearing of fractions gives β_n , in terms of resin equivalent fractions, as

$$\beta_n = 1 - \left[\frac{K_{AG} - 1}{K_{AG}} \right] (y_A)_n - \left[\frac{K_{BG} - 1}{K_{BG}} \right] (y_B)_n \quad (17)$$

An analogous derivation will supply β_n in terms of solution equivalent fractions, thus

$$\beta_n = \frac{1}{1 + (K_{AG} - 1)(x_A)_n + (K_{BG} - 1)(x_B)_n} \quad (18)$$

Equations (12), (14), and either (17) or (18) can now be used in a stepwise manner, either algebraically or graphically, to design a counter-current equilibrium stage contactor for a given operation. It is apparent that this design technique, involving the use of a variable, but linear, equilibrium relation and step-by-step calculations, is related to the Lewis and Cope⁴ method for multicomponent distillation. Examples of some of the procedures will be given in the section on the Interpretation of Data.

EQUIPMENT

General. Countercurrent ion exchange requires that the resin and solution pass through a contacting unit in opposite directions and at uniform flow rates. In the case of the equilibrium stage contactor, the flow is intermittent for the reasons discussed in the earlier paper.

The operations involve a series of batch equilibrations between resin and solution aliquots, followed by countercurrent transfers of the two phases.

Intermittent Mixer-Settler. These operations were carried out automatically in the intermittent mixer-settler shown in Figure 2. This equilibrium stage contactor was described in a previous paper.³

Briefly, the assembly consisted of ten mixers and ten reservoirs. Each resin aliquot was retained throughout a run in its respective mixer. The solutions were transferred from one mixer to the next by way of the reservoirs. Countercurrent operation was obtained by advancing the

solution feed position in the same direction and at half the rate of the advance of solutions within the apparatus. In this manner, the movement of the feed position substituted for physical transfer of the resin aliquots.

Solution transfers were made by applying air pressure to the proper vessels, and equilibration of the two phases was promoted by air agitation.

The equipment was so arranged that, at any one time, one mixing stage was devoted to saturation of the resin while nine stages were used for elution or stripping of the resin. The actual separation of the ions took place in the saturating section, where the feed solution containing the ions to be separated was introduced. Here, the resin preferentially retained one of these ions. The other ion to be separated, being less strongly held by the resin, remained largely in the solution phase and was removed in the exhausted saturant. The resin was regenerated by eluting with a third ion. This regenerated resin was, in effect, recycled to the saturating section. The saturation phase of the cycle was of primary interest in this study, whereas the elution was viewed mainly as a service function in preparing the resin for subsequent saturation.

EXPERIMENTAL PROCEDURE

General. The saturant feed solution for the mixer-settler contained Li^+ , K^+ , and H^+ , each in approximately equivalent concentrations. These cations occurred in the form of their chlorides. The performance of the equipment was based upon the degree of separation achieved between the alkali metal ions. This particular three-component system was selected because of the known separability of the metal ions, the equivalence of the ions, and the ease of analysis. The resin used, Chempro C-20, has greater affinity for K^+ than for Li^+ , and this difference served as the basis for the separation of these ions. With reference to theoretical discussion then, Li^+ corresponds to ion A, K^+ to ion B, and H^+ to ion G.

Methods of Analysis. The metal ion contents of the solutions were analyzed by flame photometry with a Beckman DU spectrophotometer, and H^+ ion concentrations were determined with an automatic titrator. In the metal analysis, corrections were made for interference (by reinforcement) of the HCl on the emission and for mutual interference of the Li^+ and K^+ . The resin samples were eluted with HCl, and the resulting elutants were analyzed in the same manner. These results were then converted to resin concentrations. The H^+ content of the resin was found as the difference between the ultimate capacity and the reported alkali metal concentrations.

Determination of Equilibrium Constants. The proposed calculation method for multicomponent gross ion exchange is predicated upon an absence of activity effects, i.e., the other ions have no effect on the mass equilibrium constant (based on concentrations) for each binary exchange. To determine the validity of this assumption, a number of resin and solution samples were equilibrated, so that the equilibrium relations for the system could be established. The data were obtained by mechanical shaking, for about eight hours, flasks containing resin samples originally in the hydrogen form with solution samples having total equivalent concentrations of 0.10N and containing varying $Li^+ : K^+ : H^+$ ratios. The equilibrated samples were analyzed for cation contents by the techniques described above. These results are indicated in Figure 3, where the slopes of the lines are equivalent to the equilibrium constants for the three binaries.

From Equation (5) any one equilibrium constant can be defined in terms of the other two for a three component system, as

$$K_{BA} = \frac{y_B x_A}{x_B y_A} = \frac{K_{BG}}{K_{AG}} \quad (19)$$

Actually, the lines in the plots of Figure 3 were located not only from the applicable data but also from the necessity for satisfying the above theoretical relation. Thus, the slopes were adjusted to obtain the least

deviation of the points from the line and still yield a consistent set of equilibrium constants. This is apparent from Figure 3, since

$$K_{KLi} = \frac{y_K x_{Li}}{x_K y_{Li}} = \frac{K_{KH}}{K_{LiH}} = \frac{3.16}{1.00} = 3.16$$

It should be pointed out that most of the $K^+ - Li^+$ equilibrium data could not be located on the plot, because they were concentrated at the lower end of the line. On an expanded scale, these omitted points also led to the indicated slope.

Experimental Runs. The mixer-settler was operated in accordance with the previously described procedure.³ The operation was such that the saturant solution made equilibrium contacts with two resin aliquots, and the elutant solution (HCl) made contacts with eighteen resin aliquots. Note that $N_C = 2N_S$, where N_C is the number of equilibrium contacts in a given section and N_S is the corresponding number of physical stages in that section. Also, for the reasons discussed in the previous paper, Equation (9A), which defines the dimensionless E'_A factor in terms of resin and solution flowrates, must be modified to apply to the intermittent operation, as

$$E'_A = \frac{K_{AG} W_P Q}{V_F C_A} \quad (20)$$

where

W_P = oven dry weight of resin aliquot, g.

V_F = volume of solution aliquot, cc.

The total ionic concentration in both saturant and elutant was ~ 1.0 N. The equilibration time between phases was five minutes. The volume of the saturant aliquot was 45 cc, and the weight of resin in each stage was approximately 6.5 g. The runs were continued until the steady state was attained. As reported earlier, the contact efficiency in the stages was

essentially 100% under similar operating conditions in the trace region; that is, the attainment of equilibrium between the phases was essentially complete within the limits of experimental accuracy.

The detailed operating conditions for the two experimental runs are given in Table I.

The saturant and elutant feed solutions and all the exhausted solutions removed during a run were analyzed for cation contents. The equilibrated resin and solution aliquots remaining in the apparatus at the end of the run were also removed for analysis. Of the equilibrium data obtained in this manner, those points which could be shown on the scale used for Figure 3 were plotted thereon, and agreement between equilibria from batch tests and from runs was observed.

