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The Separation of Aqueous Two-Salt Solutions in Horizontal Thermal Diffusion Columns: The System $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$

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To the Graduate Council:

I am submitting herewith a thesis written by Gerald Thomas Fisher entitled "The Separation of Aqueous Two-Salt Solutions in Horizontal Thermal Diffusion Columns: The System $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

Dr. J.W. Prados, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

December 2, 1960

To the Graduate Council:

I am submitting herewith a thesis written by Gerald Thomas Fisher entitled "The Separation of Aqueous Two-Salt Solutions in Horizontal Thermal Diffusion Columns: The System $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

AS Recd 29
Dec 60

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Major Professor

We have read this thesis and
recommend its acceptance:

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J. D. Tillman
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H. E. Spivey
Acting Dean of the Graduate School

THE SEPARATION OF AQUEOUS TWO-SALT SOLUTIONS IN
HORIZONTAL THERMAL DIFFUSION COLUMNS:
THE SYSTEM $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$

A Dissertation
Presented to
the Graduate Council of
University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Gerald Thomas Fisher

December 1960

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THE SEPARATION OF AQUEOUS TWO-SALT SOLUTIONS IN

HORIZONTAL THERMAL DIFFUSION COLUMNS:

THE SYSTEM $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$

SUMMARY

In the preparation and processing of nuclear fuels and materials of reactor construction, metallic elements occur in mixtures which are difficult to separate by conventional methods; for example, the desirable reactor material, zirconium, is difficult to separate from its partner in nature, hafnium. The possibility exists that these elements may be separated by liquid phase thermal diffusion of their aqueous salt solutions. The Union Carbide Nuclear Company through the Chemical Technology Division of the Oak Ridge National Laboratory has sponsored a research program at the Chemical and Metallurgical Engineering Department of the University of Tennessee to study the separation of two-salt aqueous solutions by thermal diffusion techniques.

The objectives of the present part of the project were 1) to design, construct, and operate Von Halle-Jury thermal diffusion columns for the separation of a convenient salt mixture, 2) to compare the heights of a transfer unit and the equilibrium coefficients for the separations with estimates from Soret (single thermal diffusion stage) data, 3) to determine the effect of certain operating variables, such as length, width, and temperature difference, on these separation parameters, and 4) to develop a design procedure for

commercial separation processes, including columns in a cascade.

Two horizontal thermal diffusion columns were constructed and operated using solutions of $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ of concentrations 0.5 molar in each salt. The smaller of the two columns was 22-3/4 in. long, 3/4 in. wide, and 1/16 in. deep in each flow channel, with a total mass transfer area of 0.106 ft². The larger column had a flow channel 22 ft. long and 1/2 in. wide; this channel was laid out on a flat plate 17 x 17 in. and had a mass transfer area of 0.915 ft². A du Pont PD-600 cellophane membrane separated the two flow channels in each column. The small column was operated with flow rates between 2 and 10 ml/hr, with the wall temperatures maintained at 40°F and 140°F on the top and bottom, respectively. The large column was operated with flow rates between 10 ml/hr and 30 ml/hr, with the wall temperatures at 52°F and 122°F on the top and bottom, respectively. The small column was operated with single-salt solutions and two-salt solutions at total reflux; both columns were operated with a product withdrawal using two-salt solutions.

The following results were obtained from the small column. The equilibrium constant K for mass transfer equilibrium between the two channel sections was estimated to be 0.944 for the separation of CuSO_4 from H_2O and 0.962 for the separation of CoSO_4 from H_2O . The corresponding separation factor, α , for CuSO_4 relative to CoSO_4 is 1.02. The heights of the transfer unit, h_L , based on the cold side compositions and flow rates were estimated to be 0.26 ft. for CuSO_4 and 0.24 ft. for CoSO_4 from H_2O at a flow rate of

2.0 ml/hr. The heights of the transfer unit were estimated from Soret data and the theory of laminar operation for these operating conditions, and the corresponding values were 0.91 ft. for the CuSO_4 and 0.78 ft. for the CoSO_4 . The salts always concentrated near the cold wall under steady-state conditions and the concentrations of the salts for the cases of maximum separation were 0.367 molar and 0.511 molar for the effluents from the hot and cold sides, respectively.

From the large column, the separation parameters of K and h_L were measured at steady state. The observed values could be correlated with the values observed from the small column using the form of the equations developed under the assumption of laminar flow. These correlations were in error by no more than 10 per cent.

An unusual and unexplained transient concentration distribution was observed when the large column was first started up. The salt initially concentrated at the hot wall, and the concentration continued to vary with time over a long period (about 40 days). After the column finally reached a steady state of operation, the flow rates were changed, and the transient behavior was not observed; the column was not shut down between changes of the flow rates.

All solutions were chemically analyzed with a spectrophotometer. The design of a commercial-scale operation for separating a component from a given two-salt mixture is considered in an Appendix using data and theory from this investigation. The separation would be carried out in horizontal thermal

diffusion columns arranged in a cascade. Calculations based on data for the $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ system indicate that in order to change the ratio of salt compositions by a factor of 10, about 3×10^5 square feet of thermal diffusion surface area would be required per pound of dry salt product per day.

The conclusions of the investigation were that 1) the horizontal thermal diffusion column can be used for separating the salt mixtures but would be extremely expensive, 2) the height of the transfer unit is proportional to the flow rate for the conditions investigated, 3) the separation of each salt from water is independent of the presence of the additional salt, 4) the theory developed based on Soret cell separations fails to predict the column behavior quantitatively, although the equations predict the correct dependence of heights of a transfer unit and equilibrium constants on operating conditions, and can be used for scale-up.

Although the laminar flow model may be useful for preliminary estimation of the behavior of a thermal diffusion column, it is necessary to obtain data on a scale model column in order to design a commercial plant for a specific separation with confidence.

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CHAPTER I

INTRODUCTION

Thermal diffusion is the process of separation of substances by the use of a temperature gradient as a separation potential. The effect was first reported for liquid solutions by C. Ludwig (35) in 1856; he placed one leg of an inverted U-tube filled with sodium sulfate and water in an ice bath and the other leg in boiling water. He discovered that after three days, the salt concentration in the cold leg was greater than that in the other. Thermal diffusion in liquid solutions was extensively investigated by C. Soret (42) in 1879-81; because of this extensive work, the effect in liquids bears Soret's name. Soret observed with additional salt systems that the establishment of a temperature gradient in the solutions also caused a concentration gradient; the concentration of the salt was always greater in the cold regions, as Ludwig had observed.

Thermal diffusion is one of a broad group of separation techniques used in chemical engineering that include liquid-liquid extraction, distillation, ion exchange, sorption processes, and crystallization. Thermal diffusion has not been put to use as the other operations because its large heat requirements usually make it economically unattractive where one of the other operations will work satisfactorily. However, Brown and Jones (4) state that "commercialization of the process is not far away".

Previous investigators of thermal diffusion have used either a Soret cell,

or a multistage column often referred to by the name of its inventors, Clusius and Dickel (13). The Soret cell, which is sketched in Figure 1, consists of two parallel horizontal surfaces with the solution under study contained between them; one wall is heated and the other cooled. In the absence of convection currents, a concentration gradient is established; separation obtainable in such a device corresponds to that of a single "equilibrium stage" in conventional mass transfer terminology. The Clusius-Dickel column, which is

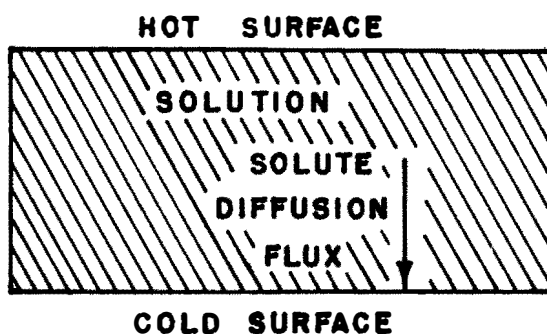


FIGURE 1

SCHEMATIC REPRESENTATION OF A SORET CELL

sketched in Figure 2, consists of vertical concentric tubes or parallel plates with a reservoir connected to each end of the channels. One wall is heated, usually the inside tube in the circular geometry, and the other wall is cooled. The concentration gradient is established in a direction perpendicular to the walls. The temperature gradient also causes a density gradient to be estab-

lished in this same direction; this density gradient causes a bulk flow upward along the hot wall and a bulk flow downward along the cold wall. As the concentration is not the same at both walls, this bulk flow causes an enrichment in the lower reservoir if the solute diffuses toward the cold wall. Hence this column operates as a multistage countercurrent-flow device. Clusius and Dickel were

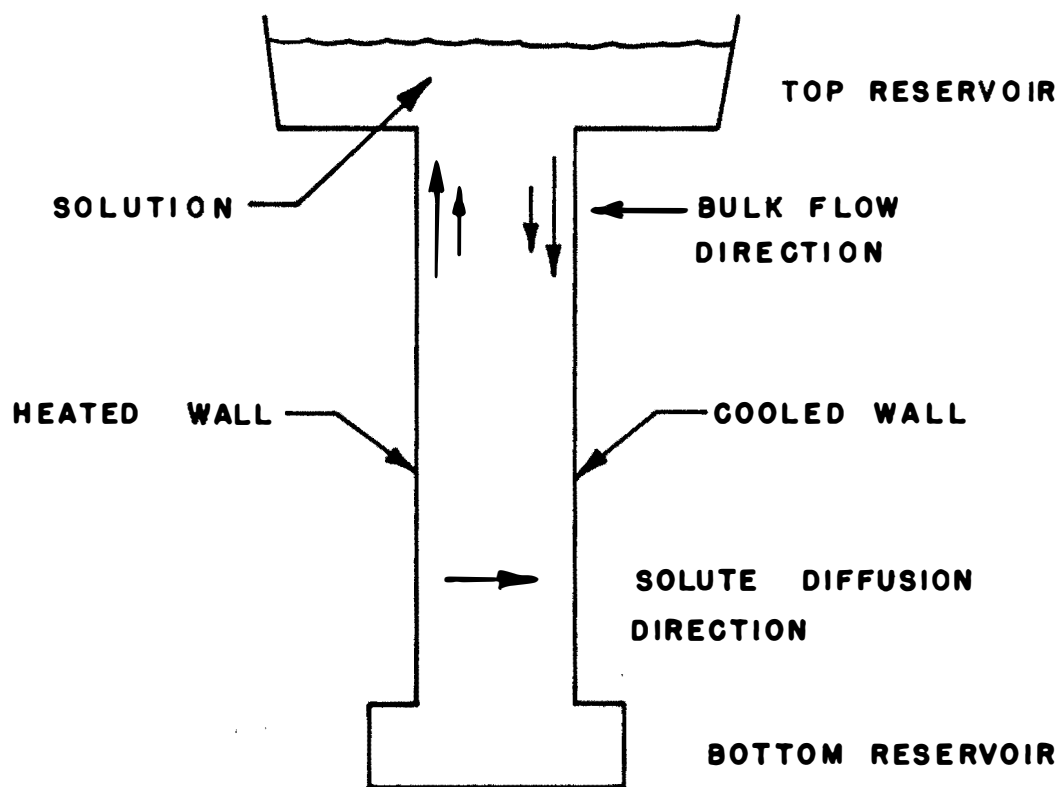


FIGURE 2

SCHEMATIC REPRESENTATION OF A CLUSIUS-DICKEL COLUMN

able to obtain a separation equivalent to 800 single stages in a tubular column 36 meters long (30). All other multistage devices have been a variation of this

basic design, except that of Von Halle and Jury (51), which is described below.

In 1956, Von Halle and Jury designed, constructed and operated a continuous multistage thermal diffusion apparatus which does not employ thermal convection currents to induce the bulk flow. Their device creates two flow channels by the use of a porous membrane, such as cellophane. Figure 3 shows the schematic arrangement of the apparatus. Each channel is bounded by a

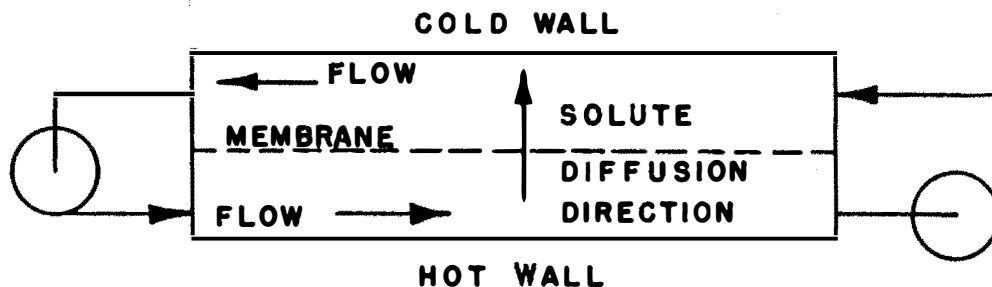


FIGURE 3

SCHEMATIC REPRESENTATION OF A VON HALLE-JURY
HORIZONTAL THERMAL DIFFUSION COLUMN

heat transfer surface and the membrane, together with appropriate side walls. Entrance and exit lines are placed at each end and the solution is pumped through the channel by external pumps. Thermal diffusion takes place through the membrane. The column is operated in a horizontal position to

prevent density gradients from causing bulk flow inside a channel as in the vertical Clusius-Dickel column. The advantages of this device are that the bulk flows can be controlled externally and independently of the temperature gradient or the spacing between the walls, and that any system which exhibits the Soret effect can be separated continuously. Some systems, such as the ethyl alcohol-water system at low alcohol concentrations, cannot be separated in the Clusius-Dickel column, but separate quite effectively in the Von Halle-Jury column. This phenomenon is believed to be due to the "forgotten effect", which is discussed in Chapter III. Another advantage is that narrow and extremely uniform wall spacing is not essential; according to Brown and Jones (4), "slit widths in a Clusius-Dickel column should be on the order of 0.01-0.06 in." An extremely uniform plate spacing is necessary in the vertical column to prevent parasitic mixing, that is, turbulent mixing of the stream flowing up and the stream flowing down.

In the preparation and processing of nuclear fuels and materials of reactor construction, metallic elements occur in mixtures which are difficult to separate by conventional methods; for example, the desirable reactor material, zirconium, is difficult to separate from its partner in nature, hafnium. In September, 1956, a research project was begun at the Department of Chemical and Metallurgical Engineering of the University of Tennessee through the support of Union Carbide Nuclear Company under Contract No. W-7405 eng 26, S-1056 to study the feasibility of separating metallic salts

in aqueous solutions by thermal diffusion techniques. The purposes of the present part of the project were 1) to design, construct, and operate Von Halle-Jury columns for the separation of a convenient salt mixture, 2) to compare the heights of a transfer unit and the equilibrium coefficients for the separations with estimates from Soret (single-stage) data, 3) to determine the effect of certain operating variables such as length, width and temperature difference on these separation parameters, and 4) to develop a design procedure for commercial separation processes including columns in a cascade.

Two horizontal thermal diffusion columns of the type used by Von Halle and Jury have been constructed and operated using the copper sulfate-cobalt sulfate-water system. This system was selected because solutions of each salt were known to exhibit the Soret effect, and because analysis of two-salt solutions could be easily performed by spectrophotometric methods. The columns were similar in construction, with the smaller having 0.106 ft^2 of transfer area and the other 0.915 ft^2 of area. The larger column was constructed in order to test the validity of the descriptive mathematics on a scaled up piece of equipment. The columns were operated with reflux ratios ranging from infinity to one; both single salt solutions and two salt solutions were used. Feed solutions were approximately 0.45 molar in each salt for all operations.

The small column of 0.106 ft^2 active area was $22\frac{3}{4}$ in. long, $\frac{3}{4}$ in. wide, and $\frac{1}{16}$ in. deep in each channel, with a cellophane membrane separat-

ing the two channels. On each side of the cellophane, a 1/2 mil Teflon gasket was used, with an opening $20\frac{1}{4}$ by $3\frac{3}{4}$ open for mass transfer; the Teflon itself is essentially impervious to diffusion of salt. Flow rates were varied from 2 ml/hr to 10 ml/hr. The wall temperatures of the system were 140°F and 40°F for all operations, with the cold wall on top.

The large column of 0.915 ft² area was constructed of two flat plates, each 17 in. x 17 in. A flow channel 22 ft. long and 1/2 in. wide was laid out on the plates; the distance between the heat transfer surfaces was 0.15 in. The channels were 20 parallel rectangular slots, alternately connected on the ends to form one continuous channel. A 1/2 mil teflon gasket covered the last channel on each end, which left 18 active channels for diffusion. Flow rates were varied from 10 ml/hr to 30 ml/hr. The wall temperatures were 52°F and 122°F for the 4 completed runs; the cold wall was on top.

The design of a cascade for separating two salt mixtures using horizontal thermal diffusion columns is considered in Appendix F. An example problem for a separation by a factor of 10 of the $\text{CuSO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ system is considered. The number of stages, the total and individual interstage flow, and a cost estimate are given.

CHAPTER II

PHENOMENOLOGICAL THEORY

The following development, except for minor changes, has appeared in a previous report by the author (18), but is repeated here in order to make the present document more complete. The development under the heading "Continuous Separation Processes" is similar in principle to that of Furry, Jones, and Onsager (21) for the Clusius-Dickel column and to that of Von Halle (51) for the horizontal column.

The existence and magnitude of the thermal diffusion effect in gases can be predicted from the kinetic theory. Unfortunately, no satisfactory explanation for thermal diffusion in liquids has been proposed, and expressions for the rate of diffusion are written by analogy with the expressions derived for gases. The form of expression adopted in the present work is that given by Grew and Ibbs (22) for the diffusion rate effected by a temperature gradient. These authors relate the thermal gradient and the rate of mass transfer caused by the thermal gradient through the equation

$$J_{At} = - \rho D' \xi (1 - \xi) \frac{dT}{dr} \quad (1)$$

where

J_{At} = diffusion rate caused by the thermal gradient, moles/area-time

ξ = mole fraction of diffusing component

$\frac{dT}{dr}$ = temperature gradient in the "r" direction, degrees/length

ρ = molar density, moles/volume

D' = coefficient of thermal diffusion, area/time-degree

For dilute solutions the quantity $(1 - \xi) \cong 1$, and this approximation will be used throughout the calculations in the present work. The theory is not applied to any operations in which ξ is greater than 0.01. Values of ξ as large as 0.02 do occur in certain parts of the work, but no attempt was made to apply the developed theories to these operations. When a concentration gradient has been established because of the thermal gradient, normal diffusion causes back mixing, and the net rate of diffusion is given by

$$J_A = \rho \left[-D' \xi \frac{dT}{dr} - D \frac{d\xi}{dr} \right] \quad (2)$$

where

J_A = the net rate of diffusion, moles/area-time

D = coefficient of diffusion, area/time

Equation (2) defines the thermal diffusion coefficient D' .

I. THE SORET CELL

In a Soret cell (Figure 1), a concentration gradient and a thermal gradient are established between two parallel walls which are respectively heated and cooled. At steady state, there is no net transfer of mass from one part of the system to another; hence $J_A = 0$. If equation (2) is equated to zero, then

$$-D' \xi \frac{dT}{dr} - D \frac{d\xi}{dr} = 0 \quad (3)$$

or

$$-\frac{D'}{D} \frac{dT}{dr} = \frac{1}{\xi} \frac{d\xi}{dr} \quad (4)$$

and it follows that

$$-\frac{D'}{D} dT = \frac{d\xi}{\xi} \quad (5)$$

If equation (5) is integrated between limits of ξ_1 , T_1 , and ξ_2 , T_2 , then

$$-\frac{D'}{D} (T_2 - T_1) = \ln \frac{\xi_2}{\xi_1} \quad (6)$$

The quantity $\frac{D'}{D}$ is defined as the Soret coefficient σ , and

$$\xi_2 = \xi_1 e^{-\sigma(T_2 - T_1)} \quad (7)$$

II. CONTINUOUS SEPARATION PROCESSES

The horizontal thermal diffusion column operates with two independently flowing streams between which diffusion occurs across the cellophane barrier. In developing a solution to the problem of obtaining concentration profiles for the column in terms of operating conditions and system properties, the following notation will be adopted. The relationships between the notation and the physical system are shown in Figure 4.

Parameters of the channel bordered by the wall that is:

| <u>hot</u> | <u>cold</u> | |
|------------|-------------|---|
| z | z' | coordinate length of channel, measured in the direction of flow, length |
| Z | Z | total length of channel, length |
| r | s | coordinate distance from the membrane, length |
| a | a | depth of channel, length |

| <u>hot</u> | <u>cold</u> | |
|-------------|---------------|--|
| $v(r)$ | $v'(s)$ | velocity distribution between the wall and the membrane, length/time |
| V | L | average flow rate, moles/time, assumed constant throughout the channel |
| $\xi(z, r)$ | $\xi'(z', s)$ | mole fraction of diffusing component |
| y | x | average mole fraction of diffusing component |
| J_r, J_z | $J_s, J_{z'}$ | diffusion rate in the coordinate direction, moles/area-time |

Parameters of the membrane:

| | |
|----------|--|
| l | coordinate distance measured from the hot channel, length |
| δ | thickness of the membrane, length |
| b | width of the membrane (and channel), length |
| J_o | diffusion rate through the membrane in the coordinate direction, moles/area-time |

The coordinate system is defined in this manner to permit the solution of the diffusion equation in one channel to be applied to the other channel by symmetry.

If equation (2) is applied to the membrane, the rate of diffusion across the membrane, J_o , as shown in Appendix D, is

$$J_o = \frac{\sigma \tau_M D \phi \rho}{(1 - e^{-\sigma \tau_M \delta})} (\xi_o' - \xi_o e^{\sigma \tau_M \delta}) \quad (8)$$

where

$$\tau_M = -\frac{dT}{dl}$$

$\xi_o' =$ the concentration on the cold surface of the membrane

ξ_0 = the concentration on the hot surface of the membrane

The quantity ϕ is the fraction of the total area of the membrane that the pores occupy; the rate of diffusion was derived assuming that the membrane has no effect on diffusion except to reduce the free area by the quantity ϕ . If the system is operated with $J_0 = 0$, i.e., as Soret cell with no net diffusion, equation (8) gives

$$\xi_0' = \xi_0 e^{\sigma \tau M \delta} \quad (9)$$

If a composition $\xi_0'^*$ is defined as the "equilibrium" concentration, i.e., that which will exist in equilibrium with ξ_0 , when $J_0 = 0$, then equation (9) gives for $\xi_0'^*$ that

$$\xi_0'^* = \xi_0 e^{\sigma \tau M \delta} \quad (10)$$

This is "equilibrium" in the sense of a steady or stationary state of no net mass transfer; it is not equilibrium in the thermodynamic sense. If equation (10) is combined with equation (8), then

$$J_0 = \frac{\sigma \tau M^D \phi \rho}{1 - e^{\sigma \tau M \delta}} (\xi_0' - \xi_0'^*) \quad (11)$$

In conventional mass transfer terminology, equation (11) states that the rate of diffusion is proportional to the difference between the actual concentration and the concentration that would exist in equilibrium with the actual concentration on the other side of the membrane.

If a column is operated as shown in Figure 4 with a product withdrawal rate from one end of D moles/time, of composition x_D , then a material balance on that end of the column gives

$$Vy = Lx + Dx_D \quad (12)$$

$$V = L + D \quad (13)$$

A material balance on a section of differential length dz yields, under the assumption of no longitudinal diffusion,

$$Lx = J_o b dz + L(x + dx) \quad (14)$$

or

$$J_o = -\frac{L}{b} \frac{dx}{dz} = \frac{L}{b} \frac{dx}{dz'} \quad (15)$$

The diffusion equation (15) and the material balance equation (12) may be readily solved simultaneously using either of two assumptions:

1. that complete mixing takes place on either side of the membrane, or
2. that no mixing takes place in either channel.

The assumption of complete mixing might better apply to a column operating with the cold wall on top, as this arrangement should induce convectional currents between the plates and the membrane; the assumption of no mixing should apply more closely to operation with the hot wall on top, as this would discourage convectional currents. The actual operating condition of a column would be expected to lie between these two assumptions.

Complete Mixing Operation

If perfect mixing in the individual channels is assumed, then

$$x = \xi' = \xi_o', \quad y = \xi = \xi_o, \quad x^* = \xi_o'^* = \xi'^* \quad (16)$$

and equation (11) becomes, using equation (16)

$$J_0 = k_L' (x^* - x) \quad (17)$$

where

$$k_L' = \frac{\sigma \tau_M D \phi \rho}{e^{\sigma \tau_M \delta} - 1} \quad (18)$$

By combining equations (10) and (16), one obtains

$$K' x^* = y \quad (19)$$

where

$$K' = e^{-\sigma \tau_M \delta} \quad (20)$$

Laminar Flow Operation

Under the assumption that physical properties are independent of temperature and composition, the solution to the equations of viscous flow between two parallel plates of infinite width is given below (this situation is approximated in the columns, since the channel width is large compared with the vertical depth):

$$v(r) = \frac{6V}{a^3 b \rho} (ar - r^2) \quad (21)$$

$$v'(s) = \frac{6L}{a^3 b \rho} (as - s^2) \quad (22)$$

If no longitudinal diffusion is assumed, then the transport relations are

$$J_r = \rho \left[-D' \xi \tau - D \frac{d\xi}{dr} \right] \quad (23)$$

$$J_z = \rho v \xi \quad (24)$$

$$J_s = \rho \left[-D' \xi' \tau' - D \frac{d\xi'}{ds} \right] \quad (25)$$

$$J_{z'} = \rho v' \xi' \quad (26)$$

where

$$\frac{dT}{dr} = -\frac{dT}{ds} = \tau = -\tau' = \text{constant}$$

The continuity equation at steady state is

$$\frac{\partial(\rho \xi)}{\partial t} = 0 = -\text{div } \vec{J} \quad (27)$$

or

$$\frac{\partial}{\partial r} J_r + \frac{\partial}{\partial z} J_z = 0 \quad \text{and} \quad \frac{\partial}{\partial s} J_s + \frac{\partial}{\partial z'} J_{z'} = 0 \quad (28)$$

If the values of the components of \vec{J} from equations (23) through (26) are substituted into equation (28), then

$$\frac{\partial}{\partial r} \left[-D' \xi \tau - D \frac{\partial \xi}{\partial r} \right] + \frac{\partial}{\partial z} (\rho v(r) \xi) = 0 \quad (29)$$

$$\frac{\partial}{\partial s} \left[-D' \xi' \tau' - D \frac{\partial \xi'}{\partial s} \right] + \frac{\partial}{\partial z'} (\rho v(s) \xi') = 0$$

The boundary values are

$$\begin{aligned} J_r(0) &= J'_0 = -J_0 & J_s(0) &= J_0 \\ J_r(a) &= 0 & J_s(a) &= 0 \end{aligned} \quad (30)$$

As the differential equations and boundary conditions are identical, it is necessary to solve only one of the differential equations. The details of the solution are given in Appendix C. The solution yields the average mole fraction in the hot channel, y , at any point z as

$$y = \xi_0 f_1(c) - \frac{V}{\sigma \tau b \rho D} \frac{dy}{dz} f_2(c) \quad (31)$$

where

$f_1(c)$ and $f_2(c)$ are constants defined in Appendix C

$$c = \sigma \tau a$$

The average mole fraction in the cold channel, x , at any point z' is

$$x = \xi_0' f_1(c') - \frac{L}{\sigma \tau' b \rho D} \frac{dx}{dz'} f_2(c') \quad (32)$$

where

$$c = \sigma \tau' a = -\sigma \tau a = -c$$

Equations (8), (15), (31), and (32) may be combined to give

$$J_0 = \frac{\sigma D \rho}{\left[\frac{1 - e^{\frac{\sigma \tau M \delta}{\tau M \phi}}}{\tau M \phi} + \frac{f_2(-c)}{\tau f_1(-c)} - \frac{f_2(c) e^{\frac{\sigma \tau M \delta}{\tau f_1(c)}}}{\tau f_1(c)} \right]} \left[\frac{x}{f_1(-c)} - \frac{y e^{\frac{\sigma \tau M \delta}{f_1(c)}}}{f_1(c)} \right] \quad (33)$$

If the composition x^* is defined as the average cold channel concentration in "equilibrium" with the average hot channel concentration y , i.e., when

$J_0 = 0$, then equation (33) gives

$$x^* = y \frac{f_1(-c)}{f_1(c)} e^{\frac{\sigma \tau M \delta}{\tau f_1(c)}} = \frac{1}{K''} y \quad (34)$$

where

$$K'' = \frac{f_1(c) e^{-\frac{\sigma \tau M \delta}{\tau f_1(c)}}}{f_1(-c)} \quad (35)$$

Equation (33) then becomes

$$J_o = k''_L (x^* - x) \quad (36)$$

where

$$k''_L = \frac{\sigma D \rho \tau_M}{\left[\frac{(e^{\sigma \tau_M \delta} - 1) f_1(-c)}{\phi} - \frac{\tau_M f_2(-c)}{\tau} + \frac{\tau_M f_1(-c) f_2(c) e^{\sigma \tau_M \delta}}{\tau f_1(c)} \right]} \quad (37)$$

From Appendix C, the ratio $f_1(c)/f_1(-c)$ is shown to be

$$f_1(c)/f_1(-c) = e^{-c} = e^{-\sigma \tau a} \quad (38)$$

Therefore K'' is given by

$$K'' = e^{-\sigma (\tau_M \delta + \tau a)} \quad (39)$$

If the temperature drop across the membrane is small compared to the temperature drop in one of the channels, then

$$K'' \cong e^{\frac{-\sigma \Delta T}{2}} \quad (40)$$

Comparison of equations (20) and (40) should indicate limiting values for K ; the equations also indicate that the separation obtained with laminar flow operation can be increased by inducing complete turbulence in the channels, provided the same temperature drop can be maintained. It should be noted that this would entail a greater rate of heat dissipation across the channel,

and hence the additional separation would not be obtained gratis.

