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I hereby recommend that the thesis prepared under my supervision by Henry B. Smith

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A STUDY OF DIALYZER DESIGN

A dissertation submitted to the

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DOCTOR OF PHILOSOPHY

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by

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TABLE OF CONTENTS

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TERMINOLOGY

a	Atoms of anions per molecule
A	Area, L^2
c	Condenser capacity, L
C	Concentration, ML^{-3}
C_1	Rich concentration, ML^{-3}
C_2	Dilute concentration ML^{-3}
C_A	Anion concentration, equivalents /liter
C_M	Cation concentration, equivalents/liter
D_d	Dielectric constant
D	Diffusivity coefficient, L^2T^{-1}
d	Distance between condenser plates, L
d_1	Density of gas, ML^{-3}
E	Potential difference, volts, $M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}$
E_m	Membrane potential, volts
E_d	Diffusion potential, volts
E_t	Thermodynamic potential, volts
F	The Faraday
F_e	Free energy, ML
f	Force, MLT^{-2}
g	Weight of solute, M
h	Height of the liquid level, L
H	Potential gradient, volts/cm.
i	Ratio of the actual number of particles to the number if ionization did not take place
I	Electrical Current, amperes
k'	Boltzman's constant, erg/deg.A.
l	Length of flow path, L
L	Lean liquor flow rate, L^3T^{-1}
m	Atoms of cation per molecule
M	Molecular weight
n	Valence of the reversible ion
N_a	Anion transference number
N_c	Cation transference number
N_f	Frictional resistance
O	Osmose, L^3
O_e	Electroosmose, L^3
P_o	Osmotic pressure, ML^{-2}
p	Vapor pressure of of the solution, m.m. Hg.
p_o	Vapor pressure of the solvent, m.m. Hg.
P	Pressure, $ML^{-1}T^{-2}$
q	Quantity of solute transferred, M
q	Charge density, $M^{\frac{1}{2}}L^{-\frac{1}{2}}T^{-1}$
Q	Total effective area, L^2
r	Radius of a tube or sphere, L
R	Rich liquor flow rate, L^3T^{-1}

TERMINOLOGY (Cont.)

R_g	The Gas Constant, suitable units of work per deg. A.
s	Distance from tube wall, L
t	Thickness of transfer path, L
T	Absolute temperature, °A.
T_c	Temperature, °C.
u	Migration velocity of cation, cm^2./sec. volt
U	Linear velocity, LT^{-1}
v	Migration velocity of the anion, cm^2./sec. volt
V	Volume of solution, L^3
V'	Volume of solvent, L^3
V_1	Volume of rich liquor, L^3
V_2	Volume of lean liquor, L^3
W	Work, suitable units of work
x_f	Mole fraction of solute
x_c	Donnan equilibrium concentration, moles/liter
x	Ratio of volumes
α	Temperature coefficient, deg.$^{-1}$
γ	Osmotic coefficient, $L^4M^{-1}T^{-1}$
Γ	Lee's transfer coefficient, LT^{-1}
δ	Thickness of electrical double layer, cm.
Δ	Concentration difference, ML^{-3}
$\bar{\Delta}$	Mean path of Brownian movement, cm.
μ	Ion mobility, cm^2./sec. volt
θ	Time, T
η	Viscosity of fluid, $ML^{-1}T^{-1}$
ϵ	Potential of the solid, volts
ϵ_l	Potential of the liquid bulk, volts
ϵ_r	Potential at the rigid electrical layer boundry, volts
K	Concentration change coefficient, T^{-1}
κ	Surface conductivity, $ohm^{-1}cm.^{-1}$

I INTRODUCTION

From many of the steeping and extraction processes, waste liquors occur which are discarded because of colloidal pollution and recovery difficulties. Also, it is often necessary to purify a colloidal solution from accompanying crystalloids. For these two cases, dialysis offers a widely applicable and economical method of solute recovery or sol purification.

