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ION EXCHANGE OF TRACE COMPONENTS IN A COUNTERCURRENT EQUILIBRIUM STAGE CONTACTOR

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PREFACE

The attached report covers one completed phase of the countercurrent ion exchange program carried out by Stanford Research Institute for the Atomic Energy Commission. It is concerned with the theory, design, and operation of an intermittent mixer-settler type of resin-solution contactor as applied to the separation of ionic components.

A portion of the contents of this report was included in Technical Report II (AEC Report No. COO-59), May 1st, 1952. However, the theory has been extended to more generalized cases than were previously considered, and the majority of the experimental work was carried out after the above report was submitted.

This report was prepared with the Atomic Energy Commission's approval for presentation at the Los Angeles National Meeting, American Chemical Society, March 18, 1953, and for submission to *Industrial and Engineering Chemistry* for publication.

In the attached report, reference is made to a "companion" paper, "Countercurrent Ion Exchange with Trace Components," which was presented at the Cleveland meeting of the American Institute of Chemical Engineers in December 1952. That paper will be submitted to the Atomic Energy Commission as Technical Report No. V after current experimental work, at high solution flowrates, is interpreted and included in the manuscript.

The results of the present experimental work lead to the following conclusions:

1. The equipment described in the report can be used as a satisfactory intermittent equilibrium-stage contactor for countercurrent ion exchange between resins and solutions.

2. Under trace conditions, the operation of the unit can be accurately predicted by the modified Kremser equation as long as equilibration times are adequate.

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Technical Report III

**ION EXCHANGE OF TRACE COMPONENTS IN A COUNTERCURRENT
EQUILIBRIUM STAGE CONTACTOR**

ABSTRACT

A calculation method is outlined for the design of a countercurrent exchange unit for the separation or removal of ions under trace conditions. This design method permits the determination of the number of countercurrent contacts required for any degree of separation, if the feed conditions and equilibrium constants for the system are available.

An intermittent mixer-settler was developed as an approach to the problem of countercurrent contact. This automatic apparatus consists of a number of separate stages in which resin and solution are intimately mixed, then separated. The solutions are then transferred to adjacent stages for another contact. Although contact in the stages is intermittent and repeated, the over-all operation is essentially continuous.

A series of runs under trace conditions was made with the mixer-settler unit. The results were quite satisfactory in that the observed degree of separation matched quite well with theoretically predicted values as long as the known operational criteria were obeyed.

INTRODUCTION

Multi-stage mixer-settler units have been developed for liquid-liquid and solid-liquid extraction operations to improve the extraction efficiency over single-stage contactors and are now in common use. In an investigation

of countercurrent ion exchange, Stanford Research Institute has developed design theories and equipment for the analogous multi-stage contact between ion exchange resins and solutions to be treated. The method provides a different approach to the removal and separation of ionic components than the traditional chromatographic, fixed-bed technique.

Much of the background for the present work on the mixer-settler was reported in a companion paper.¹

THEORETICAL CONSIDERATIONS

General The separation of ions by ion exchange operates by the transfer of ions between a solid resin phase and a fluid solution phase. The differences in affinities of the resin for the ions to be separated, say ions A and B, lead to an enrichment of one, say A, in the fluid phase and of the other in the solid phase. In countercurrent practice the two phases move in opposing directions, and thus components A and B are carried to opposite ends of the contacting apparatus. In order that both product streams be fluid, it is necessary that ion B in the resin phase be re-transferred to a solution. This requires a third component, say ion G, to elute or remove B from the resin.

Thus, in the simplest ion exchange separation system, three components (ions A, B, and G) and two phases (resin and solution) are involved. The only design theory that is presently available to handle this complex system is the trace theory.

Trace exchange is the case in which ion exchange occurs between a gross component (G) with which a resin is saturated and a trace component (A) present in the solution in a very small concentration, along with a very large concentration of component G. Vermeulen and Hiester⁶ have defined the relative concentrations of A and G which lead to this case. Under trace conditions, a linear relationship exists between the concentration of the trace component on the resin and its concentration in the solution.

This exchange may be represented as

In a companion paper¹ the mass action equilibrium constant, K_{AG} , for this reaction was defined as

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

where y_A and y_G are the mol fractions of components A and G with respect to the total ionic capacity of the resin per unit weight, x_A and x_G are the mol fractions of components A and G with respect to the total ionic concentration of the solution per unit volume, and where x_G/y_G is a constant under trace conditions.

Expressed as mol fractions, the equilibrium concentrations are

$$y_A^* = M_A x_A \quad (3)$$

and

$$x_A^* = \frac{y_A}{M_A} \quad (4)$$

where the asterisks denote equilibrium, and $M_A = \frac{K_{AG} y_G}{x_G}$. The slope of the equilibrium line, M_A , is a constant for a given trace ion exchange, so these are the Henry's law (or linear isotherm) forms.

In Figure 1, countercurrent contact between ion exchange resin and an ionic solution is represented diagrammatically. For the purposes of the theoretical discussion, continuous flow of the two phases has been assumed. The effect of intermittent operation will be considered in the section on Equipment. Resin of a constant molal composition, $(y_A)_{entr}$, is fed into one end of the contactor at a constant weight rate, $R_p \rho_p$, as the effluent resin of composition $(y_A)_{exit}$ is removed at the same rate. Simultaneously,

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FIG. 1

COUNTERCURRENT ION EXCHANGE

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the solution of constant molal composition $(x_A)_{entr}$ is introduced countercurrently into the contactor at a constant volume rate, R_F , and is removed at the corresponding rate at a composition of $(x_A)_{exit}$.

There are two methods for predicting the compositions of the effluents. One, which is based on the statistical residence contact time of a resin particle in the countercurrent section and the kinetics of the process, was discussed and experimentally evaluated in another paper.¹ The second method is based on the assumption that the section is composed of a finite number of equilibrium stages.

For such continuous countercurrent contact in discrete equilibrium stages, the design relations of Kremser² for the absorption of lean components, as given in the Souders and Brown⁴ form, were adapted to ion exchange. In ion exchange nomenclature, the relation between the degree of approach to equilibrium transfer in the solution phase and the countercurrent operation factors is

$$\gamma_A = E_A \frac{E_A^{N_C} - 1}{E_A^{N_C + 1} - 1} \quad (5)$$

where E_A , the product of the equilibrium isotherm constant and the ratio of the total molal flow rates in the resin and solution phases, is defined as

$$E_A = \frac{M_A R_P \rho_P Q}{R_F C_\Sigma} \quad (6)$$

In Equation (5) N_C is the number of equilibrium contacts between the two phases or the contact number counted from the solution inlet end, and γ_A , the approach to equilibrium transfer of component A in the solution, is defined as

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$$\gamma_A = \frac{(X_A)_{entr} - (X_A)_{exit}}{(X_A)_{entr} - (X_A^*)_{exit}} = E_A \frac{(Y_A)_{entr} - (Y_A)_{exit}}{(Y_A)_{entr} - (Y_A^*)_{exit}} \quad (7)$$

It can be seen from the above relation that the degree of approach to equilibrium transfer for the resin phase is given by γ_A/E_A .