Solution of the Diffusion Equation and the Material Balances

Whether the column operates with perfect mixing in the channels or no mixing, the rate of diffusion across the membrane may be represented by the equation

$$J_o = k_L (x^* - x) \quad (41)$$

where

$$x^* = \frac{y}{K}$$

k_L is given by equation (18) or (37)

K is given by equation (20) or (35)

If equations (15) and (41) are combined, then

$$-\frac{L}{b} \frac{dx}{dz} = k_L (x^* - x) \quad (42)$$

By combining equation (12) with equation (42), one finds that

$$-\frac{L}{b} \frac{dx}{dz} = k_L \left(\frac{L}{KV} x + \frac{D}{KV} x_D - x \right) \quad (43)$$

If one defines the height of a transfer unit based on the cold stream as

$$h_L = \frac{L}{b k_L} \quad (44)$$

then equation (43) becomes

$$h_L \frac{dx}{dz} = \left(1 - \frac{L}{KV} \right) x - \frac{D}{KV} x_D \quad (45)$$

Integrating equation (42) between the limits of $z = Z$ at $x = x_D$ and $z = z$ at $x = x$, one finds

$$\int_x^{x_D} \frac{dx}{\left(1 - \frac{L}{KV}\right)x - \frac{D}{KV}x_D} = \int_z^Z \frac{dz}{h_L} \quad (46)$$

The resulting expression for x and z is

$$\frac{x}{x_D} = \frac{D}{KV-L} + \left[\frac{V(1-L)}{L-KV} \right] e^{\left[\frac{L}{KV} - 1 \right] \left[\frac{Z-z}{h_L} \right]} \quad (47)$$

The number of transfer units is given by

$$\frac{Z-z}{h_L} = N_L \left(1 - \frac{z}{Z} \right) \quad (48)$$

where

N_L = the number of transfer units in the column based on the cold stream.

If equation (47) is rewritten in terms of the reflux ratio R , then the resulting expression is

$$\frac{x}{x_D} = \frac{1}{K(R+1) - R} - \left[\frac{(R+1)(1-K)}{K(R+1) - R} \right] e^{\left[\frac{R-K(R+1)}{K(R+1)} \right] \left[\frac{Z-z}{h_L} \right]} \quad (49)$$

where

$$R = \frac{L}{D}$$

It is seen from the above expression that the separation obtained for a given column is a function of the equilibrium constant K , the reflux ratio R , and

the height of the transfer unit h_L . Both the height of the transfer unit h_L and the equilibrium constant K may be obtained from any two runs made with the same cold side flow rate L , as h_L is not a function of the hot side flow rate. Any two runs made in such a manner determine a locus of possible values of h_L and K with the reflux ratio R and the separation ratio x/x_D as characteristic parameters; any two runs will determine a unique set of values of h_L and K . Also, any number of runs should determine the same set of values if the cold side flow is common to all of them and if h_L is truly flow-rate independent. Figures 15 through 20 are plots of sets of the parametric equations for h_L and K , and there should be a unique (h_L, K) common to all of the curves on any figure. Experiments to develop these curves are easy to perform, as only the flow rate on the hot side is changed; the data required are the compositions at the ends of the column and the flow rates.

If equation (49) is written using the definition of h_L from equation (44), one obtains

$$\frac{x}{x_D} = \frac{1}{K(R+1)-R} - \frac{(R-1)(1-K)}{K(R+1)-R} e^{\left[\frac{R-K(R+1)}{K(R+1)}\right] \left[\frac{(Z-z)bk_L}{L}\right]} \quad (50)$$

From this equation, one can see that the total area, $(Z-z)b$, is the variable of interest, rather than the length alone. Alternate expressions show the area-to-flow-rate ratio π or the flow per unit width λ to be the controlling factors. These are defined by

$$\pi = \frac{Zb}{L} = \text{area-to-flow-rate ratio} \quad (51)$$

$$\lambda = \frac{L}{b} = \text{flow per unit width of channel} \quad (52)$$

If the column is operated at total reflux, its analysis by equation (47) is somewhat simplified. At total reflux, $D = 0$, and $L = V$. Equation (47) reduces to

$$\frac{x}{x_D} = e^{(\frac{1}{K} - 1) (\frac{Z-z}{h_L})} \quad (53)$$

These developments are for a single component in a dilute solution. The equations should apply equally well in describing the separation of each of several solutes from a solvent, provided that the presence of additional components does not affect the binary diffusion coefficients between solute and solvent.

CHAPTER III

LITERATURE SURVEY

The following literature survey is intended to cover 1) data on salt solutions from Soret cells, 2) the theory and observed behavior of the Clusius-Dickel column, 3) modifications of the Clusius-Dickel column, 4) the horizontal thermal diffusion column and certain effects associated with its operation, such as "thermal osmosis", and 5) a survey of irreversible thermodynamics as applied to thermal diffusion. This field apparently holds some promise of phenomenologically describing the thermal diffusion effect in terms of other transport properties of the system. No attempt is made to consider thermal diffusion in gases or solids. A complete literature survey of all aspects of thermal diffusion through 1956 is given by Von Halle (51).

I. GENERAL ASPECTS OF THERMAL DIFFUSION

Brown and Jones (4) review the latest advances in thermal diffusion, including new equipment and theories.

Jones (28) discusses thermal diffusion as a technique of laboratory separation, and gives a history of the effect and a description of the various types of apparatus used in 1956. Jones points out that many difficultly separable pairs, such as optical isomers, and the ortho-meta and ortho-para isomers of xylene, are separable by thermal diffusion techniques. For such systems,

standard separation methods such as distillation or solvent extraction fail almost completely. Jones observes that many attempts have been made to predict directions and magnitudes of separations in the liquid state by thermal diffusion, but no theory is yet satisfactory; all theories at present have exceptions even in predicting direction of separation. Lack of an adequate kinetic theory of liquids has prohibited a satisfactory development of thermal diffusion theory.

II. SORET CELL STUDIES OF SALT SOLUTIONS

Tanner (46) (47), Tyrrell (49) (50), and Chapman, Tyrrell and Wilson (11) have investigated the Soret coefficients of a large number of electrolytes in aqueous solution, including copper sulfate and cobalt sulfate. They used a method devised by Tanner in which the concentration distribution between two parallel horizontal heat transfer surfaces is determined by measuring the refraction of a light beam passing between the surfaces. Transient concentration data were obtained and used to calculate diffusion coefficients. Chipman (12) used a conductivity method to measure coefficients from a Soret cell; he reports data for many electrolytes, including copper sulfate. Long (32) has measured Soret coefficients for copper sulfate and cobalt sulfate, both in single salt solutions and in solutions of a mixture of the two. Bosanquet (10) studied the same systems as Long in an improved cell, and obtained Soret coefficients reproducible within ± 2 per cent. Agar and Turner (2) have developed a new apparatus for measuring Soret coefficients in salt solutions, which is particularly

suited for dilute solutions. They worked with salt solutions of concentration between 0.01 and 0.045 molar, using a conductivity method for analysis. A complete summary of data on liquid-phase Soret coefficients reported through 1956 has been presented by Von Halle (51).

Except for the work of Bosanquet, the various investigators have had difficulty in reproducing their own experiments with the accuracy of their own analytical methods; a very large discrepancy in values between investigators appears. Von Halle noted that the Soret coefficients of a particular salt increased with temperature according to one author, and decreased according to a different author.

Other anomalous effects have been observed in Soret cell operation. Long (32) constructed a Soret cell which developed the entire temperature gradient across a cellophane membrane; salt solutions were on either side of the membrane, and gradients in the solutions were prevented by thorough agitation of the solution. Temperature profiles in the solutions were measured which indicated that almost the entire temperature drop occurred across the membrane. Although the theory indicates that a concentration difference in the same range as the others he measured should be developed, no measurable concentration difference was ever observed. Bosanquet observed that if the hot surface of his copper cell was cleaned with emery paper before the start of a run, a reproducible separation was not obtained. Watson (52), Long, and the author have observed that if an external electrical current path exists between the two

surfaces of a cell, a reproducible separation cannot be obtained.

The use of Soret data in predicting the operation of a thermal diffusion column requires an understanding of the effect in Soret cells. The discrepancy in values of Soret coefficients reported by different authors and the difficulties observed by Long, Bosanquet, Watson, and the author indicate that predictions of separations cannot be reliable until the controlling variables of the Soret cell are understood.

III. THE CLUSIUS-DICKEL COLUMN

The literature on experimental thermal diffusion before 1938 described only measurements of Soret coefficients using Soret cells. In 1938, Clusius and Dickel (13) reported the operation of the first continuous countercurrent contacting device to use thermal diffusion as the separation driving force; they studied the separation of gaseous isotopes in a "separation tube" consisting of a cooled outer jacket with a heated wire in the center. The thermal gradient created a positive density gradient toward the cold wall. The horizontal density gradient causes a velocity of the fluid in a vertical direction. The direction of flow is up near the hot wall and down near the cold wall. Diffusion from the hot to the cold wall therefore moves material from one stream to another flowing countercurrently. This results in a concentration gradient along the vertical direction of the column. An end reservoir connected at the top would be depleted in salt, and the one at the bottom would increase in concentration. A column

with a feed stream in the center can be operated continuously by withdrawing two products from the end reservoirs.

The Forgotten Effect

Jones (28) discusses an unusual effect observed with certain systems in the Clusius-Dickel column. This phenomenon, known as the "forgotten effect", is the initial transient enrichment of one of the components in the top reservoir, followed by enrichment of the other component in the same reservoir, which prevails at steady state. It is caused by the density gradient in a horizontal direction due to the concentration gradient being negatively larger than the density gradient due to the temperature gradient. At short times after start up, the temperature gradient is established, but the concentration gradient in the horizontal plane is not fully developed. The temperature gradient causes flow upward along the hot wall and downward along the cold wall. When the concentration gradient due to thermal diffusion becomes established, the density gradient reverses direction and flow upward along the cold wall results. As the direction of flow is changed without changing the direction of diffusion, the opposite reservoirs become enriched. Evidently, the forgotten effect can occur only if the heavier component tends to concentrate at the hot wall. The effect is called the forgotten effect because initial investigators "forgot" to take transient concentration measurements at small time values.

Jones presents an illustration of the forgotten effect by showing the

concentration-time data for the reservoirs of a Clusius-Dickel column separating the toluene-cyclohexane system.

Theory of Operation of the Clusius-Dickel Column

Furry, Jones, and Onsager (21) have solved the hydrodynamic and diffusion equations for the Clusius-Dickel column by considering the column as two parallel plates. Furry and Jones (20) solved the rigorous equations for the cylindrical tube. Jones and Furry (30) derive the transport equations with "mathematical simplicity and clarity which brings out the nature of the processes occurring in the separation column." They show that a stream of average velocity \bar{v} exists in each half of the channel and consider diffusion between these two streams flowing countercurrently. This is a simplification of the actual diffusion problem. The advantages and disadvantages of operating the Clusius-Dickel column continuously and discontinuously (i. e., batchwise separations) are pointed out; the only application considered is the separation of gaseous isotopes, but the solution of the general problem can be applied to liquids as well.

Powers and Wilke (39) constructed and operated a Clusius-Dickel column in the form of two parallel plates. Two columns were studied, one 4 feet long and the other 8 feet long. The effects of varying the temperature differences between the plates, of inclination of the columns, of length, and of varying the feed rate while keeping the end draw-off rates equal were studied. A compari-

son of the experimental data for the ethanol-water system and the n-heptane-benzene system was made with that predicted from the theory of Furry and Jones. A solution to the general problem of the Clusius-Dickel column was developed for equal product withdrawal rates assuming that $\frac{d\xi}{dz}$ varies linearly with r , the coordinate between the heat transfer surfaces. The solution is developed in terms of an infinite series which does not converge beyond small product withdrawal rates. Beyond the range of convergence, a correlation of the data in terms of the characteristic constants of the series is advocated. It is pointed out that the equation of Furry and Jones becomes inaccurate at large product rates; however, over the range of convergence of the series solution, the equation of Furry and Jones fits the data as well as that of Powers and Wilke. Design equations to be used in optimizing the design of a Clusius-Dickel column are given. A second paper by Powers and Wilke (38) presents the results of a study of column operation with unequal product withdrawal rates.

Longmire (33) investigated the separation of organic liquid mixtures in a vertical column, and reported the results of the separations in terms of dimensionless numbers. He used log-log plots involving Reynolds numbers, Schmidt numbers, a thermal diffusion number, and an absolute temperature number.

Emery (17) developed a theory for the Clusius-Dickel column taking into account variations in liquid properties with temperature. He used the power laws to represent the dependence of viscosity and diffusivity on temperature, $\eta = aT^{-n}$, and $D = bT^{n+1}$.

Ableson, Rosen, and Hoover (1) present a summary of the work done by the U. S. Atomic Energy Commission during World War II in the field of liquid thermal diffusion. Extensive mathematical theory of the Clusius-Dickel column, a history of thermal diffusion, and a description of the operating facilities used for isotope separation in the liquid phase is given. The operation of a number of columns in series-parallel arrangements is treated mathematically.

The equations for thermal diffusion between streams in countercurrent laminar flow may be extended with appropriate modifications from the Clusius-Dickel column to the horizontal column, as was done in the present work, and by Von Halle (51).

IV. MODIFIED CLUSIUS-DICKEL COLUMN STUDIES

Baranowski and Demichowicz (6) (7) studied the copper sulfate-water system in a modified Clusius-Dickel column. Instead of using a central tube in the column as a heat source, an electric current was passed through a vertical capillary tube containing the solution; the entire column was immersed in a water bath to remove the heat. The internal generation of heat creates a radial temperature gradient which causes thermal diffusion. This type of device is restricted to the use of electrolytes, as the solution inside the tube must conduct the electrical current. From equations derived by Baranowski (5) for the electrothermodiffusion process, the Soret coefficients for copper sulfate were calculated; the observed values were 10 per cent smaller than those calculated

by other methods. Witkowski (56) made a theoretical study of electrothermo-diffusion; a new method of separation using combined thermal diffusion and distillation is proposed by Witkowski (55).

Jones and Milberger (29) used a Clusius-Dickel column with a membrane in the annulus for separation of liquids; the membrane prevented parasitic convection currents between the two streams in the column and improved separations in forgotten effect pairs. Sullivan, Ruppel, and Willingham (44) (45) operated Clusius-Dickel columns packed with glass wool and annular columns with a rotating center member; they reported that separations for both types of columns were greater than those observed in conventional Clusius-Dickel columns. Lorenz and Emery (34) have applied the cost analysis work of Powers and Wilke (39) to the packed thermal diffusion column. Tilvis (48), Niini (36), and Ramser (41) have also studied various types of Clusius-Dickel columns with moving walls. Papayannopoulos (37) used a horizontal thermal diffusion column packed with filter paper. A spirally wound nichrome wire in the plane of the flat plate provided a variable heat input. Frazier (19), and White and Fellows (54) have worked on the problem of increasing efficiency by improved design of ports, feed manifolds, and novel end feed arrangements.

V. HORIZONTAL THERMAL DIFFUSION COLUMN STUDIES

Von Halle (51) studied the separation of the ethanol-water system in a horizontal thermal diffusion column using a cellophane membrane to separate

the counterflowing streams; this column is identical in principle to those used in the present study. The column design was conceived by Dr. S. H. Jury as the result of a search for a thermal diffusion device that would not be subject to the complications of the forgotten effect. Previous investigators had been unable to separate ethanol and water in a Clusius-Dickel column if the ethanol concentration was less than 30 per cent by weight; Von Halle carried out such separations successfully in a horizontal column. He demonstrated that the Soret coefficient changes sign at this concentration, and that the forgotten effect prevented investigators using Clusius-Dickel columns from separating the mixtures. Von Halle presents extensive developments of the theory of operation of Soret cells, Clusius-Dickel columns and horizontal columns. Included are equations for predicting transient behavior and for the design of horizontal column cascades for effecting two-component separations.

VI. SEPARATION OF BINARY SALT SOLUTIONS

Guthrie, Wilson, and Schomaker (23) developed a theory for thermal diffusion in solutions of mixed electrolytes based on the assumption that an electric field is created by the unequal migration rates of the charged ions. Their theory was developed in an attempt to explain the reversal of direction of enrichment of an electrolyte in a Clusius-Dickel column when another electrolyte is added. The theory is quantitative and predicts the enrichment obtained for both electrolytes. Hirota (24) studied the separation of electrolytes in a

Clusius-Dickel column and found that Guthrie's formula held only in special cases. In monovalent electrolyte mixtures, the equations held if the initial concentrations of each salt were equal; the theory did not describe the results for mixtures of unequal concentrations nor for the system sodium chloride-sodium hydroxide at any concentration. Long (32) and Bosanquet (10) found that Guthrie's theory does not appear to hold for the copper sulfate-cobalt sulfate system from measurements in Soret cells. Bosanquet observed that the Soret coefficient of each salt in the two salt solution was decreased by about 10 per cent below its value in a single salt solution. This is contrary to the Guthrie theory which predicts that one of the salts will exhibit a higher Soret coefficient in a two salt solution than it does alone.

Baranowski and Fulinski (8) (9) have derived relations for Soret coefficients from the thermodynamics of irreversible processes for liquid multicomponent mixtures. For the case of ideal electrolyte solutions, these equations reduce to those of Guthrie et al.

VII. THE THERMAL OSMOSIS EFFECT

Alexander (2) reported the appearance of a "thermal osmosis" effect in cells used for measurement of Soret coefficients. When a temperature gradient is applied across a Soret cell with a porous membrane dividing the space between the heat transfer surfaces, a pressure difference across the membrane

may be observed, even if the material in the cell is a pure substance such as distilled water. This effect is given the name of "thermal osmosis". If a pressure gradient across the membrane cannot be maintained by the cell, then there is a net transport of material across the membrane. Jones (31) observed the thermal osmosis effect in the distilled water system using the cellophane membrane material employed in the present investigation; however, the effect was not reproducible. After observing the effect on an initial run, he was successful in reproducing the developed pressure only by using eleven membranes in series as a single membrane. Long (32) attempted to measure the thermal osmosis effect for the copper sulfate-cobalt sulfate-water system in a Soret cell with a cellophane membrane; he was successful in obtaining a measurable pressure difference only by using multiple membranes.

Von Halle (51) observed that on start up of the horizontal column, a large quantity of solution would be transported through the membrane from the hot region to the cold region. This flow decreased with time, but a steady state flow existed. The flow per unit length of column was assumed constant, and the phenomenon was taken into account in the analysis of his results.

In the present work, a transport of material from the hot side to the cold side was observed during transient periods. However, no measurable effect was observed during any steady state operations. This is not in agreement with the observations of Von Halle.

VIII. IRREVERSIBLE THERMODYNAMIC STUDIES

Most of the irreversible thermodynamic treatments of thermal diffusion are based on studies of De Groot (15) and Prigogine (40); a good summary of all work in the field, including the work of de Groot and Prigogine, is given in a recent work by Denbigh (16). The approach of irreversible thermodynamics is to relate the transport properties of the systems to other measurable quantities; for instance, the thermal osmosis pressure effect is related to a heat of transport of the material across the membrane. Unfortunately, the best method of measurement of these variables is to measure the Soret coefficients and the thermal osmosis pressure directly. The field of irreversible thermodynamics attempts to relate the simultaneous transport of heat, mass, and electricity in terms of each of the basic driving forces of temperature gradient, concentration gradient, and gradients in electrical potential.

Ikeda (25) measured the emf developed across a porous membrane with 0.1 N potassium chloride on each side as a function of the temperature difference across the membrane; from the measurements, Soret coefficients were calculated using the coupling relations between heat, mass and charge transfer derived from the methods of irreversible thermodynamics. Ikeda (26) has also developed a method of calculating Soret coefficients from the transference numbers of salts using the coupling relations.

Although they did not use the principles of irreversible thermodynamics,

White and Fellows (53) have concluded from classical thermodynamics that Clusius-Dickel columns are operating near their limiting efficiency, and do not believe that further work with packed columns, moving wall columns, etc., is practical.

CHAPTER IV

DESCRIPTION OF THE INVESTIGATION

I. EXPERIMENTAL EQUIPMENT

Thermal Diffusion Columns

Two thermal diffusion columns similar in construction but of different size were used in the present investigation. The large column had a diffusion area of 0.915 ft^2 , and the small column had a diffusion area of 0.106 ft^2 . The two columns are described in detail in the following sections.

The Small Column. The small thermal diffusion column used in the present investigation was constructed from two copper bars, each $24 \times 2 \times 1$ in. The top bar was milled longitudinally to receive a $1/2$ in. copper tube, which was soldered to the bar flush with the top and which carried the refrigerant. A $1-3/4$ -in. by 22 in. "Chromalox" 1500 watt electric strip heater was fastened to the bottom bar with screws. Figure 5 shows a detailed cross section of the column. The bars were machined on the side opposite the thermal sources to fit a plastic strip $1/4$ in. deep by $5/8$ in. wide; the strip had the same dimensions on the side and on the ends. The plastic surface extended $1/16$ in. beyond the surface of the copper bar; this depression formed the flow channel of the column. Parallel to the flow channel surface $1/16$ in. away, three holes of $1/16$ in. diameter were drilled for thermocouple wires; holes were drilled

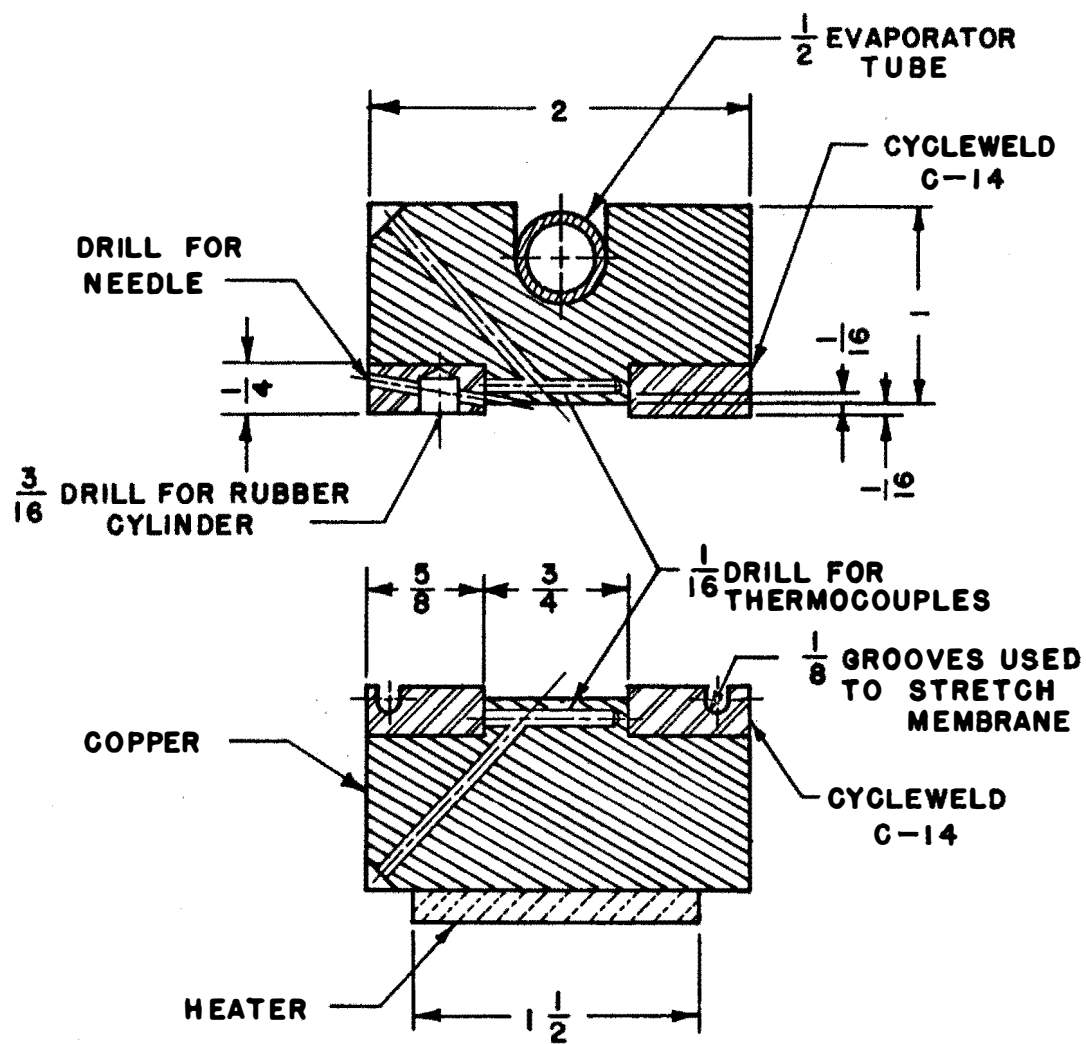


FIGURE 5

FULL SCALE

CROSS SECTIONAL VIEW OF THE THERMAL DIFFUSION COLUMN

through the copper bar for access to these thermocouple wells. In each end of each bar, 1/16-in. holes were drilled through the bar to the center of the channel for flow entry. To the outside of these were soldered lengths of 1/8 in copper tubing for external connection to flexible plastic tubing. At the point of entrance of the fluid to the cold side, small Y shaped channels were cut in the plastic at the end of the flow channel on both the top and bottom bars; stainless steel tubing of 0.072 in. O.D. was glued into the plastic to provide an external connection. The Y shaped entrance ports were constructed in an effort to solve a problem of membrane failure, which is discussed in the Experimental Procedure section of this report. As they did not stop membrane failure the entrance ports were plugged and not used. Baffles over the entrance port through the bar made of 0.005 in. copper, and baffles made of 0.03 in. Teflon were tried, but did not solve the problem. A gasket for the entire column was made from 1/2 mil teflon; the gasket had a hole in the center 20-1/4 in. by 3/4 in., or 0.106 ft², and extended 1-1/4 in. on each end beyond the entrance port into the diffusion channel. One of these gaskets on each side of the membrane ended the membrane breakage. In the region of the channel not covered by the 1/2 mil teflon gasket, there was no problem of membrane failure. The two halves of the column were held together at the ends by small vices, aided in the middle by two "C" clamps spaced at equal distances along the column, as shown in Figure 6.

The plastic used to form the side walls was a combination of "Cycleweld C-17" and "Cycleweld C-14", both resin products of Chrysler Corporation.

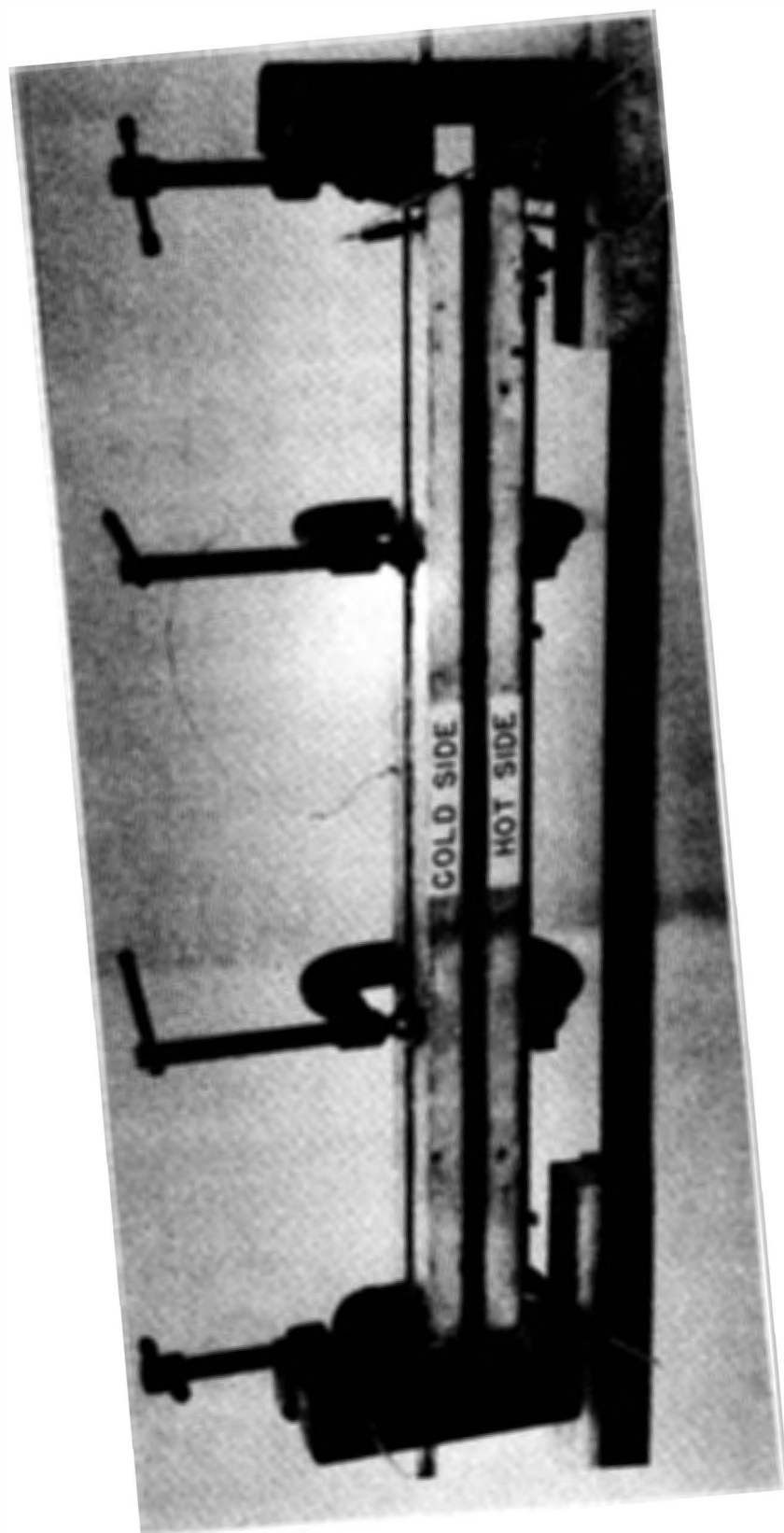


FIGURE 6
THE THERMAL DIFFUSION COLUMN

The C-17 is a high temperature product which softens at 300°F, and the C-14 softens at a relatively low 150°F. The C-17 sets very quickly when pouring, and, hence, is difficult to work with; the C-14 presents no such difficulty. The C-17 was poured in a thin layer onto the copper bar and allowed to set; a thick layer of C-14 was then poured on top of the C-17. After proper curing, the walls were machined down to proper thickness. The purpose of the initial layer of C-17 was to use its high temperature and strength properties next to the bar. As shown in Figure 5, slots were machined in the Cycleweld on the bottom half to take two 1/8-in. Monel welding rods which were 1/2 in. longer than the copper bar. A du Pont PT-600 (PD-600) cellophane membrane 2 in. wide with a 2 in. wide Teflon gasket on each side was stretched between the Monel rods. The walls of the Cycleweld between the groove and the outside were machined 0.005 in. lower than the center so that all pressure holding the column together would be exerted where the membrane was stretched tight. Figure 7 shows a photograph of the two separate halves of the channel.