Essentially, dialysis consists of imposing a permeable membrane between a concentrated impure solution and a dilute pure solution, and permitting diffusion to take place. The net result is to retain all materials colloidally dispersed on one side of the membrane, while the materials in true solution diffuse through the membrane, thus depleting the impure solution of its crystalloids. Since its discovery, dialysis has been successfully employed in laboratories for the purification of toxins, media, viruses, and various sols.

Within the last decade, the use of dialysis has appeared in industrial operations. Dialyzers are used in large scale units for the recovery of caustic soda in the viscose rayon process. It is also being experimented with as a method of purifying rubber latex before congealing, and in the recovery of sugar from non-crystallizable syrups.

In this country there are two types of industrial dialyzers employed, namely, the box and membrane type (Cerini) and the filter press type (Asahi). Of these, the Asahi type is the most efficient. However, the Cerini type lends itself more readily to the rayon industry. Neither of these is mechanically satisfactory, and both have inherent operating difficulties.

The rapid growth of dialysis as a reclamation process is represented by the following figures for sodium hydroxide alone.[17]

1934 ---- 25,000,000 lb. caustic recovered by dialysis.
1935 ---- 40,000,000 " " " " "

Thus, it is seen that the value of dialysis in the rayon industry was rapidly recognized.

Dialysis is capable of being employed with both relatively concentrated and quite dilute solutions. The operation proceeds entirely by virtue of concentration gradients, and therefore is economically favorable. The process may be executed equally well with electrolytes and non-electrolytes. Furthermore, dialyzed solutions attain a very high degree of purity.

It is the object of this investigation to study the effect of the variables involving the rate of dialysis and to develop a basis for dialyzer design. It is also desirable to evaluate the employment of the dialyzer with regard to type and adaption.

II HISTORICAL

The first important work in the field of dialysis was that of Thomas Graham's.[12] During his studies of preferential diffusion, he found that certain substances evidenced a negligible diffusivity through such septa as gelatin, gelatinous starch, coagulated albumin, animal mucus, and parchment paper.[13] From this, he differentiated between true and colloidal solutions. This famous work was eventually verified by Zsigmondy's invention of the ultramicroscope. Furthermore, Graham observed that diffusion in colloidal gels proceeded without interference from the colloid. Coincident with this, he observed that two salts exhibited their usual relative diffusivity unchanged by the introduction of a septum, while a colloid was completely withheld.

Another interesting observation was that over the range of temperatures where free water diffusivity doubled, the rate of dialysis increased by only one third. Possibly, this may have been due to convection currents in his free water diffusion apparatus.

Although Graham was the first important investigator of dialysis, he was not the first to work with the properties of membranes. Abbe' Nollet in 1748 reported the phenomenon of osmosis.[1] Pfeffer first carried out a series of reliable quantitative experiments.[25] He employed clay cells with a film of copper ferrocyanide deposited in the interstices.

Van't Hoff found that the ratio of osmotic pressure to concentration was a constant.[40] Eventually, he arrived at a relation similar to the gas law, or

$$PV = nRT$$

$$P = cRT$$

More recently, Morse and Frazer in America,[20] the Earl of Berkely and Hartly in England[15] have obtained excellent data which shows the relation between association, dissociation, and the osmotic pressure.

Since the advent of Graham's discovery of the dialyzer, it has been intimately associated with colloidal chemistry. It has also been widely employed in biochemical and bacteriological work. However, adaptions of dialyzers have been made which serve certain purposes more effectively than the dialyzer proper. These modifications are given as follows:

Electrodialysis: The process whereby the rate of removal of crystalloids from a sol is increased by imposing an electrical potential across the sol, which is separated from surrounding solvent by a permeable membrane. The electrolytes are removed by ionic migration, and the non-electrolytes by electroosmosis. The colloids are retained by the membrane. This technique is especially adapted for the purification of simple inorganic and clay sols, and is widely employed in the purification of lyophilic colloids such as mastic, agar and proteins.[43]

