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# An investigation of the fluid resistance to dialysis mass transfer in a tubular membrane

Nicholas C. Kafes  
*Lehigh University*

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AN INVESTIGATION OF THE FLUID  
RESISTANCE TO DIALYSIS MASS TRANSFER  
IN A TUBULAR MEMBRANE

by

Nicholas C. Kafes

A Dissertation  
Presented to the Graduate Faculty  
of Lehigh University  
in Candidacy for the Degree of  
Doctor of Philosophy

Lehigh University

1964

CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a  
dissertation in partial fulfillment of the requirements  
for the degree of Doctor of Philosophy.

\_\_\_\_\_  
(date)

\_\_\_\_\_  
Professor in Charge

Accepted \_\_\_\_\_  
(date)

Special committee directing the doctoral work of  
Mr. Nicholas C. Kafes.

- Prof. C. W. Clump, Chairman \_\_\_\_\_
- Prof. A. S. Foust \_\_\_\_\_
- Prof. L. A. Wenzel \_\_\_\_\_
- Prof. W. E. Schiesser \_\_\_\_\_
- Prof. J. Daen \_\_\_\_\_

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I. ABSTRACT

An experimental system has been developed for a study of the dialysis mass transfer operation. A cellulose dialysis membrane in tubular form was suspended in a column and the effect of flow conditions on the mass transfer coefficient was determined by passing water through the tubular membrane counter-current to a circulating brine solution in the annulus.

The suitability of this apparatus for obtaining data which can be utilized in the study of the laminar and turbulent mass transport mechanism is demonstrated. Theories of mass transfer in fluids, which have evolved primarily by analogy to the heat transfer operation and from data acquired in wetted wall columns and from pipe dissolution studies, can now be compared with data collected from an apparatus which has certain advantages over these two mass transfer systems.

The equation  $n' = K A (\Delta C)$ , analogous to the general expression for heat transfer  $q' = U A (\Delta T)$ , was used to calculate the over-all mass transfer coefficient,  $K$ , from flow data, the terminal concentrations, and the transfer area.

The over-all resistance to transfer,  $(1/K)$ , bears the same relation to the reciprocals of the film



coefficients and membrane coefficient as does the over-all heat transfer resistance to the individual coefficients in the heat transfer operation, i.e.,

$$\frac{1}{K} = \frac{1}{k_I} + \frac{1}{k_m} + \frac{1}{k_{II}} \quad (I-1)$$

where  $(1/k_m)$  is the membrane resistance and  $(1/k_I, 1/k_{II})$  are the resistances to diffusion which occur in the boundary layers of fluid adjacent to the membrane surface.

The experiment was conducted under such conditions that the Wilson technique for graphically interpreting heat transfer coefficients could be adapted to our present situation of continuous dialysis for the determination of the tubular film coefficients from measurements of the over-all resistance to material transfer.

A comparison with the transfer coefficients predicted from various theories of mass and heat transfer indicates that the system herein employed can be quite useful in the study of the convective mass transport mechanism.

The results in the turbulent regime fall approximately 15% and 25% below the Lin and Deissler predictions respectively, and are correlated by

the equation

$$N_{Sh} = .069 N_{Re}^{.90} \quad (I-2)$$

The laminar regime results lie between the Leveque and Linton solutions for the parabolic and constant velocity distributions respectively.

## II. INTRODUCTION

### A. Background in Dialysis

A fluid is characterized by a constant state of random molecular motion. If molecules of a particular kind are more concentrated at one point in a fluid than at another, their spontaneous mixing tendency will bring about a net rate of entry of these molecules into the region of low concentration. This flux of molecules, known as molecular diffusion, occurs between regions of unequal concentration and induces in any fluid an inclination toward uniform concentration throughout the space which it occupies.

If a solution containing equal numbers of two kinds of molecules is entered into a body of fluid, and if a sample of the fluid is taken at some point remote from the point of entry before diffusion is complete, this sample will be found to contain more of one kind of molecular species than the other. The difference in mobility of the species in solution is responsible for this action, and it is this differential diffusion which can be utilized to accomplish a partial separation of the constituents.

Dialysis involves the use of a porous membrane to accomplish the above-mentioned separation. A simple case

is illustrated in Figure 1. The diagram shows a dialysis membrane interposed between a pure solvent stream and a liquor stream containing two solute species. A spontaneous transfer of the solute particles through the membrane occurs, and it is this phenomenon of unequal diffusion of dissolved species through porous septums which is termed "dialysis". The capillary pores of the membrane are large enough to permit molecular motion, but small enough to prevent bulk intermingling of the two fluids. The exit solvent stream contains, relative to the exit liquor stream, a proportionately greater concentration of the more mobile species than of the less mobile species. Mass transfer by molecular motion through the membrane is induced by the difference in concentration between the two solutions in the drive to attain chemical equilibrium between the phases.

This process is not to be confused with osmosis, a phenomenon in which only one component of solution, solvent or solute, can pass through a semi-permeable membrane. The porous dialysis membrane permits an interchange of molecules between the two phases in such a manner that the mass flux in both directions is equal.

Practical advantage can be taken of the unequal diffusion rates of the solutes to provide a partial separation of high molecular weight substances from low

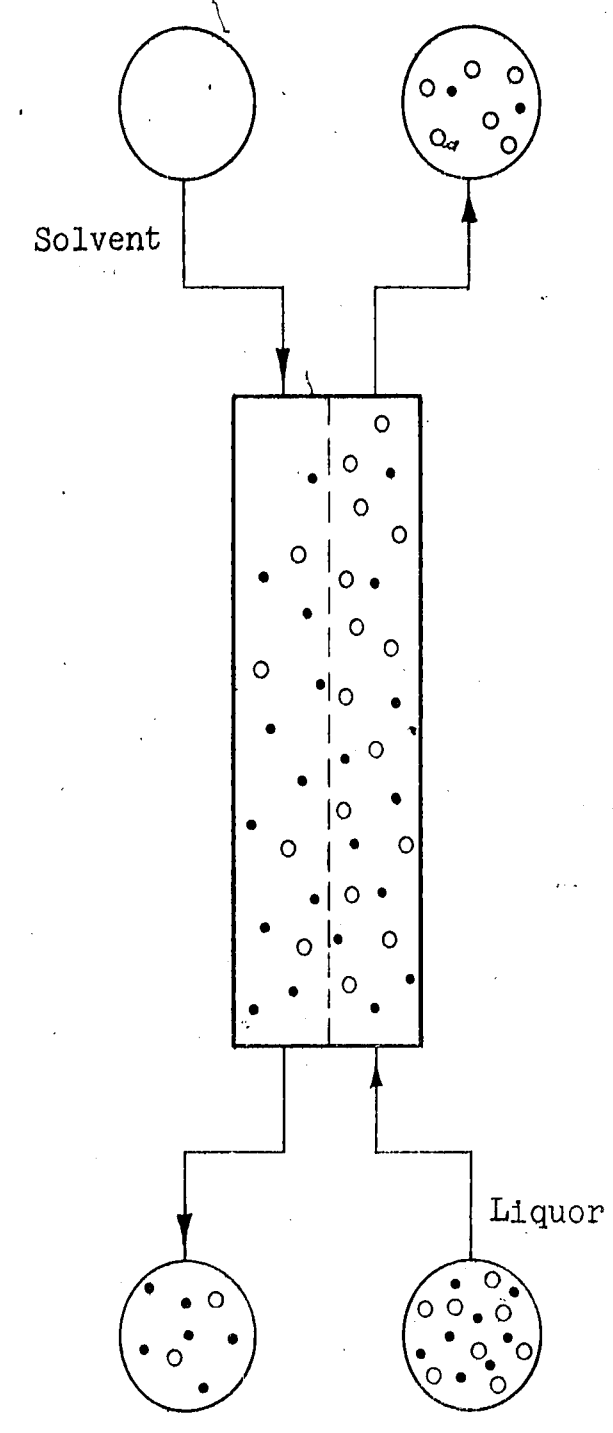


Figure 1 Diagrammatic Representation of Dialysis

molecular weight substances. In its most general conception, dialysis can be regarded as a process of fractional diffusion where the small, light molecules "dialyze" at a greater rate than the large, heavy molecules.

As a laboratory tool, dialysis has enjoyed extensive application in the removal of electrolytes and small water soluble particles (57). To date, relatively few industries have employed this technique on a large scale basis. Limitations inherent in dialysis are slowness of the diffusion process, and inefficiency at low concentrations. Other limitations are encountered in the unavailability of durable and uniformly selective membranes and the lack of technical skill in the field.

The principal application of plant scale dialysis has been in the recovery of industrial waste products where it has proven to be a very efficient and economic method, the best known example being in the viscose rayon industry where a relatively easy separation of a crystalloid (caustic soda), from a colloid (hemi-cellulose) is involved (1, 16, 39, 44, 61). Other large scale uses of this operation have been limited to areas where restrictions, such as temperature sensitivity of materials (8), do not permit utilization of more conventional separation techniques. However, the inherent simplicity

of this operation and the low power consumption involved should warrant a closer look at this method for wider areas of industrial application.

In the recent literature (4, 60) there is evidence that the dialysis technique is at long last emerging from its confining shell of process limitations. New developments of more chemically resistant membranes with better selective properties (49, 50), combined with the utilization of more efficient dialyzing units (22), indicate a wider applicability of this operation to the separation of crystalloid mixtures. For example, in the copper refining industry use of this technique effected economic recovery of sulfuric acid from a liquor containing dissolved metal sulfates (14, 33, 59, 62). It is not unreasonable to expect that the future evolution of dialysis, as a chemical engineering unit operation, will be more extensive with the continued improvement in dialyzing equipment and with a more complete understanding of the principles involved to ascertain the conditions for optimum utilization and to define areas of successful application.

The terminology of dialysis varies widely; in this thesis, the more modern terminology is employed. The liquor denotes the liquid to be dialyzed, and after some or all of the permeable solutes have been removed,

this liquid is termed the dialyzate. The liquid which receives the diffusible solutes is called the solvent. After some or all of the diffusible solute has passed into the receiving solvent, it is referred to as the diffusate.

The majority of the modern plant scale dialyzers are of the plate and frame type, similar to a filter press arrangement. A simple schematic diagram is shown in Figure 2. Membranes are held between alternate liquor and solvent frames and the two streams are passed countercurrent to each other to achieve a maximum concentration gradient and hence a maximum rate of transfer.



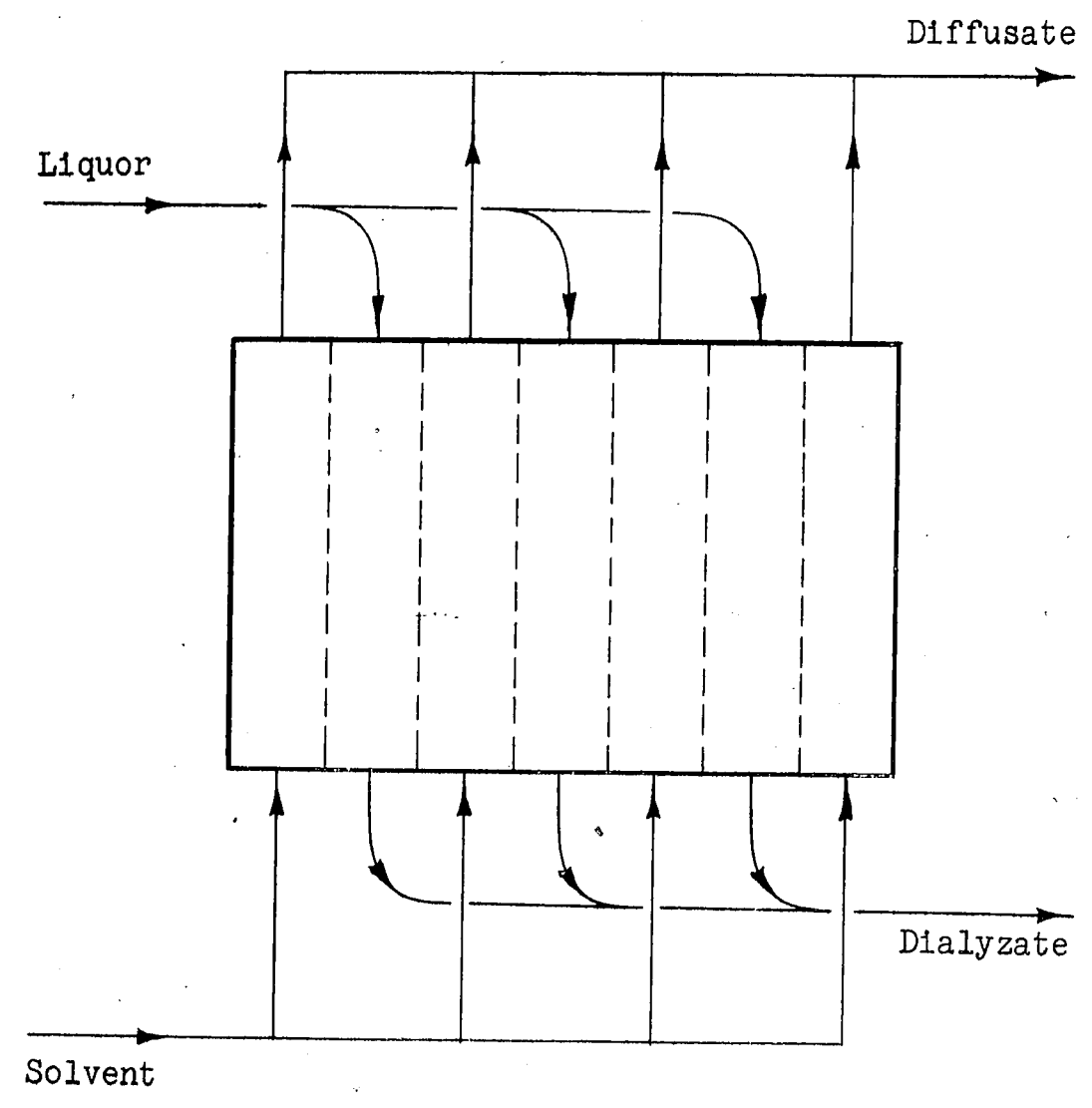


Figure 2 Schematic Representation of Modern Dialyzer

### B. Dialysis Mass Transport Equations

As previously explained, diffusion results from molecular motion in a fluid. If on two sides of a given planar boundary molecules of a certain species exist in unequal concentrations, there will occur a flux of such molecules from the side containing them in greater density to the side containing them in lesser density.

It has been shown (2) that the general relationship for a binary liquid mixture,

$$n_A = X_A (n_A + n_B) - \mathcal{D}_{AB} \nabla c_A \quad (\text{II-1})$$

describes the mass flux of molecules of species A with respect to the stationary coordinate system, where

$C$  = mass concentration, g./cu.cm.

$\mathcal{D}$  = mass diffusivity, sq.cm./min.

$n$  = mass flux, g./ (min.) (sq.cm.)

$X$  = mass fraction

For the special case of equi-mass counter-diffusion of A and B, this equation reduces to Fick's law of diffusion,

$$n_A = - \mathcal{D}_{AB} \nabla c_A \quad (\text{II-2})$$

which describes the diffusion of species A in an immobile medium.

When the fluid is in motion Fick's relationship can be substituted into the equation of continuity, which expresses the law of conservation of matter, to yield the expression

$$(\vec{V} \cdot \nabla) c_A = \mathcal{D}_{AB} \nabla^2 c_A \quad (\text{II-3})$$

for the diffusion of species A through an incompressible fluid in steady motion.

Depending on the hydrodynamic conditions in the tube, this motion can be either laminar or turbulent. In the laminar flow regime the instantaneous velocity at each point is constant in time, and the streamlines at neighboring points are parallel to each other. Once the velocity profile, obtained from the Navier-Stokes relation, and boundary conditions are defined for a particular geometry, equation (II-3) can be subject to a solution. The mechanism of the transfer of matter is essentially the same as in an immobile medium, the transfer taking place by molecular diffusion and only the external conditions varying as a result of the fluid motion. The turbulent flow regime is characterized by a disordered type of motion wherein the velocity at any point changes

continually with time in a random fashion. Transfer of mass takes place by turbulent pulsations, in other words, by disordered movement of small volumes or eddies of fluid superimposed upon the slower molecular diffusion process.

For the turbulent mass transfer operation, equation (II-3) is not easily susceptible to an analytical solution. Many investigators have utilized the expression

$$n_A = - (D_{AB} + \epsilon_M) \nabla C_A \quad (\text{II-4})$$

as the starting point for the most recent theories of mass transport in a turbulent fluid.

The above equation defines the eddy mass diffusivity  $\epsilon_M$ , and assumes the molecular and eddy transport to take place by parallel processes so that the two coefficients are additive. Practically speaking, however, even this simpler relation is not of direct use to the engineer in dealing with systems of other than the simplest type. Such problems are usually approached with the aid of the empirical mass transfer coefficient  $k$ , defined by

$$n_A = k \Delta C_A \quad (\text{II-5})$$

This expression is similar to the commonly used heat transfer equation

$$q = h \Delta T \quad (\text{II-6})$$

which defines  $h$ , the individual heat transfer coefficient.

The form of equation (II-5) was originally obtained from the use of Fick's equation in the film theory, in which it is postulated that the transfer of mass is controlled by a stagnant film of fluid adjacent to the transfer boundary; the transport mechanism being that of molecular diffusion in this region. Despite its inadequacies, the utility of the film theory depends not on the existence of a stagnant film, but on the basic assumption that the mass transfer rate is proportional to the concentration difference between the bulk of the fluid and the boundary.

In the "penetration" model, proposed by Danckwerts (7), there is no controlling film at the wall. The transfer mechanism involves small eddies of fluid which come in contact with the boundary for short periods of time. By using the equations for unsteady state diffusion, the rate is found to be also proportional to the concentration difference.

Thus, the film concept and the transient eddy theory provide entirely different models of the physical process, yet the above equation (II-5) is applicable to both. The present qualitative picture which has evolved is one of continuous increase in turbulence from the interface to the main body, with molecular diffusion playing the major role near the surface and eddy diffusion being of predominant importance in the core of a turbulent stream.

It is seldom possible to find the value of the mass transfer coefficient by analytical calculation. In the majority of cases, it is necessary to make use of experimental data with the similitude theory providing a means for the generalization of the experimental data. This approach rests on the postulate that the real laws of nature cannot depend on the choice of the system units of measurement. Representation of any real law in the form of an expression between dimensionless parameters can therefore be carried out.

Application of this theory to the fluid mass transfer operation results in the following relation showing the effect of the pertinent variables expressed in the form of the dimensionless magnitudes involved;

$$\left(\frac{k D}{\mathcal{D}}\right) = \phi \left(\frac{D U \rho}{\mu}\right) \psi \left(\frac{\mu}{\rho \mathcal{D}}\right)$$

$$N_{Sh} = \phi N_{Re} \psi N_{Sc} \quad (\text{II-7})$$

where

$D$  = diameter, cm.

$\mathcal{D}$  = mass diffusivity, sq.cm./min.

$k$  = individual mass transfer coefficient,  
g./((sq.cm.)(min.))(g./cu.cm.)

$\mu$  = viscosity, g./((min.)(cm.))

$\rho$  = density, g./cu.cm.

$U$  = average velocity, cm./min.

$N_{Re}$  = Reynolds number, dimensionless

$N_{Sc}$  = Schmidt number, dimensionless

$N_{Sh}$  = Sherwood number, dimensionless

The functional relationship between the dimensionless parameters can be ascertained with experimental data taken under given geometric and physical conditions. This relationship can further serve for the calculation of other processes taking place under the same geometric and physical restrictions, but with different dimensions, velocities, and physical properties of the substances.

Many investigators, working with various models or hypotheses to establish the functional relation between the above parameters, focus on systems of the simplest kind, such as flow over a flat plate and through a tube, where the hydrodynamic conditions are reasonably well defined.

Concerning the present situation of mass transfer from one moving fluid through a permeable membrane to another moving fluid, the equation

$$n = K \Delta C \quad (\text{II-8})$$

(similar to the over-all heat transfer equation  $q = U \Delta T$ ) defines  $K$ , the over-all coefficient of mass transfer. This coefficient is related to the individual coefficients by the expression

$$\frac{1}{K} = \frac{1}{k_I} + \frac{1}{k_m} + \frac{1}{k_{II}} \quad (\text{II-9})$$

which follows directly if the linear relationship between the rate and the potential driving force,  $\Delta C$ , is accepted (see Appendix A).

The terms  $1/k_I$  and  $1/k_{II}$  can be considered to represent the resistance to mass transfer residing in the



boundary layers of fluid adjacent to the surface, and  $1/k_m$  represents the resistance of the membrane to diffusion.

The liquid film coefficients, obtained from the above equation, can be expressed in terms of the Reynolds and Schmidt dimensionless moduli for the particular system geometry and fluid employed.

Reference will be made later to various relationships and techniques developed to describe the transfer of heat through moving fluids. Under certain well-defined conditions the mechanisms of heat and mass transfer are analogous and the equations describing the transport operations are similar. The following tabulation summarizes the corresponding equations for these two processes. The mass/heat transfer analogy is directly applicable for the situation of mass transfer in a system where there is counter-diffusion of the constituents A and B such that the mass flux in both directions is equal.

ANALOGOUS EQUATIONS OF HEAT AND MASS TRANSFER

Heat Transfer

$$q = -k \nabla T.$$

$$(\vec{V} \cdot \nabla) T = \frac{k}{\rho c} \nabla^2 T$$

$$q = u \Delta T$$

$$\frac{1}{u} = \frac{1}{h_I} + \frac{\delta}{k} + \frac{1}{h_{II}}$$

$$N_{Nu} = \phi N_{Re} \Psi N_{Pr}$$

Mass Transfer

$$n_A = -\mathcal{D}_{AB} \nabla c_A$$

$$(\vec{V} \cdot \nabla) c_A = \mathcal{D}_{AB} \nabla^2 c_A$$

$$n_A = K \Delta c_A$$

$$\frac{1}{K} = \frac{1}{k_I} + \frac{1}{k_m} + \frac{1}{k_{II}}$$

$$N_{Sh} = \phi N_{Re} \Psi N_{Sc}$$

Many investigators, dealing with mass transfer devices such as the wetted wall column and the pipe dissolution apparatus, apply the foregoing equations with a correction factor to compensate for the fact that the net transfer is unidirectional; in other words, the boundaries of these systems are permeable to only one constituent. This correction is subject to conjecture, since it does not adequately describe the effect of the attendant bulk motion on the transfer mechanism. The bulk motion, necessary for material balance considerations, can be neglected only if the transfer rate is very slight.

It is apparent, however, that for dialysis mass transfer, the above analogy with the heat transfer mechanism is valid. The restriction of zero net mass flux is satisfied by virtue of the membrane permeability to all mixture constituents, thereby permitting the direct use of the analogous forms of the heat transfer relations.

### C. Review of Literature

It has been shown above that the equation

$$n = K \Delta C \quad (\text{II-10})$$

relates the amount of material transferred per unit time to the over-all dialysis coefficient, the dialyzer area, and the concentration driving force. The over-all resistance to mass transfer ( $1/K$ ), bears the same relation to the individual resistances of films and materials as does the over-all heat transfer coefficient to the individual coefficients in heat transfer calculations. Therefore, the over-all dialysis resistance is related to the membrane resistance ( $1/k_m$ ) and the liquid side resistances ( $1/k_I$ ,  $1/k_{II}$ ) by the equation

$$\frac{1}{K} = \frac{1}{k_I} + \frac{1}{k_m} + \frac{1}{k_{II}} \quad (\text{II-11})$$

With respect to various designs of laboratory and plant scale dialyzers, the literature indicates only isolated values of over-all dialysis coefficients calculated from the terminal conditions of these units. Very little has been accomplished concerning the

particularization of the over-all resistance into the individual membrane and liquid film resistances.

Marshall (45), in an experimental study on the dialysis of caustic soda solutions, was the first to evaluate the individual resistances to dialysis mass transfer. He determined the membrane coefficient ( $k_m$ ) with a batch dialyzer by stirring the solution on both faces of the membrane to eliminate the liquid film resistances. Using a continuous dialyzer of the filter press type, with two frames, he obtained the liquid film resistances from measurements of concentration profiles. This work, though of excellent quality, was of limited value since the prime emphasis was focused on the recovery of sodium hydroxide from steeping press liquors in viscose rayon production. More importantly, however, the apparatus used for determining the liquid film coefficients was not of a sufficiently universal nature to permit the coefficients to be translated in terms of the generalized parameters describing the hydrodynamic conditions and properties of the fluid.

Lane and Riggle (36), with an apparatus similar to Marshall's batch dialyzer, determined and correlated membrane dialysis coefficients ( $k_m$ ) for different membranes in various solutions. No experimental work was carried out for the evaluation of the liquid film

coefficients, but they did set up an empirical means, of questionable validity, for determining the sum of the liquid side resistances  $(1/k_I + 1/k_{II})$  as a function of the diffusion coefficient.

Both of the above investigations were unsatisfactory in their treatment of the liquid film resistances primarily because the geometry of the filter press type system precluded an analysis and correlation of the coefficients in terms of the usual dimensionless moduli: the Reynolds number and Schmidt number parameters for fluid flow and mass transfer. That the resistance to diffusion which occurs in the boundary layers of fluid adjacent to the membrane surface is significant is indicated by Marshall, who working with flow conditions comparable to plant operation, showed that the liquid films contributed up to 50% of the total resistance to mass transfer.

In this thesis, an apparatus was designed and successfully tested for the purpose of studying the dialysis mass transport phenomena. In particular, the aim was to determine the effect of flow conditions on the liquid film coefficient in a system where the characteristic Reynolds criteria could be defined. For this reason a dialysis section of cylindrical geometry was chosen. A tubular dialysis membrane was supported in

a column and a water stream was passed through the tube counter-current to a saturated salt solution circulating in the annulus. By utilizing the measured over-all coefficients, with an adaption of Wilson's graphical analysis for over-all heat transfer resistances, the tube side individual mass transfer coefficient was determined as a function of the hydrodynamic conditions in the tube.

In addition to the practical advantage of obtaining information for the study of the dialysis mass transport operation, this apparatus, in view of the simplicity of design, the determinability of the mass transfer surface, and the fairly well defined hydrodynamic conditions of the tubular liquid stream, presents interest for a theoretical study of the fluid mass transfer mechanism in general. The data acquired with the system employed herein can serve as another means for the testing of the existing theories of mass transfer which are based on data collected in devices such as wetted wall columns and the dissolution of pipes in moving fluids.

### III. DESCRIPTION OF EQUIPMENT

The dialysis experimental apparatus consists of the contact section (a column containing the tubular membrane), and the auxiliary equipment (pumps, rotameters, pipework and feed drums), necessary for the circulation and measurement of the streams flowing through the system. A schematic diagram of the system showing the pertinent features is presented in Figure 3.

The liquids are driven through the system by means of an Ingersoll-Rand centrifugal pump (Model No. 1 $\frac{1}{2}$ K2) and a Robbins & Myers "Moyno" screw pump (Model No. 2L3). Feeds to the pumps are from 55 gallon drums.

The centrifugal machine is used to pump Bethlehem city water, employed as the solvent, through the tubular membrane and then discharges the stream to the sewer. The water flow is regulated with globe valves in the by-pass and pump outlet lines, and its measurement is obtained with the use of three rotameters in parallel to cover the range of tubular flow conditions investigated in this study.

The saturated salt solution is circulated through the annular section of the column in a closed circuit by means of the "Moyno" constant displacement pump. Under the conditions set up in this experiment



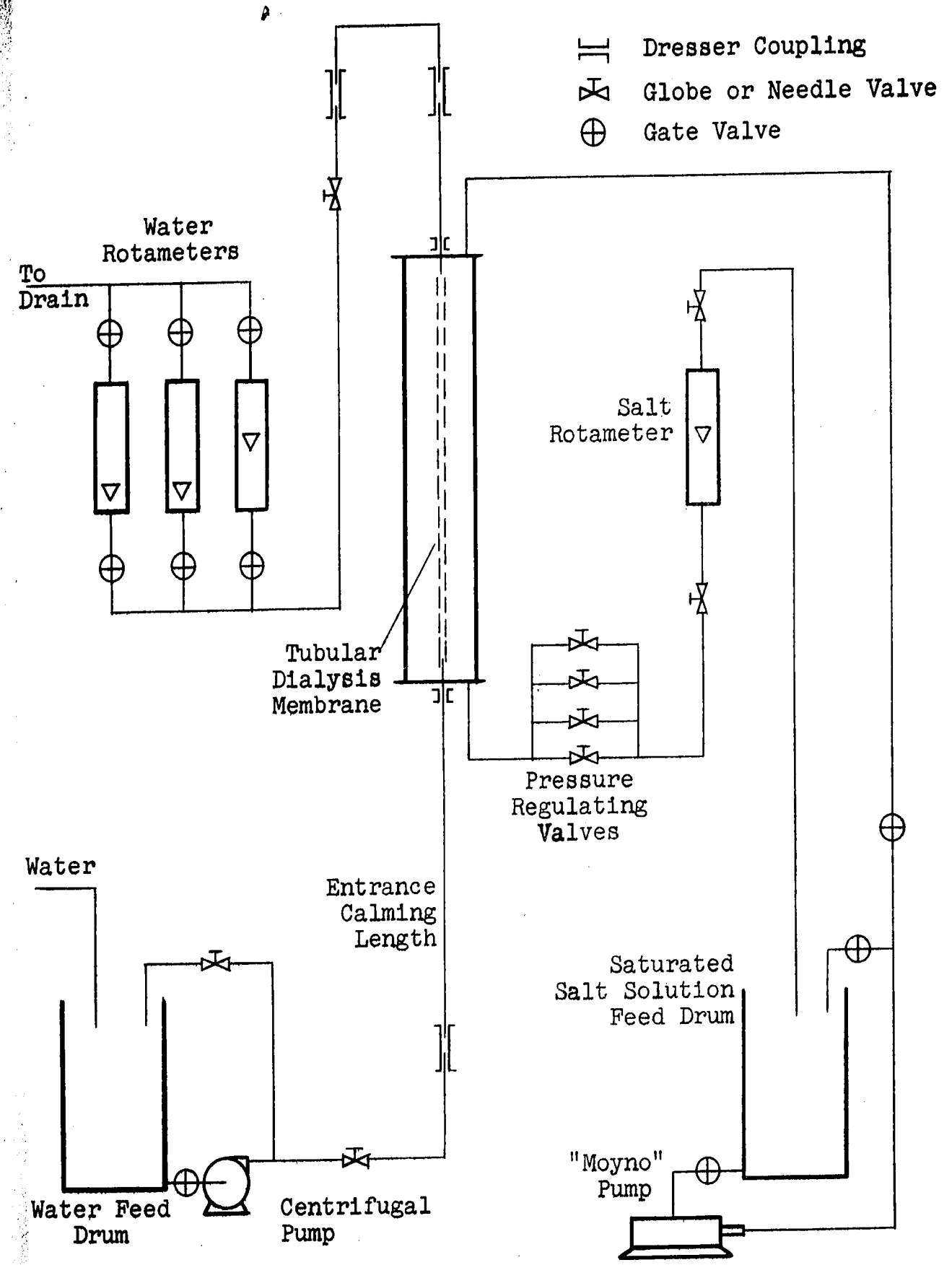


Figure 3 Schematic Flow Diagram of Experimental System

the pump by-pass valve is closed to maintain essentially constant flow conditions in the annular section of the column. A rotameter was employed to observe the salt stream flow rate. The very small amount of salt solute diffusing through the membrane is replenished from the excess salt added to the salt feed drum at the beginning of each run to maintain saturation of the liquor stream at all times.