In order to permit withdrawal of samples for obtaining concentration versus length data, three holes 1/4 in. in diameter were drilled partially into the Cycleweld at distances along the channel equally spaced from the feed ports; soft rubber cylinders were inserted in these holes. Holes were drilled through the Cycleweld from the outside face of the channel wall to the inside face through the cylinder wells to take a hypodermic needle; the rubber cylinders

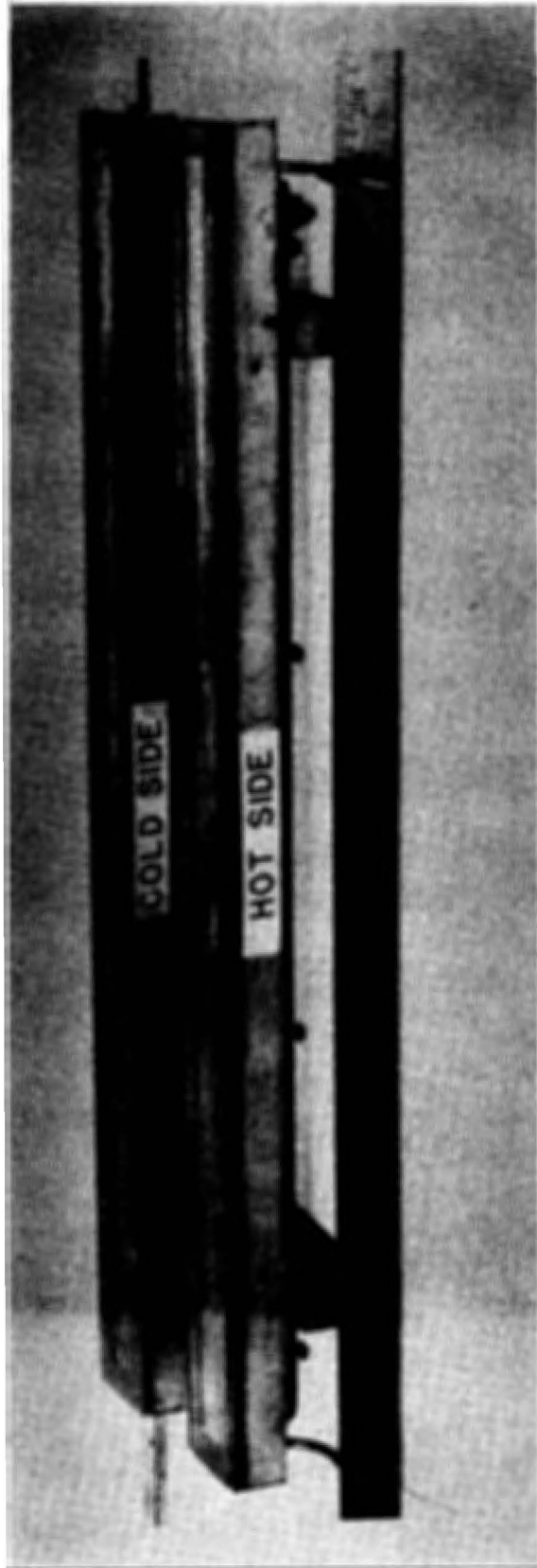


FIGURE 7
VIEW OF THE INDIVIDUAL CHANNEL SECTION

sealed off these sample ports to prevent leaks, but would allow the insertion of the needles. The details of this arrangement are shown in Figure 5. Although this method allowed satisfactory samples to be taken, no data are reported for concentration versus length, as a single analysis proved that the analytical technique did not possess sufficient accuracy to warrant use of this method. Although the concentrations monotonically increased from the cold entrance to the cold exit, the differences in concentrations between successive points exhibited no reasonable trend whatsoever. The heights of a stage and the equilibrium constant theoretically could be extracted from such data (see 18) if a very accurate (0.005%) analytical method were available.

The Large Column. The large thermal diffusion column was constructed from two silicon bronze (95% Cu, 4% Si, and 1% Mn) plates, each 17 x 17 x 1/2 in., and a press constructed from 18 x 24 x 2 in. steel plates, with a network of refrigerant channels in one plate and ten 5/8 x 16 in. cartridge heaters inserted in drilled holes in the other. This was the same press as used by Von Halle (51), with only one modification; on the lower plate which moved on 1 in. diameter steel guides, the steel bushings were replaced with special Bakelite bushings. Each silicon bronze plate was machined flat and a 1/8 in. cork sheet glued on with Glyptal No. 1202 clear varnish. Sheets of 1/16 in. cork were tried, but the spacing was too narrow to allow flow; it was thought that the membrane deformed and completely shut off the flow. Twenty flow channels 14-5/8 x 1/2 in. were cut in the sheet cork and alternate ends

connected to form one continuous channel. The detailed layout is shown in Figure 8. A solid border of cork of 1-1/8 in. width was left around the outside of the plates to form an external seal; a 1-1/4 in. width was left on the sides containing the entrance ports. This geometry gave an area of 1.020 ft²; because of the impervious Teflon covers over the end channels, only 0.915 ft² was available for diffusion. In each of the end channels, a slot was milled of 1/4 in. maximum depth and 1/2 in. width; the depth of the slot was tapered out about 1-1/2 in. along the channel. An entrance port of 1/16 in. diameter and of 1-1/4 in. length was drilled from the outside to the bottom of the tapered slot. The purpose of this entrance port configuration was to permit entry of the fluid in a direction as nearly parallel to the membrane as possible. The 1/16 in. holes were further drilled and tapped from the outside to take a 10-32 screw. A 0.072 in. neck of 1/2 in. length was turned on a 10-32 Everdure (silicon bronze) screw of 1 in. total length; a 0.052 in. hole was drilled completely through the screw. This screw was covered with Glyptal No. 1201 red enamel and screwed into the entrance port of the flat plate; each entrance and exit port in each plate was constructed in this manner. The screw in the port where the fluid entered the hot side corroded out three times, and was finally replaced by a Lucite screw of identical dimensions; no trouble was experienced with the Lucite screw or with any of the other metal screws. Care was taken, however, not to let the temperature of the hot plate rise close to the softening temperature of Lucite (180°F). Along the end of the column where the entrance

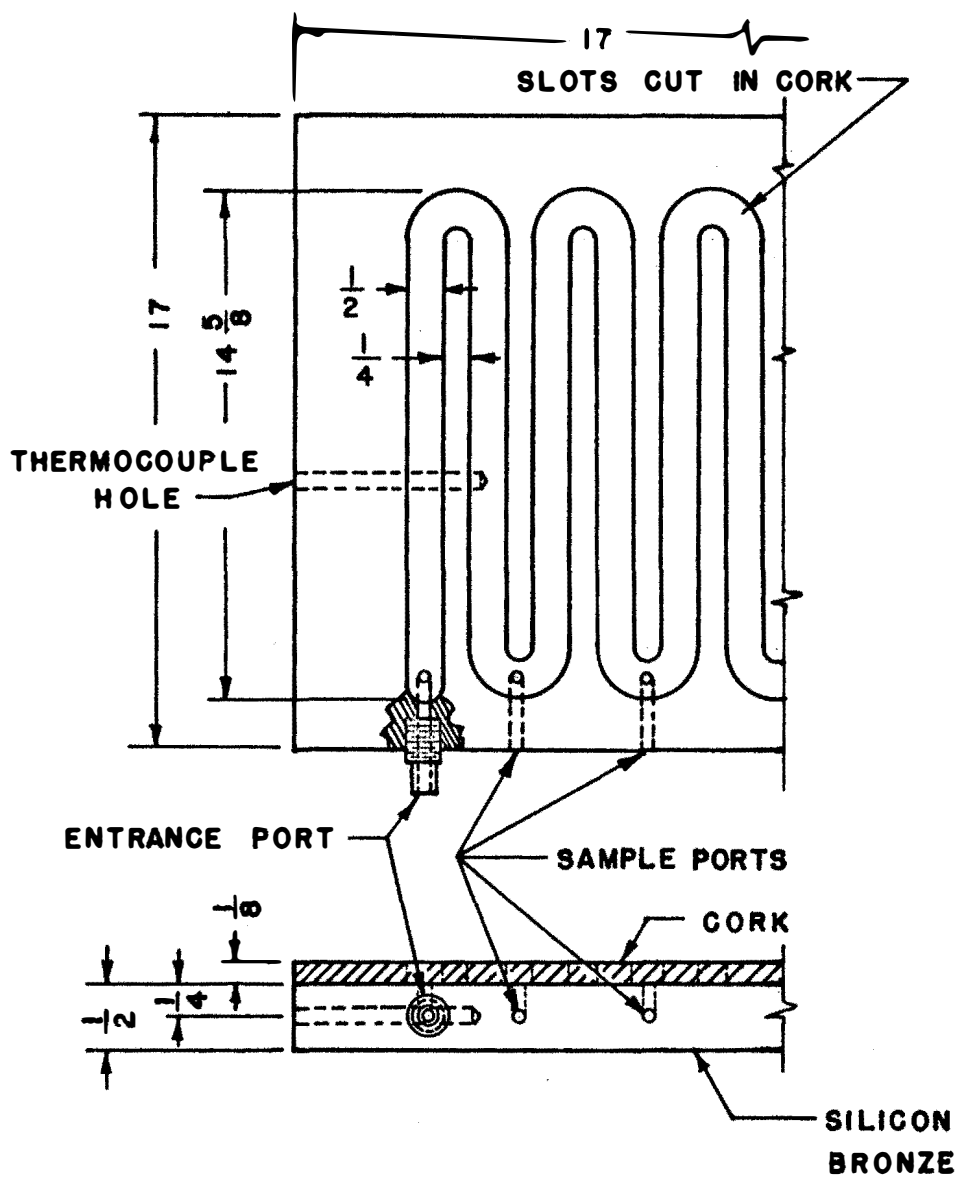


FIGURE 8

LAYOUT OF PLATES USED IN LARGE COLUMN

ports were located, holes were drilled in each channel for sample ports. Nine holes of $1/16$ in. diameter were drilled in the surface of each plate to $1/4$ in. depth; $3/32$ in. holes were drilled from the outside until they met the $1/16$ holes perpendicularly; these $3/32$ holes were plugged with $3/32$ in. Teflon rods. These holes were in the center of the return slots which connected two channels. On the side of the plates, $1/16$ in. holes were drilled 2 in. deep and $1/4$ in. below the surface of the plates to take thermocouples.

Flow System

The flow system is shown in Figure 9; the schematic applies to each of the two columns. The rotameters used were model G 9142 B with sapphire and stainless steel floats made by Manostat Corporation and distributed by the Emil Greiner Company; the rotameters were used only as qualitative indicators of flow. The pumps were "Sigmamotor" Model T6 pumps. These units are commonly called "fingerpumps", as they pump with the action of fingers pressing progressively a flexible tube between a fixed wall and the moving fingers. The tubing used in the pumps was $1/16$ I. D. by $1/16$ wall Tygon R3603. The tubing used for all connections was either $1/16 \times 1/32$ Tygon or approximately the same size tubing of another material; this unknown composition tubing had been previously obtained from Jessall Plastic Company in Connecticut. It was determined from its physical properties that it was neither polyethylene nor Tygon. It was rather stiff and resembled polyethylene in many ways. The tubing was con-

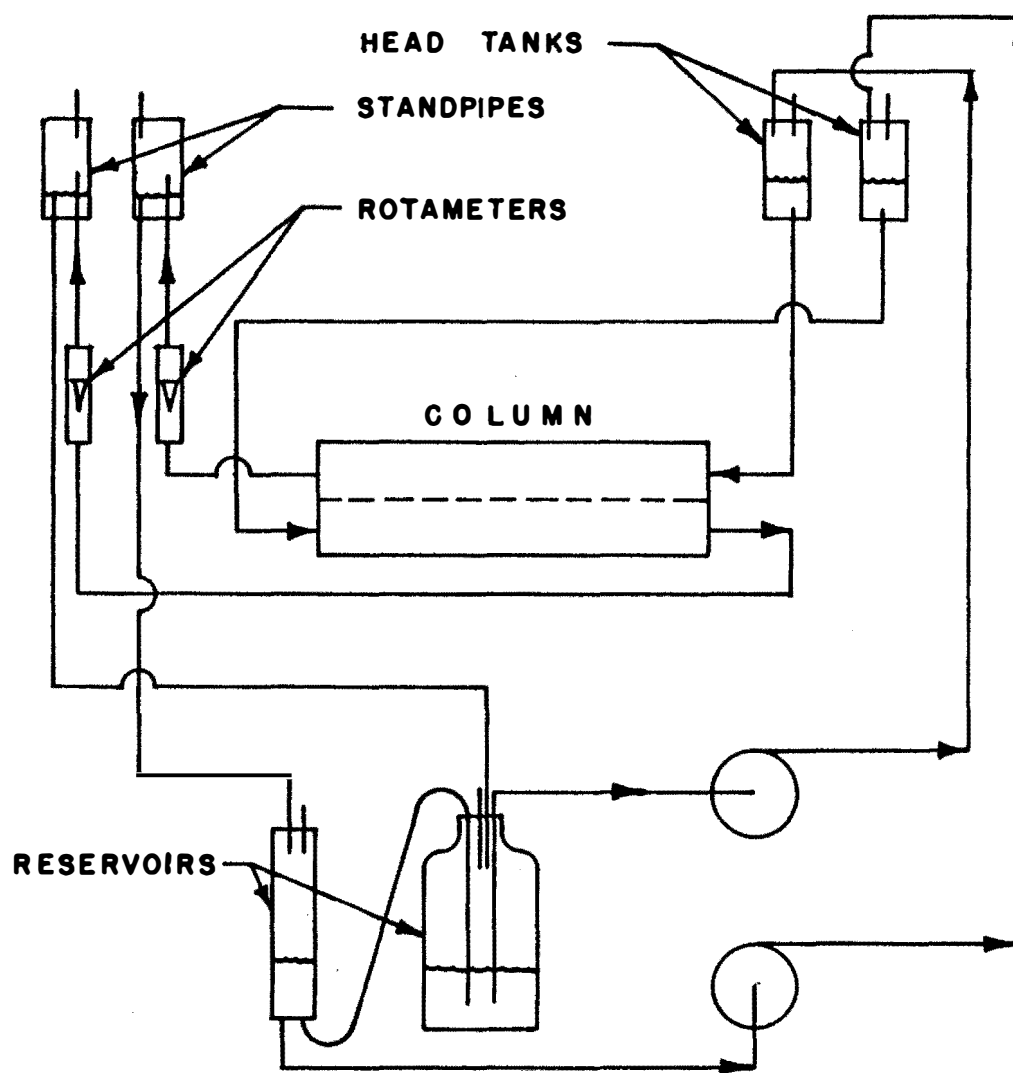


FIGURE 9

SCHEMATIC OF THE FLOW SYSTEM (EITHER COLUMN)

nected directly to the necked screws on the large column, but on the small column, it was necessary to make connections using pieces of 0.072-in. O.D. by 0.009-in. wall, type 18-8 stainless steel tubing 1 in. long with rubber tubing placed between the stainless steel and the column. Other tubing connections were made using this stainless steel tubing, but nowhere in the system was the stainless steel directly connected to any other metal; this was done to prevent electrolytic corrosion. For the reservoirs, one 50-ml burette and one 5-gal carboy were used on each column. The burette and the carboy were connected together so that the liquid level in the two would always be approximately the same; this allowed the product material from the small reservoir to flow back into the large reservoir and permitted operation as a completely closed system. The solution was pumped from one reservoir into a small vented head tank made from 3/4 in. diameter glass tubing; it flowed by gravity through the column and out into a standpipe made of the stainless tubing; the overflow from the standpipe drained into a similar glass tube and then back into the other reservoir. The circuit back to the first reservoir was identical.

Refrigeration System.

Figure 10 shows the refrigeration system of the small column. The top half of the column was cooled by the evaporation of "Freon 12" inside the 1/2-in. copper tube. An "AP" Model 209 expansion valve was used to throttle the refrigerant into the evaporator tube. Approximately 5 feet of copper tubing

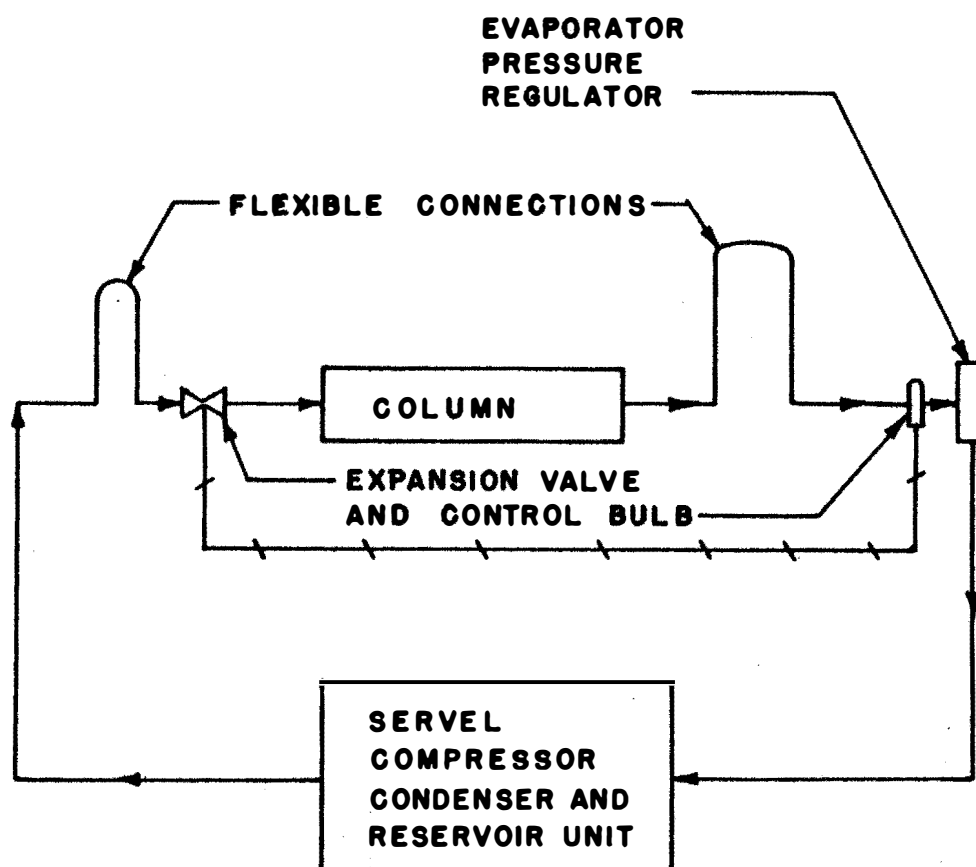


FIGURE 10

SCHEMATIC OF THE REFRIGERATION SYSTEM

and a 6-in. flexible connection were placed between the evaporator tube and an "AP" Model 235 Type S evaporator pressure regulator. Between the evaporator and the evaporator pressure regulator were the control bulb for the expansion valve and a Bourdon pressure gage, graduated in intervals of 1 psi. The expansion valve kept the superheat of the vapor at a set value and the evaporator pressure regulator kept the pressure constant. A change in the setting of the evaporator pressure regulator was the only adjustment required to change the temperature of the evaporator. A "Servel" compressor and condenser unit completed the refrigeration system. All controls and the compressor were rated at 1/2 ton of refrigeration. All low pressure tubing surfaces and the top of the column were wrapped in a commercial refrigeration insulation tape to reduce the heat load and the condensation of atmospheric moisture. A 24-in. flexible connection was located between the compressor and the expansion valve to permit movement of the column to a vertical position for filling.

The refrigeration system on the large column was identical in principle to that of the small column. The hardware was slightly different, and is described in detail by Von Halle (51).

Electrical System

Figure 11 shows the electrical system. Because of the concentration difference of the electrolyte on each side of the membrane, a concentration cell is produced which will cause an electrical current in an external circuit with

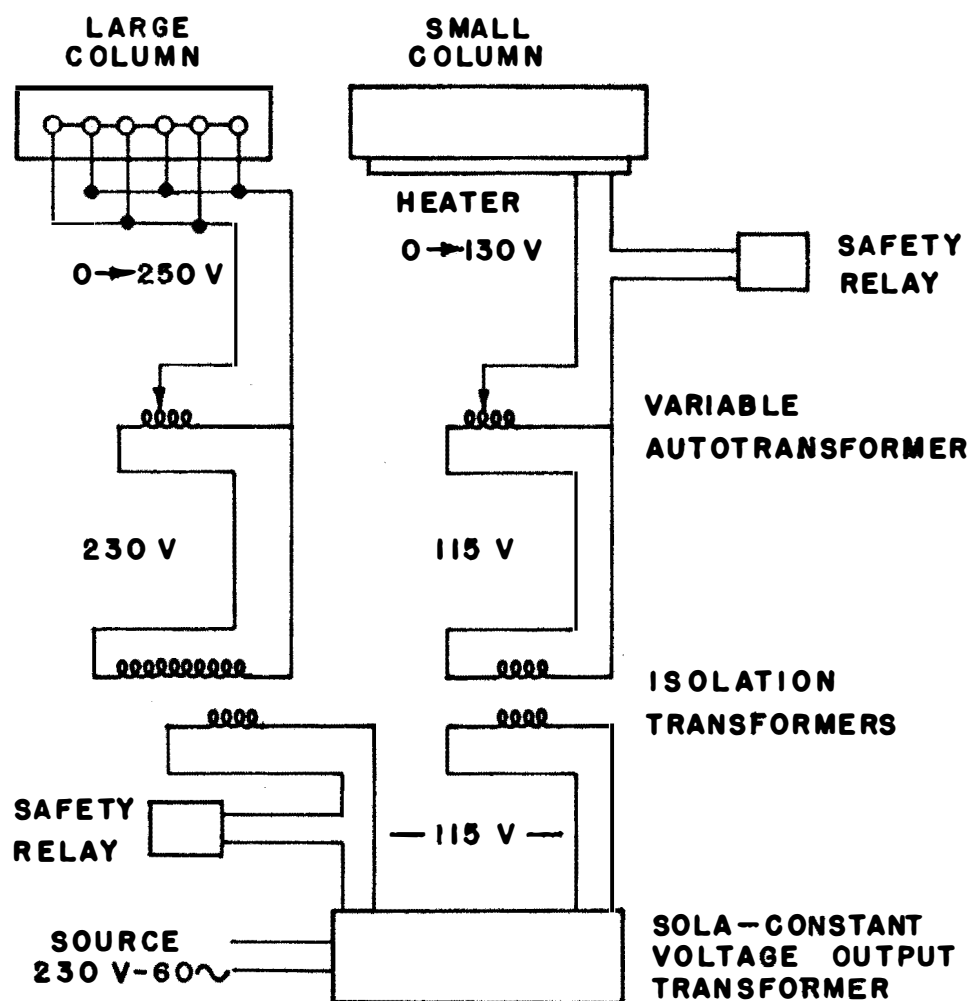


FIGURE 11

SCHEMATIC OF THE ELECTRICAL SYSTEM

the walls of the channel as the electrodes. This external current will cause transport of material in the column and cause an effect other than thermal diffusion to be measured. To prevent this, it was necessary to insulate electrically one side of the channel from the other. As the body of the electric heaters used was not completely isolated from their electric taps, an isolation transformer was installed in the line; a 1-KW "Stancor" was used for the small column and a 5-KW "Raytheon" step down-isolation transformer was used for the large column. Without the transformers, one side of the power supply was grounded, and the thermally hot side would be grounded through a high resistance circuit. The cold wall was grounded and could not be electrically insulated because of the nature of its construction. Bakelite plastic spacers were inserted between all clamps and the small column to provide electrical insulation; Bakelite bushings were used on the large column for the same reason. A variable auto-transformer was installed between the isolation transformer and each heater. The power supply was through a "Sola" 3000 watt constant voltage output transformer.

Temperature Measurement System

The thermocouple wires inserted in the column wells were #24 gage iron-iron constantan. The temperatures were recorded on a "Weston" multipoint recorder, whose guaranteed reproducibility was $\pm 1.5^{\circ}\text{F}$. However, no discrepancy was ever observed between the temperature indicated by the recorder

and a reference voltage signal from a potentiometer. The scale on the recorder was graduated in two-degree intervals. Some (but not all) of the thermocouples used were calibrated at a temperature of 32°F against the NBS tables; as no discrepancy was observed in any of the thermocouples, further calibration was not done. The thermocouple beads were formed by condenser-discharge welding.

Using the power input rates of the electric heaters as the heat transfer flux, the temperature gradients in the heat transfer surfaces were calculated with the aid of known thermal conductivities. The temperature drop in the copper bars of the small column was less than 1 per cent of the total measured temperature drop; the temperature drop in the silicon bronze plates of the large column was 15 per cent of the total measured temperature drop. This correction is applied to the data from the large column.

II. EXPERIMENTAL PROCEDURE

Column Operation

The thermal diffusion columns were operated in a horizontal position; the small column was operated as shown in Figure 6. The cold channel was placed on top to cause vertical mixing from the generated convection currents; it was believed that vertical mixing in each section of the channel would cause most of the temperature gradient to develop across the membrane and lead to a maximum separation of the salts. The columns were operated with countercurrent flow for all runs.

The flow through each channel was externally controlled by changing the input rate to the small vented head tank; the level in this tube was allowed to change until the output rate was equal to the input rate. The flow rates on the small column were between 2 and 10 ml/hr, and on the large column they were between 10 and 35 ml/hr. A fine control adjustment constructed and mounted on the speed control gear box of the finger pumps allowed the flow rates to be closely regulated. No noticeable difficulty was experienced with the flow rates changing over a long period of time due to changing characteristics of the tubing in the pump.

The flow rates into the column were measured by connecting the pump input lines to 50 ml burettes and measuring the time-volume relation; the outputs of the column were measured by allowing the overflow of the small standpipes to drain into 50 ml burettes, and measuring the appropriate time. The input and output measurements were performed simultaneously. The product rate was measured by allowing the small burette reservoir to fill. At least 12 ml of each solution was caught in each measurement.

The transient time of the system was quite long; at the lowest flow rates, the small column took 21 days to come to a steady state. This problem was circumvented to some degree, however, by placing a dilute solution in the cold side feed reservoir and allowing the system to come to steady state from an over-separated condition rather than from a condition of no separation. Runs of 2 to 4 days length could be completed in this manner. The small reservoirs

were operated with 5-10 ml holdup, and the large reservoirs with 7 liters.

Each column was operated with the output standpipes located about 2 feet above the actual column; hence, the columns were under a static pressure of 2 feet of water. This ensured that air could not leak into the column.

The cold-side of the small column was operated at 38 to 40°F and the hot side was maintained between 142 and 148°F. Because of the nonuniformities in the Chromalox heater used on the small column, there was a temperature rise on the hot-side of 6°F along the length of the column from the hot- to the cold-side exit port. No appreciable gradient was observed in the refrigerated bar. The power consumption of the heater with these operating temperatures was 350 watts.

The cold side of the large column was operated at 52°F and the hot side at 122°F. Only one temperature was measured on each plate; Von Halle (51) had a more elaborate arrangement for measuring more temperatures on the surface, and he found that the edge temperature of the plates was a satisfactory measurement of the plate temperatures. The power consumption of the heater was 1060 watts.

Solution samples for chemical analyses were withdrawn from the overflow from the standpipes; this allowed direct products of the column to be analyzed without disturbing its operation.

The condition of the membrane could be determined from the measurements of the flow rates. Difficulty was experienced with failure of the mem-

brane during operation, and it was important to determine if a hole existed in the membrane at the time of any concentration measurement. If the entrance and exit flow rates from one channel were equal within experimental error, it was concluded that the membrane was in good condition; however, if essentially all of the flow out of the column came from one of the exit ports, it was concluded that there was a hole in the membrane. Several times the conclusion was reached that there was a hole in the membrane, and subsequent shutdown and inspection of the membrane always confirmed the conclusion. During operation with only cellophane between the channels, the cellophane would fail at the cold entrance point. The introduction of the flow parallel to the membrane through the small Y shaped entrance ports on the small column and through the entrance ports on the large column was intended to stop this failure, originally believed to be the result of erosion. However, the parallel introduction of the flow did not solve the problem of membrane failure in either of the two columns. The membrane would fail in a brittle manner after about four days operation; the membrane would disintegrate or dissolve in the region where cold fluid first contacted the membrane with small tears leading in all directions from the hole. It was not a pressure-caused rupture; this type of rupture was observed in the large column a few times, and it resulted in deformation of the membrane with a directional slit in the deformation. A slight additional problem with the determination of membrane failure of the large column was occasioned by the presence of the transport of water through the membrane at start-up; a balance of channel flow rates was not

used as the criterion of a good membrane, but rather the reproducibility of flow rates from day to day.

Start-Up Procedure

Small Column. A cellophane membrane was placed on the hot side bar with a Teflon gasket both beneath and above it; the Monel rods were laid in place and the lower bar placed in position in the vices. The vices were tightened and the clamps added, which forced the Monel rods into the slots and stretched the cellophane membrane very satisfactorily. A few times, after the rods had been forced into the grooves by clamping the column together, the column was taken apart to inspect the membrane; the membrane was always found in good condition; this was easy to observe, as the Monel rods stayed in the grooves when the column was taken apart.

The assembled column was then raised to a vertical position and filled from the bottom with water. With the column full of water, all lines were sealed off and a burette attached to check for leaks. The column leaked 0.10 to 0.13 ml/hr, but this leak was never externally detected. As no salts were deposited on the outside of the column during a run, it was felt that even this small leak was not present during operation.

After measuring the leak rate for a few hours, the column was drained and refilled from the bottom with the salt solution; this vertical filling was necessary to remove all air from the flow channels. The vertical filling of the

column required cocurrent flow of the solution in each channel; to prevent switching entrance and exit lines, one side of the column was filled through the standpipe exit. Once filled, the column was lowered to its normal position.

After filling, the pumps were started and the flows adjusted approximately to the desired value. The heater and the refrigeration compressor were turned on and the system allowed to come to steady state. It took about 15 minutes for the system to come to thermal steady state.

When it was ascertained that the column was at steady state, the flow rates were changed and a new run was begun. It was not necessary to shut down the column unless it could be determined by material balances on individual channels that the membrane had failed.

Large Column. Because of the geometry of the large column, there was no advantage to using any kind of inclined filling. A 1/2 mil Teflon sheet was placed over the end channels on both sides of the cellophane membrane and the membrane laid in place on the bottom plate. The two plates were mated, and placed into the press. After clamping the press together, the column was filled through the head tanks and the standpipes. The pumps were adjusted, and the heater turned on. After the system reached 125°F, the refrigeration was turned on; it took the system about 1 hour to reach this temperature.