Ultrafiltration: A method of separation whereby a sol is placed under pressure thereby forcing the crystalloids to pas through a permeable membrane, the colloidal material being retained. This device is the favorite instrument for biological fluid purification and concentration. It is widely employed for the separation of germs and viruses.[44]

A method of separation which combines the advantages of the ultrafilter and the electrodialyzer. The cathod is placed under the ultrafilter membrane, and the anode inside a compartment containing water and separated from the sol by a permeable membrane. Suction is applied from beneath, and the imposition of a potential across the electrodes causes a rapid purification.[45]

These devices are differentiated from the normal dialyzers in that they require work external to the system to facilitate the purification. The dialyzer operates by virtue of its concentration potentials alone.

This work is to be limited purely to the auto-active process of normal dialysis, and all of the subsequent matter shall deal with this subject.

Large Scale Uses of Dialysis. The first large scale employment of dialysis was in the manufacture of beet sugar. It was found that after the first washing of the cut sugar beets, sugar dialyzed through the tissue walls resulting in a very pure solution not contaminated with colloidal matter. Actually the process of beet sugar extraction is designed around this fundamental operation. Also, it has been found feasible in some plants to use dialyzers to purify the juice of the ground beets.

The next and most successful dialysis operation appeared in the rayon and viscose products industry. It is employed in the recovery of caustic soda used for steeping purposes. This is still the most widespread application of dialysis.

The first caustic soda dialyzer patent was filed by F. H. Griffin in 1923 for the Viscose Company of Pennsylvania.[37] This dialyzer was in limited use for awhile. However, in 1927 L. Cerini,[35] an Italian, filed a patent in this country on a much superior cell which is now in widespread use. Cerini also patented a method of preparation of membranes,[36] in 1928. E. Heibig, a Frenchman, patented in 1932 a dialyzer plate,[38] which consisted of an ingenious system of baffles to insure greater flow path, the baffles being supported in a frame. This dialyzer apparently was used in Europe. S. Tachikawa, a Japanese, patented an (39) automatic pressure adjuster for use on dialyzers. Through the use of this device he hoped to obtain the rapid transfer rate facilitated by some of the more fragile membranes such as Cellophane.

Dialysis has also been employed to some extent in the recovery of crystallizable sugars from syrups in the cane sugar industry.

General Employment. Dialysis is widely employed in laboratories to effect a separation of ionic solutes from solutes in the colloidal range. Also, it may be employed preferentially to separate ions of varying diffusion rates. Generally, the laboratory employment falls into the following three classes:

(1) Separation of ionic solutes from sols which are to form gels, such as hydrated oxides.

(2) Purification of toxins, serums, bacteriological media, etc.

(3) Purification and analytical examination of sugars and other carbohydrates.

Examples of (1) are:

(a) Hydrated Fe_2O_3, and other oxides of Cr, Al, and Sn which are to be purified from acids, such as HCl.

(b) Gelatin, glue, albumin, and lyophils.

(c) Sodium silicate sol purification, and other sols where it is desirable to remove the peptizing agent.

Examples of (2) are:

(a) Hemoglobin preparations

(b) Blood examinations

(c) Diphtheria toxins

(d) Serum albumin purifications

Examples of (3) are:

(a) Dextrin purification

(b) Recovery of non-crystallizable sugars

(c) Fats examinations

(d) Alkaloid purification

(e) Pharmaceuticals manufacture

(f) Agar-agar purification

Commercial Applications. Commercially, dialysis has been applied to the following manufacturing processes:

(1) Serum and toxin manufacture

(2) Sugar reclamation

(3) Rubber purification

(4) Caustic soda recovery in the rayon industry

The two most successful applications have been (1) and (4).