INTERPRETATION OF DATA

General. The experimental data were evaluated by a trial-and-error procedure to give the composition of the effluent solution which should have resulted from two equilibrium contacts and the equivalent aliquot ratio (i.e., the ratio of the total number of ion equivalents in the solution aliquot to the total in the resin aliquot) and the composition of the feed solution used for the run. The results then were compared with the experimental effluent composition in order to establish the validity of the calculation method.

For each trial, an effluent solution composition was assumed, and the composition of the effluent resin was adjusted to give a 100% material balance for each ion of interest (Li^+ and K^+) by the use of Equation (6). Although the analysis of this resin was available, not too much confidence was placed in these results for several reasons:

- (a) Only one sample of resin was obtained (at the end of the run), and previous work³ had shown deviations of 5% to 10% among resin samples receiving similar treatments.

- (b) The resin analysis was more involved than the solution analysis; and thus a higher margin of error was associated with the resin results.

Once this resin composition was established, the distribution of the H^+ between the phases (β value) was determined for the first equilibrium contact by Equation (17). Then the composition of the solution resulting from this first contact was calculated using the β value in Equations (12A) and (12B). These steps were repeated to find the result of the second contact. If these solution values matched the experimental effluent, then the calculations were complete.

In most cases, however, it required slightly more or less than two contacts to match the solution composition assumed for the first trial. If more contacts were needed, the stepwise procedure was continued to determine the effect of a third contact. Then the number of contacts required to give the assumed effluent were totaled, including fractional contacts where necessary.

The deviation between the calculated number of contacts and the known number was used to obtain an assumed effluent composition for the succeeding trial. These calculations were continued until a match was obtained between assumed and experimental effluent compositions at exactly two contacts for both Li^+ and K^+ .

Evaluation of Run No. 18. A semi-graphical, rather than a completely analytical, method was used to evaluate the experimental data, but the general procedure was identical with that outlined above

A. First Trial.

1. An y-x (resin-solution equivalent fraction) diagram was prepared for the Li^+-H^+ exchange and one for the K^+-H^+ exchange (Figure 4). The slope of the operating line was calculated from the ratio of the equivalents in the solution and resin aliquots:

$$\frac{V_{FC}}{W_p Q} = \frac{(45 \text{ ml})(1.00 \text{ meq/ml})}{(6.36 \text{ g})(5.11 \text{ meq/g})} = 1.38$$

and this slope applied to both the Li^+ and K^+ diagrams.

The lower end of this line was located by the intersection of the influent resin composition and the effluent solution composition, i.e., these combinations;

$$\begin{aligned} (x_{\text{Li}})_{\text{exit}} &= 0.160 & \text{and} & & (y_{\text{Li}})_{\text{entr}} &= 0.0025 \\ (x_{\text{K}})_{\text{exit}} &= 0.052 & \text{and} & & (y_{\text{K}})_{\text{entr}} &= 0.0023 \end{aligned}$$

The solid operating line was then drawn in, and it intercepted the feed composition to give these combinations at the upper end:

$$\begin{aligned} (x_{\text{Li}})_{\text{entr}} &= 0.308 & \text{and} & & (y_{\text{Li}})_{\text{exit}} &= 0.207 \\ (x_{\text{K}})_{\text{entr}} &= 0.302 & \text{and} & & (y_{\text{K}})_{\text{exit}} &= 0.349 \end{aligned}$$

In effect, the above operations gave the adjusted effluent resin composition, just as did the use of Equation (6).

2. The β_1 value was then calculated from Equation (17),

$$\begin{aligned} \beta_1 &= 1 - \left[\frac{K_{\text{LiH}} - 1}{K_{\text{LiH}}} \right] (y_{\text{Li}})_{\text{exit}} - \left[\frac{K_{\text{KH}} - 1}{K_{\text{KH}}} \right] (y_{\text{K}})_{\text{exit}} \\ \beta_1 &= 1 - \left[\frac{1 - 1}{1} \right] (0.206) - \left[\frac{3.16 - 1}{3.16} \right] (0.349) \\ \beta_1 &= 0.761 \end{aligned}$$

It was entirely fortuitous that the equilibrium constant for the $\text{Li}^+ - \text{H}^+$ exchange was unity, so that the Li^+ term could be eliminated from the equation.

3. Then, instead of applying Equations (12A) and (12B) directly, the slope of the equilibrium line was established for both Li^+ and K^+ at the first contact,

$$\begin{aligned} \beta_1 K_{\text{LiH}} &= (0.761)(1.00) = 0.761 \\ \beta_1 K_{\text{KH}} &= (0.761)(3.16) = 2.40 \end{aligned}$$

Lines with these slopes and passing through the origin were drawn in on the respective plots. Actually, only that portion of the equilibrium line which intersected the $(y)_{\text{exit}}$ composition was required. Then the first contact was stepped off from point A to B to C on each plot. The result was the composition of the solution after the first contact:

$$(x_{\text{Li}})_1 = 0.270$$

$$(x_{\text{K}})_1 = 0.146$$

4. Simultaneously, the composition of the resin after the second contact was indicated:

$$(y_{\text{Li}})_2 = 0.154$$

$$(y_{\text{K}})_2 = 0.132$$

5. Then β_2 was calculated:

$$\beta_2 = 1 - \left[\frac{3.16 - 1}{3.16} \right] 0.132$$

$$\beta_2 = 0.910$$

6. The β_2 value was used to establish the slope of the equilibrium lines for the second contact:

$$\beta_2 K_{\text{LiH}} = (0.910)(1.00) = 0.910$$

$$\beta_2 K_{\text{KH}} = (0.910)(3.16) = 2.88$$

These lines were drawn in over the range of interest, and the second contact was stepped off from C to D to E on each diagram. The indicated composition of the solution after two contacts was:

$$(x_{\text{Li}})_2 = 0.170$$

$$(x_{\text{K}})_2 = 0.046$$

as compared with the experimental effluent:

$$(x_{\text{Li}})_{\text{exit}} = 0.160$$

$$(x_{\text{K}})_{\text{exit}} = 0.052$$

Thus, while the indicated K^+ content had been passed, the Li^+ content had not yet been reached, and it was necessary to step off one more contact for the Li^+ .

7. Since the resin from the hypothetical third contact could have no lower K^+ content than $(y_K)_{entr}$, this equivalent fraction was used in the calculation of β_3 .

$$\beta_3 = 1 - \left[\frac{3.16 - 1}{3.16} \right] (0.0023)$$

$$\beta_3 = 0.998$$

8. The slope of this Li^+ equilibrium line was thus 0.998 also. Stepping off from E to F to G led to a solution composition,

$$(x_{Li})_3 = 0.016$$

9. The number of equilibrium contacts required to give the experimental effluent composition was then summarized for both Li^+ and K^+ ,

$$\Sigma (N_c)_{Li} = 2 + \frac{0.170 - 0.160}{0.170 - 0.016} = 2.06$$

$$\Sigma (N_c)_K = 1 + \frac{0.146 - 0.052}{0.146 - 0.046} = 1.94$$

It is fundamental that the number of equilibrium contacts be identical for both the Li^+ - H^+ exchange and the K^+ - H^+ exchange in an equilibrium stage contactor, so the effluent composition must be adjusted until the same N_c is indicated for each exchange. In effect, this is what was done in the succeeding trials, except that the data were adjusted to indicate exactly two contacts. It was no doubt merely chance that the average of the above N_c values was just 2.00.