Rearrangement of Equation (5) gives a more convenient form for the determination of N_C from γ and E .

$$N_C = \frac{\ln \left[\frac{E_A - \gamma_A}{E_A(1 - \gamma_A)} \right]}{\ln E_A} \quad (8)$$

Separations in a Two-Section Unit A complete unit for separating ions into two fluid streams would have at least two sections of the type shown in Figure 1. A feed stream containing a mixture of A and B ions would be introduced between the two sections, as indicated in Figure 2. The least strongly held ion, say A, would remain largely in the solution phase traveling to the right through the saturating section. Thus the effluent solution from this section (the upper product) would be enriched in ion A, while the effluent resin would be enriched in ion B. The transfer of the trace ions from the resin to the solution phase would require another exchange step. In the eluting section, the resin would be contacted with an elutant free of ions A and B. The spent elutant from this section would be enriched in B and would be considered the lower product. The eluted resin would be returned to the saturating section to complete the cycle.

This two-section unit is the most simple arrangement of groups of countercurrent contacting devices that will separate ions A and B. As will be shown, its main drawback is that although nearly pure A can be obtained in the spent feed solution, there is a much lower limit to the purity in which B can be obtained in the spent elutant.

FIG. 2
TWO-SECTION SEPARATIONS UNIT

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The design theory applying to a two-section unit is based on the relations among N_c , γ and E presented earlier and also on the desired purity and/or recovery of one of the separated components. The ratio of component A to component B in a given aliquot has been termed the concentration factor for A, ϕ_{AB} . The concentration factor for A in the spent feed would thus be

$$(\phi_{AB})_U = \frac{(x_A)_U}{(x_B)_U} = \frac{1}{(\phi_{BA})_U} \quad (9)$$

where x is the mol fraction of the component designated by the subscript and U denotes the upper product.

The purity of a component, say A, in an aliquot is the fraction of that component in a mixture of several, say A and B, and is related to the concentration factor.

Thus

$$P_A = \frac{x_A}{x_A + x_B} = \frac{\frac{x_A}{x_B}}{\frac{x_A}{x_B} + 1} = \frac{\phi_{AB}}{1 + \phi_{AB}} \quad (10)$$

Likewise, the recovery of A, R_A , is the fraction of component A in a given product with respect to the amount in the feed, over the same time interval, as follows:

$$(R_A)_U = \frac{(x_A)_U}{(x_A)_F} = 1 - (R_A)_L \quad (11)$$

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where the subscripts F and L denote the feed and lower product streams. The last expression results from a consideration of the over-all material balance. For A this is

$$F(x_A)_F = U(x_A)_U + L(x_A)_L \quad (12)$$

Obviously, concentration factors and recoveries are somewhat related. For instance, if $(\phi_{AB})_U$ and $(R_A)_U$ are specified, then

$$(\phi_{BA})_L = \frac{(\phi_{AB})_U (\phi_{BA})_F - (R_A)_U}{(\phi_{AB})_U [1 - (R_A)_U]} \quad (13)$$

and

$$(R_B)_L = 1 - \frac{(R_A)_U}{(\phi_{AB})_U (\phi_{BA})_F} \quad (14)$$

The relations between γ , the degree of approach to equilibrium transfer in the solution phase, and the recovery, $(R)_U$, are of importance in any design considerations. From the definitions given in Equations (7) and (11) several relations can be obtained:

$$(\gamma)_{sat} = \frac{1 - [(x)_{exit} / (x)_{entr}]_{sat}}{1 - [(x^*)_{exit} / (x)_{entr}]_{sat}} = \frac{1 - (R)_U}{1 - [(y)_{entr} / M(x)_{entr}]_{sat}} \quad (15)$$

$$\left(\frac{\gamma}{E}\right)_{sat} = \frac{1 - [(y)_{exit} / (y)_{entr}]_{sat}}{1 - [M(x)_{entr} / (y)_{entr}]_{sat}} \quad (16)$$

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The term $[M(x)_{entr} / (y)_{entr}]_{sat}$ can now be eliminated between these two equations to give

$$(\gamma)_{sat} = \frac{[1 - (R)_U] \{1 - [(y)_{entr}/(y)_{exit}]_{sat}\}}{\{1 - [(y)_{entr}/(y)_{exit}]_{sat}\} + \{[(y)_{entr}/(y)_{exit}]_{sat} [1 - (R)_U]/(E)_{sat}\}} \quad (17)$$

But also, analogous to (16),

$$\left(\frac{\gamma}{E}\right)_{elut} = \frac{1 - [(y)_{exit}/(y)_{entr}]_{elut}}{1 - 0} = 1 - \left[\frac{(y)_{exit}}{(y)_{entr}}\right]_{elut} \quad (18)$$

since in most cases the elutant is free of the ion to be stripped. From Figure 2 it is obvious that the exit resin from the saturating section is the entrance resin to the eluting section, and vice versa, so

$$\left[\frac{(y)_{exit}}{(y)_{entr}}\right]_{elut} = \left[\frac{(y)_{entr}}{(y)_{exit}}\right]_{sat}$$

This latter term can now be eliminated from Equation (17), through Equation (18), to obtain a completely general relation between $(\gamma)_{sat}$ and $(R)_U$ involving the degree of approach to equilibrium removal in the resin phase during elution:

$$1 - (R)_U = \frac{(\gamma)_{sat}}{1 + [(\gamma)_{sat}/(E)_{sat}] \{[E/\gamma]_{elut} - 1\}} \quad (19)$$

In those cases where the resin is nearly completely eluted, $[E/\gamma]_{elut} \sim 1$, Equation (19) reduces to the approximate form

$$1 - (R)_U \cong (\gamma)_{sat}$$

//

For specific ions A and B this gives

$$1 - (R_A)_U = (\gamma_A)_{sat} \quad (20)$$

and

$$1 - (R_B)_U = (\gamma_B)_{sat} = (R_B)_L = 1 - \frac{(R_A)_U}{(\phi_{AB})_U (\phi_{BA})_F} \quad (21)$$

where Equation (14) is used to obtain the final form.

DESIGN CONSIDERATIONS

General Under the simplifying assumption that the resin from the eluting section of the two-section unit shown in Figure 2 is essentially free of ions A and B, the design procedure is straightforward and the simple relations, (20) and (21), can be used. Since the elutant is free of ions A and B, it is possible to elute (strip) the resin almost completely to this point by operating with an E_A and E_B in this section of less than unity and a large number of equilibrium contacts. This is apparent from Equation (5), since under these conditions of $E < 1$ and $N_C \rightarrow \infty$, γ approaches E . Equation (18) then shows that, as γ approaches E , y_{exit} must approach zero. The significance of E less than one is a higher total equilibrium molal flowrate in the solution than in the resin. For any one section, the difference between the values of E for ions A and B is in the equilibrium isotherm, so that

$$\frac{E_B}{E_A} = \frac{M_B}{M_A} = \frac{K_{BG}}{K_{AG}} = \delta_{BA} \quad (22)$$

where δ is the separation factor between components A and B. Since it has been assumed that B is held more strongly by the resin than A, then E_B is

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$> E_A$, or δ is greater than one. Thus the only operating requirement for the eluting section is that E_B be less than one, since then E_A will necessarily be less than one.