All metal pipework of the equipment is of galvanized iron; 1 inch size piping being used for the salt system and  $1\frac{1}{2}$  inch piping for the water system.

The column (53 inches in length) was constructed with two parallel sides of Plexi-glass to permit the photographic determination of the membrane diameter. The other two sides consist of the halves of a five-inch diameter aluminum pipe which was split along its length. Aluminum end plates provide inlet and outlet connections for the salt and water streams. The tubular solvent stream and the annular liquor stream are introduced at the bottom and top of the column respectively, thereby providing a counter-current motion of the fluids.

The dialyzer tubing is a seamless product made of regenerated cellulose, and is manufactured by the Arthur H. Thomas Company of Philadelphia for the use of the chemist and biologist in their colloid-crystalloid

separations. The inflated diameter of the tubing is  $1 \frac{1}{8}$  inches and the pore diameter averages 48 Angstrom units (11). The length of the tubing is four feet long and was chosen in order to provide adequate transfer area for a measurable amount of solute to diffuse into the solvent stream over the range of flows considered in this study. The rate of diffusion in liquid systems is quite slow so that the change in concentration of the solvent stream is in the order of 100 to 15000 parts per million, thereby permitting the effective utilization of a conductivity cell for measurement.

The Plexi-glass sides of the column not only permit the visual determination of the membrane diameter, but also allow the performance of the tubular membrane to be clearly visible during the operation. Rupture of the membrane can be readily detected. Also, a pressure differential between the two counter-current streams can be observed by the choking action of the membrane ( $P_{\text{liquor}} > P_{\text{solvent}}$ ) or by the excessive inflation of the membrane tube ( $P_{\text{solvent}} > P_{\text{liquor}}$ ). The primary pressure control of the contact section, to maintain a constant tubular geometry, is attained by the use of four globe and needle valves arranged in parallel and located in the salt system pipework downstream from the column.

The extremities of the membrane are slipped over 1.25" O.D. steel tubes (I.D. = 1.084") which were machined to 1.125" O.D. at the connecting ends. The junctures are wrapped with masking tape and clasped tightly with hose clamps in order to prevent leakage. These steel tubes serve as the calming lengths to establish and maintain normal velocity gradients in the water stream leading to and from the column. The entrance calming length is fifty times the diameter of the tubular membrane while the exit calming length is twenty-five times the membrane diameter. Each calming length tube is concentrically aligned and secured by means of a Dresser coupling assembly which is fastened to the aluminum end plate, and which is in turn joined to the flange plates of the column.

The free end of each calming length tube is passed through the Dresser coupling assembly and connected to the external pipework by means of a four-inch long Dresser coupling. These Dresser compression fittings are ideal for this application since they provide the necessary play to permit the steel tubes to be moved up or down in order to maintain the tubular membrane in a taut position. No twisting or turning is involved as would be the case if screw fittings were used.

#### IV. PROCEDURE

In the system set up for this investigation, a tubular dialysis membrane was supported within a column and a water stream passed through the tube counter-current to a saturated salt solution in the annulus.

Before its installation in the column, the membrane was steeped in a salt solution for at least 48 hours so as to allow it to achieve its maximum degree of swelling. Once the start-up was successfully carried out without rupture of the membrane, the system was operated for approximately two hours to attain steady state conditions. Each run lasted about three quarters of an hour, during which time rotameter readings and photographs of the tube were taken; also samples of the solvent and diffusate streams were collected in 1000 cubic centimeter Erlenmeyer flasks.

The salt solution was circulated in a closed loop and therefore had a tendency to increase in temperature. This stream was cooled by the direct addition of chipped ice to the salt feed drum so as to match the temperature of the solvent water stream. Excess salt was also added at the same time to maintain saturation conditions of the liquor stream at all times. During the course of a set of runs, the water stream

temperature held constant to within  $3^{\circ}\text{F}$  and the difference in temperature between the two fluids was maintained below  $0.5^{\circ}\text{F}$  in most instances and always within  $1.0^{\circ}\text{F}$ .

In the first phase of this research, data were collected for a tubular flow rate in the turbulent regime ranging from a Reynolds number of 2,500 to 45,000. The second phase involved the acquisition of laminar flow data from a Reynolds number of 150 to 1000. Over this whole range of tubular flow conditions the annular brine stream flow rate was essentially constant. The salt system rotameter readings were observed to vary by less than two percent.

To maintain the tubular geometry of the membrane, no pressure differential between the two streams could be tolerated for either choking or excessive inflation of the membrane would result. The pressure in the dialysis tubing increased with increasing solvent flow rate, so that the pressure in the annulus had to be increased to balance that in tube. This was accomplished by the manipulation of the four different size globe and needle valves arranged in parallel and located in the salt system pipework downstream from the column. These were used to exert a back pressure in the annulus and thereby compensate for the pressure increase in the tube accompanying the increased tubular flow rate.

The membrane diameter, both at the top and bottom of the column, was obtained with the use of a Polaroid camera. A two percent difference in this diameter was noted.

Samples of the solvent and diffusate streams were analyzed for total ion content utilizing a conductivity cell and a Serfass conductance bridge. (See APPENDIX B).

## V. RESULTS AND DISCUSSION

### A. Wilson Method

In order to isolate the tubular side fluid resistance from measured values of the over-all resistance to transfer, the valuable method of Wilson (65) can be utilized. This technique, which has been used to graphically interpret over-all heat transfer coefficients, can be readily adapted to the evaluation of the dialysis mass transfer data obtained in the subject investigation. Specifically, the value of the resistance to transfer of the membrane and annular salt side fluid,  $(1/k_m + 1/k_s)$ , can be determined from measurements of the over-all resistance,  $1/K$ , under the hydrodynamic conditions of turbulent flow in the tube. Tubular film coefficients for both the laminar regime and turbulent regime can be subsequently obtained by subtracting this constant from the measured over-all coefficients.

For the case of heat transfer taking place between two moving fluids separated by a wall, the general rate equation takes the form

$$q = \frac{\Delta T}{1/u} \quad (V-1)$$



This is an Ohm's law type of relation where the over-all resistance  $(1/u)$  can be expressed as the sum of the resistances to transfer residing in the wall separating the two phases and the boundary layers of fluids adjacent to the wall.

$$\frac{1}{u} = \frac{1}{h_I} + \frac{\delta}{k} + \frac{1}{h_{II}} \quad (V-2)$$

The additivity of the thermal resistances to transfer, in terms of the reciprocals of the film coefficients, is the basis of the Wilson method.

For a particular fluid under isothermal conditions, the film coefficient is a function solely of velocity. Hence, if an experiment is conducted in which the over-all coefficient,  $u$ , is measured over a range of tube stream velocities while maintaining the hydrodynamic conditions of the fluid outside the tube constant, the above equation reduces to

$$\frac{1}{u} = a + b \frac{1}{u^c} \quad (V-3)$$

where  $a$ ,  $b$ , and  $c$  are constants.

If the total resistance to transfer  $1/U$  is plotted as ordinate versus  $1/U^c$  as abscissa, a straight line is obtained with slope  $b$  for the appropriate value of  $c$ . The intercept  $a$ , obtained by extrapolation to infinite velocity (indicating zero resistance of the tubular side fluid), represents the thermal resistance of the tube wall and the fluid at constant flow conditions outside the tube. Heat transfer data have been reasonably correlated with the exponent of velocity  $c$  taking on the value 0.8.

The value of the intercept can be subtracted from the over-all resistance to give the tubular side fluid resistance, and hence the tubular film coefficient which can be expressed as a function of the variables describing the flow conditions in the tube and the properties of the fluid.

Actually, however, this technique has usually been used to obtain the constant  $a$ , representing  $(1/h_I + \delta/\lambda)$ , from which the annular film coefficient  $h_I$  can be determined with a knowledge of the tube wall properties (18, 35, 47). The 0.8 value for the exponent  $c$  has been determined generally from experimental systems, such as the electrical heating of a tube wherein only the inside film coefficient is involved.

Experimental data for the turbulent heat transfer process in a tubular geometry have established

$$N_{Nu} = .023 N_{Re}^{.80} N_{Pr}^{.33}$$

$$N_{Nu} = \frac{f}{2} N_{Re} N_{Pr}^{.33} \quad (V-4)$$

as the functional relationship, within  $\pm 40\%$  (46), between the dimensionless parameters, where

$$\frac{f}{2} = .023 N_{Re}^{-.20} \quad (V-5)$$

is taken as the relation between friction and the hydrodynamic conditions of the fluid. The Nusselt criterion and hence the film coefficient is shown to be related to the velocity with the 0.80 exponent, i.e.,

$$h \sim u^{.80} \quad (V-6)$$

This is therefore the justification for the value of  $c$  used in the Wilson plot.

The direct proportionality between the heat transfer coefficient and the friction factor is to be noted. The relationship between the transfer of heat and

momentum is emphasized by the Chilton and Colburn empirical equation

$$J_H = \frac{h}{c_G} N_{Pr}^{.67} = \frac{f}{2} \quad (V-7)$$

which in essence juxtaposes these two transport processes (6).

The use of equation (V-5) in the Nusselt relation (V-4) is justified by the correlation of heat transfer data with this form of the dimensional equation, even though friction/pressure drop data in the turbulent flow regime are better correlated (34), up to a Reynolds number of 100,000, by the Blasius equation

$$\frac{f}{2} = .0395 N_{Re}^{-.25} \quad (V-8)$$

The above relationships have their mass transfer counter-part in the Sherwood equivalent of the Nusselt relation

$$N_{Sh} = .023 N_{Re}^{.80} N_{Sc}^{.33}$$

$$N_{Sh} = \frac{f}{2} N_{Re} N_{Sc}^{.33} \quad (V-9)$$

while the Chilton-Colburn  $j$  - factor for mass transfer (5) takes the form

$$j_M = \frac{k}{U} N_{Sc}^{.67} = \frac{f}{2} \quad (V-10)$$

For the case of mass transfer taking place between two fluids separated by a dialysis membrane, it has been shown previously that the following relationships are applicable:

$$n = \frac{\Delta c}{1/K} \quad (V-11)$$

$$\frac{1}{K} = \frac{1}{k_w} + \frac{1}{k_m} + \frac{1}{k_s} \quad (V-12)$$

It is apparent that the direct application of the aforementioned graphical technique to the present case of dialysis is suitable for the determination of the individual mass transfer coefficients. The over-all mass transfer coefficient can be calculated from

$$n' = K A (\Delta c)$$

$$Q_w (C_{w2} - C_{w1}) = K A (C_s - C_w) \quad (V-13)$$

with a knowledge of the membrane area, the liquor saturation concentration, the volumetric flow, and the inlet and exit concentrations of the water stream.

The data are shown in Figure 4, the dialysis mass transfer analog of the Wilson graph. The data collected from all the sets of runs in the turbulent regime are presented. The over-all resistance to mass transfer ( $1/K$ ) is plotted versus the reciprocal of the tube stream velocity to the 0.8 power. The best straight line through the data points was drawn using the method of least squares. The intercept value of 79.05, obtained from the intersection of this line extrapolated to the ordinate, represents the sum of the membrane resistance and the salt side resistance ( $1/k_m + 1/k_s$ ).

The individual tube side coefficients determined from this plot are presented in Figure 5 in the form of the Chilton-Colburn  $j$  - factor as a function of the Reynolds number of the tubular water stream.

Some doubt is indicated concerning the validity of the value of the exponent used with the velocity in the Wilson dialysis plot. A number of recent theories of heat and mass transport (10, 40, 41) do not predict this direct proportionality between the film coefficient and the friction factor as indicated above in the Nusselt and Sherwood relations, equations (V-4) and (V-9). The 0.8

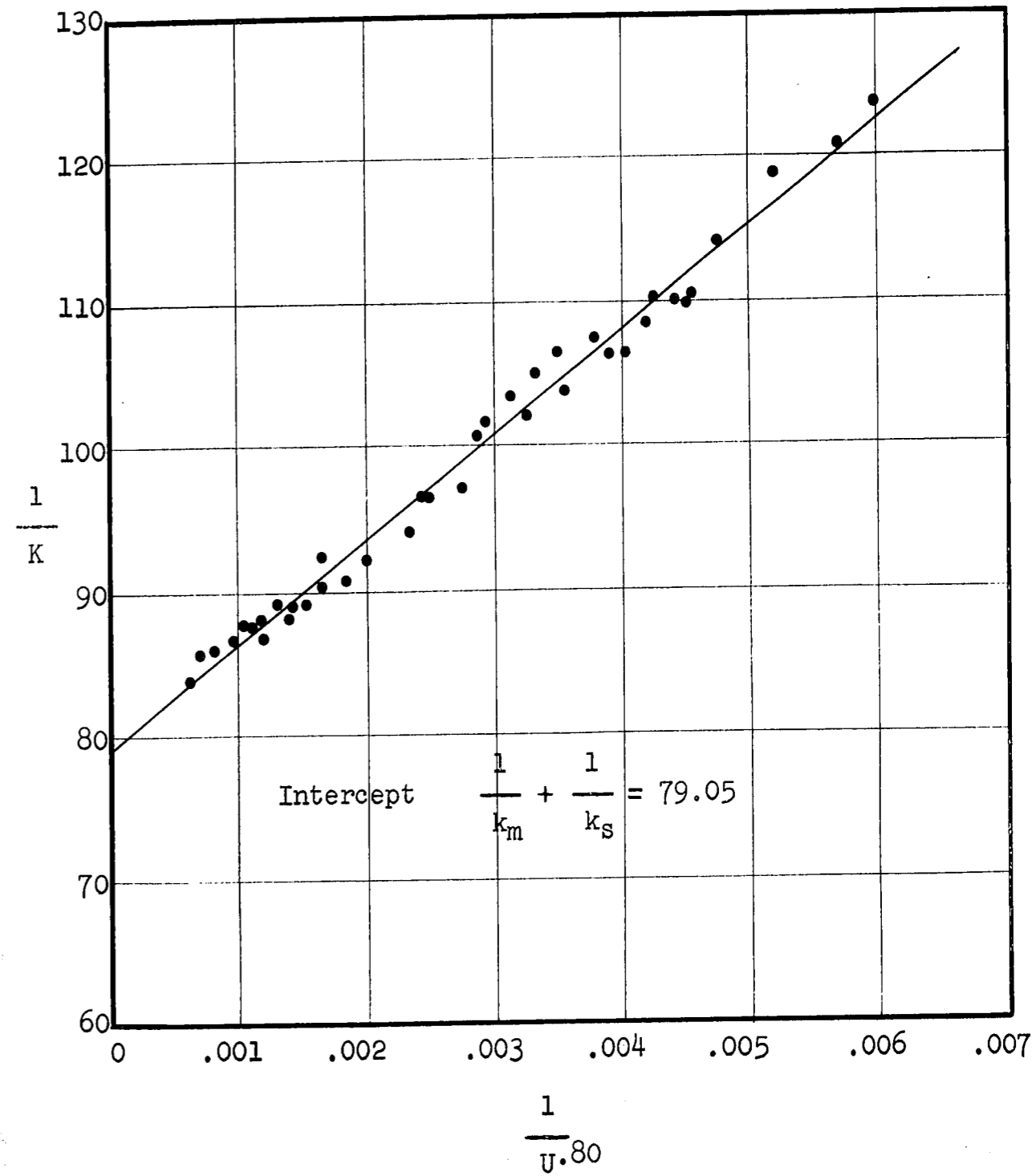
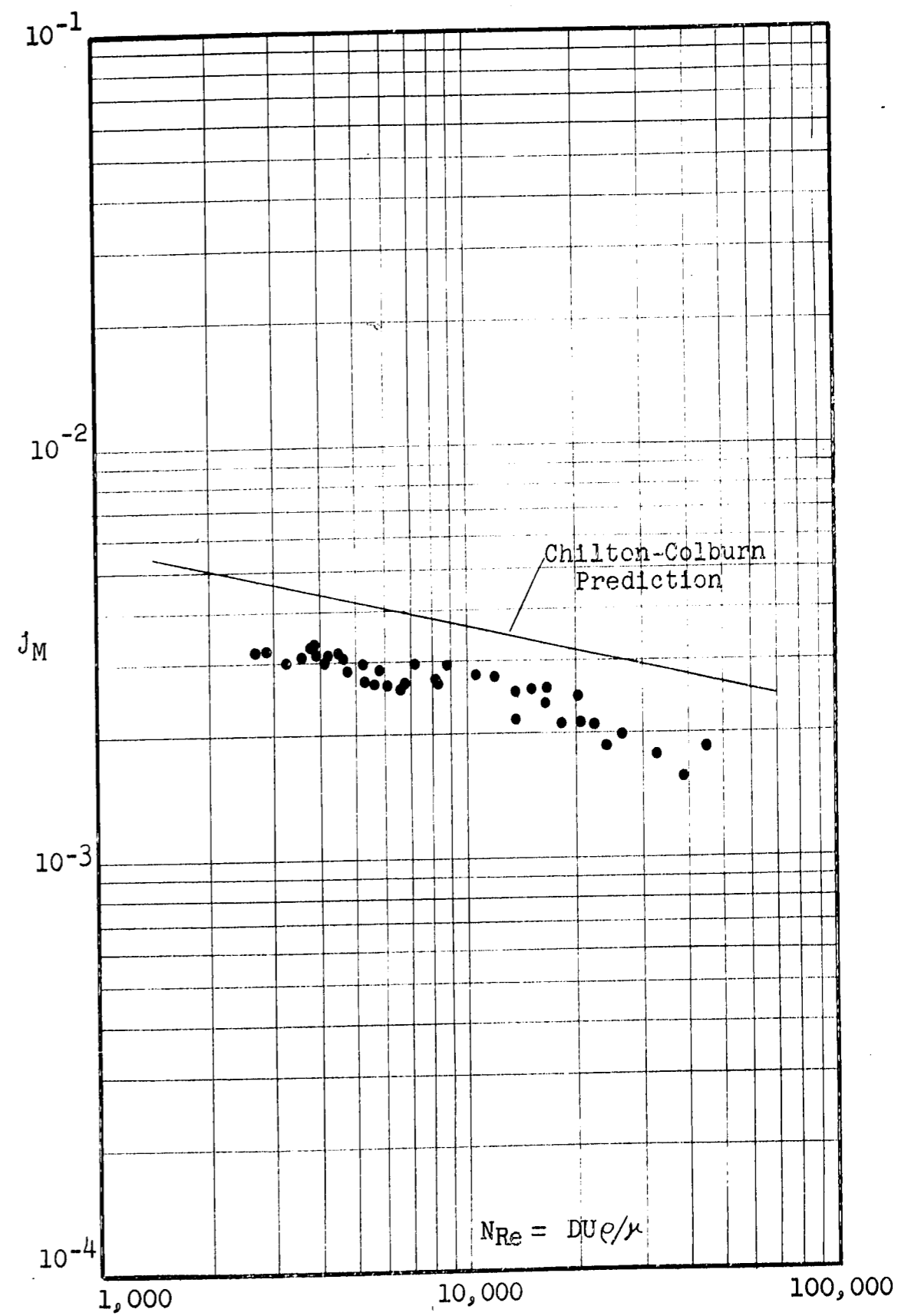


Figure 4 Wilson Plot, 0.80 Exponent

Figure 5 Chilton-Colburn  $j$  - factor Plot



exponent on the velocity was employed simply because it was found that in heat transfer studies, the straight line obtained with this exponent correlated the experimental data and conformed reasonably well with the dimensional equations presented above.

A closer look at this technique, however, indicates that the assumption of a value for this exponent fixes, a priori, the functional relation between the coefficient and the velocity. The recently advanced hypotheses, when extrapolated to high Schmidt number systems, show the film coefficient to be proportional to the square root of the friction factor, corresponding to a velocity exponent of 0.875 (employing the Blasius relation). The difference between these two exponents is small; therefore, fixing the exponent at 0.8 would reasonably correlate the data even though an exponent of 0.875 could possibly give a better fit of the data.

Thus, instead of assuming the exponent on the velocity, it was decided to determine its value from the data beginning with the assumption that these experimental points could be correlated with an equation of the form

$$\frac{1}{K} = a + b \frac{1}{U^c} \quad (V-14)$$

The constants  $a$ ,  $b$ , and  $c$  do not enter the formula linearly, and no transformation of the formula will give a linear relation among them. The determination of the constants by the method of least squares requires that the equation be linear in the constants or that the equation be reduced to a form linear in the constants. The method of differential correction (51, 54) was utilized in this case. This method involves assuming initial values for  $a$ ,  $b$ , and  $c$  and determining the corrections  $\alpha$ ,  $\beta$ , and  $\gamma$  for each of these constants. Application of Taylor's theorem for a function of several variables results in a series of residual equations (one for each data point), linear in the corrections  $\alpha$ ,  $\beta$ , and  $\gamma$ , which can then be subject to a least square analysis.

The above iterative procedure was carried out using initial values for the coefficients determined from a least square analysis of the data plotted in the form of a Wilson graph taking 0.8 as the exponent on the velocity, as indicated in Figure 4. Successive trials were carried out using the results of each previous trial until the values for the constants converged (See APPENDIX E). With the results of these trials, the above equation (V-14) then reduces to

$$\frac{1}{K} = 80.94 + 13450 \frac{1}{U^{.90}} \quad (V-15)$$

The intercept value of 80.94, so determined, is within 2½% of the value obtained with the use of the 0.80 exponent. A direct conclusion from the above analysis is that the tubular film coefficient varies with the velocity to the 0.90 power

$$k_w \sim u^{.90} \quad (V-16)$$

The results tend to support the most recent theories of turbulent transport in which the film coefficient is predicted to be proportional to the square root of the friction factor for high Schmidt number systems. The dimensional equation describing the turbulent dialysis mass transfer process then takes the form

$$N_{Sh} \sim N_{Re}^{.90} \Psi N_{Sc}$$

$$N_{Sh} \sim \sqrt{\frac{f}{2}} N_{Re} \Psi N_{Sc} \quad (V-17)$$

The data are plotted in Figure 6 in the form of a Wilson graph with this 0.90 exponent.

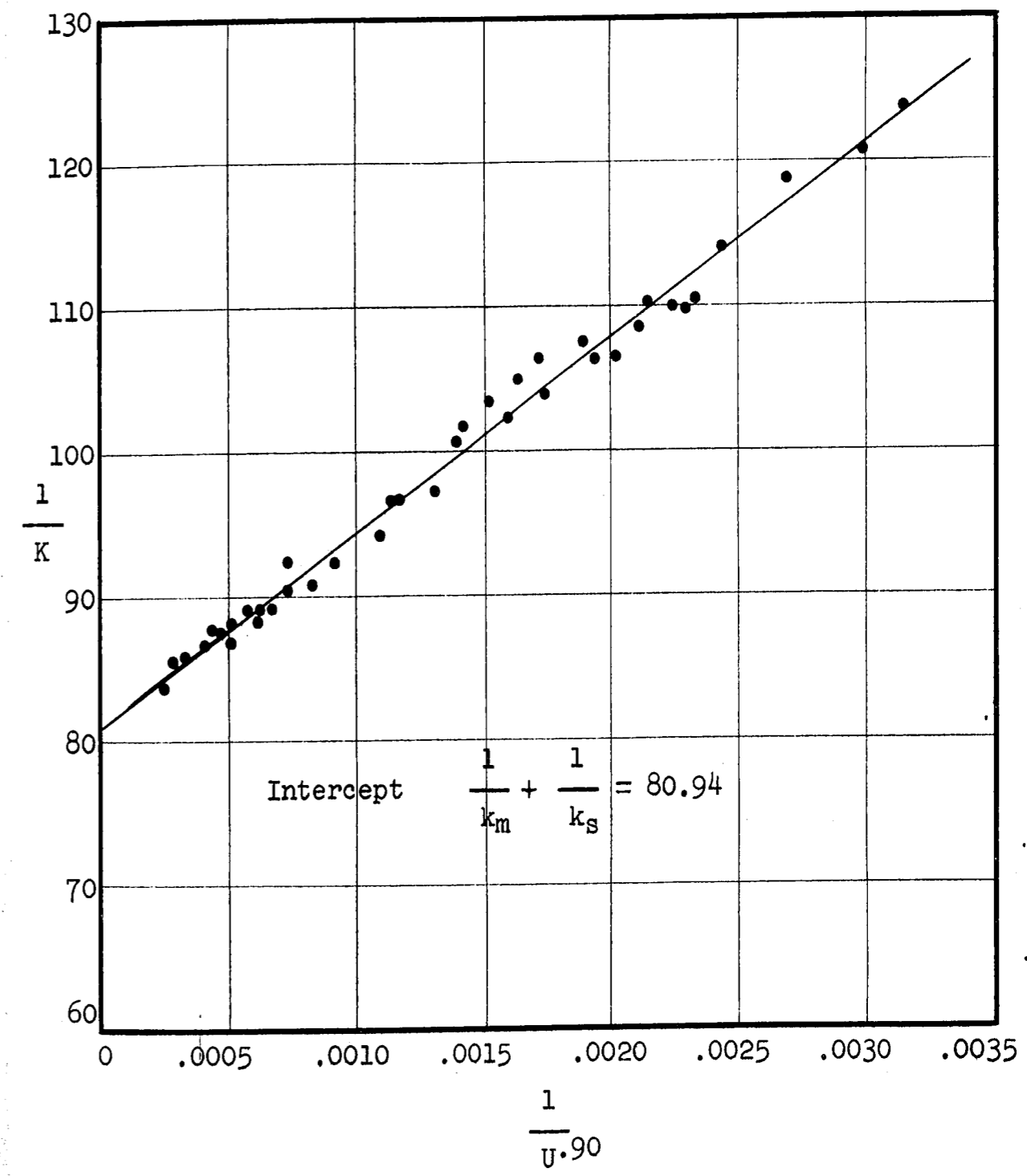


Figure 6 Wilson Plot, 0.90 Exponent

### B. Turbulent Flow Regime

No previous data for the evaluation of the dialysis liquid film coefficients in a tubular system have been reported in the literature, which therefore precludes a direct comparison with the subject investigation. However, mass transfer data have been collected in geometrically similar systems and numerous hypotheses have been advanced to describe the turbulent transport process.

Before considering some of these theories, a brief description of the experimental devices employed to obtain data for their verification is appropriate, particularly to note the differences and similarities of experimental conditions relative to those prevailing in the dialysis system utilized in this investigation.

Two types of apparatus have been used to obtain mass transfer data in a tubular geometry, the wetted wall column and the pipe dissolution system. The wetted wall column basically consists of a vertical section of pipe in which a gas usually flows upward counter-current to a film of evaporating or absorbing liquid flowing down the inside surface of the pipe. The significant operational consideration encountered is with rippling effects inherent in such a system. The difficulty of determining the actual area of the disrupted vapor-liquid interface and the effect of this disruption on the fluid near the

interface is apparent. Typical of gas phase diffusion, the Schmidt mass transfer parameter is of the order of unity, ranging from 0.5 to 2.5.

The other method for obtaining data in a tubular system is to use pipes cast from some soluble material and to pass a solvent through the pipe. This system is better adapted for mass transfer studies since the geometry is better defined. However, fissures at the surface have been noticed (43) which would be expected to have an effect on the fluid conditions near the wall. Diffusion in liquids is about a thousand fold slower than in gases, and for systems studied to date, the Schmidt parameter has ranged from about 850 to 3000.

In both these systems there is a net transfer of mass in one direction. The effect of the attendant bulk motion, necessary for material balance considerations, is not accounted for satisfactorily. This is demonstrated by considering the pipe dissolution system with solute species A and solvent species B as depicted in Figure 7. A concentration gradient of the constituents is set up causing species A to diffuse away from the surface and species B to diffuse towards the surface. The counter-diffusion mechanism involved is a unique feature of the mass transport operation. Because the interface is impermeable to species B, a total concen-

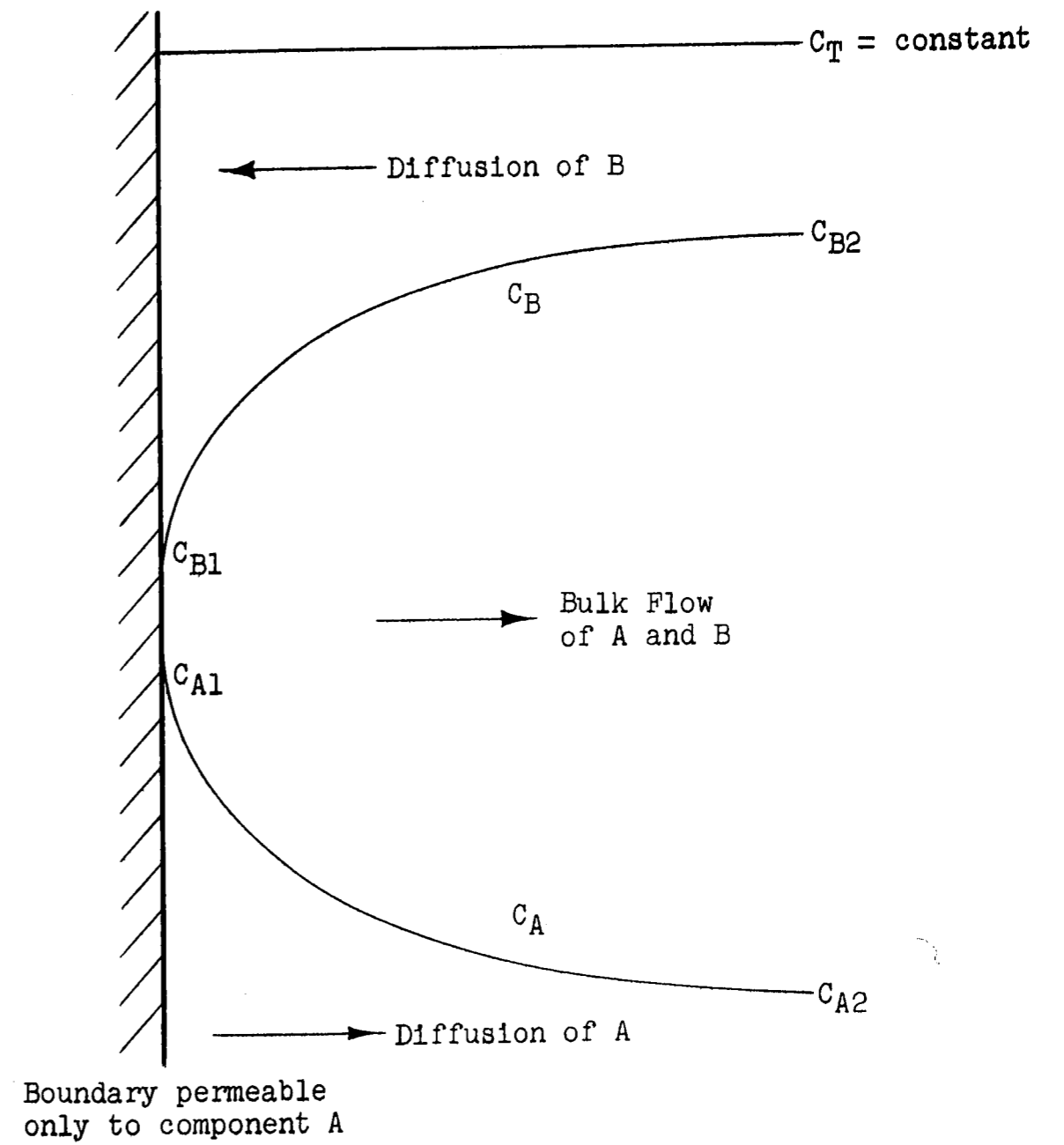


Figure 7 Concentration Gradients for the Pipe Dissolution System

tration gradient is produced causing a bulk flow of A and B away from the surface, in addition to the transfer of A by diffusion. It is the radial velocity of this bulk motion which would be expected to influence the fluid in the region near the interface.