B. Second Trial. The operating line was relocated on both plots (Figure 4) to obtain a closer match to the assumed effluent composition in two contacts. This was done by assuming that the Li^+ and K^+ contents of the effluent were half way between the experimental values which were used

in the first trial ($x_{Li} = 0.160$ and $x_K = 0.052$) and the values obtained at two contacts for that trial (0.170 and 0.046 respectively). The new values were thus:

$$(x_{Li})_{exit} = \frac{0.160 + 0.170}{2} = 0.165$$

$$(x_K)_{exit} = \frac{0.052 + 0.046}{2} = 0.049$$

The lower end of the operating line was established at these abscissa values, and these led to the composition of the effluent resin:

$$(y_{Li})_{exit} = 0.200$$

$$(y_K)_{exit} = 0.353$$

Neither this second trial nor the third are indicated on the plot for Li^+ , since all the lines were so close. The operating lines for only the final trial (No. 2 for K^+ and No. 4 for Li^+) are shown. The graphical determinations of the number of contacts for the final trials are indicated by ticks at intersections rather than by complete steps, which might have obscured the diagram. Again two contacts were stepped off, leading to an effluent composition of

$$(x_{Li})_2 = 0.154$$

$$(x_K)_2 = 0.049$$

Although there was a perfect match between the assumed and calculated values for K^+ , the assumed Li^+ value was reached in 1.92 contacts, thus necessitating a third trial.

C. Third Trial. The graph of N_c vs $(X_{Li})_{exit}$ shown in Figure 5 was used to obtain the assumed $(X_{Li})_{exit}$ for the third trial. If the equilibrium constant for the $Li^+ - H^+$ exchange had not been 1.00, it would have been necessary to prepare a similar plot for K^+ and continue the step-by-step calculations for K^+ as well as for Li^+ until a simultaneous match was obtained for both components. It will be recalled that the first trial was based on the Li^+ content of the experimental effluent (0.169) and the calculations indicated that 2.06 contacts would be required to obtain this concentration.

The $(X_{Li})_{exit} = 0.165$ used for the second trial gave 1.92 contacts. These points were plotted and were connected with a straight line. At $N_c = 2$ the indicated $(X_{Li})_{exit}$ was 0.162, so the end of the operating line was located at this abscissa. The β values for this trial were the same as those calculated in trial 2, because they are affected only by the K^+ concentrations, which remained unchanged. Thus, the same equilibrium lines applied. After two contacts this led to a new point on Figure 5 indicated by trial 3. The dashed curve connecting trials 1, 2, and 3 was drawn, and an $(X_{Li})_{exit}$ assumed for trial 4. This was found to give the same calculated value in two contacts, so no more trials were necessary.

In summary, the positions of the operating lines were shifted in an orderly fashion until the assumed effluent composition was obtained after exactly two contacts. This effluent composition was

$$(X_{Li})_{exit} = 0.163$$

$$(X_K)_{exit} = 0.049$$

The results of the two experimental runs are compared with the calculated results in Table I, and the experimental effluent compositions are plotted against the calculated values in Figure 6.

DISCUSSION OF RESULTS

Interpretation of Results. As can be seen from Table I and more strikingly from Figure 6, there was reasonably good agreement between the predicted and experimental results. These checks demonstrate the applicability of the design method. The deviations which did occur were probably the result of experimental inaccuracies, as reflected in the material balance data. It might be pointed out that, in Run No. 18, where the material balance was reasonably good, the results of the first trial calculations would have been acceptable for most engineering purposes.

The purity and recovery of the desired ionic component in the product streams have been used to assess the degree of separation achieved between two ions. Purity is the fraction of a component in a specific stream to the quantity of all the components in that stream other than the common or eluting ion. Recovery is the fraction of the amount of a component in an effluent stream with respect to the amount in a feed stream over the same time interval. In Run 16, the purity of the lithium was increased from 0.53 in the feed to 0.75 in the effluent, in which 45% of the lithium was recovered. In Run 18, the purity of lithium was 0.76 in the product as compared with 0.50 in the feed, and the recovery was 52%.

Effect of Operating Variables on Separation. The effects of varying the resin-solution equivalent aliquot ratio (slope of operating line) and the number of equilibrium contacts on the separation of trace components were reviewed in a previous paper.³ Qualitatively, the same effects would be anticipated for gross components. In essence, the use of more resin should increase the purity at the expense of reduced recovery, and the use of additional contacts at the same equivalent aliquot ratio should have the same effect.

Interrelation of Design Factors. There are five fundamental factors to consider in the design of an equilibrium stage contactor for the

exchange separation of ionic components: (1) the feed composition, (2) the equivalent solution-resin aliquot ratio, (3) the number of equilibrium contacts, (4) the purity, and (5) the recovery of the desired component in the effluent. The calculation method presented above demonstrates the determination of the purity and recovery in the effluent for a set feed composition, aliquot ratio, and number of contacts.

The interrelation among these five design factors is outlined in Table II, where the four most important types of design situations are given. Design approach A is represented, to a degree, by the first trial in the calculations. The approach B design is exemplified by the complete sample calculations.

The table shows that when any three of the five factors are set, the values of the other two can be calculated. Moreover, there is only one combination of specific values for these unknown factors which will be congruent with the initial design elements.

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NOMENCLATURE

- A,B,G = ionic components A, B and G, G being the eluting ion.
- C_{Σ} = total ionic level in the solution phase in meq/cc, equal to the ionic concentrations of components A, B, and G.
- E = ratio of the slope of the equilibrium line to the slope of the operating line, dimensionless.
- E' = βE dimensionless.
- K = chemical equilibrium constant for exchange, dimensionless.
- M = slope of the equilibrium line, dimensionless.
- N_c = number of equilibrium contacts.
- N_s = number of physical stages.
- P = purity or the fraction of a given component in a specific stream with respect to the amount of all components, excluding the elutant ion, in that stream.
- Q = total ionic concentration of the resin or the ultimate capacity, meq/g oven-dried resin.
- R = recovery or the fraction of a given component in a specific stream with respect to the amount in the incoming feed stream over the same time interval.
- R_F = volumetric flow rate of the solution, cc/sec.
- R_p = volumetric flow rate of the resin, cc of actual solids/sec ($R_p \rho_p$ is the weight flowrate of the resin, g/sec.)
- V_F = volume of solution aliquot introduced to the equilibrium-stage contactor.
- W_p = weight of resin aliquot introduced to the equilibrium-stage contactor.
- x = mol fraction of a component in solution with respect to the total ionic level of the solution, dimensionless.
- y = mol fraction of a component on the resin with respect to the total capacity of the resin, dimensionless.
- β = distribution of eluting ion G between the resin and solution phases, $\beta = y_G/x_G$.
- Δ' = the net transfer within a contactor, i.e., the difference between the amount of a component being carried in the resin phase, at a given cross-section, and that being carried in the opposite direction, at the same point, by the solution phase.
- ρ_p = density of resin, g oven-dried resin per ml of true resin volume saturated with the carrier component.