The values of γ obtained by Equations (20) and (21) can then be used to determine the number of equilibrium contacts and the values of E_A and E_B from Equation (8). When equilibrium is attained in each contact, the number of equilibrium contacts should be identical for both A and B, or

$$N_C = \frac{\ln \left[\frac{E_A - \gamma_A}{E_A(1-\gamma_A)} \right]}{\ln E_A} = \frac{\ln \left[\frac{E_B - \gamma_B}{E_B(1-\gamma_B)} \right]}{\ln E_B} = \frac{\ln \left[\frac{\delta E_A - \gamma_B}{\delta E_A(1-\gamma_B)} \right]}{\ln \delta E_A} \quad (23)$$

since from Equation (22)

$$E_B = \delta E_A$$

Thus there is only one value of E_A (or E_B) and the number of contacts, N_C , which will satisfy a given set of γ_A and γ_B (or $(R_A)_U$ and $(P_A)_U$) values.

The value of E_A obtained in this manner for the saturating section can now be used in the design of the eluting section. The relation between the E_A values in the two sections will depend only upon the relative solution flow rates and total solution ionic levels, since the resin flow rate and the total resin ionic level will remain constant throughout the entire unit in steady state operation.

Thus

$$(E_A)_{elut} = (E_A)_{sat} \frac{F(c_z)_F}{E(c_z)_E} \quad (24)$$

and from Equation (22)

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$$(E_B)_{elut} = \delta(E_A)_{elut} = \delta(E_A)_{sat} \frac{F(c_{\Sigma})_F}{E(c_{\Sigma})_E} \quad (25)$$

where E is the flow rate of the elutant.

Complete removal of B from the resin would require an infinite number of contacts in the elution section, so a small amount of leakage must be permitted to obtain a finite contactor. It may be assumed that, if almost none, or say 0.5%, of the B ion entering in the resin stays on, the resin can be recycled without affecting the accuracy of the simplified design Equations (20-21). This may be expressed mathematically from Equation (18), when the elutant is free of B, as

$$\left(\frac{\gamma_B}{E_B}\right)_{elut} = 1 - \frac{(y_B)_{exit}}{(y_B)_{entr.}} = 1 - 0.005$$

Therefore, $(\gamma_B/E_B)_{elut}$ may be taken as 0.995, or essentially unity, when applying design equation (8) to the elution section.

Normally, certain of the items considered would be fixed in any design problem, such as $(x_A)_F$, $(x_B)_F$, F, $(c_{\Sigma})_F$, K_A , K_B , and Q. Of the remaining seven items usually considered, $R_p \rho_p$, E, $(c_{\Sigma})_E$, $(\phi_{AB})_U$, $(R_A)_U$, $(N_C)_{sat}$, and $(N_C)_{elut}$, the choice of any four, subject to the limitation that $(E_B)_{elut} < 1$ when the simplified design equations are used, immediately fixes the other three. The four chosen (these usually include at least $(\phi_{AB})_U$ and $(R_A)_U$) can be subjected to an economic balance to determine the optimum choice.

Theoretical Limits of Separation in a Two-Section Unit It is of

interest at this point to consider the ultimate enrichments and recoveries that can be obtained in this two-section unit. For values of E_B less than

one, i.e. $E_A < \frac{1}{\delta}$, it has been pointed out previously that γ will approach E at a large number of contacts. That is, as $N_c \rightarrow \infty$, $\gamma_A \rightarrow E_A$ and $\gamma_B \rightarrow E_B$ with the limitation that E_A (and thus E_B) must be greater than zero.

At the limit, since $\delta E_A = E_B$ then $\delta \gamma_A = \gamma_B$ and from Equations (20-21)

$$\delta [1 - (R_A)_U] = 1 - \frac{(R_A)_U}{(\phi_{AB})_U (\phi_{BA})_F} \quad (26)$$

Rearranging

$$(R_A)_U = \frac{\delta - 1}{\delta - [1/(\phi_{AB})_U (\phi_{BA})_F]} \quad (27)$$

or

$$\frac{(\phi_{AB})_U}{(\phi_{AB})_F} = \frac{(R_A)_U}{1 - \delta[1 - (R_A)_U]} \quad (27a)$$

Thus, at any given purity the calculated recovery is the highest that can be achieved, and likewise for each recovery there is an ultimate purity (for values of $(R_A)_U$ less than $\frac{\delta-1}{\delta}$ this ultimate purity is unity). That is, at anything less than infinite plates these ultimate recovery - purity combinations will not quite be achieved. An example may clarify this. If an absolutely pure steam of A is desired for the top product, i.e. $(\phi_{AB})_U/(\phi_{AB})_F = \infty$ so that $(p_A)_U = 1$, then the highest possible recovery is

$$(R_A)_U = \frac{\delta - 1}{\delta} \quad (28)$$

Under these same conditions, using Equations (13-14),

$$(\phi_{BA})_L / (\phi_{BA})_F = \delta \quad (29)$$

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or

$$(P_B)_L = \frac{\delta}{\delta + 1} \quad (29a)$$

with

$$(R_B)_L = 1 \quad (30)$$

By a similar procedure, the ultimate enrichments and recoveries, with an infinite number of contacts, at other values of E_A , are found to be

$$1 > E_A \geq \frac{1}{\delta}, \quad (\phi_{AB})_U / (\phi_{AB})_F = \infty, \quad (R_A)_U = 1 - E_A \quad (31)$$

$$E_A \geq 1, \quad (\phi_{AB})_U / (\phi_{AB})_F = \infty, \quad (R_A)_U = 0 \quad (32)$$

The effects of other values of N_C and of E_A are shown in Figure 3. For the particular case illustrated, a feed solution containing equal amounts of ions A and B with a separation factor of 3.79 has been assumed. Also, complete removal of the trace ions from the resin, in the elution section, has been assumed. It is apparent that, at a recovery of 0.50, one contact would yield a solution of 0.70 purity while 10 counter-current contacts would give 0.99 purity, and an infinite number would produce a pure solution. The E_A values show that, for a given feed rate, ten contacts would require one-half as much resin per contact as the single contact, and thus a total of only five times as much resin in the saturating unit. As can be seen, it is not possible to obtain purity-recovery combinations above the $N_C = \infty$ curve in a simple two-section unit. To obtain such combinations, either these units must be cascaded as discussed below, or the principle of reflux applied.

Effect of Cascading Separate Two-Section Units As pointed out, above, in a single two-section unit, the enrichment of B in the bottom product

FIG. 3
 RELATION BETWEEN THEORETICAL RECOVERY AND
 PURITY AT VARIOUS VALUES OF N_C AND E_A
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can never exceed the value of δ no matter how many equilibrium contacts are used. However, it may be possible to attain further enrichment of B by using this bottom product stream as the feed to another two-section unit. This second cascade would then remove more A from the feed thus leaving the new bottom product more pure in B. The effect of the number of cascades can best be shown by considering the highest possible enrichment per cascade, i.e. the case of infinite contacts in the saturating section. Consider, as an example, that the original enrichment factor of B in the feed is $[(\phi_B)_F]$, and that the enrichment of B in the lower product, from the first cascade (or two-section unit) is $[(\phi_B)_L]_1$. Then, from Equation (29), under conditions of complete purity of A in all the top products, i.e. $(\phi_A)_U = \infty$ and $(R_B)_L = 1$,

$$\frac{[(\phi_B)_L]_1}{[(\phi_B)_F]_1} = \delta \quad (33)$$

also, for the second cascade

$$\frac{[(\phi_B)_L]_2}{[(\phi_B)_F]_2} = \delta \quad (34)$$

But, since the bottom product from cascade 1 is used as the feed to cascade 2

$$[(\phi_B)_F]_2 = [(\phi_B)_L]_1$$

then

$$\frac{[(\phi_B)_L]_2}{[(\phi_B)_F]_1} = \delta \cdot \frac{[(\phi_B)_L]_1}{[(\phi_B)_F]_1} = \delta^2 \quad (35)$$