It will be shown later that a small disturbance in the boundary layer of fluid near the wall has a predominant effect on the turbulent transport operation, particularly for systems of high Schmidt number, where the change in concentration occurs practically entirely across the region near the interface.

In such uni-directional mass transfer systems the correction factor  $C_T/C_{Bm}$  is usually employed. This term is obtained by considering a static system in which there is molecular transfer of component A through stationary component B. For the turbulent flow of component B through a tube, this correction is not valid, however the correlations of experimental data have been adjusted on this basis since none of component B passes through the boundary. It is apparent that only if the net mass transfer is minimal can the effect of the bulk motion be neglected.

With the wetted wall apparatus, the above described problem has been circumvented by operating the system as a rectifying column, such that the falling film



surface can be considered fully permeable. For a gaseous system at constant total pressure the total molar concentration is constant.

$$C_T = C_A + C_B = \text{constant} \quad (\text{V-18})$$

$$\frac{dC_A}{dx} = - \frac{dC_B}{dx} \quad (\text{V-19})$$

Hence, it follows from Fick's relation that the condition of equi-molar counter-diffusion

$$N_A = -N_B \quad (\text{V-20})$$

exists at every point in the gas.

For this system of equi-molar counter-diffusion, it has been shown (23) that if the species are of significantly different molecular weight, there will be a net transfer of mass which again can be expected to result in an unascertainable disturbance of the fluid near the interface.

Along with the above mentioned difficulty encountered with the formation of ripples, there is the problem in this rectification system of evaluating the mean values of the properties; these properties vary considerably

along the contact section and thereby render uncertain conclusions resulting from such an analysis (3, 27, 58).

We have noted previously that in order for the analogy between heat and mass transfer to be strictly applicable, the similarity of boundary conditions must be satisfied. This pre-supposes a zero net transfer of mass, which in turn requires the interface to be completely permeable to all constituents. This condition is satisfied with the dialysis system herein employed.

For a liquid system the total density is constant and hence the total mass concentration must remain constant throughout the fluid.

$$C_T = C_A + C_B = \text{constant} \quad (\text{V-21})$$

$$\frac{d C_A}{d x} = - \frac{d C_B}{d x} \quad (\text{V-22})$$

It follows that the mass flux in both directions is equal,

$$n_A = - n_B \quad (\text{V-23})$$

The porous nature of the dialysis membrane permits the counter-diffusion of the solute and solvent species to occur, thereby fulfilling the above condition. The surface is always smooth and well defined in this system. Also, the experiment can be carried out in such a manner that the transfer of mass is quite small concomitant with a very slight change in properties.

Theories of mass transfer in fluids have evolved primarily from the relations developed for the analogous heat transfer operation and from data acquired in the two mass transfer devices discussed above. The salient consideration of any hypothesis attempting to describe the turbulent transport of heat or mass must be a postulation of a model or picture of the hydrodynamic behavior of the fluid, particularly in the region close to the wall.

Momentum transfer from a moving fluid results in a shear stress at the tube wall, causing a decrease in fluid pressure along the tube length. This momentum transport is represented by the Navier-Stokes equation

$$\frac{g_c}{\rho} \frac{\partial P}{\partial x} = \frac{\nu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) \quad (V-24)$$

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which can be solved for a fluid in steady laminar motion to yield the parabolic velocity distribution across the tube.

In turbulent flow, this same relation is still applicable if instantaneous values of velocity and pressure are employed. However, the chaotic and random nature of the fluctuations renders insoluble this momentum balance. Reynolds modified the relation by substituting the mean values and fluctuating values of the flow quantities

$$\begin{aligned} u_1 &= u + u' \\ v_1 &= v + v' \end{aligned} \quad (V-25)$$

in place of the instantaneous values. Upon substitution, the above equation reduces to

$$\frac{g_c}{\rho} \frac{\partial P}{\partial x} = \frac{\nu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) - \frac{1}{r} \frac{\partial}{\partial r} (r \overline{u'v'}) \quad (V-26)$$

The first term on the right hand side of the equation represents the shear stresses in the fluid due to the mean velocity and molecular viscosity, while the last term represents stresses in the fluid attributable to turbulent fluctuations.

It would appear that a statistical approach to this problem of turbulence would be appropriate. However, knowledge of velocity fluctuations and their correlations would be required. To date, limited data are available for bounded turbulent flow (anisotropic turbulence), hence the problem of predicting mean values of velocity has not been satisfactorily resolved. Furthermore, the mathematical complexity of such problems make it difficult to count on significant success in the very near future in the application of statistical theory to the study of anisotropic turbulence.

The semi-empirical or phenomenological theories of turbulence, as initiated by Prandtl in 1925, have proven to be reasonably successful in predicting mean flow character. Prandtl's "mixing length" concept, though over-simplified, has some justification in that it was derived by analogy with the kinetic theory of gases, and considers the migration of fluid eddies rather than molecular motion. In essence, he visualized the "mixing length" as the distance a particle of fluid moved transverse to the mean flow, before it lost its identity and mingled with molecules of other particles to form new particles of fluid.

There has been criticism of the phenomenological models, stemming mainly from objections to the detailed inferences regarding the structure of turbulent flow.

However, it should also be noted that theories based on this approach result in relations of only nominal mathematical complexity, when compared to those obtained by the statistical approach, and have found surprising usefulness in predicting the behavior of turbulent transport.

Prandtl defined the mixing length by the equation

$$u' = l \frac{du}{dy} \quad (V-27)$$

and considered the fluctuating components of velocity,  $u'$  and  $v'$ , as being of the same order of magnitude. The turbulent shear stress can then be expressed as

$$\tau_t = \frac{e}{g_c} \overline{u'v'} = \frac{e}{g_c} \left( l \frac{du}{dy} \right)^2 \quad (V-28)$$

If the eddy diffusivity of momentum is defined as

$$\epsilon = l^2 \frac{du}{dy} \quad (V-29)$$

then

$$\tau_t \frac{g_c}{\rho} = \epsilon \frac{du}{dy} \quad (V-30)$$

Employing the Prandtl mixing length concept and the eddy diffusivity, equation (V-26) can be written

$$\frac{g_c}{\rho} \frac{\partial P}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r (\nu + \epsilon) \frac{\partial u}{\partial r} \right] \quad (V-31)$$

For tubular flow

$$\tau = \frac{r}{2} \left( - \frac{\partial P}{\partial x} \right) = \tau^0 \frac{r}{R} \quad (V-32)$$

$$\frac{g_c}{\rho} \frac{\partial P}{\partial x} = \frac{2\tau^0 g_c}{\rho R} \quad (V-33)$$

Substitution in equation (V-31) and integration yield

$$\frac{\tau g_c}{\rho} = - (\nu + \epsilon) \frac{du}{dr} \quad (V-34)$$



Since  $y = R - r$  and  $dy = -dr$

$$\tau_{\xi c} = (\nu + \epsilon) \frac{d(u\rho)}{dy} \quad (V-35)$$

which shows the additivity of the stresses due to viscous and eddy motion.

For the transfer of mass in a moving fluid, it has been shown previously that the equation

$$u \frac{\partial c}{\partial x} = \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \quad (V-36)$$

is valid for the condition of counter-diffusional mass transfer. As with the Navier-Stokes relation, this equation can be modified to include the velocity fluctuations. Additionally, the concentration fluctuations of turbulent transport can be incorporated.

$$u \frac{\partial c}{\partial x} = \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) - \frac{1}{r} \frac{\partial}{\partial r} (r \overline{v'c'}) \quad (V-37)$$

Carrying out an analysis similar to the one presented above will yield the analogous turbulent mass transfer equations

$$u \frac{\partial c}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} r (\mathcal{D} + \epsilon_M) \frac{\partial c}{\partial r} \quad (V-38)$$

$$n = - (\mathcal{D} + \epsilon_M) \frac{dc}{dy} \quad (V-39)$$

The latter shows the additive nature of the transport of mass in terms of the molecular and eddy contributions.

It is usually assumed that the mixing length for mass transfer is the same as the mixing length for momentum transfer, i.e.

$$\epsilon = \epsilon_M \quad (V-40)$$

The resulting equations,

$$\tau_{\epsilon c} = (\nu + \epsilon) \frac{d(u\rho)}{dy} \quad (V-41)$$

$$n = - (\mathcal{D} + \epsilon) \frac{dc}{dy} \quad (V-42)$$

therefore represent the formal basis for the various relations between mass transfer and momentum transfer, which have been developed to predict rates of mass transfer from friction losses and velocity profiles.

Equation (V-41) can be employed with experimental data regarding the turbulent velocity profile in order to obtain the eddy diffusivity of momentum. This procedure was facilitated by using the generalized velocity correlations relating the  $u^+$  and  $y^+$  parameters, defined as:

$$u^+ = \frac{u}{\sqrt{\frac{\tau_{gc}^0}{e}}} = \frac{u}{U \sqrt{\frac{f}{2}}} \quad (V-43)$$

$$y^+ = \frac{y}{\nu} \sqrt{\frac{\tau_{gc}^0}{e}} = \frac{y}{\nu} U \sqrt{\frac{f}{2}} \quad (V-44)$$

Upon introducing these variables, equations (V-41) and (V-42) can be rewritten as

$$\frac{du^+}{dy^+} = 1 / \left( \frac{\epsilon}{\nu} + 1 \right) \quad (V-45)$$

$$- \left( \frac{\tau_{gc}^0}{e} / n^0 \right) \frac{dc}{dy^+} = 1 / \left( \frac{\epsilon}{\nu} + \frac{1}{N_{Sc}} \right) \quad (V-46)$$

It has been assumed that  $\tau = \tau^0$  and  $n = n^0$  since most of the resistance is near the tube wall.

In principle, these equations can be integrated to yield the velocity and concentration profiles

$$u^+ = \int_0^{y_1^+} \frac{dy^+}{(\mathcal{E}/\nu + 1)} + \int_{y_1^+}^{y^+} \frac{dy^+}{(\mathcal{E}/\nu)} \quad (V-47)$$

$$\frac{c^0 - c}{n^0} \sqrt{\frac{\tau_{gc}^0}{e}} = \int_0^{y_1^+} \frac{dy^+}{(\mathcal{E}/\nu + 1/N_{Sc})} + \int_{y_1^+}^{y^+} \frac{dy^+}{(\mathcal{E}/\nu)} \quad (V-48)$$

The integrals have been separated into two parts (52) with the limit  $y_1^+$  pertaining to a distance from the tube wall beyond which the transfer due to molecular diffusion is negligible. These two equations can be subtracted to give

$$\frac{c^0 - c}{n^0} U = \frac{2}{f} + \sqrt{\frac{2}{f}} \int_0^{y_1^+} \left[ \frac{1}{(\mathcal{E}/\nu + 1/N_{Sc})} - \frac{1}{(\mathcal{E}/\nu + 1)} \right] dy^+$$

$$\frac{1}{N_{St}} = \frac{2}{f} + \sqrt{\frac{2}{f}} \Psi(N_{Sc}) \quad (V-49)$$

where  $\Psi(N_{Sc})$  depends on the relation between  $\mathcal{E}$  and  $y^+$ . Equation (V-49) shows the basic form which the mass and heat transfer analogies have taken.

For a Schmidt number of unity  $\Psi(N_{Sc}) = 0$  and equation (V-49) reduces to the well known Reynolds analogy.

$$N_{St} = \frac{f}{2} \quad (V-50)$$

or 
$$N_{Sh} = \frac{f}{2} N_{Re} N_{Sc} = \frac{f}{2} N_{Re}$$

A simple extension of this relation to include systems of higher  $N_{Sc}$  is the wholly empirical Chilton-Colburn equation (5, 6)

$$N_{St} N_{Sc}^{.67} = \frac{f}{2} \quad (V-51)$$

$$N_{Sh} = \frac{f}{2} N_{Re} N_{Sc}^{.33}$$

Both this equation, and its analogous heat transfer counterpart,

$$N_{St}' N_{Pr}^{.67} = \frac{f}{2} \quad (V-52)$$

$$N_{Nu} = \frac{f}{2} N_{Re} N_{Pr}^{.33}$$

have been extensively used in correlating transport data from a variety of heat and mass transfer systems, where skin friction rather than form drag effects are predominant. Their simplicity of form (no constants need be evaluated), and their apparent success in achieving reasonable experimental agreement, have attained for these relations a reputation as a panacea, which is remarkable in view of the fact that there is no theoretical basis for their existence. A number of investigators have employed slightly different exponents on the  $N_{Pr}$  or  $N_{Sc}$  parameter, along with an  $L/D$  function to correlate their data (26, 31, 63). In all cases however, the direct proportionality between the film coefficient and the friction factor, as established by the Reynolds analogy, is maintained.

For a more comprehensive extension of the phenomenological approach to this transport problem, an extension to encompass system Schmidt numbers differing from unity, certain further assumptions regarding the nature of the turbulent flow had to be postulated in order to solve equations (V-41) and (V-42) which have been established as the foundation of this semi-empirical procedure.

Early investigators (Prandtl and Taylor) divided the flow into two regions; they postulated a laminar

layer of fluid adjacent to the surface in which the transport processes were assumed wholly molecular, and a turbulent layer in which the molecular transport processes were neglected. This procedure resulted in an improvement over the Reynolds analogy for  $N_{Sc}$  differing moderately from unity; however, these methods suffered from an arbitrary choice of the laminar layer thickness.

The next significant improvement in advancing a more realistic mechanism of turbulent transfer was made by von Karman (30) who introduced a buffer layer between the turbulent core and a laminar sublayer near the wall. He divided the universal velocity distribution into these three regions using the same assumption as Prandtl regarding the laminar layer and turbulent core, while for the buffer region both molecular and turbulent transports were assumed. Von Karman's analysis was for the heat transfer operation; confirmation of his relation was obtained by comparison with the data of Eagle and Ferguson (15) which were extrapolated to isothermal conditions of zero heat transfer and constant fluid properties. The particular choice of the laminar sublayer thickness was intended for the range of the Prandtl number investigated (0.73 to 40).

Sherwood (55) has adapted von Karman's relation to the mass transfer operation. This expression can be

put in terms of the dimensionless parameters for fluid flow and mass transfer to yield

$$\frac{1}{N_{St}} = \frac{2}{f} + \sqrt{\frac{2}{f}} \Psi(N_{Sc})$$

$$\text{where } \Psi(N_{Sc}) = 5 \left[ (N_{Sc} - 1) + \ln \left( 1 + \frac{5}{6}(N_{Sc} - 1) \right) \right]$$

When expressed in terms of the Sherwood parameter, the above equation reduces to

$$N_{Sh} = \frac{\frac{f}{2} N_{Re} N_{Sc}}{1 + \sqrt{\frac{f}{2}} \Psi(N_{Sc})} \quad (V-53)$$

With the picture of a laminar sublayer controlling the diffusion process (at high values of  $N_{Sc}$ ), the above relation shows the mass transfer coefficient to be proportional to the first power of the molecular diffusivity, i.e.,

$$k \sim D$$

Von Karman's equation was found to be in substantial agreement with mass transfer data at low Schmidt number,



but not too effective in correlating high Schmidt number systems (of the order of a thousand). This would indicate the not wholly realistic nature of the laminar sublayer assumption in which transfer is only by molecular motion.

At low Schmidt number (gaseous systems), the contribution of the resistance to transfer of the region near the wall to the over-all resistance is not influenced too markedly by assumptions regarding the velocity distribution in this region. However, at large values of  $N_{Sc}$  (liquid systems), the region near the wall is of major importance since the concentration changes from its value at the interface to the mainstream value over a narrow region much thinner than the laminar sublayer.

In liquid systems the molecular diffusivity is very small so that slight turbulence very near the wall can be quite critical. Experimental velocity traverses lack the necessary precision to describe the variation of the eddy diffusivity in the wall region, and hence cannot provide an experimental basis for a true analogy which will be sound at high Schmidt number. Instead, empirical functions for the eddy diffusivity in this region have been successfully employed demonstrating the picture of turbulent decay all the way to the wall to be a more realistic representation of the turbulent transport phenomenon.

This behavior has been noted by Fage and Townend (17) who observed the motion of small particles in a turbulent water stream very near the wall. It was found that no fluctuation of the particles in the radial direction took place, indicating the flow to be of the laminar type. However, the motion of the particles in the laminar layer was sinuous, and no particle was observed to move in a straight path, demonstrating the effect that eddies in the turbulent core have in superimposing disturbances upon the laminar sublayer.

This phenomenon has been verified by Laufer (38) who found that velocity perturbations exist in the laminar sublayer by employing a hot wire anemometer apparatus. The results prove conclusively that the laminar sublayer velocity profile is of an oscillatory nature. However, this sublayer is indicated to be quite stable, though unsteady, with the velocity profile being very nearly linear. The random disturbances imposed upon the sublayer by the adjacent turbulent layers can be sustained without permitting them to amplify.

The most successful analyses, of the type which make certain allowance for turbulence all the way to the wall, appear to be those of Lin (41) and Deissler (10). The assumed variation of  $\epsilon$  with  $y^+$  that Lin

selected is

$$\frac{\varepsilon}{\nu} = \left( \frac{y^+}{14.5} \right)^3 \quad (V-54)$$

When substituted in equation (V-46), this gives a relation of the form shown in equation (V-49) where

$\Psi(N_{Sc})$  is a complicated function of the Schmidt parameter. At high  $N_{Sc}$  this reduces to

$$N_{Sh} = .057 \sqrt{\frac{f}{2}} N_{Re} N_{Sc}^{.33} \quad (V-55)$$

or

$$N_{Sh} = .0113 N_{Re}^{.875} N_{Sc}^{.33}$$

The mass transfer coefficient is indicated to be proportional to the two-third power of the diffusivity.

$$k \sim D^{.67}$$

The expression for eddy diffusion near the wall that Deissler employed is basically empirical, though derived from dimensional reasoning.

$$\frac{\varepsilon}{y} = n^2 u^+ y^+ (1 - e^{-n^2 u^+ y^+}) \quad (V-56)$$

He obtained the following equation for a high Schmidt number system.

$$N_{Sh} = .112 \sqrt{\frac{f}{2}} N_{Re} N_{Sc}^{.25} \quad (V-57)$$

$$N_{Sh} = .0222 N_{Re}^{.875} N_{Sc}^{.25}$$

Deissler's equation shows the mass transfer coefficient to be proportional to the three-quarter power of the diffusivity,

$$k \sim D^{.75}$$

The reduced form for each of the Lin and Deissler equations employ the Blasius expression

$$f = .079 N_{Re}^{-.25} \quad (V-58)$$

for the friction factor relation.

The variation of local Sherwood number with distance from the tube inlet was also calculated by

Deissler (10). His results indicate that for a Schmidt number of 1000, the local Sherwood number approached the fully developed Sherwood number after an entrance length of one to two tube diameters for Reynolds' numbers between 10,000 and 30,000. Meyerink, in his pipe dissolution study (48), has also verified these conclusions. Results for the dialysis system herein employed,  $N_{Sc} = 800$  and  $L/D = 48$ , can therefore be considered to be little affected by the entrance length required to achieve the fully developed concentration profile.

Both the predictions of Lin and Deissler fit the data for low and high Schmidt numbers, in spite of the different exponents of diffusivity used in equations (V-55) and (V-57). This is not surprising since the eddy diffusion assumed in the viscous layer has little effect on the transfer rate for low Schmidt numbers and the numerical constants can be adjusted to fit the data for systems of high Schmidt numbers where all the gradient is in the viscous layer.

The above relations of von Karman, Lin, and Deissler, derived from the basic transport equations (V-41) and (V-42), all show the film coefficient to be (at high  $N_{Sc}$ ) proportional to the square root of the friction factor and indicate this coefficient to be proportional to the diffusivity with an exponent value ranging from

unity (laminar film controlling) to two-thirds. It is interesting to note that the penetration theory (7, 24), in which there is no laminar sublayer at the boundary, predicts the rate to be proportional to the square root of the diffusivity, i.e.,

$$k \sim D^{.5}$$

The individual tubular film coefficients obtained in this investigation are plotted in Figure 8 in the form of the Sherwood parameter as a function of the Reynolds number for the system Schmidt number of 800. Also shown in the figure are the lines predicted by von Karman, Lin and Deissler. The Chilton-Colburn line, equation (V-51), showing a direct proportionality between the film coefficient and the friction factor, is also included.

The data points shown in Figure 8 can be represented by the equation

$$N_{Sh} = .069 N_{Re}^{.90} \quad (V-59)$$

These results appear to support the general form of the Deissler, Lin, and von Karman theories as far as the relation between the film coefficient and the friction factor is concerned.

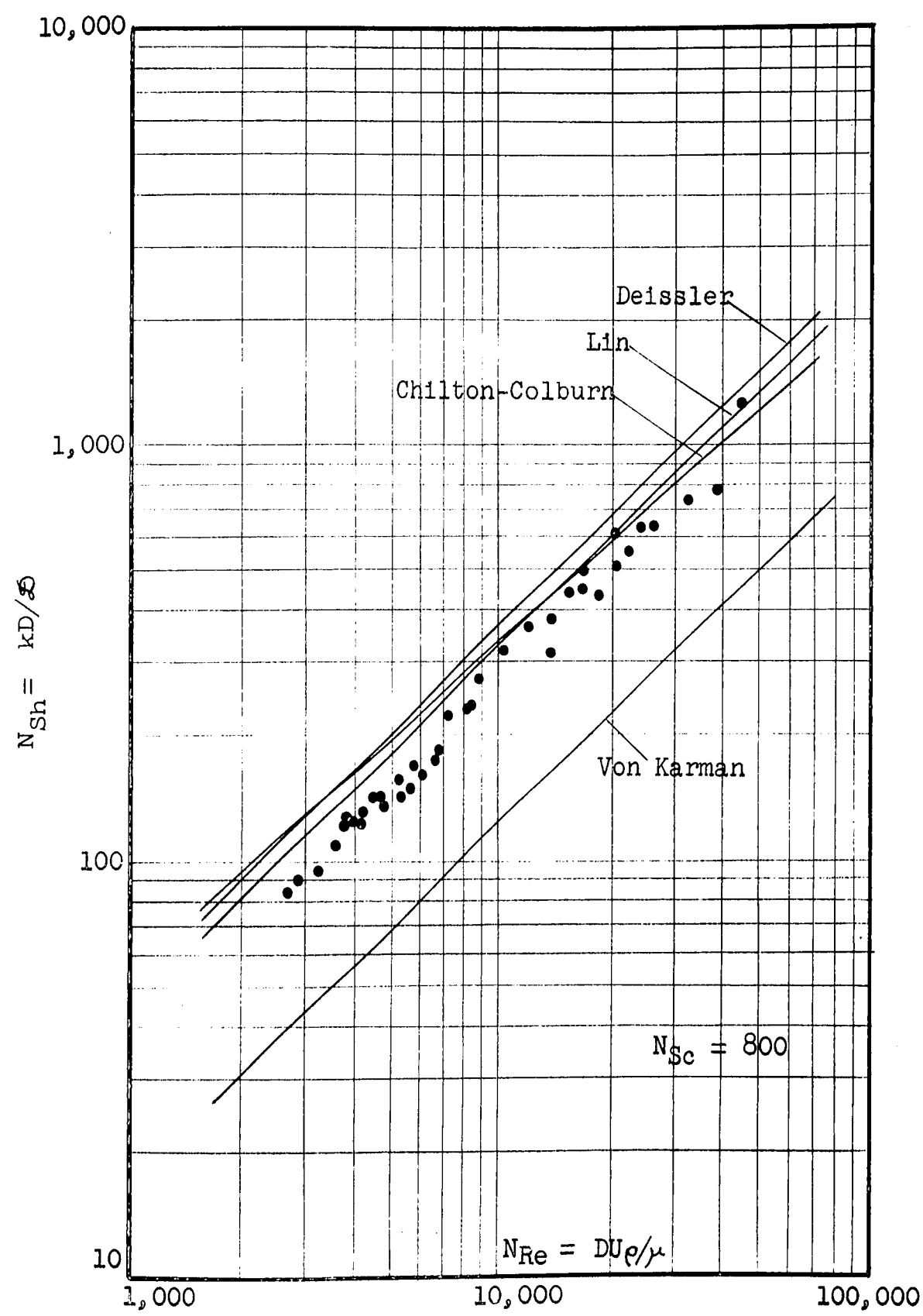


Figure 8 Turbulent Mass Transfer - Sherwood Plot

The recent pipe dissolution data of Meyerink (48) also substantiates reasonably well the square root rather than the linear relationship. For the dissolution of benzoic acid and cinnamic acid in water ( $N_{Sc} = 900$ ), he obtained

$$N_{Sh} = .070 N_{Re}^{.94} \quad (V-60)$$

and for the aspirin-water system ( $N_{Sc} = 850$ ) the equation

$$N_{Sh} = .168 N_{Re}^{.86} \quad (V-61)$$

represented the data. These experimental results fall on or slightly above the Deissler correlation for the particular system Schmidt number involved.

The recent Deissler and Lin theories use much of the same data to support their theories and to adjust the constants in their equations. Most of the high Schmidt number results were taken in systems (pipe dissolution apparatus) where the mass transfer was uni-directional and hence could be expected to be slightly higher than they should be owing to the attendant bulk motion of the fluid. This uni-directional transfer has been previously shown to result in a radial component of velocity not accounted for in the mass transfer equation employed.



With the dialysis tubing utilized in this investigation this problem is not present since the porous membrane permits the counter-diffusion of solute and solvent such that the mass flux in both directions is equal, thereby satisfying the same boundary conditions required of the analogous transport equations.

The experimental results indicated in Figure 8 fall about 25% and 15% below the lines predicted by Deissler and Lin respectively, which qualitatively is as expected due to the counter-diffusion mechanism involved in the dialysis system. However, the data are considerably above the von Karman prediction (laminar film controlling) and would tend to support the Deissler-Lin picture of transfer which allows for a decay of turbulence all the way to the wall.

The film coefficients predicted by the various theories are cross-plotted in Figure 9 in the form of the mass transfer Stanton number  $k/U$  as a function of the Schmidt parameter for a Reynolds number of 25,000. Shown also is the point calculated from equation (V-59) which represents the results of this investigation at  $N_{Sc} = 800$ .

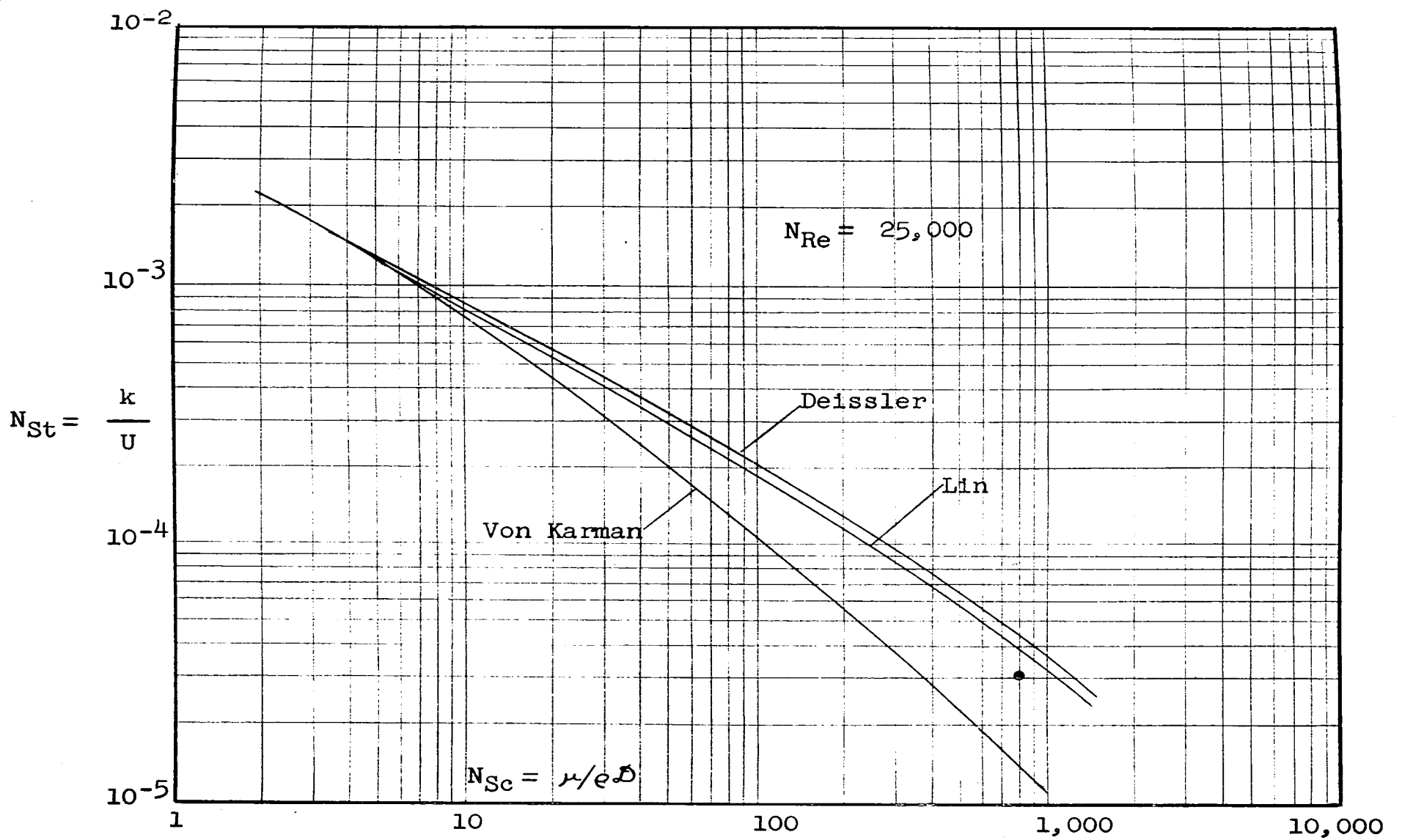


Figure 9 Turbulent Mass Transfer - Stanton Plot

An examination of the hydrostatics of the experimental system herein employed indicates that the lower results of this study may in part be due to a viscous transfer effect brought about by a pressure differential between the tubular water stream (sp. g. = 1.0) and the annular saturated salt stream (sp. g. = 1.2). A more detailed discussion of this point is presented in APPENDIX J.