Subscripts

A, B, G = components A, B, and G.

n = contact number

entr = influent composition

exit = effluent composition

Table I

DATA AND RESULTS FOR EQUILIBRIUM STAGE CONTACTOR
(SATURATING SECTION)

A. Experimental Data

	Run 16	Run 18
Solution Aliquot Volume, R_F , ml	45	45
Resin Aliquot Weight, R_{pOp} , g	6.23	6.36
Feed Solution		
$\left\{ \begin{array}{l} (x_{Li})_{entr} \\ (x_K)_{entr} \end{array} \right.$	$\left\{ \begin{array}{l} 0.217 \\ 0.191 \end{array} \right.$	$\left\{ \begin{array}{l} 0.308 \\ 0.302 \end{array} \right.$
Total Solution Concentration, C_{Σ} , meq/ml	1.036	1.000
Purity of Li^+ in Feed	$(p_{Li})_{entr}$ 0.53	0.50
Entering Resin		
$\left\{ \begin{array}{l} (y_{Li})_{entr} \\ (y_K)_{entr} \end{array} \right.$	$\left\{ \begin{array}{l} 0.0021 \\ 0.0011 \end{array} \right.$	$\left\{ \begin{array}{l} 0.0025 \\ 0.0023 \end{array} \right.$
Number of Contacts	2	2

B. Calculated Results

		Run 16		Run 18	
		Found	Calc.	Found	Calc.
Effluent Solution	$\left\{ \begin{array}{l} (x_{Li})_{exit} \\ (x_K)_{exit} \end{array} \right.$	$\left\{ \begin{array}{l} 0.097 \\ 0.032 \end{array} \right.$	$\left\{ \begin{array}{l} 0.110 \\ 0.029 \end{array} \right.$	$\left\{ \begin{array}{l} 0.160 \\ 0.052 \end{array} \right.$	$\left\{ \begin{array}{l} 0.163 \\ 0.049 \end{array} \right.$
Effluent Resin	$\left\{ \begin{array}{l} (y_{Li})_{exit} \\ (y_K)_{exit} \end{array} \right.$	$\left\{ \begin{array}{l} 0.110 \\ (0.173^*) \end{array} \right.$	$\left\{ \begin{array}{l} 0.153 \\ 0.231 \end{array} \right.$	$\left\{ \begin{array}{l} 0.192 \\ (0.207^*) \end{array} \right.$	$\left\{ \begin{array}{l} 0.203 \\ 0.353 \end{array} \right.$
Recovery of Li^+ in Effluent	$(R_{Li})_{exit}$	0.45	0.51	0.52	0.53
Purity of Li^+ in Effluent	$(p_{Li})_{exit}$	0.75	0.79	0.76	0.77
Number of Contacts	$\left\{ \begin{array}{l} (N_c)_{Li} \\ (N_c)_K \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 2.97^{**} \\ 1.90^{**} \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 2.06^{**} \\ 1.94^{**} \end{array} \right.$
Material Balance	Li	91.2%		93.4%	
	K	90.6%		96.0%	

* Based on $(x)_{entr}$, $(x)_{exit}$, and $(y)_{entr}$ values for this ion and assuming 100% material balance.

** Based on First Trial.

Table II

DESIGN FACTORS IN ION EXCHANGE

	DESIGN APPROACH			
	A	B	C	D
DESIGN FACTORS:				
1. Feed Composition	known	known	known	known
2. Equivalent Aliquot Ratio	known	known	known	desired
3. Number of Contacts	desired	known	desired	known
4. Purity in Effluent	known	desired	known	known
5. Recovery in Effluent	desired	desired	desired	desired

FIG. 1

SCHEMATIC DIAGRAM OF COUNTERCURRENT CONTACTOR

A-CU337-76

FIG. 2
INTERMITTANT MIXER-SETTLER ASSEMBLY

FIG. 3
EQUILIBRIUM RELATIONS FOR $\text{Li}^+ - \text{K}^+ - \text{H}^+$ SYSTEM
ON CHEMPRO C-20

FIG. 4

GRAPHICAL ANALYSIS OF RUN NO. 18

B-CU337-72

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FIG. 5

INDICATED NUMBER OF CONTACTS AS A
FUNCTION OF THE ASSUMED $(x_{\text{Li}})_{\text{EXIT}}$
RUN NO. 18

A-CU337-74

FIG. 6

COMPARISON OF EXPERIMENTAL AND
CALCULATED EFFLUENT COMPOSITIONS

A-CU337-75

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Technical Report No. VI, Part II

**COUNTERCURRENT ION EXCHANGE WITH GROSS COMPONENTS
IN A CONTINUOUS COUNTERCURRENT COLUMN**

ABSTRACT

The design method for the exchange of gross components described in Part I was extended to apply to a continuous, countercurrent column.

In this procedure, the number of theoretical equilibrium contacts required for a specific exchange of any two gross components, in a multi-component system, is determined graphically as before. These calculated results were then used to obtain a theoretical bed height from a modified mass transfer correlation which relates the height equivalent to an equilibrium contact with the characteristics of the ion-resin system and the operating variables in the continuous column.

Several runs made with a moving bed of resin were evaluated by this technique. Fair agreement between the theoretical and observed bed heights was obtained.

INTRODUCTION

In Part I, a calculation procedure for the design of an equilibrium stage contactor for gross ion exchange was presented. Part II is concerned with a modification of this calculation method; and its application to the evaluation of a continuous, countercurrent column used for the separation of gross components. It will be recalled that a gross ion is one which occurs at a concentration of the same order of magnitude as the total ionic concentration. The experimental equipment used in this study was described in detail earlier², and it is therefore treated more concisely here.

THEORETICAL CONSIDERATIONS

Basic Relations. The design relations for countercurrent ion exchange with a three component system (gross ions A, B, and G, G being the eluting ion) were developed in Part I³. The fundamental equilibrium and material balance relations presented there for equilibrium contact operations apply equally well to continuous, countercurrent, resin-solution contact.

For the exchange between gross ions A and G, the equilibrium between resin and solution for ion A at the n'th contact may be expressed as

$$(y_A)_n = \beta_n K_{AG} (x_A)_n \quad (1A)^*$$

where

y_A = the equivalent fraction of component A on the resin with respect to the total ionic capacity of the resin, Q.

