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Title: DESIGN OF A CONTINUOUS COUNTERCURRENT ION
EXCHANGE UNIT AND OPERATING CHARACTERISTICS
FOR THE AQUEOUS CUPRIC SULFATE-SODIUM SULFATE-
DOWEX 50W-X8 SYSTEM

Abstract approved

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A countercurrent, liquid-solids contactor was constructed,
operated and evaluated for a continuous ion-exchange operation.
The exchange of cupric and sodium ions between aqueous solutions
and Dowex 50W-X8 ion exchange resin was studied.

The countercurrent contactor consisted of two, three-inch
diameter columns with active sections ranging from one to four feet
in length. Resin was driven downward in each column by a sinusoidal
hydraulic pulse acting in conjunction with a check valve that allowed
only downward flow of solids. Resin phase velocities of 4 cm/min
and solution flow rates of 35.6 ml/cm² min were attained in the
columns. Cupric sulfate and sodium sulfate solutions were fed to
each of the two columns to simulate loading and eluting operations,
respectively.
The experimental results were correlated with a modified transfer unit model. Provision was made for a variable, composition-dependent, resin-phase diffusivity and a direction-of-ion-transfer dependent transfer-unit height in the solution phase. Although a variable resin-phase diffusivity was expected, the data were best correlated with a constant resin phase diffusivity of

\[
\bar{D}_{\text{CuNa}} = 0.807 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \pm 5\%.
\]

The solution-phase transfer unit heights were found to be relatively larger when the slower ion diffused from the solution to the resin phase.

Solution phase-resin phase equilibria were determined for the systems, cupric sulfate and sodium sulfate in 0.1, 0.2, 0.5, 1.0, and 2.0 normal aqueous solutions and Dowex 50W-X8 ion-exchange resin. These data were required to evaluate the column experiments since the available equilibrium data for cupric chloride and sodium chloride in aqueous solution and Dowex 50W-X8 were found to be inapplicable.
DESIGN OF A CONTINUOUS COUNTERCURRENT ION EXCHANGE UNIT AND OPERATING CHARACTERISTICS FOR THE AQUEOUS CUPRIC SULFATE-SODIUM SULFATE-DOWEX 50W-X8 SYSTEM

by

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DESIGN OF A CONTINUOUS COUNTERCURRENT ION EXCHANGE UNIT AND OPERATING CHARACTERISTICS FOR THE AQUEOUS CUPRIC SULFATE-SODIUM SULFATE-DOWEX 50W-X8 SYSTEM

INTRODUCTION

As with other more common unit operations continuous countercurrent ion-exchange offers several advantages over the batch method. Countercurrent ion-exchange operations require shorter columns which should result in a savings in both space and construction costs. Also continuous countercurrent operations can produce constant product flows of uniform quality which should result in higher operating efficiencies and increased adaptability to automation and integration with other units. A savings of capital, material and manpower costs should therefore result from the use of a suitable continuous countercurrent ion-exchange unit.

Although several continuous ion-exchange systems have been devised, none of them have come into wide use. This is apparently due to the mechanical complexity of the units or to the restricted ion-exchange resin and solution flow rates attained. A lack of design information for continuous systems is also apparent, and this is probably a contributing factor to the limited use of continuous ion exchange systems.

In view of the above considerations, the two objectives of the
present study were to devise an improved countercurrent, liquid-solids contactor and to formulate design criteria from the results of its operation. It was felt that a modified transfer unit analysis of an operation featuring a moving, packed bed of ion exchanging material would fulfill these objectives.

In designing the countercurrent, liquid-solids contactor, a device featuring a moving, constrained bed of resin was sought. Such a device should allow high solution flow rates without the problem of fluidization in the resin bed. Mechanical simplicity was also desirable in order to insure trouble-free operation and to minimize physical attrition of the ion-exchange resin.

The formulation of correlating and design equations should account for the resistance to mass transfer in both phases of the two-phase system and the possible variation of the solution-phase and resin-phase mass-transfer coefficients due to the ionic nature of the system. The unknown quantities in such formulas should be resolved by fitting experimental data to the theoretical formulations.

The design and principles of operation of the continuous countercurrent contactor and the methods by which its operation was analyzed are the subjects of the following sections. With the relationships derived there and known values of the appropriate system properties one should be able to design similar equipment for continuous countercurrent ion-exchange operations.
LITERATURE REVIEW

Ion-exchange operations are usually carried out in columns containing a fixed bed of solid ion-exchanging material. In most cases this solid material is initially saturated with an ion for which it has less affinity than for an ion or ions in the solutions to be processed. As the process solution passes through the bed, the ions initially on the ion-exchanging material are displaced by ions from the process solution. This exchange is not instantaneous, and so an exchange zone develops between the fresh resin still in its initial condition and the exhausted resin from which all of the original ions have been displaced. A knowledge of the behavior of this exchange zone is necessary in order to evaluate the operation of ion-exchange columns.

Kinetics of Ion-Exchange Operations

In carrying out fixed-bed, ion-exchange, displacement operations, the exchange zone will vary in width during the early stages of an operation where the equilibrium conditions are favorable, and throughout the entire operation if the equilibrium conditions are unfavorable. Although this transient behavior is not a factor in the present study, solutions of the time-dependent problem are of interest. Mass transfer coefficients and diffusivities have been
evaluated and theories of the ion-exchange mechanism formulated as a result of these studies.

Thomas (48) solved the transient problem by assuming a second order reversible mass action rate mechanism and a time dependent continuity equation. A second order reversible reaction model results from viewing the exchange of monovalent ions as being controlled by the chemical reactions involved. His solution is difficult to use since it involves integrals of Bessle functions and exponentials. Heister and Vermeulen (20) have presented Thomas' solution in graphical form. Their charts give the liquid concentration in the column in terms of parameters involving distance down the column and the time since the start of the run. They also modify the solution so that liquid- and solid-phase mass transfer coefficients can be used instead of the mass action rate constants.

Amundsen (1) used an approach similar to that of Thomas in that he assumed a mass action rate mechanism and time dependent continuity equation. However, his rate equations are for first-order reversible, second-order irreversible and second-order forward, first-order reverse chemical reactions.

Boyd, Meyers and Adamson (5) used a mass transfer model to solve the transient problem. They assumed that the operation was controlled by a diffusional resistance in the solid phase and that a linear equilibrium relationship could be used. A model employing
diffusional resistance as the rate controlling mechanism and a linear equilibrium relationship was also used by Rosen (42, 43). He accounted for the liquid- and solid-phase diffusional resistances and the spherical geometry of the ion-exchange resin particles. The solution of this more realistic problem is again unwieldy to use. In addition, the assumption of straight-line equilibrium restricts the use of both of the above solutions to the exchange of trace components or isotopes.

In order to use the solutions for the behavior of ion-exchange operations, a knowledge of the rate constants involved is required. Gilliland and Baddour (12) and Sujata, Banchero and White (47) have used differentiated forms of the Thomas solution to fit breakthrough curve data to the mathematical model. They have studied the effect of particle size, liquid flow rate, and liquid concentration on the mass-action rate constants. Relationships between the mass-action rate constants and mass transfer coefficients have also been suggested.

The solution of the transient problem is necessary if the behavior of shallow beds and the case in which equilibrium is unfavorable are to be determined. However, Cooney and Lightfoot (8) have shown that the exchange zone attains a steady-state configuration in deep beds where equilibrium is favorable and the resin composition, liquid feed concentration and flow rate are uniform. This is the case
for most ion-displacement operations. The existence of the steady-state exchange zone has led several investigators to analyze column operation from this point of view. With this approach the difficulties involved in the time dependent case are avoided, and more workable solutions result.

Mayer and Thompkins (31) assumed that a column can be described as a cascade of equilibrium stages. They also assumed a linear equilibrium relationship. From these assumptions, they derived a finite-difference formula for liquid concentration as a function of the equilibrium constant, the number of stages down the column of the point in question, and the volume of solution fed to the column. However, they did not consider the important problem of stage height.

Michaels (35) used a steady state model in which the concentration profile in the exchange zone was assumed to have attained a fixed configuration. With the assumptions of liquid-phase control and a mass-action equilibrium constant, he derived formulas for the height of the exchange zone. Glueckauf (14) also used this approach, but considered the resistances to mass transfer in both the liquid and resin phases. Moison and O'Hern (37) presented a method for determining the magnitude of the liquid and resin phase resistances from experimental data. Their derivations were also based on a steady-state model.

Graphical methods, similar to those used in gas absorption
and distillation, have been presented by Pfieffer (40) and Zeegers (54). Pfieffer suggested a Ponchon-Savarit (41, p. 146) type construction that takes account of the absorption of salt molecules in the ion exchanger particles. Zeegers used a McCabe-Thiele (41, p. 123) diagram to determine the number of stages required to carry out a given operation. Both of these authors point out that a continuous countercurrent process would be more flexible than a fixed-bed process. In a fixed-bed process, the slope of the operating line depends on the nature of the equilibrium relationship. However, in the continuous process, the slope of the operating line depends on the flow rates of the solution and resin phases.

**Diffusion in Ion-Exchange Operations**

In order to evaluate a kinetic process or operation, the magnitude of the rate constants involved must be known. In most ion-exchange operations, diffusion of the exchanging ions, and not the chemical reaction rate has been accepted as the controlling phenomenon. Accordingly, the mechanism of diffusion and the magnitude of diffusivities and mass transfer coefficients have been studied by a variety of methods.

Deep beds have been studied by various authors (12, 14, 20, 26, 47, 53). They have suggested ways of explaining breakthrough-curve data in terms of liquid phase and/or solid phase diffusion
phenomena.

A method that is better suited to the study of diffusion phenomena is that of the shallow bed. Here, the bed is shallow enough and the liquid flow rate great enough that there is only a small change in the ionic concentrations of the solution phase as it passes through the bed. Also, the change in composition of the resin is essentially uniform throughout the bed and a function of time only. These conditions result in a situation that is more easily analyzed mathematically than that of the deep bed. However, precise measurement of the ions in the effluent solution is usually required since the changes in solution compositions are necessarily small.

Grossman and Adamson (17) and Anderson and Peebles (2) used the shallow bed technique and found diffusion to be the controlling mechanism. They also found that both phases contribute to the mass transfer resistance. David and co-workers (15, 28) have avoided the difficulties in measuring small concentration changes in the solution phase by observing concentration changes in the resin phase. Their method involves monitoring the depletion of a radioactive tracer ion in the resin. They found that both phases contributed to the mass transfer resistance and that the resin phase behaves in the manner which the variable-diffusivity model of Helfferich (22) predicts.

Another method of measuring ion-exchange phenomena is that
of the stirred-tank reactor. This method has the advantage of
easier control of the contact time between resin and solution phases.
Glaski and Dranoff (13) and Smith and Dranoff (45) used the stirred-
tank reactor method with dilute solutions. They found that the ion-
exchange reaction could be described equally well by the mass-action
chemical-kinetic model, ordinary Fick's law (49, p. 18) diffusion,
or a model using a variable diffusivity in the solution phase. How-
ever, their findings are not truly applicable to the packed bed case
since the mass transfer resistance is predominantly in the liquid
phase when dilute solutions are used. Hering and Bliss (23) studied
ion-exchange reactions in a stirred batch reactor with concentrated
solutions. Their experiments were designed so that the major re-
sistance would be in the resin phase. They found the variable dif-
fusivity model of Helfferich more accurate than the Fick's law model.

In analyzing the ion-exchange process, most investigators
have assumed a constant diffusivity or mass transfer coefficient in
the resin phase. Helfferich and Plesset (22) have shown this to be
a simplification of the actual case. From consideration of the elec-
tric potential driving forces as well as the diffusional driving forces,
they have shown that the counter diffusivity of a given ion pair de-
pends on the ionic composition of the resin. They have solved the
shallow-bed problem with this model by numerical methods. Al-
though they did not obtain an analytical solution, they have presented
graphical solutions and approximation formulas. It is interesting to note that Vermeulen (51) and Cooper (9) have suggested the use of a quadratic concentration driving force model for the irreversible exchange of ions where the major resistance is in the solid phase. It appears that this is a special case of the Helfferich variable-diffusivity model when divalent ions displace monovalent ions from the resin and the diffusivity of the monovalent ions is much greater than that of the divalent ions.

Consideration of the various types of analyses applied to ion-exchange phenomena indicated a graphical method as the best approach to the case of countercurrent ion-exchange. The flexibility and accuracy of the graphical technique recommended its use.

Although the transient solutions (1, 5, 20, 43, 48) are of theoretical interest and apply to fixed bed operations, they do not apply to countercurrent ion-exchange. This is due to the time independent nature of continuous operations once steady state has been achieved.

The analytical solutions for the case of a steady-state breakthrough curve (14, 31, 35, 37) are not universally applicable to countercurrent ion-exchange. These solutions apply only to the case where the equilibrium relationship is favorable to the exchange of the two ions.

It was also found that ion-exchange operations should be dependent on variable diffusion coefficients. A mathematical model
describing countercurrent ion-exchange should therefore account for these effects. As a result a graphical method similar to those used for other countercurrent operations was modified to incorporate the effects of variable diffusion coefficients on countercurrent ion-exchange.

Apparatus for Continuous Countercurrent Ion Exchange

Various means have been suggested by which ion exchange operations can be carried out in a continuous countercurrent manner. Most of these methods rely on either a cascade of mixer-settlers or a columnar arrangement in which the two phases can be passed countercurrent to one another.

Lewis (29) has operated and evaluated a cascade of mixer-settlers. He avoided the problem of transferring the resin from one tank to the next by periodically draining the solutions from the tanks and transferring the solutions to the next tank in the cascade. This method required that the feed point and product withdrawal point also be changed from tank to tank. The chief drawback to the use of mixer-settlers is the mechanical complexity of the apparatus.

This is especially true when a large number of stages is required for a difficult operation.

Use has also been made of columns in which the resin is not confined in a packed bed. Selke and Bliss (44) caused the resin to
fall freely countercurrent to a rising flow of solution in small
diameter columns. This procedure worked well for columns on the
order of one centimeter in diameter. However, in larger columns,
turbulence develops, except at very low resin flow rates, and the
operation becomes equivalent to a single stage stirred reactor.

McNeil, Swinton and Weiss (33), Grimmett and Brown (16) and
Turner and Church (50) have used sieve trays to regulate the flow of
the resin phase in columns. These devices are similar to those used
in gas-liquid operations. The heavier resin flows across the trays
and descends to the tray below through downcomers. Simultaneously,
the lighter liquid phase rises through the perforated trays.
Grimmett and Brown (16) and Wiess, et al. (33) applied cyclic, hy-
draulic pulses to the apparatus to fluidize the resin and aid its flow
through the column.

Another method of preventing turbulent mixing was employed
by Olin, Koenig and McCarthy (39). They used a spinning cylin-
der whose axis was collinear with the axis of the column. When
the concentric cylinder was rotated at the correct angular
velocity, toroidal eddies resulted that reduced other forms of
turbulence in the column. This caused the resin to settle more
uniformly through the column than it would without the spinning
cylinder.

Heister, Fields, Phillips and Radding (19) used a column in
which the resin traveled down the column in a settled condition. Movement of the resin depended on the difference in density between the resin and solution phases. Due to the small difference in densities, this type of device is limited to low throughputs since fluidization of the resin bed completely disrupts the operation.

It is desirable to avoid the disadvantages of turbulence or low throughput that are common to operations where the resin is not constrained in the column. Several methods of moving the resin as a packed bed have been devised. In these devices, the resin is either driven continuously through the column or is moved periodically in a cyclic operation. In those featuring cyclic operation, the resin moves during one part of the cycle and solutions are passed during the other.

A straightforward approach to this problem was taken by McCormack and Howard (32). They contained the resin in a sausage-like string of porous bags. The string of bags was drawn through columns in which the process solutions were passed in a countercurrent direction.

Arehart, Bresee, Hancher and Jury (3) used a hydraulic ram to drive the resin downward through the active section of a vertical column. The ram consisted of a stream of water pumped at a high velocity in the direction of resin flow. The high-velocity stream was drawn off and recycled above the active section of the column.
Resin was metered from the bottom of the column to control the resin flow rate.

A cyclic jerked bed contactor was devised by Higgins and Roberts (24). In this device, the resin was confined in a column between two resin valves. During part of the cycle, the resin valves were closed and solution was passed downward through the packed bed of resin. After an appropriate feeding interval, the solution inlets and outlets were closed as the first part of the cycle ended. In the second half of the cycle, the resin valves were opened and a slug of resin was forcibly injected at the bottom of the column. After the upward movement of the resin, the resin valves were again closed and the cycle completed. At the present time, this is probably the most widely used of the continuous countercurrent ion-exchange devices.

Devices that moved the ion exchange resin downward and the solution upward have been devised by Porter (38) and Yomiyama (4). Both devices used the pressure of the incoming feed solution to drive the resin. The feed point was near the bottom of the column and as feeding progressed, the bed separated and a quantity of spent resin was metered out at the bottom of the column. After an appropriate amount of feed had been passed, the solution flow was shut off, the solution was drained from the bottom of the column and a resin valve at the top of the column was opened. As the volume in the column
tended to decrease, due to the drainage of solution, resin was
drawn into the column from a reservoir above the valve. When the
column was again filled with resin, the solution outlet and resin
valves were closed, and feeding resumed. In this way, continuous
but cyclic operation was achieved.

In considering the various methods available for carrying out
countercurrent ion-exchange, the confined bed techniques seemed
most advantageous. However, the systems employing cyclic move-
ment of confined resin beds, as found in the literature, all operate
on relatively long time cycles. As a result, it was decided that a
device should be constructed in which a confined bed would be moved
in a more nearly continuous manner.
THEORY

In countercurrent mass transfer operations in a packed bed, the transfer of material from one phase to the other takes place under conditions that cannot be described exactly. Therefore, a simplified model is used to describe the more complex situation. The transfer unit theory has been found to work well for countercurrent, packed-bed operations in general and has been suggested by several investigators as appropriate for packed-bed ion-exchange operations (14, 31, 35, 40, 54). Although the moving resin becomes the packing in a countercurrent ion-exchange operation it was felt that a modified transfer unit theory should apply.

It has been shown that ion-exchange operations are subject to the effects of variable diffusion coefficients. Helfferich and Plesset (22) have presented a variable diffusivity model for the counter diffusion of ions in ion-exchange resins. Dranoff and co-workers (13, 45) have found that the liquid phase is also affected by differences in the diffusivities of the counter-diffusing ions. It was found that with the use of simplifying assumptions, provision could be made in a modified transfer unit model for these variable diffusivity effects.

Transfer Unit Theory

The transfer unit theory is based on the assumption that at a
given point in a column the mass transfer rate is proportional to a concentration difference. In many cases the operation can be considered as being controlled by one phase or the other if most of the resistance to mass transfer lies in that phase. If the resistance to mass transfer is negligible in one phase, there will be a negligible difference between the bulk concentration of that phase and its interfacial concentration. As a consequence, the interfacial concentration of the phase containing the major resistance to mass transfer can be taken as being that which is in equilibrium with the other phase. If one assumes that the major resistance to ion exchange lies in the resin phase, the concentration driving force will be \((Y^*-Y)\), where \(Y^*\) and \(Y\) are the equilibrium and bulk average resin-phase equivalent fractions corresponding to the solution phase equivalent fraction \(X\). For a system with two cations \(A\) and \(B\) the equivalent fraction \(Y_A\) is the number of equivalents of \(A\) divided by the total number of equivalents of \(A\) and \(B\).

In accordance with the transfer unit theory the fluxes of the exchanging ions are assumed to be equal to the equivalent fraction driving force multiplied by the appropriate overall mass transfer coefficient \(K_R\) \((12)\).

\[
z_A J_A = - z_B J_B = K_R (Y^*-Y) \quad \text{(1)}
\]

In Equation 1 \(Y\) and \(Y^*\) are the equivalent fractions, \(z_A\) is
is the valence, and \( J_A \) is the molar flux of ion A.