### C. Laminar Flow Regime

It has been shown previously that the chaotic nature of turbulent flow renders virtually impossible a complete and definitive analysis of the turbulent mass transfer mechanism. By contrast, a fluid in laminar motion can be exactly defined mathematically with the use of the Navier-Stokes momentum equation (V-24) for the particular boundary conditions involved. For laminar flow in a tube ( $N_{Re} < 2100$ ), the parabolic velocity distribution can easily be obtained.

$$u = 2U \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \quad (V-62)$$

This relation can be visualized as representing the velocity of a series of concentric thin tubes sliding inside one another in the direction of flow. For such conditions, no radial mixing of the fluid occurs and the transfer of solute from the tube wall into the fluid stream is solely by molecular diffusion.

The inter-relationship between the fluid motion and the diffusion process can be obtained by substituting Fick's relation

$$n_A = -D_{AB} \frac{dC_A}{dx} \quad (V-63)$$

into the equation of continuity for a binary system

$$\nabla e_A \vec{v} = 0 \quad (V-64)$$

The resulting relation

$$u \frac{\partial c_A}{\partial x} = \mathcal{D}_{AB} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_A}{\partial r} \right) \quad (V-65)$$

represents the diffusion process for a fluid in streamline motion.

For the analogous laminar flow heat conduction problem, the relation

$$u \frac{\partial T}{\partial x} = \frac{k}{\rho c} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \quad (V-66)$$

can be similarly obtained.

The solution of the basic differential form for the heat transfer situation has been carried out by Graetz for the case of a normal parabolic velocity distribution and for the case of constant velocity across the tube diameter (rod-like flow). These mathematical analyses are reviewed by Drew (12) and Jakob (28). The following

are the assumptions common to these solutions when converted to the appropriate terminology of diffusion:

- 1) The radial velocity component is zero everywhere.
- 2) The diffusivity  $\mathcal{D}$  is constant throughout the liquid.
- 3)  $C = C_1$  at  $x = 0$  for all  $r$ .  
 $C = C^\circ$  at  $r = R$  for all  $x$ .
- 4) Molecular diffusion in the  $x$  direction is negligible.
- 5) The pipe diameter is uniform.
- 6) The physical properties of the fluid are constant.

The Graetz solution for the parabolic velocity solution, as applied to the mass transfer problem, is

$$\frac{C_2 - C_1}{C^\circ - C_1} = 1 - 8 \left[ .1023 e^{-14.63 \mathcal{f}} + .0122 e^{-89.22 \mathcal{f}} \right] \quad (V-67)$$

where 
$$\mathcal{f} = \frac{\pi}{4} \frac{\mathcal{D} e L}{W}$$

Concerning the assumption of uniform velocity across the pipe, the Graetz solution is

$$\frac{C_2 - C_1}{C^\circ - C_1} = 1 - 4 \left[ .1729 e^{-5.784 \mathcal{f}} + .03282 e^{-30.47 \mathcal{f}} \right] \quad (V-68)$$

When values of the term  $W/D_e L$  are very large, the evaluation of the above series solutions becomes excessively laborious and is avoided by the asymptotic approximation of Leveque. This solution applies directly to transfer from a flat plate, however, its application to flow in tubes is valid where the diffusing material penetrates but a short distance into the fluid stream while in the contact section. The solution for parabolic flow is obtained by assuming the fluid to have a linear velocity distribution equal to the limiting velocity distribution found near the wall in streamline flow. By using the same assumptions as Graetz, Leveque determined the solution to be

$$\frac{C_2 - C_1}{C^0 - C_1} = 5.55 \left( \frac{W}{D_e L} \right)^{-2/3} \quad (V-69)$$

Employing the constant velocity assumption instead of a linear distribution, Linton has shown (43), by a similar derivation, that the solution for the rod-like flow case can be expressed by

$$\frac{C_2 - C_1}{C^0 - C_1} = 4.00 \left( \frac{W}{D_e L} \right)^{-1/2} \quad (V-70)$$

For the dialysis system, the liquid diffusivity is very small and hence the basic assumption under which the simpler Leveque equations were derived is valid.

All of the above relations can be conveniently represented by a graph of  $(C_2 - C_1/C^\circ - C_1)$  versus  $(W/D_e L)$ , as shown in Figure 10. The dialysis laminar regime results obtained in this investigation are also plotted. For purposes of comparison, there are depicted as shaded areas the laminar data collected by Linton in his pipe dissolution study (43), and the wetted wall column data of Gilliland (vaporization) (20), and Haslam (absorption) (25), as taken from Sherwood's text (56).

The dialysis results fall above the line for parabolic flow and approach the rod-like flow curve as the flow rate decreases. Since the flow is viscous, the data would be expected to conform to the parabolic curve. These high values are believed to be the result of free convection effects caused by density gradients. In the laminar regime, the fluid has a higher residence time in the contact section, and hence picks up a greater amount of salt. The concentration of the exit fluid ranges from .0153 gms/cu.cm. at  $N_{Re} = 100$  to .0020 gms/cu.cm. at  $N_{Re} = 900$ . By contrast, the exit concentration of the turbulent regime results range from



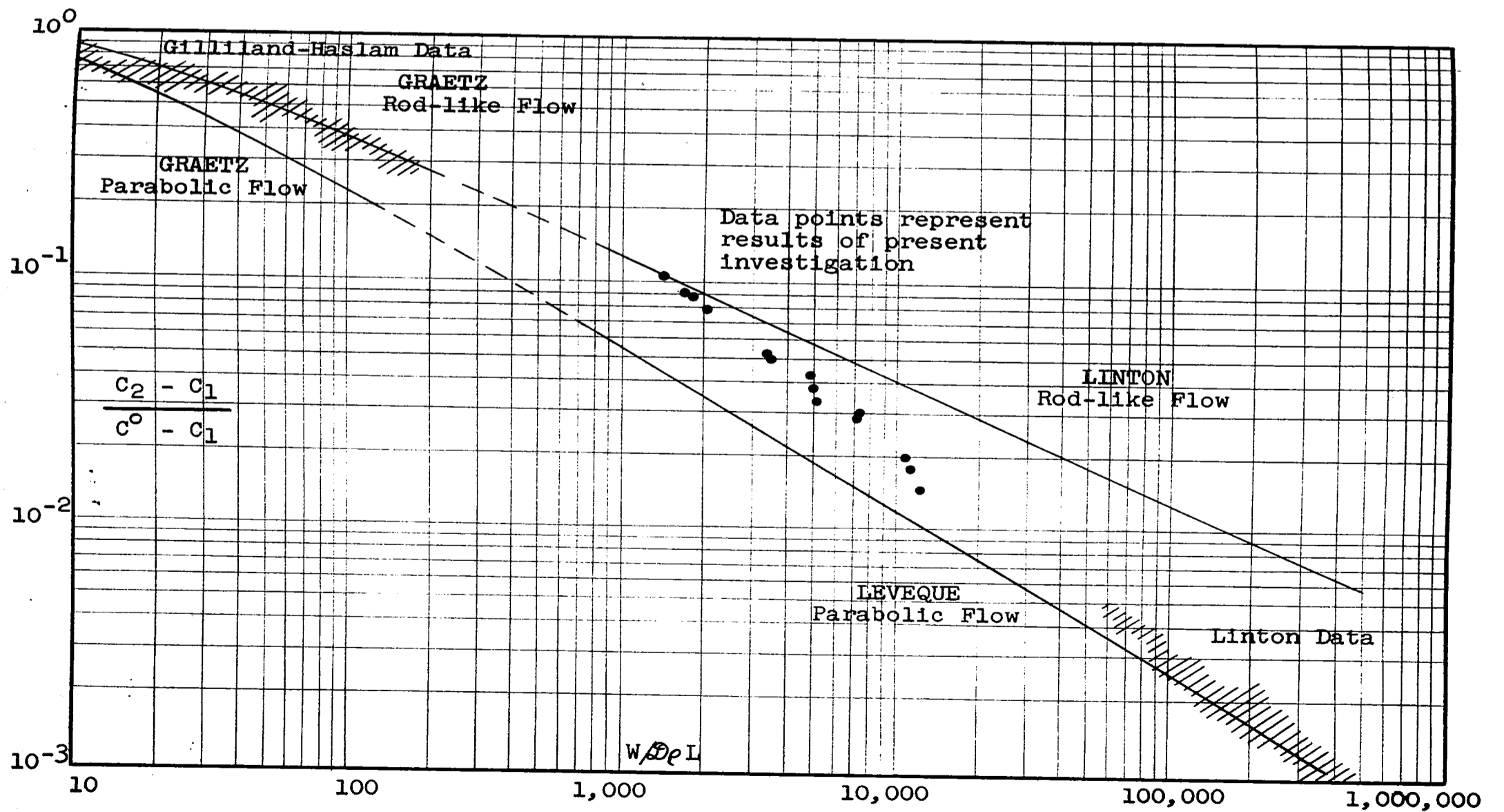


Figure 10 Mass Diffusion in Laminar Flow

.00075 gms/cu.cm. to .000075 gms/cu.cm. for a Reynolds number of 2700 and 45,000 respectively. The assumption of constant fluid properties is not entirely valid for the laminar regime. The results, as shown in Figure 10, are qualitatively in the right direction and indicate a greater divergence from the parabolic curve as the flow rate decreases. Another factor which would tend to distort and upset the normal parabolic velocity distribution established in the entrance calming length, is the slight swaying motion of the tubular membrane. Again, this can be expected to have a greater effect at the lower flow rates.

It is interesting to note that the corresponding data for the analogous laminar flow heat conduction problem conform to the same pattern as the diffusion data presented in Figure 10. This can be seen in Figure 11 in which the heat transfer data of Holden and White, as tabulated by Drew (13), are plotted.

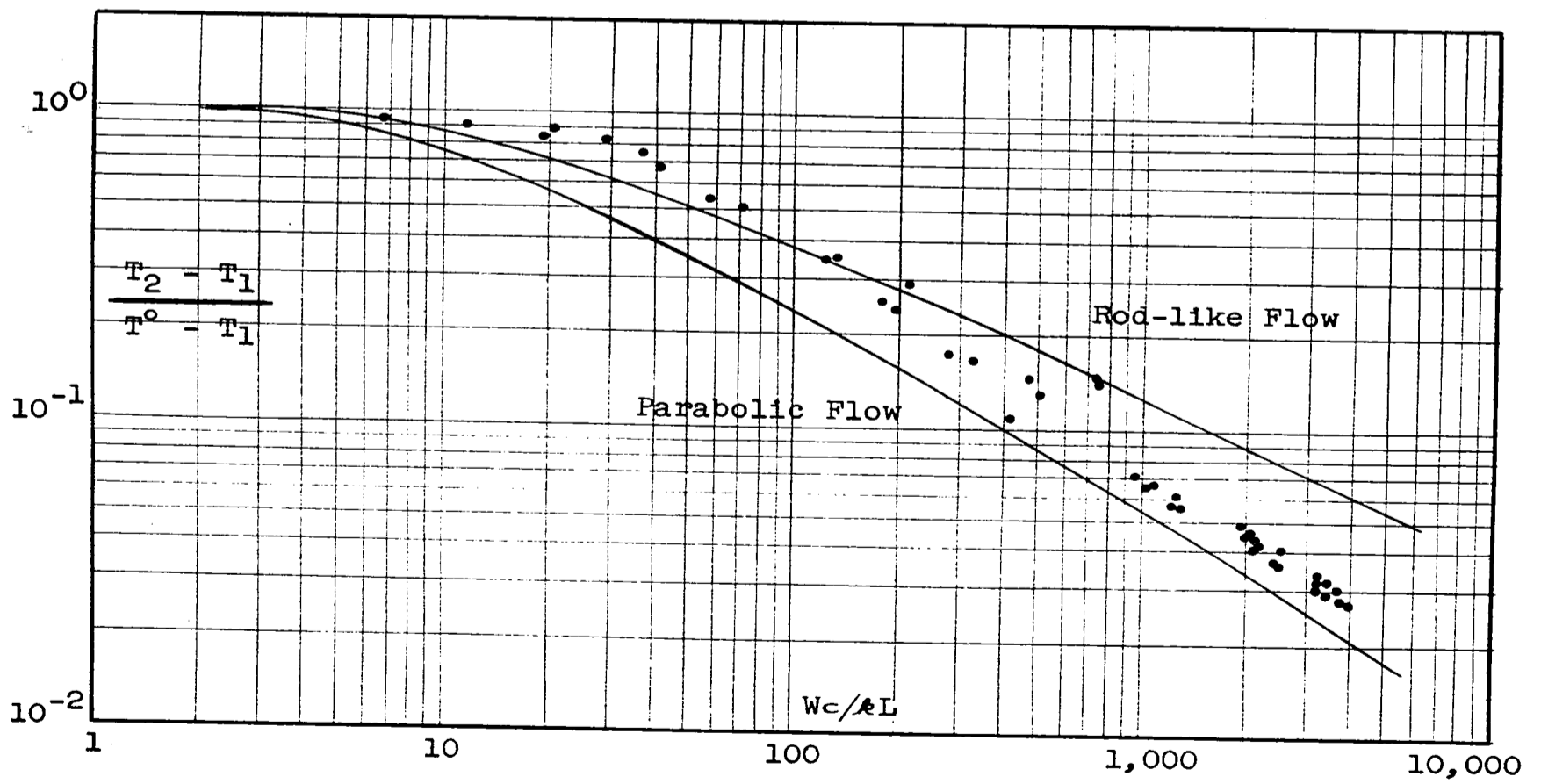


Figure 11 Heat Conduction in Laminar Flow

## VI. CONCLUSIONS

An experimental apparatus has been developed for studying the fluid resistance to the dialysis mass transfer operation. Investigation of the rate controlling factors influencing dialysis transfer with batch and filter press type dialyzers can now be complemented with a system in which the defined flow conditions permit the liquid film coefficient to be isolated and hence subject to analysis.

The results indicate that present mass transfer theory can be used to correlate the individual film coefficients obtained from a "Wilson technique" type treatment of the over-all resistance data collected. The dependence of  $N_{Sh}$  on  $N_{Re}$  is in good agreement with turbulent transport theory as far as the functional form of the friction factor is concerned, i.e.,

$$N_{Sh} \sim \sqrt{\frac{f}{2}} N_{Re} \Psi(N_{Sc})$$

Specifically

$$N_{Sh} = .069 N_{Re}^{.90}$$

for the system  $N_{Sc} = 800$ .

The laminar regime results are bounded by the theoretical equations of Leveque, and Linton for parabolic and uniform flow; and conform to the same pattern as the analogous heat conduction results in laminar flow.

The counter-diffusion mechanism involved in this process and the smooth, defined transfer surface suggests that this system can be effectively employed for studying the convective diffusion mechanism, particularly at much higher Schmidt numbers.

VII. APPENDIX

A. Derivation of Over-all Mass Transfer Equation

If a fluid flows parallel to a solid surface, the velocity increases rapidly from zero at the wall to an almost constant value a short distance away. This velocity gradient near the membrane wall is accompanied by a corresponding sharp change in the concentration of the fluid. A similar condition occurs on the other side so that the concentration distribution from a concentrated stream on one side to a dilute stream on the other will be of the form shown in Figure A-1.

It has been established that the rate of transfer, be it heat, mass, or momentum, is equal to the driving force divided by a resistance.

$$\text{Transfer Rate} = \frac{\text{Driving Force}}{\text{Resistance}} \quad (\text{A-1})$$

For mass transfer between two fluids separated by a porous membrane

$$n' = \frac{C_S - C_S^o}{1/k_S A_S} = \frac{C_S^o - C_W^o}{1/k_m A_m} = \frac{C_W^o - C_W}{1/k_W A_W} \quad (\text{A-2})$$

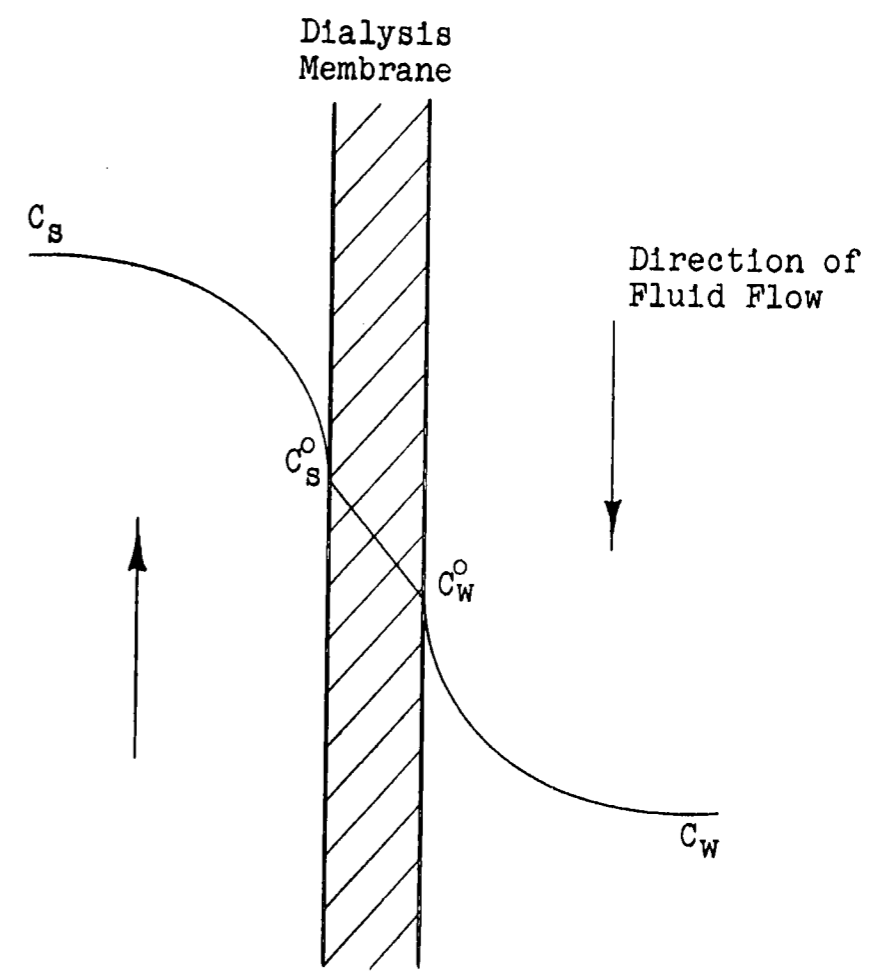


Figure A-1 Mass Transfer Between Two Fluids Separated by a Porous Membrane

or

$$c_s - c_s^o = \frac{n'}{k_s A_s} ; \quad c_s^o - c_w^o = \frac{n'}{k_m A_m} ; \quad c_w^o - c_w = \frac{n'}{k_w A_w}$$

from which

$$c_s - c_w = \Delta C = n' \left[ \frac{1}{k_s A_s} + \frac{1}{k_m A_m} + \frac{1}{k_w A_w} \right] \quad (A-3)$$

But an over-all coefficient of mass transfer  $K_m$  can be defined based on the area  $A_m$  such that

$$n' = K_m A_m \Delta C \quad (A-4)$$

Thus

$$\frac{n'}{K_m A_m} = \Delta C = n' \left[ \frac{1}{k_s A_s} + \frac{1}{k_m A_m} + \frac{1}{k_w A_w} \right]$$

giving

$$\frac{1}{K_m} = \frac{A_m}{k_s A_s} + \frac{1}{k_m} + \frac{A_m}{k_w A_w} \quad (A-5)$$

The over-all transfer coefficient may be based on the inside area, the outside area or the mean area of the tubular membrane. For the case of a very thin membrane these will not differ appreciably and the following may



be written.

$$\frac{1}{K} = \frac{1}{k_s} + \frac{1}{k_m} + \frac{1}{k_w} \quad (\text{A-6})$$

and

$$n' = K A \Delta C = K A (C_s - C_w) \quad (\text{A-7})$$

For the experimental system utilized in this investigation the above equation can be used directly by substituting the saturated salt concentration for  $C_s$  (.317 gms./cm<sup>3</sup>) and neglecting the water side concentration  $C_w$  (in the order of parts per million) to determine the over-all driving force  $\Delta C$ .

#### Mean Concentration Difference

For the sake of completeness the derivation of the mean concentration difference is shown for the situation where there is a difference, of the same order of magnitude, in  $C_s$  or  $C_w$  under the conditions that the density and mass flow of the two streams do not change appreciably. The method used by Foust, et. al. (19) in their derivation of the logarithmic mean temperature difference is adapted for dialysis mass transfer.

The salt stream flows at a constant rate of  $W_s$  gms./min. and changes in concentration from

$C_{s2}$  to  $C_{s1}$ . The water stream flows at a steady rate of  $W_w$  gms./min. and increases in concentration from  $C_{w1}$  to  $C_{w2}$ . The concentration driving force in the transfer direction at any point in the system is

$$\Delta C = C_s - C_w \quad (A-8)$$

Differentiating

$$d(\Delta C) = dC_s - dC_w \quad (A-9)$$

The mass given up by the salt stream as it passes through the dialyzer is

$$dn'_s = \frac{W_s}{e_s} dC_s \quad \text{or} \quad dC_s = \frac{e_s}{W_s} dn'_s \quad (A-10)$$

The mass gained by the water stream is

$$dn'_w = \frac{W_w}{e_w} dC_w \quad \text{or} \quad dC_w = \frac{e_w}{W_w} dn'_w \quad (A-11)$$

Combining equations (A-10) and (A-11) with equation (A-9) yields

$$d(\Delta C) = \frac{e_s}{W_s} dn'_s - \frac{e_w}{W_w} dn'_w = dn'_s \left[ \frac{e_s}{W_s} + \frac{e_w}{W_w} \right] \quad (A-12)$$

since  $dn'_s + dn'_w = 0$  at steady state. Assuming the terms in the brackets are constant this equation may be integrated between 0 and  $n'$  and between the limits of  $\Delta C_1$  and  $\Delta C_2$  to give

$$(\Delta C_2 - \Delta C_1) = n'_s \left[ \frac{e_s}{W_s} + \frac{e_w}{W_w} \right] \quad (A-13)$$

At any particular point in the system

$$dn' = K \Delta C \, dA \quad (A-14)$$

Combining equation (A-12) with equation (A-14) yields

$$dn'_s = K \Delta C \, dA = d(\Delta C) / \left[ \frac{e_s}{W_s} + \frac{e_w}{W_w} \right] \quad (A-15)$$

Rearrangement of this equation to separate variables for integration, with  $K$  being assumed constant gives

$$K \left[ \frac{e_s}{W_s} + \frac{e_w}{W_w} \right] \int_0^A dA = \int_{\Delta C_1}^{\Delta C_2} d(\Delta C) / \Delta C \quad (A-16)$$

which upon integration becomes

$$\left[ \frac{e_s}{W_s} + \frac{e_w}{W_w} \right] K_A = \ln \frac{\Delta c_2}{\Delta c_1} \quad (\text{A-17})$$

But from equation (A-13)

$$\left[ \frac{e_s}{W_s} + \frac{e_w}{W_w} \right] = \frac{\Delta c_2 - \Delta c_1}{n'_s} \quad (\text{A-18})$$

Therefore substituting equation (A-18) into equation (A-17) gives

$$\left[ \frac{\Delta c_2 - \Delta c_1}{n'_s} \right] K_A = \ln \frac{\Delta c_2}{\Delta c_1} \quad (\text{A-19})$$

Rearranging

$$n'_s = K_A \left[ \frac{\Delta c_2 - \Delta c_1}{\ln(\Delta c_2 / \Delta c_1)} \right] = K_A (\Delta c)_{lm} \quad (\text{A-20})$$

The bracketed term of equation (A-20) defines the logarithmic-mean concentration driving force  $(\Delta c)_{lm}$ .

Equations (A-7) and (A-20) are applicable for cases where the following assumptions are valid.

- a) The over-all coefficient  $K$  is constant. This is not rigorously valid, but for fluids whose

physical properties are not too sensitive to small concentration variations, the over-all coefficient based upon average fluid properties leads to little error.

- b) The densities of the two fluids do not change with concentration.
- c) The mass flow of both fluids is constant.

In this investigation the above conditions are satisfied since the amount of material transferred from one fluid to the other is quite small (as stated previously, in the order of parts per million) so that the density and the mass flow of the two fluids does not change appreciably.

VII. APPENDIXB. Details of Procedure1. Startup Procedure

The dialysis membrane was immersed in water for about three hours to remove the glycerine humectant used in its packaging. It was then allowed to soak in a 15% salt solution for at least 48 hours in order for the membrane to attain its maximum degree of swelling. This is important since obviating this step would result in the membrane resistance changing during the course of a set of runs. Before its installation it was again washed in water.

The ends of the membrane were slipped over the connecting steel tube sections and clasped tightly by means of masking tape and hose clamps. The two tubes with the membrane were lowered into the column with great care taken to insure that the membrane was not injured. The lower connecting tube section was joined to the external pipework by means of a four-inch Dresser coupling. The pumps were started, permitting the fluid in the feed drums to circulate through the by-pass lines. The stopcock valve on the upper Dresser assembly was opened to allow the air in

S

the system to escape. Saturated solution from the salt feed drum was permitted to gradually flow down from the annulus inlet line until the level of the solution was slightly above the lower connecting tube section sticking into the column. Water was poured into the upper connecting tube section down through the membrane into the lower tube section until the level in the membrane matched the level in the annulus. The salt solution was pumped gradually into the annulus while water was poured into the tubular membrane at a rate such that the liquid levels were about the same during the filling operation. The upper connecting tube was then joined to the water system pipework and fluid from the water feed drum allowed to pass upward through the tubular membrane. The flows of both streams were simultaneously increased in a gradual manner, along with the manipulation of the back pressure valves so as to maintain the streams on both sides of the membrane at essentially the same pressure. The membrane was pulled taut and any twist in the membrane corrected by manipulating the connecting tube sections and the Dresser couplings.

The system was permitted to run for approximately two hours to attain steady state conditions. Each run lasted about three quarters of an hour,

during which time rotameter readings and photographs were taken, and samples of the solvent and diffusate streams were obtained in 1000 cubic centimeter Erlenmeyer flasks.

## 2. Measurement of Flow Rates

The tubular water flow was measured with the use of three rotameters in parallel to cover the range of tubular flow conditions investigated in this study. Calibration curves for these rotameters are indicated in Figures A-2, A-3, and A-4.

The saturated salt solution in the annulus was maintained at essentially the same flow rate and its measurement was similarly obtained with a rotameter. Figure A-5 shows the calibration curve for this instrument.

## 3. Measurement of the Membrane Diameter

A Polaroid Land Camera (Speedliner Model 95A) was employed to determine the diameter of the tubular membrane. Photographs were taken at the upper and lower end of the column. Supporting stands were used to assure that the same camera position was maintained for each shot.