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Thus for the Mth cascade

$$\frac{[(\phi_B)_L]_M}{[(\phi_B)_F]_1} = \delta^M \quad (36)$$

The recovery of A in the top product from the first cascade will be

$$[(R_A)_U]_1 = \frac{\delta - 1}{\delta} \quad (37)$$

However, although the recovery of the A from its feed will be identical in the second cascade, there is less to recover since an amount $[(R_A)_U]_1$ has already been recovered. Thus, based on the original feed,

$$[(R_A)_U]_2 = \{1 - [(R_A)_U]_1\} \frac{\delta - 1}{\delta} = \{1 - \frac{\delta - 1}{\delta}\} \frac{\delta - 1}{\delta} = \frac{\delta - 1}{\delta^2} \quad (38)$$

and for the Mth cascade

$$[(R_A)_U]_M = \{1 - \sum_{i=0}^{M-1} [(R_A)_U]_i\} \frac{\delta - 1}{\delta} = \frac{\delta - 1}{\delta^M} \quad (39)$$

The sum of all the recoveries, through a given cascade, can be obtained from Equation (39)

$$\sum_{i=0}^M [(R_A)_U]_i = \frac{\delta^M - 1}{\delta^M} \quad (40)$$

For any reasonable value of δ , it can be seen that high purities of B in the bottom product and recoveries of A in the top product can be achieved with only a small number of cascades. However, it should be pointed out that the elutant flow rate is usually greater than the saturant flow rate. The effect is that each succeeding unit in a cascade will require a still

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larger quantity of resin and elutant to process the elutant from the previous unit. Thus the increase in purity of B in the bottom product, is usually obtained at the expense of pyramiding resin and elutant requirements.

EQUIPMENT

General Ion exchange in a countercurrent column implies that the resin enters one end of the unit at a constant rate and leaves the other end at the same rate. Feed solution enters and leaves the unit at the same rate but travels in the opposite direction with respect to the resin. This countercurrent contact may of course be obtained by either a continuous moving-bed type of unit* or in an equilibrium-stage unit analogous to a plate distillation column. In this latter type of unit, mechanical difficulties in transferring resin from one plate to the next, in an even stream and without solution entrainment, led to the consideration of a batch mixer-settler type of unit.

In intermittent countercurrent operations, the resin and solution aliquots are agitated batchwise in a number of individual stages where equilibrium between the two phases is approached. Following mixing, the resin and solution are separated; then one phase is transferred to the adjoining stage where the two phases are intimately contacted again. Then, after separation, the other phase is transferred countercurrently to the next adjacent stage, and the resin and solution are again mixed. This method of operation has been described by Stephenson.⁽⁵⁾

In the initial studies, this sequence of operations was carried out in beakers, separating the two phases by decantation. The somewhat erratic results indicated that manual manipulation of beakers could not be done with enough finesse to assure stable operating conditions. Moreover, the

* The moving bed studies were discussed in another paper. (1)

separation by simple decantation left an appreciable quantity of solution in the void volume of the resin which contaminated the next solution contacted with the resin. The volume of this interstitial solution could have been reduced by filtering under air pressure, but this would have involved still more manipulations. A large number of these tedious transfers was required to establish the steady state.

Consequently, a mechanical device which would simulate the beaker operations but offer greater precision was considered necessary for an adequate investigation of intermittent operations. In the ideal mechanical apparatus, operations would be automatic, transfers would be simultaneous, and the interstitial solution would be filtered from the resin under air pressure.

Intermittent Mixer-Settler The automatic intermittent mixer-settler shown in Figure 4 was designed to satisfy these requirements. In this assembly a complete cycle of saturation of resin with metal ions and subsequent elution with hydrogen ions is carried out continually until the steady state is attained. This cycle is represented by Figure 2. In effect, the resin is alternately saturated and eluted.

It will be noted that the assembly contained ten mixers and ten reservoirs. Each resin aliquot was retained in its respective mixer for the duration of a run, and the solutions were transferred from one mixer to the next by way of the reservoirs in such a manner that the operations were truly countercurrent. Both the mixing and transfer steps were accomplished with air pressure applied to the top of the appropriate vessel. It was possible by proper manifolding to operate half these mixers and settlers as a unit, while the other half was operated as an independent unit in which duplicate runs were made. It was also possible to interconnect all ten mixers and settlers into one unit.

The cyclic operations required two feed solutions, a saturant and an elutant. The relative positions of these two feed solutions were

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FIG. 4

INTERMITTANT MIXER-SETTLER ASSEMBLY

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6420 25

separated by the number of mixers being used for the saturation step. Figure 5 is a flow diagram of this apparatus showing only five mixers and five reservoirs. As shown in this diagram, the feed positions moved in a clockwise direction with the elutant feed preceding the saturant feed by one stage. Under the conditions indicated, at any one time, some one mixer was devoted to saturation, while the other four were used for elution.

The reservoirs consisted of vertical glass cylinders of about 250 ml. capacity, tapered at the bottom to a 6 mm. tube and tapered to a tubulature at the top for a stoppered outlet. Also near the top was an outlet for connection to the outer, or reservoir, air manifold. The mixers have similar external characteristics, but within the bottom taper was a horizontal fritted glass disc which retained the resin. The mixers were connected to the inner, or mixer, air manifold at the top with rubber tubing. At the bottom, the mixers were connected to the solution manifold with standard spherical joints, so they could be removed from the apparatus for replacement of resin when necessary. The solution manifold of glass and rubber tubing interconnected all the mixers and reservoirs in a unit. Check valves are indicated on the diagram as a means of controlling the direction of flow, since it was desired that each solution aliquot flow clockwise from a reservoir into the next mixer, then from that mixer into the adjoining reservoir and so on around the circle. Although tapered ground glass check valves were initially tried to control the direction of flow, they failed to seat securely, and they were supplemented with mechanical pinch valves. These consisted of sheet metal yokes around thin-wall rubber tubing. Motivated by solenoids, the yokes pinched the rubber tubing against a fixed surface and provided a positive seal. There were two groups of these solenoid pinch valves in the solution manifold system: one group controlled the flow from the reservoirs to the mixers, while the other set controlled the flow from the mixers to the reservoirs.

FIG. 5
INTERMITTENT MIXER-SETTLER FLOW DIAGRAM

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Solution transfers were made by applying air pressure on the containers which were to be emptied of solution. The air pressure was indicated by a manometer and was adjusted with a diaphragm valve. To minimize loss of water from the solutions by saturation of the low humidity air used for transferring, the air was first passed through a saturator, a vertical glass cylinder some 7.5 cm. in diameter and some 90 cm. long. Air was dispersed through a sparger into the water retained in the saturator. Contact between air and water was aided by passage through a bed of glass wool. At the upper end of the saturator, there was a disengaging zone in which entrained water was removed.