With Equation 1 as an expression for the rate of ion transfer between the two phases, a material balance can be made on a section of the column. Taking an arbitrary section of the column at a distance \( z \) from one end and of height \( dz \), expressions can be written for the corresponding resin phase equivalent fractions \( Y \) and \( Y + dY \). If the resin moves through the column at a rate \( R \) meq/cm\(^2\) sec, component A enters the section at \( z \) with the rate \( RY \). Also A leaves the section at \( z + dz \) with a rate \( R(Y + dY) \). As the resin travels through the section between \( z \) and \( z + dz \), it absorbs A at the rate \( K_R (Y^* - Y) adz \) where \( adz \) is the interfacial area for a section of column with one square centimeter cross section and height \( dz \). In a column operating at steady state, the input of A must equal the output of A or

\[
RY + K_R (Y^* - Y) adz = R(Y + dY).
\]

Cancelling like terms and solving for \( dz \) results in

\[
dz = \frac{R}{K_R a} \frac{dY}{(Y^* - Y)} \quad (2)
\]

In situations where the resistance to mass transfer is of the same order in the two phases, \( K_R \) can be found in terms of \( k_R \) and \( k_L \), the mass transfer coefficients for the resin and liquid
phases, respectively. If it can be assumed that the resistances in the two phases are additive, it can be shown (49, p. 86) that

\[
\frac{1}{K_R} = \frac{1}{k_R} + \frac{m}{k_L}
\]  

(3)

In Equation 3 \(m\) is the slope of the equilibrium curve at the point under consideration. If \(m, k_L\) and \(k_R\) are constant, or nearly constant, throughout the column, Equation 2 can be used with \(K_R\) evaluated from Equation 3. However, in the case of ion-exchange, the assumption of a constant \(m\) often does not apply. For the point in the column where the average equivalent fractions are \(X\) and \(Y\), the slope of the equilibrium curve is approximated by

\[
m = \frac{Y^* - Y}{X^* - X}
\]  

(4)

as shown in Figure 1. Also, the slope of the operating line representing the countercurrent operation is

\[
\frac{dY}{dX} = \frac{L}{R}
\]  

(5)

Substituting Equations 3, 4 and 5 into Equation 2 gives

\[
dz = \frac{R}{k_R a} \frac{dY}{(Y^* - Y)} + \frac{L}{k_L a} \frac{dX}{(X^* - X)}
\]  

(6)

Before Equation 6 was integrated, \(R/k_R a\) and \(L/k_L a\)
Figure 1. Typical Operating Diagram
were examined. Although the corresponding terms in gas-liquid absorption can usually be considered constant, the possibility of variations in the diffusivities in both phases precludes this assumption in the case of ion-exchange. Also, mass transfer in the resin phase takes place in the solid particles, and so, a relationship between the rate of mass transfer and the physical and geometrical properties of the resin was derived.

**Diffusion in the Resin Phase**

The results of basic investigations of resin-phase-controlled ion-exchange operations are often presented in terms of ionic diffusivities (15, 23, 28). Therefore $k_Ra$ should be expressed in terms of an ionic diffusivity. Such a relationship would be the result of a rigorous analysis of the operation in terms of the ionic diffusivities and concentration gradients in the resin particles. Although no solution for the exact situation was found, consideration of a simplified case gave a relationship for $k_Ra$ in terms of an ionic diffusivity and the average radius of the resin particles.

If isotopic ion exchange in a situation of equi-equivalent, countercurrent flow of resin and solution is considered, a simplified situation results. The resin will have no selectivity for one isotope or the other since the isotopes have the same chemical properties. Therefore, the equilibrium curve on an equivalent-fraction
phase-equilibrium diagram will be a straight line between \((0, 0)\) and \((1, 1)\). The condition of equal equivalent resin and solution flow rates requires that the operating line also be a straight line with a slope of one on an equivalent fraction, phase diagram. Thus, the equilibrium and operating curves will be straight and parallel lines. Since the diffusivities of the two isotopes are essentially the same, a constant diffusivity can be used. Lastly, if the column is long enough and the resin and solution rates are low enough, steady state concentration gradients should build up in the resin particles and be maintained throughout most of their travel through the column.

Time dependent diffusion in a sphere with a constant diffusivity is described by the partial differential equation \((10, \text{p. 84})\).

\[
\frac{\bar{D}}{\bar{D}_{AB}} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial Y}{\partial r} \right) = \frac{\partial Y}{\partial t} \tag{7}
\]

In the case of the exchange of ionic isotopes in an operation where the equilibrium and operating lines are parallel, one would expect constant fluxes of the ions between the two phases. This leads to the assumption that \(\partial Y/\partial t\) is constant and independent of \(r\) and \(t\) throughout most of the column. With this assumption, Equation 7 can be written as an ordinary differential equation

\[
\frac{\bar{D}}{\bar{D}_{AB}} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dY}{dr} \right) = C \tag{8}
\]
Since $D_{AB}$ is assumed to be constant, Equation 8 can be integrated with the conditions

$$\frac{dY}{dr} = 0 \quad \text{at} \quad r = 0$$

$$Y = Y^* \quad \text{at} \quad r = r_p$$

The result is

$$Y_r = Y^* - \frac{C}{6D_{AB}} \left( \frac{r^2_p}{r^2} - r^2 \right)$$  \hspace{1cm} (9)

where $Y_r$ is the resin phase equivalent fraction at a given radius, $r$. The volume average equivalent fraction can also be found by integrating $Y_r \, dV$ over the total volume of the resin bead to get

$$Y = Y^* - \frac{C}{D_{AB}} \frac{r^2_p}{15}$$  \hspace{1cm} (10)

The resin phase isotopic exchange problem can also be solved in terms of a mass transfer coefficient $k_R$. The mass transfer coefficient can then be related to the diffusivity and the particle radius. If the input of $A$ to a resin bead is set equal to the accumulation of $A$ in the bead, one gets

$$4\pi r^2_p k_R (Y^*-Y) = \frac{4}{3} \pi r^3_p Q_W \frac{\partial Y}{\partial t}$$  \hspace{1cm} (11)

where $Q_W$ is the resin-phase ionic capacity based on the volume
of the wet polymer alone.

It is more convenient to consider ion-exchange operations in terms of the wet bulk volume capacity of the resin $Q_B$. The wet bulk volume capacity of the resin is equal to the product of the wet polymer capacity, $Q_W$, and the fraction of the bed occupied by the resin, $(1-\epsilon)$. With the above relationship and again making the assumption that $\partial Y/\partial t$ is constant, Equation 11 can be simplified to

$$\frac{\partial Y}{\partial t} = C = \frac{3}{r_p} \frac{k_R (1-\epsilon)}{Q_B} (Y^* - Y)$$

(12)

The constant, $C$, can now be eliminated by substituting Equation 12 into Equation 10. The result reduces to

$$k_R = \frac{5D_{AB} Q_B}{r_p (1-\epsilon)}$$

(13)

The relationship of the interfacial area in a packed bed to the average particle radius was estimated by considering the resin beads as uniform spheres. It can be shown that the area to volume ratio in a bed of uniform spheres with void fraction $\epsilon$ is

$$a = \frac{3(1-\epsilon)}{r_p}$$

(14)

as shown in Appendix A. The product of Equations 13 and 14 is
Equation 15 was assumed to hold for the more complicated case where \( (Y^*-Y) \) is not constant and \( \overline{D}_{AB} \) varies with the composition of the resin phase. The variation of the resin phase diffusivity \( \overline{D}_{AB} \) was accounted for as indicated in the following paragraphs.

Helfferich and Plesset (22) have shown that the counter-diffusivity of an ion pair in an ion-exchange resin is a function of the diffusivity of each of the ions involved and the ionic composition of the resin. Their derivation is based on the premise that counter-diffusion of ions with different diffusivities will generate electric potential gradients in the resin. The generation of these potential gradients is due to the tendency of the faster ions to diffuse away from the oppositely charged sites in the resin faster than they can be replaced by the slower ions. The effect of the electric potentials generated can be accounted for by applying the Nernst-Planck equation (21, p. 268) for the fluxes of the two ions.

\[
J_A = J_{A_{\text{diff.}}} + J_{A_{\text{el.}}} = -\overline{D}_A (\text{grad} \overline{c}_A + z_A \overline{c}_A \frac{F}{R_G T} \text{grad} \phi)
\]

(16)

\[
J_B = J_{B_{\text{diff.}}} + J_{B_{\text{el.}}} = -\overline{D}_B (\text{grad} \overline{c}_B + z_B \overline{c}_B \frac{F}{R_G T} \text{grad} \phi)
\]

(17)
The conditions that an equal number of equivalents of the two ions must be exchanged and that all the active sites in the resin be neutralized lead to the conditions:

\[ z_A J_A + z_B J_B = 0 \]  \hspace{1cm} (18)

\[ z_A c_A + z_B c_B = Q_W \]  \hspace{1cm} (19)

Elimination of the electric potential terms between Equations 16 and 17 and application of the Equations 18 and 19 results in

\[ J_A = - \frac{D_A D_B}{D_B A} (z_A A z_B B + z_B B z_A A) \frac{\nabla c_A}{\nabla c_B} \quad \text{grad} \ c_A = -D_A \text{grad} \ c_A \]  \hspace{1cm} (20)

As indicated in Equation 20, the bracketed term can be considered as a variable diffusivity.

The variable diffusivity term in Equation 20 can be simplified by introducing a diffusivity ratio, converting the concentration terms to equivalent fractions and applying the appropriate values of the valences involved. These terms are:

\[ \frac{D_B}{D_A} = \frac{D_{Na}}{D_{Cu}} = a \]

\[ Y = \frac{z_A c_A}{Q_W} \]
1 - \( Y \) = \( z_B c_B / Q_W \)

\[ z_A = z_{Cu} = 2 \]

\[ z_B = z_{Na} = 1 \]

Introduction of these terms reduces Equation 20 to

\[
\overline{D}_{AB} = \frac{\overline{D}_{Na, Cu}}{a + (2 - a) Y} = \frac{\overline{D}_{Na}(Y + 1)}{a + (2 - a) Y}
\]  \( (21) \)

It was assumed that the variable counter diffusivity does not drastically alter the relationship of \( k_R^{a} \) to \( r_p \) and \( \overline{D}_{AB} \), and so, Equation 21 was substituted in Equation 15. Equation 15 was then substituted in Equation 6 along with the relationship that the resin velocity \( V_R \) is equal to \( R/Q_B \) to get, for the resin phase term

\[
\frac{R}{k_R^{a}} \frac{dY}{(Y^* - Y)} = \frac{r_p^2 V_R}{15 \overline{D}_{Na}} \frac{(a + (2 - a) Y)}{(Y + 1)(Y^* - Y)} dY
\]  \( (22) \)

**Diffusion in the Solution Phase**

Diffusion in the solution phase can be analyzed in much the same way as the case of ionic counter-diffusion in the resin phase. However, since the co-ion as well as the two counter-ions are mobile in this case, a Nernst-Planck equation must be written for the co-ion also. Dranoff and co-workers (13, 45) have derived a variable
counter-diffusivity for the case of monovalent ions. Their derivation was extended to the case where all three ions are of arbitrary valence.

For counter-diffusing cations A and B with common anion C the Nernst-Planck equations are:

\[ J_A = -D_A \left( \nabla c_A + z_A c_A \frac{F}{R_G T} \nabla \phi \right) \]  \hspace{1cm} (23)

\[ J_B = -D_B \left( \nabla c_B + z_B c_B \frac{F}{R_G T} \nabla \phi \right) \]  \hspace{1cm} (24)

\[ J_C = -D_C \left( \nabla c_C - z_C c_C \frac{F}{R_G T} \nabla \phi \right) = 0 \]  \hspace{1cm} (25)

There can be no net current in the system which requires that

\[ z_A J_A + z_B J_B + z_C J_C = 0 \]  \hspace{1cm} (26)

Also, the system must remain electrically neutral, or

\[ z_A c_A^c + z_B c_B^c = z_C c_C^c \]  \hspace{1cm} (27)

In this situation, in contrast to the case of diffusion in the interior of the resin particles, \( c_C \) is not necessarily constant and can vary across the solution phase diffusion film. In the resin-phase diffusion case, the fixed ionic sites corresponding to \( c_C \) are held stationary by the resin matrix. For this reason, no equation corresponding to 25 is needed in the case of resin phase diffusion.
Equations 23 through 27 can be combined to obtain a flux equation for component A or component B that is free of the electric potential term. This can be done by solving Equation 25 for \( \frac{F}{RT} \) \( \text{grad}\phi \), substituting the result into Equation 23 and 24, and solving the modified Equations 23 and 24 simultaneously for \( J_A \) under the conditions shown in Equations 26 and 27. The result is

\[
J_A = \frac{D_A D_B (z_A^2 c_A + z_B^2 c_B + z_C^2 c_C)}{D_A z_A^2 c_A + D_B (z_B^2 c_B + z_C^2 c_C)} \text{grad} c_A
\]  

(28)

Substitution of B for A and A for B in Equation 28 results in the corresponding flux equation for ion B. If Equation 28 is considered as a flux equation of the form

\[
J_A = -D_{AB} \text{grad} c_A,
\]

the bracketed term in Equation 28 can be considered as a variable diffusion coefficient.

\[
D_{AB} = \frac{D_A D_B (z_A^2 c_A + z_B^2 c_B + z_C^2 c_C)}{D_A z_A^2 c_A + D_B (z_B^2 c_B + z_C^2 c_C)}
\]  

(29)

The variable diffusivity defined in Equation 29 can be reduced to a simpler expression by substituting the appropriate valences and replacing the concentration terms with equivalent fractions. Letting
A, B and C represent Cu$^{++}$, Na$^+$ and SO$_4^{=}$, respectively

\[ z_A = 2 \]
\[ z_B = 1 \]
\[ z_C = 2 \]

\[ X = \frac{z_A c_A}{z_C c_C} \]
\[ (1-X) = \frac{z_B c_B}{z_C c_C} \]

On substitution of the above terms, Equation 29 reduces to

\[ D_{AB} = \frac{D_{CuNa}(X+3)}{(2D_{Cu} - D_{Na})X + 3D_{Na}} \] (30)

The corresponding expression for the reverse operation is

\[ D_{BA} = \frac{D_{NaCu}(X+3)}{(2D_{Na} - D_{Cu})X + 2D_{Cu} + D_{Na}} \] (31)

Equation 28 cannot be integrated for the case of mass transfer in a packed bed due to the complex nature of the flow system and unknown boundary conditions. However, one should be able to compare the relative magnitudes of the ionic fluxes in terms of the differences in the counter diffusivities for the alternate operations.

In order to do this, \(D_{Cu-Na}\) and \(D_{Na-Cu}\) must be related to
the correct directions of ionic transfer.

If $D_{Cu}$ is smaller than $D_{Na}$, Equations 23 and 24 show that the ionic flux of $Cu^{++}$ will be aided and the ionic flux of $Na^{+}$ retarded by the electrical potential, since the two fluxes must be equal but of opposite sign. Equation 25 shows that the anions, $SO_4^-$, will experience a concentration gradient in the same direction as the electric potential gradient. As a result, the total solution concentration will experience a concentration gradient in the same direction as the concentration gradient of the slower ion.

For $Cu^{++}$ diffusing from the solution to the resin, the above reasoning predicts a dilution in the diffusion film between the resin-solution interface and the bulk of the solution. The result of dilution in the diffusion film is a reduction of the diffusion rate. Therefore, diffusion of the slower ion from the solution to the resin would be slower than the reverse operation for a given concentration driving force. Examination of Equations 30 and 31 shows that if $D_{Cu}$ is smaller than $D_{Na}$, $D_{CuNa}$ is smaller than $D_{NaCu}$. Therefore, $D_{CuNa}$ corresponds to $Cu^{++}$ diffusing from the solution to the resin and $Na^{+}$ diffusing from the resin to the solution.

The alternate operation of $Na^{+}$ displacing $Cu^{++}$ on the resin is governed by $D_{NaCu}$.

Values of $D_{Cu}$ and $D_{Na}$ can be determined from electrochemical data. Lin, et al. (30) suggest that the ionic diffusivity
can be related to the equivalent conductance of an ion at infinite dilution, \( \lambda^0_A \), by the Nernst equation

\[
D_A = \frac{R G T}{z_A F^2} \lambda^0_A
\]  

(32)

In Equation 32, \( \lambda^0_A \), in \( \text{cm}^2/\text{eq. ohm} \), corresponds to \( D_A \) in \( \text{cm}^2/\text{sec} \) if \( R_G \) is 8.313 joules/gmole°K and \( F \) is 96,500 coulombs/g equivalent.

The direction dependent diffusivities derived above can be incorporated in a modified j-factor model. Carberry (6) has found that liquid phase mass transfer data for steady flow in packed beds can be correlated with the relationship

\[
J_D = \frac{k_L}{L} \epsilon Sc^{2/3} = 1.15 \text{ Re}^{-1/2}
\]

(33)

This relationship has been verified by Gopala Rao (15) for the exchange of \( \text{Cu}^{++} \) and \( \text{Na}^+ \) on Dowex 50W-X8 ion exchange resin.

In the present work, all the experimental runs were made with cupric sulfate and sodium sulfate solutions between 0.2 and 1.0 normal. In this concentration range, the Schmidt numbers were essentially constant. Therefore, the Schmidt number exponent could not be checked experimentally and was taken as 2/3. The Reynolds number, however, varied between 1.2 and 12.2 for the various runs.
Therefore, the Reynolds number coefficient and exponent were given the arbitrary values $p$ and $q$ respectively. It was expected that $p$ and $q$ should have different values than 1.15 and 0.5 as shown in Equation 33 due to the pulsed flows used in the experimental runs.

From Equation 33, with the substitution of the constants $p$ and $q$ and the definition for the height of a solution phase mass transfer unit,

$$H_{TL} = \frac{L}{k_L a} = \frac{\epsilon}{pa} Sc^{2/3} Re^q$$

(34)

Although an average diffusivity was used to estimate the magnitude of the Schmidt number, $H_{TL}$ was assumed to vary as a function of the variable counter-diffusivities defined above. Assuming that $k_L$ is proportional to $(D_{AB})^n$, the transfer unit heights for alternate operations with identical Reynolds number, Schmidt number and interfacial areas can be related by

$$\frac{H_{TLAB}}{H_{TLBA}} = \left(\frac{D_{BA}}{D_{AB}}\right)^n$$

(35)

Since $H_{TL}$ was assumed to depend on the direction of transfer of the slower ion, $H_{TL}$ as defined in Equation 34 was taken as the arithmetic average

$$H_{TL_{av.}} = \frac{H_{TLAB} + H_{TLBA}}{2}$$

(36)
Solving Equations 35 and 36 for \( H_{TL_{AB}} \) in terms of \( H_{TL_{av}} \),
\( D_{AB} \) and \( D_{BA} \) gives

\[
H_{TL_{AB}} = \frac{2H_{TL_{av}}}{1 + \left(\frac{D_{AB}}{D_{BA}}\right)^n}
\]  

Substituting Equation 37 in Equation 34 gives

\[
H_{TL_{AB}} = \frac{2}{1 + \left(\frac{D_{AB}}{D_{BA}}\right)^n} \frac{\varepsilon}{\rho a} \frac{Sc^{2/3}}{Re} q^n
\]  

Evaluation of the Operating Data

With the substitution of Equation 38 for \( L/k_s a \) in the solution phase term, and of Equation 22 for the resin phase term, it was possible to write Equation 6 in integrated form as

\[
z_{2} - z_{1} = \frac{r^2}{15} \frac{Y}{D} \int_{Y_1}^{Y_2} \left[ \frac{\alpha - (a-2)Y}{(Y+1)(Y^*-Y)} \right] dY + H_{TL_{AB}} \int_{X_1}^{X_2} \frac{X_2}{(X-X^*)} dX
\]  

In order to evaluate the integrals in Equation 39 values of \( (Y^*-Y) \) as a function of \( Y \) and \( (X-X^*) \) as a function of \( X \) were required for a given operation. These relationships can be found by constructing an operating diagram similar to the one shown in Figure 1 and measuring the indicated equivalent fraction differences.
graphically. Graphical measurement of the equivalent fraction differences is preferable to the use of analytical expressions since ion exchange equilibria are often difficult to describe accurately by analytical expressions. The equilibrium relationships for the systems investigated were measured experimentally as shown in Appendix B.