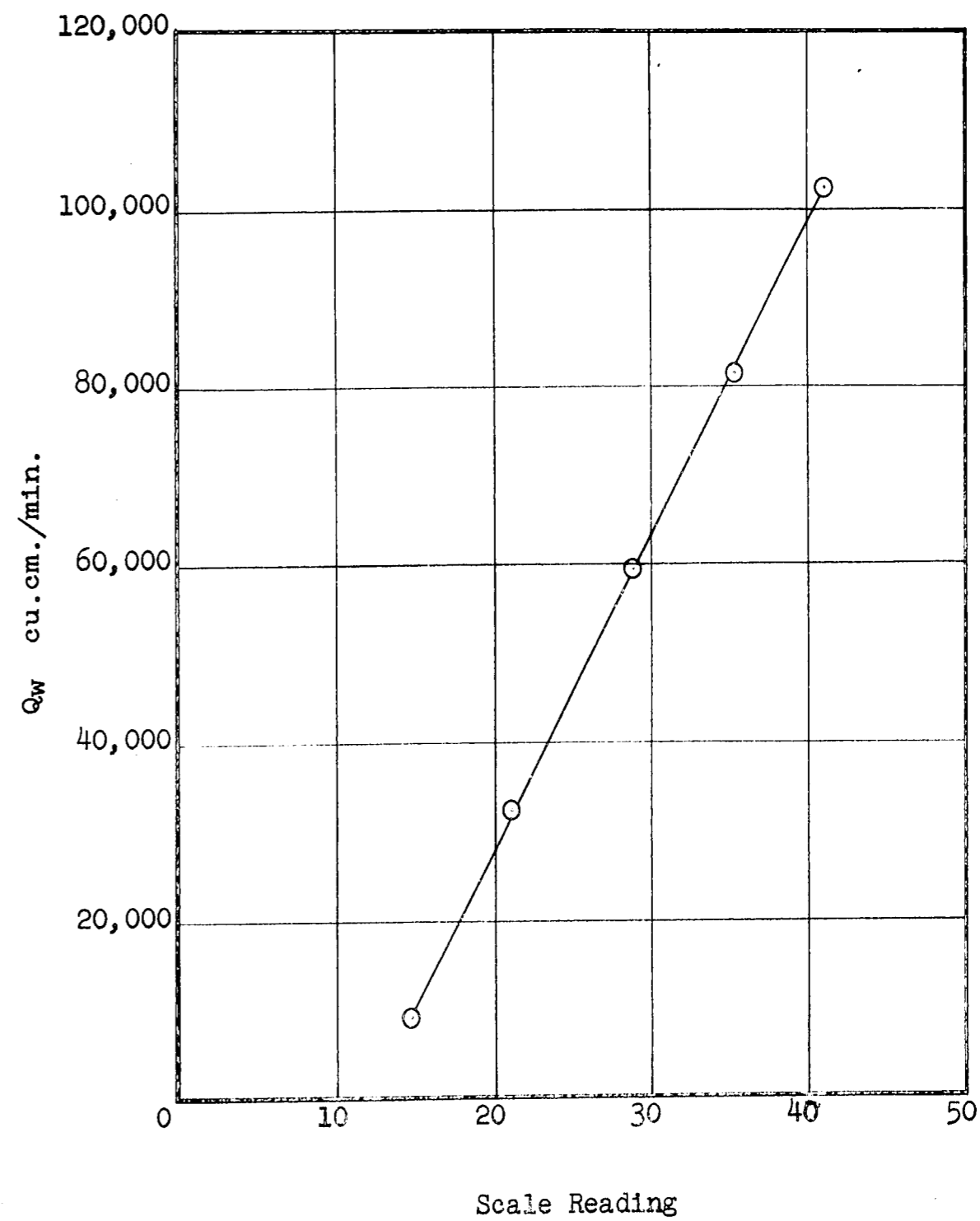


Figure A-2 Calibration Curve - Water Rotameter #1

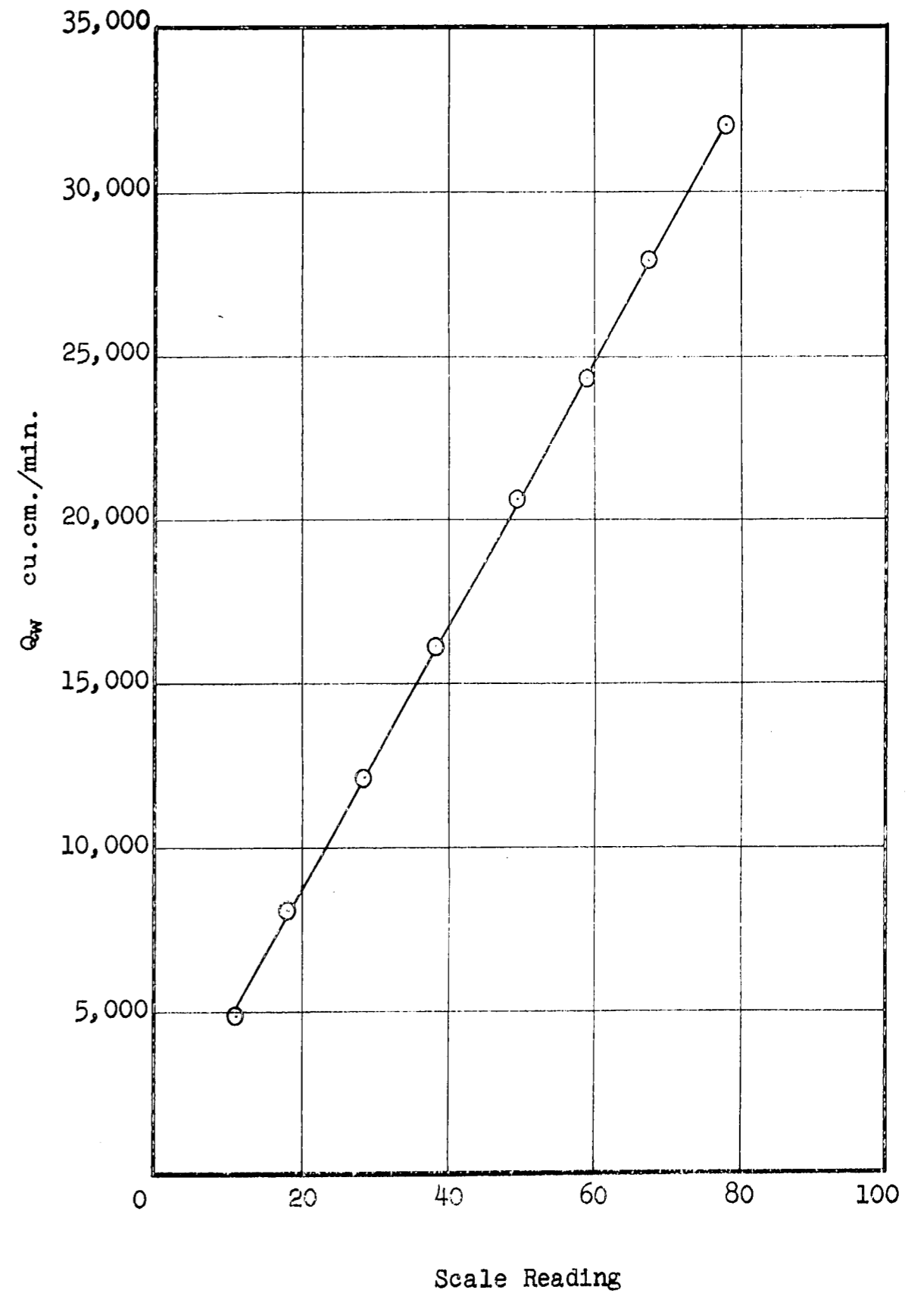


Figure A-3 Calibration Curve - Water Rotameter #2

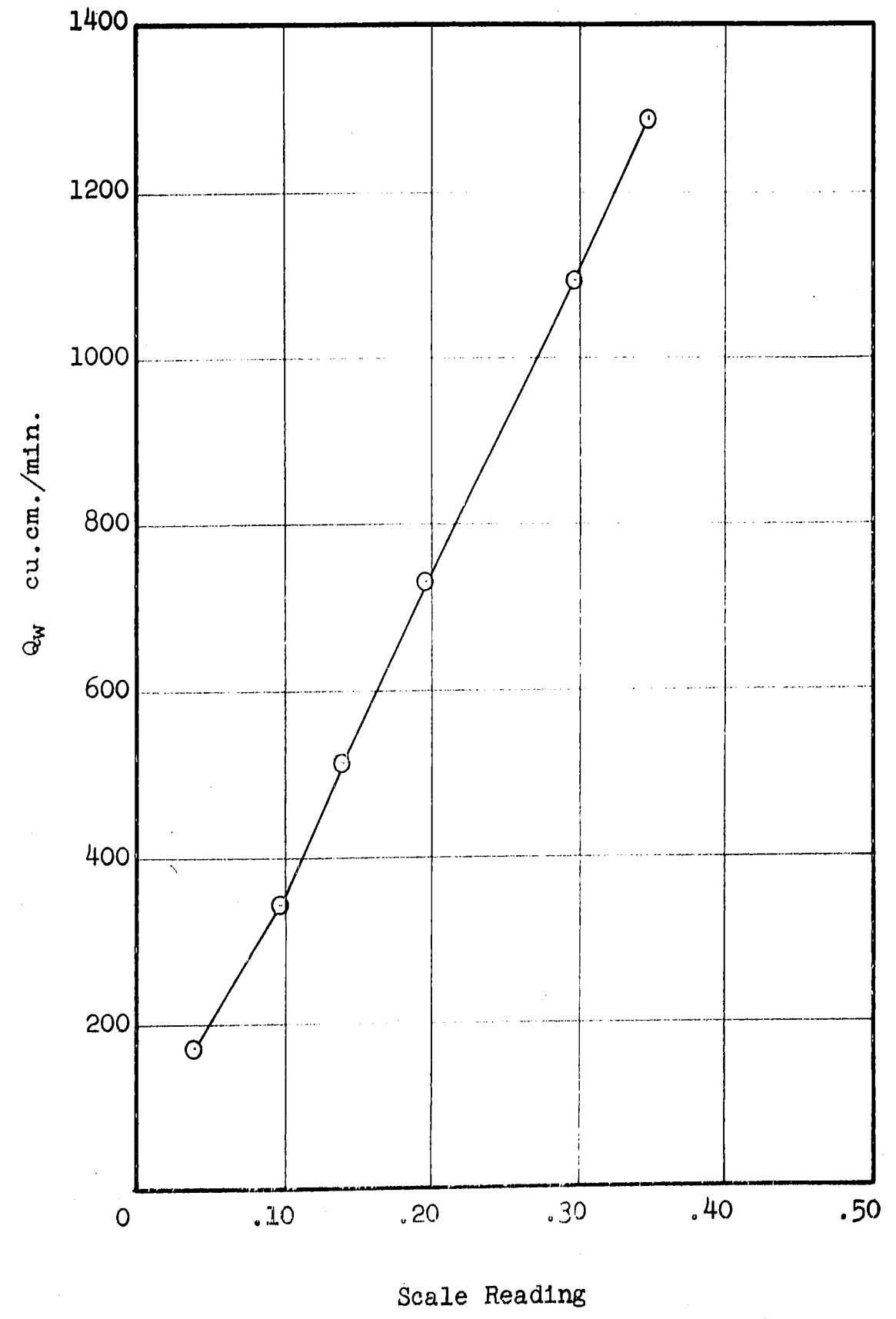


Figure A-4 Calibration Curve - Water Rotameter #3

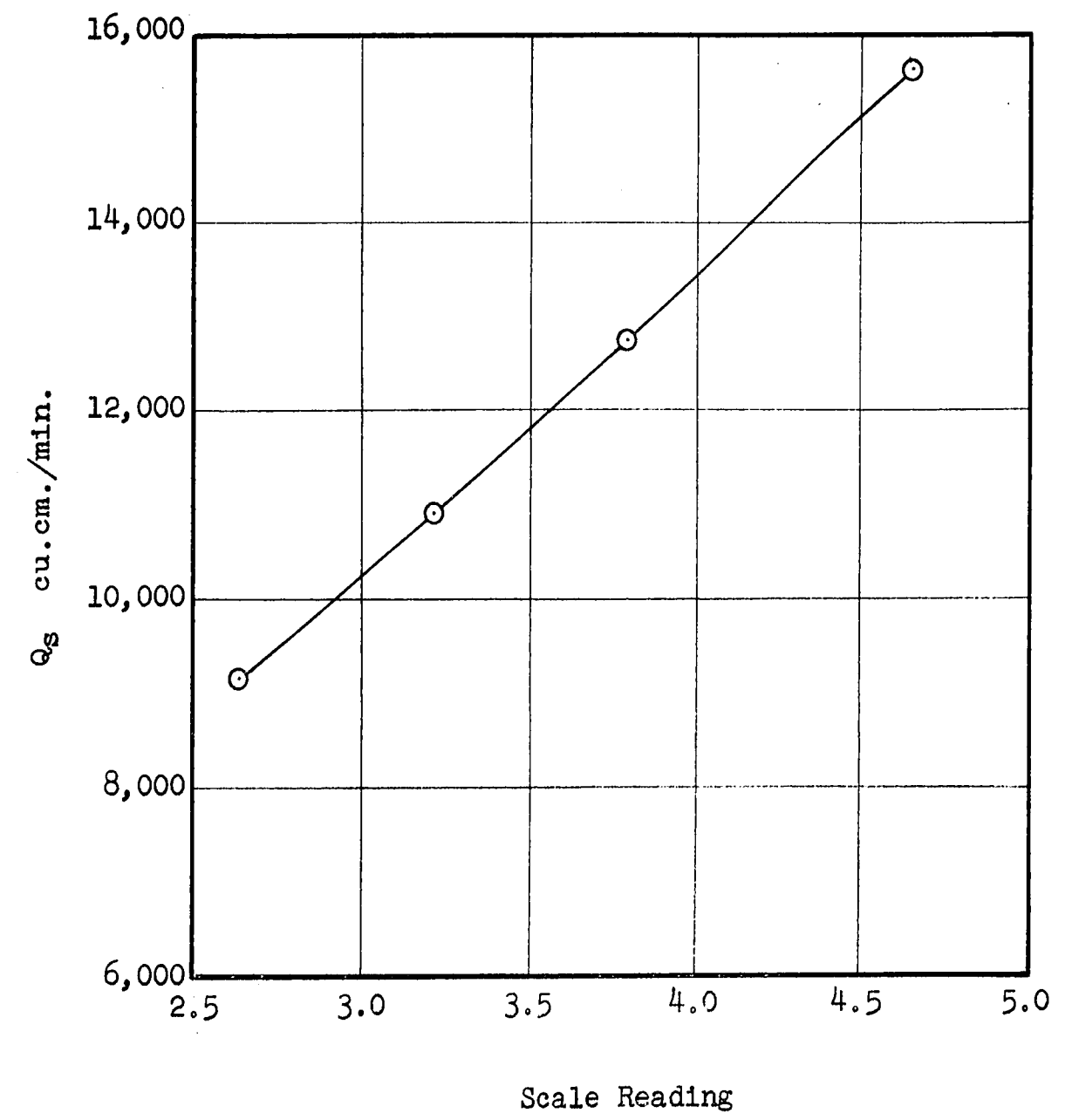


Figure A-5 Calibration Curve - Salt Solution Rotameter

Calibration of the camera was obtained by photographing a number of aluminum rods (machined to different diameters) immersed in the column filled with saturated salt solution. Figure A-6 indicates these results.

#### 4. Method of Analysis

The amount of salt solute transferred through the membrane into the water stream was very small, ranging from 75 to 750 parts per million in the turbulent regime, and from 2000 to 15300 parts per million in the laminar regime. This indicated that concentration of the solvent stream samples could be effectively measured for total ion content by means of a conductivity cell.

The electrodes were prepared by first cleaning the surface with aqua regia. The coating of platinum black was applied by immersing the electrodes in a 3% solution of chloroplatinic acid containing a trace of lead acetate. The electrodes were connected in series with two  $1\frac{1}{2}$  volt batteries and the current was regulated by means of a rheostat so that only a small amount of gas was evolved (9).

A Serfass conductance bridge was utilized to balance the circuit and conductance reading of the

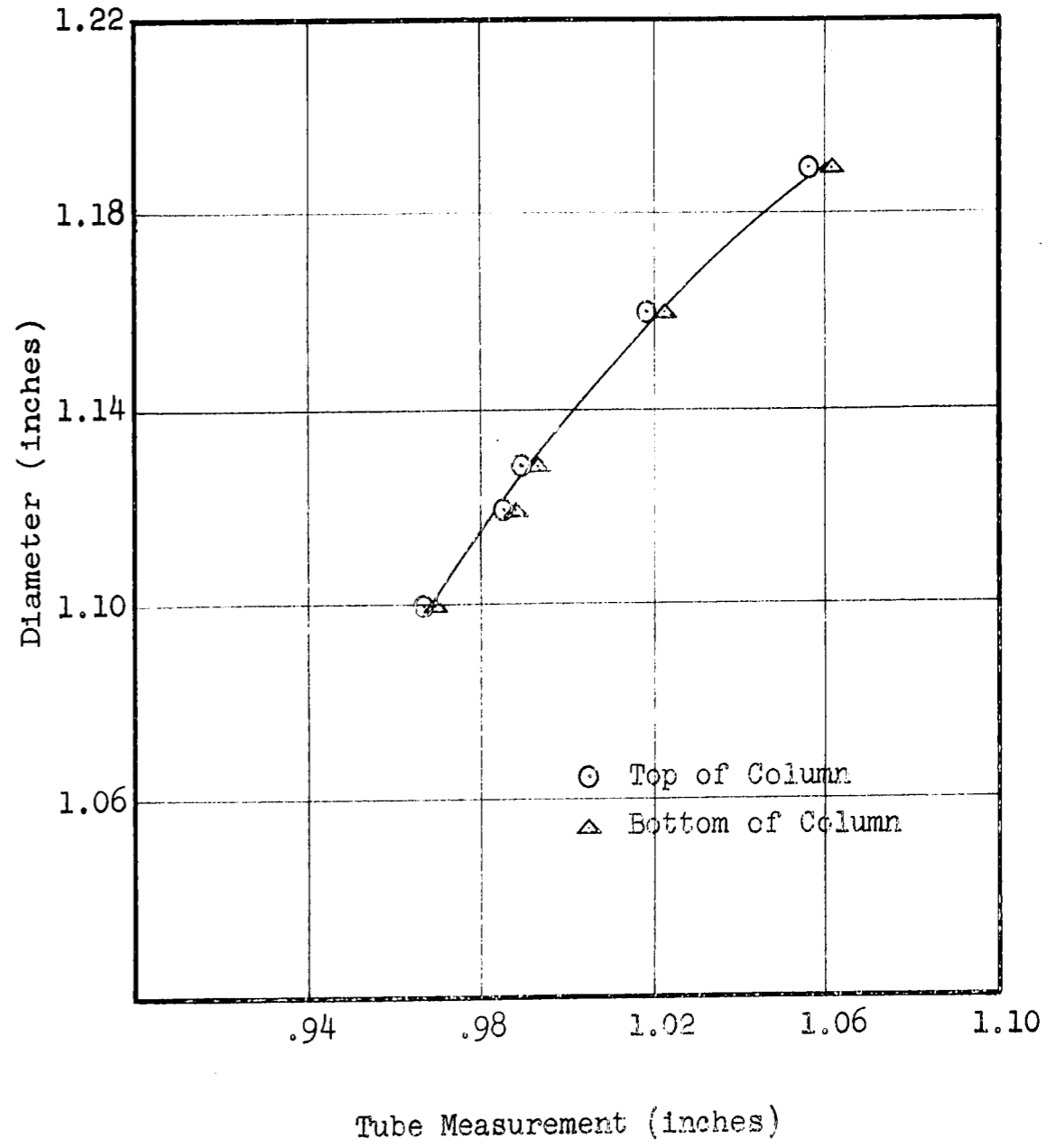


Figure A-6 Calibration Curve - Polaroid Camera

sample solution was obtained directly. Bridge balance was determined by the point of maximum shadow angle of the "magic eye" (cathode ray tube) employed in this instrument. A clear description of the operation of this particular bridge appears in the text of Willard, et al (64).

Two sets of electrodes were used; one for the measurement of the samples collected in the turbulent regime and one for the samples of higher concentration collected in the laminar regime. Calibration curves are shown in Figure A-7 and A-8.

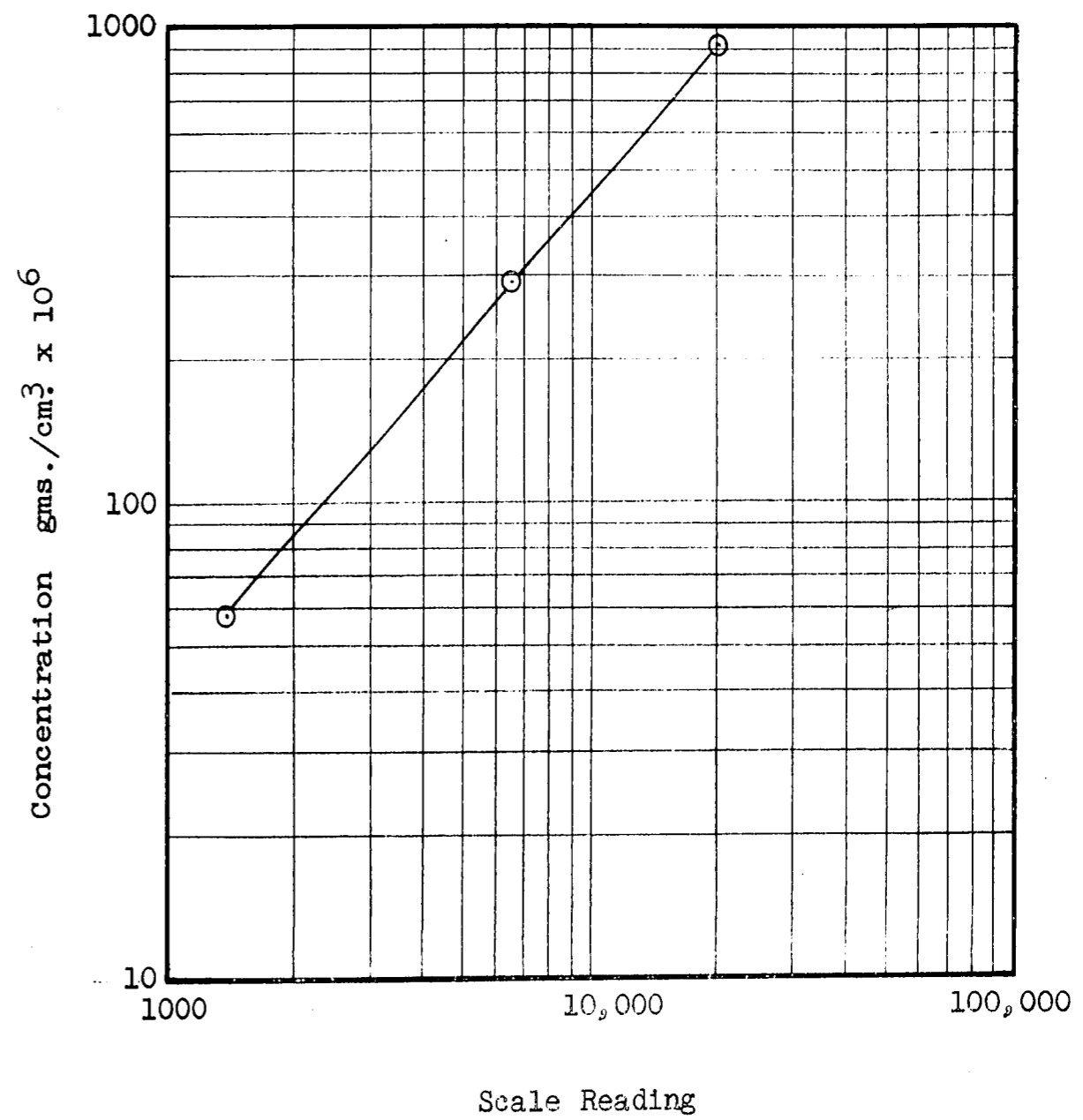


Figure A-7 Calibration Curve - Conductivity Cell #1



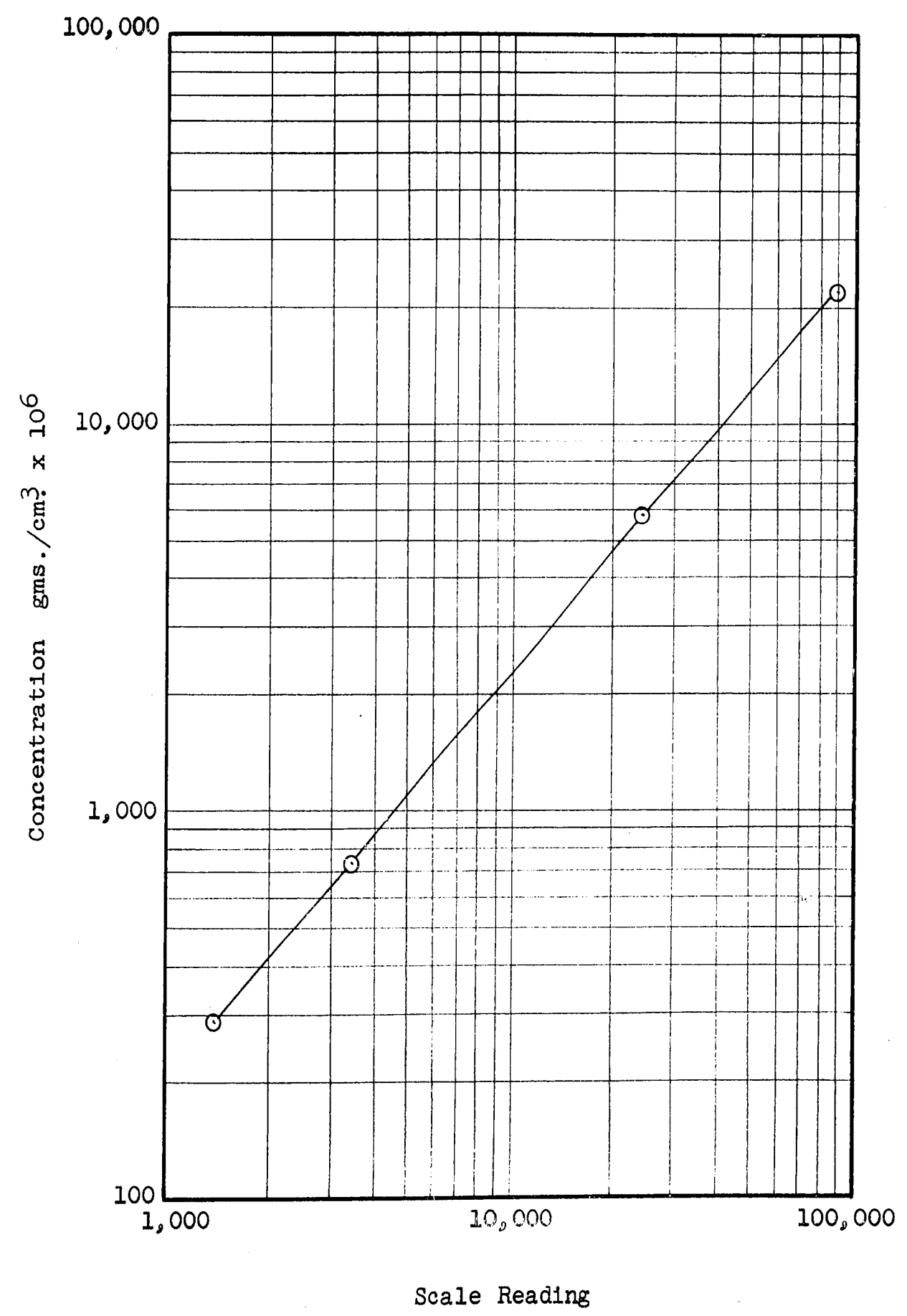


Figure A-8 Calibration Curve - Conductivity Cell #2

VII. APPENDIXC. Determination of Over-all Resistance to Transfer

RUN SET - 727

Cross-sectional area:

$$D = 1.135''$$

$$A_x = \pi D^2 / 4$$

$$A_x = (.785)(1.135)^2(2.54)$$

$$A_x = 6.5276 \text{ cm}^2$$

Tube-side velocity:

$$U_w = Q_w / A_x$$

$$U_w = (.1532) Q_w$$

Transfer area:

$$L = 49 \frac{1}{8}''$$

$$A = \pi D L$$

$$A = (3.1416)(1.135)(49.125)(2.54)^2$$

$$A = 1130.1 \text{ cm}^2$$

Concentration driving force:

$$C_s = \text{saturated salt conc. @ } 19^\circ\text{C (32)}$$

$$C_s = 26.43 \text{ wt.}\% \quad \rho_s = 1.20 \text{ gm./cm}^3$$

$$C_s = (.2643)(1.20) = 0.317 \text{ gm./cm}^3$$

$$C_w = \text{water side conc. negligible} \\ \text{relative to salt side conc.}$$

$$\Delta C = C_s - C_w = 0.317 \text{ gm./cm}^3$$

Over-all Resistance to Transfer

$$C_{w1} = 11(10)^{-6} \text{ gm./cm}^3$$

$$Q_w (C_{w2} - C_{w1}) = K A (C_s - C_w)$$

$$\frac{1}{K} = \frac{A (\Delta C)}{Q_w (C_{w2} - C_{w1})}$$

$$\frac{1}{K} = \frac{(1130.1)(.317)}{Q_w (C_{w2} - C_{w1})}$$

Over-all Resistance to Transfer

RUN SET - 727

Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )	$U_w$ ( $\text{cm}./\text{min}$ )	$C_{w2} - C_{w1}$ ( $\text{gm}./\text{cm}^3$ )	$1/K$ ( $\text{min}./\text{cm}.$ )
727-1	3930	602.1	$737 \times 10^{-6}$	123.684
727-2	5210	798.2	603	114.030
727-3	5730	877.8	568	110.071
727-4	6450	988.1	522	106.401
727-5	6930	1062	481	107.472
727-6	7690	1178	438	106.359
727-7	8870	1359	391	103.294
727-8	10480	1606	352	97.111
727-9	12820	1964	297	94.087
727-10	6020	922.2	540	110.201
727-11	17410	2667	227	90.846
727-12	21970	3366	183	89.103
727-13	26440	4051	152	89.139
727-14	32270	4944	127	87.412
727-15	37970	5817	109	86.558

C. Determination of Over-all Resistance to Transfer

RUN SET - 801

Cross-sectional area:

$$D = 1.135''$$

$$A_x = \pi D^2 / 4$$

$$A_x = 6.5276 \text{ cm}^2$$

Tube-side velocity:

$$U_w = Q_w / A_x$$

$$U_w = (.1532) Q_w$$

Transfer area:

$$L = 48.75''$$

$$A = \pi D L$$

$$A = (3.1416)(1.135)(48.75)(2.54)^2$$

$$A = 1121.5 \text{ cm}^2$$

Concentration driving force:

$$\Delta c = c_s - c_w$$

$$\Delta c = 0.317 - \text{neg.}$$

$$\Delta c = 0.317 \text{ gm./cm}^3$$

Over-all Resistance to Transfer

$$c_{w1} = 11(10)^{-6} \text{ gm./cm}^3$$

$$Q_w (c_{w2} - c_{w1}) = K A (c_s - c_w)$$

$$\frac{1}{K} = \frac{A (\Delta c)}{Q_w (c_{w2} - c_{w1})}$$

$$\frac{1}{K} = \frac{(1121.5)(.317)}{Q_w (c_{w2} - c_{w1})}$$

Over-all Resistance to Transfer

RUN SET - 801

Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )	$U_w$ ( $\text{cm}/\text{min}$ )	$C_{w2} - C_{w1}$ ( $\text{gm}/\text{cm}^3$ )	$1/K$ ( $\text{min}/\text{cm}$ )
801-1	4700	720.0	$636 \times 10^{-6}$	118.935
801-4	5500	842.6	585	110.496
801-7	8180	1253	414	104.981
801-8	9630	1475	363	101.702
801-9	11880	1820	310	96.535
801-10	15430	2364	250	92.163
801-11	19770	3029	199	90.366
801-12	24300	3723	166	88.135
801-13	29700	4550	136	88.017
801-14	34930	5351	116	87.742

C. Determination of Over-all Resistance to Transfer

RUN SET - 810

Cross-sectional area:

$$D = 1.135''$$

$$A_x = \pi D^2 / 4$$

$$A_x = 6.5276 \text{ cm}^2$$

Tube-side velocity:

$$U_w = Q_w / A_x$$

$$U_w = (.1532) Q_w$$

Transfer area:

$$L = 48 \frac{5}{8}''$$

$$A = \pi D L$$

$$A = (3.1416)(1.135)(48.625)(2.54)^2$$

$$A = 1118.6 \text{ cm}^2$$



Concentration driving force:

$$\Delta c = c_s - c_w$$

$$\Delta c = 0.317 - \text{neg.}$$

$$\Delta c = 0.317 \text{ gm./cm}^3$$

Over-all Resistance to Transfer

$$c_{w1} = 11(10)^{-6} \text{ gm./cm}^3$$

$$Q_w (c_{w2} - c_{w1}) = K A (c_s - c_w)$$

$$\frac{1}{K} = \frac{A (\Delta c)}{Q_w (c_{w2} - c_{w1})}$$

$$\frac{1}{K} = \frac{(1118.6)(.317)}{Q_w (c_{w2} - c_{w1})}$$

Over-all Resistance to Transfer

RUN SET - 810

Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )	$U_w$ ( $\text{cm}/\text{min}$ )	$C_{w2} - C_{w1}$ ( $\text{gm}/\text{cm}^3$ )	$1/K$ ( $\text{min}/\text{cm}$ )
810-1	4180	640.4	$702 \times 10^{-6}$	120.844
810-2	7600	1164	449	103.915
810-3	5580	854.8	579	109.755
810-4	6120	937.6	534	108.504
810-5	6720	1030	496	106.387
810-7	8420	1290	412	102.219
810-8	9810	1503	359	100.687
810-9	12120	1857	303	96.559
810-11	19810	3035	194	92.268
810-12	24000	3677	166	89.006
810-13	29600	4535	138	86.810
810-15	47200	7231	87.5	85.860
810-16	56000	8579	74.0	85.570
810-17	64600	9897	65.5	83.804

VII. APPENDIXD. Simple Linear Regression Analysis

The equation

$$\frac{l}{K} = a + b \frac{l}{U^c}$$

is to be subject to a least squares analysis to determine the values for  $a$  and  $b$  corresponding to velocity exponents of  $c = .80$  and  $c = .90$ . The following calculations are facilitated by writing the above equation as

$$y = a + b(x)$$

where the coefficients  $a$  and  $b$  (to be derived from the experimental data) are estimates of the population parameters  $A$  and  $B$ . An indication of the accuracy of these regression coefficients can be obtained by determining interval estimates of the true values of the population parameters (employing the "Student's"  $t$  distribution).