Serum and toxin purifications are rather slowly accomplished in the following type of apparatus:

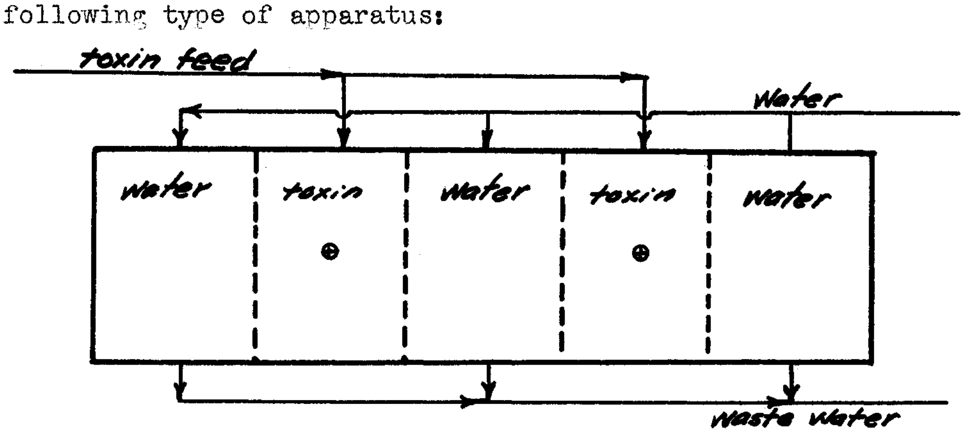


Fig. 1 A Toxin Dialytic Cell

In these cells, a cellophane or parchment paper membrane is employed. The toxin or serum is allowed to remain stagnant in their compartments, while water is slowly passed in the adjoining compartment.

This illustrates a very simple, but highly inefficient method.

Sugar purification presents a very different case, more nearly resembling preferential dialysis. In the syrups from crystallized sugar, there remains a quantity of sugar which would be crystallized under extreme conditions, but cannot be removed in pure form. However, this sugar will dialyze in preference to the non-crystallizable sugar. Thus, it is possible to recover considerable quantities of sugar that otherwise would be wasted.[42] The Stephans process of forming the calcium saccharide competes with this.

The rubber companies of Great Britain's East Indies have endeavored to purify raw latex by means of dialysis before the latex is congealed.[26] This removes an accelerator and an oxidant. Sixteen per cent of the total nitrogen is diffusible. The film from dialyzed latex is stronger than that from the regular process. Certain difficulties arose, however, due to the formation of a lightly coagulated gel in the vicinity of the membrane. By properly controlling conditions, this was partially alleviated.[27] It is apparent that the condition was not completely treated, since there was no method of latex circulation employed, and at certain limits, the latex stability could be expected to be affected. Furthermore, the apparatus employed was very crude. The British India Company has dropped their experiments since then, but there is no apparent reason why a modern dialyzer could not effect the purification.

Probably the greatest dialysis advances and the most successful applications have been in the viscose manufacturing industries. For that reason, and because of the available information, this case will be treated in detail.

Viscose is manufactured by causticizing wood pulp (essentially alpha cellulose) with sodium hydroxide, which caustic cellulose is then ripened, treated with carbon disulfide, and then dissolved in dilute sodium hydroxide solution.[17] Figure (2) represents the flow sheet that is employed by the Turbize Chatillon Corporation of Rome, Georgia.

The manufacture of viscose requires 1.25 lbs. of NaOH per lb. of viscose products, 65 per cent (or 0.813 lb.) of which is employed in the steeping baths.[17] All of the caustic is not dialyzed after each steeping since the degree of contamination does not require purification. The following procedure is employed; 220 lbs. of wood pulp (dry basis) is placed in a steeping bath, to which is added 2,998 lbs. of 17 -18 per cent caustic solution. After the specified period of steeping, the excess caustic solution is drained off. Immediately following this, pressure is applied to the causticized cellulose by means of a horizontal screw jack, thus liberating a quantity of 17 per cent NaOH solution, which is known as the "1st press". The drain and "1st press" are combined and sent to a purification unit in which suspended matter is removed. This has combined with it 0.70 lb. of hemicellulose. The causticized cellulose mass is then pressed again to yield the "2nd press". This consists of 298 lbs. of 17 per cent caustic which is contaminated with 1.9 lbs. of hemicellulose. This has reached a cellulose content too high for further steeping operations, and is, therefore, sent to the dialyzers for purification. Four hundred lbs. of 16.7 per cent caustic is retained by the causticized cellulose.[42]