The operating line for a given run can be located on the appropriate equilibrium diagram by connecting the points corresponding to the solution and resin phase equivalent fractions at $z_1$ and $z_2$ with a straight line. If conditions are such that only ions and no salt molecules diffuse between the solution and resin phases, and the feed rates of resin and solution to the column are constant, the steady-state operating curves will be straight lines. This can be shown by taking a material balance on a section of the column. Let the solution and resin phase equivalent fractions be $X$ and $Y$ at the point $z$ and $(X+dX)$ and $(Y+dY)$ at $(z+dz)$. If the resin and solution flow rates in the column are $R$ and $L$ respectively, a material balance at steady state results in

$$\frac{dY}{dX} = \frac{L}{R} \quad (40)$$

Under ideal conditions every equivalent of a given ion that transfers from one phase to the other will be replaced by an equivalent of the other ion. $R$ and $L$ are therefore constant and Equation 40 is
the differential equation of a straight line.

In reality, ion-exchange resins do absorb salt molecules from solutions, but generally in small quantities as predicted by the Donnan potential theory (21, p. 34). This was verified by Subba Rao (46) who found that Dowex 50W-X8 absorbed 0.15 meq. salt per gram of dry resin from one normal cupric chloride-sodium chloride solutions. Assuming Dowex 50W-X8 absorbs a like amount of salt from one normal cupric sulfate-sodium sulfate solutions, the change in slope of the operating line due to salt absorption can be estimated.

If the resin entered the active section with no absorbed salt and left the column with 0.15 milliequivalents of salt per gram of resin, an equal amount of salt would have been removed from the solution. Taking an input resin rate about equal to the specific dry-weight capacity of the resin or $4.30 \text{ meq/cm}^2\text{min}$, the resin would leave the column with $4.30 + 0.15 = 4.45 \text{ meq/cm}^2\text{min}$. For a designed operating line slope of one, a solution rate equal to the input resin rate of $4.30 \text{ meq/cm}^2\text{min}$ would have been chosen. Due to loss of salt to the resin, the solution would have left the column at the resin input end at $4.30 - 0.15 = 4.15 \text{ meq/cm}^2\text{min}$. The slope of the operating line for the above situation can now be calculated at the resin input and solution input ends of the column as $(L/R)_1$ and $(L/R)_2$, respectively.
\[
\left( \frac{L}{R} \right)_1 = \frac{4.15}{4.30} = 0.9651
\]

\[
\left( \frac{L}{R} \right)_2 = \frac{4.30}{4.45} = 0.9663
\]

Although the operating line slopes differ by about 3.5\% from the desired \( L/R \) of 1.00, the difference in \( L/R \) at the two ends of the column is only 0.12\%. Since this is the maximum deviation expected for the experiments to be run, the assumption of a straight operating line is valid.

With the measured values of \( (Y^* - Y) \) and \( (X - X^*) \) from the operating diagrams, the values of the integrals in Equation 39 can be determined. The integrals can be evaluated by plotting the values of the integrand over the appropriate interval and determining the area under the resulting curve.

With the above method for performing the integrations indicated in Equation 39, the operating data from a series of experiments can be used to evaluate the unknown quantities in Equations 38 and 39. These unknown quantities are \( \overline{D_{Na}} \) and \( a \) in the resin phase term of Equation 39 and \( n, p \) and \( q \) in Equation 38 for the evaluation of \( ^H_{TL} \) in Equation 39.
APPARATUS

In order to carry out a continuous countercurrent ion-exchange operation with a wide range of flow conditions, a contactor which employs a moving packed bed is desirable. Arehart, Bresee, Hancher and Jury (3), Higgins and Roberts (24), Porter (38) and Yomiyama (4) have described such devices. The apparatus of Jury, et al., and of Higgins and Roberts are quite complicated mechanically. On the other hand, those of Porter and Yomiyama move the resin in large discontinuous steps. These features were considered as undesirable; and therefore, it was decided that a new ion-exchanger should be devised.

The equipment used in this study was similar to those of Porter (38) and Yomiyama (4) in that the resin moved downward in a column and was constrained by a resin valve at the top of the column. However, a hydraulic pulsing device was used to drive the resin rather than a manipulation of process solution flow rates.

As can be seen in Figure 2, a cylindrical column served as both a container for the moving resin and solution phases and also as the body of a resin pump. A constriction and ball at the top of the column formed a resin check valve. This valve allowed resin to flow only in the downward direction. At the bottom of the column, a screened, cone-shaped member allowed a hydraulic pulse to enter
positive pulse →

Figure 2. Resin Pumping Action in Columns

negative pulse ←
and leave the column.

During the positive part of the pulse cycle, the ball seated and resin was firmly held in the column. Process solution could then pass upward through the packed bed and out through a screened member in the resin valve. At the bottom of the column, the pressure of the incoming pulse caused the bed to divide and a quantity of resin to be ejected through a resin outlet line.

As the pulsing device began the negative half of its cycle, liquid was drawn out through the screened member at the bottom of the column. This caused the bed to be drawn down to replace the volume of resin ejected during the positive half of the cycle. Downward travel of the resin bed caused the check valve to open and resin to enter the column from a reservoir above the valve. As the negative pulse ended and the positive pulse began, the valve ball seated and the cycle was complete. The solution effluent line was equipped with a check valve to prevent solution from flowing back into the column on the negative pulse.

During the complete pulse cycle, feed solution was metered into the column. However, the feed rates were much smaller than the flows caused by the pulser and so they did not interfere with the pumping action in the column.

This device did not generate constant velocity flows of resin and solution. However, the overall effect was countercurrent flow
of resin and solution in a continuous operation. Also, the pulse rate was rapid enough, i.e., on the order of ten revolutions per minute, that the stepwise movement of the resin was incremental in nature.

Figure 3 is a schematic diagram of the apparatus. Two identical columns were used, one for operating on the process solution, and one for regenerating the resin. In this case, a solution of cupric sulfate represented the process stream and Dowex 50W-X8 in the sodium form constituted the regenerated resin.

Each column was composed of the following sections (from top to bottom): a resin reservoir, a resin valve, an active section, a dead section, a rinsing section and a bottom chamber. The resin valves, bottom chambers, solution feed plate, solution outlet plates and sample plates were fabricated of stainless steel, while the columns were constructed of three-inch Pyrex pipe.

The reservoirs consisted of glass tees and three-foot sections of glass pipe. A two-foot section of two-inch Pyrex pipe was suspended in the upper part of the reservoir in column one. Resin entering column one from column two was led into the two-inch pipe. Here, it encountered an upward flowing stream of water which was introduced through an inlet port in the side arm of the glass tee. The purpose of this arrangement was to remove any fine particulate solids that had accumulated due to physical attrition of the resin.
Figure 3. Schematic Drawing of Columns and Flow Pattern
The overflow from this classifier arrangement descended through a polyethylene tube and passed out through a port in the glass tee. Column two had no classifier as one wash per cycle was found to be sufficient. However, column two was equipped with a water inlet and overflow to maintain a constant liquid level in the column. After the resin passed through the upper sections, it settled in the bottoms of the reservoirs prior to passage into the active sections.

The resin valves were constructed as shown in Figure 4. The valve body consisted of two intersecting cones in a three-inch, sheet-metal cylinder. The upper cone and the cylinder were fabricated from 16-gage stainless steel sheet, and the lower cone from 20 x 150 mesh wire cloth. The lower cone was porous so that solutions could pass out of the column at this point, but resin would be retained. A one-and-one-half-inch floating ball, in this case a ping pong ball, was located just below the intersection of the two conical sections. This ball type check valve limited flow of resin in the column to the downward direction. Flanges for connection to three-inch Pyrex pipe and a three-eighths-inch solution outlet nipple were welded to the body of the valve. Two radial holes were tapped in the lower flange to accommodate resin and solution sampling taps. One-eighth-inch stainless steel pipe nipples were threaded into these holes. The hole for the liquid sample tap was screened at its inner opening to keep resin from leaving the column during extraction of
Figure 4. Detail Drawing of Resin Valve.
the sample. A Pyrex glass stop cock was attached to the resin nipple with a short section of Tygon tubing. A section of Tygon tubing and a pinch clamp served as a solution sampling valve.

The active sections of the columns were located directly below the resin valves. One-, two- and four-foot sections of glass pipe were used for various runs. The lower three-quarters of an inch of each active section was a short stainless steel cylinder. These short cylinders held resin and solution sampling taps similar to those in the lower flanges of the resin valves.

Feed solutions entered the columns through feed plates located at the bottom of the active sections (see Figure 5). As solution entered the plate, it flowed through a large outer channel and was distributed through radial ducts to an inner concentric channel. The inner wall of this channel was 20 x 150 mesh stainless steel, wire cloth which allowed passage of the solution into the resin bed.

Below the feed plate in each column was a six-inch section of glass pipe which acted as a dead section. Flow rates into and out of the column were adjusted so that no solution passed through this section. Its purpose was to separate the active section from a rinsing section in the lower part of the column.

Solution outlet plates separated the dead sections from the rinsing sections below. These plates were identical to the feed plate shown in Figure 5.
Figure 5. Detail Drawing of Feed and Outlet Plates
A rinsing section was located in the lower part of each column for the purpose of allowing removal of any solution adhering to the resin leaving the active section. One-foot lengths of glass pipe were used for these rinsing sections.

The bottom chambers consisted of conical screened members in four-inch, cylindrical cans as shown in Figure 6. A conduit at the base of each can allowed the hydraulic pulse to be applied to the system. The conical member was porous to allow the hydraulic pulse and water rinse stream to enter the base of the resin bed. The small end of the cone intersected a conduit through which resin was ejected on the positive part of the hydraulic pulse. Sixteen-gage stainless steel sheet, 20 x 150 mesh stainless steel wire cloth and standard stainless steel pipe and pipe elbows were used in fabricating the bottom chambers.

The pulser unit, which provided the motive force for moving the resin, contained two, three-inch I. D. Teflon bellows four inches long. These bellows were driven by a variable speed, variable throw, eccentric. A 91 RPM, 3/4 HP gear motor was connected by chain and sprocket drive to an infinitely variable Link Belt gear box. A chain and sprocket drive was also used between the gear box and the crank shaft. With a motor-to-gear box ratio of 1.875:1, maximum and minimum gear box ratios of 2:1 and 1:2, and a gear box-to-crankshaft ratio of 4.09:1, the pulse rate could be varied from
Figure 6. Detail Drawing of Bottom Chamber
5.93 to 23.74 RPM. Variation in pulse amplitude was provided by variable throw cranks that could be set on a zero- to three-quarter-inch radius.

The solution and rinse water streams entering the column were pumped by stainless steel, one-third horsepower centrifugal pumps. The flow rates were controlled with stainless steel, one-quarter-inch needle valves and monitored with FM1048 Manostat, flow meters. The outlet streams were regulated and monitored with identical valves and flow meters. It was found that surge tanks were necessary in the inlet and outlet lines to dampen the variations in flow caused by the action of the hydraulic pulse. Thirty-two-ounce polyethylene bottles with about 50 percent air space, and ball type check valves were placed in the lines between the flow meters and the columns. This arrangement resulted in steady flow through the flow meters.

Nine-gallon, stainless steel oxygen bottles were used as feed-solution and rinse-water reservoirs. This volume was found to be inadequate, so 55-gallon polyethylene drums were connected in series as auxiliaries to the solution feed tanks. The rinse water tanks were refilled periodically throughout the runs. All conduits for either solution or resin flows were either stainless steel or polyethylene.

Initially, it was assumed that the resin pumping rate could be
controlled by variation of the pulse rate and amplitude. Water inlets were also placed in the resin return lines (see Figure 3) for this purpose. A small excess of water greatly reduced frictional forces between the moving resin and the return line wall. It was found that the resin rates could be controlled by adjusting the pulser and the resin-return-line water valves. However, the constant attention required to monitor and adjust the resin rates in both columns made this method impractical. For this reason, resin-rate controllers were installed.

The rate at which resin left column one was controlled by a resin metering device in the resin return line from column one to column two. The meter contained three, one-half-inch diameter, porous cylindrical baskets that were one inch long. The baskets were made to pass under the end of the resin return line, fill with resin, and then discharge the resin into the reservoir of column two. The baskets were held between two rotating disks which were, in turn, held between two stationary plates. The top plate held the terminal end of the resin return line and also had a vent hole at an angular distance of $180^\circ$ from the return line connection. The bottom plate had only a discharge port at an angular distance of $180^\circ$ from the intake. After a $360^\circ$ rotation of the disk-basket assembly, each basket had been filled and emptied once. Thus, the flow through the meter depended on the angular velocity at which the meter was
turned. A driving device with infinitely variable angular velocity was attached to the meter. This allowed precise setting and control of the resin flow rate in column one.

A photo cell-electric pinch cock device was used to control the resin rate in column two. Its purpose was to keep the resin level in the reservoir of column two constant and thus make the resin rates in both columns equal. A photo-electric relay was used to monitor the resin level in the reservoir of column two. When the resin level was above the control point, the light to the photo cell was cut off. This caused the relay, and thus the electric pinch cock, to open. Resin was then pumped at a higher rate out of column two. As the resin level fell below the control point, the photo-electric relay was activated and the pinch cock closed. The pinch cock was adjusted to only partially close the line and thus reduce, but not stop, the resin flow. Proper adjustment of the pinch cock kept the resin level in the reservoir close to the control point. A time-delay relay was included in the photo cell-pinch cock circuit to prevent excessive on-off action caused by slight oscillations of the resin-reservoir level. These oscillations were due to a slight leakage of the hydraulic pulse through the resin valve.
MATERIALS USED IN THE TEST SYSTEM

The objectives of this study were to design, operate and derive design criteria for a continuous countercurrent ion-exchanger. Therefore, it was decided that the system studied should be easy to work with and if possible the subject of previous study. The salts used should be relatively inexpensive, non-corrosive, stable, non-toxic and easily determined quantitatively. Also, the appropriate resin should have good physical and chemical properties. On the basis of these criteria, cupric sulfate, sodium sulfate and Dowex 50W-X8 ion-exchange resin were chosen.

Technical grade cupric sulfate and sodium sulfate are readily available at reasonable cost and were considered pure enough for the proposed operation. Cost was a consideration, since fairly large quantities of the salts were needed to operate columns of the size used in this work.

Both of the salts are inoffensive and easily handled. Sodium sulfate is non-toxic and cupric sulfate is dangerous only if taken internally in relatively large quantities. Both salts are stable and very soluble in water. A major consideration was that they are non-corrosive to the materials used in fabricating the apparatus.

An important reason for choosing the cupric ion was the ease with which it can be determined quantitatively. Volumetric titration
and also colorimetric methods can be used to determine cupric ion accurately. Another factor is that the blue color of solutions of the cupric ion and the amber color of the resin combine to give resin in the cupric form a deep green color. This allowed qualitative estimation of the state of the resin by visual inspection, since the sodium ion is colorless.

Equilibrium data are available for the sodium ion-cupric ion-Dowex 50W-X8 system (46). Since the position of the equilibrium isotherm changes with the total solution concentration for a monovalent-divalent ion system, equilibrium isotherms were required for each solution concentration used. Subba Rao and David (46) studied the sodium chloride-cupric chloride-Dowex 50W-X8 system in the range 0.01N to 4.0N. It was felt that this data should apply to the sodium sulfate-cupric sulfate-Dowex 50W-X8 system. However, early trial runs indicated that the equilibrium data were inapplicable to the system used in this investigation.

An experimental investigation of the equilibrium relationships showed that the data of Subba Rao and David, while correct, were not applicable. This was due to unexpected effects resulting from using sulfate rather than chloride as the common anion. Figure 7 shows a comparison of the equilibrium isotherms for the chloride and sulfate systems at a total normality of one half. Rather than change to the chloride system, which is mildly corrosive to stainless
Figure 7. Comparison of Cu$^{++}$-Na$^+$ Dowex 50W-X8 Equilibria for the 0.5N SO$_4^-$ and Cl$^-$ Systems
steel, it was decided that the use of the sulfate system should be continued. This necessitated an experimental investigation of the equilibrium relationships. The method of Subba Rao and David (46) was used. Since our problem was to evaluate column operation, no theoretical considerations were applied to the equilibrium data. However, the equilibrium data are shown in Appendix B.

Twenty- to fifty-mesh Dowex 50W-X8 was chosen as the ion exchange resin. This resin is manufactured in the form of spherical beads with only a small proportion of malformed or broken particles. The beads are structurally strong and have good resistance to physical attrition. The sphericity and mechanical strength of the resin particles kept attrition and, as a consequence, pressure drops in the bed, at a minimum. The resin is also homogeneous chemically and has a uniform capacity. This is important in a continuous operation, since it is the volumetric flow rate that is controlled. If the ionic capacity of the resin is non-uniform, the resin rate will be non-uniform, on a capacity basis, even if the volumetric flow rate is constant.

Dowex 50W-X8 is one of the most widely used ion-exchange resins. For this reason, it was used as delivered as it would be in an industrial application. The experiments described below were performed after the resin had been cycled in the apparatus for roughly 100 hours during preliminary runs.
EXPERIMENTAL PROCEDURES

Operating Procedure

One of the main objectives of the present study was to determine the effect of resin flow rate on the operating characteristics of the columns. Therefore, experiments were designed by first choosing a resin flow rate and then calculating the appropriate liquid flow rates.

All of the runs were designed to have solution flow rates equal to the resin flow rates, on an equivalent basis. This was done to avoid pinching of the equilibrium and operating lines. The flow rate for a solution of given normality was found by dividing the resin rate in milliequivalents per minute by the solution normality.

To prevent dilution of the feed stream from the rinsing section in the lower part of the column, an excess amount of solution was fed. This excess corresponded to the product of the volumetric resin flow rate and the void fraction of the bulk resin. The water rinse inlet and outlet flow rates were both set at 250 ml/min. Part of the incoming rinse water was lost from the column in the void volume of the exiting resin. This loss was equal to the feed solution excess and allowed the excess feed solution to flow down through the dead section at the same velocity as the resin. After traversing the dead section, the excess feed solution was vented through the
rinse outlet port.

After choosing a resin flow rate and calculating the corresponding solution flow rates, the apparatus was adjusted as follows: The resin meter was set to give the desired resin rate. The rotometer settings were calculated with the aid of calibration tables and correction formulas supplied with the flowmeters to compensate for viscosities and densities other than those of water at 25°C.

Start up of the equipment consisted of the following steps: The solution and rinse water flows were started and run long enough to displace the water in the active sections of the columns. When all of the water was displaced the pulser and resin meter were started. The pulse rate was then adjusted to keep pace with the resin meter. Finally, the liquid flow rates were again adjusted to compensate for any pressure effects caused by the moving resin.

During operation of the columns, the resin rates were monitored by visually observing the progress of dyed resin beads in the column. No trouble was encountered in maintaining the resin rate at a constant value. The liquid flow rates, however, required constant monitoring because of the centrifugal pumps used and the necessity of maintaining the flow rates as constant as possible.

Resin and solution samples were withdrawn periodically during the run from two points in each column. Preliminary experiments indicated that steady state was approached after the resin had
completed one cycle through the system. Therefore samples were taken at the end of one, one and one-half and two resin cycles. Typical calculations used in the design of an experiment are shown in Appendix F.

**Sampling Procedures**

A steady state countercurrent ion exchange operation should, in theory, be represented by a straight line on an operating diagram where concentrations are expressed in equivalent fractions. This was assumed to be the case; and thus the operating lines were located by determining their end points and connecting the end points with a straight line. Therefore solution and resin phase samples were extracted from two fixed points in each column.

The solution samples were withdrawn from sample taps that were screened at their inner ends to prevent the withdrawal of any resin. A portion of solution approximately equal in volume to the internal volume of the sample port was first discarded as it was not representative of the column contents. Fifty-milliliter samples were then tapped off into sixty-milliliter bottles from each of the two solution sample ports in each column.

Obtaining resin samples was complicated by the necessity of rapid removal of the solution entrained with the resin. Before taking a resin sample, a portion about equal to the internal volume
of the sample port was first discarded. The sample was then withdrawn into a plexiglass tube with a screened lower end. This tube was connected to a vacuum system, and as the sample entered the tube, the bulk of the entrained solution was quickly drawn away while the resin was retained on the screen. Twenty to thirty milliliters of water were then quickly flushed through the sample to remove the solution remaining on the surface of the resin particles. The sample tube was then removed from the vacuum system and attached to a 500-milliliter buret. Five hundred milliliters of water were percolated through the sample at 50 milliliters per minute to insure removal of all contaminating solution from the surface of the resin.

Analytical Procedures

Equivalent fractions were used as concentration parameters in both the solution and resin phases. Therefore, analytical techniques were developed to determine the cupric ion content in both phases in terms of their equivalent fractions. In both cases, cupric ion concentrations were determined quantitatively by iodometric titration. Refractive index and dry weight measurements were used to determine the total cation content of the solution and resin phases, respectively.