Run No.	$\gamma$	$\kappa$	$\kappa$
	$\frac{1}{K}$	$\frac{1}{U \cdot 80} \times 10^3$	$\frac{1}{U \cdot 90} \times 10^3$
727-1	123.684	5.9741	3.1499
727-2	114.030	4.7676	2.4440
727-3	110.071	4.4185	2.2436
727-4	106.401	4.0195	2.0193
727-5	107.472	3.7941	1.8901
727-6	106.359	3.4921	1.7218
727-7	103.294	3.1148	1.5139
727-8	97.111	2.7259	1.3030
727-9	94.087	2.3200	1.0869
727-10	110.201	4.2475	2.1462
727-11	90.846	1.8162	.8252
727-12	89.103	1.5077	.6693
727-13	89.139	1.3001	.5660
727-14	87.412	1.1085	.4735
727-15	86.558	.9733	.4090
801-1	118.935	5.1776	2.6817
801-4	110.496	4.5600	2.3278
801-7	104.981	3.3238	1.6287
801-8	101.702	2.9172	1.4063
801-9	96.535	2.4657	1.1639
801-10	92.163	2.0002	.9199
801-11	90.366	1.6404	.7359
801-12	88.135	1.3909	.6112
801-13	88.017	1.1846	.5103
801-14	87.742	1.0405	.4410
810-1	120.844	5.6863	2.9798
810-2	103.915	3.5256	1.7404
810-3	109.755	4.5135	2.2979
810-4	108.504	4.1916	2.1144
810-5	106.387	3.8895	1.9437
810-7	102.219	3.2473	1.5866
810-8	100.687	2.8736	1.3827
810-9	96.559	2.4263	1.1431
810-11	92.268	1.6378	.7346
810-12	89.006	1.4048	.6181
810-13	86.810	1.1878	.5118
810-15	85.860	.8178	.3363
810-16	85.570	.7133	.2883
810-17	83.804	.6362	.2536

Least Squares Analysis of Linear Equation ( c = .80 )

$$b = \frac{\sum(xy) - (\sum x)(\sum y)/N}{\sum(x)^2 - (\sum x)^2/N}$$

$$a = \bar{y} - b \bar{x}$$

$$N = 39$$

$$\begin{aligned} (\sum x) &= .1080322 & \bar{x} &= (\sum x)/N = .002770056 \\ (\sum x)^2 &= .011670956237 & (\sum x)^2/N &= .000299255288 \\ \sum(x)^2 &= .000385206163 & (\sum y) &= 3867.028 \end{aligned}$$

$$\bar{y} = (\sum y)/N = 99.154564$$

$$\sum(xy) = 11.335852272$$

$$(\sum x)(\sum y)/N = 10.711884114$$

$$b = \frac{11.335852272 - 10.711884114}{.000385206163 - .000299255288} = 7260$$

$$a = 99.155 - 7260 (.002770056) = 79.045$$

Calculation of Confidence Interval ( c = .80 )Standard Deviation of  $y$  for a Fixed  $x$  .

$$s_{y.x}^2 = \frac{\sum (y_e - y_p)^2}{N - 2}$$

$$s_{y.x}^2 = \frac{54.387197}{37} = 1.469924$$

$$s_{y.x} = 1.2124$$

where  $y_e$  represents experimental values of  $y$   
and  $y_p$  represents predicted values of  $y$  .

Standard Deviation of  $x$ 

$$s_x^2 = \frac{N \sum (x)^2 - (\sum x)^2}{N ( N - 1 )}$$

$$s_x^2 = \frac{39(.000385206163) - (.011670956)}{39 (38)}$$

$$s_x = .0015039$$

Calculation of Confidence Interval (  $c = .80$  )

"Student's"  $t$  Distribution for a 95% Confidence Interval  
(  $\alpha = .05$  )

$$t_{.975} (37 \text{ degrees of freedom}) = 2.025 = - t_{.025}$$

$$t_{\alpha/2} \frac{S_{y \cdot x}}{S_x \sqrt{N - 1}} = -265$$

The interval estimate for the regression coefficient  
lies on both sides of the point estimate  $b$  .

$$( b - 265 ) < \hat{B} < ( b + 265 )$$

$$(7260 - 265) < \hat{B} < (7260 + 265)$$

$$6995 < \hat{B} < 7525$$

For  $A$

$$t_{\alpha/2} S_{y \cdot \bar{x}} \sqrt{\frac{1}{N} - \frac{(\bar{x})^2}{(N - 1) S_x^2}} = -.393$$

and

$$( a - .393 ) < \hat{A} < ( a + .393 )$$

$$(79.045 - .393) < \hat{A} < (79.045 + .393)$$

$$78.652 < \hat{A} < 79.438$$

Least Squares Analysis of Linear Equation (  $c = .90$  )

$$b = \frac{\sum(xy) - (\sum x)(\sum y)/N}{\sum(x)^2 - (\sum x)^2/N}$$

$$a = \bar{y} - b \bar{x}$$

$$N = 39$$

$$(\sum x) = .0528203 \quad \bar{x} = (\sum x)/N = .001354366$$

$$(\sum x)^2 = .002789984092 \quad (\sum x)^2/N = .000071538053$$

$$\sum(x)^2 = .000096590639 \quad (\sum y) = 3867.028$$

$$\bar{y} = (\sum y)/N = 99.154564$$

$$\sum(xy) = 5.574380416$$

$$(\sum x)(\sum y)/N = 5.237371244$$

$$b = \frac{5.574380416 - 5.237371244}{.000096590639 - .000071538053} = 13450$$

$$a = 99.155 - 13450 (.001354366) = 80.94$$



Calculation of Confidence Interval ( c = .90 )Standard Deviation of  $y$  for a Fixed  $x$  .

$$s_{y.x}^2 = \frac{\sum (y_e - y_p)^2}{N - 2}$$

$$s_{y.x}^2 = \frac{50.718824}{37} = 1.370779$$

$$s_{y.x} = 1.1708$$

where  $y_e$  represents experimental values of  $y$

and  $y_p$  represents predicted values of  $y$  .

Standard Deviation of  $x$ 

$$s_x^2 = \frac{N \sum (x)^2 - (\sum x)^2}{N ( N - 1 )}$$

$$s_x^2 = \frac{39(.000096590639) - (.002789984)}{39 (38)}$$

$$s_x = .00081196$$

Calculation of Confidence Interval (  $c = .90$  )

"Student's"  $t$  Distribution for a 95% Confidence Interval  
(  $\alpha = .05$  )

$$t_{.975} (37 \text{ degrees of freedom}) = 2.025 = - t_{.025}$$

$$t_{\alpha/2} \frac{S_{y.x}}{S_x \sqrt{N-1}} = -475$$

The interval estimate for the regression coefficient  
lies on both sides of the point estimate  $b$ .

$$\begin{aligned} (b - 475) &< \beta < (b + 475) \\ (13450 - 475) &< \beta < (13450 + 475) \\ 12975 &< \beta < 13925 \end{aligned}$$

For  $A$

$$t_{\alpha/2} S_{y.\bar{x}} \sqrt{\frac{1}{N} - \frac{(\bar{x})^2}{(N-1) S_x^2}} = -.379$$

and

$$\begin{aligned} (a - .379) &< A < (a + .379) \\ (80.94 - .38) &< A < (80.94 + .38) \\ 80.56 &< A < 81.32 \end{aligned}$$

VII. APPENDIX

E. Method of Differential Correction

It has been indicated previously that the equation

$$\frac{1}{K} = a + b \frac{1}{U^c} = f(U, a, b, c) \quad (E-1)$$

cannot be directly adapted to a least squares analysis of the data for the evaluation of the constants since the latter do not enter the equation linearly. This problem can be avoided by utilizing the iterative technique outlined in the texts of Nielsen (51), and Scarborough (54) in which initial values  $a_0$ ,  $b_0$ ,  $c_0$  are assumed for the constants and the corrections  $\alpha$ ,  $\beta$ ,  $\gamma$ , determined. New values for  $a_0$ ,  $b_0$ ,  $c_0$  can be successively employed until the desired convergence is attained. Using the estimated values for the constants the above equation becomes

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}} = f(U, a_0, b_0, c_0) \quad (E-2)$$

The values of this approximating function corresponding to  $U_1$ ,  $U_2$ , -----  $U_n$  (experimental values of  $U$ )

will be

$$\frac{1}{K_1} = a_0 + b_0 \frac{1}{U_1^{c_0}} = f(U_1, a_0, b_0, c_0)$$

$$\frac{1}{K_2} = a_0 + b_0 \frac{1}{U_2^{c_0}} = f(U_2, a_0, b_0, c_0)$$

-----

$$\frac{1}{K_n} = a_0 + b_0 \frac{1}{U_n^{c_0}} = f(U_n, a_0, b_0, c_0) \quad (E-3)$$

If equation (E-1) is taken as the best or most probable function and its graph to be the best representative curve, then the residuals will be

$$v_1 = a + b \frac{1}{U_1^c} - \frac{1}{K_1}$$

$$v_2 = a + b \frac{1}{U_2^c} - \frac{1}{K_2}$$

-----

$$v_n = f(U_n, a, b, c) - \frac{1}{K_n} \quad (E-4)$$

where  $1/K_1, 1/K_2, \dots, 1/K_n$  are the observed  $1/K$ 's corresponding to  $U_1, U_2, \dots, U_n$  respectively. Substituting in (E-4) the values of  $a, b, c$ , as given by

$$\begin{aligned} a &= a_0 + \alpha \\ b &= b_0 + \beta \\ c &= c_0 + \gamma \end{aligned} \quad (E-5)$$

the first residual becomes

$$\begin{aligned} v_1 &= (a_0 + \alpha) + (b_0 + \beta) \frac{1}{U(c_0 + \gamma)} - \frac{1}{K_1} \\ v_1 + \frac{1}{K_1} &= f(U_1, a_0 + \alpha, b_0 + \beta, c_0 + \gamma) \quad (E-6) \end{aligned}$$

Considering the right-hand side of (E-6) as a function of  $a, b, c$ , and expanding it by Taylor's theorem for a function of several variables, this equation becomes

$$\begin{aligned}
 v_1 + \frac{1}{K_1} &= f(U_1, a_0, b_0, c_0) + \alpha \left( \frac{\partial f_1}{\partial a} \right)_0 + \beta \left( \frac{\partial f_1}{\partial b} \right)_0 \\
 &+ \gamma \left( \frac{\partial f_1}{\partial c} \right)_0 + \text{terms involving higher powers and products of } \alpha, \beta, \gamma. \quad (\text{E-7})
 \end{aligned}$$

where  $\left( \frac{\partial f_1}{\partial a} \right)_0$  represents

$$\left( \frac{\partial f_1}{\partial a} \right)$$

$$\begin{aligned}
 U &= U_1 \\
 a &= a_0 \\
 b &= b_0 \\
 c &= c_0
 \end{aligned}$$

Since

$$\frac{1}{K_1} = f(U_1, a_0, b_0, c_0)$$

equation (E-7) becomes

$$v_1 = \frac{1}{K_1} - \frac{1}{K_1} + \alpha \left( \frac{\partial f_1}{\partial a} \right)_0 + \beta \left( \frac{\partial f_1}{\partial b} \right)_0 + \gamma \left( \frac{\partial f_1}{\partial c} \right)_0 \quad (\text{E-8})$$

Let

$$\begin{aligned} \kappa_1 &= \frac{1}{K_1'} - \frac{1}{K_1} , & \kappa_2 &= \frac{1}{K_2'} - \frac{1}{K_2} \\ \dots & & \dots & \\ \kappa_n &= \frac{1}{K_n'} - \frac{1}{K_n} \end{aligned}$$

The residual equations are then obtained.

$$v_1 = \alpha \left( \frac{\partial f_1}{\partial a} \right)_0 + \beta \left( \frac{\partial f_1}{\partial b} \right)_0 + \gamma \left( \frac{\partial f_1}{\partial c} \right)_0 + \kappa_1$$

$$v_2 = \alpha \left( \frac{\partial f_2}{\partial a} \right)_0 + \beta \left( \frac{\partial f_2}{\partial b} \right)_0 + \gamma \left( \frac{\partial f_2}{\partial c} \right)_0 + \kappa_2$$

$$\dots$$

$$v_n = \alpha \left( \frac{\partial f_n}{\partial a} \right)_0 + \beta \left( \frac{\partial f_n}{\partial b} \right)_0 + \gamma \left( \frac{\partial f_n}{\partial c} \right)_0 + \kappa_n \quad (\text{E-9})$$

The linearity of the corrections  $\alpha$ ,  $\beta$ ,  $\gamma$ , in these residual equations permits the method of least squares to be utilized. The partial derivatives in the above equations take the form

$$\left(\frac{\partial f}{\partial a}\right)_0 = \left(\frac{\partial 1/K}{\partial a}\right)_0 = 1 \quad (\text{E-10})$$

$$\left(\frac{\partial f}{\partial b}\right)_0 = \left(\frac{\partial 1/K}{\partial b}\right)_0 = \frac{1}{U^{c_0}} \quad (\text{E-11})$$

$$\left(\frac{\partial f}{\partial c}\right)_0 = \left(\frac{\partial 1/K}{\partial c}\right)_0 = b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U} \quad (\text{E-12})$$

In order to start this iterative calculation, initial values of the constants were obtained by letting the exponent  $c_0$  take on the value 0.80 and determining the other constants from a least squares analysis since the resulting equation,

$$\frac{1}{K} = a_0 + b_0 \frac{1}{U^{.8}} \quad (\text{E-13})$$

is linear in  $a_0$  and  $b_0$ . This calculation has been carried out in APPENDIX D. The results of this calculation show that the initial values of the constants that are to be employed in the method of differential correction



are

$$a_0 = 79.045 \quad b_0 = 7260 \quad c_0 = 0.80$$

The partial derivatives in the above residual equations then reduce to

$$\left( \frac{\partial f}{\partial a} \right)_0 = \left( \frac{\partial 1/K}{\partial a} \right)_0 = 1$$

$$\left( \frac{\partial f}{\partial b} \right)_0 = \left( \frac{\partial 1/K}{\partial b} \right)_0 = \frac{1}{U^{.80}}$$

$$\left( \frac{\partial f}{\partial c} \right)_0 = \left( \frac{\partial 1/K}{\partial c} \right)_0 = 7260 \frac{1}{U^{.80}} \ln \frac{1}{U}$$

The following tables show the calculation of the coefficients for the residual equations.

Differential Correction Calculation - Trial One

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
727-1	123.684	5.9741	43.372	122.417	-1.267	-6.40043	-277.599
727-2	114.030	4.7676	34.613	113.685	-.372	-6.68236	-231.297
727-3	110.071	4.4185	32.078	111.123	1.052	-6.77742	-217.406
727-4	106.401	4.0195	29.182	108.227	1.826	-6.89578	-201.233
727-5	107.472	3.7941	27.545	106.590	-.882	-6.96791	-191.931
727-6	106.359	3.4921	25.353	104.398	-1.961	-7.07157	-179.286
727-7	103.294	3.1148	22.613	101.685	-1.636	-7.21450	-163.142
727-8	97.111	2.7259	19.790	98.835	1.724	-7.38119	-146.074
727-9	94.087	2.3200	16.843	95.888	1.801	-7.58274	-127.716
727-10	110.201	4.2475	30.837	109.882	-.319	-6.82677	-210.517
727-11	90.846	1.8162	13.186	92.231	1.385	-7.88872	-104.021
727-12	89.103	1.5077	10.946	89.991	.888	-8.12148	-88.898
727-13	89.139	1.3001	9.439	88.484	-.655	-8.30660	-78.406
727-14	87.412	1.1085	8.048	87.093	-.319	-8.50594	-68.456
727-15	86.558	.9733	7.066	86.111	-.447	-8.66854	-61.252

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\mu = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 79.045$$

$$b_0 = 7260$$

$$c_0 = 0.80$$

Differential Correction Calculation - Trial One

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
801-1	118.935	5.1776	37.589	116.634	-2.301	-6.57924	-247.307
801-4	110.496	4.5600	33.106	112.151	1.655	-6.73649	-223.018
801-7	104.981	3.3238	24.131	103.176	-1.805	-7.13329	-172.133
801-8	101.702	2.9172	21.179	100.224	-1.478	-7.29641	-154.531
801-9	96.535	2.4657	17.901	96.946	.411	-7.50660	-134.376
801-10	92.163	2.0002	14.521	93.566	1.403	-7.76811	-112.801
801-11	90.366	1.6404	11.909	90.954	.588	-8.01599	-95.462
801-12	88.135	1.3909	10.098	89.143	1.008	-8.22229	-83.029
801-13	88.017	1.1846	8.600	87.645	-.372	-8.42289	-72.437
801-14	87.742	1.0405	7.554	86.599	-1.143	-8.58505	-64.851

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\tau = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 79.045$$

$$b_0 = 7260$$

$$c_0 = 0.80$$

Differential Correction Calculation - Trial One

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
810-1	120.844	5.6863	41.283	120.328	-.516	-6.46209	-266.774
810-2	103.915	3.5256	25.596	104.641	.726	-7.05961	-180.698
810-3	109.755	4.5135	32.768	111.813	2.058	-6.75087	-221.213
810-4	108.504	4.1916	30.431	109.476	.972	-6.84332	-208.249
810-5	106.387	3.8895	28.238	107.283	.896	-6.93683	-195.882
810-7	102.219	3.2473	23.575	102.620	.401	-7.16240	-168.854
810-8	100.687	2.8736	20.862	99.907	-.780	-7.31522	-152.610
810-9	96.559	2.4263	17.615	96.660	.101	-7.52672	-132.583
810-11	92.268	1.6378	11.890	90.935	-1.333	-8.01797	-95.334
810-12	89.006	1.4048	10.199	89.244	.238	-8.20985	-83.732
810-13	86.810	1.1878	8.623	87.668	.858	-8.41958	-72.602
810-15	85.860	.8178	5.937	84.982	-.878	-8.88614	-52.757
810-16	85.570	.7133	5.179	84.224	-1.346	-9.05707	-46.907
810-17	83.804	.6362	4.619	83.664	-.140	-9.19994	-42.495

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\tau = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 79.045$$

$$b_0 = 7260$$

$$c_0 = 0.80$$

Residual Equations - Trial One

727-1	$v_1$	=	$\alpha$	+	.0059741	$\beta$	-	277.599	$\gamma$	-	1.267
727-2	$v_2$	=	$\alpha$	+	.0047676	$\beta$	-	231.297	$\gamma$	-	.372
727-3	$v_3$	=	$\alpha$	+	.0044185	$\beta$	-	217.406	$\gamma$	+	1.052
727-4	$v_4$	=	$\alpha$	+	.0040195	$\beta$	-	201.233	$\gamma$	+	1.826
727-5	$v_5$	=	$\alpha$	+	.0037941	$\beta$	-	191.931	$\gamma$	-	.882
727-6	$v_6$	=	$\alpha$	+	.0034921	$\beta$	-	179.286	$\gamma$	-	1.961
727-7	$v_7$	=	$\alpha$	+	.0031148	$\beta$	-	163.142	$\gamma$	-	1.636
727-8	$v_8$	=	$\alpha$	+	.0027259	$\beta$	-	146.074	$\gamma$	+	1.724
727-9	$v_9$	=	$\alpha$	+	.0023200	$\beta$	-	127.716	$\gamma$	+	1.801
727-10	$v_{10}$	=	$\alpha$	+	.0042475	$\beta$	-	210.517	$\gamma$	-	.319
727-11	$v_{11}$	=	$\alpha$	+	.0018162	$\beta$	-	104.021	$\gamma$	+	1.385
727-12	$v_{12}$	=	$\alpha$	+	.0015077	$\beta$	-	88.898	$\gamma$	+	.888
727-13	$v_{13}$	=	$\alpha$	+	.0013001	$\beta$	-	78.406	$\gamma$	-	.655
727-14	$v_{14}$	=	$\alpha$	+	.0011085	$\beta$	-	68.456	$\gamma$	-	.319
727-15	$v_{15}$	=	$\alpha$	+	.0009733	$\beta$	-	61.252	$\gamma$	-	.447
801-1	$v_{16}$	=	$\alpha$	+	.0051776	$\beta$	-	247.307	$\gamma$	-	2.301
801-4	$v_{17}$	=	$\alpha$	+	.0045600	$\beta$	-	223.018	$\gamma$	+	1.655
801-7	$v_{18}$	=	$\alpha$	+	.0033238	$\beta$	-	172.133	$\gamma$	-	1.805
801-8	$v_{19}$	=	$\alpha$	+	.0029172	$\beta$	-	154.531	$\gamma$	-	1.478
801-9	$v_{20}$	=	$\alpha$	+	.0024657	$\beta$	-	134.376	$\gamma$	+	.411
801-10	$v_{21}$	=	$\alpha$	+	.0020002	$\beta$	-	112.801	$\gamma$	+	1.403
801-11	$v_{22}$	=	$\alpha$	+	.0016404	$\beta$	-	95.462	$\gamma$	+	.588
801-12	$v_{23}$	=	$\alpha$	+	.0013909	$\beta$	-	83.029	$\gamma$	+	1.008
801-13	$v_{24}$	=	$\alpha$	+	.0011846	$\beta$	-	72.437	$\gamma$	-	.372
801-14	$v_{25}$	=	$\alpha$	+	.0010405	$\beta$	-	64.851	$\gamma$	-	1.143
810-1	$v_{26}$	=	$\alpha$	+	.0056863	$\beta$	-	266.774	$\gamma$	-	.516
810-2	$v_{27}$	=	$\alpha$	+	.0035256	$\beta$	-	180.698	$\gamma$	+	.726
810-3	$v_{28}$	=	$\alpha$	+	.0045135	$\beta$	-	221.213	$\gamma$	+	2.058
810-4	$v_{29}$	=	$\alpha$	+	.0041916	$\beta$	-	208.249	$\gamma$	+	.972
810-5	$v_{30}$	=	$\alpha$	+	.0038895	$\beta$	-	195.882	$\gamma$	+	.896
810-7	$v_{31}$	=	$\alpha$	+	.0032473	$\beta$	-	168.854	$\gamma$	+	.401
810-8	$v_{32}$	=	$\alpha$	+	.0028736	$\beta$	-	152.610	$\gamma$	-	.780
810-9	$v_{33}$	=	$\alpha$	+	.0024263	$\beta$	-	132.583	$\gamma$	+	.101
810-11	$v_{34}$	=	$\alpha$	+	.0016378	$\beta$	-	95.334	$\gamma$	-	1.333
810-12	$v_{35}$	=	$\alpha$	+	.0014048	$\beta$	-	83.732	$\gamma$	+	.238
810-13	$v_{36}$	=	$\alpha$	+	.0011878	$\beta$	-	72.602	$\gamma$	+	.858
810-15	$v_{37}$	=	$\alpha$	+	.0008178	$\beta$	-	52.757	$\gamma$	-	.878
810-16	$v_{38}$	=	$\alpha$	+	.0007133	$\beta$	-	46.907	$\gamma$	-	1.346
810-17	$v_{39}$	=	$\alpha$	+	.0006362	$\beta$	-	42.495	$\gamma$	-	.140

The equations on the previous page are linear in the corrections  $\alpha$ ,  $\beta$ ,  $\gamma$ , and a least squares analysis can be applied. This involves the determination of three normal equations from the above set of residuals. The first normal equation is obtained by multiplying the right-hand member of each residual equation by the coefficient of the first unknown in that member, and equating their sum to zero; to get the second normal equation the right-hand member of each residual equation is multiplied by the coefficient of the second unknown in that member, adding the products so obtained and placing their sum equal to zero; the third normal is similarly obtained. Following are the three normal equations determined in such a manner for the first trial.

$$\begin{aligned}
 39\alpha + .1080322\beta - 5627.869\gamma + .041 &= 0 \\
 .1080322\alpha + .000385206163\beta - 19.404202\gamma + .000152506 &= 0 \\
 -5627.869\alpha - 19.404202\beta + 981871.503\gamma - 49.47126 &= 0
 \end{aligned}$$

These equations can be solved for  $\alpha$ ,  $\beta$ ,  $\gamma$ , by utilizing one of the methods of Gauss, as described in Scarborough (54), for solving simultaneous linear equations. This procedure involves choosing as the pivotal equation the equation in which the largest coefficient occurs. This

Differential Correction Calculation - Trial Two

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
727-1	123.684	3.1499	36.098	117.168	-6.516	-6.40043	-231.043
727-2	114.030	2.4440	28.008	109.078	-4.952	-6.68236	-187.160
727-3	110.071	2.2436	25.712	106.782	-3.289	-6.77742	-174.261
727-4	106.401	2.0193	23.141	104.211	-2.190	-6.89578	-159.575
727-5	107.472	1.8901	21.661	102.731	-4.741	-6.96791	-150.932
727-6	106.359	1.7218	19.732	100.802	-5.557	-7.07157	-139.536
727-7	103.294	1.5139	17.349	98.419	-4.875	-7.21450	-125.164
727-8	97.111	1.3030	14.932	96.002	-1.109	-7.38119	-110.216
727-9	94.087	1.0869	12.456	93.526	-.561	-7.58274	-94.451
727-10	110.201	2.1462	24.596	105.666	-4.535	-6.82677	-167.911
727-11	90.846	.8252	9.457	90.527	-.319	-7.88872	-74.604
727-12	89.103	.6693	7.670	88.740	-.363	-8.12148	-62.292
727-13	89.139	.5666	6.493	87.563	-1.576	-8.30660	-53.935
727-14	87.412	.4735	5.426	86.496	-.916	-8.50594	-46.153
727-15	86.558	.4090	4.687	85.757	-.801	-8.66854	-40.629

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\Delta = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 81.07$$

$$b_0 = 11460$$

$$c_0 = 0.90$$

Differential Correction Calculation - Trial Two

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
801-1	118.935	2.6817	30.732	111.802	-7.133	-6.57924	-202.193
801-4	110.496	2.3278	26.677	107.747	-2.749	-6.73649	-179.709
801-7	104.981	1.6287	18.665	99.735	-5.246	-7.13329	-133.143
801-8	101.702	1.4063	16.116	97.186	-4.516	-7.29641	-117.589
801-9	96.535	1.1639	13.338	94.408	-2.127	-7.50660	-100.123
801-10	92.163	.9199	10.542	91.612	-.551	-7.76811	-81.891
801-11	90.366	.7359	8.433	89.503	-.863	-8.01599	-67.599
801-12	88.135	.6112	7.004	88.074	-.061	-8.22229	-57.589
801-13	88.017	.5103	5.848	86.918	-1.099	-8.42289	-49.257
801-14	87.742	.4410	5.054	86.124	-1.618	-8.58505	-43.389

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\Delta = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 81.07$$

$$b_0 = 11460$$

$$c_0 = 0.90$$



Differential Correction Calculation - Trial Two

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
810-1	120.844	2.9798	34.149	115.219	-5.625	-6.46209	-220.674
810-2	103.915	1.7404	19.945	101.015	-2.900	-7.05961	-140.804
810-3	109.755	2.2979	26.334	107.404	-2.351	-6.75087	-177.777
810-4	108.504	2.1144	24.231	105.301	-3.203	-6.84332	-165.820
810-5	106.387	1.9437	22.275	103.345	-3.042	-6.93683	-154.518
810-7	102.219	1.5866	18.182	99.252	-2.967	-7.16240	-130.227
810-8	100.687	1.3827	15.846	96.916	-3.771	-7.31522	-115.917
810-9	96.559	1.1431	13.100	94.170	-2.389	-7.52672	-98.600
810-11	92.268	.7346	8.419	89.489	-2.779	-8.01797	-67.503
810-12	89.006	.6181	7.083	88.153	-.853	-8.20985	-58.150
810-13	86.810	.5118	5.865	86.935	.125	-8.41958	-49.381
810-15	85.860	.3363	3.854	84.924	-.936	-8.88614	-34.247
810-16	85.570	.2883	3.304	84.374	-1.196	-9.05707	-29.925
810-17	83.804	.2536	2.906	83.976	.172	-9.19994	-26.735

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\tau = \frac{1}{K'} - \frac{1}{K}$$

$$\begin{aligned} a_0 &= 81.07 \\ b_0 &= 11460 \\ c_0 &= 0.90 \end{aligned}$$

## Residual Equations - Trial Two

727-1	$v_1$	=	$\alpha$	+	.0031499	$\beta$	-	231.043	$\gamma$	-	6.516
727-2	$v_2$	=	$\alpha$	+	.0024440	$\beta$	-	187.160	$\gamma$	-	4.952
727-3	$v_3$	=	$\alpha$	+	.0022436	$\beta$	-	174.261	$\gamma$	-	3.289
727-4	$v_4$	=	$\alpha$	+	.0020193	$\beta$	-	159.575	$\gamma$	-	2.190
727-5	$v_5$	=	$\alpha$	+	.0018901	$\beta$	-	150.932	$\gamma$	-	4.741
727-6	$v_6$	=	$\alpha$	+	.0017218	$\beta$	-	139.536	$\gamma$	-	5.557
727-7	$v_7$	=	$\alpha$	+	.0015139	$\beta$	-	125.164	$\gamma$	-	4.875
727-8	$v_8$	=	$\alpha$	+	.0013030	$\beta$	-	110.216	$\gamma$	-	1.109
727-9	$v_9$	=	$\alpha$	+	.0010869	$\beta$	-	94.451	$\gamma$	-	.561
727-10	$v_{10}$	=	$\alpha$	+	.0021462	$\beta$	-	157.911	$\gamma$	-	4.535
727-11	$v_{11}$	=	$\alpha$	+	.0008252	$\beta$	-	74.604	$\gamma$	-	.319
727-12	$v_{12}$	=	$\alpha$	+	.0006693	$\beta$	-	62.292	$\gamma$	-	.363
727-13	$v_{13}$	=	$\alpha$	+	.0005666	$\beta$	-	53.935	$\gamma$	-	1.576
727-14	$v_{14}$	=	$\alpha$	+	.0004735	$\beta$	-	46.153	$\gamma$	-	.916
727-15	$v_{15}$	=	$\alpha$	+	.0004090	$\beta$	-	40.629	$\gamma$	-	.801
801-1	$v_{16}$	=	$\alpha$	+	.0026817	$\beta$	-	202.193	$\gamma$	-	7.133
801-4	$v_{17}$	=	$\alpha$	+	.0023278	$\beta$	-	179.709	$\gamma$	-	2.749
801-7	$v_{18}$	=	$\alpha$	+	.0016287	$\beta$	-	133.143	$\gamma$	-	5.246
801-8	$v_{19}$	=	$\alpha$	+	.0014063	$\beta$	-	117.589	$\gamma$	-	4.516
801-9	$v_{20}$	=	$\alpha$	+	.0011639	$\beta$	-	100.123	$\gamma$	-	2.127
801-10	$v_{21}$	=	$\alpha$	+	.0009199	$\beta$	-	81.891	$\gamma$	-	.551
801-11	$v_{22}$	=	$\alpha$	+	.0007359	$\beta$	-	67.599	$\gamma$	-	.863
801-12	$v_{23}$	=	$\alpha$	+	.0006112	$\beta$	-	57.589	$\gamma$	-	.061
801-13	$v_{24}$	=	$\alpha$	+	.0005103	$\beta$	-	49.257	$\gamma$	-	1.099
801-14	$v_{25}$	=	$\alpha$	+	.0004410	$\beta$	-	43.389	$\gamma$	-	1.618
810-1	$v_{26}$	=	$\alpha$	+	.0029798	$\beta$	-	220.674	$\gamma$	-	5.625
810-2	$v_{27}$	=	$\alpha$	+	.0017404	$\beta$	-	140.804	$\gamma$	-	2.900
810-3	$v_{28}$	=	$\alpha$	+	.0022979	$\beta$	-	177.777	$\gamma$	-	2.351
810-4	$v_{29}$	=	$\alpha$	+	.0021144	$\beta$	-	165.820	$\gamma$	-	3.203
810-5	$v_{30}$	=	$\alpha$	+	.0019437	$\beta$	-	154.518	$\gamma$	-	3.042
810-7	$v_{31}$	=	$\alpha$	+	.0015866	$\beta$	-	130.227	$\gamma$	-	2.967
810-8	$v_{32}$	=	$\alpha$	+	.0013827	$\beta$	-	115.917	$\gamma$	-	3.771
810-9	$v_{33}$	=	$\alpha$	+	.0011431	$\beta$	-	98.600	$\gamma$	-	2.389
810-11	$v_{34}$	=	$\alpha$	+	.0007346	$\beta$	-	67.503	$\gamma$	-	2.779
810-12	$v_{35}$	=	$\alpha$	+	.0006181	$\beta$	-	58.150	$\gamma$	-	.853
810-13	$v_{36}$	=	$\alpha$	+	.0005118	$\beta$	-	49.381	$\gamma$	+	.125
810-15	$v_{37}$	=	$\alpha$	+	.0003363	$\beta$	-	34.247	$\gamma$	-	.936
810-16	$v_{38}$	=	$\alpha$	+	.0002883	$\beta$	-	29.925	$\gamma$	-	1.196
810-17	$v_{39}$	=	$\alpha$	+	.0002536	$\beta$	-	26.735	$\gamma$	+	.172

Following are the three normal equations determined from the Trial Two residual equations on the previous page.

$$39 \alpha + .0528203 \beta - 4320.622 \gamma - 99.978 = 0$$

$$.0528203 \alpha + .000096590639 \beta - 7.635582 \gamma - .18530757 = 0$$

$$- 4320.622 \alpha - 7.635582 \beta + 570961.531 \gamma + 14631.081 = 0$$

Solution of these normal equations yields

$$\alpha = - 0.13 \quad \beta = 1995 \quad \gamma = .00005$$

Therefore

$$a = a_0 + \alpha = 81.07 - 0.13 = 80.94$$

$$b = b_0 + \beta = 11460 + 1995 = 13455$$

$$c = c_0 + \gamma = 0.90 + .00005 = 0.90$$

The results of the Trial Two calculation indicate that no further trials are necessary to establish the convergence of the velocity exponent. However, a final differential correction calculation was carried out for each of the three individual sets of turbulent regime runs to establish what sort of agreement exists between the sets as far as the exponent is concerned. For this final

calculation initial values of the constants that were employed are

$$a_0 = 80.94 \quad b_0 = 13450 \quad c_0 = 0.90$$

The value of 0.90 was taken for  $c_0$ ; and  $a_0$ ,  $b_0$  were determined from a least squares analysis of the data. This analysis for equation

$$\frac{1}{K} = a_0 + b_0 \frac{1}{U^{.90}}$$

is indicated in APPENDIX D.