When steady state was reached, the flow rates were changed and a new run was started, as with the small column.

Analytical Procedure

Chemical analysis of all solutions was carried out using a Beckman Model DU Spectrophotometer. This instrument provided a very reliable and convenient method of analysis. The instrument required a sample of about 0.6 ml; the light path through this small sample was 0.097 or 0.100 cm. Daily analyses were made until the analyses of the end reservoirs checked on three succeeding days.

The spectrophotometric method utilizes the relation between the concentration of a solution and its ability to absorb light. The concentrations were obtained from the light absorbancy by the use of Lambert-Beer's law, which states that

$$T_s = 10^{-a_s b c} \quad (54)$$

or

$$A_s = -\log_{10} T_s = a_s b c \quad (55)$$

where

T_s = transmittancy, the ratio of light transmittance of the solution to that of the solvent

A_s = absorbancy

a_s = absorbancy index

b = thickness of the solution light path

c = concentration

The instrument gives T_s (or A_s) directly by comparing light absorption

in the solution to that of the solvent alone. The cell thickness is known and the absorbancy index may be determined by using standard solutions of known concentrations. From these data the unknown concentrations may be computed. If only the ratio of the concentration of two solutions is desired, only the absorbancies need be known, as the ratio of two absorbancies measured in the same cell depends only on the concentrations; that is,

$$\frac{A_s}{A'_s} = \frac{c}{c'} \quad (56)$$

For single-salt solutions, the transmittancy value at only one wave length is required for solution of equation (54) or (55). For two salts in solution, the assumption is usually made that the light absorbancy of the two solutes is additive at each of two wave lengths, i. e.

$$A_s = -\log_{10} T_s = (a_{s1}c_1 + a_{s2}c_2)b \quad (57)$$

where the subscripts 1 and 2 refer to absorbancies and concentrations of components 1 and 2. One equation at each of two wave lengths may be written for c_1 and c_2 and these solved simultaneously. The method of analyzing two-salt solutions is given in detail in Appendix B. Long's (32) and the author's own data show that the assumption of additive absorbancies applies well to the copper sulfate-cobalt sulfate system at 0.3 to 0.9 molar concentrations; the only deviations from the additivity assumption occurred at dilute concentrations of 0.01 molar. If the ratio of two concentrations of two salt solutions is desired,

both absorbancy indexes must be known. For a two salt solution, one has the equations for absorbancy at one wave length of

$$\frac{c_1}{c_1'} = \frac{A_S - a_{S2}c_2b}{A_S' - a_{S2}c_2'b} \quad (58)$$

However, at the wave lengths used, the value of $a_{S2}c_2b$ was only about 2 per cent of the value of A_S , and the ratio of concentrations could be approximated with less than 1 per cent error by the ratio of absorbancies at one wave length. This effectively is using equation (56) for analysis. The corrected absorbancies were used in this work, but no appreciable error would be introduced by the use of uncorrected values.

Although the analyses give the concentrations in units of moles per unit volume, the ratio of two concentrations in these units is not significantly different in dilute solution from the ratio of the two corresponding mole fractions. This has been shown previously by the author (18). The error in this approximation is much less than the uncertainty introduced by the analytical error. As only ratios of mole fractions are ever used in the analysis of the results, conversions from the molar concentrations are not made.

CHAPTER V

PRESENTATION OF DATA AND RESULTS

I. DATA

Separations at Total Reflux

The separations of single salts from water obtained at total reflux from the small column are given in Table I. Column 3 gives the flow rate, in ml/hr, through each channel section. Columns 4 and 5 give the effluent composition x' of the hot and cold side, respectively, in molar units (moles of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ per 1000 ml of solution). Column 6 gives the separation ratio of the effluent streams, $x_{\text{cold}}/x_{\text{hot}} = x_L/x_D$, which is the ratio of columns 5 to 4. Runs 1 through 3 are for CuSO_4 , and Run 4 is for CoSO_4 .

The data are plotted for CuSO_4 in Figure 12; this figure shows the relation between the natural logarithm of the separation ratio of the column x_L/x_D (Column 6, Table I) and the inverse flow rate $1/m$, given in hr/ml (Column 3, Table I); equation (53) predicts that the plot should be linear.

The data for the two-salt total reflux runs from the small column are tabulated in Table I. Columns 1 through 6 are as presented for the single salt operations. Column 2 gives the salt for which each horizontal row of data apply. Column 7 shows the separation factor for the column, Ω , for each run, where Ω is defined for the effluent streams as

$$\Omega = \frac{[x_L/x_D]_{\text{CuSO}_4}}{[x_L/x_D]_{\text{CoSO}_4}} \quad (59)$$

TABLE I

TOTAL REFLUX SEPARATIONS
FROM SMALL COLUMN

| Run No. | Salt | Flow Rate ml/hr | Concentration of Effluent from: | | Separation | |
|-------------------------------|-------------------|-----------------------|------------------------------------|--------------------|--------------------|--------------------|
| | | | Hot Side molar | Cold Side molar | Ratio x_L/x_D | Factor Ω |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| <u>Single-Salt Operations</u> | | | | | | |
| 1 | CuSO ₄ | 9.3 | .373 | .410 | 1.10 | |
| 2 | " | 6.8 | .470 | .489 | 1.14 | |
| 3 | " | 2.6 | .407 | .555 | 1.36 | |
| 4 | CoSO ₄ | 2.4 | .455 | .500 | 1.10 | |
| <u>Two-Salt Operations</u> | | | | | | |
| 5 | CuSO ₄ | 2.8 | .373 | .511 | 1.37 | 1.10 |
| | CoSO ₄ | | .385 | .481 | 1.25 | |
| 6 | CuSO ₄ | 2.6 | .367 | .511 | 1.39 | 1.11 |
| | CoSO ₄ | | .386 | .481 | 1.25 | |
| 7 | CuSO ₄ | 4.3 | .409 | .511 | 1.25 | 1.06 |
| | CoSO ₄ | | .408 | .481 | 1.18 | |
| 8 | CuSO ₄ | 6.3 | .416 | .511 | 1.22 | 1.04 |
| | CoSO ₄ | | .410 | .481 | 1.17 | |

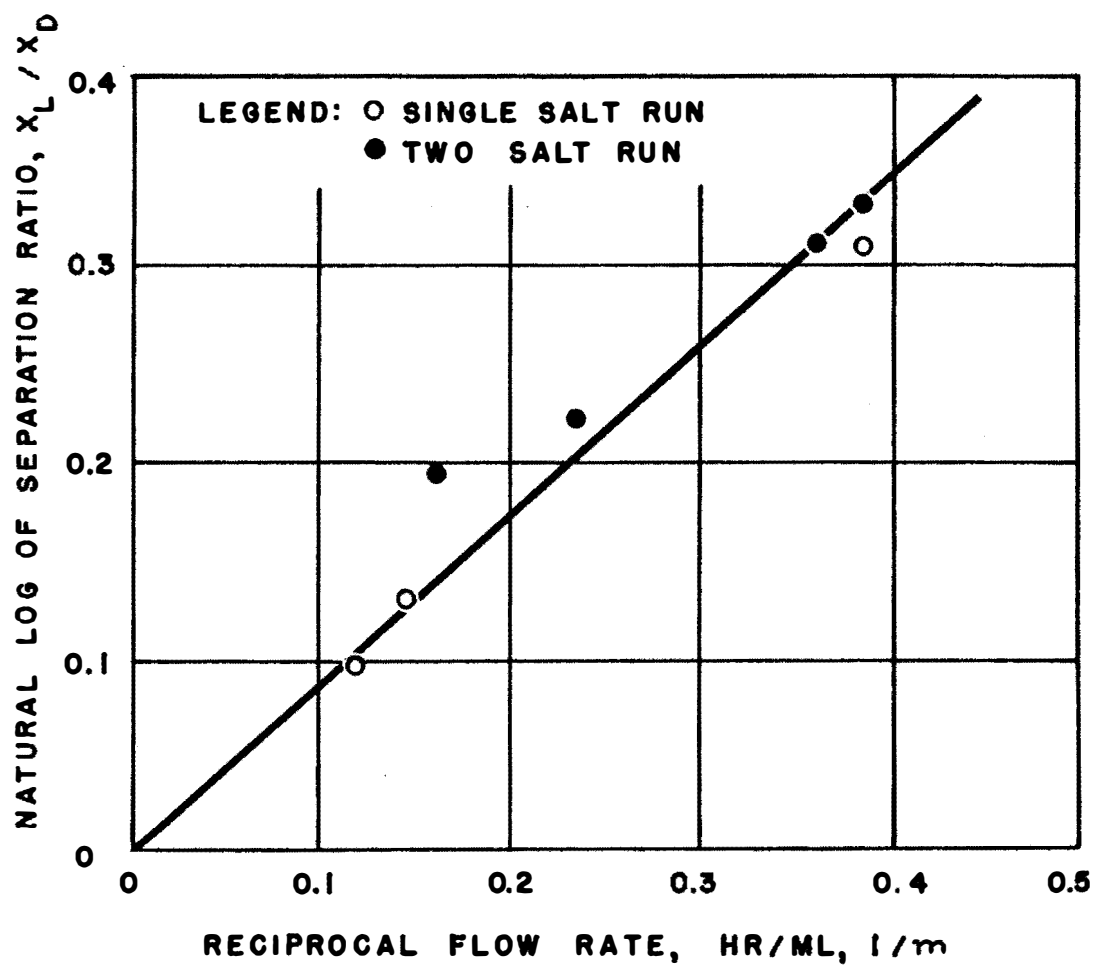


FIGURE 12

LOGARITHM OF THE SEPARATION RATIO VERSUS THE RECIPROCAL
OF THE FLOW RATE FOR TOTAL REFLUX SEPARATION
OF CuSO_4 FROM H_2O

Runs 5 through 8 represent two-salt runs. The data for the separation of CuSO_4 from H_2O in the two-salt solutions are presented in Figure 12, and for the separation of CoSO_4 from H_2O in Figure 13. Equation (53) predicts that these two plots of separation ratio versus reciprocal flow rate should be straight lines through the origin.

These data at total reflux were taken prior to the data for operation with product withdrawal. Neither the measurement technique for the flow rates nor the flow system previously described had been worked out when the total reflux data were obtained. The flow rates were measured by counting drops coming from a fixed stainless steel tube of 0.072 in. O.D. during a timed interval and calculating the rate from a calibration of the drop size. The flow system was essentially the same, but the flow had slight instabilities in the output rates over long periods of time; also, the finger pumps were hooked directly to the column and therefore caused pulsed flow of short periods. In addition, the column was operated without the Teflon gasket or any type of baffle over the entrance ports. Operation of the column without the Teflon gasket could never be reproduced because of the problem of membrane failure at the cold entrance port region. It was never fully understood why the cellophane membrane would not last long enough to reproduce the original method of operation. Successful attainment of steady state with product withdrawal required use of the Teflon gasket. Many of the runs at total reflux resulted in very short runs because of a different method of operation; this could partially explain the success of the first method.

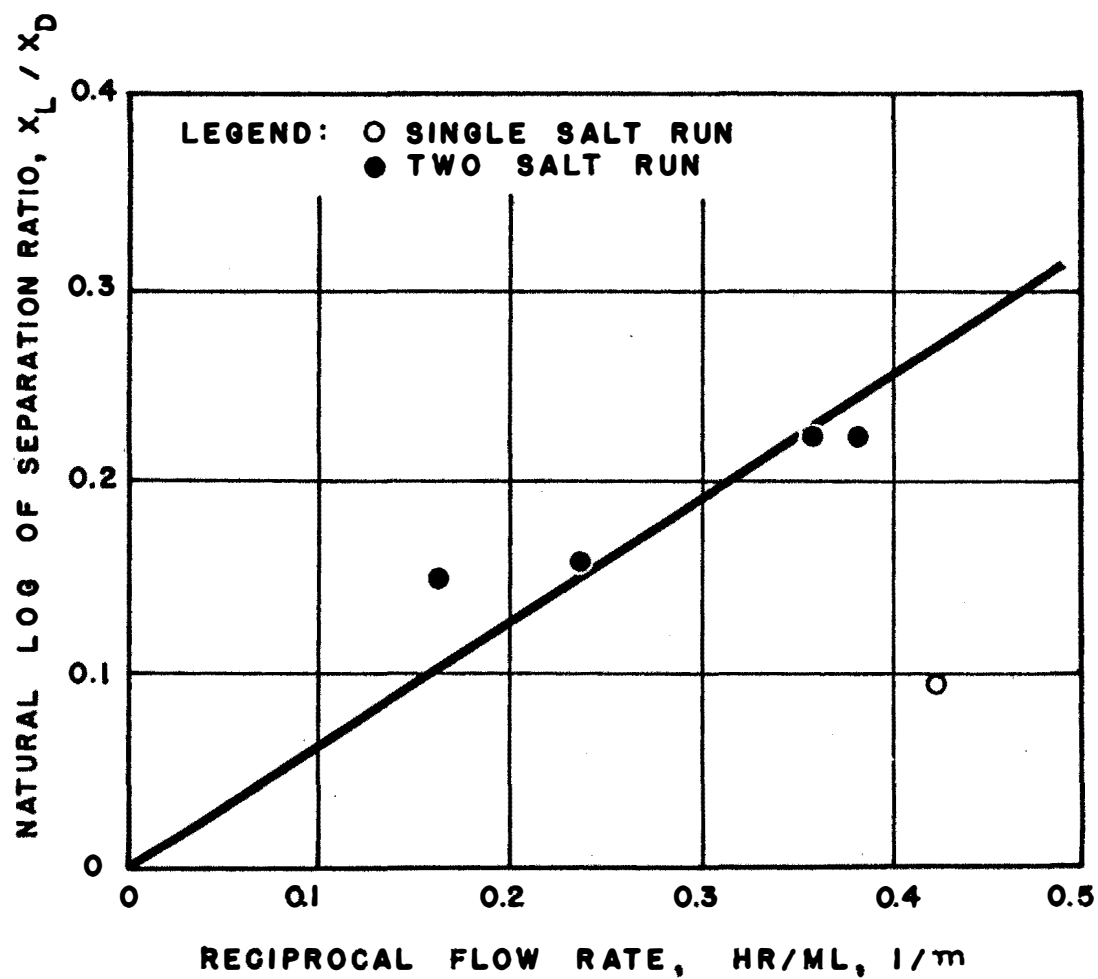


FIGURE 13

LOGARITHM OF THE SEPARATION RATIO VERSUS THE RECIPROCAL
OF THE FLOW RATE FOR TOTAL REFLUX SEPARATION
OF CoSO_4 FROM H_2O

Separations with Product Withdrawal

The data for the small column with product withdrawal are presented in Table II; the data for product withdrawal on the large column are in Table III. The following explanation applies to both tables. In columns 4 and 5 are the input flow rates to the cold and hot sides, respectively. The measured product rate is given in column 6; this measurement is independent of the other two flow rate measurements, and hence is not equal to the difference in the figures in columns 5 and 4, although it very closely approximates this difference. Column 6 gives the reflux ratio, which is the ratio of the cold side flow rate (column 3) to the product rate (column 5); this is the actual reflux ratio at the return end of the column. Columns 7 and 8 show the concentration of the effluent from the hot and cold sides, respectively. Column 9 contains the separation ratio for the individual salts; this is the ratio of the two numbers in columns 7 and 8. The numbers in columns 7, 8, and 9 correspond to the salt listed in the same line in column 2. Column 10 contains the overall separation factor for the two salts; this is the ratio of the two numbers in column 9.

Anomalous Behavior of the Large Column

In Table IV are presented the time-concentration data for the effluent streams from the large thermal diffusion column; these same data are presented graphically in Figure 14. The separation ratio of each salt between the two ends of the column is presented in columns 2 and 3, with the actual concentrations of the salts in the effluent from the hot side being given in columns 5 and 6. The separation factor for the column is in column 4. From

TABLE II

PRODUCT WITHDRAWAL DATA FROM SMALL COLUMN

| Run No. | Salt | Cold Side ml/hr | Hot Side ml/hr | Product ml/hr | Reflux Ratio | Concentration of Effluent from | | Separation Ratio x_L/x_D | Factor Ω |
|---------|--|--------------------|-------------------|------------------|-----------------|-----------------------------------|--------------------|-------------------------------|--------------------|
| | | | | | | Hot Side molar | Cold Side molar | | |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) |
| 10 | CuSO ₄ CoSO ₄ | 1.97 | 2.33 | 0.318 | 6.3 | .369 | .477 | 1.293 | 1.137 |
| | | | | | | .408 | .464 | 1.137 | |
| 11 | CuSO ₄ CoSO ₄ | 1.97 | 2.50 | .52 | 3.8 | .384 | .477 | 1.242 | 1.098 |
| | | | | | | .411 | .466 | 1.131 | |
| 12 | CuSO ₄ CoSO ₄ | 2.00 | 2.97 | .85 | 2.35 | .404 | .475 | 1.178 | 1.056 |
| | | | | | | .420 | .468 | 1.115 | |
| 13 | CuSO ₄ CoSO ₄ | 1.97 | 3.75 | 1.72 | 1.16 | .428 | .475 | 1.110 | 1.037 |
| | | | | | | .436 | .466 | 1.070 | |
| 14 | CuSO ₄ CoSO ₄ | 4.05 | 4.46 | .58 | 6.94 | .384 | .469 | 1.220 | 1.061 |
| | | | | | | .402 | .462 | 1.150 | |
| 15 | CuSO ₄ CoSO ₄ | 4.04 | 4.45 | .62 | 6.52 | .389 | .474 | 1.217 | 1.044 |
| | | | | | | .402 | .468 | 1.166 | |
| 16 | CuSO ₄ CoSO ₄ | 4.13 | 5.68 | 1.61 | 2.56 | .410 | .477 | 1.163 | 1.043 |
| | | | | | | .420 | .468 | 1.115 | |
| 17 | CuSO ₄ CoSO ₄ | 4.04 | 7.51 | 3.52 | 1.15 | .430 | .479 | 1.113 | 1.023 |
| | | | | | | .438 | .476 | 1.088 | |
| 18 | CuSO ₄ CoSO ₄ | 6.15 | 6.80 | .675 | 9.11 | .397 | .465 | 1.173 | 1.051 |
| | | | | | | .418 | .466 | 1.116 | |
| 19 | CuSO ₄ CoSO ₄ | 6.30 | 9.60 | 3.30 | 1.91 | .425 | .477 | 1.123 | 1.026 |
| | | | | | | .434 | .474 | 1.094 | |

TABLE III

PRODUCT WITHDRAWAL DATA FROM LARGE COLUMN

| Run No. | Salt | Cold Side ml/hr | Hot Side ml/hr | Product ml/hr | Reflux Ratio | Concentration of Effluent from | | Separation Ratio x_L/x_D | Factor Ω |
|---------|--|--------------------|-------------------|------------------|-----------------|-----------------------------------|--------------------|----------------------------------|--------------------|
| | | | | | | Hot Side molar | Cold Side molar | | |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) |
| 20 | CuSO ₄ CoSO ₄ | 16.1 | 17.4 | 1.51 | 10.7 | .384 | .451 | 1.177 | 1.066 |
| | | | | | | .380 | .419 | 1.104 | |
| 21 | CuSO ₄ CoSO ₄ | 16.2 | 29.8 | 14.2 | 1.14 | .418 | .449 | 1.073 | 1.035 |
| | | | | | | .400 | .413 | 1.036 | |
| 22 | CuSO ₄ CoSO ₄ | 10.7 | 11.4 | 0.84 | 12.7 | .367 | .455 | 1.240 | 1.082 |
| | | | | | | .371 | .426 | 1.146 | |
| 23 | CuSO ₄ CoSO ₄ | 10.6 | 19.7 | 8.15 | 1.30 | .416 | .459 | 1.103 | 1.050 |
| | | | | | | .407 | .428 | 1.050 | |

TABLE IV

SOME TRANSIENT DATA FOR LARGE COLUMN

| Time days | Separation Ratio | | Separation Factor Ω | Concentration of Effluent From Hot Side | |
|--------------|------------------------------|------------------------------|----------------------------------|--|-----------------|
| | CuSO_4 x_L/x_D | CoSO_4 x_L/x_D | | CuSO_4 | CoSO_4 |
| (1) | (2) | (3) | (4) | (5) | (6) |
| 0 | 1.00 | 1.00 | 1.00 | .445 | .410 |
| 5 | .535 | .483 | 1.11 | .740 | .745 |
| 9 | .751 | .695 | 1.08 | .518 | .498 |
| 10 | .813 | .730 | 1.11 | .495 | .485 |
| 13 | .875 | .811 | 1.08 | .472 | .445 |
| 19 | .935 | .875 | 1.07 | .458 | .446 |
| 21 | .945 | .902 | 1.05 | .455 | .432 |
| 24 | .950 | .925 | 1.03 | .450 | .426 |
| 27 | .970 | .950 | 1.02 | .446 | .422 |
| 31 | 1.00 | .950 | 1.05 | .442 | .417 |
| Shut Down | | | | | |
| 36 | .940 | .911 | 1.03 | .452 | .430 |
| 41 | 1.015 | 1.00 | 1.01 | .443 | .398 |
| 42 | 1.03 | 1.00 | 1.03 | .423 | .398 |
| 44 | 1.03 | 1.00 | 1.03 | .436 | .406 |
| 48 | 1.06 | 1.015 | 1.05 | .429 | .406 |
| 51 | 1.07 | 1.04 | 1.03 | .429 | .404 |
| 53 | 1.06 | 1.045 | 1.01 | .429 | .404 |
| 55 | 1.07 | 1.05 | 1.02 | .429 | .398 |
| 56 | 1.07 | 1.04 | 1.03 | .429 | .404 |
| 58 | 1.07 | 1.05 | 1.02 | .430 | .404 |
| Minimum | .312 | .293 | 1.06 | 1.22 | 1.18 |

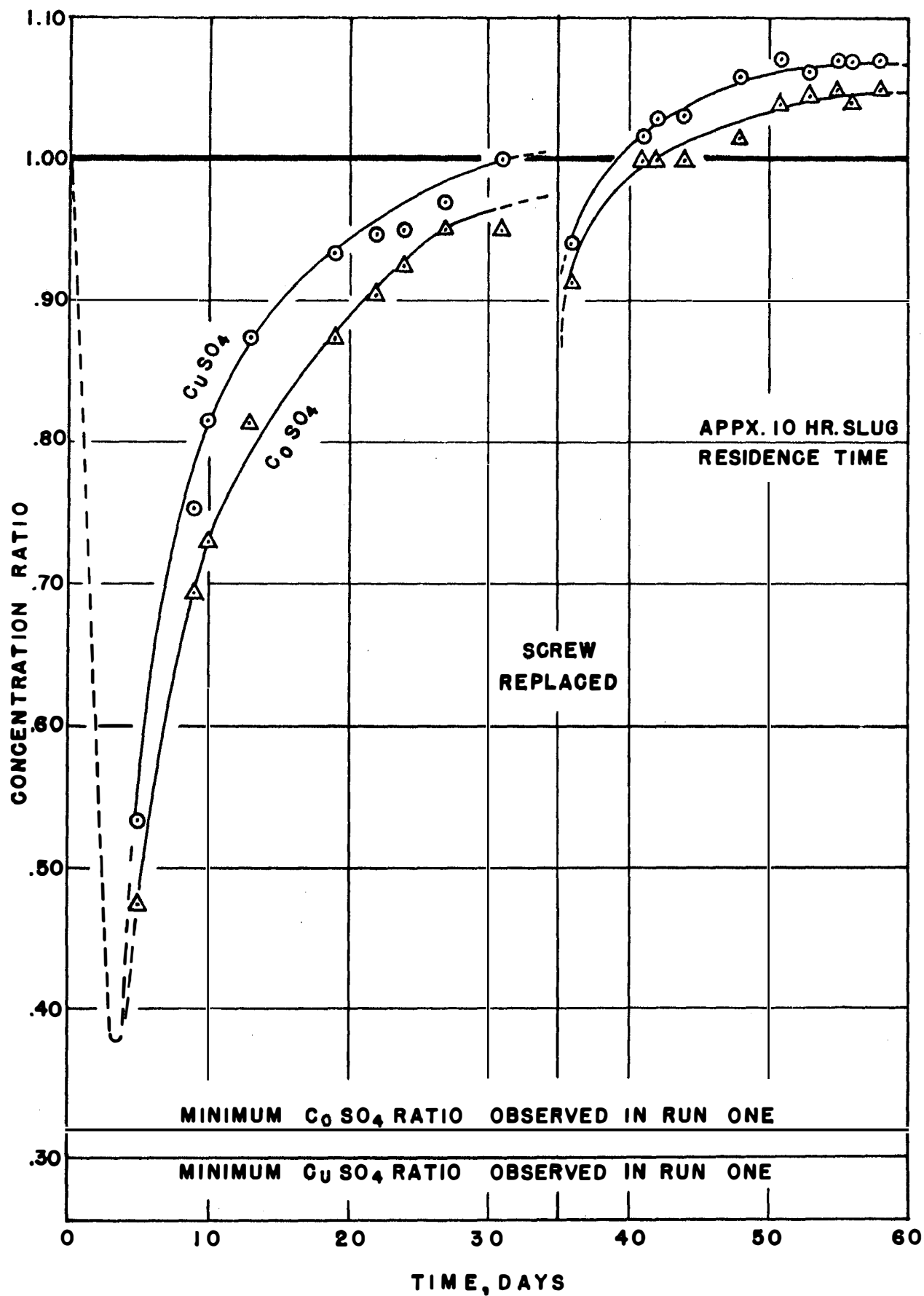


FIGURE 14

TRANSIENT CONCENTRATION RATIOS OF THE LARGE COLUMN

Table IV and from Figure 14, it may be observed that the column starts with a uniform solution, and then creates a large concentration change in a short time. This change for each salt is not only unusually large, but also is in the direction opposite to that predicted by Soret data and opposite to that in the column at steady state; it can result only from a transport of salt from the cold channel to the hot channel. During the early stages of this transient (first 15 days), a large amount of water is transported through the membrane. The hot side feed was 30 ml/hr and the exit 19 ml/hr; the cold side feed was 16 ml/hr and the exit 27 ml/hr. This flow of water is from the hot side to the cold side, which is the usual direction for thermal osmosis observed by others (3) (31) (51). One might think that the water alone is transported through the membrane and that the concentration increase along the hot side is due to the loss of a large amount of water; however, material balances were calculated for the column, and showed that each salt was definitely being transported from the cold side to the hot side at approximate rates of 0.125 m-moles/hr. The material balances on each channel of the column checked within the accuracy of the experimental measurements; the net rates of salt transport were accurate within ± 10 per cent. The transport of water through the membrane gradually decreased, until it was not significant at the end of the 58 day transient period. After the 31st day, the screw in the entrance port of the hot side feed corroded out and had to be replaced; the heat and the refrigerant were shut off and the screw replaced with one made of Lucite; no difficulty was experienced with this screw. At the end of 40 days, the transport of salt occurred in the opposite and usual direction. After ascertaining that steady state had been attained, the flow rates were

changed and the data reported in Table III were taken. This particular type of transient behavior was observed in three runs; the first run resulted in solutions so concentrated that they crystallized and plugged the cold side entrance port. These measured concentrations are given at the bottom of Table IV and at the bottom of Figure 14. After the first run, the column was taken apart and the cellophane membrane replaced with a new one; after the second run, the wall of the hot side channel was scraped of a green deposit, and the same membrane replaced in the column for the third run. The data obtained after this treatment are reported in Table IV and Figure 14. No satisfactory explanation of this behavior has yet been proposed. It should be noted that changes of column flow rates did not cause anomalous behavior; the behavior resulted only after shutdowns involving taking the column apart.

The conjecture of the author is that the transient behavior was caused by a surface activity effect of the silicon bronze plate on the hot side. No difficulty was experienced with the small column which was constructed of copper. Bosanquet (10) experienced some difficulties in Soret measurements which he attributed to surface effects of the hot side. His Soret cell was constructed from the same copper bar stock as was the small column used in this work, however, so one cannot conclude that it was strictly an effect of the silicon bronze. The explanation of the behavior as a membrane effect was fairly well eliminated, as far as the author is concerned, by the fact that the same membrane was used in two of the runs in which the behavior was observed, with only a water rinse of one side of the membrane between runs. In the author's opinion, the cleaning of the hot surface caused the anomalous behavior. It is not attributed to an electrolytic corrosion and

transport effect, however, as sufficient material was not found deposited on the hot surface to account for the large quantity of salt which was transported.

II. ANALYSIS OF THE RESULTS

In order to extract the height of a transfer unit h_L and the equilibrium constant K from the data, plots of possible values of h_L versus K , as determined from equation (45), must be made. Any two runs with the same cold side flow rate L should have the same h_L , and all runs at constant temperature difference, wall spacing, etc., should have the same value of K . Figures 15, 16, and 17 are plots of h_L and K values from equation (49) and the data of Table II for the separation of copper sulfate in the small column; the reflux ratio R is listed on each curve as the parameter. Figures 18, 19, and 20 are similar curves for cobalt sulfate. Figures 21 and 22 are from data on the large column for copper sulfate; Figures 23 and 24 are for cobalt sulfate in the large column. For each figure, the cold side flow rate is constant, indicating, theoretically, a constant value for h_L . Hence, on each plot, all of the curves should intersect at a common point. The locus of possible values of h_L and K from total reflux data are also plotted on Figures 15 through 20; total reflux operations are not shown in Figures 21 through 24, as no total reflux data were taken on the large column.