In the solution phase, the equivalent fraction was found by dividing the normality of cupric sulfate in a given sample by its
total normality. The cupric-sulfate normality was found by iodo-
metric titration of an aliquot of solution. The refractive index of
the solution phase was found to be dependent on both its total nor-
mality and its cupric-sulfate normality. The relationship between
these properties was found experimentally and expressed in the form
of a nomogram. With a knowledge of the refractive index and cupric-
sulfate normality for a given solution, the total normality could be
determined from the nomogram. Thus, measurement of the cupric-
sulfate normality and refractive index of a solution sample allowed
calculation of its cupric ion equivalent fraction. More detailed
descriptions of the procedures used, and of the total-normality
nomogram are given in Appendix C.

Determination of the equivalent fraction of cupric ion in the
resin phase was based on the dry-weight capacity of the resin. Ac-
cordingly, the resin samples were dried overnight at 105°C and
cooled in a desiccator. The resin was then weighed into a 50-milli-
liter buret and the cupric ions were eluted with concentrated sodium
sulfate. The effluent solution, containing the cupric ions, was ti-
trated iodometrically to determine the amount of cupric ion original-
ly in the resin sample. The total ionic capacity of the sample was
found by multiplying the sample's dry weight by the dry-weight
specific capacity of the resin. The resin-phase equivalent fraction
was then the cupric ion content of the sample divided by its total ionic capacity. Details of the analytical procedures used and the determination of the dry-weight specific capacity of the resin are given in Appendix D.
The best values of the unknown quantities in Equations 38 and 39 were determined by a trial and error method. This consisted of choosing values of the unknown quantities, calculating the corresponding column length \((z_2 - z_1)\) from Equations 38 and 39, and comparing the calculated column lengths with those used in the experiments. The values of the unknown parameters that gave the least column-length error were taken as the best values for the system studied.

Several of the quantities appearing in Equations 38 and 39 were directly measurable or could be estimated from data available in the literature. The size dependent parameters \(r_p\) and \(\epsilon\) were measured experimentally. The average particle radius, \(r_p\), was found by microscopic examination of a number of wet resin samples. The packed-bed void volume, \(\epsilon\), was measured by titrating the water required to fill the voids in a known bulk volume of resin. The measured values of \(r_p\) and \(\epsilon\) were used to determine the interfacial area to bulk volume ratio, \(a\). The methods used and the values found are shown in Appendix A.

The solution-phase term in Equation 39 contains three dimensionless groups other than the integral. As shown in Equation 38, the height of a liquid phase mass transfer unit was assumed to be proportional to a direction-of-transfer group, the Schmidt number.
to the two-thirds power, and the Reynolds number to an unknown power.

The counter diffusivities, $D_{Cu,Na}$ and $D_{Na,Cu}$, in the direction-dependent group were found by application of the individual ionic diffusivities $D_{Na}$ and $D_{Cu}$ to Equations 30 and 31. The ionic diffusivities $D_{Na}$ and $D_{Cu}$ were evaluated with Equation 32 and values of $\lambda_{Cu}^0$ and $\lambda_{Na}^0$ as given by Conway (7, p. 145). It was found that the ratio of $D_{Cu,Na}$ to $D_{Na,Cu}$ showed little variation with change in $X$. Therefore the ratio was considered constant and evaluated at $X = 0.5$ for use in Equation 38.

Calculation of the Schmidt number in Equation 38 required values of the viscosity and density of the solution and an average diffusivity of the counter diffusing ions in the solution. An average diffusivity was taken as the arithmetic average of the two ionic diffusivities $D_{Cu}$ and $D_{Na}$. Average values of the solution viscosity and density were also determined. Thus, a constant average Schmidt number was used in correlating the experimental results. The viscosity and density of the solution were taken as the arithmetic averages of these properties for 0.5N cupric sulfate and 0.5N sodium sulfate in aqueous solution.

In evaluating the Reynolds number, the effects of solution concentration on the viscosity and density were taken into account. However, a constant average viscosity and density were taken for
each solution normality investigated. The velocity term in the
Reynolds group was taken as the average solution velocity with
respect to the resin phase, $V_L + V_R$. The velocities $V_L$ and
$V_R$ are the absolute values of the average solution and resin phase
linear velocities, respectively. The values of the known parameters
used in the solution phase Equation 38 and the methods by which
they were obtained are shown in Appendix A.

With the above constants and dimensionless groups considered
as known quantities, $\bar{D}_{Na}$ and $a$ in the resin phase term of
Equation 39 and $n$, $p$ and $q$ in Equation 38 for the determination
of $H_{TLAB}$ remained as unknown quantities. Although $\bar{D}_{Na}$ and
$a$ have been investigated by Gopala Rao (15), they were taken as
unknowns since Rao's data were found for shallow bed experiments
where conditions were quite different from those found in counter-
current ion-exchange.

In fitting the operating data to Equations 38 and 39, the best
values of $\bar{D}_{Na}$, $a$, $n$, $p$ and $q$ were taken as those which, when
applied to Equations 38 and 39 would most closely reproduce the
actual column lengths $(z_2 - z_1)$ used in the experiments. The
following trial and error procedure was used to find $\bar{D}_{Na}$, $a$, $n$,
$p$ and $q$.

1. An arbitrary value of the resin phase diffusivity ratio

$\alpha$ was chosen and the values of the integrals
were evaluated for all the runs.

2. With the values of the integrals, the column lengths used, and the Reynolds numbers corresponding to the various runs, the magnitudes of $\frac{r^2}{\mu Na}$ and $H_{TL_{AB}}$ were approximated for runs of equal Reynolds number and the same direction of ion transfer, but different resin velocity and solution normality. The pairs of runs 61 and 101, 71 and 111, 62 and 102, 72 and 112 satisfied these conditions. In these pairs of runs, the solution flow rates and Reynolds numbers were nearly identical and thus $H_{TL_{AB}}$ should be nearly the same. The value of $\frac{r^2}{\mu Na}$ was considered as the same for all the runs.

Therefore, it was possible to solve the pairs of Equations 39, corresponding to the above mentioned paired runs, simultaneously for $\frac{r^2}{\mu Na}$ and $H_{TL_{AB}}$. The average of the four values of $\frac{r^2}{\mu Na}$ for the four pairs, was taken as a first approximation of the best value for the value of $a$ under consideration.

3. With the average value of $\frac{r^2}{\mu Na}$ as found in Step 2, $H_{TL_{AB}}$ was evaluated for all the runs by rearranging Equation 39 in the form
4. The results of Step 3 were then plotted as $\log_{10} H_{TL_{AB}}$ as a function of $\log_{10} Re$ as shown in Figures 8 and 9. Since $H_{TL_{AB}}$ was assumed to be dependent on the direction of ion transfer, $H_{TL_{Cu, Na}}$ and $H_{TL_{Na, Cu}}$ were plotted on separate graphs. The slopes of the lines and their intercepts at $Re = 1.0$ were used to obtain expressions for $H_{TL_{AB}}$ as a function of Reynolds number of the form

$$H_{TL_{AB}} = C_{AB} Re^q$$

(42)

5. The values of $\frac{r^2}{p} 15 \overline{D}_{Na}$ were recalculated with Equation 42, and the appropriate Reynolds number, and Equation 39 rearranged in the form

$$\frac{r^2}{p} 15 \overline{D}_{Na} = \frac{(z_2 - z_1)^2}{H_{TL_{AB}}} \left( \int_{X_1}^{X_2} \frac{dX}{X - X^*} \right) - V_R \int_{Y_1}^{Y_2} \frac{[a-(a-2)Y]dY}{(Y+1)(Y^*-Y)}$$

(43)
Solution normality $O = 1.0$

Reynolds numbers

Figure 8. Solution Phase Transfer Unit Height as a Function of Reynolds Number for Na$^+$ Displacing Cu$^{++}$ from the Resin
Figure 9. Solution Phase Transfer Unit Height as a Function of Reynolds Number for Cu^{++} Displacing Na^{+} from the Resin
Upon carrying out the above procedure, it was found that end effects had to be considered. This became apparent when runs with identical solution normalities, direction of transfer, solution flow rates and resin flow rates, but with different column lengths, were compared. The presence of an end effect was shown by an apparent decrease in $r_p^2/15D_{Na}$ with increasing column length. This was assumed to be the result of non uniform solution distribution in the solution input end of the column. Since the feed plates were peripheral in design, (see Figure 5) and the solution outlets in the resin valve bodies were conical in nature, the end effect was assumed to lie entirely in the region of the feed plate.

6. The values of $r_p^2/15D_{Na}$ as found in Step 5 were graphed as a function of $1/(z_2-z_1)$, as shown in Figure 10, and extrapolated to $1/(z_2-z_1) = 0$. The value of $r_p^2/15D_{Na}$ at $1/(z_2-z_1) = 0$ was taken as the true value, since the end effect would be negligible in comparison to an infinite column.

7. The magnitude of the end effect was estimated by considering the difference in $r_p^2/15D_{Na}$ for a finite and infinite column as indicated below.

$$
\Delta z_e = \left[ \left( \frac{r_p^2}{15D_{Na}} \right)_{finite} - \left( \frac{r_p^2}{15D_{Na}} \right)_{infinite} \right] V_R \int_{Y_1}^{Y_2} \frac{Y^2}{(Y+1)(Y^{a-2} - Y)} dY
$$

(46)
Figure 10. Apparent \( \frac{2}{15} \bar{D}_{\text{Cu, Na}} \) as a Function of Reciprocal Column Length, No End Effects Considered
The magnitude of $\Delta z_e$ was found to be less sensitive to differences in flow rate than to experimental error. Thus, an average constant value was used in evaluating all the experiments.

8. Equations 39, 41 and 43 were modified to incorporate the end effect.

$$H_{TLAB} = \frac{(z_2 - z_1) - \Delta z_e}{\frac{r_p^2}{15 D_{Na}}} V_R \int_{Y_1}^{Y_2} \frac{[a-(a-2)Y]dY}{(Y+1)(Y^*-Y)}$$

$$= \frac{\int_{X_1}^{X_2} \frac{dX}{(X-X^*)}}{V_R \int_{Y_1}^{Y_2} \frac{[a-(a-2)Y]dY}{(Y+1)(Y^*-Y)}}$$

$$= \frac{r_p^2}{15 D_{Na}} \frac{(z_2 - z_1) - \Delta z_e}{H_{TLAB}} \int_{X_1}^{X_2} \frac{dX}{(X-X^*)}$$

$$= \frac{\int_{X_1}^{X_2} \frac{dX}{(X-X^*)}}{V_R \int_{Y_1}^{Y_2} \frac{[a-(a-2)Y]dY}{(Y+1)(Y^*-Y)}}$$

$$z_2 - z_1 = \frac{r_p^2}{15 D_{Na}} V_R \int_{Y_1}^{Y_2} \frac{[a-(a-2)Y]dY}{(Y+1)(Y^*-Y)} + H_{TLAB} \int_{X_1}^{X_2} \frac{dX}{X-X^*} + \Delta z_e$$

9. Steps 2 through 5 were repeated using Equations 47 and 48 instead of Equations 41 and 43 to calculate the resin phase constant $\frac{r_p^2}{15 D_{Na}}$ and the constants $C_{Cu, Na}$, $C_{Na, Cu}$ and $q$ defined in Equation 42.
10. The column lengths \((z_2 - z_1)\) were calculated for all the runs using Equation 49, the approximate values of the constants found in Step 9, and the end effect found in Step 7.

11. The column lengths calculated in Step 10 were compared to the actual column lengths by calculating the percent error.

\[
e = \left[ \frac{(z_2 - z_1)_{\text{calc.}} - (z_2 - z_1)_{\text{act.}}}{(z_2 - z_1)_{\text{act.}}} \right] \times 100\% \tag{50}
\]

The sum of the absolute values of the errors for all the runs was found and used as a measure of the correctness of the values of \(\alpha, \overline{D}_{Na}, C_{Cu, Na}, C_{Na, Cu}\) and \(q\) used in its calculation.

12. A different value of \(\frac{r_p^2}{15\overline{D}_{Na}}\) was chosen, and Steps 3 through 5, 10 and 11 were carried out. It was found that the change in \(\Delta z_e\) was negligibly small for a small change in \(\frac{r_p^2}{15\overline{D}_{Na}}\). Therefore, repetition of Steps 6 through 9 was not necessary at this point.

13. The error resulting from the new value of \(\frac{r_p^2}{15\overline{D}_{Na}}\) was compared with that for the initial choice; and a third approximation was made for the best value of \(\frac{r_p^2}{15\overline{D}_{Na}}\). This process was aided by constructing a graph of the sum of the absolute values of the error as a function of
Figure 11 shows one of these graphs.

14. Other values of α were chosen and Steps 1 through 13 were repeated for each value of α.

15. The minimum values of the sums of the absolute error for each α investigated were graphed as functions of α as shown in Figure 12. The values of the unknown quantities that corresponded to the minimum error on this curve were taken as the best values of α, $\overline{D}_{Na}$, $C_{Cu, Na}$, $C_{Na, Cu}$ and q. The values of α and $\frac{r^2}{p}/15\overline{D}_{Na}$ investigated and their corresponding errors are shown in Table 1.

16. The values of n and p as used in Equation 38 were extracted from $C_{Cu, Na}$ and $C_{Na, Cu}$ with the relationships

\[
n = \frac{\log(C_{Na, Cu}/C_{Cu, Na})}{\log(D_{Cu, Na}/D_{Na, Cu})} \quad (51)
\]

\[
p = \frac{2}{(C_{Cu, Na} + C_{Na, Cu})} \frac{\epsilon}{a} S_c^{2/3} \quad (52)
\]

Although the j-factor correlation was not used in the form of Equation 33 in analyzing the experimental data, the $H_{TLAB}$ values corresponding to the best values of the unknown parameters were transformed to correspond to the j-factor. This was done in order
Table 1. Summation of the Absolute Error Values for the 21 Experiments as a Function of $\frac{r_p^2}{15 \overline{D}_\text{Na}}$ and $\frac{\overline{D}_\text{Na}}{\overline{D}_\text{Cu}}$

| $\frac{\overline{D}_\text{Na}}{\overline{D}_\text{Cu}}$ | $\frac{r_p^2}{15 \overline{D}_\text{Na}}$ | $\sum |e|$ |
|---|---|---|
| $\alpha$ | seconds | % |
| 1.0 | 98.9 | 99.2 |
| 1.0 | 100.5 | 97.5 |
| 1.0 | 101.2 | 97.3 |
| 1.0 | 102.1 | 98.7 |
| 1.0 | 103.7 | 101.4 |
| 2.0 | 69.0 | 146.4 |
| 2.0 | 72.6 | 113.8 |
| 2.0 | 74.4 | 103.1 |
| 2.0 | 76.2 | 119.2 |
| 4.0 | 44.0 | 144.4 |
| 4.0 | 50.1 | 127.0 |
| 4.0 | 51.0 | 126.3 |
| 4.0 | 52.2 | 130.2 |
| 4.0 | 53.4 | 134.1 |
| 6.0 | 33.6 | 147.9 |
Figure 11. The Sum of the Absolute Values of the Errors for the Twenty-one Runs as a Function of $\frac{r^2}{15D_{\text{Cu, Na}}}$ seconds
Figure 12. Minimum Absolute Error Value Sums for the Twenty-one Runs as a Function of the Resin Phase Diffusivity Ratio.
to compare the solution phase portion of the ion-exchange operation under investigation with the more common liquid-phase, mass transfer operations described in the literature. An average j-factor graph for all the runs was desired; therefore, the direction-of-transfer effect was compensated for in converting the experimental values to \( j_D \) values.

\[
j_D = \left( \frac{2C_{AB}}{C_{AB} + C_{BA}} \right) \left( \frac{\varepsilon}{\alpha} \right) \left( \frac{Sc^{2/3}}{H_{TLAB}} \right)
\]

In Equation 53, the quotient \( \frac{2C_{AB}}{C_{AB} + C_{BA}} \) counterbalances the direction of ionic transfer effect on \( H_{TLAB} \). A graph of \( \log_{10} j_D \) as a function of \( \log_{10} Re \) is shown in Figure 13.

Application of the above procedures to the experimental data resulted in the following values for the unknown quantities.

\[
\alpha = 1.0 \\
r_p^2 / 15 \overline{D}_{Cu, Na} = 101 \text{ sec} \\
C_{Cu, Na} = 0.84 \text{ cm} \\
C_{Na, Cu} = 0.75 \text{ cm} \\
q = 0.69
\]

Since \( \alpha \) was found to be unity the resin phase diffusivity corresponded to the constant counter-diffusivity \( \overline{D}_{Cu, Na} \). The
Figure 13. j-factor as a Function of Reynolds Number
magnitude of $\bar{D}_{Cu, Na}$ was found by converting the values of 

$$r_p^2/15 \bar{D}_{Cu, Na}$$

for all the runs to the corresponding diffusivities and finding their mean value. For $r_p = 0.0348 \text{ cm}$ the resin phase diffusivity was found to be

$$\bar{D}_{Cu, Na} = 0.807 \times 10^{-6} \text{ cm}^2/\text{sec} \pm 5\% .$$

The deviation of $\bar{D}_{Cu, Na}$ was estimated within 95% confidence limits as shown in Appendix E.

The values of $n$ and $p$ were found by inserting the values of $C_{Cu, Na}$ and $C_{Na, Cu}$ in Equations 51 and 52.

$$n = 0.32$$

$$p = 0.79$$

The above values of $n$ and $p$ correspond to a $j$-factor relation of the form

$$j_D = \frac{k_L}{L} \epsilon Sc^{2/3} = 0.79 Re^{-0.69}$$

(54)

The end effect as defined in Equation 46 was found to be 4.0 cm when the best values listed above were used. This value was found with respect to the sample port at the solution input end of the column. Since the sample ports were 2.0 cm above the feed plates, the true end effect was 6.0 centimeters or roughly one column diameter (7.6 cm). Therefore, in designing columns of the type
described, one column diameter should be added to the column length as calculated with Equations 38 and 39.

The calculations involved in correlating the experimental data are shown in more detail in Appendix F. The calculated values of $\Delta z_c$, $H_{TL_{AB}}$, $r_p^2/15 \overline{D_{Cu, Na}}$, $\overline{D_{Cu, Na}}$ and $(z_2-z_1)$ for each run and the operating data on which they were based are also shown in Appendix F.
DISCUSSION

Operating Characteristics of the Apparatus

The operating characteristics of the countercurrent ion-exchange apparatus were quite good in most respects. It was found that the resin phase could be moved through the columns countercurrent to the solution flows with no difficulty. However, improvements could be made in the equipment used to pump and meter the solutions into and out of the columns.

The average velocity of the resin in the columns was checked periodically during the runs by observing the progress of dyed ion-exchange resin particles. By measuring the time required for a dyed resin bead to travel between points in the column a known distance apart, the average resin velocity could be evaluated. In all cases, the desired resin velocity was maintained throughout the run.

The solutions and water rinse streams were pumped into the columns by centrifugal pumps. These flows and also the column effluents were regulated with needle valves and monitored with rotometers. Although this arrangement allowed adequate control of the operation, the eight flow rates required frequent adjustment. This was particularly troublesome when the operator's attention was diverted during the taking of the samples.
The use of metering pumps in the input and outlet lines to the column would eliminate the above control problem and also increase the efficiency of the pulser in moving the resin. The use of centrifugal pumps caused part of the negative pulse to be nullified by solution entering at an increased rate through the inlet lines. The same effect was present during the positive part of the pulse cycle due to increased flow through the column outlets. These effects would be eliminated if the solutions and rinse streams were pumped at constant rates into and out of the columns with metering pumps. Thus, the installation of metering pumps would make the apparatus much easier to operate and would also improve the resin pumping action in the column.

The maximum resin and solution flow rates used in the runs were 4.0 cm/min. and 35.6 ml/cm² min. respectively. A resin rate of 4.0 cm/min. was the maximum that could be accurately metered by the resin meter. The solution flow rate corresponding to this resin rate for equal-equivalent flow of 0.2N solution was 35.6 ml/cm² min. Since the maximum flow rate suggested for fixed bed ion exchange operations is on the order of 40 ml/cm² min. (11, p. 66), it was possible to operate the apparatus at solution rates corresponding to those used in fixed bed operations.
Comparison of the Experimental Results with Values Appearing in the Literature

Values of the resin phase diffusivities of cupric ion and sodium ion in Dowex 50W-X8 are available in the literature (15). Therefore, the resin phase diffusivity found in this investigation could be compared with the findings of others. However, it was impossible to make a quantitative comparison of the parameters used to correlate the solution-phase mass-transfer phenomena. This was due to the unique flow regime in which the ion-exchange operation was performed.