Differential Correction Calculation - Final Trial

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
727-1	123.684	3.1499	42.366	123.306	- .378	-6.40043	-271.161
727-2	114.030	2.4440	32.872	113.812	- .218	-6.68236	-219.663
727-3	110.071	2.2436	30.176	111.116	1.045	-6.77742	-204.515
727-4	106.401	2.0193	27.160	108.100	1.699	-6.89578	-187.289
727-5	107.472	1.8901	25.442	106.362	-1.110	-6.96791	-177.115
727-6	106.359	1.7218	23.158	104.098	-2.261	-7.07157	-163.763
727-7	103.294	1.5139	20.362	101.322	-1.992	-7.21450	-146.902
727-8	97.111	1.3030	17.525	98.465	1.354	-7.38119	-129.355
727-9	94.087	1.0869	14.619	95.559	1.472	-7.58274	-110.852
727-10	110.201	2.1462	28.866	109.806	- .395	-6.82677	-197.062
727-11	90.846	.8252	11.099	92.039	1.193	-7.88872	- 87.557
727-12	89.103	.6693	9.002	89.942	.839	-8.12148	- 73.110
727-13	89.139	.5666	7.621	88.561	- .578	-8.30660	- 63.305
727-14	87.412	.4735	6.369	87.309	- .103	-8.50594	- 54.174
727-15	86.558	.4090	5.501	86.441	- .117	-8.66854	- 47.686

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\tau = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 80.94$$

$$b_0 = 13450$$

$$c_0 = 0.90$$

Residual Equations - Final Trial - RUN SET 727

727-1	$v_1$	=	$\alpha$	+	.0031499 $\beta$	-	271.161 $\gamma$	-	.378
727-2	$v_2$	=	$\alpha$	+	.0024440 $\beta$	-	219.663 $\gamma$	-	.218
727-3	$v_3$	=	$\alpha$	+	.0022436 $\beta$	-	204.515 $\gamma$	+	1.045
727-4	$v_4$	=	$\alpha$	+	.0020193 $\beta$	-	187.289 $\gamma$	+	1.699
727-5	$v_5$	=	$\alpha$	+	.0018901 $\beta$	-	177.115 $\gamma$	-	1.110
727-6	$v_6$	=	$\alpha$	+	.0017218 $\beta$	-	163.763 $\gamma$	-	2.261
727-7	$v_7$	=	$\alpha$	+	.0015139 $\beta$	-	146.902 $\gamma$	-	1.992
727-8	$v_8$	=	$\alpha$	+	.0013030 $\beta$	-	129.355 $\gamma$	+	1.354
727-9	$v_9$	=	$\alpha$	+	.0010869 $\beta$	-	110.852 $\gamma$	+	1.472
727-10	$v_{10}$	=	$\alpha$	+	.0021462 $\beta$	-	197.062 $\gamma$	-	.395
727-11	$v_{11}$	=	$\alpha$	+	.0008252 $\beta$	-	87.557 $\gamma$	+	1.193
727-12	$v_{12}$	=	$\alpha$	+	.0006693 $\beta$	-	73.110 $\gamma$	+	.839
727-13	$v_{13}$	=	$\alpha$	+	.0005666 $\beta$	-	63.305 $\gamma$	-	.578
727-14	$v_{14}$	=	$\alpha$	+	.0004735 $\beta$	-	54.174 $\gamma$	-	.103
727-15	$v_{15}$	=	$\alpha$	+	.0004090 $\beta$	-	47.686 $\gamma$	-	.117

Normal Equations

$$15\alpha + .0224623\beta - 2133.509\gamma + .450 = 0$$

$$.0224623\alpha + .000043162057\beta - 3.981333\gamma - .001316473 = 0$$

$$-2133.509\alpha - 3.981333\beta + 368533.831\gamma + 99.431142 = 0$$

$$\alpha = -0.23 \quad \beta = 720 \quad \gamma = 0.006$$

$$a = a_0 + \alpha = 80.94 - 0.23 = 80.71$$

$$b = b_0 + \beta = 13450 + 720 = 14170$$

$$c = c_0 + \gamma = 0.90 + 0.006 = 0.906$$

Differential Correction Calculation - Final Trial

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
801-1	118.935	2.6817	36.069	117.009	-1.926	-6.57924	-237.307
801-4	110.496	2.3278	31.309	112.249	1.753	-6.73649	-210.913
801-7	104.981	1.6287	21.906	102.846	-2.135	-7.13329	-156.262
801-8	101.702	1.4063	18.915	99.855	-1.847	-7.29641	-138.012
801-9	96.535	1.1639	15.654	96.594	.059	-7.50660	-117.508
801-10	92.163	.9199	12.373	93.313	1.150	-7.76811	-96.115
801-11	90.366	.7359	9.898	90.838	.472	-8.01599	-79.342
801-12	88.135	.6112	8.221	89.161	1.026	-8.22229	-67.595
801-13	88.017	.5103	6.864	87.804	-.213	-8.42289	-57.815
801-14	87.742	.4410	5.931	86.871	-.871	-8.58505	-50.918

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\tau = \frac{1}{K'} - \frac{1}{K}$$

$$a_0 = 80.94$$

$$b_0 = 13450$$

$$c_0 = 0.90$$

Residual Equations - Final Trial - RUN SET 801

801-1	$v_1$	=	$\alpha$	+	.0026817	$\beta$	-	237.307	$\gamma$	-	1.926
801-4	$v_2$	=	$\alpha$	+	.0023278	$\beta$	-	210.913	$\gamma$	+	1.753
801-7	$v_3$	=	$\alpha$	+	.0016287	$\beta$	-	156.262	$\gamma$	-	2.135
801-8	$v_4$	=	$\alpha$	+	.0014063	$\beta$	-	138.012	$\gamma$	-	1.847
801-9	$v_5$	=	$\alpha$	+	.0011639	$\beta$	-	117.508	$\gamma$	+	.059
801-10	$v_6$	=	$\alpha$	+	.0009199	$\beta$	-	96.115	$\gamma$	+	1.150
801-11	$v_7$	=	$\alpha$	+	.0007359	$\beta$	-	79.342	$\gamma$	+	.472
801-12	$v_8$	=	$\alpha$	+	.0006112	$\beta$	-	67.595	$\gamma$	+	1.026
801-13	$v_9$	=	$\alpha$	+	.0005103	$\beta$	-	57.815	$\gamma$	-	.213
801-14	$v_{10}$	=	$\alpha$	+	.0004410	$\beta$	-	50.918	$\gamma$	-	.871

Normal Equations

$$10 \alpha + .0124267 \beta - 1211.787 \gamma - 2.532 = 0$$

$$.0124267 \alpha + .000020811 \beta - 1.952783 \gamma - .005550845 = 0$$

$$-1211.787 \alpha - 1.952783 \beta + 184109.708 \gamma + 508.247384 = 0$$

$$\alpha = - 0.66 \quad \beta = - 1220 \quad \gamma = - 0.020$$

$$a = a_0 + \alpha = 80.94 - 0.66 = 80.28$$

$$b = b_0 + \beta = 13450 - 1220 = 12230$$

$$c = c_0 + \gamma = 0.90 - 0.020 = 0.880$$



Differential Correction Calculation - Final Trial

Run No.	$\frac{1}{K}$	$\frac{1}{U^{c_0}} \times 10^3$	$b_0 \frac{1}{U^{c_0}}$	$\frac{1}{K'}$	$\frac{1}{K'} - \frac{1}{K}$	$\ln \frac{1}{U}$	$b_0 \frac{1}{U^{c_0}} \ln \frac{1}{U}$
810-1	120.844	2.9798	40.078	121.018	.174	-6.46209	-258.988
810-2	103.915	1.7404	23.408	104.348	.433	-7.05961	-165.251
810-3	109.755	2.2979	30.907	111.847	2.092	-6.75087	-208.649
810-4	108.504	2.1144	28.439	109.379	.875	-6.84332	-194.617
810-5	106.387	1.9437	26.143	107.083	.696	-6.93683	-181.350
810-7	102.219	1.5866	21.340	102.280	.061	-7.16240	-152.846
810-8	100.687	1.3827	18.597	99.537	-1.150	-7.31522	-136.041
810-9	96.559	1.1431	15.375	96.315	-.244	-7.52672	-115.723
810-11	92.268	.7346	9.880	90.820	-1.448	-8.01797	-79.218
810-12	89.006	.6181	8.313	89.253	.247	-8.20985	-68.248
810-13	86.810	.5118	6.884	87.824	1.014	-8.41958	-57.960
810-15	85.860	.3363	4.523	85.463	-.397	-8.88614	-40.192
810-16	85.570	.2883	3.878	84.818	-.752	-9.05707	-35.123
810-17	83.804	.2536	3.411	84.351	.547	-9.19994	-31.381

$$\frac{1}{K'} = a_0 + b_0 \frac{1}{U^{c_0}}$$

$$\tau = \frac{1}{K'} - \frac{1}{K}$$

$$\begin{aligned} a_0 &= 80.94 \\ b_0 &= 13450 \\ c_0 &= 0.90 \end{aligned}$$

Residual Equations - Final Trial - RUN SET 810

810-1	$v_1$	=	$\alpha$	+	.0029798	$\beta$	-	258.988	$\gamma$	+	.174
810-2	$v_2$	=	$\alpha$	+	.0017404	$\beta$	-	165.251	$\gamma$	+	.433
810-3	$v_3$	=	$\alpha$	+	.0022979	$\beta$	-	208.649	$\gamma$	+	2.092
810-4	$v_4$	=	$\alpha$	+	.0021144	$\beta$	-	194.617	$\gamma$	+	.875
810-5	$v_5$	=	$\alpha$	+	.0019437	$\beta$	-	181.350	$\gamma$	+	.696
810-7	$v_6$	=	$\alpha$	+	.0015866	$\beta$	-	152.846	$\gamma$	+	.061
810-8	$v_7$	=	$\alpha$	+	.0013827	$\beta$	-	136.041	$\gamma$	-	1.150
810-9	$v_8$	=	$\alpha$	+	.0011431	$\beta$	-	115.723	$\gamma$	-	.244
810-11	$v_9$	=	$\alpha$	+	.0007346	$\beta$	-	79.218	$\gamma$	-	1.448
810-12	$v_{10}$	=	$\alpha$	+	.0006181	$\beta$	-	68.248	$\gamma$	+	.247
810-13	$v_{11}$	=	$\alpha$	+	.0005118	$\beta$	-	57.960	$\gamma$	+	1.014
810-15	$v_{12}$	=	$\alpha$	+	.0003363	$\beta$	-	40.192	$\gamma$	-	.397
810-16	$v_{13}$	=	$\alpha$	+	.0002883	$\beta$	-	35.123	$\gamma$	-	.752
810-17	$v_{14}$	=	$\alpha$	+	.0002536	$\beta$	-	31.381	$\gamma$	+	.547

Normal Equations

$$14 \alpha + .0179313 \beta - 1725.587 \gamma + 2.148 = 0$$

$$.0179313 \alpha + .000032617190 \beta - 3.027313 \gamma + .006906303 = 0$$

$$-1725.587 \alpha - 3.027313 \beta + 282067.979 \gamma - 609.978541 = 0$$

$$\alpha = -0.13 \quad \beta = -3460 \quad \gamma = -0.036$$

$$a = a_0 + \alpha = 80.94 - 0.13 = 80.81$$

$$b = b_0 + \beta = 13450 - 3460 = 9990$$

$$c = c_0 + \gamma = 0.90 - 0.036 = 0.864$$

VII. APPENDIXF. Determination of Chilton-Colburn j - factor

It has been shown in APPENDIX D that the intercept of the Wilson graph takes on the value  $a = 79.05$  for a velocity exponent  $c = 0.80$ . Therefore

$$\frac{1}{K} = \frac{1}{k_s} + \frac{1}{k_s} + \frac{1}{k_w}$$

$$\frac{1}{K} = 79.05 + \frac{1}{k_w}$$

Reynolds number:

$$D = 1.135''$$

$$\nu/e = .01072 \text{ cm}^2/\text{sec. @ } 19^\circ\text{C (53)}$$

$$N_{Re} = \frac{D U_w}{\nu/e}$$

$$N_{Re} = \frac{(1.135)(2.54)}{(.01072)(60)} U_w = 4.482 U_w$$

Schmidt number:

$$D = 1.34(10^{-5}) \text{ cm}^2/\text{sec. @ } 19^\circ\text{C (21)}$$

$$N_{Sc} = \frac{\nu/e}{D}$$

$$N_{Sc} = 800$$

Chilton-Colburn j - factor:

$$j_M = \frac{k_w}{U_w} N_{Sc}^{.67} = \frac{86.176}{(1/k_w) U_w}$$

Determination of Chilton-Colburn j - factor

RUN SET - 727

Run No.	1/K (min./cm.)	1/k <sub>w</sub> (min./cm.)	U <sub>w</sub> (cm./min)	N <sub>Re</sub>	J <sub>M</sub> × 10 <sup>3</sup>
727-1	123.68	44.63	602.1	2700	3.206
727-2	114.03	34.98	798.2	3580	3.086
727-3	110.07	31.02	877.8	3930	3.164
727-4	106.40	27.35	988.1	4430	3.188
727-5	107.47	28.42	1062	4760	2.855
727-6	106.36	27.31	1178	5280	2.678
727-7	103.29	24.24	1359	6090	2.615
727-8	97.11	18.06	1606	7200	2.971
727-9	94.99	15.04	1964	8800	2.917
727-10	110.20	31.15	922.2	4130	2.999
727-11	90.85	11.80	2667	11950	2.738
727-12	89.10	10.05	3366	15090	2.547
727-13	89.14	10.09	4051	18160	2.108
727-14	87.41	8.36	4944	22160	2.084
727-15	86.56	7.51	5817	26070	1.972

Determination of Chilton-Colburn j - factor

RUN SET - 801

Run No.	1/K (min./cm.)	1/k <sub>w</sub> (min./cm.)	U <sub>w</sub> (cm./min)	N <sub>Re</sub>	j <sub>M</sub> ×10 <sup>3</sup>
801-1	118.94	39.89	720.0	3230	3.000
801-4	110.50	31.45	842.6	3780	3.251
801-7	104.98	25.93	1253	5620	2.652
801-8	101.70	22.65	1475	6610	2.579
801-9	96.54	17.49	1820	8160	2.707
801-10	92.16	13.11	2364	10600	2.780
801-11	90.37	11.32	3029	13580	2.513
801-12	88.14	9.09	3723	16690	2.546
801-13	88.02	8.97	4550	20390	2.111
801-14	87.74	8.69	5351	23980	1.853

Determination of Chilton-Colburn j - factor

RUN SET - 810

Run No.	1/K (min./cm.)	1/k <sub>w</sub> (min./cm.)	U <sub>w</sub> (cm./min)	N <sub>Re</sub>	J <sub>M</sub> × 10 <sup>3</sup>
810-1	120.84	41.79	640.4	2870	3.220
810-2	103.92	24.87	1164	5220	2.976
810-3	109.76	30.71	854.8	3830	3.282
810-4	108.50	29.45	937.6	4200	3.120
810-5	106.39	27.34	1030	4610	3.060
810-7	102.22	23.17	1290	5780	2.883
810-8	100.69	21.64	1503	6740	2.649
810-9	96.56	17.51	1857	8320	2.650
810-11	92.27	13.22	3035	13600	2.147
810-12	89.01	9.96	3677	16480	2.353
810-13	86.81	7.76	4535	20330	2.448
810-15	85.86	6.81	7231	32410	1.750
810-16	85.57	6.52	8579	38450	1.540
810-17	83.80	4.75	9897	44360	1.833

VII. APPENDIXG. Determination of Sherwood Parameter

Application of the method of differential correction shows the exponent on the velocity to converge to a value 0.90 . The corresponding intercept of the Wilson graph is 80.94 . Therefore

$$\frac{1}{K} = \frac{1}{k_s} + \frac{1}{k_m} + \frac{1}{k_w}$$

$$\frac{1}{K} = 80.94 + \frac{1}{k_w}$$

Reynolds number:

$$D = 1.135''$$

$$\mu/e = .01072 \text{ cm}^2/\text{sec. @ } 19^\circ\text{C}$$

$$N_{\text{Re}} = \frac{D U_w}{\mu/e}$$

$$N_{\text{Re}} = 4.482 U_w$$

Schmidt number:

$$D = 1.34 (10^{-5}) \text{ cm}^2/\text{sec. @ } 19^\circ\text{C}$$

$$N_{\text{Sc}} = \frac{\mu/e}{D}$$

$$N_{\text{Sc}} = 800$$



Sherwood Parameter:

$$N_{Sh} = \frac{k_w D}{\mathcal{D}}$$

$$N_{Sh} = \frac{(1.135)(2.54)}{(1/k_w)(1.34)(10^{-5})(60)}$$

$$N_{Sh} = \frac{3586}{(1/k_w)}$$

Determination of Sherwood Parameter

RUN SET - 727

Run No.	1/K (min./cm.)	1/k <sub>w</sub> (min./cm.)	U <sub>w</sub> (cm./min)	N <sub>Re</sub>	N <sub>Sh</sub>
727-1	123.68	42.74	602.1	2700	83.9
727-2	114.03	33.09	798.2	3580	108.4
727-3	110.07	29.13	877.8	3930	123.1
727-4	106.40	25.46	988.1	4430	140.8
727-5	107.47	26.53	1062	4760	135.2
727-6	106.36	25.42	1178	5280	141.1
727-7	103.29	22.35	1359	6090	160.4
727-8	97.11	16.17	1606	7200	221.8
727-9	94.09	13.15	1964	8800	272.7
727-10	110.20	29.26	922.2	4130	122.6
727-11	90.85	9.91	2667	11950	361.9
727-12	89.10	8.16	3366	15090	439.5
727-13	89.14	8.20	4051	18160	437.3
727-14	87.41	6.47	4944	22160	554.3
727-15	86.56	5.62	5817	<del>2870</del>	638.1

Determination of Sherwood Parameter

RUN SET - 801

Run No.	1/K (min./cm.)	1/k <sub>w</sub> (min./cm.)	U <sub>w</sub> (cm./min)	NRe	NSh
801-1	118.94	38.00	720.0	3230	94.4
801-4	110.50	29.56	842.6	3780	121.3
801-7	104.98	24.04	1253	5620	149.2
801-8	101.70	20.76	1475	6610	172.7
801-9	96.54	15.60	1820	8160	229.9
801-10	92.16	11.22	2364	10600	319.6
801-11	90.37	9.43	3029	13580	380.3
801-12	88.14	7.20	3723	16690	498.1
801-13	88.02	7.08	4550	20390	506.5
801-14	87.74	6.80	5351	23980	527.4

Determination of Sherwood Parameter

RUN SET - 810

Run No.	1/K (min./cm.)	1/k <sub>w</sub> (min./cm.)	U <sub>w</sub> (cm./min)	N <sub>Re</sub>	N <sub>Sh</sub>
810-1	120.84	39.90	640.4	2870	89.9
810-2	103.92	22.98	1164	5220	156.0
810-3	109.76	28.82	854.8	3830	124.4
810-4	108.50	27.56	937.6	4200	130.1
810-5	106.39	25.45	1030	4610	140.9
810-7	102.22	21.28	1290	5780	168.5
810-8	100.69	19.75	1503	6740	181.6
810-9	96.56	15.62	1857	8320	229.6
810-11	92.27	11.33	3035	13600	316.5
810-12	89.01	8.07	3677	16480	444.4
810-13	86.81	5.87	4535	20330	610.9
810-15	85.86	4.92	7231	32410	728.9
810-16	85.57	4.63	8579	38450	774.5
810-17	83.80	2.86	9897	44360	1253.8

VII. APPENDIXH. Diffusion in Laminar FlowTransfer Area:

$$D = 1.135''$$

$$L = 49.5''$$

$$A = \pi D L$$

$$A = (3.1416)(1.135)(49.5)(2.54)^2$$

$$A = 1138.7 \text{ cm}^2$$

Laminar Flow Diffusion Parameter:

$$D = 1.34(10)^{-5} \text{ cm}^2/\text{sec.}$$

$$\rho = 0.998 \text{ gm./cm}^3$$

$$\frac{W}{DeL} = \frac{W}{(1.34)(10)^{-5}(60)(2.54)(.998)}$$

$$\frac{W}{DeL} = \frac{W}{101(10)^{-3}}$$

Concentration Driving Force:

$$C_s = 0.317 \text{ gm./cm}^3$$

$$C_{w1} = \text{negligible relative to salt side conc.}$$

$$C_{w2} = \text{exit water stream concentration}$$

$$\Delta C_1 = 0.317 - \text{neg.} = 0.317$$

$$\Delta C_2 = 0.317 - C_{w2}$$

Concentration Driving Force: (Cont'd)

$$\Delta C_{1m} = \frac{\Delta C_1 - \Delta C_2}{\ln(\Delta C_2 / \Delta C_1)}$$

$$\Delta C_{1m} = \frac{C_{w2}}{\ln \frac{.317}{.317 - C_{w2}}}$$

Over-all Resistance to Transfer:

$$Q_w (C_{w2} - C_{w1}) = K A \Delta C_{1m}$$

$$\frac{1}{K} = \frac{(1138.7)(\Delta C_{1m})}{Q_w (C_{w2} - C_{w1})}$$

Water-side Film Coefficient:

The value of  $(1/k_s + 1/k_m)$  has been determined from the turbulent regime results and found to be 80.94 from the "Wilson technique" type treatment of the data.

$$\frac{1}{k_w} = \frac{1}{K} - 80.94$$

Water-side Wall Concentration:

With reference to Figure A-1

$$n' = K A (C_S - C_W) = k_W A (C_W^{\circ} - C_W)$$

Therefore if  $C_W$  is assumed negligible relative to  $C_S$ , then

$$C_W^{\circ} = \frac{(1/k_W)}{(1/K)} (C_S)$$

where  $C_S$  and  $C_W$  are bulk stream concentrations.

Diffusion in Laminar Flow

Run No.	W (gm./min)	Q <sub>w</sub> (cm <sup>3</sup> /min)	W/D <sub>e</sub> L	C <sub>w2</sub> - C <sub>w1</sub> (gm./cm <sup>3</sup> )	ΔC <sub>lm</sub> (gm./cm <sup>3</sup> )
823-1	150.1	150.4	1490	.0153	.30934
823-2	218.5	218.9	2160	.0110	.31153
823-3	191.7	192.0	1900	.0124	.31078
823-4	182.5	182.8	1810	.0129	.31054
829-1	1302	1305	12890	.00200	.31654
829-2	1197	1199	11850	.00228	.31630
829-3	1146	1148	11340	.00245	.31620
829-4	762	764	7540	.00362	.31538
829-5	763	765	7550	.00365	.31525
905-1	358	358.7	3545	.00709	.31360
905-2	366	366.7	3624	.00689	.31364
905-3	539	540.0	5340	.00466	.31490
905-4	528	529.0	5230	.00499	.31466
905-5	515	515.9	5100	.00531	.31461



Diffusion in Laminar Flow

Run No.	$\frac{l}{K}$	$\frac{l}{k_w}$	$C_w^o$	$\frac{C_{w2} - C_{w1}}{C_w^o - C_{w1}}$
823-1	153.08	72.14	.14939	.1024
823-2	147.32	66.38	.14284	.0770
823-3	148.64	67.70	.14438	.0859
823-4	149.96	69.02	.14590	.0884
829-1	138.10	57.16	.13121	.0152
829-2	131.75	50.81	.12225	.0187
829-3	128.02	47.08	.11658	.0210
829-4	129.85	48.91	.11940	.0303
829-5	128.56	47.62	.11742	.0311
905-1	140.41	59.47	.13426	.0528
905-2	141.35	60.41	.13548	.0509
905-3	142.50	61.56	.13694	.0340
905-4	135.74	54.80	.12798	.0390
905-5	130.77	49.83	.12079	.0439

VII. APPENDIXI. Summary of DataTubular Water Stream Flow Rates

Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )	Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )
727-1	3930	801-1	4700
727-2	5210	801-4	5500
727-3	5730	801-7	8180
727-4	6450	801-8	9630
727-5	6930	801-9	11880
727-6	7690	801-10	15430
727-7	8870	801-11	19770
727-8	10480	801-12	24300
727-9	12820	801-13	29700
727-10	6020	801-14	34930
727-11	17410		
727-12	21970		
727-13	26440		
727-14	32270		
727-15	37970		

Tubular Water Stream Flow Rates

Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )	Run No.	$Q_w$ ( $\text{cm}^3/\text{min}$ )
810-1	4180	823-1	150.4
810-2	7600	823-2	218.9
810-3	5580	823-3	192.0
810-4	6120	823-4	182.8
810-5	6720		
810-7	8420	829-1	1305
810-8	9810	829-2	1199
810-9	12120	829-3	1148
810-11	19810	829-4	764
810-12	24000	829-5	765
810-13	29600		
810-15	47200	905-1	358.7
810-16	56000	905-2	366.7
810-17	64600	905-3	540.0
		905-4	529.0
		905-5	515.9

Annular Salt Solution Flow Rates

Run No.	$Q_s$ ( $\text{cm}^3/\text{min}$ )	Run No.	$Q_s$ ( $\text{cm}^3/\text{min}$ )
727-1	15310	801-1	15310
727-2	15350	801-4	15310
727-3	15350	801-7	15310
727-4	15380	801-8	15350
727-5	15380	801-9	15350
727-6	15400	801-10	15350
727-7	15400	801-11	15350
727-8	15440	801-12	15350
727-9	15440	801-13	15380
727-10	15440	801-14	15380
727-11	15440		
727-12	15440		
727-13	15460		
727-14	15440		
727-15	15440		

Annular Salt Solution Flow Rates

Run No.	$Q_s$ ( $\text{cm}^3/\text{min}$ )	Run No.	$Q_s$ ( $\text{cm}^3/\text{min}$ )
810-1	15310	823-1	15240
810-2	15350	823-2	15310
810-3	15350	823-3	15380
810-4	15380	823-4	15400
810-5	15380		
810-7	15380	829-1	15180
810-8	15380	829-2	15220
810-9	15380	829-3	15240
810-11	15380	829-4	15240
810-12	15380	829-5	15220
810-13	15380		
810-15	15380	905-1	15220
810-16	15380	905-2	15240
810-17	15380	905-3	15350
		905-4	15350
		905-5	15350

Diameter Measurements

Run No.	Top (inches)	Bottom (inches)	Difference (inches)
727-1	1.145	1.123	.022
727-2	1.141	1.120	.021
727-3	1.150	---	--
727-4	1.139	1.123	.016
727-5	1.146	1.127	.019
727-6	1.141	1.118	.023
727-7	1.141	1.120	.021
727-8	1.145	1.127	.018
727-9	1.139	1.127	.019
727-10	1.135	1.117	.018
727-11	1.141	1.120	.021
727-12	1.152	1.131	.021
727-13	1.145	1.127	.018
727-14	1.141	1.118	.023
727-15	1.139	1.122	.017
801-1	1.141	1.120	.021
801-4	1.148	1.131	.017
801-7	1.150	1.131	.019
801-8	1.146	1.124	.022
801-9	1.146	1.131	.015
801-10	1.135	1.118	.017
801-11	1.139	1.123	.016
801-12	1.139	1.120	.019
801-13	1.141	1.118	.023
801-14	1.145	1.124	.021

Diameter Measurements

Run No.	Top (inches)	Bottom (inches)	Difference (inches)
810-1	1.139	1.120	.019
810-2	1.152	1.135	.017
810-3	1.146	1.124	.022
810-4	---	1.123	--
810-5	1.141	1.120	.021
810-7	1.146	1.131	.015
810-8	1.139	1.123	.016
810-9	1.141	1.118	.023
810-11	1.141	1.118	.023
810-12	1.141	---	--
810-13	1.152	1.135	.017
810-15	1.150	1.127	.023
810-16	1.145	1.129	.016
810-17	1.135	1.118	.017
823-1	1.146	1.124	.022
823-2	1.141	1.123	.018
823-3	1.139	1.116	.023
823-4	1.146	1.123	.023
829-1	1.150	1.129	.021
829-2	---	1.123	--
829-3	1.141	1.123	.018
829-4	1.148	1.125	.023
829-5	1.146	1.125	.021
905-1	1.146	1.123	.023
905-2	1.146	1.125	.021
905-3	1.139	1.120	.020
905-4	1.141	1.118	.023
905-5	1.150	1.129	.021

Concentration of Exit Water Stream

Run No.	$C_{w2}$ (gm./cm. <sup>3</sup> )	Run No.	$C_{w2}$ (gm./cm. <sup>3</sup> )
727-1	$748 \times 10^{-6}$	801-1	$647 \times 10^{-6}$
727-2	614	801-4	596
727-3	579	801-7	425
727-4	533	801-8	374
727-5	492	801-9	321
727-6	449	801-10	261
727-7	402	801-11	210
727-8	363	801-12	177
727-9	308	801-13	147
727-10	551	801-14	127
727-11	238		
727-12	194		
727-13	163		
727-14	138		
727-15	120		