* The letter in the equation number designates that it applies to that particular ion and that a similar expression could be derived for ion B.

x_A = the equivalent fraction of component A in the solution with respect to the total ionic level of the solution, c_{Σ} ,

K_{AG} = chemical equilibrium constant for the exchange between ions A and G:

$$K_{AG} = \frac{x_G y_A}{y_G x_A}, \quad (2A)$$

and

β = distribution of the eluting ion, G, between the resin and solution phases:

$$\beta = \frac{y_G}{x_G} = \frac{1 - y_A - y_B}{1 - x_A - x_B} \quad (3)$$

The material balance equation relates the concentration of the ion on the resin at any equilibrium contact with the concentration in the solution from the previous contact:

$$(y_A)_n = \frac{K_{AG}}{E'_A} (x_A)_{n-1} + \frac{\Delta'_A}{R_p \rho_p Q} \quad (4A)$$

where

E'_A = the dimensionless product of the equilibrium constant and the ratio of the equivalent flowrates in the resin and solution phases

$$E'_A = K_{AG} \frac{R_p \rho_p Q}{R_f c_{\Sigma}} \quad (5A)$$

and

Δ'_A = net transfer of ion A within the column, i.e. the difference between the amount of ion A being carried in the resin phase, at any

given cross section, and that being carried in the opposite direction, at the same point, by the solution phase,

$$\Delta'_A = R_p \rho_p Q (y_A)_n - R_F c_{\Sigma} (x_A)_{n-1} \quad (6A)$$

and

R_p = volumetric resin flowrate

R_F = volumetric solution flowrate

ρ_p = density of the resin

Q = ultimate capacity of the resin

c_{Σ} = total ionic concentration of the solution.

Application of Relations to Continuous Operation. Where true equilibrium contact between the phases is achieved, as in the intermittent mixer-settler, there is a unique β value (ratio of the G ion concentration in the resin and solution phases) for each contact which can be determined directly and analytically from effluent resin and solution compositions of that contact. However, in the continuous, countercurrent column there is a continuous concentration gradient for every ion in each phase, and thus equilibrium contacts are hypothetical, but accepted, means for expressing column performance. Each such equilibrium contact represents a physical segment of the column which can be defined mathematically by the compositions of the resin and solution streams entering and leaving that segment. However, the G content of the resin from such a hypothetical contact cannot be used with the G content of the effluent solution from the contact to obtain a β value since these effluent streams are not representative of the contact as a whole. Consequently, the β value used for each contact is derived from the compositions of the resin and solution phases at the midpoint of the contact since this is the most representative average for that portion of the column.

Moreover, because of different rates of ionic transfer, and unlike equilibrium constants, the number of contacts obtained in a given bed height is different for every ion pair in the system. Therefore, it follows that the length of the segment corresponding to the first contact for A will probably not coincide with the length for the first B contact. Thus the calculation of the eluting ion distribution at the midpoint of the first A contact will involve not only the A content of the resin and solution at that point, but also the respective B content at that partial B contact which corresponds to the same physical position in the column.

Obviously, some knowledge of the relative number of contacts for each ion concerned is required for the design of the exchange column. However, the number of contacts is interdependent with the β distribution through the column, which is also unknown. Thus, a single estimated average β value is first assumed to apply over the entire column to permit the calculation of a preliminary number of contacts for each ion. The resultant ratio of contacts allows a more accurate estimation of the β distribution which, in turn, leads to a better value for the number of contacts for each ion, etc. This approach is similar to the distillation design method of Hummel⁴, in which he made an approximation of the temperature distribution through the column as a starting point for plate-to-plate calculations.

Correlation of Data. A previously reported relation² permits the correlation of the height of a transfer unit with the column operating variables and the characteristics of the ion-resin system. This relation is

$$\left[\frac{(Ht_A)_{OF}}{d_p} \right] = \frac{1.6}{f_E (Re \cdot Sc)^{0.5}} \left[\frac{d_p R_F}{6(1 - f_E)S(D_A)_F} \right] + \frac{0.6}{(1 - f_E)E_A} \left[\frac{d_p R_P}{6(1 - f_E)S(D_A)_P} \right] \quad (7A)$$

where

$(Ht)_{OF}$ = height of a transfer unit

d_p = average diameter of resin particles

f_E = void fraction

$(Re \cdot Sc)$ = product of Reynolds and Schmidt numbers for the solution flow

S = cross-sectional area of column

D_F = counter-diffusivity of ion with the eluting ion in fluid phase

D_p = counter-diffusivity of ion with the eluting ion in resin phase

$$E_A = \frac{y_G}{x_G} \cdot \frac{K_{AG} R_p \rho_p Q}{R_F c_\Sigma} = \beta E'_A$$

For the present case, however, it is desirable to express the above relationship in terms of the height of an equilibrium contact $(H_c)_A$. For countercurrent exchange of trace components, if the terminal conditions (concentrations and flowrates) are known, the performance of an ion exchange unit may be expressed in terms of either transfer units or equilibrium contacts without knowing whether the contact between the phases is continuous or intermittent and stagewise. Under such conditions it is possible to relate the number of transfer units and the number of equilibrium contacts which, for a given E ratio, would lead to the same degree of exchange²; this relation is

$$\frac{(Nt)_{OF}}{N_c} = \frac{E \ln E}{E - 1} \quad (8)$$

It will be noted that $(Nt)_{OF}/N_c$ is the reciprocal of the plates per transfer unit (P.T.U.), defined by Gerster, et al.¹.

Equation (8) is predicated on the linear equilibrium isotherm for trace exchange. In gross ion exchange, on the other hand, the equilibrium relation is dependent upon the eluting ion distribution, which is variable

through the contactor. In a continuous column, the equilibrium relation for a gross ion is different at every level in the column. For purposes of the calculation method, the β value applying to each equilibrium contact was assumed to be that indicated at the midpoint of each hypothetical contact. Presumably, this β value would also apply to the calculation of the number of transfer units over the same interval of the column. Since the E value for trace exchange is equivalent to the $\beta E'$ product for gross exchange, the relation between transfer units and contacts under gross conditions is considered to be

$$\frac{(Nt)_{OF}}{N_c} = \frac{\beta E' \ln \beta E'}{\beta E' - 1} = \frac{H_c}{(Ht)_{OF}} \quad (9)$$

where $H_c = h/N_c$ and $(Ht)_{OF} = h/(Nt)_{OF}$.

When applying this relation, it must be kept in mind that a different β value is associated with each equilibrium contact, and hence a unique $H_c/(Ht)_{OF}$ ratio holds for each contact.

In terms of equilibrium contacts, the correlation equation for gross ion exchange is thus

$$\begin{aligned} \frac{(H_c)_A}{d_p} = & \frac{1.6 \beta E'_A \ln (\beta E'_A)}{f_E (\beta E'_A - 1) (Re \cdot Sc)^{0.5}} \left[\frac{d_p R_F}{6(1 - f_E) S(D_A)_F} \right] \\ & + \frac{0.6 \ln (\beta E'_A)}{(1 - f_E) (\beta E'_A - 1)} \left[\frac{d_p R_P}{6(1 - f_E) S(D_A)_P} \right] \quad (10A) \end{aligned}$$

EQUIPMENT

Continuous, countercurrent flow of the resin and the solution streams was accomplished in the 9.5 cm i.d. column illustrated in Figure 1. The accessory equipment included two resin transfer valves, and a tapped screen insert.