A quantity frequently used for analysis of mass transfer data is the separation factor, α , for a point in the column z , which is defined as the ratio of two components in one phase (or channel) divided by (or into) the ratio of the same two components in the other phase that would exist at equilibrium with the concentrations in the former phase. If the ratio of

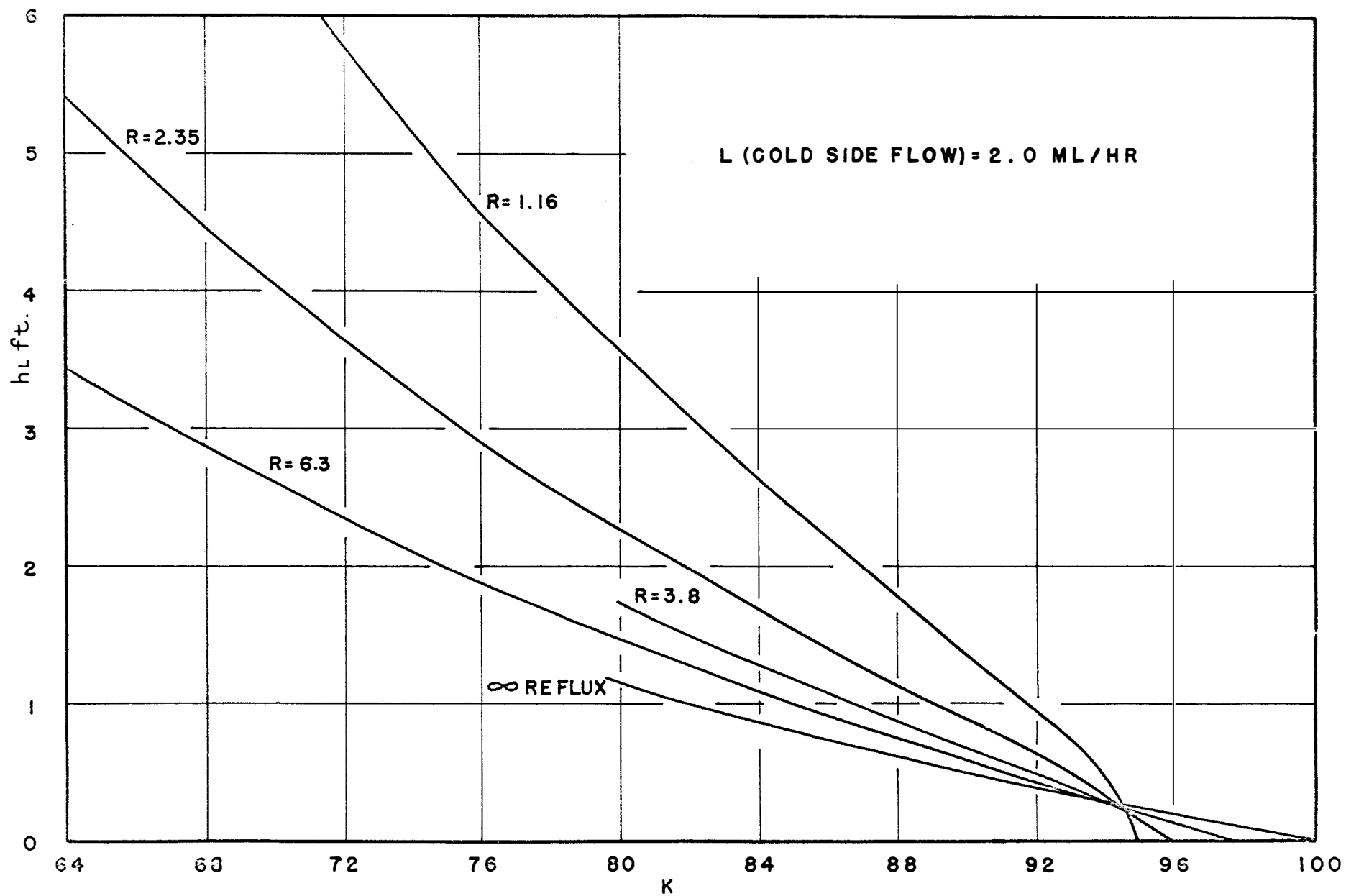


FIGURE 15

DETERMINATION OF THE SMALL COLUMN SEPARATION PARAMETERS FOR CuSO_4 : I

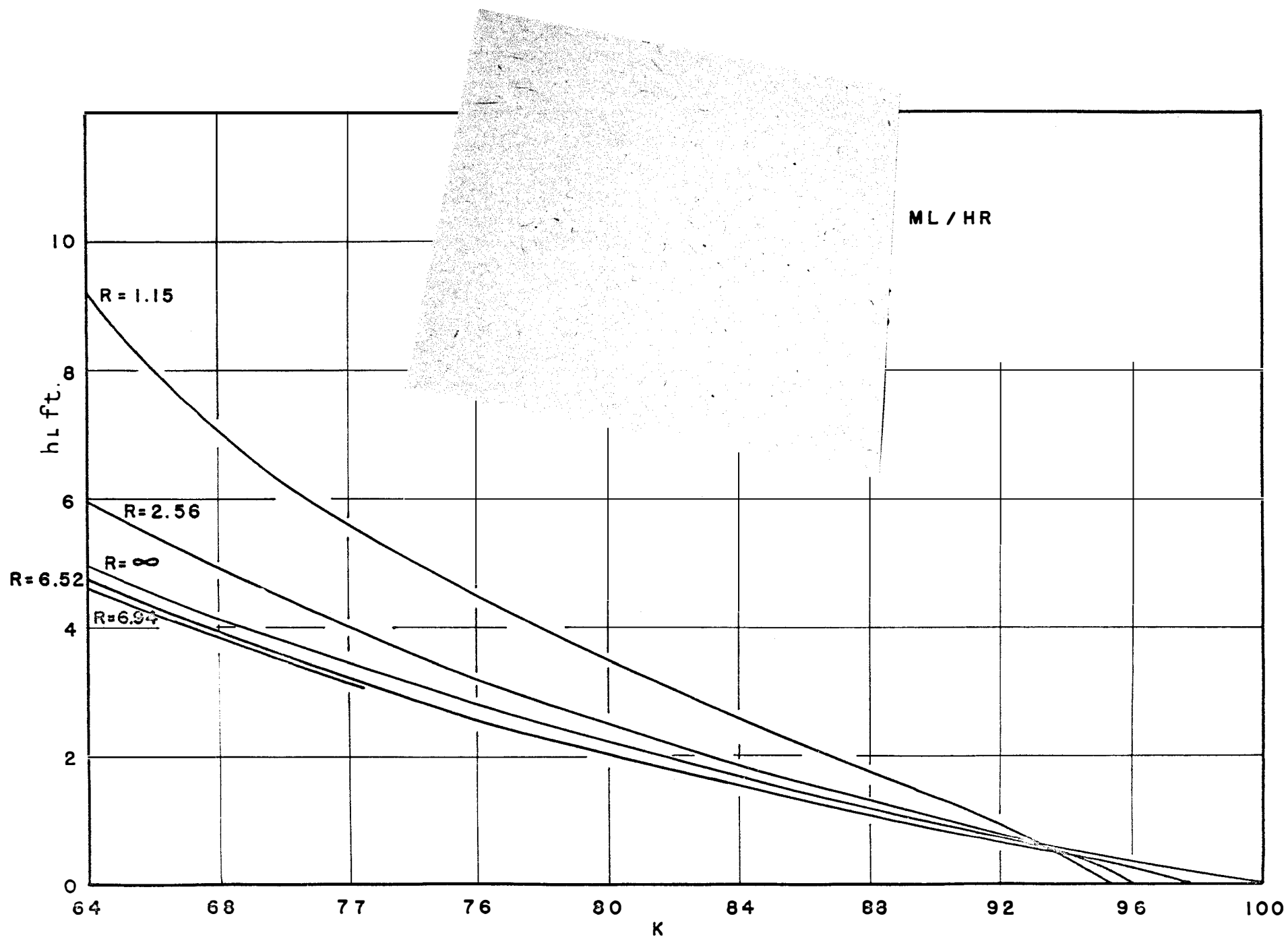


FIGURE 16

DETERMINATION OF THE SMALL COLUMN SEPARATION PARAMETERS FOR CuSO_4 : II

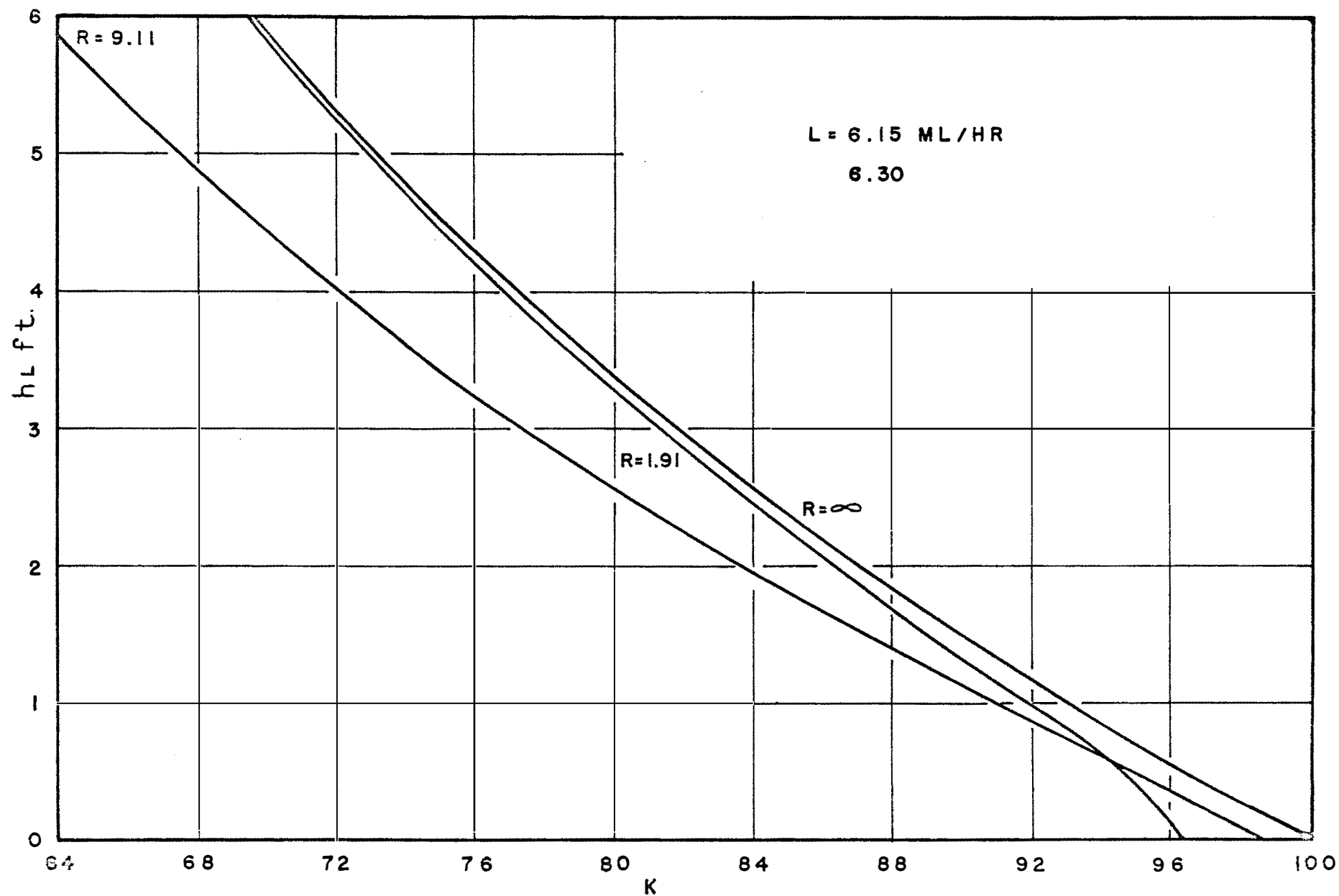


FIGURE 17

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DETERMINATION OF THE SMALL COLUMN SEPARATION PARAMETERS FOR CuSO_4 : III

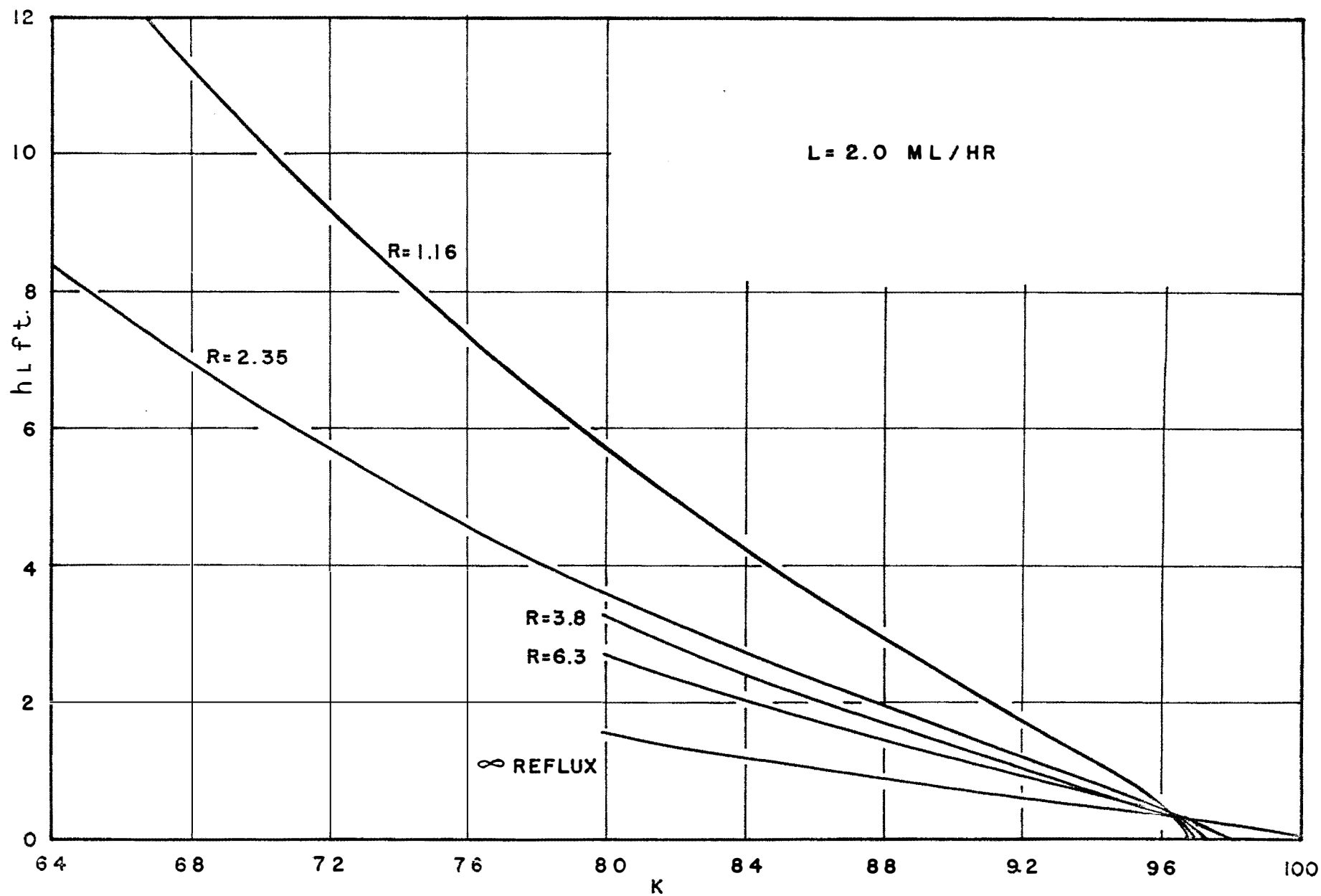


FIGURE 18

DETERMINATION OF THE SMALL COLUMN SEPARATION PARAMETERS FOR CoSO_4 : I

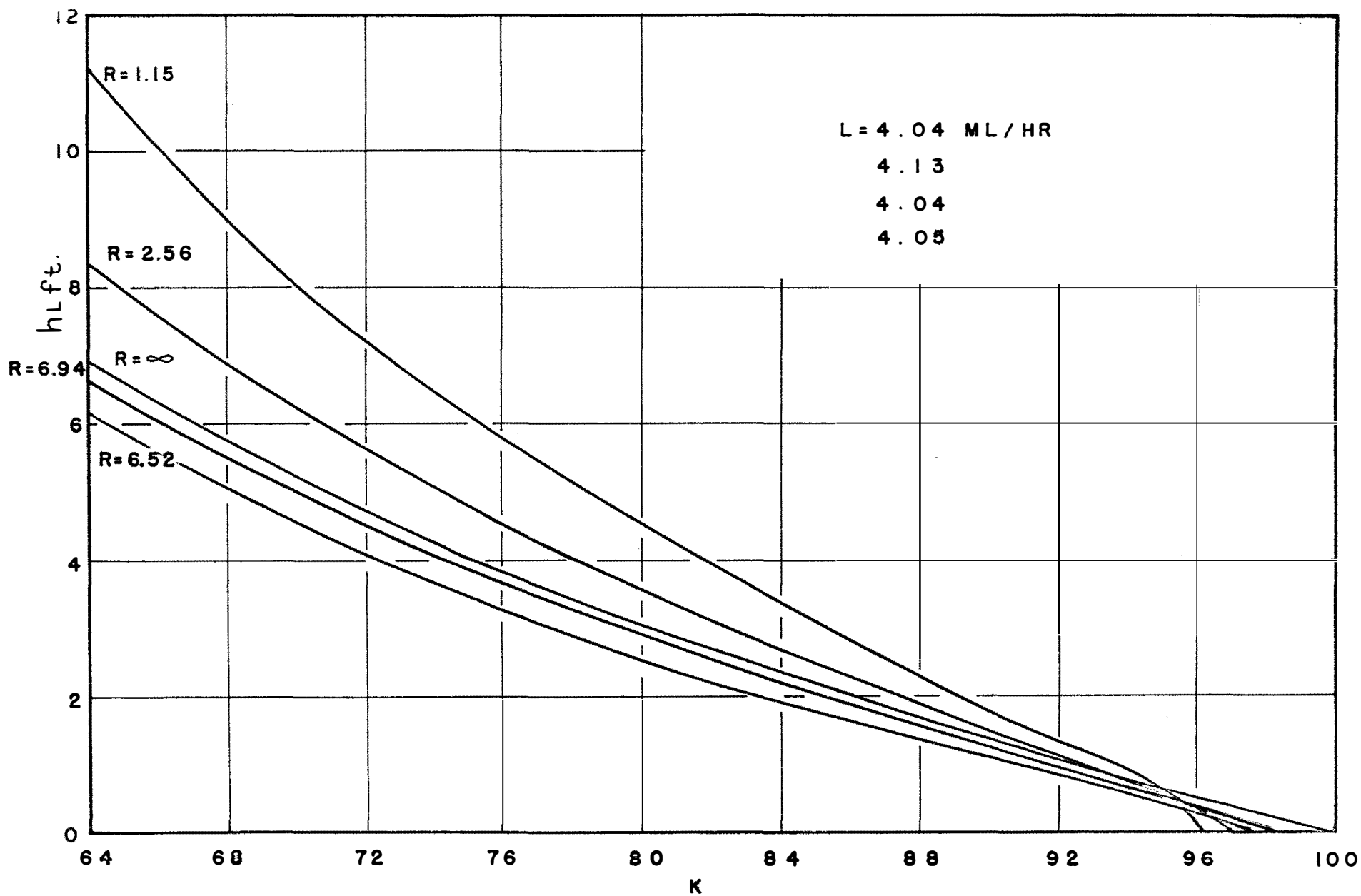


FIGURE 19

DETERMINATION OF THE SMALL COLUMN SEPARATION PARAMETERS FOR $\text{CoSO}_4: \text{I}$

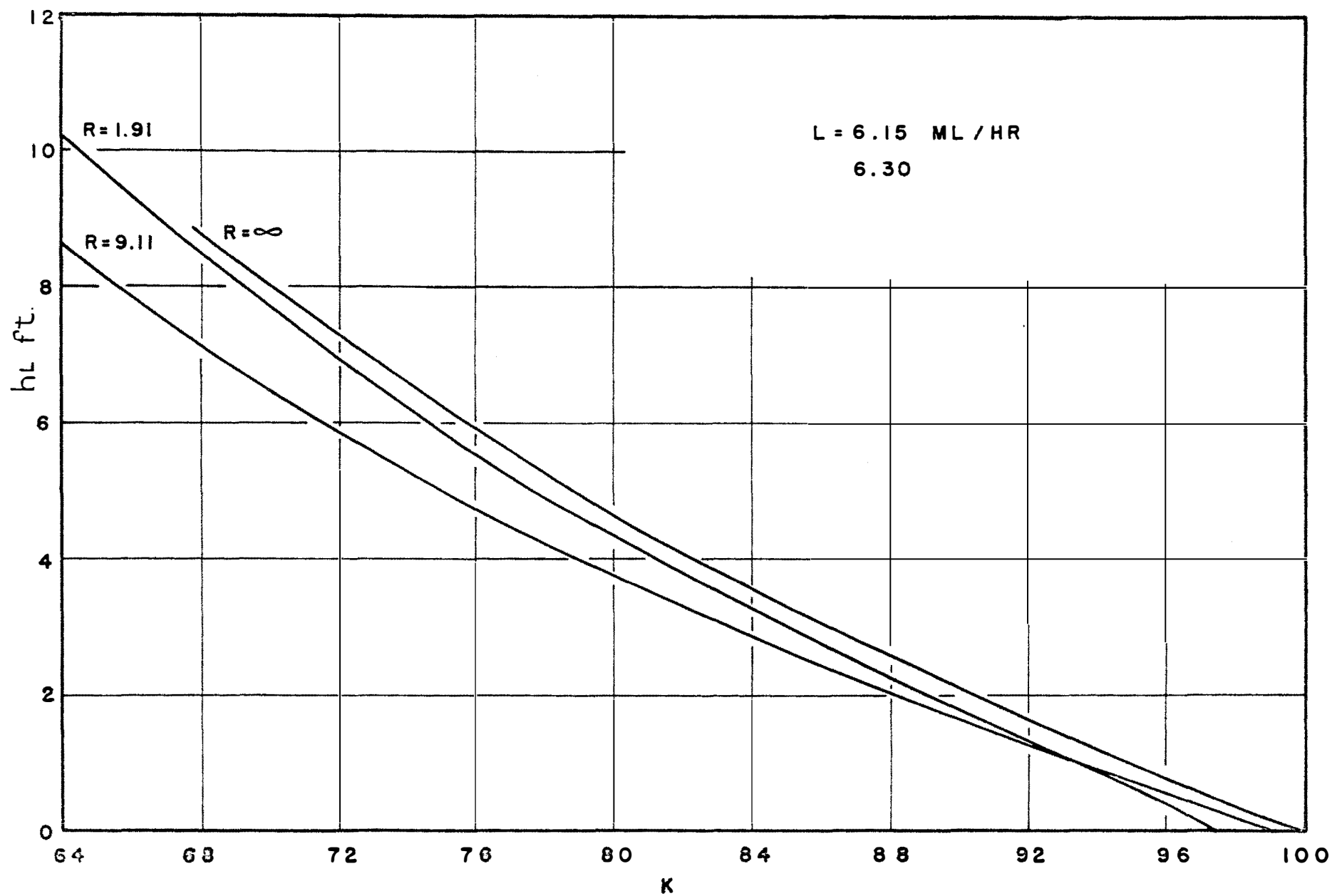


FIGURE 20

DETERMINATION OF THE SMALL COLUMN SEPARATION PARAMETERS FOR CoS_4 : III

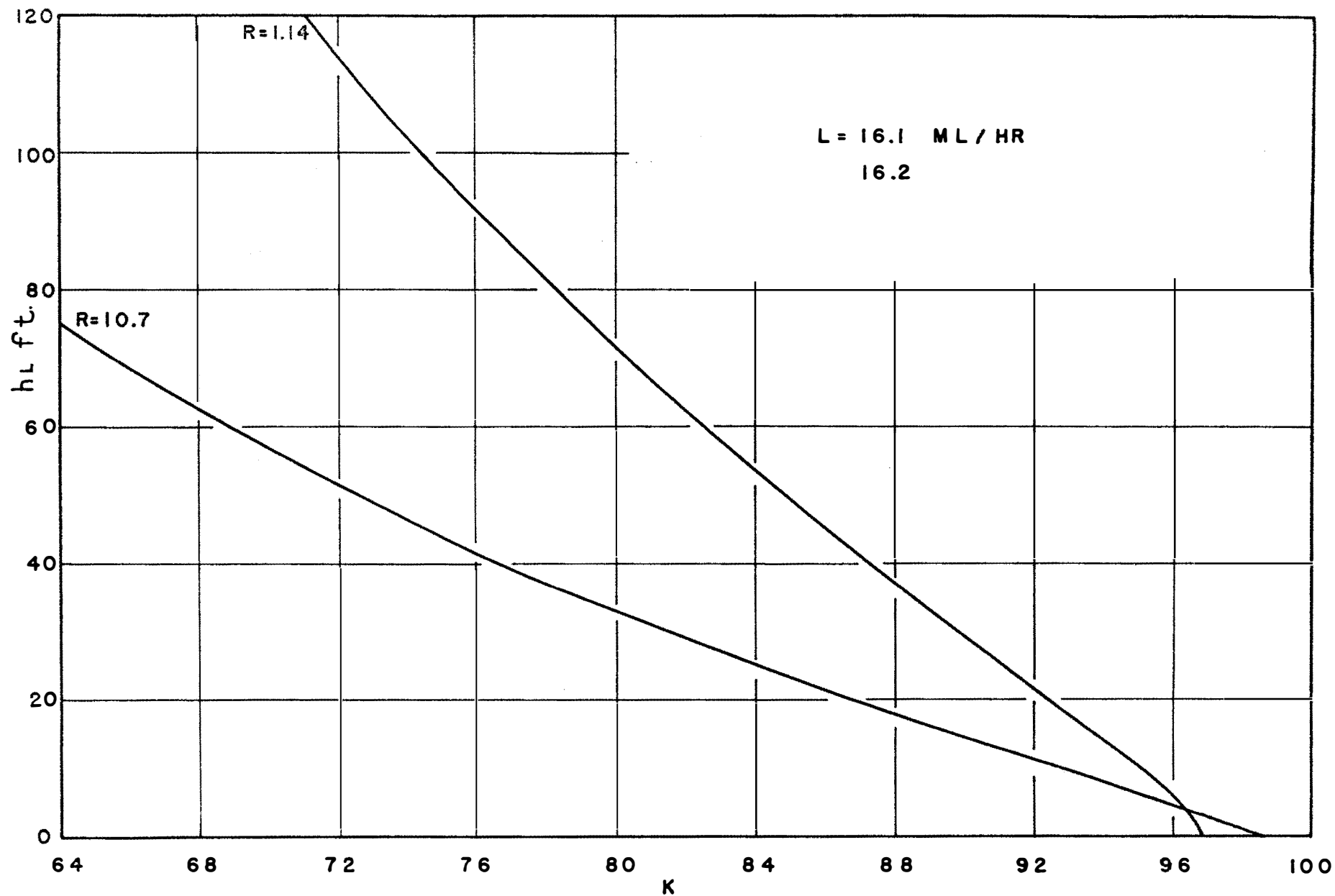


FIGURE 21

DETERMINATION OF THE LARGE COLUMN SEPARATION PARAMETERS FOR $\text{CuSO}_4 \cdot \text{I}$

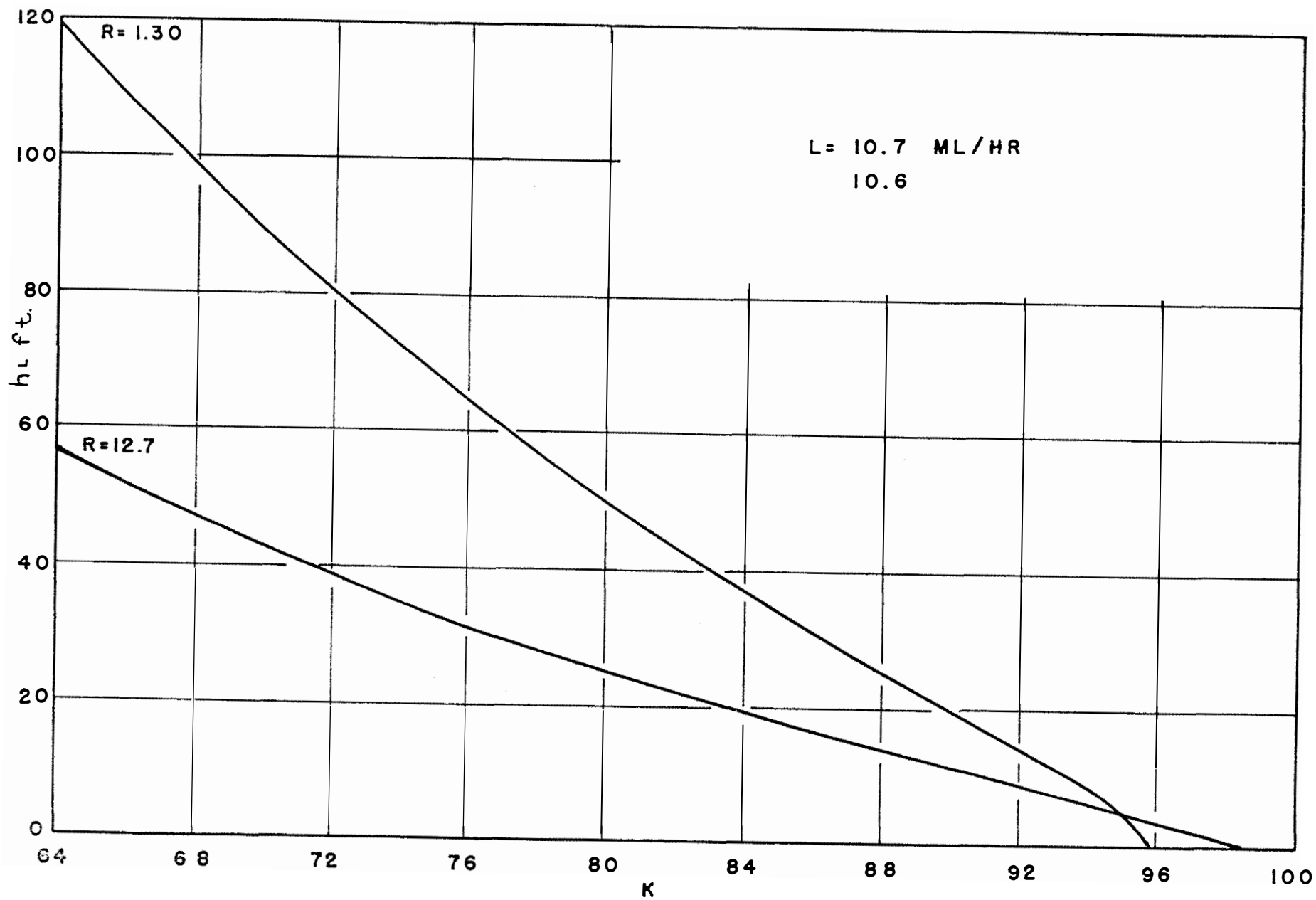


FIGURE 22

DETERMINATION OF THE LARGE COLUMN SEPARATION PARAMETERS FOR $\text{CuSO}_4 \cdot \text{II}$

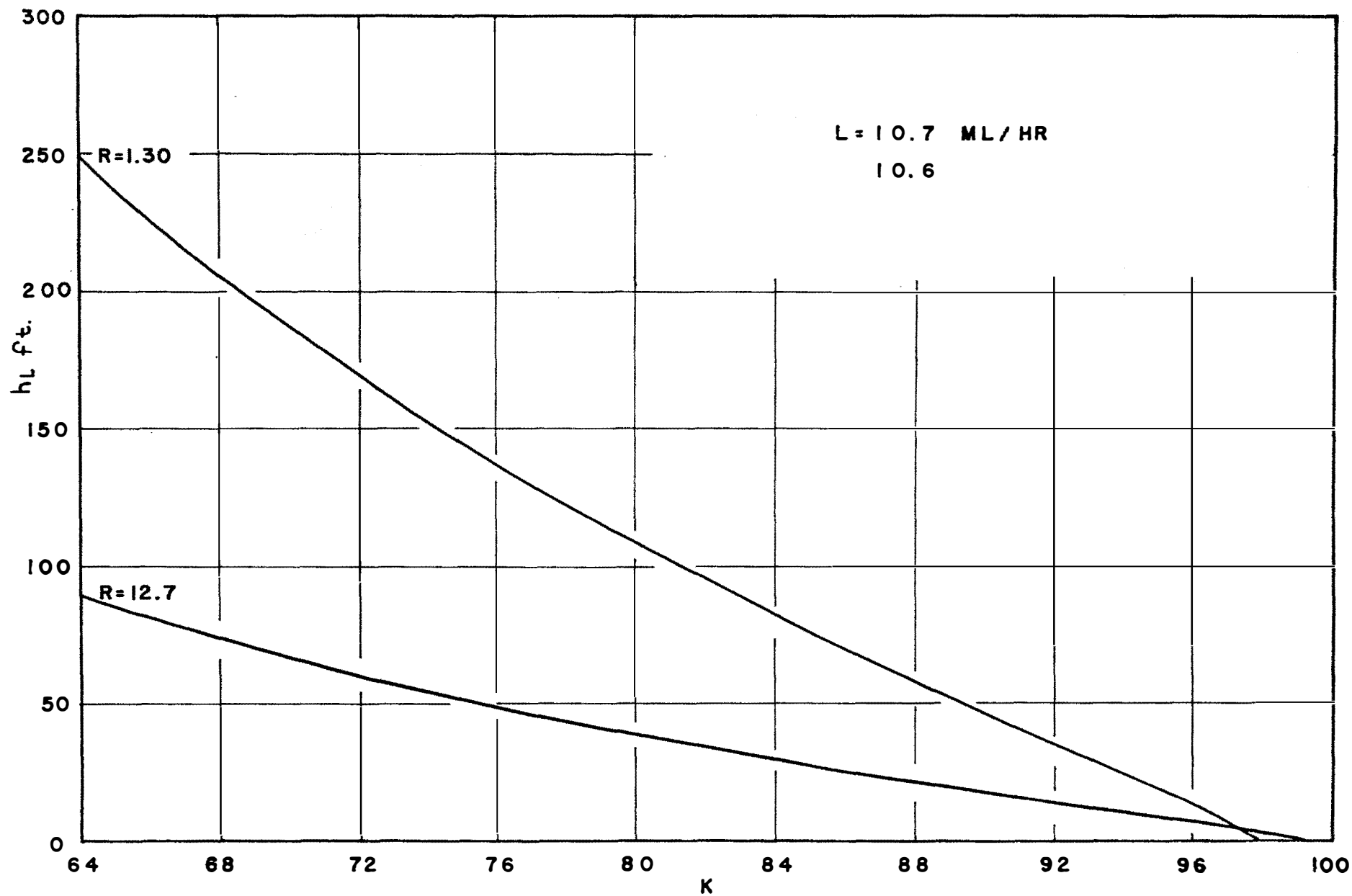


FIGURE 24

DETERMINATION OF THE LARGE COLUMN SEPARATION PARAMETERS FOR $\text{CoSO}_4: \text{II}$

interest is the ratio of the concentrations of the two salts and α is defined to be greater than 1, then

$$\alpha = \frac{x_{\text{CuSO}_4}^* / x_{\text{CoSO}_4}^*}{y_{\text{CuSO}_4} / y_{\text{CoSO}_4}} = \frac{K_{\text{CoSO}_4}}{K_{\text{CuSO}_4}} \quad (60)$$