The method by which an ion-exchange operation is carried out should not affect the diffusivities of the ions in a given ion-exchange material. Therefore, the resin phase diffusivity data found in the literature for cupric ion and sodium ion in Dowex 50W-X8 should be comparable to that found in this investigation.

Gopala Rao and David (15) have studied the counter diffusion of cupric and sodium ions in Dowex 50W-X8 resin. They used a shallow bed technique that resulted in a situation corresponding to transient diffusion in a sphere with constant boundary conditions. It was found that their data could be correlated with a constant diffusivity model or, with somewhat better agreement, with the variable diffusivity model of Helfferich (22). The constant diffusivity model resulted in a resin phase diffusivity, \( \overline{D}_{Cu,Na} \) of
0.90 \times 10^{-6} \text{cm}^2/\text{sec} \quad \text{while the variable diffusivity model gave a}
ratio, a, \quad \text{of six and a sodium ion diffusivity,} \quad D_{Na}, \quad \text{of}
1.60 \times 10^{-6} \text{cm}^2/\text{sec}.

The constant counter diffusivity found in this investigation, \text{i.e.,}
\overline{D}_{Cu,Na} = 0.807 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}} \quad \text{was 10\% less than that found by Gopala Rao and David. This was felt to be good agreement considering the}
widely different methods used in the two studies.

A comparison of the experimental results with the theory of
ion exchange showed that the data contradicted the variable diffusivity
theory of Helfferich (22) as adapted to the case of countercurrent ion-
exchange. Although simplifying assumptions were made in adapting
the variable diffusivity theory to the case of countercurrent ion-
exchange, no reason could be found for the failure of the theory to
differentiate between the diffusivities of the two ions. This contra-
diction indicates that more sensitive experiments should be performed
to further investigate resin phase diffusion phenomena in counter-
current operations.

Aside from the end effects and the accuracy of the experimental
procedures the magnitude of the resin-phase counter-diffusivity de-
pended on two factors. First, the relative magnitudes of the resis-
tances in the two phases have a direct bearing on the size of the
entire resin phase term in Equation 48 and in turn on the value of the
diffusivity. Secondly, the group \( r_p^2/15 \overline{D}_{Cu,Na} \), as defined in
Equation 15, was derived using an idealized diffusion model and may not be an accurate representation of the real case. No data were available for a comparison of the relative resistances in the two phases. However, other authors have suggested relationships corresponding to Equation 15 to relate the resin phase, mass transfer coefficient to the particle size and the diffusivity of the ions in the resin phase.

Factors corresponding to $\frac{r_p^2}{15} \overline{D}_{AB}$ appearing in Equation 15 have been suggested by Glueckauf (14, p. 39) and Gilliland (12). Glueckauf indicated that $\frac{r_p^2}{14.1} \overline{D}_{AB}$ should be used and Gilliland presented a choice of either $\frac{r_p^2}{\pi^2 \overline{D}_{AB}}$ or $\frac{r_p^2}{12} \overline{D}_{AB}$ as appropriate. The factor 14.1 suggested by Glueckauf is 6% less than that derived from the idealized isotopic exchange model while the factors $\pi^2$ and 12 given by Gilliland are 34% and 20% less than that derived in this study. This indicates that the factor 15 is of the right order of magnitude but may be too large.

It was impossible to make a quantitative comparison of the solution phase results with corresponding literature values. This was due to the unique fluid dynamic conditions in which the operation was performed and to the absence of any correlations relating ion-exchange rates to the direction of ion transfer in paced bed operations. However, a qualitative comparison of the solution phase j-factor (Equation 54) with that for steady flow (Equation 33) indicated
a decreased efficiency due to the pulsed nature of the flow system.

It was suspected that hydraulic pulsing in the system would have two major effects on the operation. First, the alternating flow should cause an increase in the solution mass-transfer coefficient due to increased instantaneous velocities (27). Second, the alternating flow in the bed should cause an increase in the backmixing of the solutions. A comparison of the j-factor relationship suggested by Carberry (6) and that for the present case is shown in Figure 13. This graph shows that the j-factors for the present case were considerably smaller than for the case of steady flow. This indicates that the predominant effect of pulsing on the system was to increase backmixing. Although this was detrimental to the operation, it was of minor importance since the larger resistance to ion-exchange was in the resin phase. Therefore, the slight increase in column height due to backmixing should be more than counterbalanced by the advantages of continuous operation.

Solution phase ion-exchange has been studied with respect to dependence on the direction of ion transfer. However, these studies have been confined to the case of the stirred tank reactor (13, 45). The transient behavior of the stirred tank case was sufficiently different from that for countercurrent operation that no comparison between the two could be made.

No design equations comparable to Equations 38 and 49 were
found in the literature. Therefore, a determination was made of the accuracy with which Equations 38 and 49 would reproduce the column lengths used in the experimental runs. With the best values of the various unknowns as shown in the previous section and the estimated values of the remaining parameters, it was possible to calculate the column lengths corresponding to the operating data for the various runs. The column lengths were calculated with Equations 38 and 49 and compared to the actual column lengths with Equation 50. The results of these calculations are shown in Figure 14 and Table 13 of Appendix F.

Figure 14 shows that the percent error for all but two of the runs are less than 11%. The runs four-two and five-one that do not show agreement within 11% probably did not attain steady state.

The runs number four were made with half-normal solutions whereas the preceding runs number three were made with one-normal solutions. The main effect of this change in solution normality was that the equilibrium relationship was less favorable to the adsorption of sodium ion in the runs number four. Therefore, the average cupric ion content of all the resin in the system had to attain a higher level in order to attain steady state. Run four-two indicates that steady state was not achieved, since the error involved is due to the operating line lying too far below the equilibrium curve, as would be the case if the resin phase cupric ion content were too low.
Figure 14. Percent Error in the Calculated Column Lengths as a Function of Resin Velocity.

- Shaded symbols, Cu\textsuperscript{++} displacing Na\textsuperscript{+} from resin
- Open symbols, Na\textsuperscript{+} displacing Cu\textsuperscript{++} from resin
- Solution normality: ○ = 1.0, □ = 0.5, Δ = 0.2
The same effect is apparent in run five-one. The runs number five were made after shortening the active sections from two feet to one foot. This required that the resin be removed and later replaced in the apparatus. The large error in run five-one shows the effect of the operating line being too close to the equilibrium curve. This was probably due to the resin's average initial cupric ion concentration being too low. The effect of an initial major disturbance in the system, added to an expected error of two to thirteen percent at steady state, was the probable cause of the large deviations shown in runs four-two and five-one. Compensating experimental errors and non attainment of steady state errors probably reduced the overall errors in runs four-one and five-two. The probable errors of two to thirteen percent were estimated by the methods suggested by Mickley, Sherwood and Reed (36, 53-59) as shown in Appendix E.

All but two of the runs show errors of an expected magnitude. Therefore, the results were considered as reasonably accurate considering the nature of the operation investigated. It was also found that the results were of the same order of accuracy as those obtained in other ion-exchange, mass transfer investigations (23).
RECOMMENDATIONS FOR FURTHER WORK

The present work should be extended to a more intensive investigation of three factors found to influence countercurrent ion-exchange. The most important of these is the variable diffusivity effect in the resin phase and the apparent contradiction of the Helfferich variable diffusivity model (22) found in this work. The effects of the direction of transfer and of the Reynolds number on the rate of solution phase ion-exchange should also be studied more intensively.

Examination of the Resin Phase Operation

The dependence of resin-phase ion-exchange on the resin-phase composition could be checked more conclusively by one of two methods. Either experiments could be designed in which the resin compositions would be confined to a series of limited ranges; or runs could be made with essentially complete conversion of the resin in each column and with samples taken at several points along the length of the column.

The first method could be carried out in the same manner as the experiments described in the present work with the exception that the equivalent fractions of the feed solutions would be other than 0.0 and 1.0. In this case, the solution feed compositions would have
to be chosen such that the corresponding resin phase compositions would lie in the desired range. A series of experiments would then be required to cover the entire range of resin phase equivalent fractions for a given resin rate and solution normality. If a series of resin flow rates and solution normalities were to be investigated, this method would involve a large number of experiments.

The second method is more attractive, since progressive stages of the ion-exchange operation could be determined from one run. With this method, individual sections of the operating line on an operating diagram would correspond to the sections of the column between the sample taps. Thus, the average resin phase diffusivity could be found for each segment of the column. A comparison of these diffusivities would show their relationship to the resin phase compositions in the corresponding sections of the column. This method would also allow inspection of the straight-operating-line assumption and should allow a more accurate estimation of end effects.

The drawback to taking several samples from various points in the column is that more sophisticated sampling and analytical procedures would be required. If relatively large samples were taken from several points in the column, the operation would be upset, and a relatively long recovery period would have to be allowed before more samples could be taken. Withdrawal of large samples
would also require that all the samples be withdrawn simultaneously in order that the samples be representative of the column conditions at steady state. If large samples were withdrawn sequentially, all but the first would be subject to the variation in resin and/or solution flows caused by removing the previous samples.

The difficulties involved in taking large samples could be avoided by taking small samples. A sample could be considered small if the resin and solution flow rates in the column remained essentially constant during the sample withdrawal. This alternative would, however, necessitate the development of refined analytical techniques in order to analyze the small samples with sufficient accuracy.

### Examination of the Solution Phase Operation

The constants $n$, $p$ and $q$ appearing in Equation 38 should be verified. This could be done by comparing the results of experiments in which different ion pairs were used and of those covering a wider range of Reynolds numbers. The constancy of $n$, $p$ and $q$ should also be determined by withdrawing and analyzing samples from several points in the column.

The value of $n$ should be tested by examining a system in which the two ions have widely different diffusivities. Hydrogen ion has an equivalent conductance of roughly six times that of the other
cations (7, p. 144) and should have a correspondingly greater dif-
fusivity. Therefore, the use of hydrogen ion as one of the exchang-
ing cations should give a good test of the value of \( n \).

The system used to verify \( p \) and \( q \) should contain ions
with diffusivities as nearly the same as possible and with the same
valence. With ions of like diffusivity, uncertainty as to the form of
the direction dependent term in Equation 38 and to the value of \( n \)
would be eliminated. Ions of like valence should be used, since the
equilibrium relationships for such systems are essentially indepen-
dent of the total solution normality. Therefore, a wide range of so-
lution flow rates could be investigated without the necessity of ex-
perimentally determining the equilibrium relationships for the cor-
responding total solution normalities.
SUMMARY

The apparatus used in the continuous countercurrent ion-exchange experiments was found to operate reliably over a fairly wide range of solution flow rates. Resin velocities between 1.0 and 4.0 cm/min. and solution flow rates between 3.5 and 35.6 ml/cm² min. were maintained with no difficulty.

Two continuous ion-exchange columns containing 20-50 mesh Dowex 50W-X8 ion-exchange resin were used. Cupric sulfate solution was fed to one column to simulate a loading operation with favorable equilibrium conditions. Sodium sulfate was fed to the second column to simulate an eluting operation with unfavorable equilibrium conditions. The system was operated with constant solution and resin flow rates in order that a steady state be attained.

Resin and solution samples were taken periodically from two points in each column during the experiments. These samples were analyzed to determine the composition of the resin and solution phases at known points in the columns. The resulting end point data, combined with experimentally determined equilibrium data, were used to evaluate the unknown quantities in a modified transfer unit model.

The mathematical model used in correlating the experimental data accounted for possible variations of the resin-phase diffusivity...
as a function of ionic composition. The effect of the direction of ion transfer on the rate of ion-exchange in the solution phase was also considered.

It was found that diffusion in the resin phase corresponded to a system with a constant resin-phase diffusivity. For the cupric ion-sodium ion-Dowex 50W-X8 system, the resin phase diffusivity was found to be \( \overline{D}_{\text{CuNa}} = 0.807 \times 10^{-6} \text{ cm}^2/\text{sec.} \pm 5\% \).

The experimental data also showed that the rate of ion-exchange was dependent on the direction of travel of the ions. This was attributed to the migration of co-ions in the solution phase. The resulting co-ion shift should result in higher ion-exchange rates when the faster moving ion displaces the slower moving ion from the resin. The experimental results showed the effect of this phenomenon.

The solution phase transfer unit heights were found to be represented by

\[
\begin{align*}
H_{\text{TL}_{\text{Cu,Na}}} &= 0.84 \Re^{0.69} \text{ cm.} \\
H_{\text{TL}_{\text{Na,Cu}}} &= 0.75 \Re^{0.69} \text{ cm.}
\end{align*}
\]

\( H_{\text{TL}_{\text{AB}}} \) indicates the height of a solution-phase transfer unit when ion \( A \) displaces ion \( B \) from the resin. The Reynolds numbers were based on the solution-phase linear velocity with respect to the resin.

The mathematical model used to correlate the experimental
data should be suitable for the design of countercurrent columns similar to those described in this study. A good estimate of the column length required for a given operation can be obtained from a knowledge of the resin particle size, the diffusivity of the ions in the resin phase, the kinematic viscosity of the solution, the solution-phase ionic diffusivities, and the phase equilibrium relationships.
NOMENCLATURE

\( a \) \hspace{1cm} \text{interfacial area to bulk volume ratio, cm}^2/\text{cm}^3

\( A_C \) \hspace{1cm} \text{cross sectional area of the column, cm}^2

\( C \) \hspace{1cm} \text{constant defined in Equation 7, sec}^{-1}

\( C_{AB} \) \hspace{1cm} \text{constant defined in Equation 42, cm}

\( c_A \) \hspace{1cm} \text{concentration of A in the solution phase, mmoles/cm}^3

\( \overline{c}_A \) \hspace{1cm} \text{concentration of A in the resin phase, mmoles/cm}^3

\( d_p \) \hspace{1cm} \text{average diameter of the resin particles, cm}

\( D_A \) \hspace{1cm} \text{diffusivity of ion A in the solution phase, cm}^2/\text{sec}

\( \overline{D}_A \) \hspace{1cm} \text{diffusivity of ion A in the resin phase, cm}^2/\text{sec}

\( D_{AB} \) \hspace{1cm} \text{counterdiffusivity of ions A and B in the solution phase where A displaces B from the resin, cm}^2/\text{sec}

\( \overline{D}_{AB} \) \hspace{1cm} \text{counter diffusivity of A and B in the resin phase, cm}^2/\text{sec}

\( e \) \hspace{1cm} \text{error defined in Equation 50, %}

\( F \) \hspace{1cm} \text{Faraday's constant, 96,500 coul/g. eq.}

\( g \) \hspace{1cm} \text{weight of dry resin, grams}

\( H_{TL_{AB}} \) \hspace{1cm} \text{height of a solution phase transfer unit when A displaces B from the resin, cm}

\( I_X \) \hspace{1cm} \text{solution phase integral}

\( I_Y \) \hspace{1cm} \text{resin phase integral}

\( j_D \) \hspace{1cm} \text{solution phase j-factor, see Equation 33}

\( J_A \) \hspace{1cm} \text{molar flux of component A, mmoles/cm}^2\text{ sec}
\( J_{A_{\text{diff.}}} \)  molar flux of component A due to a concentration gradient, mmoles/cm\(^2\) sec

\( J_{A_{\text{el.}}} \)  molar flux of component A due to an electric potential gradient, mmoles/cm\(^2\) sec

\( k_L \)  ionic mass transfer coefficient in the solution phase, meq/cm\(^2\) sec

\( k_R \)  ionic mass transfer coefficient in the resin phase, meq/cm\(^2\) sec

\( K_R \)  overall ionic mass transfer coefficient in the resin phase, meq/cm\(^2\) sec

\( L \)  solution flow rate, meq/cm\(^2\) sec

\( L_V \)  volumetric solution flow rate, ml/cm\(^2\) sec

\( m \)  slope of equilibrium curve

\( n \)  constant defined in Equation 35

\( N \)  total solution normality, meq/ml

\( N_A \)  normality of ion A in solution, meq/ml

\( N_T \)  normality of standardized sodium thiosulfate solution, meq/ml

\( p \)  constant defined in Equation 34

\( q \)  constant defined in Equation 34

\( Q_B \)  bulk capacity of the wet resin, meq/cm\(^3\)

\( Q_W \)  capacity of the wet resin polymer, meq/cm\(^3\)
$Q_0$ specific, dry weight capacity of the resin in the Na\(^+\) form, meq/gram

$Q_Y$ specific, dry weight capacity of the resin with a cupric ion equivalent fraction $Y$, meq/gram

$R$ resin flow rate, meq/cm\(^2\) sec

$R_G$ gas constant $= 8.313$ joules/mole\(^\circ\)K

$r$ radial coordinate in a resin bead, cm

$r_p$ average radius of the resin beads, cm

t time, seconds

$T$ absolute temperature, \(^\circ\)K

$v_A$ volume of aliquot, ml

$v_T$ volume of titrated sodium thiosulfate solution, ml

$V_L$ average solution phase linear velocity, cm/sec

$V_R$ average resin phase linear velocity, cm/sec

$X$ equivalent fraction of cupric ion in the solution phase

$X^*$ equivalent fraction of cupric ion in the solution at equilibrium with a resin phase equivalent fraction $Y$

$Y$ equivalent fraction of cupric ion in the resin phase

$Y^*$ equivalent fraction of cupric ion in the resin at equilibrium with a solution phase equivalent fraction $X$

$z$ axial distance in column, cm

$z_A$ absolute valence of ion $A$, eq/mole

$\Delta z_e$ inactive column length due to end effects, cm
\( \alpha \) diffusivity ratio in the resin phase, \( \frac{D_{Na}}{D_{Cu}} \)

\( \epsilon \) void fraction in the packed bed, \( \text{cm}^3 / \text{cm}^3 \)

\( \lambda_A^0 \) equivalent conductance of ion A at infinite dilution, \( \text{cm}^2 / \text{ohm} \)

\( \mu \) solution viscosity, poise, gram/cm sec

\( \rho \) solution density, grams/cm\(^3\)

\( \phi \) electric potential, volts

\( \text{Re} \) Reynolds number = \( \frac{d_p (V_R + V_L) \rho}{\mu} \)

\( \text{Sc} \) Schmidt number = \( \frac{\mu}{\rho D} \)
BIBLIOGRAPHY


34. Meyer, Walter. Equilibria in the ion-exchange systems

\[
\begin{align*}
H^+ &- Cs^+ + 1, H^+ &- Sr^+ + 2, H^+ &- Ce^{+3}, Cs^+ &- Sr^+ + 2, Sr^+ &- Ce^{+3}, \\
H^+ &- Cs^+ - Sr^+ + 2, H^+ &- Cs^{+1} &- Ce^{+3} \text{ and } H^+ &- Sr^+ + 2 &- Ce^{+3}.
\end{align*}
\]


46. Subba Rao, H. C. and M. M. David. Equilibrium in the system Cu
++-Na


APPENDIX A

PROPERTIES OF THE RESIN AND SOLUTION PHASES

Several properties of the resin phase-solution phase system could be measured experimentally or estimated from data found in the literature. The properties of the resin included the average radius and capacity of the resin beads and the porosity and interfacial area of the packed resin bed. The densities and viscosities of the solutions and the diffusivities of the ions in the solution phase could also be estimated.

The Dowex 50W-X8 ion-exchange resin was used as delivered. This resin is manufactured in the form of rigid spheres and the batch used had a size range of 20 and 50 mesh. The average diameter, porosity and ionic capacity of this material were measured experimentally.

The ion-exchange resin had been cycled in the system for roughly 100 hours prior to the column experiments described in this work. It was therefore assumed that the resin was in a used state and that its properties did not change appreciably during the experiments. The resin phase properties were measured at the conclusion of the column experiments.
Determination of the Resin Particle Diameter

The average particle diameter was found by microscopic examination of samples of the wet resin. The samples were placed in a drop of water between two glass slides and positioned on the stage of an American Optical Microstar Trinocular microscope. The microscope was fitted with a Filar eyepiece and calibrated with a Bausch and Lomb glass scale that was ruled in tenths of a millimeter. With this arrangement, the particle diameters could be measured to the nearest micron. The particle sizes for the used, 20-50 mesh resin were distributed as shown in Table 2.