The upper resin valve was used to remove resin from a reservoir, to filter off the interstitial solution, and to deliver the resin into the top of the column. The resin fell through a rising stream of solution to the top of a moving resin bed maintained at a predetermined height above the solution inlet. As resin was added to the top of the bed, it was removed at an equivalent rate by the lower resin valve. The interstitial solution removed in this valve was returned to the base of the column.

Contact between the resin and solution was promoted with a tapped screen assembly, Figure 2. This unit consisted of a group of horizontal disc screens, spaced about 5 cm apart on a light framework. A rod, extending through the center of these screens and connected to them, was tapped with a light hammer, and these impacts caused the screens to oscillate vertically. The tapped screen assembly was inserted into the column, and its action produced continual movement of the resin particles, thereby minimizing channeling.

EXPERIMENTAL PROCEDURE

General. The same ion-resin system was employed in the continuous column work as in the intermittent mixer-settler studies reported in Part I, namely, Li^+ , K^+ , and H^+ exchanging on Chempro C-20 resin. The applicable constants for the system (equilibrium constants, diffusivities, and resin characteristics) are given in Table I. The methods of analysis were identical with those described in Part I, and the range of experimental concentrations was similar.

Experimental Runs. Three gross runs were made in the column, all under similar operating conditions, but the composition of the feed solution was varied somewhat. As can be seen in Table I, the entering resin, essentially stripped of Li^+ and K^+ was transferred into the column at ~ 0.3 cc/sec. The feed solution flow rate was ~ 1.5 cc/sec. These rates were equivalent to superficial velocities of 0.0042 and 0.021 cm/sec respectively through the column. The level of the resin bed above the feed position was maintained at 7.6 cm, and the screen assembly was tapped 200 times/minute.

During a run, samples of effluent solution and resin were collected and measured volumetrically over 15-minute intervals. A portion of each sample was retained for later analysis. The equilibria favored the retention of Li^+ in the effluent solution and the transfer of the K^+ to the effluent resin. It was necessary to continue a run for about six hours before the steady state was assured. Parenthetically, it might be noted that the steady state was obtained in about two hours under trace conditions with comparable flowrates.

INTERPRETATION OF DATA

General. Unlike the equilibrium stage contactor, in which the actual number of equilibrium contacts was known, and identical for each component, neither the number of contacts for a given exchange nor the relative number with respect to the exchange for another component was known for the continuous column. These factors had to be established before the calculation of the theoretical bed height from the correlation equation could be made.

A graphical method for the evaluation of the continuous, countercurrent column results was developed. Briefly, this procedure involved the use of two y-x diagrams, one for the $\text{Li}^+ - \text{H}^+$ exchange and one for $\text{K}^+ - \text{H}^+$. The slope of the operating lines was established by material balance considerations. Initially, the average H^+ distribution between the phases (β value),

derived from the compositions at the top and bottom of the column, was used to set the slope of the equilibrium line for each ion pair. On each diagram the contacts necessary to reach the effluent solution composition were stepped off between the operating and equilibrium lines. This gave an initial ratio of Li^+ to K^+ contacts, which was then used in the second trial to obtain a more accurate β distribution through the column.

After sufficient trials had been carried out to obtain an unchanging β value distribution through the column, the correlation relation was used to obtain the theoretical bed height for each component.

Application of Calculation Method. The graphical method outlined above was applied to the evaluation of the moving bed runs, and the procedure for Run No. 18C is detailed below. The pertinent data for the run are contained in Table I. The step-by-step evaluation of this information follows:

1. The slope of the operating lines can be calculated either from
 - (a) the ratio of the equivalent solution-resin flowrates or
 - (b) the experimental equivalent fractions of each ion in the entering and exiting streams at the top and bottom of the column, although the former method is probably more accurate.

$$(a) \quad \frac{R_F c_{\Sigma}}{R_P \rho_P Q} = \frac{(1.61 \text{ cc/sec}) (0.905 \text{ meq/cc})}{(0.248 \text{ cc/sec}) (0.64 \text{ g/cc}) (5.11 \text{ meq/g})}$$

$$= 1.79$$

- (b) The operating line slopes were determined graphically by connecting the terminal concentrations on the y-x diagrams for the $\text{Li}^+ - \text{H}^+$ and $\text{K}^+ - \text{H}^+$ exchange as shown in Figure 3. These slopes were 1.79 and 1.78 respectively, which agree with the result from method (a). These operating, or material balance lines, express Equation (4) graphically.

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2. The distribution of the H^+ between the phases at the top and bottom of the column was established next with Equation (3).

$$\begin{aligned}\beta_{top} &= \frac{(y_H)_{entr}}{(x_H)_{exit}} = \frac{1 - (y_{Li})_{entr} - (y_K)_{entr}}{1 - (x_{Li})_{exit} - (x_K)_{exit}} \\ &= \frac{1 - 0.0005 - 0.0004}{1 - 0.212 - 0.0177} = 1.240\end{aligned}$$

$$\begin{aligned}\beta_{bottom} &= \frac{(y_H)_{exit}}{(x_H)_{entr}} = \frac{1 - (y_{Li})_{exit} - (y_K)_{exit}}{1 - (x_{Li})_{entr} - (y_K)_{entr}} \\ &= \frac{1 - 0.235 - 0.540}{1 - 0.343 - 0.322} = 0.672\end{aligned}$$

3. The average distribution of the eluting ion between the phases was calculated from the top and bottom values:

$$\begin{aligned}\beta_{av} &= \frac{\beta_{top} + \beta_{bottom}}{2} \\ &= \frac{1.240 + 0.672}{2} = 0.956\end{aligned}$$

4. The slopes of the equilibrium lines for Figure 3 were calculated, using β_{av} :

$$\beta_{av} K_{LiH} = (0.956) (1.00) = 0.956$$

$$\beta_{av} K_{KH} = (0.956) (3.16) = 3.02$$

and these lines were constructed through the origins of the respective plots. The equilibrium lines represent Equation (1).

5. The contacts were stepped off in the conventional manner, starting at the upper end of the operating line, and the indicated number of theoretical contacts were:

$$(N_c)_{Li} = 1.18$$

$$(N_c)_K = 3.97$$

6. From the resulting ratio of $(N_c)_{Li} : (N_c)_K (= 0.297)$, the positions on the Li stage corresponding to the midpoints of the K stages were located and also the positions of the K stages corresponding to the midpoints of the Li stages.

For instance, at the midpoint of the first Li contact, the $N_c/(N_c)_{total}$ ratio is 0.424 ($= 0.50/1.18$), and the corresponding position on the K plot occurs at 1.68 contacts ($= 0.424 \times 3.97$). These points are designated on the respective operating lines in Figure 3 as A and A'. At this position the β value was calculated from the resin and solution compositions at points A and A', Equation (3):

$$\beta = \frac{1 - y_{Li} - y_K}{1 - x_{Li} - x_K} = \frac{1 - 0.147 - 0.186}{1 - 0.294 - 0.122} = 1.143.$$

Similarly, with indicated values of x_{Li} , x_K , y_{Li} , and y_K at the midpoints, the β_1^* value for each stage was calculated. The results, which include the end positions as well as the midpoints of each contact, are tabulated in Table II as Trial 1.