Representation of Total Reflux Separations

The total reflux data of Figures 12 and 13 for the separation of the individual salts from H_2O may be represented by the equations, fitted by the method of least squares

$$\frac{x_L}{x_D} = e^{\frac{0.87}{m}} \quad \text{for CuSO}_4 \quad (61)$$

$$\frac{x_L}{x_D} = e^{\frac{0.63}{m}} \quad \text{for CoSO}_4 \quad (62)$$

Figures 12 and 13 indicate that these equations may be used to represent either single-salt separations or the separation in two-salt solutions of the two. Although the data in Figures 12 and 13 show some random distribution, there is no trend which indicates a consistent deviation from the straight lines.

The single-salt run for CoSO_4 was not used in the least squares treatment because the separation was much lower than that of the two salt solutions. As there was no effect of the presence of CoSO_4 on the separation of CuSO_4 , it is reasonable to assume that there is no reverse interaction. The small separation of the single salt run could be explained by lack of steady state, or by a

hole in the membrane which was undetected at the time of measurement.

Comparisons of the Results

In Table V, values of the separation parameters K and h_L as determined from experimental data are compared with theoretical predictions based on Soret coefficient data alone. In Table VI, the use of the theoretical equations in predicting the effect of operating conditions on separations is illustrated by a comparison between observed values of K and h_L for the large column with predictions based on the experimental results with the small column.

The values of K and h_L for the small column estimated from the perfect mixing theory using equations (18), (44), and (53) appear in columns 2 and 5 of Table V. The values in columns 3 and 6 were estimated from laminar flow theory using equations (37), (44), and (53). The best values from consideration of Figures 15, 16, and 17 for CuSO_4 , and of Figures 18, 19, and 20 for CoSO_4 , appear in columns 4 and 7. The values in line 1 are for CuSO_4 and in line 2 for CoSO_4 . The values of h_L reported are for a cold side flow rate of 2.0 ml/hr. For some runs, the intersection point of the curves was not as well defined as in others. In cases where doubt existed as to the exact location of the intersection point, conservative values of h_L are indicated by the total reflux curves.

The data for the separation of copper sulfate in the large column are not in complete agreement as to the real value of the equilibrium constant K . Figure 21 indicates that $K = 0.964$ and Figure 22 indicates $K = 0.952$. The value of K from Figure 21 is reported in Table VI, column 2. All values in line 1 are for CuSO_4 , and all numbers in line 2 are for CoSO_4 . The data from

TABLE V

SEPARATION PARAMETERS OF
THE SMALL COLUMN

| Salt | K_{mix} | K_{lam} | K_{obs} | $h_{\text{L-mix}}$ ft | $h_{\text{L-lam}}$ ft | $h_{\text{L-obs}}$ ft |
|-------------------|------------------|------------------|------------------|--------------------------|--------------------------|--------------------------|
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| CuSO ₄ | 0.68 | 0.82 | 0.944 | 1.2 | 0.91 | 0.26 |
| CoSO ₄ | 0.74 | 0.86 | 0.962 | 1.6 | 0.78 | 0.24 |

TABLE VI

SEPARATION PARAMETERS OF
THE LARGE COLUMN

| Salt | K_{obs} | $K_{\text{scale up}}$ | $h_{\text{L-obs}}$ ft | $h_{\text{L-scale up}}$ ft |
|-------------------|------------------|-----------------------|--------------------------|-------------------------------|
| (1) | (2) | (3) | (4) | (5) |
| CuSO ₄ | 0.964 | 0.965 | 3.8 | 3.75 |
| CoSO ₄ | 0.980 | 0.977 | 4.0 | 3.50 |

the large column for cobalt sulfate in Figures 23 and 24 provide values of K in much better agreement. The value of K at the intersection of curves is reported in Table VI, column 2. The values of h_L estimated from Figures 21 and 23 are reported in Table VI, column 4.

From the equilibrium constants for the operation of the small column, the separation factor, α , as defined by equation (60), can be computed from the ratio of the values of K, or

$$\alpha = \frac{K_{\text{CoSO}_4}}{K_{\text{CuSO}_4}} = \frac{0.962}{0.944} = 1.02 \quad (63)$$

Discussion of Results

A value of K nearer 1 would be expected in the data from the large column than from the small, because the temperature difference between the heat transfer surfaces was only 60°F in the large column, where it was 100°F in the small column. The difference in the refrigeration capacities of the units and the high-temperature limitation imposed by the Lucite screw in the large column caused these differences. If the exponential dependence of the equilibrium constant with the temperature difference is valid, as indicated by equations (20) and (40), then the values of K reported for the small column at a temperature difference of 100°F in Table V, column 4, would become the values reported in Table VI, column 3, for a temperature difference of 60°F. It should be pointed out that while the large column was undergoing the transient effect illustrated in Figure 14, the separation would be described by an equilibrium constant greater than 1. Whether or not the physical situation causing the transient effect had any effect on the normal steady state separation

is unknown. The disagreement between the corresponding figures for the values of K could be caused to a large degree by inherent errors in the analytical technique; even 1 per cent errors in the separation ratio have a large effect on the location of the curves, because all data are obtained for small separations.

If the dependence on flow rate, channel width, channel depth and temperature of the height of the transfer unit h_L found for the small column is applied through equation (126) of Appendix C, one obtains the predicted values for a flow in the large column of 16.1 ml/hr found in Table VI, column 5. These values compare favorably with the values estimated from Figures 21 and 23. The values in Figures 21 and 22, and Figures 23 and 24, are approximately in proportion for the flow rates in the two cases.

From the data, one can conclude that the height of the transfer unit is proportional to the flow rate, but that neither the laminar flow model nor the complete mixing model can adequately represent the physical situation; the complete mixing model is certainly inadequate. From the limited data on the two columns, and with the data on the large column somewhat questionable, one might conclude that the form of the correlations is valid, but the equations are in error by a constant of proportionality.

The disagreement between the experimental values of K and the values predicted from Soret data can probably best be explained by effects resulting from the presence of the cellophane membrane which have not been determined and taken into account. In the theoretical developments it was assumed that the Soret coefficients within the membrane pores were the same as in the bulk solutions. With the cold wall on top natural convection currents could be

generated in each channel; according to the developed theory, these should improve separation. However, Long (32) induced complete mixing in the solutions on either side of a cellophane membrane in a Soret cell and measured the resulting temperature profile. Although almost the entire temperature drop was developed across the membrane, no measureable separation was observed. The physical situation in the horizontal column is somewhat analogous; not only do the natural convection currents caused by the temperature gradient exist, convection currents induced by the flow through the column are possible. If these convection currents are present, one would expect, if the data of Long are valid, a value of K nearer 1 than would be predicted by the theory. Long's data suggest that thermal diffusion does not exist in the membrane. If it is necessary to get away from convection currents in the operation of the horizontal column, then better separations should be observed with the hot wall on top. The difference in predicted and observed values of h_L could be explained by the above effects; also, the measurement of the membrane free area ϕ could have a large effect on the agreement. The height of the transfer unit is approximately inversely proportional to the membrane free area; hence, if the free area should be larger than the value of $\phi = 0.02$ reported by Couch (14), then the height of the transfer unit would be correspondingly smaller. Von Halle (51) observed values as large as $\phi = 0.4$ for the ethanol-water system.

It was assumed in the analysis that there was no interaction between the two salts. The separation from H_2O obtained for $CuSO_4$ as a single salt and in the presence of $CoSO_4$ indicates that the diffusion properties of $CuSO_4$ are essentially independent of the addition of the other component, and conversely;

Bosanquet (10) observed a slight dependence, but this was of a magnitude that would not be significant in the present work.

Suggestions for Further Work

In order to improve on the accuracy of the experimental work in this report, either a very accurate method ($\pm 0.005\%$) of chemical analysis or a much larger piece of experimental equipment would be needed; probably the latter would be preferred if the extremely long steady state times of a large piece of equipment could be tolerated. The worst experimental errors in this work are probably those in the spectrophotometric measurements; at best, only a measurement to 0.5 per cent could be obtained; combining the errors of two measurements necessary to obtain a separation ratio, then the separation ratio contained errors on the order of 1.0 per cent. This error is significant since the separation ratios had magnitudes near 1.10 and it is essential to distinguish these ratios from that corresponding to no separation, i.e., 1.00.

Other problems connected with this work which have not been answered include the problem of the behavior of the column if the hot wall is on the top. It would be interesting also to know if the semi-empirical relations hold for other salt pairs, and also for salt mixtures with no common anions.

Two interesting and unexpected effects were observed in this work; one is the failure of the cellophane membrane at the point where it was first contacted by solution from the cold channel entrance port. The present work seemed to indicate that the failure was not caused by mechanical erosion. The other unexpected effect is the reverse separation of the large column

observed on start-up; it would be very valuable from a standpoint of obtaining better separations if this effect could be explained and controlled.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this work are that:

1. CuSO_4 and CoSO_4 may be separated from each other and from water using the Von Halle-Jury horizontal thermal diffusion column.
2. Based on experimental data, the best estimate of the equilibrium constant, K , for CuSO_4 is 0.944, and for CoSO_4 is 0.962 when the column is operated with a flow rate of 2.0 ml/hr, a temperature gradient of $800^\circ\text{F}/\text{in.}$, and a wall spacing of $1/8$ in. The height of the transfer unit at these operating conditions is found to be 0.26 ft for the separation of CuSO_4 from water, and 0.24 ft for the separation of CoSO_4 from water.
3. At the concentrations studied, the separation of each salt from water is independent of the presence of the additional salt; hence the values of the equilibrium constants and the heights of the transfer unit cited above are valid for either single-salt separations or two-salt separations.
4. The height of the transfer unit for the separation of either salt from water is proportional to the flow rate.
5. The value of the equilibrium separation factor α for CuSO_4 relative to CoSO_4 is found to be $\alpha = 1.02$ for the operating conditions given above.
6. The theory developed based on Soret cell separations fails to predict the column behavior quantitatively, although the parameter groups that arise in the equations can be used for determining the effects of operating variables on heights of a transfer unit and equilibrium constants.
7. The phenomenological theory of thermal diffusion in salt solutions

is not fully understood, as illustrated by the anomalous effects observed in the present work and by prior investigators (24).

Although the laminar flow model may be useful for preliminary estimation of the behavior of a thermal diffusion column, it is necessary to obtain operating data on a scale model column in order to design a commercial plant for a specific separation with confidence.

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APPENDICES

APPENDIX A

SAMPLE CALCULATIONS

I. CALCULATIONS OF EQUILIBRIUM CONSTANTS AND HEIGHTS
OF A TRANSFER UNIT CuSO_4

Data:

| | |
|---|--|
| Membrane thickness | $\delta = 0.0014 \text{ in.}$ |
| Membrane free area (14) | $\phi = 0.02$ |
| Channel width | $b = 0.75 \text{ in.}$ |
| Soret coefficient for CuSO_4 (32) | $\sigma = 3.9 \times 10^{-3}/^\circ\text{F}$ |
| Soret coefficient for CoSO_4 (32) | $\sigma = 3.0 \times 10^{-3}/^\circ\text{F}$ |
| Diffusion coefficient for CuSO_4 (27) | $D = 1.36 \times 10^{-5} \text{ ft}^2/\text{hr}$ |
| Diffusion coefficient for CoSO_4 (estimated) | $D = 1.36 \times 10^{-5} \text{ ft}^2/\text{hr}$ |
| Column length | $Z = 1.9 \text{ ft}$ |
| Volumetric flow rate (on cold side for product withdrawal run) | $L/\rho = 2.0 \text{ ml/hr}$ |
| Reflux ratio for product withdrawal run | $R = 6.52$ |
| Feed composition for product withdrawal run | $x_F = 0.474 \text{ molar}$ |
| Product composition for product withdrawal run | $x_D = 0.495 \text{ molar}$ |
| Temperature difference between heat transfer surfaces | $\Delta T = 100^\circ\text{F}$ |
| Distance between surfaces | $2a = 0.125 \text{ in.}$ |

A. Calculations for Laminar flow model

1. The equilibrium constant K:

$$K = \frac{f_1(c)}{f_1(-c)} e^{-\sigma \tau M^\delta} = e^{-\sigma (\delta \tau M + \tau a)} = e^{-\sigma \frac{\Delta T}{2}}$$

$$K = e^{-3.9 \times 10^{-3}/^\circ\text{F} \times \frac{100^\circ\text{F}}{2}} = e^{-0.20} = 0.82$$

2. The height of a transfer unit calculated from Soret data:

$$h_L = \frac{L}{bk_L} = \frac{L/\rho}{b \sigma D \tau_M} \left[(e^{\sigma \tau_M \delta} - 1) \frac{f_1(-c)}{\phi} - \left(\frac{\tau_M}{\tau}\right) f_2(-c) + \frac{\tau_M}{\tau} \frac{f_2(c)}{K} \right]$$

$$f_1(c) = \frac{6}{c^3} [e^{-c} (c + 1) - (c - 2)]$$

$$f_1(-0.2) = -\frac{6}{(0.2)^3} [e^{0.2} (1.8) - 2.2] = 1.125$$

$$f_2(c) = 0.3714c - 0.1250c^2 - 0.0529c^3$$

$$\begin{aligned} f_2(0.2) &= 0.3714(0.2) - 0.1250(0.2)^2 - 0.0529(0.2)^3 \\ &= 0.0789 \end{aligned}$$

If the conductivity of the membrane does not differ appreciably from that of the solution, $\tau_M = \tau$, and

$$\tau = \tau_M = \frac{\Delta T}{2\bar{a}} = \frac{100^\circ\text{F}}{0.125 \text{ in.}} = 800^\circ\text{F/in.}$$

$$h_L = \left[\frac{2.0 \text{ ml/hr} \times 3.53 \times 10^{-5} \text{ ft}^3/\text{ml}}{0.75 \text{ in.} \times 3.9 \times 10^{-3}/^\circ\text{F} \times 1.36 \times 10^{-5} \text{ ft}^2/\text{hr} \times 800^\circ\text{F/in.}} \right] \times$$

$$\left[\frac{(1.00439-1)}{0.02} \times 1.125 + (1) 0.0789 + (1) \frac{0.07014}{0.82} \right]$$

$$h_L = 0.91 \text{ ft}$$

3. The height of a transfer unit estimated from total reflux data for arbitrary K:

$$\frac{x_L}{x_D} = e^{\left(\frac{1}{K} - 1\right) \frac{Z}{h_L}} = e^{\frac{0.87}{m}}$$

for $K = 0.82$

$$\left(\frac{1}{0.82} - 1 \right) \frac{1.9 \text{ ft}}{h_L} = \frac{0.87}{2.2}$$

$$h_L = 1.04 \text{ ft}$$

4. The height of a transfer unit estimated from product withdrawal data for arbitrary K : Run No. 15:

$$\frac{x}{x_D} = \frac{D}{KV-L} + \frac{V(1-K)}{L-KV} e^{\left(\frac{L}{KV} - 1 \right) \frac{(Z-z)}{h_L}}$$

or in terms of the reflux ratio $R = L/D$

$$\frac{[R - K(R+1)] \frac{x_W}{x_D} + 1}{(1-K)(R+1)} = e^{\left[\frac{R}{K(R+1)} - 1 \right] \left[\frac{Z}{h_L} \right]}$$

for $K = 0.80$

$$\frac{[6.52 - .80(7.52)] \frac{1.217}{7.52} + 1}{(1-.80)(7.52)}$$

$$\left[\frac{6.52}{0.80 \times 7.52} \right] - 1 = \frac{1.7}{h_L}$$

$= e$

$$h_L = 2.02 \text{ ft}$$

B. Calculations for complete mixing model:

1. The equilibrium constant K:

$$K = e^{-\sigma \tau_M \delta} = e^{-\sigma \Delta T}$$

$$K = e^{-3.9 \times 10^{-3}/^{\circ}\text{F} \times 100^{\circ}\text{F}} = e^{-.39} = 0.678$$

2. The height of the transfer unit estimated from Soret data:

$$h_L = \frac{L}{bk_L} = \frac{L/\rho}{b\sigma D \tau_M \phi}$$

$$\tau_M = \Delta T / \delta$$

$$h_L = \frac{2.0 \text{ ml/hr} \times 3.53 \times 10^{-5} \text{ ft}^3/\text{ml} \times 1.4 \times 10^{-3} \text{ in.}}{0.75 \text{ in.} \times 3.9 \times 10^{-3}/^{\circ}\text{F} \times 1.36 \times 10^{-5} \text{ ft}^2/\text{hr} \times 100^{\circ}\text{F} \times 0.02}$$

$$h_L = 1.24 \text{ ft}$$

II. CALCULATION OF THE CHEMICAL ANALYSIS OF THE HOT RESERVOIR FOR RUN 8

Data:

| | |
|---|---------------------------|
| Transmittancy @ 700 mμ | T _s = 56.2% |
| @ 525 mμ | T _s = 63.1% |
| Cell light path length | b ^s = 0.097 cm |
| *Absorbancy index of CuSO ₄ @ 700 mμ | a _{s1} = 6.02 |
| @ 525 mμ | a _{s1} = 0.073 |
| CoSO ₄ @ 700 mμ | a _{s2} = 0.154 |
| @ 525 mμ | a _{s2} = 4.86 |

$$-\frac{\log_{10} T_{\lambda}}{b} = a_{s_1} c_1 + a_{s_2} c_2$$

$$-\frac{\log 0.562}{0.097 \text{ cm}} = 6.02 c_1 + 0.073 c_2$$

$$-\frac{\log 0.631}{0.097 \text{ cm}} = 0.154 c_1 + 4.86 c_2$$

$$c_1 = .416 \text{ molar}$$

$$c_2 = .410 \text{ molar}$$

APPENDIX B

TREATMENT OF SPECTROPHOTOMETRIC DATA

Quantitative determinations may be obtained from spectrophotometric data by applying simple equations derived from the Lambert-Beer Law. This law may be stated as:

$$T_s = 10^{-a_s bc} \quad (64)$$

where

- T_s = transmittancy
- a_s = absorbancy index
- c = concentration
- b = cell thickness

Other quantities used in spectrophotometric calculations are the relations

$$A_s = \log_{10} \frac{1}{T_s}$$

$$k_s = a_s c \frac{\log_{10} \frac{1}{T_s}}{b} = \frac{a_s c}{b} A_s \quad (66)$$

where

- k_s = absorbancy coefficient
- A_s = absorbancy

Stearns (43) shows several methods of reducing these data to the desired

concentration values. The simplest of these is for the case of additive absorbancies. Absorbancies are additive for a single-salt solution if there is a linear relationship between solution concentration and absorbancy. Absorbancies are additive for mixtures of two or more salts in solution if the sum of the absorbancies of the individual components equals the absorbancy of the mixture.

For the case of a single solution having additive absorbancies, the unknown concentration may be determined by solving the equation

$$C_a = \frac{(k_s) m W_1}{(a_s) a W_1} \quad (67)$$

where

C_a = concentration of component a, moles/volume

$(k_a) m W_1$ = absorbancy coefficient of the solution unknown concentration at wavelength W_1 .

$(a_s) a W_1$ = absorbancy index of component at wavelength W_1 .

This may be done by measuring T_s for a standard solution having a known concentration. The value for $(a_s) a W_1$ is calculated using equation (66). Having established this value, unknown concentrations may be found by substituting the measured values of $(k_s) m W_1$ in equation (67).

For the case of two solutes in solution, transmittancy values at two wavelengths must be obtained. Assuming additive absorbancies, one may write

$$C_a(a_s) a W_1 + C_d(a_s) d W_1 = (k_s) m W_1 \quad (68)$$

$$C_a(a_s) a W_2 + C_d(a_s) d W_2 = (k_s) m W_2 \quad (69)$$

Values for the absorbancy indices may be found using standard solutions as indicated for the case of a single solute. Concentrations C_a and C_d may be found by solving these two equations simultaneously with values of the absorbancy coefficients measured at the two wave lengths. Choice of wave lengths is discussed by Stearns.

Table VII shows the values of the absorbancy indices determined and used in the present investigation.

TABLE VII

ABSORBANCY INDEX VALUES FOR THE SYSTEM
 $\text{CuSO}_4 - \text{CoSO}_4 - \text{H}_2\text{O}$

| Molarity | a_{saw_1} | a_{saw_2} | a_{sdW_1} | a_{sdW_2} |
|----------|-------------|-------------|-------------|-------------|
| 0.50 | 6.02 | 0.073 | 0.153 | 4.86 |

APPENDIX C

DETERMINATION OF THE AVERAGE CONCENTRATION AT
A CHANNEL CROSS-SECTION

The physical situation is sketched in Figure 4 of the text. The problem is to determine the average concentration in a cross section as a function of the point concentrations on the membrane-channel boundary.

The following assumptions are utilized:

1. The flow between the boundaries is laminar with an infinite aspect ratio (width to depth).
2. The physical properties of viscosity, density, and diffusion coefficients are independent of temperature and composition.
3. The solutions are dilute, which means that

$$\xi (1 - \xi) \cong \xi$$

4. The flow rates V and L are constant throughout the column, which results from the dilute solution assumption and implies that there is no thermal osmosis.
5. The concentration gradient is independent of the vertical coordinate; hence

$$\frac{d\xi}{dz} \cong \frac{dy}{dz}$$

6. The temperature gradient is constant, hence

$$\frac{dT}{dr} \cong -\frac{dT}{ds} \cong \tau = -\tau' = \text{constant}$$

7. No longitudinal diffusion.

The differential equation, as set up in equation (29),

is

$$\frac{\partial}{\partial r} \rho \left[-D' \xi \tau - D \frac{d\xi}{dr} \right] + \frac{\partial}{\partial z} (\rho v \xi) = 0 \quad (70)$$

with the boundary conditions of equation (30)

$$J_r(0) = -J_0 \quad (71)$$

$$J_r(a) = 0$$

As the velocity $v(r)$ is a function only of the height r , ρ is assumed constant, and $\frac{d\xi}{dz} = \frac{dy}{dz}$, then

$$\frac{\partial}{\partial z} (\rho v \xi) = \rho v \frac{\partial \xi}{\partial z} = \rho v \frac{dy}{dz} \quad (72)$$

The differential equation becomes

$$\frac{\partial}{\partial r} \left[-D' \xi \tau - D \frac{d\xi}{dr} \right] + v \frac{dy}{dz} = 0 \quad (73)$$

If equation (73) is integrated from $r = r$ to $r = a$, then

$$\int_r^a \frac{d}{dr} \left[-D' \xi \tau - D \frac{d\xi}{dr} \right] dr + \int_r^a v \frac{dy}{dz} dr = 0 \quad (74)$$

$$\left[-D' \xi \tau - D \frac{d\xi}{dr} \right]_r^a = - \int_r^a v \frac{dy}{dz} dr \quad (75)$$

But

$$\left[-D' \xi \tau - D \frac{d\xi}{dr} \right] = J_r \quad (76)$$

Hence

$$J_r(a) - J_r = - \int_r^a v \frac{dy}{dz} dr \quad (77)$$

With the boundary conditions (71), then equation (77) becomes

$$J_r = -D' \xi \tau - D \frac{d\xi}{dr} = \int_r^a v \frac{dy}{dz} dr \quad (78)$$

and

$$J_r(0) = \int_0^a v \frac{dy}{dz} dr \quad (79)$$

If equation (78) is rearranged, then

$$\frac{d\xi}{dr} + \frac{D'}{D} \xi \tau = - \frac{1}{D} \int_r^a v \frac{dy}{dz} dr \quad (80)$$

If one uses an integrating factor $e^{\sigma \tau r}$, where $\sigma = \frac{D'}{D}$,

then

$$\int_0^r d(e^{\sigma \tau r} \xi) = \int_0^r \left[\frac{d\xi}{dr} + \sigma \xi \tau \right] e^{\sigma \tau r} dr$$

$$= -\frac{1}{D} \frac{dy}{dz} \int_0^r e^{\sigma \tau r} dr \int_r^a v dr \quad (81)$$

and

$$e^{\sigma \tau r} \xi(r) - \xi_0 = -\frac{1}{D} \frac{dy}{dz} \int_0^r e^{\sigma \tau r} dr \int_r^a v dr \quad (82)$$

or

$$\xi(r) = \xi_0 e^{-\sigma \tau r} - \frac{e^{-\sigma \tau r}}{D} \frac{dy}{dz} \int_0^r e^{\sigma \tau r} dr \int_r^a v dr \quad (83)$$

The total flow rate in the z direction is

$$Vy = \int_0^a \rho b v(r) \xi(r) dr \quad (84)$$

If equation (83) is substituted into equation (84) and rearranged, then

$$y = \frac{\rho b \xi_0}{V} \int_0^a v(r) e^{-\sigma \tau r} dr - \frac{\rho b}{DV} \frac{dy}{dz} \int_0^a v(r) e^{-\sigma \tau r} dr \int_0^r e^{\sigma \tau r} dr \int_r^a v dr \quad (85)$$

In order to facilitate the evaluation of the integrals, let

$$\Theta = \sigma \tau r \quad c = \sigma \tau a \quad 0 < \Theta < c \quad (86)$$

then

$$\begin{aligned}
 \int_0^a v(r) e^{-\sigma \tau r} dr &= \frac{6V}{a^3 b \rho} \int_0^a (ar - r^2) e^{-\sigma \tau r} dr \\
 &= \frac{6V}{a^3 b \rho} \int_0^c \left[\frac{a\Theta}{\sigma \tau} - \frac{\Theta^2}{\sigma^2 \tau^2} \right] e^{-\Theta} \frac{d\Theta}{\sigma \tau} = \frac{6V}{b \rho} \int_0^c \left[\frac{\Theta}{c} - \frac{\Theta^2}{c^2} \right] e^{-\Theta} \frac{d\Theta}{c} \\
 &= \frac{6V}{c^3 b \rho} \int_0^c (c\Theta - \Theta^2) e^{-\Theta} d\Theta = \frac{V}{b \rho} f_1(c)
 \end{aligned} \tag{87}$$

Equation (87) defines $f_1(c)$; thus

$$f_1(c) = \frac{6}{c^3} \int_0^c (c\Theta - \Theta^2) e^{-\Theta} d\Theta \tag{88}$$

Also

$$\begin{aligned}
 \int_0^a v(r) e^{-\sigma \tau r} dr \int_0^r e^{\sigma \tau r} dr \int_r^a v dr &= \\
 \frac{36V^2}{c^6 b^2 \rho^2} \int_0^c (c\Theta - \Theta^2) e^{-\Theta} d\Theta \int_0^\Theta e^\Theta \frac{d\Theta}{\sigma \tau} \int_\Theta^c (c\Theta - \Theta^2) d\Theta
 \end{aligned}$$

$$= \frac{V^2 f_2(c)}{\sigma \tau b^2 \rho} \quad (89)$$

Equation (89) defines $f_2(c)$; thus

$$f_2(c) = \frac{36}{c^6} \int_0^c (c\theta - \theta^2) e^{-\theta} d\theta \int_0^\theta e^{-\theta} d\theta \int_\theta^c (c\theta - \theta^2) d\theta \quad (90)$$

If $f_1(c)$ and $f_2(c)$ are substituted into equation (85), then

$$y = \xi_0 f_1(c) - \frac{V}{D\sigma\tau b\rho} \frac{dy}{dz} f_2(c) \quad (91)$$

By analogy,

$$x = \xi'_0 f_1(c') - \frac{L}{D\sigma\tau' b\rho} \frac{dx}{dz'} f_2(c') \quad (92)$$

where

$$c' = \sigma\tau'a = -\sigma\tau a = -c$$

As $z + z' = Z$, then

$$\frac{dx}{dz} = -\frac{dx}{dz'} \quad (93)$$

Hence

$$x = \xi'_0 f_1(-c) + \frac{L}{D\sigma\tau' b\rho} \frac{dx}{dz} f_2(-c) \quad (94)$$

The value of $f_1(c)$ is

$$f_1(c) = \frac{6}{c^3} \left[e^{-c} (c + 2) + (c - 2) \right] \quad (95)$$

and the value of $f_2(c)$ is

$$f_2(c) = \frac{36}{c^3} \left[4 \left[e^{-c} (1 + c) - 1 \right] + c^2 (e^{-c} + 1) - \frac{1}{3} c^3 e^{-c} - \frac{c^4}{6} (e^{-c} + 1) + \frac{c^5}{30} + \frac{c^6}{72} \right] \quad (96)$$

If e^{Θ} and $e^{-\Theta}$ in equation (90) are approximated by

$$e^{\Theta} \approx 1 + \Theta \quad (97)$$

then $f_2(c)$ can be approximated by

$$f_2(c) \approx 0.3714 c - 0.1250 c^2 - 0.0529 c^3 \quad (98)$$

This approximation is valid for small values of c , as $0 < \Theta < c$; the approximation was checked for $c = 0.20$, the maximum value of c encountered in this work. The value of $f_2(c)$ from equation (96) is

$$f_2(0.2) \approx 0.0701$$

and the approximate value computed from equation (98) is

$$f_2(0.2) \approx 0.0689$$

The approximation is in error by less than 2 per cent. The approximation was used because the calculation by equation (96) required 10 place tables of

the exponential function and the calculation is very tedious; no such difficulty is encountered with the approximation of equation (98).