Automatic control of the sequence of operations in the mixer-settler was achieved with a motor-driven multi-cam mechanism. These cams actuated mercury switches which in turn controlled the electrical circuits involved in the operations. The principal circuits were those controlling each group of solution valves and those controlling the magnetic valves for supplying air pressure to or for venting the air manifolds.

A selsyn transmitter was also geared directly to the cam mechanism drive shaft. The associated selsyn receiver was mounted at the center of the top board on the mixer-settler. The receiver motivated an indicator which at the proper time pointed to the reservoirs which must be drained and then filled with fresh feed solutions.

Operation of the Mixer-Settler The operation of the unit can be understood best by following the sequence of events which occurred during an operating cycle. At the beginning of a cycle, the solution aliquots were all in reservoirs and the resin aliquots were in the mixers. Upon starting the cam mechanism, air pressure was applied in the top of all the solution reservoirs through the outer air manifold. Simultaneously, the proper group of solenoid pinch valves opened to permit the solutions to transfer in a clockwise direction from the reservoirs to the mixers. Also simultaneously, the inner air manifold, connected to the mixers, was

vented to the atmosphere.

Air flow was continued into the bottom of the mixers for the duration of the desired equilibration period. This air flow served two purposes: first, to keep the solution in the mixer and second, by its dispersion through the fritted disc, to provide turbulence for keeping the slurry well agitated.

At the end of this pre-determined contact period, the cam mechanism caused the air flow to reverse, so that pressure was applied to the mixers and the reservoirs were vented. At the same time, the reservoir-to-mixer pinch valves were closed and those permitting flow from the mixers to the reservoirs opened. This combination of events caused the solutions in the mixers to flow through the fritted glass discs into the reservoirs in a clockwise direction. Air flow was continued through the resin retained on the fritted discs long enough to assure adequate removal of free solution from the resin. Then all the pinch valves and air valves were closed, leaving the apparatus in a momentary quiescent condition. Then the cam mechanism repeated the cycle. At the end of the second cycle, the drive motor shut off and a buzzer sounded to indicate the end of a cycle. At the end of this second cycle, the selsyn-driven indicators pointed to the reservoirs which contained the spent, saturant and elutant samples to be removed and replaced with fresh feed solutions. This was done manually, although an automatic selector valve arrangement for removing the exhausted samples and filling the empty reservoirs with fresh feed could have been provided.

From this point on, the operations described above were repeated, starting with the transfer of solutions into the mixers. The experimental runs made with this apparatus required that a large number of cycles be completed before dynamic equilibrium could be assured. Figure 6 outlines the physical transfers of solutions for a run in a five-stage unit with one saturation stage and four elution stages. One might imagine that this figure were shaped as a cylinder with Mixer 5 adjacent to and just

Nomenclature:

R - Reservoir
M - Mixer
F - Saturant Feed
E - Elutant Feed

Sequence a - transfer into mixer and agitate
Sequence b - transfer out of mixer
Sequence c - empty proper reservoir
Sequence d - fill this reservoir

Solution Out
↑ Feed In

FIG. 6
INTERMITTENT MIXER-SETTLER OPERATIONS (5 Units)
For 5 Mixers and 5 Reservoirs, 1 Mixer on Saturation,
4 Mixers on Elution

XXXI
Final
Cycle
for
Run #5

Comment: The resin originally in Mixer 1 remains in Mixer 1 throughout all operations, etc. 1A-CU337-69

preceding Reservoir 1 to complete the cycle.

Initially, equal, pre-determined quantities of hydrogen resin were placed in the mixers. Approximately equal quantities of distilled water were placed in all but two reservoirs. Into one of the empty reservoirs, R-1, the first elutant sample, E-1, was transferred volumetrically. Reservoir R-5 was filled with the first saturant, F-1. It will be noted that F-1 subsequently contacted resin in two mixers and was then removed from the system. Similarly, the elutant, E-1, contacted resin in eight stages before removal. Thus it can be seen that two equilibrium contacts were attained per stage in a given cycle. This follows Ravenscroft's⁽³⁾ reasoning with regard to batch countercurrent operations.

The outline of operations given in Figure 6 is practically self-explanatory. Here again, it should be pointed out that samples were withdrawn and feed solutions were introduced only every other cycle. As a consequence, it may be observed that the position of the saturant feed, for instance, moves one reservoir while the saturant solution is transferred through two stages. Specifically, the initial saturant feed, F-1, was placed in R-5; the next saturant feed, F-2, was placed in R-1, the adjacent reservoir. Meanwhile, F-1, had passed to R-2, from which it was withdrawn after two contacts.

The lower dashed line across the figure indicates that the same physical situation existed at Cycle XVIII, sequence a, as at the upper dashed line, Cycle VIII, sequence a. Cycle XVIII is the first one which duplicated a previous cycle after all the reservoirs had been filled with active solutions. In other words, it may be assumed that dynamic equilibrium existed no earlier than at the lower dashed line. The experimental runs were usually carried even further to assure a steady state. The locations of solutions at the end of an early run, for instance, are shown on the last line of the diagram.

Although not indicated on the diagram, it is obvious that the distilled water initially present in the system was replaced with active

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solutions as the run progressed. The water served only to prevent dehydration, by air, of the resin aliquots which were not all in contact with active solutions during the filling cycles.

Operations in a ten-stage unit were substantially identical with those in the five stage unit, except that a larger number of contacts was made. The essence of operations with the ten stage unit is outlined in Figure 7 which shows only the last few cycles, ending with conditions existing at the end of the first run of this type.

In the case of the ten-stage unit, it will again be found that two equilibrium contacts were attained per stage. In terms of the number of actual physical stages, N_s , then, the Kremser relation, Equation (8), must be modified as follows:

$$N_s = \frac{N_c}{2} = \frac{\ln \left[\frac{E_A - \gamma_A}{E_A (1 - \gamma_A)} \right]}{2 \ln E_A} \quad (41)$$

or

$$\gamma_A = \frac{E_A^{2N_s+1} - E_A}{E_A^{2N_s+1} - 1} \quad (42)$$

The ratio of the solution and resin flowrates used in E must also be expressed in terms of aliquot (or intermittent flowrate) ratios because of the intermittent operation of the units. The value of E is then defined as

$$E_A = \frac{M_A}{V_{F\Sigma} C_{\Sigma} / W_P Q} = \frac{M_A W_P Q}{V_{F\Sigma} C_{\Sigma}} \quad (43)$$

FIG. 7
INTERMITTENT MIXER-SETTLER OPERATIONS (10 Units)
For 10 Mixers and 10 Reservoirs, 1 Mixer on Saturation, 9 Mixers on Elution

Nomenclature:

R - Reservoir
M - Mixer
F - Saturant Feed
E - Elutant Feed

Sequence a - transfer into mixer and agitate
Sequence b - transfer out of mixer
Sequence c - empty proper reservoir
Sequence d - fill this reservoir

Solution Out
↑
Feed In

where V_F is the volume of the solution aliquot and W_p is the weight of the resin aliquot.