7. From this information, a plot of β vs $N_c/(N_c)_{total}$, Figure 4, was prepared. Also indicated in Figure 4 is the contact distribution in the column for this first trial.
8. The values of β_1 found in Step 6 were used to locate the equilibrium line at each pertinent contact for the second trial as indicated in Figure 3. This set of equilibrium lines was not

* The subscript refers to the first trial values.

completely drawn in, but all pass through the origin. The contacts (indicated as ticks) were stepped off between the operating line and these adjusted equilibrium lines on each plot. These operations gave the new number of theoretical stages as

$$(N_c)_{Li} = 0.949$$

$$(N_c)_K = 3.56$$

9. Again, the $N_c/(N_c)_{total}$ ratios were calculated for the midpoints of these stages, and the value of β_2 for each stage was determined. The calculations were identical to those performed in step 6, so only the results are tabulated in Table II as Trial 2. The plotted results are indicated by the dashed line on Figure 4. A reasonably good agreement will be noted between the two trials. Further trials did not affect the dashed curve appreciably, so they are not indicated.
10. Then the theoretical height of each individual equilibrium contact was determined from the correlation equation, and the sum of the heights was compared with the experimental height of the moving bed. The detailed calculations for the one Li contact are given below:

The $\beta E'$ product was calculated,

$$\begin{aligned} \beta E' &= \frac{\beta K Q R_p \rho_p}{R_F c_\Sigma} \\ &= \frac{(1.172) (1.00) (5.11) (0.248) (0.64)}{(1.61) (0.905)} \\ &= 0.650 \end{aligned}$$

The product of the Reynolds and Schmidt numbers is defined and calculated below:

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$$\begin{aligned}
 [\text{Re} \cdot \text{Sc}] &= \left[\frac{d_p f_E}{6(1 - f_E)} \right] \left[\frac{\frac{R_F}{f_E} + \frac{R_P}{(1 - f_E)}}{S} \right] \left[\frac{1}{D_F} \right] \\
 &= \left[\frac{(0.07)(0.39)}{(6)(0.61)} \right] \left[\frac{\frac{1.61}{0.39} + \frac{0.248}{0.61}}{71.4} \right] \left[\frac{1}{1.85 \times 10^{-5}} \right] \\
 &= 25.7
 \end{aligned}$$

$$[\text{Re} \cdot \text{Sc}]^{0.5} = 5.07$$

The correlation equation (10A) is repeated below for ease of reference:

$$\begin{aligned}
 \left[\frac{(H_c)_A}{d_p} \right] &= \frac{1.6 \beta E'_A \ln(\beta E'_A)}{f_E(\beta E'_A - 1)(\text{Re} \cdot \text{Sc})^{0.5}} \left[\frac{d_p R_F}{6(1 - f_E) S (D_A)_F} \right] \\
 &+ \frac{0.6 \ln(\beta E'_A)}{(1 - f_E)(\beta E'_A - 1)} \left[\frac{d_p R_P}{6(1 - f_E) S (D_A)_P} \right]
 \end{aligned}$$

and substitution of the numerical values gives

$$\begin{aligned}
 \left[\frac{(H_c)_{Li}}{d_p} \right] &= \frac{(1.6)(0.65) \ln(0.65)}{(0.39)(0.65 - 1)(5.07)} \left[\frac{(0.07)(1.61)}{(6)(0.61)(71.4)(1.85 \times 10^{-5})} \right] \\
 &+ \frac{(0.6) \ln(0.65)}{(0.61)(0.65 - 1)} \left[\frac{(0.07)(0.248)}{(6)(0.61)(71.4)(3.46 \times 10^{-6})} \right] \\
 &= 15.1 + 23.2 = 38.3
 \end{aligned}$$

Hence, the height of a transfer unit was found as

$$\begin{aligned}(H_c)_{Li} &= (38.3) (0.07) \\ &= 2.68 \text{ cm}\end{aligned}$$

Since only a partial Li contact was involved, the indicated bed height was calculated as

$$h = (2.68) (0.949) = 2.5 \text{ cm}$$

Similarly, the sum of the calculated bed heights for the 3.56 K contacts was 8.8 cm.

An alternate method of presenting the results is to compare the height of a transfer unit (H_t) with those heights achieved in this same column under trace conditions. In the earlier work² the data were presented by plotting

$$D_A \frac{(D_A)_P}{(D_A)_F} \left[\frac{hf_E}{(Nt_A)_{OF} d_p} \right] \left[\frac{6(1 - f_E) S (D_A)_F}{d_p R_F} \right] \text{ vs } D_A \frac{(D_A)_P}{(D_A)_F} (Re \cdot Sc)^{-0.5}$$

as shown in Figure 5. Here

$$D_A = \frac{\beta K_{AG} Q \rho_P (1 - f_E)}{c \Sigma f_E}$$

The solid dots are for Li and K trace exchange at solution flowrates of 100 cc/min and tapping rates of 200 per min.

In the present procedure the height of a transfer unit, $h/(Nt_A)_{OF}$ depends on the value of β and on the height of an equilibrium contact, h/N_c , according to Equation (9). Since the actual height of each contact is not known, it is necessary to use the average value for the whole column and the average value of β . This last can be obtained from the β distribution curve by determining the integrated average value. As an example, for

Run 18C, the β_{av} value was obtained from Figure 4 as 1.17, and was used to calculate $h/(Nt_{Li})_{OF}$ from $h/N_c = 7.6/0.949$ and to calculate D_{Li} . From these the values of the ordinate and abscissa were obtained and plotted on Figure 5. The data for Runs 15C and 16C were treated similarly.

DISCUSSION OF RESULTS

The results of the three runs are assembled in Table III. The calculated bed heights ranged from 2.5 to 14.3 cm, as compared with the observed 7.6 cm; the average deviation from 7.6 cm was 50%. If, instead, the gross transfer heights are compared to those for the trace exchange runs in the same equipment, it will be noticed that, except for the Li point for Run 18C, the deviations of the data from the correlation curve in Figure 5 are of the same order of magnitude. However, contrary to expectations, the Li points fell consistently above the respective K points.

Even these results show that the method represents a considerable advance over empirical design procedures. It is hoped that the method will provide the impetus for further development of design techniques for continuous countercurrent exchange of gross components based on fundamental concepts.

In Table III, the separation achieved between Li^+ and K^+ was again expressed in terms of the purity and recovery of Li^+ in the effluent solution. It will be noted that the higher the purity, the lower the recovery and the higher the indicated number of equilibrium contacts. This is consistent with similar results predicted and observed in the experiments made in this same column under trace conditions.

In conclusion, it appears that the proposed calculation method for continuous, countercurrent gross exchange may be useful for some engineering purposes. However, is certainly less accurate than the corresponding equilibrium stage method for gross exchange and less accurate too than the design of continuous columns for trace ion exchange.