The values for $f_1(c)$ and $f_2(c)$ are listed in Table VIII for the range $0.01 < c < 0.25$.

Value of Equilibrium Constant for the Laminar Flow Model

The value of the equilibrium constant K from equation (35) of the text is

$$K \equiv \frac{f_1(c)}{f_1(-c)} e^{-\sigma \tau_M \delta}$$

If the value of $f_1(c)$ is substituted from equation (95), then

$$\begin{aligned} K &= \frac{[e^{-c}(c+2) + (c-2)] e^{-\sigma \tau_M \delta}}{-[e^c(-c+2) + (-2-c)]} \\ &= \frac{[e^{-c}(c+2) + (c-2)] e^{-\sigma \tau_M \delta}}{e^c[(c-2) + (c+2)e^{-c}]} \\ &= e^{-\sigma \tau_M \delta - c} \\ &= e^{-\sigma(\tau_M \delta + \tau a)} \end{aligned} \tag{99}$$

TABLE VIII

VALUES OF FUNCTIONS OF "c"

| c | $f_1(c)$ | $f_1(-c)$ | $f_2(c)$ | $-f_2(-c)$ | $F(c, \dots)^*$ |
|------|----------|-----------|----------|------------|-----------------|
| 0.01 | .99442 | 1.0060 | .00370 | .00373 | |
| 0.02 | .98959 | 1.0101 | .00693 | .00793 | |
| 0.03 | .98489 | 1.0169 | .01103 | .01125 | |
| 0.04 | .98021 | 1.0210 | .01465 | .01505 | |
| 0.05 | .97532 | 1.0260 | .01843 | .01905 | |
| 0.06 | .97055 | 1.0309 | .02182 | .02272 | |
| 0.07 | .96573 | 1.0358 | .02537 | .02659 | |
| 0.08 | .96093 | 1.0409 | .02888 | .03048 | |
| 0.09 | .95619 | 1.0463 | .03237 | .03440 | |
| 0.10 | .95147 | 1.0515 | .03584 | .03834 | 1.96 |
| 0.11 | .94677 | 1.0569 | .03927 | .04230 | 1.96 |
| 0.12 | .94210 | 1.0622 | .04268 | .04628 | 1.97 |
| 0.13 | .93746 | 1.0676 | .04605 | .05028 | 1.98 |
| 0.14 | .93285 | 1.0730 | .04940 | .05430 | 1.99 |
| 0.15 | .92826 | 1.0785 | .05272 | .05834 | 2.00 |
| 0.16 | .92371 | 1.0840 | .05601 | .06241 | 2.01 |
| 0.17 | .91918 | 1.0895 | .05926 | .06649 | 2.02 |
| 0.18 | .91467 | 1.0951 | .06249 | .07059 | 2.03 |
| 0.19 | .91019 | 1.1006 | .06569 | .07472 | 2.04 |
| 0.20 | .90574 | 1.1063 | .06886 | .07886 | 2.05 |
| 0.21 | .90174 | 1.1119 | .07199 | .08302 | 2.06 |
| 0.22 | .89692 | 1.1176 | .07509 | .08719 | 2.07 |
| 0.23 | .89254 | 1.1233 | .07817 | .09139 | 2.09 |
| 0.24 | .88820 | 1.1291 | .08120 | .09560 | 2.10 |
| 0.25 | .88388 | 1.1349 | .08421 | .09984 | 2.11 |

* $F(c, \dots) = F(c, \tau_M/\tau, \delta/a, \phi)$
 $= F(c, 1, 0.0224, 0.02)$

APPENDIX D

RATE OF DIFFUSION ACROSS THE MEMBRANE

The physical situation is shown in Figure 4 of the text. The rate of diffusion across the membrane, neglecting longitudinal diffusion and assuming that thermal diffusion in the membrane obeys the same equations as in the free solution, is

$$J_o = \rho \phi \left[-D' \xi(l) \frac{dT}{dl} - D \frac{d\xi(l)}{dl} \right] \quad (100)$$

Let

$$-\frac{dT}{dl} = \tau_M \quad (101)$$

I. CASE OF NO NET DIFFUSION

If there is no net diffusion through the membrane, i.e., as in the steady state operation of the Soret cell, then

$$J_o = 0 \quad (102)$$

$$D' \xi(l) \tau_M - D \frac{d\xi(l)}{dl} = 0 \quad (103)$$

If one integrates the equation between the limits $\xi(l=0) = \xi_o$ and $\xi(l=\delta) = \xi_o'$, then

$$\int_{\xi_o}^{\xi_o'} \frac{d\xi(l)}{\xi(l)} = \frac{D'}{D} \tau_M \int_0^\delta dl = \sigma \tau_M \int_0^\delta dl \quad (104)$$

thus

$$\xi_0' = \xi_0 e^{\sigma \tau M \delta} \quad (105)$$

If the values of ξ_0' and ξ_0 from equations (91) and (94) are substituted in the above expression, then

$$\frac{x}{f_1(-c)} + \frac{L}{D\sigma\tau b\rho} \frac{dx}{dz} f_2(-c) = \left[\frac{y}{f_1(c)} + \frac{V}{D\sigma\tau b\rho} \frac{dy}{dz} f_2(c) \right] e^{\sigma\tau M \delta} \quad (106)$$

But as there is no transport of material,

$$L = V = 0 \quad (107)$$

then

$$x = y \frac{f_1(-c)}{f_1(c)} e^{\sigma\tau M \delta} \quad (108)$$

Let

$$\frac{f_1(c)}{f_1(-c)} e^{-\sigma\tau M \delta} = K \quad (109)$$

Then

$$y = Kx \quad (110)$$

This means that the "equilibrium concentration" in one channel can be expressed as a linear function of the actual concentration in the other.

II. FINITE DIFFUSION RATE CASE

At steady state, the diffusion rate through the membrane J_0 is a con-

stant at any point z . Equation (100) becomes

$$D' \xi(l) \tau_M - D \frac{d\xi(l)}{dl} = \frac{J_0}{\rho\phi} \quad (111)$$

If the variables are separated and the equation integrated between the limits

$\xi(l=0) = \xi_0$ and $\xi(l=\delta) = \xi_0'$, then

$$\int_{\xi_0}^{\xi_0'} \frac{d\xi}{\frac{J_0}{\rho\phi D} + \sigma \tau_M \xi} = \int_0^\delta dl \quad (112)$$

and

$$\frac{1}{\sigma \tau_M} \ln \left[\frac{\sigma \tau_M \xi_0' - \frac{J_0}{\rho\phi D}}{\sigma \tau_M \xi_0 - \frac{J_0}{\rho\phi D}} \right] = \delta \quad (113)$$

If one solves equation (113) for J_0 , then

$$J_0 = \frac{\rho\phi D \sigma \tau_M}{(e^{\sigma \tau_M \delta} - 1)} (\xi_0 e^{\sigma \tau_M \delta} - \xi_0') \quad (114)$$

If the values of ξ_0 and ξ_0' from equations (91) and (94) are substituted into equation (108), then

$$J_0 = \frac{\rho\phi D \sigma \tau_M}{(e^{\sigma \tau_M \delta} - 1)} \left[\frac{ye^{\sigma \tau_M \delta}}{f_1(c)} + \frac{Ve^{\sigma \tau_M \delta}}{D\sigma\tau b\rho} \frac{dy}{dx} \frac{f_2(c)}{f_1(c)} - \frac{x}{f_1(-c)} + \frac{L}{D\sigma\tau b\rho} \frac{dx}{dz} \frac{f_2(-c)}{f_1(-c)} \right] \quad (115)$$

If a material balance is written on a section of the column of length dz , one obtains

$$L(x + dx) + Vy = Lx + V(y + dy) \quad (116)$$

or

$$L dx = V dy \quad (117)$$

If equation (117) is combined with equations (115) and (15), one obtains

$$J_o = \frac{\rho \phi D \sigma \tau_M}{(\sigma \tau_M^\delta - 1)} \left[\frac{ye^{\sigma \tau_M^\delta}}{f_1(c)} - \frac{e^{\sigma \tau_M^\delta} J_o}{D \sigma \tau \rho} \frac{f_2(c)}{f_1(c)} - \frac{x}{f_1(-c)} + \frac{J_o}{D \sigma \tau \rho} \frac{f_2(-c)}{f_1(-c)} \right] \quad (118)$$

Again, if this equation is solved for J_o , then

$$J_o \left[\frac{e^{\sigma \tau_M^\delta} - 1}{\rho \phi D \sigma \tau_M} + \frac{f_2(c)e^{\sigma \tau_M^\delta}}{\rho D \sigma \tau f_1(c)} - \frac{f_2(-c)}{\rho D \sigma \tau f_1(-c)} \right] = \left[\frac{ye^{\sigma \tau_M^\delta}}{f_1(c)} - \frac{x}{f_1(-c)} \right] = \frac{1}{f_1(-c)} \left[\frac{y}{K} - x \right] = \frac{e^{\sigma \tau_M^\delta}}{f_1(c)} [y - Kx] \quad (119)$$

where K is defined by equation (109). If y^* is defined as the theoretical value of y that would exist in equilibrium with x , and x^* defined accordingly with y , then equation (113) may be put into the forms

$$J_o = k_V(y - y^*) = k_L(x^* - x) \quad (120)$$

as a result of equation (110), where

$$y^* = Kx, \quad x^* = \frac{y}{K} \quad (121)$$

and

$$k_V = \frac{\rho D \sigma \tau_M}{(1 - e^{-\sigma \tau_M \delta / \phi}) \frac{f_1(c)}{\phi} + \frac{\tau_M}{\tau} f_2(c) - \frac{\tau_M}{\tau} \frac{f_2(-c)f_1(c)e^{-\sigma \tau_M \delta}}{f_1(-c)}} \quad (122)$$

$$k_L = \frac{\rho D \sigma \tau_M}{(e^{\sigma \tau_M \delta} - 1) \frac{f_1(-c)}{\phi} - \frac{\tau_M}{\tau} f_2(-c) + \frac{\tau_M}{\tau} \frac{f_2(c)f_1(-c)e^{\sigma \tau_M \delta}}{f_1(c)}} \quad (123)$$

Equation (120) is analogous to the equation commonly used in diffusion processes to describe the rate process. Equation (123) can be further rewritten as

$$k_L = \frac{\rho D \tau_M / \tau a}{\frac{1}{c} [e^{c(\tau_M / \tau) (\delta/a)} - 1) \frac{f_1(-c)}{\phi} - \frac{\tau_M}{\tau} f_2(-c) + \frac{\tau_M}{\tau} \frac{f_2(c)f_1(-c)}{f_1(c)} e^{c(\tau_M / \tau) (\delta/a)}]} \quad (124)$$

A function F can be defined by

$$F(c, \tau_M / \tau, \delta/a, \phi) =$$

$$\frac{1}{c} [e^{c(\tau_M / \tau) (\delta/a)} - 1) \frac{f_1(-c)}{\phi} - \frac{\tau_M}{\tau} f_2(-c) + \frac{\tau_M}{\tau} \frac{f_2(c)f_1(-c)}{f_1(c)} e^{c(\tau_M / \tau) (\delta/a)}] \quad (125)$$

and therefore

$$k_L = \frac{\rho D \tau_M / \tau}{a F(c, \tau_M / \tau, \delta / a, \phi)} \quad (126)$$

Table VIII gives values of $F(c, \tau_M / \tau, \delta / a, \phi)$ for different values of c .

APPENDIX E

ORIGINAL DATA

Tables IX and X are tabulations of original data taken on experimental runs in this investigation. These data will be found recorded on pages 21051-21100, pages 23051-23100 and pages 16951-16990 of the Original Record of Research, Department of Chemical and Metallurgical Engineering, University of Tennessee, Knoxville, Tennessee. Pages 2851-2900 were used for calculation purposes.

TABLE IX

ORIGINAL DATA FROM SMALL COLUMN

| | A _S 525 m μ | A _S 700 m μ | L ml/hr | V ml/hr | Product ml/hr |
|------|-------------------------------|-------------------------------|------------|------------|------------------|
| Hot | .206 | .246 | 6.15 | 6.80 | .675 |
| Cold | .230 | .288 | | | |
| Hot | .216 | .266 | 4.04 | 7.51 | 3.52 |
| Cold | .235 | .296 | | | |
| Hot | .207 | .254 | 4.13 | 5.68 | 1.61 |
| Cold | .231 | .295 | | | |
| Hot | .198 | .241 | 4.04 | 4.45 | .62 |
| Cold | .231 | .293 | | | |
| Hot | .198 | .238 | 4.05 | 4.46 | .584 |
| Cold | .228 | .290 | | | |
| Hot | .214 | .263 | 6.30 | 9.60 | 3.30 |
| Cold | .234 | .295 | | | |
| Hot | .195 | .233 | 1.93 | 2.36 | .436 |
| Cold | .232 | .298 | | | |
| Hot | .224 | .293 | | | |
| Cold | .214 | .283 | 2.00 | 2.33 | 0.318 |
| Hot | .203 | .238 | | | |
| Cold | .230 | .295 | 1.97 | 2.50 | 0.52 |
| Hot | .207 | .250 | | | |
| Cold | .231 | .294 | 2.00 | 2.97 | 0.852 |
| Hot | .215 | .265 | | | |
| Cold | .230 | .294 | 1.97 | 3.75 | 1.72 |

TABLE X

ORIGINAL DATA OF PRODUCT WITHDRAWAL DATA ON LARGE COLUMN

| | A _S 525 mμ | A _S 700 mμ | L | V | Product |
|------|--------------------------|--------------------------|------|------|---------|
| Hot | .180 | .228 | 16.1 | 17.4 | 1.51 |
| Cold | .199 | .268 | | | |
| Hot | .189 | .248 | 16.2 | 29.8 | 14.2 |
| Cold | .196 | .266 | | | |
| Hot | .176 | .218 | 10.7 | 11.4 | 0.842 |
| Cold | .202 | .270 | | | |
| Hot | .193 | .247 | 10.6 | 19.7 | 8.15 |
| Cold | .203 | .272 | | | |

APPENDIX F

THE DESIGN OF A THERMAL DIFFUSION PLANT TO SEPARATE
COMMERCIAL QUANTITIES OF A TWO-SALT MIXTURE

In the design of a commercial thermal diffusion plant, a major problem is that of minimizing the area of the installation, for the fixed costs as well as the operating costs for heat and coolant requirements are proportional to the area.

Optimum Concentration. A question which first arises concerns the concentrations of the solutions for most efficient operation; would the best efficiency be obtained in concentrated or dilute solutions? If one considers the material balances for column operation with a concentrated solution and with a dilute solution, one obtains the equations

$$x_D D = x_V V - x_L L \quad (127)$$

$$x_D' D' = x_V' V' - x_L' L' \quad (128)$$

where the primed quantities denote the dilute conditions. For the ratio of the two equations, one obtains

$$\frac{x_D D}{x_D' D'} = \frac{x_V V - x_L L}{x_V' V' - x_L' L'} = \frac{x_V V}{x_V' V'} \cdot \frac{1 - \frac{x_L}{x_V} \frac{L}{V}}{1 - \frac{x_L'}{x_V'} \frac{L'}{V'}} \quad (129)$$

If the two methods of operation are restricted by requiring the feed quantities of salt to be equal in the two cases, and for the reflux ratio and the separation ratio for the column to be equal in both cases; that is,

$$x_V V = x_{V'} V'$$

$$R = L/D = R' = L'/D' \quad (130)$$

$$\omega = \frac{x_L}{x_D} = \omega' = \frac{x_{L'}}{x_{D'}}$$

then the ratio of material balances may be simplified to

$$\frac{x_D D}{x_{D'} D'} = \frac{1 - \frac{x_L}{x_V} \frac{R}{R+1}}{1 - \frac{x_{L'}}{x_{V'}} \frac{R'}{R'+1}} \quad (131)$$

The separation ratio may be obtained from equation (127);

$$\frac{x_D D}{x_L L} = \frac{x_V V}{x_L L} - 1 \quad (132)$$

or

$$\frac{1}{\omega} \frac{1}{R} = \frac{x_V}{x_L} \frac{R+1}{R} - 1 \quad (133)$$

From this equation one can see that if R and ω are fixed, then $\frac{x_V}{x_L}$ must remain constant. From equation (131), one then has

$$\frac{x_D D}{x_{D'} D'} = 1 \quad (134)$$

As $x_D D$ is the product rate of salt, one has that the product rate is constant.

These conditions can be met if the area to flow rate ratio in the L channel is

fixed; this is a result of the exponential term in equation (49) which contains the term Z/h_L . As h_L is proportional to the flow rate, the area required for the separation varies directly as the flow rate; as the flow rate varies inversely with the concentration of the feed stream, x_V , the area required for the separation will be a minimum when the feed has a maximum concentration. The only upper limit to the concentration is that which will cause crystallization of the salt in the channels. Although the discussion has treated one salt only, the same will hold for the other salt, and hence for the separation of the two salts as well.

Optimum reflux ratio. Von Halle (51), and Abelson, Rosen, and Hoover (1) have considered the problem of a continuously varying cross section of a column or a cascade of horizontal thermal diffusion columns and of Clusius Dickel columns, respectively. They have obtained an optimum reflux ratio as a function of composition by minimizing the integral expression for the total area. A similar analysis for the diffusion equations in the present problem leads to the integral

$$\frac{\text{Area}}{h_L D / \lambda} = \int_{\frac{x_L}{x_D}}^1 \frac{R d(\frac{x}{x_D})}{(1 - \frac{R}{K(R+1)}) (\frac{x}{x_D}) - \frac{1}{K(R+1)}} \quad (135)$$

The restriction is made that the product rate D and composition x_D are fixed, along with the flow rate per unit width λ ; holding λ constant restricts h_L to a constant value, as

$$h_L = \frac{L}{bk_L} = \frac{\lambda}{k_L} \quad (44)$$

where

$$\lambda = \frac{L}{b} \quad (52)$$

Hence, a minimization of the integral with respect to R at any arbitrary composition x will minimize the area. This integral can be minimized with respect to R for values of $x/x_D > 1/K$. No minimum exists for smaller values; that is, for separations that can be obtained in a single equilibrium stage. The optimum reflux ratio in the region of its existence is given by

$$R_{op} = \frac{1 - K \frac{x}{x_D} - \left[\left(1 - K \frac{x}{x_D} \right) \left(1 - \frac{x}{x_D} \right) \right]^{1/2}}{(K - 1) \frac{x}{x_D}} \quad (136)$$

The lower values of R are limited by pressure drop in the V channel; as the reflux ratio decreases under the condition of constant flow per unit area in the L channel, the flow rate in the V channel per unit width increases without limit; hence, pressure drop in the V channel would also limit the reflux ratio R .

Use of Evaporation. As previously shown, it is desirable to operate with solutions of maximum permissible concentrations. In the separation of one salt from another, separation of the salts from water also occurs. It would seem desirable then to remove some of the excess water from the solutions at the feed point of a column by evaporation in order to prevent the use of dilute

solutions.

Let us consider the treatment of L_2 ft³ of a salt mixture of a given composition by two processes: 1) separation by thermal diffusion only, and 2) separation by initial evaporation and subsequent diffusion. These are shown schematically in Figure 25.

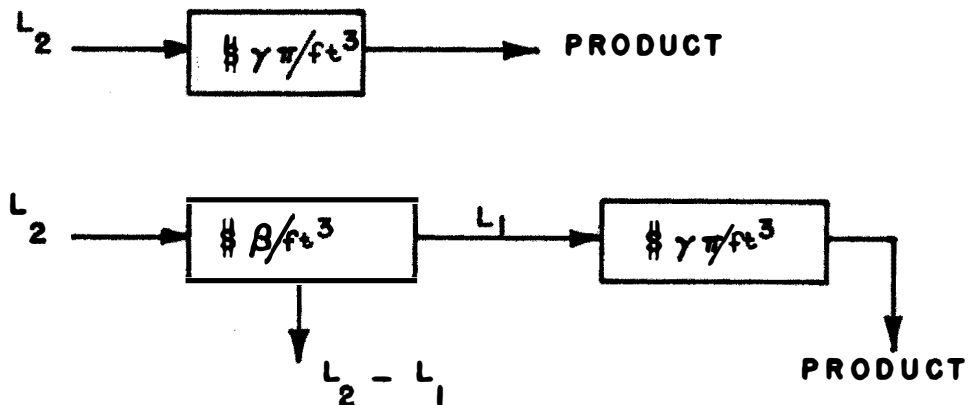


FIGURE 25

SCHEMATIC OF POSSIBLE PROCESSING METHODS

If the cost of thermal diffusion is $\$ \gamma \pi / \text{ft}^3$ of solution and the cost of evaporation is $\$ \beta / \text{ft}^3$ of solution evaporated, then the cost of process 1 is $\gamma \pi L_2$; the cost of process 2 is $\beta (L_2 - L_1) + \gamma \pi L_1$, where $L_2 - L_1$ is the quantity of liquid evaporated. If the cost of the two processes is equated, then

$$\gamma \pi L_2 = \beta (L_2 - L_1) + \gamma \pi L_1 \quad (137)$$

or

$$\gamma \pi (L_2 - L_1) = \beta (L_2 - L_1) \quad (138)$$

and

$$\gamma\pi = \beta$$

(139)

The cost of treating 1 ft³ of solution by thermal diffusion is the product of the cost per hour of 1 ft² of thermal diffusion area, γ , times the area-to-flow-rate ratio, $\pi = A/(L/\rho)$. With $\gamma = 3.00$ mills/hr-ft² and $\beta = 110$ mills/ft³ as discussed in the following paragraph, then the value of π which would equate the cost of the two processes is $\pi = 37$ hr/ft; if the flow rate is converted to ml/hr, then $\pi = 1.30 \times 10^{-3}$ ft²/ml/hr. Hence, if this area-to-flow-rate ratio were used on each column, no advantage would be obtained by intermediate evaporation; if any ratio larger than this is used, then evaporation would be desirable. This development does not take into account that with evaporation, a more concentrated product would be obtained, although the quantity of salt and the ratio of one salt to the other would be the same in both cases; this more concentrated product would possibly be a more valuable product, particularly if it were desired to manufacture a dry product.

Power and Equipment Costs. The following data on power and equipment costs were taken from Vilbrandt and Dryden (50).

| | |
|--|-----------------------|
| Steam (242°F) | \$0.50/1000 lbs. |
| Thermal diffusion capacity | \$50/ft ² |
| All stainless 10,000 ft ² units | |
| Evaporative capacity | \$500/ft ² |
| All copper, 100 ft ² units | |

The cost of the thermal diffusion equipment was estimated as 10 times the cost of evaporative capacity for the same size unit and of the same construction material. By amortizing the cost of the equipment over 5 years, the cost of evaporation is 16 mills/hr-ft² with a capacity of 9 lbs/hr-ft², or 110 mills/ft³ of water evaporated. The costs of thermal diffusion capacity is 3.00 mills-hr-ft²,

if the wall spacing is 0.125 in.