The proper identification of the entering and exiting solutions and resins is more difficult with the intermittent contactor than it would be for a continuous unit. This identification is quite important since the value of γ , the degree of approach to equilibrium transfer in the solution phase, depends on the compositions of these streams. For the saturating section, the entering solution concentration is obviously that of the feed and, at the steady state, the exiting concentration can be obtained from the spent feed leaving the unit. The resin compositions must be obtained from those aliquots that have received the proper number of contacts. In the case of the five stage unit outlined in Figure 6 the exiting (or saturated) resin aliquot would be that which had just completed two contacts with feed solutions and the entering (or eluted) resin would be that which had just gone through eight equilibrations with elutant aliquots.

The position of these resin aliquots will depend on the cycle since the feed position changes every two cycles. For instance, at Cycle XVI b (on Figure 6) the resin in mixer M-2 has just finished its second equilibration with feed solution, i.e. it had been contacted only with F-7 and F-8 since its last elution. Likewise the resin in mixer M-3 has just had eight elutions, with E-1 to E-8. These resins, M-2 and M-3 respectively, would then be exiting and entering resins respectively, for the saturating section.

It will be noted that all of the short cycles, i.e. cycles not involving solution removal and addition, will exhibit a similar behavior after the steady state is reached. For example, in the case of Cycle XVIII the proper aliquots would be M-3 and M-4, respectively. Since these resin aliquots can not be obtained during a run, it would be necessary, after the unit has reached the steady state, to shut down at such a short cycle. At this shutdown point, none of the solutions in the reservoirs correspond

to entering or exiting aliquots. This is not important, however, as such solutions will have been obtained from the previous long cycles and, at the steady state, their compositions would not change.

The proper aliquots involved in calculating γ from Equation (7) can now be identified in terms of the operating program. For the case outlined in Figure 6, the compositions would be those for the samples indicated:

$$[(X)_{entr}]_{sat} = [(X)_{R-3}]_{XVII\ d}$$

$$[(X)_{exit}]_{sat} = [(X)_{R-4}]_{XVII\ b}$$

$$[(Y)_{entr}]_{sat} = [(Y)_{exit}]_{elut} = [(Y)_{M-3}]_{XVI\ b}$$

$$[(Y)_{exit}]_{sat} = [(Y)_{entr}]_{elut} = [(Y)_{M-2}]_{XVI\ b}$$

$$[(X)_{entr}]_{elut} = [(X)_{R-4}]_{XVII\ d}$$

$$[(X)_{exit}]_{elut} = [(X)_{R-3}]_{XVII\ b}$$

where the subscripts indicate reservoir or mixer number and cycle number.

EXPERIMENTAL PROCEDURE

General The mixer-settler apparatus was evaluated by carrying out the separation of Li^+ and K^+ , in trace concentrations with respect to the H^+ carrier (or gross) component, in a feed solution. The resin was also eluted with H^+ . This ion system was chosen because of the equal valence of the three ions, the ease of analysis and the known feasibility of separating the metal ions. The resin has greater affinity for the K^+ than the Li^+ , so, in reference to the theoretical discussion, Li^+ corresponds to the A ion and K^+ to the B ion, and H^+ is the G ion. The determination of the parameters of this system, and a detailed

description of the analytical methods were given in a companion paper.¹

The affinity between an ion species and the resin was expressed as the distribution coefficient, M . In the trace region, in which the experimental work was conducted, the distribution between the resin and solution phases is a linear isotherm as shown in Figure 8, and thus the distribution coefficient is a constant as desired. For the above ion system and the Chempro C-20 cation resin used for these studies, the coefficients were: $M_{LiH} = 0.87$ and $M_{KH} = 3.30$.

The ultimate capacity of the resin was 5.11 meq./g. of oven dried resin.

Methods of Analysis The alkali metals in solution were analyzed with a Beckman DU spectrophotometer with a flame attachment. Corrections were made for interference, by reinforcement, of the HCl on the emission and for mutual interference of the Li^+ and K^+ . The H ion concentrations were determined with a Beckman automatic titrator.

The resin analysis entailed an elution of the metal ions from resin aliquots weighing about 10 g., which had been washed with water to displace interstitial solution. These samples were retained in a tube and were eluted with 250 ml. of 2N HCl. The resulting elutants were diluted to 1N and then analyzed for alkali metal concentrations by flame photometry as above, the samples were oven-dried, and the concentrations were reported on that basis.

Experimental Runs Prior to each run, eluted resin aliquots having equal settled volumes were transferred to all the mixers. The unit was then started up and operated according to the method indicated in the section on Operation of the Mixer-Settler. The equilibration or mixing time was varied for different runs from 1.5 to 28 minutes by changing the gear trains and the positions of the cams in the control mechanism. The solution transfer time was originally 1.5 minutes but was later reduced to 0.5 minutes.

FIG. 8
EQUILIBRIUM ISOTHERMS

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The saturant feed was composed of HCl and approximately equimolar quantities of K ions, and Li ions, in the form of their chlorides. These ions were in trace concentrations ($\sim 0.03N$) with respect to the approximately 1.0 N HCl carrier. The elutant $\sim 1.0 N$ HCl. Saturant aliquots varied for different runs from 40 to 100 ml and elutant aliquots from 150 to 200 ml. All feed and product solutions were measured in graduates.

All samples removed from the apparatus and aliquots of both feed and elutant solutions were analyzed for cation contents. At the end of the run the resin samples and the solutions left in the various reservoirs were removed, and their metal ion contents were determined. The oven-dried weights of the resin samples were also obtained. Typical weights of the resin aliquots used in separate runs varied from 5 to 35 g.

A run was continued until there was reasonable assurance that the steady state had been attained. As was pointed out earlier, this necessitated operation until at least one complete series of cycles had been completed subsequent to the filling of all of the reservoirs with active solutions.

In the case of the longer equilibration time, 28 minutes, this required a run of about 28 hours. For one of the shorter mixing times, say 2.5 minutes, a run could be completed in 3 hours.

The detailed operating conditions for all the runs are given in Table I. It will be noticed that the E values, which will be used in the calculations, have been given rather than the individual values for the solution and resin aliquots. These E values were calculated from M , the slope of the equilibrium isotherm and the average molal aliquot ratio, $V_F C_{\Sigma} / W_P Q$, according to Equation (43).

INTERPRETATION OF RESULTS

General The experimental data were obtained in terms of solution concentrations (later converted to mol fractions) for both the upper and

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TABLE I

EXPERIMENTAL CONDITIONS AND RESULTS

RUN NO.	EQUILI- BRATION TIME (min.)					RECOVERY OF LI IN THE UPPER PRODUCT %	ENRICHMENT OF LI IN THE UPPER PRODUCT
		$(E_{Li})_{sat.}$	$(E_{Li})_{elut.}$	$(E_K)_{sat.}$	$(E_K)_{elut.}$	$(R_{Li})_U$	$(\phi_{LiK})_U / (\phi_{LiK})_F$
4	28	0.73	0.30	1.84	0.75	35	3.23
5	28	0.39	0.31	1.02	0.79	68	2.59
6	28	0.42	0.21	1.66	0.84	55	3.85
7	28	0.49	0.24	1.94	0.95	56	2.97
8	28	0.23	0.12	0.86	0.47	84	2.55
9	28	1.52	0.85	5.76	3.24	17	1.44
10	12	0.60	0.20	2.26	0.74	48	4.10
11	28	1.10	0.18	4.19	0.69	29	6.56
12*	28	0.62	—	2.34	—	48	4.09
13	5.0	0.58	0.21	2.20	0.78	49	3.65
14	3.5	0.57	0.25	2.16	0.94	51	3.59
15	5.0	0.34	0.13	1.27	0.51	64	2.16
19	2.5	0.60	0.24	2.28	0.91	52	3.89
20	**	0.58	—	2.21	—	66	1.85
21	1.5	0.55	0.25	2.08	0.93	57	3.27

* The reproducibility of results in the saturation section was evaluated.