Concentration of Exit Water Stream

Run No.	$C_{w2}$ (gm./cm. <sup>3</sup> )	Run No.	$C_{w2}$ (gm./cm. <sup>3</sup> )
810-1	$713 \times 10^{-6}$	823-1	$15300 \times 10^{-6}$
810-2	460	823-2	11000
810-3	590	823-3	12400
810-4	545	823-4	12900
810-5	507		
810-7	423	829-1	2010
810-8	370	829-2	2290
810-9	314	829-3	2460
810-11	205	829-4	3630
810-12	177	829-5	3660
810-13	149		
810-15	98.5	905-1	7100
810-16	85.0	905-2	6900
810-17	76.5	905-3	4670
		905-4	5000
		905-5	5320

Temperature Readings

Run No.	Water Side ( °F )	Salt Side ( °F )	Difference ( F° )
727-1	67.0	67.3	0.3
	66.8	67.0	0.2
727-2	66.5	66.9	0.4
	66.2	67.0	0.8
727-3	67.2	67.0	- 0.2
	67.7	67.7	0.0
727-4	67.0	66.8	- 0.2
	66.9	67.2	0.3
727-5	66.8	66.1	- 0.7
	66.8	66.7	- 0.1
727-6	66.8	66.7	- 0.1
	66.8	67.2	0.4
727-7	66.8	67.0	0.2
	66.8	67.5	0.7
727-8	66.6	66.2	- 0.4
	66.6	66.6	0.0
727-9	66.6	66.8	0.2
	66.6	67.2	0.6
727-10	66.9	66.6	- 0.3
	66.9	67.0	0.1
727-11	67.4	67.0	- 0.4
	67.5	67.5	0.0
727-12	67.2	66.9	- 0.3
	67.2	67.2	0.0
727-13	66.8	66.3	- 0.5
	66.8	66.9	0.1
727-14	66.3	66.5	0.2
	66.2	66.9	0.7
727-15	66.0	66.2	0.2
	66.0	66.6	0.6

Temperature Readings

Run No.	Water Side ( °F )	Salt Side ( °F )	Difference ( F° )
801-1	66.7 66.3	66.2 66.7	- 0.5 0.4
801-4	66.6 66.6	66.1 67.0	- 0.5 0.4
801-7	66.7 66.8	67.0 67.3	0.3 0.5
801-8	66.8 66.8	66.0 66.9	- 0.8 0.1
801-9	66.8 66.8	66.7 67.2	- 0.1 0.4
801-10	66.7 66.7	66.3 67.2	- 0.4 0.5
801-11	66.2 66.2	66.4 67.2	0.2 1.0
801-12	66.0 65.8	66.2 66.6	0.2 0.8
801-13	66.3 66.3	66.0 66.5	- 0.3 0.2
801-14	66.2 66.2	66.2 67.0	0.0 0.8

Temperature Readings

Run No.	Water Side ( °F )	Salt Side ( °F )	Difference ( F° )
810-1	67.2	66.6	- 0.6
	67.2	67.0	- 0.2
810-2	66.8	67.1	0.3
	66.7	66.4	- 0.3
810-3	66.7	66.3	- 0.3
	66.7	66.9	0.2
810-4	66.5	66.3	- 0.2
	66.5	66.9	0.4
810-5	66.7	66.3	- 0.4
	66.7	67.0	0.3
810-7	66.5	66.3	- 0.2
	66.6	66.8	0.2
810-8	66.5	66.2	- 0.3
	66.3	66.7	0.4
810-9	66.1	66.0	- 0.1
	66.1	66.5	0.4
810-11	65.6	65.3	- 0.3
	66.5	66.0	- 0.5
810-12	66.0	65.8	- 0.2
	66.0	66.8	0.8
810-13	66.2	65.8	- 0.4
	66.2	66.3	0.1
810-15	65.3	65.3	0.0
	65.2	65.2	0.0
810-16	64.9	65.1	0.2
	64.9	65.1	0.2
810-17	64.7	65.0	0.3
	64.7	65.0	0.3

Temperature Readings

Run No.	Water Side ( °F )	Salt Side ( °F )	Difference ( F° )
823-1	67.0	66.8	- 0.2
	67.0	67.2	0.2
823-2	67.2	66.9	- 0.3
	67.2	67.2	0.0
823-3	67.2	66.2	- 1.0
	67.2	66.4	- 0.8
823-4	67.2	67.2	0.0
	67.2	67.3	0.1
829-1	70.2	69.0	- 1.2
	70.1	69.8	- 0.3
829-2	70.0	69.3	- 0.7
	69.8	69.9	0.1
829-3	69.5	68.3	- 1.2
	69.4	69.1	- 0.3
829-4	69.3	68.5	- 0.8
	69.3	69.0	- 0.3
829-5	69.0	68.2	- 0.8
	69.0	69.0	0.0
905-1	68.0	67.0	- 1.0
	68.0	67.2	- 0.8
905-2	68.1	67.7	- 0.4
	68.2	68.0	- 0.2
905-3	68.2	67.0	- 1.2
	68.3	67.4	- 0.9
905-4	68.3	67.6	- 0.7
	68.3	68.0	- 0.3
905-5	68.4	67.9	- 0.5
	68.4	68.6	0.2

VII. APPENDIXJ. Viscous Transfer Due To A Pressure Differential

A closer examination of the hydrostatics of the experimental system used in this work indicates that the pressure of the tubular water stream (sp. g. = 1.0), and the pressure of the annular saturated salt stream (sp. g. = 1.2), can be exactly balanced only at one point along the vertical length of the tube. Depending upon its magnitude, the pressure differential between the two fluids can be expected to influence the transfer rate by causing the transfer of mass by a viscous flow mechanism; this transfer mechanism would be superimposed upon the diffusion of mass induced by the concentration gradient that is present. The latter mechanism has been the one exclusively adopted in the development of the transport theories presented previously.

In Figure A-9 there is shown an accentuated representation of the tubular system herein employed. The experiment was conducted under such conditions that the fluid pressures were balanced at the lower end of the tube. By considering only the hydrostatics of the situation, the pressure difference between the two fluids was calculated and found to range from zero at the bottom to 0.35 p.s.i. at the top.

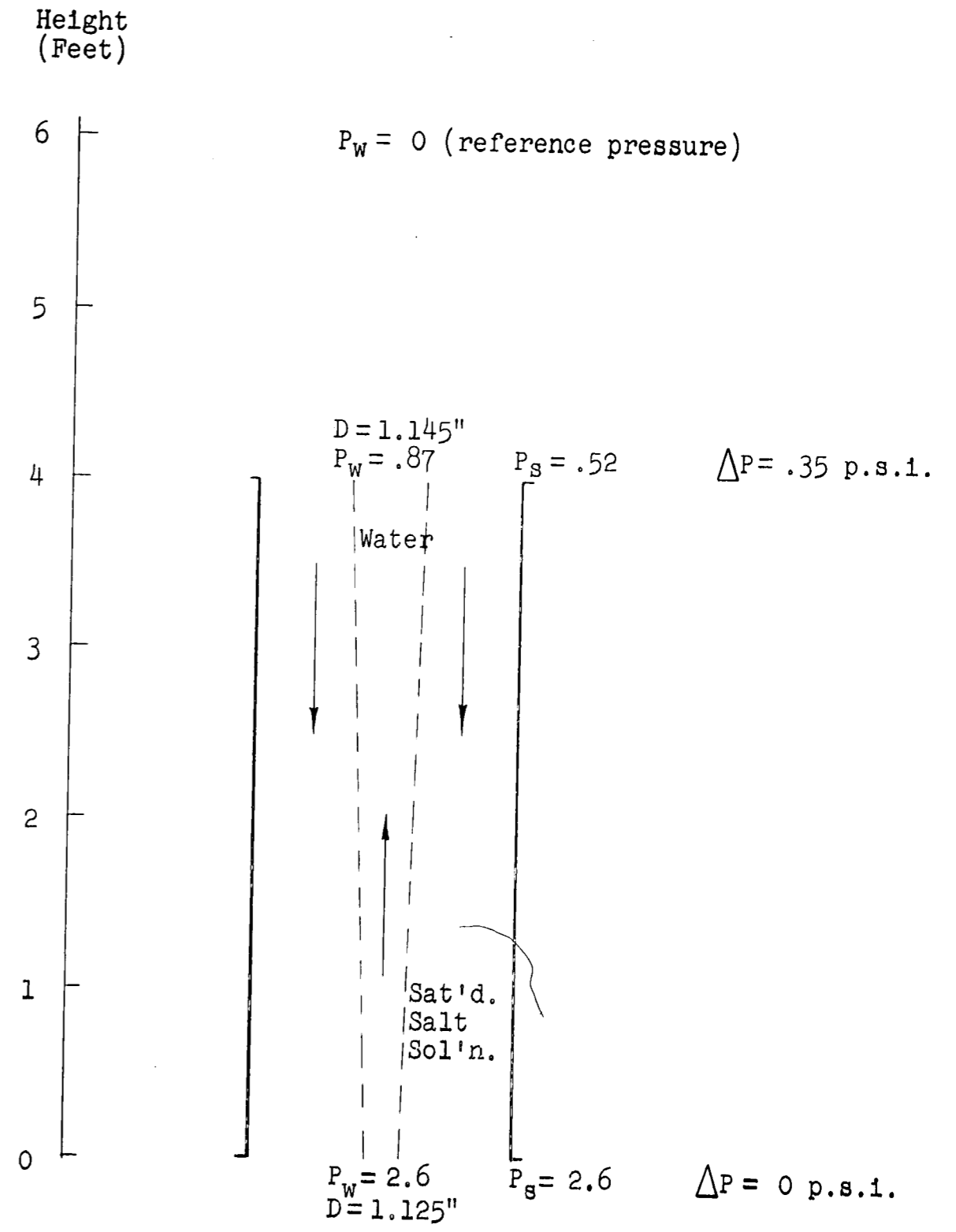


Figure A-9 Hydrostatics of Present Investigation

The pressure in the tube is greater than the pressure in the annulus, and therefore can be expected to impede the diffusional transfer of salt solute from the annulus side to the tube side. This would tend to indicate that the low results obtained in the present investigation, relative to other transport studies, may not only be due to the counter-diffusion mechanism inherent in the dialysis system, but may also be caused by the pressure differential between the two fluids.

It would be difficult to ascertain analytically the influence of the pressure gradient effect on the transfer coefficient. In addition to the necessary information on the membrane properties such as size range and distribution of pores, additional experimental data would be required concerning the viscous transfer of fluid through the membrane as a function of the pressure head involved. However, in order to obtain an estimate of the magnitude of this pressure differential effect on the transport rate, the author's previous results are cited; Master of Science, 1961 (29).



The M.S. thesis was essentially a feasibility study to determine the operability of a dialysis system such as that employed in the present investigation. The essential difference between the two dialyses studies was that the preliminary study, in contrast to the present work, was conducted with the saturated salt solution flowing through the tube counter-current to a water stream in the annulus. In Figure A-10 there is shown an accentuated representation of the tubular system employed in the preliminary study. The experiment was conducted under such conditions that the fluid pressures were balanced at the upper end of the tube. Again, if the hydrostatics of the situation are only considered, the pressure differential is found to range from zero at the top to 0.44 p.s.i. at the bottom of the column, with the pressure in the tube being greater than the pressure in the annulus. However, in this case the transfer takes place from the tube side to the annular side of the membrane, and the pressure gradient is now in the direction such that the viscous flow transfer mechanism should complement rather than hinder the diffusional transfer mechanism. The resulting rate coefficients would now be expected to be higher than they should be (if only a concentration gradient were considered) due to the additional transfer induced by this pressure differential between the two fluids.

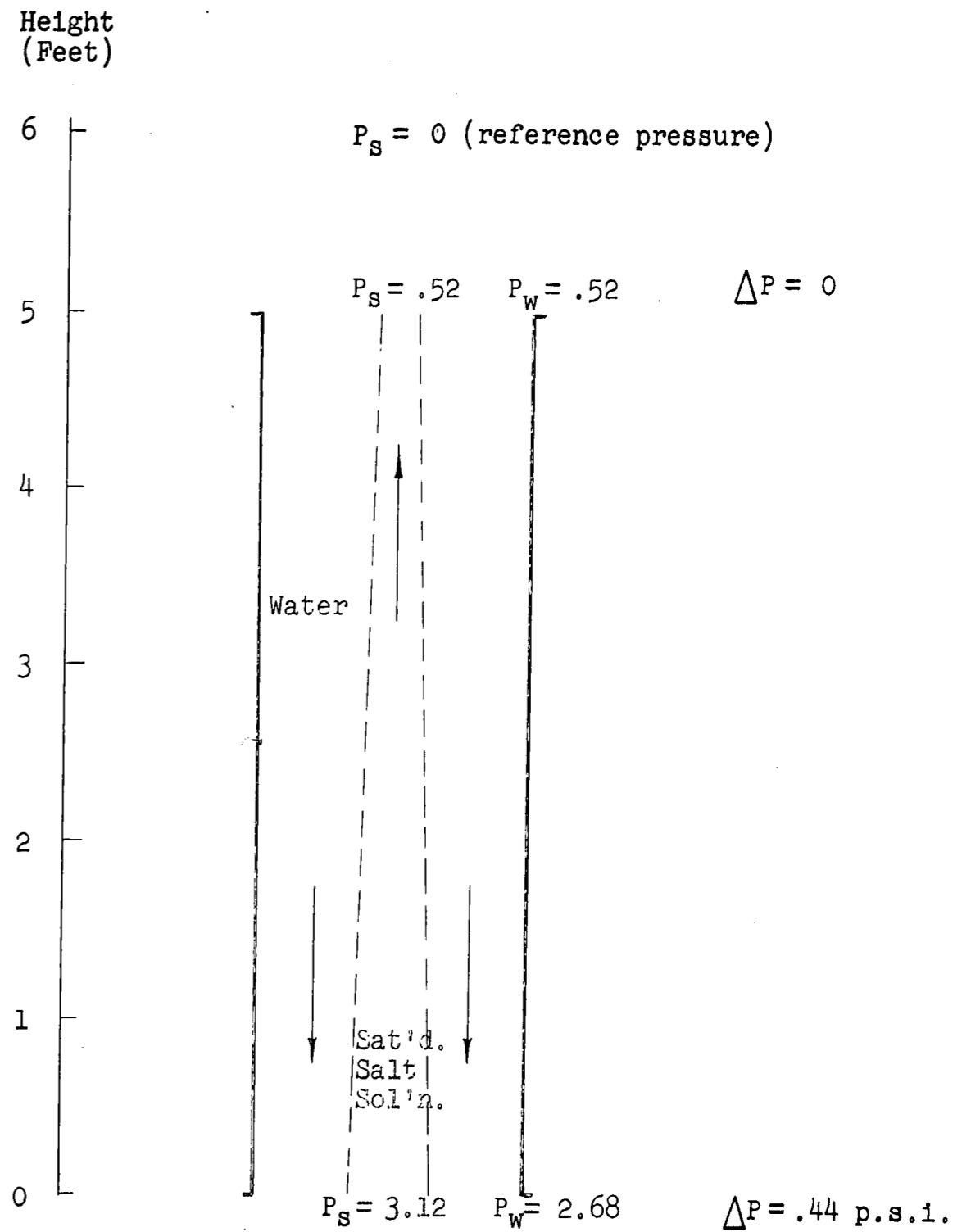


Figure A-10 Hydrostatics of Preliminary Investigation

Calculation of the individual film coefficients for the preliminary study was complicated by the fact that the annular stream velocity was not maintained constant throughout the range of tubular flows. It was therefore necessary that the two liquid films be analyzed concurrently (the Chilton-Colburn relation was employed); in addition, a knowledge of the membrane resistance was required. This constant was determined from over-all  $K$  data using an adaptation of the Wilson technique. However, an incorrect value for the saturation concentration was used in the calculations, hence the M. S. data were recalculated and the membrane resistance,  $1/k_m$ , was found to be  $79.2 \text{ (gm./min.)}/(\text{cm}^2)(\text{gm./cm}^3)$ . This value conforms reasonably well with the data collected by H. B. Lange in a subsequent batch dialysis study (37). Lange determined that  $1/k_m = 71.0$ .

The resulting tubular side resistance,  $1/k_s$ , can then be expressed in the form of the Chilton-Colburn  $j$  - factor as a function of the Reynolds parameter. In Figure A-11 these results are shown along with the results of the present investigation. The M. S. results indicate considerable scatter, which is not surprising in view of the inattention paid to experimental details such as entrance effects and precise temperature control. However, in spite of the partial overlap of the two sets

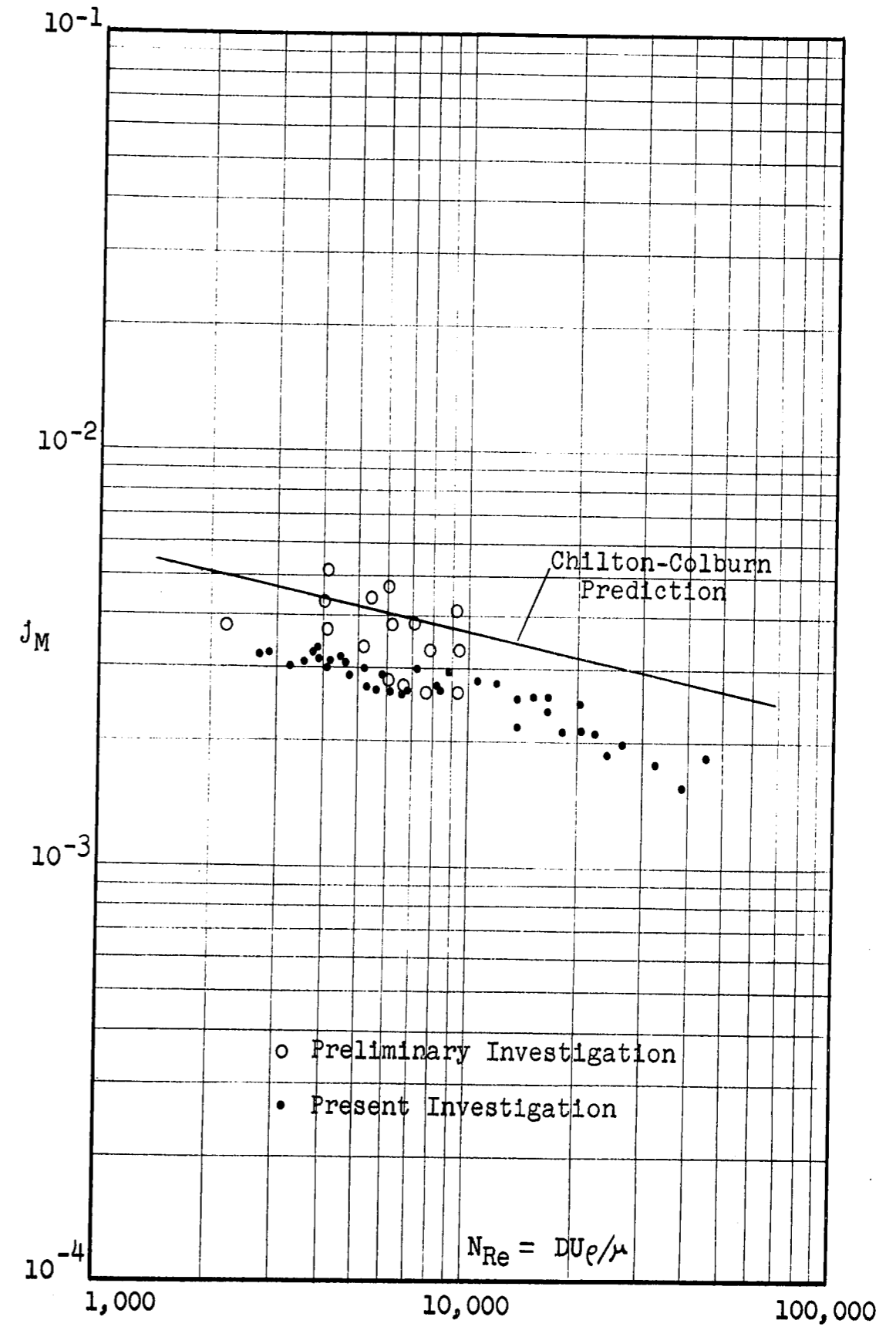
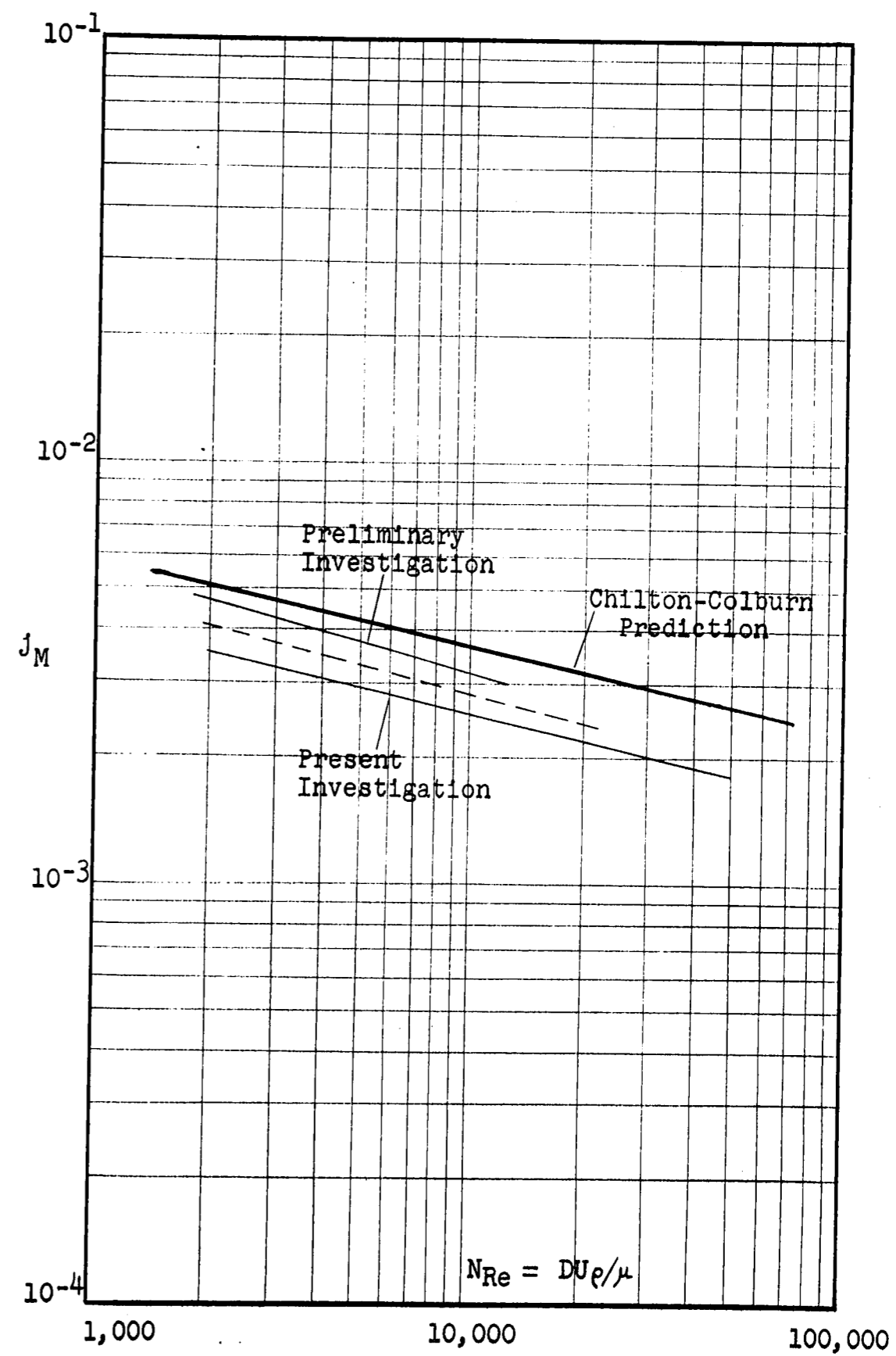


Figure A-11 Chilton-Colburn  $j$  - factor Plot

of data, many of the M. S. experimental points fall in a region somewhat higher than the results of the present investigation and would tend to indicate that a viscous transfer mechanism is present along with the assumed diffusional transfer mechanism.

In order to ascertain the magnitude of this pressure differential effect, the lines representing the data of these dialyses studies are shown in Figure A-12. There is approximately a 20% difference between the two curves. If the results of the present investigation are considered to be lower than they should be and the preliminary results are considered to be higher than they should be, due to the pressure gradient, then the actual results (representing transfer caused only by a concentration gradient), must lie somewhere in between the two lines, as represented by the dotted line. As indicated, the effect of the viscous transfer mechanism upon the results of this present investigation is about 10%. However, it is to be noted that the dialyses results generally fall below the Chilton-Colburn and Deissler predictions and support the conclusion presented previously that the counter-diffusion mechanism involved in the dialysis operation is primarily responsible for the lower results obtained in the present investigation. This is in contrast to the mass transfer results obtained by

Figure A-12 Pressure Diffusion Effect  $j$  - factor Plot

other investigators employing uni-directional experimental systems, as represented by the Chilton-Colburn and Deissler curves.



VIII. NOMENCLATURE

A	transfer area, sq.cm.
$A_x$	cross-sectional area, sq.cm.
$A$	population parameter
a	constant in equations (V-3) and (V-14)
$\alpha$	correction to constant a
$\beta$	population parameter
b	constant in equations (V-3) and (V-14)
$\beta$	correction to constant b
c	constant in equations (V-3) and (V-14)
$\gamma$	correction to constant c
C	molar concentration, g.mols/cu.cm.
c	mass concentration, g./cu.cm.
$C'$	concentration fluctuation of turbulent transport
$C^\circ$	mass concentration at wall, g./cu.cm.
$C_{Bm}$	$(C_{B2} - C_{B1})/\ln(C_{B2}/C_{B1})$
c	specific heat, cal./(g.)(°C)
D	diameter, cm.
$\mathcal{D}$	mass diffusivity, sq.cm./min.
$\delta$	tube wall thickness, cm.
$\Delta$	difference
$\epsilon$	eddy momentum diffusivity, sq.cm./min.
$\epsilon_H$	eddy heat diffusivity, sq.cm./min.
$\epsilon_M$	eddy mass diffusivity, sq.cm./min.



$f$	friction factor, $2g_c \tau / \rho U$
$f$	function
$\phi$	function
$G$	mass velocity, g./ (min)(sq.cm.)
$h$	individual heat transfer coefficient, cal./ (min)(sq.cm.)(°C)
$J_H$	Chilton-Colburn factor for heat transfer $(h/\rho G) N_{Pr}^{2/3}$
$J_M$	Chilton-Colburn factor for mass transfer $(k/U) N_{Sc}^{2/3}$
$K$	over-all dialysis mass transfer coefficient, g./ (sq.cm.)(min)(g./cu.cm.)
$K'$	predicted value of $K$
$k$	individual mass transfer coefficient, g./ (sq.cm.)(min)(g./cu.cm.)
$k$	thermal conductivity, cal./ (min)(sq.cm.)(°C/cm.)
$l$	Prandtl mixing length, cm.
$L$	length of tubular membrane, cm.
$\mu$	viscosity, g./ (min)(cm.)
$N$	totality of data points
$\mathcal{N}$	molar flux, g.mols/ (min)(sq.cm.)
$N_{Nu}$	Nusselt number, $(hD/k)$
$N_{Pr}$	Prandtl number, $(c_p \mu / k)$
$N_{Re}$	Reynolds number, $(DU\rho/\mu)$
$N_{Sc}$	Schmidt number, $(\mu/\rho D)$
$N_{Sh}$	Sherwood number, $(kD/D)$
$N_{St}$	Stanton number for mass transfer, $(k/U)$

$N_{St}'$	Stanton number for heat transfer, $(h/cG)$
$n$	mass flux, $g./(\text{min})(\text{sq.cm.})$
$n^\circ$	mass flux at wall, $g./(\text{min})(\text{sq.cm.})$
$n'$	mass transfer rate, $g./\text{min.}$
$\eta$	constant in Deissler equation (V-56)
$\nu$	kinematic viscosity $(\mu/\rho)$ , $\text{sq.cm.}/\text{min.}$
$P$	pressure, psi absolute
$\Psi$	function
$\xi$	laminar mass transfer parameter, $(\pi/4)(ScL/W)$
$Q$	volumetric flow rate, $\text{cu.cm.}/\text{min.}$
$q$	heat flux, $\text{cal.}/(\text{min})(\text{sq.cm.})$
$q'$	heat transfer rate, $\text{cal.}/\text{min.}$
$R$	tube radius, $\text{cm.}$
$r$	radial distance, $\text{cm.}$
$\kappa$	error in prediction $(1/K' - 1/K)$
$\rho$	density, $g./\text{cu.cm.}$
$S_x$	standard deviation of $x$
$S_{y.x}$	standard deviation of $y$ for a fixed $x$
$T$	temperature, $^\circ\text{C}$
$T^\circ$	temperature at wall, $^\circ\text{C}$
$t_{a/2}$	"Student's" $t$ distribution
$\tau$	shear stress,
$\tau^\circ$	shear stress at wall,
$U$	over-all heat transfer coefficient, $\text{cal.}/(\text{min})(\text{sq.cm.})(^\circ\text{C})$

U	average velocity, cm./min.
u, v, w	components of velocity, cm./min.
u', v', w'	fluctuating components of velocity, cm./min.
u <sub>i</sub> v <sub>i</sub> w <sub>i</sub>	instantaneous components of velocity, cm./min.
$\nu$	residual
W	mass flow rate, g./min.
X	mass fraction
x, y, z	Cartesian coordinates
$\bar{x}$	data point, least squares analysis
$\bar{y}$	data point, least squares analysis

#### Subscripts

m	refers to membrane
n	refers to any number
o	refers to initial values of constants a, b, c
s	refers to salt solution stream
T	refers to total
t	refers to turbulent
w	refers to water stream
A, B	refers to species A and B
1, 2	refers to terminal conditions
I, II	refers to the fluid on either side of the membrane

Vector Notation

$$\nabla c_A = \frac{\partial c_A}{\partial x} + \frac{\partial c_A}{\partial y} + \frac{\partial c_A}{\partial z}$$

$$\nabla^2 c_A = \frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2}$$

$$(\vec{v} \cdot \nabla) c_A = u \frac{\partial c_A}{\partial x} + v \frac{\partial c_A}{\partial y} + w \frac{\partial c_A}{\partial z}$$

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X. VITA

The author was born in New York City on May 28, 1933, the son of Mr. and Mrs. Comminos Kafes.

Upon graduation from Straubenmuller Textile High School in 1951, he attended Lehigh University for two years before transferring to the Massachusetts Institute of Technology where he received a B.S. in Chemical Engineering in 1955.

He was employed by the Republic Aviation Corporation in their thermodynamics department until May, 1956 at which time he joined the Lummus Company as a process engineer. After two years with Lummus, and a three-month tour of duty in the U. S. Navy (Critical Skills Program), he returned to Lehigh University in the Fall of 1958 and subsequently received his M.S. degree in Chemical Engineering in 1961.