Cascade Design. Cascade operation of thermal diffusion columns has been considered and the following design procedures arrived at. The individual stage of the cascade, stage s , is sketched in Figure 26; the L stream is fed to the next stage above, and the D stream is fed to the next stage below (as in Figure 27). The equation of separation of a single stage is, from (49),

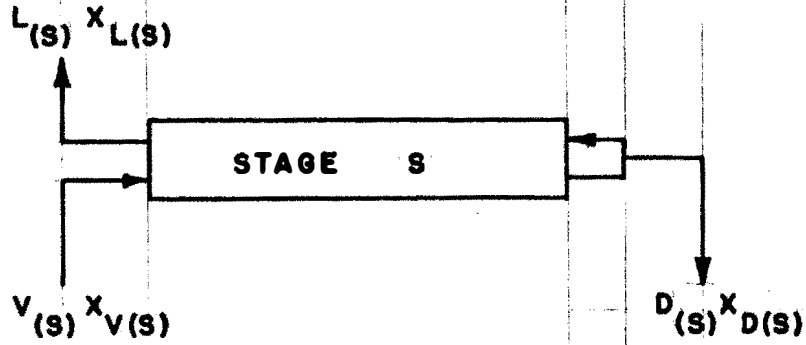


FIGURE 26

SINGLE STAGE OF THE CASCADE

$$\frac{x_L}{x_D} = \frac{1}{K(R+1)-R} - \frac{(R+1)(1-K)}{K(R+1)-R} e^{\frac{R-K(R+1)}{K(R+1)} \frac{Z}{h_L}} \quad (49)$$

If one defines the overhead fraction θ by

$$\theta = \frac{D}{V} = \frac{1}{R+1} \quad (140)$$

then the equation becomes

$$\frac{x_L}{x_D} = \frac{\theta}{K+\theta-1} - \frac{(1-K)}{K+\theta-1} e^{\frac{-K+\theta-1}{K} \frac{Z}{h_L}} \quad (141)$$

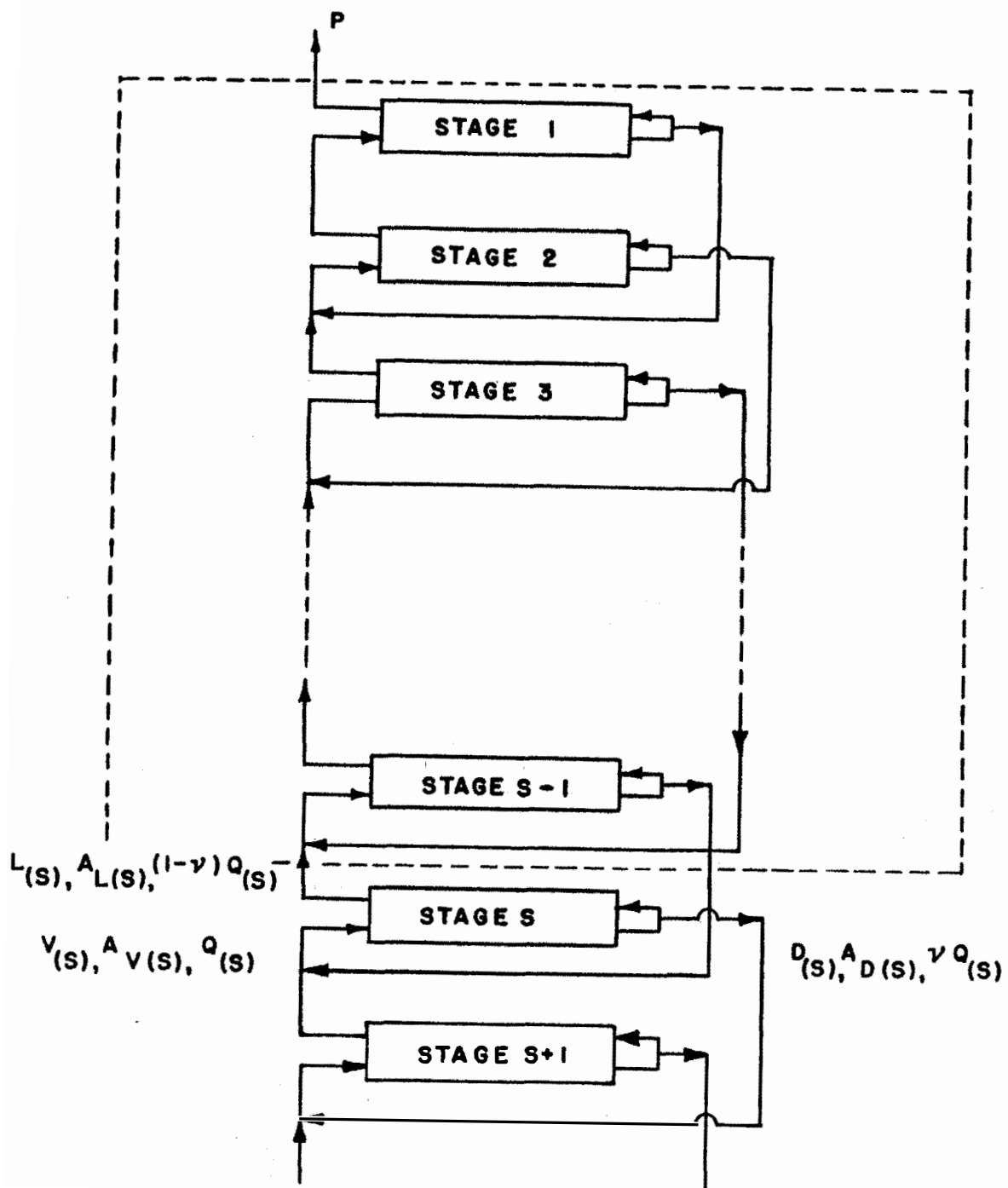


FIGURE 27

THE CASCADE

For salt a, this quantity is defined as ω ; thus

$$\omega = \frac{a^x_L}{a^x_D} \quad (142)$$

If the ratio of the concentrations of the salts, A, is defined as

$$A = \frac{a^x}{b^x} \quad (143)$$

where x is the mole fraction and the pre-subscripts refer to the particular salt, then the separation of the column may be expressed in terms of the stage separation factor, Ω , as

$$A_{L(s)} = \Omega A_{D(s)} \quad (144)$$

where the post-subscripts refer to the stream leaving the stage numbered by the letter in the parentheses. The quantities Ω and ω therefore define the separation in the L stream. Let the fraction of salt "a" leaving a stage that appears in the D stream be denoted by ν ; thus

$$\nu = \frac{a^x_D}{a^x_V} \frac{D}{V} \quad (145)$$

If $Q_{(s)}$ is the quantity of salt "a" fed to stage s, then $\nu_{(s)} Q_{(s)}$ is the quantity removed in the D stream and $(1 - \nu_{(s)}) Q_{(s)}$ is the quantity removed in the L stream. The quantity $\nu_{(s)}$ is related to θ by

$$\nu_{(s)} = \frac{\theta}{\theta + \omega(1 - \theta)} \quad (146)$$

The usual arrangement for cascades is for the products of stage s to be fed to stage s + 1 and to stage s - 1, as shown in Figure 27. A material balance of salt "a" over the first s - 1 stages is

$$(1 - \nu_{(s)}) Q_{(s)} = \nu_{(s-1)} Q_{(s-1)} + P \quad (147)$$

where P is the overhead product rate. A material balance for salt "b" is

$$A_{L(s)} (1 - \nu_{(s)}) Q_{(s)} = A_{D(s-1)} Q_{(s-1)} \nu_{(s-1)} + P A_{L(1)} \quad (148)$$

The separation of stage (s-1) is expressed by the relation

$$A_{L(s-1)} = \Omega_{(s-1)} A_{D(s-1)} \quad (149)$$

If equation (147) is substituted into equation (148), then one has

$$\nu_{(s-1)} Q_{(s-1)} \left[A_{L(s)} - \frac{A_{L(s-1)}}{\Omega_{(s-1)}} \right] = P [A_{L(1)} - A_{L(s)}] \quad (150)$$

If equation (149) is substituted into equation (150), then

$$A_{L(s)} - \frac{A_{L(s-1)}}{\Omega_{(s-1)}} = \frac{P [A_{L(1)} - A_{L(s)}]}{[1 - \nu_{(s)}] Q_{(s)} - P} \quad (151)$$

If one adds and subtracts $A_{L(s)}/\Omega_{(s-1)}$, then one has

$$\frac{1}{\Omega_{(s-1)}} [A_{L(s)} - A_{L(s-1)}] = \frac{P [A_{L(1)} - A_{L(s)}]}{(1 - \nu_{(s)}) Q_{(s)} - P} + A_{L(s)} \left[\frac{1}{\Omega_{(s-1)}} + 1 \right] \quad (152)$$

If the number of stages is large and the change in salt ratio per stage is small, then the system may be described with small loss of accuracy by considering the salt ratio, $A_{L(s)}$, to be a continuous function of the variable s, and the difference in salt ratios for adjacent stages becomes approximately equal to the derivative of $A_{L(s)}$ with respect to s. Thus,

$$A_{L(s)} - A_{L(s-1)} \cong \frac{d A_{L(s)}}{d s} = \frac{d A_L}{d s} \quad (153)$$

then

$$\frac{d A_L}{d s} = -A_L(\Omega_{(s-1)}^{-1}) + \frac{P \Omega_{(s-1)} [A_{L(1)} - A_L]}{[1-\nu_{(s)}] Q_{(s)} - P} \quad (154)$$

A material balance on the feed line of stage $s + 1$ is

$$[1 - \nu_{(s+2)}] Q_{(s+2)} + \nu_{(s)} Q_{(s)} = Q_{(s+1)} \quad (155)$$

An examination of equations (141), (143), and (145) shows that each stage of the cascade can be operated with a constant cut θ and have a constant stage separation factor Ω for each stage if the area-to-flow-rate ratio π is constant for each stage. The restriction of constant θ for each stage of the cascade will be made in the development to follow. With this restriction, equation (155) is a second order difference equation with constant coefficients, and the "initial conditions" are

$$Q_{(0)} = 0$$

$$\frac{Q_{(1)}}{P} = \frac{1}{1-\nu} \quad (156)$$

The complete solution of the difference equation (155) is then

$$\frac{Q_{(s)}}{P} = \frac{1}{1-2\nu} \left[1 - \left(\frac{\nu}{1-\nu} \right)^s \right] \quad \nu \neq \frac{1}{2} \quad (157)$$

$$\frac{Q_{(s)}}{P} = 2s \quad \nu = \frac{1}{2} \quad (158)$$

The differential equation (154) then becomes

$$\frac{d A_L}{d s} = -A_L (\Omega - 1) + \frac{(1-2\nu)}{\nu} \Omega \frac{[A_{L(1)} - A_L]}{1 - \left(\frac{\nu}{1-\nu} \right)^{s-1}} \quad (159)$$

for $\nu \neq \frac{1}{2}$, and for $\nu = \frac{1}{2}$,

$$\frac{d A_L}{d s} = -A_L(\Omega-1) + \Omega \frac{[A_{L(1)} - A_L]}{s-1} \quad (160)$$

It should be noted that with total cascade reflux, $P = 0$, and the D.E. is

$$\frac{d A_L}{d s} = -(\Omega - 1) A_L \quad (161)$$

This total cascade reflux can be obtained for arbitrary ν by returning the product of the first stage to its feed. By the use of the integrating factor method, it may be shown that the solution of equation (159) is, for $\nu \neq \frac{1}{2}$,

$$\frac{A_{L(N+1)}}{A_{L(1)}} = \Omega \left(\frac{1-g}{g} \right) e^{-(\Omega-1)N} (1-g^N) \left[\frac{\Omega}{\ln g} \left(\frac{1-g}{g} \right) \right] I \quad (162)$$

where

$$g = \frac{1-\nu}{\nu} \quad (163)$$

and

$$I = \int_0^N e^{(\Omega-1)r} (1-g^r) - \left[\frac{\Omega}{\ln g} \left(\frac{1-g}{g} \right) - 1 \right] dr \quad (164)$$

The quantity $A_{L(N+1)}$ is the composition of the feed to the cascade, and $A_{L(1)}$ is the product composition. For the case where $\nu = \frac{1}{2}$, the solution of equation (160) is

$$\frac{A_{L(N+1)}}{A_{L(1)}} = \Omega e^{-(\Omega-1)N} N^{-\Omega} \int_0^N e^{(\Omega-1)r} r^{(\Omega-1)} dr \quad (165)$$

As no analytical expression for either of the above integrals is known, the integrals must be evaluated numerically for specific cases.

An alternate attack on the solution of the differential equation is to program the problem for a computer; the author has programmed the problem for the PACE 221-R analog computer in the Department of Chemical and Metallurgical Engineering at the University of Tennessee and investigated the effect of the variable ν on solutions of the equation. Both equation (159) and equation (160) were programmed for computation. The basic computer circuits are shown in Figure 28.

The total flow in the cascade per unit of product is given by

$$\sum_{s=1}^N \frac{Q(s)}{P} = \sum_{s=1}^N \frac{1}{1-2\nu} \left[1 - \left(\frac{\nu}{1-\nu} \right)^{s-1} \right] = \frac{1}{(1-2\nu)^2} \left[N(1-2\nu) - \nu + \nu \left(\frac{\nu}{1-\nu} \right)^N \right] \quad (166)$$

for $\nu \neq 1/2$, and for $\nu = 1/2$ is

$$\sum_{s=1}^N \frac{Q(s)}{P} = \sum_{s=1}^N 2s = N(N+1) \quad (167)$$

The quantity of salt "a" that must be fed to the cascade per unit mass of "a" in the product stream is

$$\frac{F}{P} = \frac{Q_{(N+1)}}{P} = \frac{1}{1-2\nu} \left[1 - \left(\frac{\nu}{1-\nu} \right)^{N+1} \right] \quad (168)$$

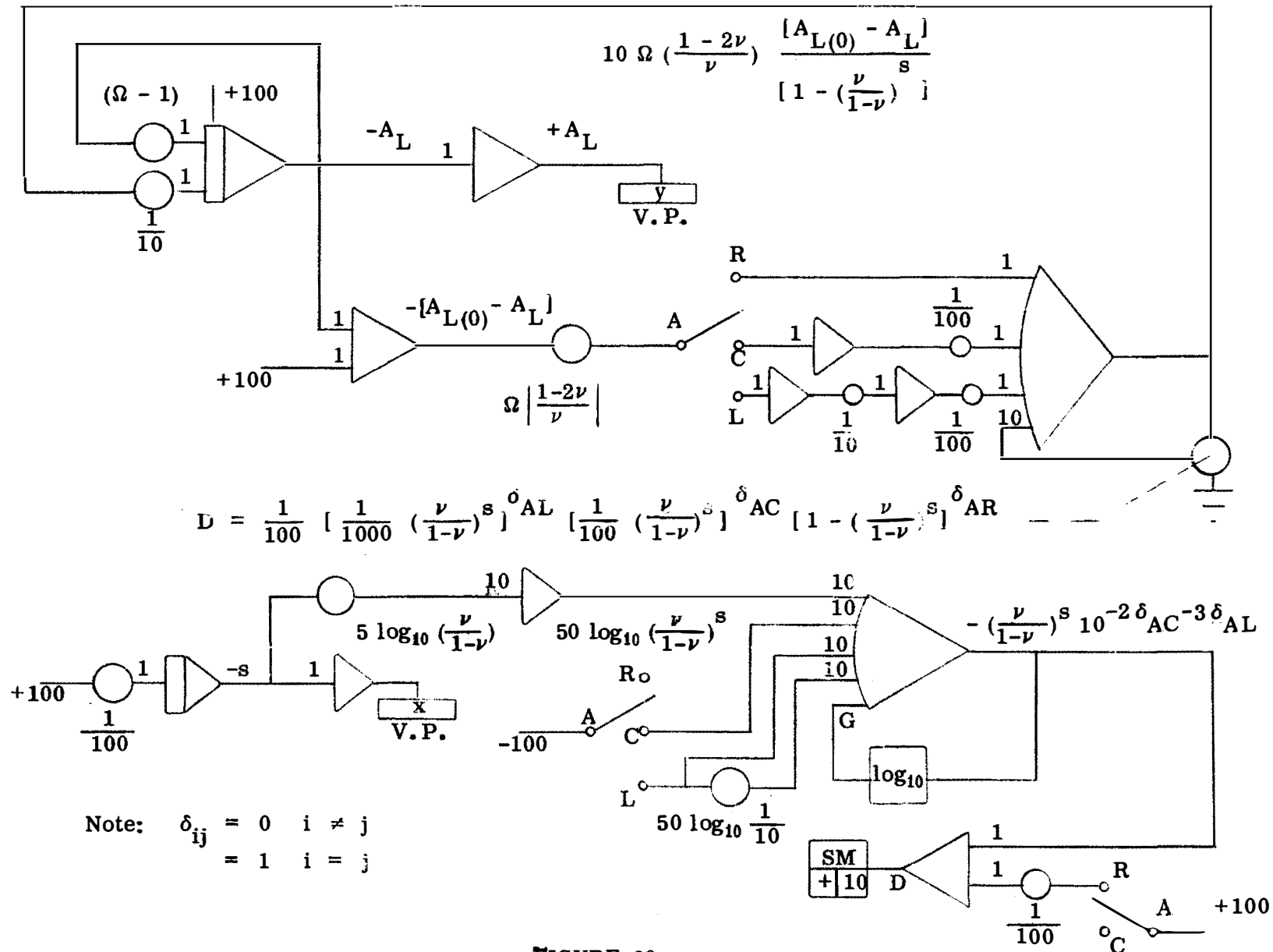


FIGURE 28

ANALOG COMPUTER CIRCUIT FOR THE SOLUTION OF THE CASCADE DIFFERENTIAL EQUATION

for $\nu \neq 1/2$, and for $\nu = 1/2$ is

$$\frac{F}{P} = 2 (N + 1) \quad (169)$$

It will be noted that processing costs are proportional to $\frac{\sum Q(s)}{P}$; while feed costs are proportional to $\frac{F}{P}$. Hence one wishes to minimize both of these quantities.

A Cascade Example. The differential equation for the cascade was solved with the following operating conditions, which were determined in the experimental part of the present work:

$$K_{\text{CuSO}_4} = 0.944$$

$$K_{\text{CoSO}_4} = 0.962$$

$$Z/h_{L-\text{CuSO}_4} = 6.54$$

$$Z/h_{L-\text{CoSO}_4} = 7.08$$

$$\pi = A/(L/\rho) = 0.053 \text{ ft}^2/\text{ml/hr}$$

The area-to-flow-rate ratio π used was that for the operation of the small column at a flow rate of 2 ml/hr; this was considerably higher, but much more convenient from a control standpoint, than the value of 0.0013 found in the previous section, which was the ratio which would give no advantage to the use of evaporation.

After the separation parameters are determined from the operating conditions, the number of stages required for the desired separation may be calculated from the solution of differential equation (159). The values of the cascade variables for a fixed separation are given in Table XI. Values of

TABLE XI

VALUES OF THE SIZE-DETERMINING
FACTORS OF A CASCADE

| ν | Ω | N | $\Sigma \frac{Q}{P} \text{ (s)}$ | $\frac{F}{P}$ |
|-------|----------|----------|----------------------------------|---------------|
| | | | $\times 10^{-4}$ | |
| .534 | 1.036 | 70 | 207 | 264,000 |
| .528 | 1.037 | 75 | 75.6 | 80,500 |
| .521 | 1.038 | 77 | 18.9 | 15,500 |
| .518 | 1.038 | 80 | 12.8 | 8,900 |
| .512 | 1.039 | 87 | 5.6 | 4,160 |
| .508 | 1.039 | 100 | 5.2 | 1,440 |
| .504 | 1.040 | 125 | 5.1 | 915 |
| .500 | 1.040 | 250 | 6.2 | 502 |
| .480 | 1.042 | ∞ | ∞ | 25 |

$\Sigma \frac{Q_{(s)}}{P}$ and $\frac{F}{P}$ are calculated from equations (166) through (169) for the corresponding values of ν and Ω ; the number of stages, N , indicated will give a change in salt ratio between feed and product by a factor of 10, that is, $A_{L(1)} = 10 A_{L(N+1)}$. For example, such a cascade could produce a product containing 0.05 per cent CoSO_4 from a feed containing 0.5 per cent CoSO_4 in CuSO_4 . From Table XI, it can be seen that $\Sigma \frac{Q_{(s)}}{P}$ goes through a relatively flat minimum in the region $0.500 < \nu < 0.518$. $\frac{F}{P}$ decreases with decreasing ν . Hence, unless feed costs were inordinately low, it would appear desirable to operate the cascade in the neighborhood of $\nu = 0.500$ in order to minimize the total cost of a unit of product. If ν is increased greatly, the number of stages would increase, as the stage separation factor, Ω decreases with increasing ν . On the other hand, a situation of minimum reflux is reached if ν is decreased; a value of $\nu = 0.48$ in this problem prevented the product to feed composition ratio from becoming larger than 1.5.

In order to calculate the area of a cascade, the quantity of product desired must be known. For the example, let $P = 100 \text{ lbs/day} = 181 \text{ g-moles of CuSO}_4/\text{day}$. If the maximum permissible concentration in the feed is restricted to 0.90 molar, then the total interstage flow is

$$P \Sigma_{s=1}^N \frac{Q_{(s)}}{P} \times \frac{1}{0.90} \text{ moles/liter}$$

or

$$\frac{1}{0.90} 6.25 \times 10^4 \times 181 \text{ g-moles/day} = 12.6 \times 10^6 \text{ liters/day}$$

With an area-to-flow-rate ratio of $\pi = 0.053 \text{ ft}^2\text{ml/hr}$, one has that the total

area A is

$$\begin{aligned}
 A &= \frac{12.6 \times 10^6}{24 \text{ hr/day}} \text{ l/day} \times 0.053 \text{ ft}^2/\text{ml/hr} \times 10^3 \frac{\text{ml}}{\text{l}} \\
 &= 28.8 \times 10^6 \text{ ft}^2 \\
 &= 0.288 \times 10^6 \text{ ft}^2/\text{lb of product/day}
 \end{aligned}$$

At a construction cost of \$50/ft² the capital investment I would be

$$I = 28.8 \times 10^6 \text{ ft}^2 \times \$50/\text{ft}^2 = \$1.38 \times 10^9$$

or per unit of product

$$I = \$13.8 \times 10^6 / \text{lb of product/day}$$

With the capital investment amortized over a 5 year period, the sum of fixed and operating costs on a daily basis, C, is computed from the value of

$$\gamma = 3.00 \text{ mills/hr-ft}^2$$

$$\begin{aligned}
 C &= 28.8 \times 10^6 \text{ ft}^2 \times \$3.00 \times 10^{-3}/\text{hr-ft}^2 \times 24 \frac{\text{hr}}{\text{day}} \\
 &= \$2.00 \times 10^6/\text{day}
 \end{aligned}$$

or

$$C = \$20.0 \times 10^3/\text{lb of product}$$

The feed required would be

$$F = 50.2 \times 10^3 \text{ lbs of CuSO}_4/\text{day}$$

or

$$F = 502 \text{ lb/lb of product}$$

For the cascade considered, interstage dilution rather than evaporation would be required since total salt concentration tends to increase toward the product end. It was assumed that process water would be available at a sufficiently low cost to have no effect on the large separation cost above.

Practical Equipment. The question arises of what shape such a large installation should take. The author conceives of a commercial installation being built of batteries of columns; each battery would be of the approximate size and shape of the large column used in the present investigation, but there would be several columns on one set of guide rods. Each set of plates would have a spacer between it and the next set; the fluid of the thermal sink would circulate between the plates, and the spacers would be the exterior walls. This arrangement would give alternate columns with the cold plate on top and alternate plates with the hot plate on top. The author does not believe that the reversal of position of the hot plates would have any appreciable effect on the separation. The thermal fluids would be, of course, steam and cool water. This apparatus would resemble a common plate-and-frame filter press, except the plates would be horizontal rather than vertical as in a filter press. Each "stage" would actually consist of a number of column units fed in parallel so as to maintain the area to flow rate ratio constant, while permitting the necessary flow rate changes from stage to stage in order to maintain the optimum value of ν .

Consideration of an "Ideal Cascade". It was originally hoped that the cascade could be operated in such a manner that it would not be necessary to mix streams of unequal salt ratios, that is, as an ideal cascade. This condition implies that

$$A_{L(s+1)} = A_{V(s)} = A_{D(s-1)} \quad (170)$$

A quantity φ may be defined by

$$A_{V(s)} = \varphi A_{D(s)} \quad (171)$$

It can be shown that φ is constant for all stages if Θ is held constant. If the definition of φ is combined with the relations for an ideal cascade, then one obtains

$$A_{D(s+n)} = \varphi^{-n} A_{D(s)} \quad (172)$$

$$A_{V(s+n)} = \varphi^{-n} A_{V(s)} \quad (173)$$

and

$$A_{L(s)} = \varphi^2 A_{D(s)} = \Omega A_{D(s)} \quad (174)$$

With these relations, one may show that Θ is given by

$$\Theta = \frac{\omega}{\omega + \varphi} \quad (175)$$

If equation (150) of the combined material balances of the cascade is combined with the relations for the ideal cascade, one has that

$$Q_{(s)} = P \frac{\varphi [\varphi^s - 1]}{\nu [\varphi - 1]} \quad (176)$$

If this equation is substituted into equation (155) for arbitrary s , one may show that

$$\nu = \frac{1}{1 + \frac{1}{\varphi}} \quad (177)$$

If this value of ν is substituted into equation (146), one may obtain

$$\Theta = \frac{\omega}{\omega + \frac{1}{\varphi}} \quad (178)$$

Comparison of this equation with equation (175) reveals that both equations can be satisfied only if $\varphi = 1$, that is, only if no separation occurs in the column. This implies that ideal cascade operation for constant Q as defined by equation (171), is impossible.

LIST OF SYMBOLS

LIST OF SYMBOLS

| | |
|------------------|---|
| A | - ratio of salt 1 to salt 2 |
| A | - total area of cascade |
| A _s | - absorbancy |
| C | - operating cost of cascade |
| C _a | - concentration of component a, molar |
| D | - coefficient of diffusion, area/time |
| D | - product withdrawal rate, moles/time |
| D' | - coefficient of thermal diffusion area/time-degree |
| F | - feed rate, moles/time |
| F (c, . .) | - function defined by equation (125) |
| I | - value of integral in equation (164) |
| I | - capital investment required for cascade |
| J | - diffusion rate, moles/time-area |
| J _A | - net rate of diffusion, moles/time-area |
| J _{At} | - diffusion rate caused by the thermal gradient, moles/time-area |
| J _O | - diffusion rate through the membrane in the coordinate -1- direction, moles/time-area |
| J _O ' | - ≈ -J _O |
| J _r | - diffusion rate in the coordinate direction, moles/time-area |
| J _s | |
| J _z | |
| J _z ' | |

| | |
|------------|--|
| K | - equilibrium constant, dimensionless |
| K' | - equilibrium constant for the complete mixing model |
| K'' | - equilibrium constant for the laminar flow model |
| L | - average flow rate in the cold-side channel, moles/time |
| L/ρ | - average flow rate in the cold-side channel, volume/time |
| N | - total number of stages in cascade |
| N_L | - the number of transfer units in the column based on the cold stream |
| P | - product rate of cascade |
| Q | - feed rate of dry salt 1 |
| R | - reflux ratio, L/D |
| S | - stage number |
| T | - temperature, degrees |
| ΔT | - total temperature drop between the top and bottom walls, degrees |
| T_s | - transmittancy, the ratio of light transmittance of the solution to that of the solvent |
| V | - average flow rate in the hot-side channel, moles/time |
| W | - wave length of light |
| Z | - total length of the flow channel, length |
| a | - depth of the channel, length |
| a_s | - absorbancy index |
| b | - width of the membrane (and channel), length |

| | |
|----------|---|
| b | - distance of the solution light path in the spectrophotometer, length |
| c | - concentration of the solution used in the spectrophotometer, molar |
| c | - $\sigma \tau a$ |
| c' | - $\sigma \tau' a$ ($\approx -c$) |
| $f_1(c)$ | - function defined by equation (88) |
| $f_2(c)$ | - function defined by equation (90) |
| g | - variable defined in terms of ν |
| h_L | - height of a theoretical stage based on the cold side, length |
| k_L | - mass transfer coefficient based on the cold side, moles/time-area |
| k'_L | - mass transfer coefficient based on the cold side and the complete mixing model, moles/time-area |
| k''_L | - mass transfer coefficient based on the cold side and the laminar flow model, moles/time-area |
| k_s | - absorbancy coefficient |
| k_v | - mass transfer coefficient based on the hot side and the laminar flow model, moles/time-area |
| l | - coordinate distance in the membrane measured from the hot channel, length |
| m | - flow rate in a channel, ml/hr |
| r | - 1) coordinate in the direction of diffusion, length 2) specifically, in the hot-side channel |
| r | - integration variable |

- s - coordinate in the direction of diffusion in the cold-side channel, length
- t - time
- v - linear velocity of the fluid, length/time
- x - average mole fraction of the diffusing component in the cold-side channel
- x^* - equilibrium average mole fraction in the cold-side channel
- x' - concentration of solution, molar
- x_D - mole fraction of product
- x_L - mole fraction of product
- x_V - mole fraction of feed
- y - average mole fraction of the diffusing component in the cold-side channel
- y^* - equilibrium average mole fraction in the hot-side channel
- y_F - mole fraction of feed
- z } - coordinate length of channel, measured in the direction of
- z' } - flow, length
- α - separation factor of CuSO_4 to CoSO_4
- β - cost of evaporation per unit volume
- γ - cost per unit of thermal diffusion area
- δ - thickness of the membrane, length
- η - viscosity
- θ - integration variable, $\sigma \tau r$

| | |
|------------|---|
| θ | - fraction of solution removed in product stream |
| λ | - flow per unit width of channel |
| ν | - fraction of salt 1 removed in product stream |
| ξ | - 1) mole fraction of the diffusing component 2) specifically, in the hot-side channel |
| ξ' | - mole fraction of the diffusing component in the cold-side channel |
| ξ'^* | - equilibrium mole fraction in the cold-side channel |
| ξ_0 | - mole fraction on the hot surface of the membrane |
| ξ'_0 | - mole fraction on the cold surface of the membrane |
| ξ'_0^* | - equilibrium mole fraction on the cold surface of the membrane |
| ξ_0^* | - equilibrium mole fraction on the hot surface of the membrane |
| π | - area to flow-rate ratio |
| ρ | - molar density, moles/volume |
| σ | - Soret coefficient, (degrees) ⁻¹ |
| τ | - temperature gradient in the hot-side channel, degrees/length |
| τ' | - temperature gradient in the cold-side channel, degrees/length |
| τ_M | - the negative of the temperature gradient in the membrane, degrees/length |
| ϕ | - membrane free area, dimensionless |
| φ | - cascade separation factor |
| ω | - separation factor for a single salt |
| Ω | - separation factor for the column |

VITA

VITA

The author was born on July 5, 1935, at Greenbrier, Tennessee, the younger of two sons of C. F. and Lois Greer Fisher. He received a diploma from Greenbrier High School in May, 1952. He entered the University of Tennessee in September, 1952, and graduated with a B. S. in Chemical Engineering in June, 1956. He completed his M. S. in June, 1959, with a major in chemical engineering.

The author was employed as a surveyor by East Tennessee Natural Gas Co. during the summer of 1953. He worked as a production engineer with E. I. du Pont de Nemours and Co. in Charleston, W. Va., during the summer of 1955. He was employed as an Instructor in Chemical Engineering at the University of Tennessee in June, 1956, and has served in this capacity along with the duties of a Research Assistant until the present. The author has accepted a position of Assistant Professor of Chemical Engineering at Vanderbilt University, Nashville, Tennessee, and will take up his duties there upon completion of this dissertation.

The author is a member of the A. I. Ch. E., Tau Beta Pi, Sigma Xi, Phi Kappa Phi, Phi Eta Sigma, and Alpha Chi Sigma. He was the recipient of a Freshman Scholarship, the Lockett Scholarship, and the Kruesi Prize, all at the University of Tennessee.

The author was married on June 11, 1960 to Nancy E. Willis. His hobbies are fishing, flying, water skiing, tennis, and basketball.

COMMENTARY

The question exists of the effect of a more accurate treatment of the hydrodynamic problem on the predicted values of the mass transfer parameters, K and h_L . In order to justify a different model, the representation should improve the agreement between theory and observation for both mass transfer parameters. As the effect on h_L of assuming various flow patterns is tedious to calculate, only the variation of K with flow pattern was considered.

In the analysis, it was assumed that the form of equations (31) and (32) is valid; thus the effect of changing the flow model is only to change the values of $f_1(c)$ and $f_2(c)$. These equations were derived on the assumption that $\frac{dy}{dz} = \frac{d\xi}{dz}$. As the term involving $\frac{\xi}{z} \frac{d}{dz}$ was not significant in determining the values of h_L and K from the experimental data, the form of equations (31) and (32) is further justified. If in equation (35) one replaces $f_1(-c)$ by $f_1'(-c)$, this equation for K is valid for any laminar velocity distribution, where $f_1(c)$ and $f_1'(-c)$ are defined for the hot and cold channels, respectively, by equation (87). The evaluation of $f_1(c)$ and $f_1'(-c)$ requires the use of the proper velocity function and value of τ (τ or τ').

From numerical calculations, it was ascertained using the viscosity data for water that the maximum velocity occurred at a distance of approximately 0.4 of the channel depth above the hot wall in the lower channel and above the membrane in the upper channel. As further investigation would require numer-

ical integration, the effect of certain assumed velocity profiles was determined.

It was determined that the assumptions of 1) a constant viscosity fluid (as in the text), 2) of a constant velocity, and 3) of a linear profile with zero velocity at the upper boundary of each channel (slip at the other boundaries) give rise to identical expressions for K . The assumption of a constant viscosity fluid in the lower channel and of a constant velocity in the upper channel gives a K for $c = 0.2$ of 95 per cent of the theoretical value reported in the text. If one switches these velocity profiles between the two channels, one obtains 99.9 per cent of the theoretical value in the text for $c = 0.2$.

It is apparent that the calculation of K is quite independent of the laminar flow model assumed. One can therefore conclude that improved agreement between theory and practice probably can not be obtained by more accurate treatment of the hydrodynamic problem.

It has been suggested that an ideal cascade might be possible if the individual stages of the cascade were center-fed instead of simple reflux stages. Also, it might be possible to obtain a more efficient cascade if the reflux ratio of an individual stage were optimized by equation (136). This should be carefully examined, however, as this is the optimum for the separation of a single salt from water. The problem, of course, is the separation of the two salts. Equation (136) defines a different optimum for each salt; any average of these two would not necessarily be the optimum for two-salt separation.