It is the "2nd press" liquor which it is desired to discuss in detail. This liquor has the following approximate composition:

Density -----------1.2 gm./cm^3

Caustic -----------16% NaOH

Carbonates --------4% (Ca, Mg, Na, K)

Organic Matter ----2% (mostly hemicellulose)

Suspended solids, silicates, metallic impurities, etc.

This liquid passes into a storage tank, where part of the suspended solids pass out. From here the liquor passes to dialyzers of the Cerini type, where 90 per cent of the dissolved hemicellulose is removed, nearly all carbonates, and all the shreds and metallic impurities. This is delivered as 8 per cent NaOH solution, the impure liquid being reduced to 1.5 per cent NaOH. The recovery efficiency is specified as 90 per cent.[42] There is some increase in the impure liquor volume, while the pure liquid has a volume twice that of the impure solution. The concentration of the solution must be built up before further use in the steeping baths, or reduced in strength for use in mixing with treated cellulose. Incidentally, some plants have found it advantageous to dialyze some of the first press liquor expressly for the purpose of the mixing solution, thus deriving the advantage of high purity of the dialyzed solutions.

The value of dialysis as a reclamation process is established by the record of its rapid growth in the caustic-viscose industry.

Some of the immediate feasible industries where dialysis could be profitably employed are given by Basset, a worker in the field.[1] These are as follows:

(1) Sugar refining - large per cent of crystallizable sugar may be obtained from molasses.

(2) Textile industry - recovery of waste mercerizing caustic, waste sodium sulfate, etc.

(3) Gel purification - alumina, silica gel, glues, gelatins, etc.

(4) Organic wastes may be flocculated by removing soluble salts.

(5) Tartaric and citric acid recovery.

Other than sugar reclamation, there has been little work done in any of these fields.

Diffusion Theory.

Diffusion of a solute in the liquid state is governed by multiple factors, a working relation between which has never been satisfactorily realized. However, certain fundamental relations hold rather well for limited cases.

The rate of diffusion in long paths is defined by

$$\frac{\partial q}{\partial \theta} = DA\frac{\partial^2 c}{\partial t^2} \tag{1}$$

This relation indicates that the diffusivity coefficient is a function of the concentration. However, where the diffusion path is relatively short, the concentration gradient across the path may be assumed to be linear in path length. Therefore we may write[8]

$$\frac{dq}{d\theta} = DA\frac{dc}{dt} = \frac{DA}{t}(C_1 - C_2) \tag{2}$$

Furthermore, for any system, it may be written that

$$k = \frac{D}{t} \tag{3}$$

Substituting (3) in (2)

$$\frac{dq}{d\theta} = kA(C_1 - C_2) \tag{4}$$

The equation (4) is the most convenient to use in the case of dialysis, and will be employed in some of the subsequent work. Equations

(1) and (2) only define the diffusivity coefficient.

An analogy for dilute solutions may be drawn from Graham's effusion law, which is given as

$$\frac{\theta_1}{\theta_2} = \frac{D_2}{D_1} = \sqrt{\frac{M_1}{M_2}} = \sqrt{\frac{\rho_1}{\rho_2}} \qquad (5)$$

and

$$D_2 = D_1 \frac{\theta_1}{\theta_2} = D_1 \sqrt{\frac{M_1}{M_2}} \qquad (6)$$

This relation is objectional because M does not consider solute solvation.