** The effect of equilibration time on approach to equilibrium was evaluated. The average values for equilibration times of 2-5 minutes are given.

lower products. A typical set of such data (for Run 19) is represented in Figure 9. The approach to steady state at the end of the run is readily apparent.

In addition, upon completion of the run, data were obtained in terms of resin concentrations for each mixer (say in M-1) along with the concentration of the solution (say R-2) that had just been equilibrated with that resin. This equilibration data, for the later runs, was plotted, as shown on Figure 8, and checked the equilibrium isotherms obtained previously.¹

The steady state K^+ data for Run No. 19 are shown graphically in Figure 10. This diagram is a graphical representation of the Kremser relations, Equations (5, 7, 43), and is similar to the McCabe-Thiele representation of distillation column data.

The points along the equilibrium line were obtained at the end of the run as previously described. In agreement with the value of M_{KH} its slope was 3.30. The operating lines express the material balances for the individual sections and have slopes equivalent to the molal aliquot ratios, $V_F C_2 / W_P Q (=M/E)$. For the saturating section, this slope is 1.45 ($= 3.30 / 2.28$) and for the eluting section is 3.63 ($= 3.30 / 0.91$). In the case of the saturating section, the upper end of the operating line was fixed by the composition of the resin leaving the saturating section and the saturant feed composition. The lower end of this line was established by the compositions of the eluted resin entering the saturation section and of the upper product (exhausted saturant). It is apparent from Figure 2 that the eluted resin entering the saturating section is identical with the resin leaving the eluting section. Similarly, the saturated resin leaving the saturating section is also the resin entering the eluting section.

Thus, the upper end of the operating line for the eluting section is fixed by the compositions of the saturated resin and of the lower product (exhausted elutant). Since the elutant feed contains no K^+ , the lower

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FIG. 9
COMPOSITIONS OF EFFLUENT
SOLUTIONS FOR RUN NO. 19

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FIG.10
GRAPHICAL REPRESENTATION
OF K^+ DATA FOR RUN NO. 19

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end of this line must fall on the ordinate axis at a height equivalent to the composition of the eluted resin.

The number of countercurrent equilibrium contacts between the resin and solution phases, required for a given ionic transfer may be determined graphically as shown. For the saturating section, this was two contacts and for the eluting section, eighteen. It will be recalled that two contacts were made for each stage and that in the ten stage unit, one stage was devoted to saturation and nine to elution. The equilibrium data were obtained for each physical stage and thus for every other contact.

In general it is more convenient to use the modified Kremser relation, Equation (41), than the graphical method for the determination of the number of physical stages required for an exchange of ions, but the graphical approach is more illustrative of the stepwise and cyclic operations involved.

Evaluation of Data Values of γ were calculated for both the saturating and eluting sections by use of Equation (7) and the proper steady state data. Although solution information was available for the upper and lower products at the end of each two cycles, resin could be obtained only upon completion of the run as pointed out earlier.

For a given section, four values of γ were obtained: one based on the change in the fraction of Li^+ in solution, one based on the K^+ in solution, and the two corresponding values obtained from the resin concentration information. The two γ values based on Li^+ were averaged as were the two γ values based on K^+ . This was done to compensate for any inaccuracies due to a poor material balance over the section in question. These average values of γ are given in Table II.

The material balance for the unit was checked in two ways. First, the amount of a given ion (say Li^+) entering the contactor per unit time was compared to the amount leaving over the same period. This was known

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TABLE II

COMPARISON OF EXPERIMENTAL AND PREDICTED RESULTS

RUN NO.	AVERAGE APPROACH TO EQUILIBRIUM				AVERAGE RATIO OUTPUT TO INPUT OF SOLUTIONS		PREDICTED APPROACH TO EQUILIBRIUM*				OVER-ALL MATERIAL BALANCE %	
	$(\gamma_{Li})_{sat.}$	$(\gamma_{Li})_{elut.}$	$(\gamma_K)_{sat.}$	$(\gamma_K)_{elut.}$	Li ⁺	K ⁺	$(\gamma_{Li})_{sat.}$	$(\gamma_{Li})_{elut.}$	$(\gamma_K)_{sat.}$	$(\gamma_K)_{elut.}$	Li ⁺	K ⁺
4	0.54	0.36	0.68	0.87	1.06	0.87	0.56	0.30	0.84	0.75	107	96
5	0.20	0.28	0.60	0.95	0.98	0.96	0.35	0.31	0.67	0.79	99	95
6	0.30	0.35	0.65	1.20	0.94	1.00	0.38	0.21	0.82	0.83	94	86
7	0.47	0.24	0.82	1.12	1.06	1.11	0.42	0.24	0.85	0.92	97	92
8	0.14	0.14	0.61	0.58	1.09	1.21	0.22	0.12	0.62	0.47	106	94
9	0.77	0.92	0.95	1.35	1.00	0.56	0.79	0.84	0.98	1.00	95	102
10	0.48	0.19	0.86	0.75	0.96	0.95	0.48	0.20	0.88	0.74	95	92
11	0.60	0.17	0.93	0.69	0.84	0.94	0.70	0.18	0.96	0.69	94	89
12	0.53	-	0.86	-	-	-	0.50	-	0.89	-	95	95
13	0.44	0.21	0.88	0.72	0.91	1.14	0.48	0.21	0.88	0.78	90	96
14	0.46	0.25	0.82	1.00	0.97	1.11	0.47	0.25	0.87	0.92	96	98
15	0.35	0.12	0.70	0.55	0.96	1.13	0.31	0.13	0.74	0.51	87	92
19	0.47	0.23	0.89	0.89	0.97	1.02	0.48	0.24	0.88	0.89	97	98
20	0.31	-	0.67	-	-	-	0.35	-	0.68	-	90	100
21	0.42	0.26	0.86	0.95	0.97	1.11	0.46	0.25	0.87	0.91	96	104

* Based on one stage in the saturation zone and nine in the elution (except for Runs 4 and 5 which had 4 elution stages) and the values of E actually existing during the run.

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as the instantaneous output-input ratio and was calculated from the content of the saturant and elutant feeds and of the two product streams only, since the resin was recirculated internally. A recurring ratio of unity indicates that none of the component is being accumulated or depleted in the unit and that steady state operation is occurring. The second method involved a material balance on the unit over the entire run. The input for a component was calculated from the amount fed in the saturant and elutant solutions and the amount in the initial resin aliquots. The output was based on the upper and lower products and on the amounts in the resin and solution aliquots left in the contactor at the end of the run. The overall material balance was then expressed as the percent of the input that was found in the output. Both the instantaneous output-input ratio and the overall material balance are presented in Table II.

Comparison with Predicted Data

The known number of physical stages in a given section, along with the E values for that section, were used in Equation (42), to predict theoretical γ values. In the majority of the runs there were one saturation stage and nine elution stages. For a given run, four values of γ were predicted: one for Li^+ in the saturating section, one for the eluting section, and the two corresponding values for K^+ . This information is also indicated in Table II and has been plotted against the pertinent experimental values of γ in Figure 11.