Table 2. Resin Particle Size Distribution

<table>
<thead>
<tr>
<th>Diameter range cm</th>
<th>Number of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04-0.05</td>
<td>7</td>
</tr>
<tr>
<td>0.05-0.06</td>
<td>45</td>
</tr>
<tr>
<td>0.06-0.07</td>
<td>55</td>
</tr>
<tr>
<td>0.07-0.08</td>
<td>51</td>
</tr>
<tr>
<td>0.08-0.09</td>
<td>25</td>
</tr>
<tr>
<td>0.09-0.10</td>
<td>15</td>
</tr>
<tr>
<td>0.10-0.11</td>
<td>6</td>
</tr>
</tbody>
</table>

The arithmetic-average, particle diameter of the 204 particles measured was found to be 0.0697 cm.
Resin Bed Porosity

The porosity of the resin bed was measured by titrating the quantity of water required to fill the voids in a known bulk volume of water saturated resin. A quantity of wet resin was centrifuged in a screened basket at 1500 RPM to remove the surface water. The resin was then transferred to a graduated cylinder and a titrated quantity of water was added. The graduated cylinder was swirled to remove all air bubbles and tapped to cause the resin to settle as much as possible. The volume of the settled resin and the total volume of the resin and water in the graduated cylinder were then noted.

The void fraction was calculated as follows. Let:

\[ v_C = \text{total volume in the graduated cylinder} \]
\[ v_T = \text{titrated volume of water} \]
\[ v_R = \text{bulk volume of the resin} \]

The void volume fraction or porosity of the resin bed was related to the measured volumes by the following relationship:

\[ \epsilon = \frac{v_T - (v_C - v_R)}{v_R} \]  \hspace{1cm} (55)

The void volume fractions found by this procedure ranged between 0.328 and 0.346 and had an average value of 0.339. Therefore the
average void fraction was taken as

\[ \epsilon = 0.34. \]

**Surface Area to Bulk Volume Ratio**

The interfacial area to bulk volume ratio of the packed resin was calculated from the average particle radius, \( r_p \), and the bed porosity, \( \epsilon \). The surface area of the spherical particles in a unit volume was taken as

\[ a = 4\pi r^2 \frac{n_p}{P} \quad (56) \]

where \( n_p \) is the number of spheres per unit volume. The value of \( n_p \) was taken as

\[ n_p = \frac{(1-\epsilon)}{4/3 \pi r^3_p} \quad (57) \]

where \( (1-\epsilon) \) is the volume of resinous material per unit volume. Thus the interfacial area per unit volume was found as the product of Equations 56 and 57.

\[ a = \frac{3(1 - \epsilon)}{r_p} \quad (58) \]

Insertion of the experimentally determined values of \( r_p \) and \( \epsilon \) in Equation 58 resulted in

\[ a = 56.8 \text{ cm}^2/\text{cm}^3 \]
Ionic Capacity of the Resin

The resin capacity for Dowex 50W-X8 in the sodium-ion form was found to be 4.329 meq/gram as shown in Appendix D. The wet bulk volume capacity was also required in calculating the solution flow rate corresponding to the resin rate chosen for a given column experiment. The wet, bulk volume capacity was found by Meyer (34, p. 139) to be 1.78 meq/ml for the same batch of resin used in the present study.

The resin phase properties are summarized below.

\[ \begin{align*}
  d_p &= 0.0697 \text{ cm} \\
  r_p &= 0.0348 \text{ cm} \\
  \epsilon &= 0.34 \\
  a &= 56.8 \text{ cm}^2/\text{cm}^3 \\
  Q_0 &= 4.329 \text{ meq/gram} \\
  Q_B &= 1.78 \text{ meq/ml}
\end{align*} \]

Solution Phase Viscosities

The viscosities of sodium sulfate and cupric sulfate solutions and their arithmetic averages for the solution normalities used in the experiments are shown in Table 3. The data for the pure salt solutions were taken from the International Critical Tables (52, p. 14, 15).
Table 3. Solution Phase Viscosities

<table>
<thead>
<tr>
<th>Solution Normality</th>
<th>Viscosity of Na$_2$SO$_4$ @25°C cp</th>
<th>Viscosity of CuSO$_4$ @25°C cp</th>
<th>Average Viscosity cp</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.040</td>
<td>1.061</td>
<td>1.050</td>
</tr>
<tr>
<td>0.5</td>
<td>1.106</td>
<td>1.161</td>
<td>1.133</td>
</tr>
<tr>
<td>1.0</td>
<td>1.227</td>
<td>1.357</td>
<td>1.292</td>
</tr>
</tbody>
</table>

Solution Phase Densities

The densities of the sodium sulphate and cupric sulfate solutions and their arithmetic averages are shown in Table 4. The data for the pure salts were taken from the Handbook of Chemistry and Physics (25, p. 1855, 1913).

Table 4. Solution Phase Densities

<table>
<thead>
<tr>
<th>Solution Normality</th>
<th>Density of Na$_2$SO$_4$ @20°C grams/ml</th>
<th>Density of CuSO$_4$ @20°C grams/ml</th>
<th>Average Density grams/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.013</td>
<td>1.015</td>
<td>1.014</td>
</tr>
<tr>
<td>0.5</td>
<td>1.029</td>
<td>1.033</td>
<td>1.031</td>
</tr>
<tr>
<td>1.0</td>
<td>1.060</td>
<td>1.077</td>
<td>1.069</td>
</tr>
</tbody>
</table>

Solution Phase Diffusivities

The solution-phase diffusivities of cupric ion and sodium ion
were determined by applying the equivalent conductance data of Conway (7, p. 145) to Equation 32. The equivalent conductances and the corresponding diffusivities are listed in Table 5.

Table 5. Solution Phase Diffusivities

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>Equivalent conductance cm²/ohm</th>
<th>Diffusivity cm²/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺⁺</td>
<td>54</td>
<td>7.2 x 10⁻⁶</td>
</tr>
<tr>
<td>Na⁺</td>
<td>50.1</td>
<td>13.3 x 10⁻⁶</td>
</tr>
</tbody>
</table>
APPENDIX B

RESIN PHASE-SOLUTION PHASE EQUILIBRIUM

Equilibrium data for the interaction of Dowex 50W-X8 ion-exchange resin and aqueous solutions of sodium chloride-cupric chloride mixtures are available. However, these data were found to be inapplicable due to the presence of chloride rather than sulfate as the common anion in the solution phase. Therefore the equilibrium relationships for Dowex 50W-X8 ion-exchange resin and aqueous solutions of sodium sulfate and cupric sulfate mixtures were determined experimentally.

The resin was exposed to solutions of known cupric ion equivalent fraction and total normality in 50 ml burets. Since the stop cocks on the burets were only partially opened during the operation, no special arrangement was needed to hold the resin in the burets. Duplicate determinations were made with each solution tested. Although the weight of the resin in each sample did not enter into the equilibrium calculations, the samples were weighed to the nearest milligram in the dry, hydrogen-ion form. This was done in order that the dry weight capacity of the resin could be determined as described in Appendix D.

The resin was brought to equilibrium by passing 150 ml of test
solution through the resin samples. Percolation rates of less than one-half milliliter per minute allowed ample time for the attainment of equilibrium. After passage of the test solution a water rinse was flushed through each sample to remove all of the test solution from the surface of the resin. A volume of 150 ml passed at about 15 ml/min was used in rinsing the resin.

The cupric ion in the equilibrated resin was removed by elution with concentrated sodium sulfate. A volume of 100 ml of 2N sodium sulfate was percolated through the sample at less than 0.5 ml/min. This procedure was found to remove all detectable amounts of cupric ion from the resin.

The effluent from the elution operation was analyzed for cupric ion by iodometric titration. The methods suggested by Hamilton and Simpson (18, p. 263-270) were used. This analysis gave the amount of cupric ion contained in the resin in equilibrium with the test solution in question, expressed as milliliters of titrating agent used in neutralizing the effluent solution.

When the above procedure was carried out using a test solution of pure cupric sulfate the total capacity of the resin was saturated with cupric ion. Thus the volume of titrating agent corresponding to the resin capacity was determined by an identical equilibrating, eluting and titrating procedure for a pure cupric sulfate test solution.
The equivalent fraction in the resin phase corresponding to the equivalent fraction of a given test solution was found as the amount of cupric ion adsorbed from that particular solution divided by the capacity of the resin. In making this calculation, the volumes of titrating agent corresponding to the amounts of cupric ion eluted from the resin were used.

The results of these determinations are shown in Table 6 and Figure 15.
Table 6. Equilibrium Between Dowex 50W-X8 Resin and Aqueous Sodium Sulfate-Cupric Sulfate Solutions

<table>
<thead>
<tr>
<th>N</th>
<th>X</th>
<th>( Y_a )</th>
<th>( Y_b )</th>
<th>( Y_{av} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>0.379</td>
<td>0.381</td>
<td>0.380</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.525</td>
<td>0.523</td>
<td>0.524</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>0.680</td>
<td>0.678</td>
<td>0.679</td>
</tr>
<tr>
<td>0.10</td>
<td>0.375</td>
<td>0.815</td>
<td>0.810</td>
<td>0.812</td>
</tr>
<tr>
<td>0.10</td>
<td>0.625</td>
<td>0.919</td>
<td>0.910</td>
<td>0.915</td>
</tr>
<tr>
<td>0.10</td>
<td>0.80</td>
<td>0.966</td>
<td>0.968</td>
<td>0.967</td>
</tr>
<tr>
<td>0.20</td>
<td>0.10</td>
<td>0.385</td>
<td>0.385</td>
<td>0.385</td>
</tr>
<tr>
<td>0.20</td>
<td>0.20</td>
<td>0.520</td>
<td>0.523</td>
<td>0.522</td>
</tr>
<tr>
<td>0.20</td>
<td>0.40</td>
<td>0.729</td>
<td>0.730</td>
<td>0.730</td>
</tr>
<tr>
<td>0.20</td>
<td>0.60</td>
<td>0.851</td>
<td>0.858</td>
<td>0.854</td>
</tr>
<tr>
<td>0.20</td>
<td>0.80</td>
<td>0.942</td>
<td>0.944</td>
<td>0.943</td>
</tr>
<tr>
<td>0.50</td>
<td>0.10</td>
<td>0.209</td>
<td>0.209</td>
<td>0.209</td>
</tr>
<tr>
<td>0.50</td>
<td>0.20</td>
<td>0.356</td>
<td>0.356</td>
<td>0.356</td>
</tr>
<tr>
<td>0.50</td>
<td>0.40</td>
<td>0.594</td>
<td>0.595</td>
<td>0.595</td>
</tr>
<tr>
<td>0.50</td>
<td>0.60</td>
<td>0.772</td>
<td>0.772</td>
<td>0.772</td>
</tr>
<tr>
<td>0.50</td>
<td>0.80</td>
<td>0.905</td>
<td>0.908</td>
<td>0.906</td>
</tr>
<tr>
<td>1.00</td>
<td>0.20</td>
<td>0.229</td>
<td>0.232</td>
<td>0.231</td>
</tr>
<tr>
<td>1.00</td>
<td>0.40</td>
<td>0.452</td>
<td>0.449</td>
<td>0.450</td>
</tr>
<tr>
<td>1.00</td>
<td>0.50</td>
<td>0.558</td>
<td>0.561</td>
<td>0.560</td>
</tr>
<tr>
<td>1.00</td>
<td>0.60</td>
<td>0.697</td>
<td>0.675</td>
<td>0.686</td>
</tr>
<tr>
<td>1.00</td>
<td>0.80</td>
<td>0.855</td>
<td>0.848</td>
<td>0.852</td>
</tr>
<tr>
<td>2.00</td>
<td>0.2</td>
<td>0.163</td>
<td>0.187</td>
<td>0.175</td>
</tr>
<tr>
<td>2.00</td>
<td>0.4</td>
<td>0.385</td>
<td>0.394</td>
<td>0.390</td>
</tr>
<tr>
<td>2.00</td>
<td>0.6</td>
<td>0.620</td>
<td>0.626</td>
<td>0.623</td>
</tr>
<tr>
<td>2.00</td>
<td>0.8</td>
<td>0.824</td>
<td>0.819</td>
<td>0.822</td>
</tr>
</tbody>
</table>
Figure 15. Equilibria of Cupric Ion and Sodium Ion Between Aqueous Sulfate Solutions and Dowex 50W-X8
APPENDIX C

SOLUTION PHASE ANALYSIS

The equivalent fractions of cupric ion in the solution phase were calculated as the quotient of the normality of cupric sulfate and the total normality of the solution. The cupric ion normalities were determined by iodometric titration. The total normalities of the solutions were determined by a refractive index method.

In the determination of cupric ion in the solution phase, aliquots of solution were titrated iodometrically as suggested by Hamilton and Simpson (18, p. 263-270). This method is based on the liberation of free iodine, in stoichiometric amounts, from potassium iodide by the reduction of cupric ion to cuprous iodide. The titration of iodine with sodium thiosulfate using starch as an indicator is one of the most accurate of the volumetric determinations.

The normality of cupric ion was calculated from the aliquot volume, titrant volume and normality of the titrant as follows: Let

\[ v_T = \text{volume of standardized } \text{Na}_2\text{S}_2\text{O}_3 \text{ solution, ml} \]

\[ N_T = \text{normality of thiosulfate solution, meq/ml} \]

\[ v_A = \text{volume of sample, ml} \]

\[ N_{Cu} = \text{normality of cupric ion, meq/ml} \]

Since the milliequivalents of cupric ion were equal to the
milliequivalents of thiosulfate used in the titration

\[ N_{Cu} = \frac{v_T N_T}{v_A} \]  

(59)

The total normalities of the solutions were determined from the refractive indexes of the solutions and their cupric sulfate normalities. To find the relationship between concentration and refractive index, a series of solutions with known total and cupric sulfate normalities were prepared. The refractive indexes of these solutions were measured at 35°C. The Bausch and Lomb Precision Refractometer (Model 33-45-01) used did not give the refractive index directly, but rather, a scale reading that could be converted to a refractive index with appropriate charts. Since a characteristic number and not the actual index was required the refractometer scale reading was used directly.

The cupric sulfate and total solution normalities were related to the refractometer scale reading on a nomogram as shown in Figure 16. A linear scale graduated in cupric sulfate normality formed the left hand ordinate. The right hand ordinate was a linear scale of total solution normality. Between the ordinates an appropriately ruled refractive index scale curve was located to relate the three variables.

It was found that the refractometer scale reading was linear with respect to the normality of pure cupric sulfate in the 0.0-1.0N
Figure 16. Total Normality of Cupric Sulphate–Sodium Sulphate Solutions as a Function of Cupric Sulphate Normality and Refractometer Scale Reading at 35°C
concentration range studied. The refractive index scale was located vertically such that a horizontal line on the monogram would cut the left hand ordinate at a given cupric sulfate normality and also cut the refractive index curve at the refractometer scale reading corresponding to that normality. The refractive index curve was then located by drawing tie lines between the total normality and cupric sulfate normality ordinates corresponding to the prepared solutions of known composition. The refractive index curve was positioned horizontally such that the tie lines intersected the curve at the correct scale reading.

The refractometer was accurate enough that total normalities could be measured to \( \pm 0.005 \, \text{N} \). This of course assumes that the value of the cupric sulfate normality was correct. Appendix E shows the expected errors in the measurements leading to the calculation of the equivalent fraction in the liquid phase.
APPENDIX D

RESIN PHASE ANALYSIS

The equivalent fraction of cupric ion in a resin sample was found by determining the concentration of cupric ion in the sample and its total ionic capacity. Cupric ion was determined by iodo-metric titration of the solution eluted from the resin sample. The total ionic capacity was found by relating the dry weight of the sample to its specific, dry weight capacity.

It is difficult to remove all of the surface solution from resin samples. Also ion exchange resins absorb varying amounts of water depending on the ionic state of the resin. Therefore it was decided that the resin should be analyzed on a dry weight basis.

The resin was dried overnight in an oven at 105°C. It was then cooled in a vacuum desiccator over anhydrous calcium chloride for at least six hours. This technique was suggested by the manufacturer (11, p. 36) as the correct method for drying the resin. The use of a vacuum desiccator was not specified, however.

Two to three grams of resin weighted to the nearest tenth of a milligram, were placed in a 50 ml buret. The cupric ions were then eluted from the weighed samples with 100 ml of concentrated (about 2N) sodium sulfate solution. A percolation rate of less than
one-half milliliter per minute was found to remove all of the cupric ion from the resin. The absence of cupric ion in the effluent solution was checked during the later stages of the elution. A small quantity of the effluent was mixed with a solution of potassium iodide and starch. The presence of cupric ion would cause liberation of free iodine and the characteristic deep blue color of starch in the presence of iodine. No color change with this very sensitive test indicated the complete removal of copper from the resin.

The cupric ions eluted from the resin were titrated iodimetrically. The techniques suggested by Hamilton (18, p. 263-270) were used in this analysis. The result of the titration and the weight of the sample gave the milliequivalents of cupric ion per gram of resin in the original sample. This value divided by the ionic capacity of the sample yielded the equivalent fraction of cupric ion in the resin.

The total ionic capacity was the product of the sample weight and its specific capacity. The specific capacity of the resin was measured before and after the column experiments were run. It was found initially by weighing out quantities of dry resin in the hydrogen ion form, saturating the samples with cupric ion, eluting the cupric ion, and analyzing for cupric ion iodimetrically. The specific capacity was found to be $4.787 \pm 0.014$ milliequivalents per gram of resin in the hydrogen ion form. When corrected for the
weight difference between sodium ion and hydrogen ion this corresponded to a specific capacity of $4.332 \pm 0.013$ milliequivalents per gram in the sodium ion form. The final specific capacity analysis consisted of saturating the resin with cupric ion, drying the samples, weighing out known quantities of dry resin, eluting the cupric ions, and titrating the effluent iodimetrically. The specific capacity was found to be $4.167 \pm 0.008$ milliequivalents per gram of resin in the cupric ion form. This is equivalent to a capacity of $4.326 \pm 0.008$ milliequivalents per gram in the sodium ion form. Since the initial and final analyses varied by only 0.16% an average of the two was used in the calculation of the equivalent fraction. The specific capacity of the resin in the sodium ion form was taken as $4.329$ milliequivalents per gram.

The change in specific capacity with ionic content of the resin is due to the difference in equivalent weights of the ionic components. Since the milliequivalent weights of cupric ion and sodium ion are $0.0318$ and $0.0230$, respectively, a gram of resin originally in the sodium form will weigh

$$1 + 4.329(0.0318 - 0.0230) = 1.038$$

grams in the cupric form. The change in specific capacity of the resin with cupric ion content was accounted for in calculating the equivalent fraction in the resin phase.
The following procedure was used in calculating the cupric ion equivalent fraction: Let

\[ g = \text{weight of dry resin sample, grams} \]
\[ v_T = \text{volume of sodium thiosulfate solution used in the titration, milliliters} \]
\[ N_T = \text{normality of sodium thiosulfate solution, meq/ml} \]
\[ Q_0 = \text{dry weight, specific capacity of Dowex 50W-X8 in the sodium form} = 4.329 \text{ milliequivalents per gram} \]
\[ Q_Y = \text{dry weight specific capacity of Dowex 50W-X8 with an equivalent fraction } Y \]
\[ Y = \text{equivalent fraction of cupric ion in the resin} \]

Since sodium-form resin was taken as a basis, the excess weight due to cupric ion in a given resin sample will be

\[ \Delta g = v_T N_T (0.0318 - 0.0230) \quad (60) \]

The excess weight per gram of sample will be

\[ \frac{\Delta g}{g} = \frac{v_T N_T (0.0088)}{g} \quad (61) \]

Due to the excess weight of cupric ion, resin containing cupric ion will have a smaller specific capacity

\[ Q_Y = Q_0 (1 - \frac{\Delta g}{g}) \]
\[ = 4.329 \left( 1 - \frac{0.0088 v_T N_T}{g} \right) \quad (62) \]
The equivalent fraction of cupric ion is then given by

\[ Y = \frac{v_{NT}}{gQ_Y} = \frac{v_{NT}}{0.0088v_{NT}} \frac{4.329(1 - \frac{g}{4})}{g} \]  

(63)
APPENDIX E

ESTIMATION OF EXPERIMENTAL ERROR

The column lengths calculated from Equation 49 and the best values of \( \frac{r^2}{15} \overline{D}_{Cu, Na} \), \( \Delta z_e \), and \( H_{TL}^{AB} \) showed deviations from the actual column lengths used. If one assumed that \( \frac{r^2}{15} \overline{D}_{Cu, Na} \) and \( \Delta z_e \) were constant and that \( H_{TL}^{AB} \) could be calculated from Equation 38, the deviations in the calculated column lengths would be due to errors in the integrals appearing in Equation 49. Therefore, an estimation of the probable errors in the integrals was made to compare with the deviations found in the calculated column lengths.