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NOMENCLATURE

- A,B,G = ionic components A, B, and G, G being the eluting ion.
- C_{Σ} = total ionic level in the solution phase in meq/cc; equal to the sum of the ionic concentrations of components A, B, and G.
- d_p = mean diameter of swollen resin particles, cm.
- D = distribution ratio or partition coefficient for a component.
- D_F = effective diffusivity of designated ion diffusing against the eluting ion in the solution phase, sq cm/sec.
- D_p = effective diffusivity of designated ion diffusing against the eluting ion in the resin phase, sq cm/sec.
- E = ratio of the slope of the equilibrium line to the slope of the operating line, dimensionless.
- E' = E/β , dimensionless.
- f_E = ratio of void space outside resin particles to total volume of contacting zone, dimensionless.
- h = height of contact zone, cm.
- $(Ht)_{OF}$ = height of contact zone equivalent to a transfer unit based on fluid films, cm.
- H_c = height of contact zone equivalent to an equilibrium contact, cm.
- K = chemical equilibrium constant for exchange, dimensionless.
- N_c = number of equilibrium contacts, dimensionless.
- $(Nt)_{OF}$ = number of transfer units, dimensionless.
- P = purity or the fraction of a given component in a specific stream with respect to the amount of all components, excluding the eluting ion, in that stream.
- Q = total ionic concentration of the resin or the ultimate capacity, meq/g, oven-dried basis.
- R = recovery or the fraction of a given component in a specific stream with respect to the amount in the incoming feed stream over the same time interval.
- Re = Reynolds number, dimensionless.

$$\left(Re = \frac{\left[\frac{d_p f_E}{6(1 - f_E)} \right] \left[\frac{R_F}{f_E} + \frac{R_p}{1 - f_E} \right]}{S} \cdot \frac{\rho}{\mu} \right)$$

- R_F = volumetric flowrate of solution, cc/sec.
- R_p = volumetric flowrate of the resin, cc of actual solids/sec.
($R_p \rho_p$ is the weight flowrate of the resin, g/sec).
- S = cross-sectional area of column, sq cm.
- Sc = Schmidt number, dimensionless.
$$(Sc = \frac{\mu}{\rho D_F})$$
- x = equivalent fraction of a component in solution with respect to the total ionic level of the solution, dimensionless.
- y = equivalent fraction of a component on the resin with respect to the total capacity of the resin, dimensionless.
- β = distribution of the eluting ion G between the resin and solution phases, dimensionless ($\beta = y_G / x_G$).
- Δ' = the net transfer within the column, i.e., the difference between the amount of a component being carried in the resin phase, at a given cross section, and that being carried in the opposite direction, at the same point, by the solution phase.
- μ = viscosity of the solution, poise.
- ρ = specific gravity of the solution, g/cc.
- ρ_p = density of the resin, g of oven-dried resin per cc of true resin volume, saturated with the eluting component.

Subscripts

- A, B, G = components A, B, and G.
- n = contact number.
- entr = influent composition.
- exit = effluent composition.

Table I

EXPERIMENTAL CONDITIONS AND SYSTEM CONSTANTS

	Run 15C	Run 16C	Run 18C
Solution Flowrate, R_F , cc/sec	1.48	1.59	1.61
Resin Flowrate, R_p , cc/sec	0.274	0.307	0.248
Feed Solution			
$(x_{Li})_{entr}$	0.262	0.253	0.343
$(x_K)_{entr}$	0.238	0.240	0.322
Total Soln. Concentration, c_Σ , meq/cc	0.938	0.970	0.905
Purity of Li^+ in Feed, $(p_{Li})_{entr}$	0.52	0.51	0.52
Entering Resin			
$(y_{Li})_{entr}$	0.0004	0.0004	0.0005
$(y_K)_{entr}$	0.0002	0.0003	0.0004
Resin Bed Height, h , cm	7.6	7.6	7.6
Cross-sectional area of column, S	71.4 sq cm		
Resin capacity, Q	5.11 meq/g		
Resin density, ρ_p	0.64 g/cc		
Ave. wet particle diameter, d_p	0.07 cm		
Void fraction, f_E	0.39		
Equilibrium constants			
K_{LiH}	1.00		
K_{KH}	3.16		
Diffusion constants*			
Li^+ in solution, $(D_{Li})_F$	1.85×10^{-5} sq. cm./sec		
Li^+ in resin, $(D_{Li})_p$	3.46×10^{-6} " " "		
K^+ in solution, $(D_K)_F$	2.18×10^{-5} " " "		
K^+ in resin, $(D_K)_p$	4.08×10^{-6} " " "		

* Based on counter-diffusion of designated ion and H^+ .

Table II
CALCULATION OF β DISTRIBUTION

Trial 1				
N_C	$(N_C)_{Li}$	$(N_C)_K$	β_1	$\beta_1 K_{KH}$
$(N_C)_{total}$			$(= \beta_1 K_{LiH})$	
0	0	0	0.612	
0.126	0.149	0.500	0.897	2.83
0.252	0.297	1.000	1.047	
0.378	0.446	1.500	1.119	3.54
0.424	0.500	1.682	1.143	
0.504	0.594	2.000	1.180	
0.630	0.743	2.500	1.215	3.84
0.754	0.891	3.000	1.250	
0.847	1.000	3.364	1.262	
0.882	1.040	3.500	1.278	4.04
1.000	1.179	3.970	1.297	

Trial 2			
N_C	$(N_C)_{Li}$	$(N_C)_K$	β_2
$(N_C)_{total}$			$(= \beta_2 K_{LiH})$
0.140		0.500	0.958
0.281		1.000	
0.421		1.500	1.149
0.501	0.475		1.172
0.562		2.000	
0.702		2.500	1.236
0.843		3.000	
0.921		3.280	1.284
1.000	0.949	3.560	

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Table III

EXPERIMENTAL AND DERIVED RESULTS

	<u>Run 15c</u>	<u>Run 16c</u>	<u>Run 18c</u>
Effluent Solution			
$(x_{Li})_{exit}$	0.117	0.123	0.212
$(x_K)_{exit}$	0.002	0.004	0.018
Effluent Resin			
$(y_{Li})_{exit}$	0.231	0.196	0.235
$(y_K)_{exit}$	0.362	0.353	0.540
Recovery of Li^+ in Effluent, $(R_{Li})_{exit}$	0.46	0.49	0.62
Purity of Li^+ in Effluent, $(p_{Li})_{exit}$	0.99	0.97	0.92
Number of Contacts			
$(N_c)_{Li}$	2.74	1.63	0.95
$(N_c)_K$	5.91	4.57	3.56
Calculated Bed Height, h, cm			
Li	4.2	4.0	2.5
K	14.3	11.3	8.8
Material Balance			
Li	1.02	0.99	1.00
K	0.99	1.02	0.95

FIG. 1 - COLUMN ASSEMBLY
P-CU337-90

FIG. 2
TAPPED SCREEN ASSEMBLY

FIG. 3
GRAPHICAL ANALYSIS OF RUN NO. 18 C

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FIG. 4
ELUTING ION DISTRIBUTION THROUGH COLUMN FOR RUN NO. 18C

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FIG. 5
CORRELATION PLOT

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