Overall, the agreement between predicted and experimental results was satisfactory. In general, those points showing the greatest deviations from the norm were from the earlier runs (4 through 8). These runs were made before the analytical techniques reported here were fully refined, and the generally poor material balances for these runs probably reflect the analytical inaccuracies, especially for potassium. For this reason also, the equilibrium data for these runs were not represented in Figure 8.

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FIG. II
COMPARISON OF EXPERIMENTAL AND PREDICTED
 γ VALUES

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In addition to possible analytical problems, Runs No. 4, 5 and 6 were not entirely satisfactory. Plots of product composition, similar to Figure 9, revealed that Run No. 4 had not yet reached the steady state at the end of the run. With respect to Run Nos 5 and 6, they were inadvertently terminated at the improper cycle, i.e., after the resin in the saturating section had received only one contact with saturant. It was thus necessary to extrapolate the concentrations on the resin aliquots at the end of the run to obtain estimated concentrations of the resin out of the saturating section after two contacts and that out of the eluting section after eighteen contacts. These estimated values were used to calculate the approaches to equilibrium transfer for these runs and the results must therefore be viewed with reserve.

In Table II, it will be noted that there is a large discrepancy between the experimental and predicted $(\gamma_K)_{elut}$ for Run No. 9. In fact, this point could not be plotted on Figure 11. In this run, the steady state was never attained, for potassium at least, and therefore the experimental value of γ has no meaning. Because the E_K was more than one, potassium accumulated on the recycled resin, and it had not reached a stable concentration at the end of the run. The most important point about Run No. 9 is that incomplete elution and thus slower attainment of the steady state could have been anticipated from the E_K value.

Reproducibility of Effluent Resin Compositions One possible source of uncertainty in the calculation of the experimental values of γ is in the composition of the saturated and eluted resins. As was pointed out previously only one sample of each, obtained at the end of the run, is available, whereas the steady-state compositions for solutions are based on quite a few product samples. There was thus some question as to the accuracy of the values obtained from the single resin samples.

A run (No. 12) was therefore made to check on the range of deviations encountered on duplicate samples. The ten mixers of the unit were each

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filled with similar aliquots of an eluted resin and all but the first resin sample received two countercurrent contacts with saturant solution according to the usual operating procedure. However, after receiving its two contacts, each resin aliquot was removed from the system rather than carrying out an elution in the unit. Although the first three samples were contacted either the improper number of times or with solutions which had received the improper number of prior equilibrations, the last six or seven samples should be indicative of steady state operations in a saturation section. The actual compositions of the effluent solution and resin samples for this run are plotted in Figure 12. The predicted values of the compositions, based on the average E values and two equilibrium contacts are also indicated.

It is apparent that, although the resin compositions are relatively constant, deviations of 5 - 10% exist between samples. This variation may be partially responsible for the cases of disagreement between predicted and experimental values of γ and for the unsatisfactory overall material balances.

Effect of Equilibration Time on Results

As can be seen from Table II, there appears to be no effect of equilibration time on the agreement between predicted and experimental results, at least for times of 1.5 minutes or greater. However, because of minor differences in conditions between the runs this conclusion can only be tentative. In order to further check this factor a special run (No. 20) was made. Again the ten mixers of the unit were each filled with similar aliquots of an eluted resin. The first two mixers were then each contacted, for one minute, with separate saturant aliquots which were then removed. The next two mixers were contacted for two minutes with new saturant aliquots, etc., until the last two mixers were contacted for five minutes. The average values of γ and overall material balances for both Li^+ and K^+ , were calculated in the usual manner from the quantities and compositions of the solution

FIG. 12

REPRODUCIBILITY OF DATA
(RUN NO. 12)

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and resin aliquots, before and after equilibration. The duplicate results, from the two mixers, have been plotted against equilibration time in Figure 13. The predicted values of γ , based on the average values of E and one equilibrium contact are also indicated on the figure. The results agree with the previous observation that equilibration times of 1.5 minutes or longer are sufficient for these ions in the equipment used. An adverse affect on γ is apparent at one minute however.

The poorer material balance for Li^+ , as indicated in Figure 13, is probably responsible for the less satisfactory agreement between the experimental and predicted values of γ for Li^+ .

Conclusions The results all appear to indicate that the present equipment can be used as a satisfactory equilibrium stage contactor for countercurrent ion exchange between resins and solutions. Under trace conditions, the operation of the unit can be accurately predicted by the modified Kremser equation as long as equilibration times are adequate.

The apparatus may also be useful in the investigation of other unit operations involving fluid-solid contacting, such as leaching, adsorption, and catalysis.

Further work is in progress on the equilibrium-stage theory and the use of this contactor for exchange under gross conditions. This will be reported in a later paper.

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FIG. 13

EFFECT OF EQUILIBRATION TIME ON γ

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NOMENCLATURE*

A, B, G	=	trace components A, B, and gross component G.
C_T	=	total ionic level in the solution phase in meq/cc., equal to the ionic concentrations of components A, B, and G.
D	=	distribution or partition parameter, dimensionless.
E	=	ratio of the slope of the equilibrium line to the slope of the operating line, dimensionless.
E	=	volume of elutant solution aliquot introduced to the equilibrium-stage contactor.
F	=	volume of feed solution aliquot introduced into the equilibrium-stage contactor.
K	=	chemical equilibrium constant for exchange, dimensionless.
L	=	volume of lower product solution aliquot removed from the equilibrium-stage contactor.
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 trace component in a specific stream with respect to the amount of all trace components 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.)
U	=	volume of upper product solution aliquot removed from the equilibrium-stage contactor.
V_F	=	volume of solution aliquot introduced to the equilibrium-stage contactor. If the solution is elutant, $V_F = E$, or if feed, $V_F = F$.
W_P	=	weight of resin aliquot introduced to the equilibrium-stage contactor.

* Note that the light and bold D and E symbols have been interchanged with respect to Technical Report II. The bold symbols are now used mainly for dimensionless factors.

- x = mol fraction of a component in solution with respect to the total ionic level of the solution, dimensionless.
- x^* = mol fraction in the solution in equilibrium with a given mol fraction on the resin, dimensionless. $(x^*)_{\text{exit}} = (y)_{\text{entr}}/M$.
- y = mol fraction of a component on the resin with respect to the total capacity of the resin, dimensionless.
- y^* = mol fraction on the resin in equilibrium with a given mol fraction in the solution, dimensionless, $(y^*)_{\text{exit}} = M(x)_{\text{entr}}$.
- γ = degree of approach to equilibrium transfer for a component in the solution phase, dimensionless. (The degree of approach to equilibrium transfer for a component in the resin phase is γ/E)
- δ = separation factor between B and A. $\delta = K_{BG}/K_{AG}$.
- ϕ = the concentration factor or the ratio of the concentration of one trace component to that of another in a given stream.
- ρ_p = density of resin, g; oven-dried resin per ml of true resin value saturated with the carrier component.

Subscripts

- A, B, G = components A, B, and G.
- E = elutant stream
- elut = elution section
- entr = influent composition
- exit = effluent composition
- F = feed stream
- L = lower product or spent elutant stream
- sat = saturation section
- U = upper product or spent feed stream

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