The experimental results showed that the diffusivity ratio should be unity. As a result, the values of

\[
\int_{Y_1}^{Y_2} \frac{dY}{(Y^* - Y)} \quad \text{and} \quad \int_{X_1}^{X_2} \frac{dX}{(X - X^*)}
\]

were of about the same magnitude for a given run, and it was assumed that the percent errors in the calculated column lengths would be of the same magnitude as those found in the resin phase integral. Therefore, the probable errors in the determination of the end point equivalent fractions and their affect on the value of the resin phase integrals were estimated.
The methods suggested by Mickley, Sherwood, and Reed (36, p. 53-59) were used in the error analysis. If a quantity $G$ is related to a number of other variables by a relationship of the form $G = \gamma(g_1, g_2, \ldots, g_n)$, the variation of $G$ with respect to $g_1, g_2, \ldots, g_n$ will be

$$dG = \frac{\partial \gamma}{\partial g_1} dg_1 + \frac{\partial \gamma}{\partial g_2} dg_2 + \ldots + \frac{\partial \gamma}{\partial g_n} dg_n$$  \hfill (64)

If the differentials $dg_i$ in Equation 64 are replaced by sufficiently small increments $\Delta g_i$, it can be shown (36, p. 54) that

$$\Delta G = \frac{\partial \gamma}{\partial g_1} \Delta g_1 + \frac{\partial \gamma}{\partial g_2} \Delta g_2 + \ldots + \frac{\partial \gamma}{\partial g_n} \Delta g_n$$  \hfill (65)

is a good approximation to $\Delta G$. If the quantities $\Delta g_i$ are considered as errors in the values of the $g_i$ used to evaluate $G$, Equation 65 gives an estimation of the maximum errors in $G$ corresponding to the errors $\Delta g_i$. A maximum estimate results since the $\Delta g_i$ are all assumed to be additive; thus no compensation of the errors is considered.

In the present investigation, the evaluation of the integrals depended upon the values of the equivalent fractions $X_1, Y_1, X_2$ and $Y_2$ which determined the location of the operating line on the operating diagram. The expected variations in the equivalent fractions were found as indicated by Equation 65. The expected
variations of the integrals corresponding to the deviations of $X_1', Y_1', X_2$ and $Y_2$ were then calculated for runs corresponding to typical operating conditions.

The resin phase equivalent fraction, $Y$, was found by the procedure described in Appendix D. Equation 63 in Appendix D gives the relationship of $Y$ to the measured quantities involved as

$$Y = \frac{v_T N_T}{g Q_Y}$$

The quantities $N_T$, the normality of the sodium thiosulfate solution used in the titrations, and $Q_Y$, the resin capacity, were considered as not contributing to the error involved.

The normality of the sodium thiosulfate solution was standardized by the same procedure in all cases (18, p. 269). Although errors may have been involved, the replicate standardizations were found to agree within 0.2%. Therefore, any errors due to the standardization of the thiosulfate solution should have the same effect on all the runs and not be apparent in the variation of the $Y$ values.

The specific dry-weight capacity, $Q_0$, on which $Q_Y$ was based, was determined before and after the column experiments were performed. These values of $Q_0$ were found to differ; however, the variation was small and considered to be negligible. Therefore, an average value of $Q_0$ was applied to all the runs.
The value of $Q_Y$ depended on the measured quantities $v_T$ and $g$. However, the value of $Q_Y$ was insensitive to errors in $v_T$ and $g$, as shown by Equation 62, and therefore the errors in $Q_Y$ were considered as being negligible.

The error in $Y$ according to Equation 65 and the above assumptions was

$$\Delta Y = \frac{N_T}{gQ_Y} \Delta v_T + \frac{N_T v_T}{g^2 Q_Y} \Delta g \tag{66}$$

Values of $Y$ were found at the ends of the operating lines. Therefore, $\Delta Y$ was estimated for a typical high value of $\Delta Y = 0.9$ and a typical low value of $\Delta Y = 0.3$.

The copper rich samples with a high value of $Y$ contained about two grams of dry resin. These samples were weighed on a Type 86 Mettler balance to the nearest tenth of a milligram. Therefore, $\Delta g$ was taken as $\pm 0.0005$ grams. The sodium thiosulfate solution used had a normality of about 0.35. With a two gram sample whose specific, dry-weight capacity was about 4.17 meq/gram, an equivalent fraction of $Y = 0.9$, and a sodium thiosulfate normality of 0.35, about 23 ml of sodium thiosulfate were required to titrate the cupric ion eluted from the resin. A 50 milliliter, zero filling buret was used in the titrations. This buret could be read directly to 0.10 ml. Therefore, a value of $\pm 0.025$ was taken
for $\Delta v_T$. The values of the above variables appearing in Equation 66 are summarized as follows:

- $g = 2$ grams
- $\Delta g = 0.00005$ grams
- $v_T = 23$ ml
- $\Delta v_T = 0.025$ ml
- $N_T = 0.35$ meq/ml
- $Q_Y = 4.17$ meq/gram

Insertion of these values in Equation 66 resulted in

$$\Delta Y = 0.001$$

The appropriate values for the resin samples with lower cupric ion content ($Y = 0.3$) were

- $g = 3$ grams
- $\Delta g = 0.00005$ grams
- $v_T = 11$ ml
- $\Delta v_T = 0.025$ ml
- $N_T = 0.35$ meq/ml
- $Q_Y = 4.33$ meq/g

Substitution of these values in Equation 66 resulted in an error to the nearest thousandth of

$$\Delta Y = 0.001$$

The errors involved in the determination of the solution-phase equivalent fraction depended on the accuracy with which the cupric ion normality and the total normality of the solutions were determined. The solution phase equivalent fraction was found as indicated
in Appendix C as

\[ X = \frac{N_{Cu}}{N} = \frac{v_T N_T}{v_A N} \]  

(67)

In Equation 67, \( v_A \) is the sample volume used in determining the cupric ion normality and \( N \) is the total normality of the solution. It was assumed that the pipets used in taking the aliquots were sufficiently accurate, (18, p. 125), that no random error would be involved in the sample volume \( v_A \). It was also assumed that errors in \( N_T \) would be negligible for the reasons previously stated. Application of Equation 65 to Equation 67 with the above assumptions resulted in

\[ \Delta X = \frac{N_T}{v_A N} \Delta v_T + \frac{v_T N_T}{v_A N^2} \Delta N \]  

(68)

As stated above, the titrated volume, \( v_T \), was assumed to be accurate to \( \Delta v_T = 0.025 \text{ml} \) and \( N_T \), the thiosulfate normality, was assumed to be free of random error. The total solution normality, \( N \), was determined from refractive index measurements. As shown in Appendix C, the total solution normality could be determined to \( \Delta N = 0.005 \text{meq/ml} \). It can be seen that the second term on the right hand side of Equation 68 will increase as the total normality of the solution decreases. Therefore, estimates of \( \Delta X \) were made for 0.5N and 1.0N solutions. Values of \( \Delta X \) were
also estimated for typical low and high values of \( X = 0.15 \) and \( X = 0.80 \). Aliquots of 25 ml were used in all cases except where \( X \) was large and 1.0N solutions were used. In this case 10 ml aliquots were taken.

The magnitude of \( \Delta X \) was calculated for the appropriate values of \( X \) and \( N \) by first calculating the titrated volume required in the determination of the cupric ion normality and then inserting it and the other appropriate values indicated above in Equation 68. The results of these determinations are shown below:

<table>
<thead>
<tr>
<th>( N )</th>
<th>( X )</th>
<th>( \Delta X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.15</td>
<td>0.002</td>
</tr>
<tr>
<td>0.5</td>
<td>0.80</td>
<td>0.009</td>
</tr>
<tr>
<td>1.0</td>
<td>0.15</td>
<td>0.001</td>
</tr>
<tr>
<td>1.0</td>
<td>0.80</td>
<td>0.005</td>
</tr>
</tbody>
</table>

The values of \( \Delta X \) and \( \Delta Y \) found above, were added to, or subtracted from, the operating line end point values of \( X \) and \( Y \) for two series of runs. It was apparent that the errors would increase as the operating line was brought closer to the equilibrium curve. Therefore, runs with the operating lines relatively close to the equilibrium curve and runs with the operating lines relatively far from the equilibrium curve were investigated.

For the runs number six, the operating line and equilibrium curve were relatively close together. When the equivalent fraction deviations were applied to the end points found for the 0.5N run
six-one, the following end point equivalent fractions resulted

\[
\begin{align*}
X'_{2} &= 0.065 + 0.002 = 0.067 \\
Y'_{2} &= 0.342 - 0.001 = 0.341 \\
X'_{1} &= 0.628 + 0.009 = 0.637 \\
Y'_{1} &= 0.870 - 0.001 = 0.869
\end{align*}
\]

The value of the integral \( \int_{Y_{1}}^{Y_{2}} \frac{dY}{(Y_{2} - Y)} \) corresponding to these end points was evaluated by graphical integration and found to have the value 7.14. This amounted to an error of 13% when compared to the value of 6.32 found for the original end point values.

The same procedure was applied to the 0.5N run six-two for which the modified end points were:

\[
\begin{align*}
X'_{1} &= 0.387 - 0.02 = 0.385 \\
Y'_{1} &= 0.424 + 0.001 = 0.425 \\
X'_{2} &= 0.989 - 0.009 = 0.980 \\
Y'_{2} &= 0.979 + 0.001 = 0.980
\end{align*}
\]

These end point values resulted in an integral value of 6.97 which was 11% greater than 6.23 as found from the original end point values.

The data of runs number ten were taken as being typical of experiments in which the operating line and equilibrium curve were relatively far apart. The modified end point values for the
1. ON run ten-one were found to be:

\[
\begin{align*}
X'_2 &= 0.025 + 0.001 = 0.026 \\
Y'_2 &= 0.210 - 0.001 = 0.209 \\
X'_1 &= 0.585 + 0.005 = 0.590 \\
Y'_1 &= 0.845 - 0.001 = 0.844
\end{align*}
\]

These changes in the operating line location corresponded to an increase in the value of the integral from 3.509 to 3.571. This amounted to a difference of about 2%.

The modified end point values for the 1. ON run ten-two were:

\[
\begin{align*}
X'_1 &= 0.455 - 0.001 = 0.454 \\
Y'_1 &= 0.343 + 0.001 = 0.344 \\
X'_2 &= 0.968 - 0.005 = 0.963 \\
Y'_2 &= 0.876 + 0.001 = 0.877
\end{align*}
\]

These modifications resulted in an increase from 3.536 to 3.655 in the integral or an increase of about 3%.

It is apparent that the relatively small deviations in the values of the equivalent fractions \( X \) and \( Y \) evaluated at the end points of the column can have a rather large effect on the value of the integral \( \int_{Y_1}^{Y_2} \frac{dY}{(Y^*-Y)} \). It is also apparent that this effect decreases as the operating line is placed further from the equilibrium curve. Therefore, the analysis of the errors involved in
calculated column lengths indicated that these errors should range from 2% to 13%.
APPENDIX F

SAMPLE CALCULATIONS

The calculations are shown in detail for the run ten-one. However, the results of the calculations for the other runs are given in tabular form. The calculations involved in the trial and error procedure used in correlating the data are demonstrated with the best values found for the various unknown quantities. Operating diagrams are included for both run ten-one and ten-two to show the relationship of the operating line and equilibrium curve for the cases of sodium ion displacing cupric ion from the resin and cupric ion displacing sodium ion from the resin, respectively.

Design of Column Experiments

The experiments were designed by choosing a resin phase flow rate and calculating the corresponding solution flow rate for equal-equivalent flow. For a resin phase velocity of 0.067 cm/sec as chosen for run ten-one.

\[
R = \frac{Q}{B} V_R
\]

\[
R = (1.78)(0.067) = 0.119 \text{ meq/cm}^2\text{sec}
\]

\[
L = R = 0.119 \text{ meq/cm}^2\text{sec}
\]

\[
L_V = \frac{L}{N} = \frac{0.119}{1.00} = 0.119 \text{ ml/cm}^2\text{sec}
\]
\[ L_V A_C = (0.119)(\pi)(3.81)^2 = 5.42 \text{ ml/sec} \]
\[ = 325 \text{ ml/min} \]
\[ V_L = \frac{L_V}{\varepsilon} = \frac{0.119}{0.34} = 0.349 \text{ cm/sec} \]
\[ Re = \frac{d_p(V_R + V_L)\rho}{\mu} \]
\[ = \frac{(0.0697)(0.067 + 0.349)(1.069)}{0.01292} = 2.40 \]

The operating conditions for all the column experiments were calculated in this manner and the results are listed in Table 9.

**Evaluation of the Integrals**

The integrals appearing in Equation 49 were evaluated by graphical integration. The values of the end point equivalent fractions and their smoothed values, on which the graphical integrations for run ten-one were based, are shown in Table 7 and Figure 17. The values in Table 7 indicated as occurring at infinite time are the extrapolated values from the curves in Figure 17.

Table 7. End Point Equivalent Fractions for Run Ten-one

<table>
<thead>
<tr>
<th>Time from start, min.</th>
<th>( X_1 )</th>
<th>( Y_1 )</th>
<th>( X_2 )</th>
<th>( Y_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>soln. phase</td>
<td>res. phase</td>
<td>soln. phase</td>
<td>res. phase</td>
</tr>
<tr>
<td></td>
<td>eq. fr.</td>
<td>eq. fr.</td>
<td>eq. fr.</td>
<td>eq. fr.</td>
</tr>
<tr>
<td>60</td>
<td>0.562</td>
<td>0.823</td>
<td>0.022</td>
<td>0.209</td>
</tr>
<tr>
<td>80</td>
<td>0.567</td>
<td>0.860</td>
<td>0.023</td>
<td>0.213</td>
</tr>
<tr>
<td>100</td>
<td>0.587</td>
<td>0.846</td>
<td>0.027</td>
<td>0.217</td>
</tr>
<tr>
<td>( \infty )</td>
<td>0.585</td>
<td>0.845</td>
<td>0.025</td>
<td>0.210</td>
</tr>
</tbody>
</table>
Figure 17. End Point Cu^{++} Equivalent Fractions as a Function of Time for Run Ten-one
The average end point equivalent fractions for all the runs are shown in Table 8.

Table 8. End Point Equivalent Fractions

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1₂</td>
<td>0.230</td>
<td>0.235</td>
<td>0.995</td>
<td>0.976</td>
</tr>
<tr>
<td>2₁</td>
<td>0.725</td>
<td>0.886</td>
<td>0.019</td>
<td>0.161</td>
</tr>
<tr>
<td>2₂</td>
<td>0.305</td>
<td>0.239</td>
<td>0.975</td>
<td>0.948</td>
</tr>
<tr>
<td>3₁</td>
<td>0.730</td>
<td>0.866</td>
<td>0.016</td>
<td>0.119</td>
</tr>
<tr>
<td>3₂</td>
<td>0.255</td>
<td>0.203</td>
<td>0.990</td>
<td>0.956</td>
</tr>
<tr>
<td>4₁</td>
<td>0.642</td>
<td>0.890</td>
<td>0.033</td>
<td>0.315</td>
</tr>
<tr>
<td>4₂</td>
<td>0.357</td>
<td>0.385</td>
<td>0.984</td>
<td>0.965</td>
</tr>
<tr>
<td>5₁</td>
<td>0.565</td>
<td>0.850</td>
<td>0.035</td>
<td>0.350</td>
</tr>
<tr>
<td>5₂</td>
<td>0.495</td>
<td>0.480</td>
<td>0.990</td>
<td>0.935</td>
</tr>
<tr>
<td>6₁</td>
<td>0.628</td>
<td>0.870</td>
<td>0.065</td>
<td>0.342</td>
</tr>
<tr>
<td>6₂</td>
<td>0.387</td>
<td>0.424</td>
<td>0.989</td>
<td>0.979</td>
</tr>
<tr>
<td>7₁</td>
<td>0.605</td>
<td>0.821</td>
<td>0.075</td>
<td>0.314</td>
</tr>
<tr>
<td>7₂</td>
<td>0.175</td>
<td>0.333</td>
<td>0.993</td>
<td>0.994</td>
</tr>
<tr>
<td>8₁</td>
<td>0.575</td>
<td>0.796</td>
<td>0.025</td>
<td>0.219</td>
</tr>
<tr>
<td>8₂</td>
<td>0.404</td>
<td>0.358</td>
<td>0.952</td>
<td>0.946</td>
</tr>
<tr>
<td>9₁</td>
<td>0.725</td>
<td>0.886</td>
<td>0.051</td>
<td>0.219</td>
</tr>
<tr>
<td>9₂</td>
<td>0.136</td>
<td>0.224</td>
<td>0.954</td>
<td>0.966</td>
</tr>
<tr>
<td>10₁</td>
<td>0.585</td>
<td>0.845</td>
<td>0.025</td>
<td>0.210</td>
</tr>
<tr>
<td>10₂</td>
<td>0.455</td>
<td>0.343</td>
<td>0.968</td>
<td>0.876</td>
</tr>
<tr>
<td>11₁</td>
<td>0.565</td>
<td>0.821</td>
<td>0.038</td>
<td>0.167</td>
</tr>
<tr>
<td>11₂</td>
<td>0.355</td>
<td>0.314</td>
<td>0.962</td>
<td>0.946</td>
</tr>
</tbody>
</table>
The end point equivalent fractions were used to construct operating diagrams as shown in Figures 18 and 19. Values of $X$ and $X^*$ and of $Y$ and $Y^*$ were obtained from the operating diagrams. These values were used in evaluating the integrals as shown in Figures 20 and 21. For run ten-one the following values were found.

$$I_X = \int_{X_1}^{X_2} \frac{dX}{(X-X^*)} = 3.35$$

$$I_Y = \int_{Y_1}^{Y_2} \frac{dY}{(Y^*-Y)} = 3.51$$

The values of the integrals for all the experiments are shown in Table 9.

**Correlation of the Experimental Data**

The correlation of the experimental data depended on the values of the integrals, the column lengths used, the resin phase velocities and the Reynolds numbers corresponding to the various experiments. The values of these quantities are shown in Table 9. The procedures used are described in the "Correlation of the Experimental Data" section.
Solution phase Cu^{++} equivalent fraction, X

Resin phase Cu^{++} equivalent fraction, Y

Figure 18. Operating Diagram for the Eluting Run Ten-one
Figure 19. Operating Diagram for the Loading Run Ten-two
Solution phase Cu$^{++}$ equivalent fraction, $X$

\[ \text{Area} = \int_{X_1}^{X_2} \frac{dX}{(X-X^*)} = 3.35 \]

Figure 20. Graphical Integration of the Solution Phase Integral for Run Ten-One

Resin phase Cu$^{++}$ equivalent fraction, $Y$

\[ \text{Area} = \int_{Y_1}^{Y_2} \frac{dY}{(Y^*-Y)} = 3.51 \]

Figure 21. Graphical Integration of the Resin Phase Integral for Run Ten-one
Table 9. Operating Conditions and Values of Integrals

<table>
<thead>
<tr>
<th>Run</th>
<th>N</th>
<th>V&lt;sub&gt;R&lt;/sub&gt;</th>
<th>V&lt;sub&gt;L&lt;/sub&gt;</th>
<th>Re</th>
<th>z&lt;sub&gt;2&lt;/sub&gt; - z&lt;sub&gt;1&lt;/sub&gt;</th>
<th>I&lt;sub&gt;X&lt;/sub&gt;</th>
<th>I&lt;sub&gt;Y&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total normality</td>
<td>resin velocity</td>
<td>solution velocity</td>
<td>Reynolds number</td>
<td>column length</td>
<td>solution phase integral</td>
<td>resin phase integral</td>
</tr>
<tr>
<td></td>
<td>meq/ml</td>
<td>cm/sec</td>
<td>cm/sec</td>
<td>cm</td>
<td>cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.067</td>
<td>0.349</td>
<td>2.40</td>
<td>123.8</td>
<td>14.60</td>
<td>14.39</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.067</td>
<td>0.349</td>
<td>2.40</td>
<td>62.9</td>
<td>7.71</td>
<td>7.26</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>0.050</td>
<td>0.262</td>
<td>2.40</td>
<td>62.9</td>
<td>9.75</td>
<td>9.52</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.050</td>
<td>0.262</td>
<td>2.40</td>
<td>62.9</td>
<td>8.10</td>
<td>8.94</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.067</td>
<td>0.698</td>
<td>4.85</td>
<td>62.9</td>
<td>6.77</td>
<td>6.26</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.067</td>
<td>0.698</td>
<td>4.85</td>
<td>62.9</td>
<td>4.13</td>
<td>5.55</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>0.067</td>
<td>0.698</td>
<td>4.85</td>
<td>32.4</td>
<td>4.27</td>
<td>3.76</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.033</td>
<td>0.349</td>
<td>2.42</td>
<td>32.4</td>
<td>2.47</td>
<td>3.28</td>
</tr>
<tr>
<td>9</td>
<td>0.5</td>
<td>0.033</td>
<td>0.349</td>
<td>2.42</td>
<td>32.4</td>
<td>2.47</td>
<td>3.28</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>0.067</td>
<td>1.745</td>
<td>12.20</td>
<td>32.4</td>
<td>2.47</td>
<td>3.28</td>
</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>0.033</td>
<td>0.174</td>
<td>1.19</td>
<td>32.4</td>
<td>2.47</td>
<td>3.28</td>
</tr>
<tr>
<td>12</td>
<td>0.88</td>
<td>0.033</td>
<td>0.174</td>
<td>1.19</td>
<td>32.4</td>
<td>2.47</td>
<td>3.28</td>
</tr>
</tbody>
</table>
Estimation of End Effects

The end effects were estimated by assuming a transfer-unit-height relationship of the form of Equation 42 and performing the operations indicated by Equations 43 and 46. The best values found for the unknowns in Equation 42

\[ H_{RL} = C_{AB} R^q \]  (42)

gave the following relationships

\[ H_{TL_{Cu, Na}} = 0.84 R^{0.69} \]

\[ H_{TL_{Na, Cu}} = 0.75 R^{0.69} \]

With the above relationships Equation 43

\[ \frac{r_p^2}{15 D_{\text{Cu, Na}}} = \frac{(z_2 - z_1)^{-1} - H_{TL_{AB}} \int_{X_1}^{X_2} \frac{dX}{(X - X^*)}}{V_R \int_{Y_1}^{Y_2} \frac{dY}{(Y^* - Y)}} \]  (43)

gave the following value for run ten-one.

\[ \frac{r_p^2}{15 D_{\text{Cu, Na}}} = \frac{32.4 - (0.75)(2.40)^{0.69}(3.35)}{(0.067)(3.51)} = 118.3 \text{ sec} \]
The values of \( \frac{r_p^2}{15} \bar{D}_{Cu, Na} \) were calculated for all the 1.0N runs and are shown in Table 10.

The values of \( \frac{r_p^2}{15} \bar{D}_{Cu, Na} \) given in Table 10 were plotted as functions of \( \frac{1}{(z_2-z_1)} \) as shown in Figure 10. A line drawn through the points in Figure 10 and extrapolated to zero indicated a value of \( \frac{r_p^2}{15} D_{Cu, Na} = 101 \) sec for an infinitely long column.

Therefore Equation 46

\[
\Delta z_e = \left( \frac{r_p^2}{15 \bar{D}_{Cu, Na}} \right)_{\text{finite}} - \left( \frac{r_p^2}{15 \bar{D}_{Cu, Na}} \right)_{\text{infinite}} \quad V_R \int_{Y_1}^{Y_2} \frac{dY}{Y^*-Y} \quad (46)
\]

resulted in

\[
\Delta z_e = (118.1-101)(0.067)(3.51) = 4.1 \text{ cm}
\]

when applied to run ten-one. The values for each experiment are given in Table 10, and the average value was found to be 4.0 cm.

**Estimation of the Solution Phase Transfer Unit Height**

The solution phase transfer unit heights were estimated with an assumed \( \frac{r_p^2}{15} \bar{D}_{Cu, Na} \) of 101 sec, a \( \Delta z_e \) of 4.0 cm and the known column lengths and values of the integrals. Equation 47
Table 10. Estimation of End Effects

<table>
<thead>
<tr>
<th>Run</th>
<th>( H_{TL} )</th>
<th>( L_{AB} )</th>
<th>( V_e )</th>
<th>( Z_2 )</th>
<th>( Z_1 )</th>
<th>( \frac{r_p}{15D_{Cu,Na}} )</th>
<th>( \frac{1}{r_p} )</th>
<th>( \Delta \left[ \frac{r_p}{15D_{Cu,Na}} \right] )</th>
<th>( \Delta z_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_2</td>
<td>22.5</td>
<td>123.8</td>
<td>0.964</td>
<td>105.1</td>
<td>0.0081</td>
<td>4.1</td>
<td>3.9</td>
<td>4.1</td>
<td>1.0</td>
</tr>
<tr>
<td>2_1</td>
<td>10.55</td>
<td>62.9</td>
<td>0.486</td>
<td>107.7</td>
<td>0.0159</td>
<td>6.7</td>
<td>3.3</td>
<td>6.7</td>
<td>1.0</td>
</tr>
<tr>
<td>2_2</td>
<td>10.65</td>
<td>62.9</td>
<td>0.508</td>
<td>102.9</td>
<td>0.0159</td>
<td>1.9</td>
<td>1.0</td>
<td>1.9</td>
<td>0.0</td>
</tr>
<tr>
<td>3_1</td>
<td>11.0</td>
<td>62.9</td>
<td>0.476</td>
<td>109.0</td>
<td>0.0159</td>
<td>8.0</td>
<td>3.8</td>
<td>8.0</td>
<td>3.8</td>
</tr>
<tr>
<td>3_2</td>
<td>10.2</td>
<td>62.9</td>
<td>0.447</td>
<td>117.9</td>
<td>0.0159</td>
<td>16.9</td>
<td>7.5</td>
<td>16.9</td>
<td>7.5</td>
</tr>
<tr>
<td>8_1</td>
<td>4.85</td>
<td>32.4</td>
<td>0.230</td>
<td>119.8</td>
<td>0.0309</td>
<td>18.8</td>
<td>4.3</td>
<td>18.8</td>
<td>4.3</td>
</tr>
<tr>
<td>9_1</td>
<td>5.4</td>
<td>32.4</td>
<td>0.194</td>
<td>138.1</td>
<td>0.0309</td>
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<td>17.3</td>
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<td>3.4</td>
<td>14.4</td>
<td>3.4</td>
</tr>
<tr>
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<td>5.75</td>
<td>32.4</td>
<td>0.218</td>
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<td>4.6</td>
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<tr>
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<td>6.25</td>
<td>32.4</td>
<td>0.249</td>
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<td>0.0309</td>
<td>4.0</td>
<td>1.0</td>
<td>4.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

average 4.0
\[
H_{TL_{AB}} = \frac{(z^2 - z^1) - \Delta z_e - \frac{r^2}{15D_{Cu,Na}}}{VR \int_{Y_1}^{Y_2} \frac{dY}{(Y^* - Y)}} 
\int_{X_1}^{X_2} \frac{dX}{(X - X^*)}
\]

resulted in

\[
H_{TL_{Na,Cu}} = \frac{32.4 - 4.0 - (101)(0.067)(3.51)}{3.35} = 1.40 \text{ cm}
\]

for run ten-one. The results for all the experiments are shown in Table 11 and Figures 8 and 9. The slopes and intercepts of the lines drawn through the points in Figures 8 and 9 were used to determine \(q, C_{Cu,Na}\) and \(C_{Na,Cu}\).

\[
q_{Cu,Na} = \log_{10} \frac{4.13}{0.84} = 0.69
\]

\[
q_{Na,Cu} = \log_{10} \frac{3.68}{0.75} = 0.69
\]

\[
C_{Cu,Na} = \left[ H_{TL_{Cu,Na}} \right]_{Re=1.0} = 0.84
\]

\[
C_{Na,Cu} = \left[ H_{TL_{Na,Cu}} \right]_{Re=1.0} = 0.75
\]

The above constants applied to Equation 42
Table 11. Calculation of $H_{TILAB}$

<table>
<thead>
<tr>
<th>Run</th>
<th>Reynolds number</th>
<th>$z_2 - z_1 - \Delta z_e$</th>
<th>$101 V_{RIY}$</th>
<th>$I_X$</th>
<th>$H_{TIL_{Na, Cu}}$ from Eq. 47</th>
<th>$H_{TIL_{Cu, Na}}$ from Eq. 47</th>
<th>$j_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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<td>119.8</td>
<td>97.4</td>
<td>14.60</td>
<td>1.53</td>
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</tr>
<tr>
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<td>51.3</td>
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<td>1.10</td>
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<tr>
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<td>8.10</td>
<td>1.70</td>
<td>0.392</td>
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<td>42.3</td>
<td>6.77</td>
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<tr>
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<td>37.6</td>
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<td>5.16</td>
<td>0.129</td>
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<tr>
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<td>28.4</td>
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<td>1.47</td>
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<tr>
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<td>23.9</td>
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<tr>
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<td>28.4</td>
<td>22.0</td>
<td>6.76</td>
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<td>0.622</td>
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</tr>
<tr>
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<td>1.19</td>
<td>28.4</td>
<td>25.1</td>
<td>6.60</td>
<td>0.50</td>
<td>1.334</td>
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</tr>
</tbody>
</table>
resulted in the following equations for the solution phase transfer unit heights.

\[ H_{TL_{Cu, Na}} = 0.84 \text{Re}^{0.69} \]

\[ H_{TL_{Na, Cu}} = 0.75 \text{Re}^{0.69} \]

Calculation of \( \frac{r^2}{15 \overline{D}_{Cu, Na}} \)

The values of \( \frac{r^2}{15 \overline{D}_{Cu, Na}} \) were calculated for all the runs. The average of these values should be the same as that initially assumed in calculating the solution-phase transfer-unit heights. With the solution-phase transfer-unit-height relationships found in the previous section, \( \Delta z_e = 4.0 \text{ cm} \) and the appropriate column length and values of the integrals, Equation 49

\[
\frac{r^2}{15 \overline{D}_{Cu, Na}} = \frac{(z_2 - z_1) - \Delta z_e - H_{TL_{AB}} \int_{X_1}^{X_2} \frac{dX}{(X - X^*)}}{V_R \int_{Y_1}^{Y_2} \frac{dY}{(Y^* - Y)}} \quad (49)
\]

\[
\frac{r^2}{15 \overline{D}_{Cu, Na}} = \frac{3.24 - 4.0 - (0.75)(2.40^{0.69})(3.35)}{(0.067)(3.51)} = 101.3 \text{ sec}
\]
for run ten-one.

The values for all the experiments are listed in Table 12. An average value of 101.2 sec was found which is essentially the same as the value of 101 sec originally assumed.

**Calculation of Column Lengths**

The end effect, solution-phase transfer-unit-height relationships and average $r_p^2/15 D_{Cu,Na}$ found in the previous paragraphs were used to calculate the corresponding column lengths. The calculated column lengths were then compared to those actually used. For run ten-one application of the above terms and the appropriate integrals to Equation 49

\[
(z_2-z_1) = \frac{r_p^2}{15 D_{Cu,Na}} v R \int_{Y_1}^{Y_2} \frac{dY}{(Y^*-Y)} + h_{TLAB} \int_{X_1}^{X_2} \frac{dX}{(X-X^*)} + \Delta z e
\]  \hspace{1cm} (49)

resulted in

\[
(z_2-z_1) = (101.2)(0.067)(3.51)+(0.75)(2.400.69)(3.35)+4.0 = 32.3 \text{ cm}
\]

The corresponding error according to Equation 50

\[
e = \left[ \frac{(z_2-z_1)_{\text{calc.}} - (z_2-z_1)_{\text{act.}}}{(z_2-z_1)_{\text{act.}}} \right] 100\% \hspace{1cm} (50)
\]
Table 12. Calculation of $\frac{r^2}{D_{\text{Na,Cu}}}^{15}$ and $\overline{D_{\text{Cu,Na}}}$

<table>
<thead>
<tr>
<th>Run</th>
<th>$z^2 - z_1 - \Delta z$</th>
<th>$H_{\text{TL}}$</th>
<th>$I_{\text{AB}}$</th>
<th>$X$</th>
<th>$V$</th>
<th>$R$</th>
<th>$Y$</th>
<th>$\frac{r^2}{15D_{\text{Cu,Na}}}$ from Eq. 48</th>
<th>$D_{\text{Cu,Na}}$</th>
<th>$\Delta D_{\text{Cu,Na}}^2$</th>
<th>$(\Delta D_{\text{Cu,Na}})^2$</th>
</tr>
</thead>
<tbody>
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<td>0.964</td>
<td>100.9</td>
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<td>49</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>10.55</td>
<td>0.486</td>
<td>99.5</td>
<td>0.811</td>
<td>+4</td>
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<td></td>
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</tr>
<tr>
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<td>0.476</td>
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<tr>
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</tr>
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<td>99.7</td>
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<td>9</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>28.4</td>
<td>10.15</td>
<td>0.184</td>
<td>99.2</td>
<td>0.814</td>
<td>7</td>
<td>49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>10000</td>
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</table>

average = 101.2, 0.807, sum = 160, 974
The calculated column lengths and their corresponding errors are shown in Table 13.

**Calculation of \( \overline{D}_{\text{Cu}, \text{Na}} \)**

The resin phase diffusivities were calculated as

\[
\overline{D}_{\text{Cu}, \text{Na}} = \frac{r_p^2}{15 \left[ \frac{r_p^2}{\overline{D}_{\text{Cu}, \text{Na}}_{\text{calc.}}} \right]}
\]

The value for run ten-one was

\[
\overline{D}_{\text{Cu}, \text{Na}} = \frac{(0.0348)^2}{(15)(101.3)} = 0.797 \times 10^{-6} \text{ cm}^2/\text{sec}
\]

The calculated values of \( \overline{D}_{\text{Cu}, \text{Na}} \) and \( \Delta(\overline{D}_{\text{Cu}, \text{Na}}) \) are listed in Table 12. The average was found to be

\[
\overline{D}_{\text{Cu}, \text{Na}} = 0.807 \times 10^{-6} \text{ cm}^2/\text{sec}
\]

The 95% confidence limits of the average value of the resin phase diffusivity were calculated by the method suggested by Mickley, Sherwood and Reed (36, p. 66-77). They show that the population mean value of \( \overline{D}_{\text{Cu}, \text{Na}} \) should lie within the range
Table 13. Comparison of Calculated and Actual Column Lengths

<table>
<thead>
<tr>
<th>Run</th>
<th>$10^1 V_{RX}$</th>
<th>$H_{TL}$</th>
<th>$I_X$</th>
<th>$z_2 - z_1$ calculated from Eq. 49</th>
<th>$z_2 - z_1$ actual</th>
<th>$\epsilon$ error from Eq. 50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>cm</td>
<td></td>
<td></td>
<td>cm</td>
<td>%</td>
</tr>
<tr>
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<td>22.5</td>
<td></td>
<td>123.9</td>
<td>123.8</td>
<td>0.1</td>
</tr>
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<td>63.7</td>
<td>62.9</td>
<td>1.3</td>
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<td>62.9</td>
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<td>32.6</td>
<td>32.4</td>
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<td>10.1</td>
<td></td>
<td>32.7</td>
<td>32.4</td>
<td>0.9</td>
</tr>
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<td>32.1</td>
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<tr>
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<td>6.2</td>
<td></td>
<td>35.3</td>
<td>32.4</td>
<td>9.0</td>
</tr>
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</table>
\( (\overline{D}_{\text{Cu}, \text{Na}})_{\text{av}} \pm s_m t_s \), where \( s_m \) is the square root of the sample variance of the mean, and \( t_s \) is "Student's t". The value of \( s_m \) was estimated as

\[
\begin{align*}
    s_m &= \left[ \frac{n}{n(n-1)} \sum (\Delta \overline{D}_{\text{Cu}, \text{Na}})^2 \right]^{1/2} \\
    &= \left[ \frac{3833 \times 10^{-16}}{(21)(20)} \right]^{1/2} = 1.96 \times 10^{-8} \text{ cm}^2/\text{sec}
\end{align*}
\]

The value of \( t_s \) for 21 measurements and 95% confidence limits was found in Table 2-1 of Mickley, Sherwood and Reed (36, p. 68) as

\[
t_s = 2.09
\]

Therefore

\[
\begin{align*}
    \overline{D}_{\text{Cu}, \text{Na}} &= 0.807 \times 10^{-6} \pm (1.96 \times 10^{-8})(2.09) \text{ cm}^2/\text{sec} \\
    &= (0.807 \pm 0.041) \times 10^{-6} \text{ cm}^2/\text{sec} \\
    &= 0.807 \times 10^{-6} \text{ cm}^2/\text{sec} \pm 5\%
\end{align*}
\]

**Calculation of \( n, p \) and the \( j \)-factors**

The values of the Schmidt number and the solution phase diffusivity ratio were required in evaluating \( n, p \) and the \( j \)-factors. The magnitude of the Schmidt number was estimated from the properties shown in Appendix A.
\[ \text{Sc} = \frac{\mu}{D_{av}} \]
\[ D_{av} = \frac{D_{Na} + D_{Cu}}{2} \]
\[ = \frac{(7.2 + 13.3) \times 10^{-6}}{2} = 10.2 \times 10^{-6} \text{ cm}^2/\text{sec} \]
\[ \text{Sc}^{2/3} = \left[ \frac{0.01133}{(1.031)(10.2 \times 10^{-6})} \right]^{2/3} = 105 \]

The solution phase diffusivity ratio at \( X = 0.5 \) was found by applying the ionic diffusivities listed in Appendix A to the quotient of Equations 30 and 31

\[ D_{Cu, Na} = \frac{D_{Cu} D_{Na} (X+3)}{(2D_{Cu} - D_{Na})X + 3D_{Na}} \]  \hspace{1cm} (30) \]
\[ D_{Na, Cu} = \frac{D_{Cu} D_{Na} (X+3)}{(2D_{Cu} - D_{Na})X + 2D_{Cu} + D_{Na}} \]  \hspace{1cm} (31) \]
\[ \frac{D_{Cu, Na}}{D_{Na, Cu}} = \frac{(2D_{Cu} - D_{Na})X + 2D_{Cu} + D_{Na}}{(2D_{Cu} - D_{Na})X + 3D_{Na}} \]

\[ \left[ \frac{D_{Cu, Na}}{D_{Na, Cu}} \right]_{X=0.5} = \frac{(2)(7.2) - 13.3)(0.5) + 2(7.2) + 13.3}{(2)(7.2) - 13.3)(0.5) + 3)(13.3)} \]
\[ = 0.698 \]

The values of \( n \) and \( p \) were found as indicated by
Equations 51 and 52, respectively

\[ n = \frac{\log \left( \frac{C_{Na,Cu}}{C_{Cu,Na}} \right)}{\log \left( \frac{D_{Cu,Na}}{D_{Na,Cu}} \right)} \quad (51) \]

\[ n = \frac{\log (0.75/0.84)}{\log 0.698} = 0.34 \]

\[ p = \frac{2}{(C_{Cu,Na} + C_{Na,Cu})} \left( \frac{\epsilon}{a} \right) \frac{\epsilon}{\text{Sc}^{2/3}} \quad (52) \]

\[ p = \frac{(2)(0.34)(105)}{(0.75+0.84)(56.8)} = 0.79 \]

The \( j \)-factor values corresponding to the calculated solution phase transfer unit height were calculated with Equation 53

\[ j_D = \frac{2C_{AB}}{C_{AB} + C_{BA}} \left( \frac{\epsilon}{a} \right) \left( \frac{\epsilon}{\text{Sc}^{2/3}} \right) \frac{1}{H_{TL_{AB}}} \quad (53) \]

The \( j \)-factor corresponding to run ten-one was

\[ j_D = \frac{(2)(0.75)(0.34)(105)}{(0.75 + 0.84)(56.8)(1.40)} = 0.422 \]

The \( j \)-factors found for the various experiments are listed in Table 11 and shown in Figure 13.