Nernst[21] found that the diffusion of electrolytes could be related to their ionic mobilities, and gives the following equation

$$dq = -\frac{2uv}{u+v} R_6 T A \frac{dc}{dt} d\theta \qquad (7)$$

Comparison of equations (7) and (2) indicates that

$$D = \frac{2uv}{u+v} R_6 T \qquad (8)$$

Using the data of W. Öholm,[24] the following calculations indicate the applicability of equation (8).

TABLE I

Substance	D (obs.) 18°C.	D(Calc.) 18°C.	Substance	D (obs.) 18° C.	D (Calc.) 18° C.
KCl	1.460	1.460	KOH	1.903	2.109
NaCl	1.170	1.173	NaOH	1.432	1.558
LiCl	1.000	0.994	KI	1.460	1.467
HCl	2.324	2.431	CH_3COOH	0.930	1.370

Note: All values of D were measured at Normality = 0.01
D is expressed in cm.^{2}/day.

Equation (8) was later modified, and found to give better results.

The modified form is given as

$$D = 0.044856\left(\frac{uv}{u+v}\right)\left[1 + 0.0034(T_c - 18)\right] \tag{9}$$

In general, it may be said that the above equation holds for electrolytes, where the ionization is nearly complete, over a range of temperatures in the vicinity of 18 degrees C.

In an effort to correlate D with the variation of temperature, Oholm[23] compiled the following table for the approximate value of α, the temperature coefficient per degree for various ranges of the diffusion coefficient.

TABLE II

D =	2.4	2.0-1.8	1.6-1.4	1.2-1.1	0.8-0.7	0.4-0.3
α =	0.0018	0.020	0.022	0.025	0.029	0.035

The value of alpha is defined by

$$\frac{D_2}{D_1} = 1 + \alpha(T_2 - T_1) \tag{10}$$

In the use of Equations (8) and (9) it must also be remembered that the values of u and v vary with temperature. Kohlrausch[29] gives the following equations for determining the temperature coefficient for solutes in aqueous solution.

$$\alpha = 0.0136 + \left(\frac{0.67}{18.5+\mu}\right) = 0.0134 + \left(\frac{0.640}{\mu}\right) - \left(\frac{6.94}{\mu^2}\right)$$

$$\alpha = 0.0065 + 0.0683\left(\frac{1}{\mu}\right)^{0.3545} \tag{11}$$

$$\alpha = 0.0348/(\ln \mu - 0.207)$$

These may be employed to yield a more accurate value for diffusivity.

Thovert[32] found the relation $DM^{1/2}$ = constant to hold for some solutes. This would be anticipated from Graham's law of effusion. From this it may be concluded that the relation holds only for dilute solutions where the solute is not solvated.

Einstein's equation[7] combined with Stoke's law yields the relation[45]

$$D = \left(\frac{R_G T}{N}\right)\left(\frac{1}{6\pi\eta r}\right) \tag{12}$$

This equation has been found to hold fairly well in non-aqueous solutions, but fails in the case of electrolytes in aqueous solution.

The problem of any systematic and mathematically related system of diffusivity data over ranges of temperature and concentration is extremely involved. However, the sources of published data may be used, but with caution. Various authors report variant values of D under identical conditions of temperature and concentration. The reliability of the data is best estimated by determining the relative advantages of the authors technique.

The Debye-Huckel Theory of solutions[5] postulates several points that are of value in the explanation of diffusivity irregularities. These are:

(1) All electrolytes are completely ionized.

(2) All ions have associated with them an envelope of electrically bound solvent.

(3) The amount of hydration depends upon the charge on the ion, and the dielectric constant of the solvent.

(4) At high concentrations ion groups of the following type begin to form.

$$2M^{+} + A^{-} = (MAM)^{+}$$

<u>Colloidal Diffusivity.</u>

Colloidal diffusivity must also be considered in dialysis.

Some membranes will permit colloidal transfer to take place. However, the rate of colloidal diffusion is much less than that of crystalloid transfer, the ratio between the two being roughly 1 to 25.

The best equation for estimating colloidal diffusivity is that of Sutherland (28) and Einstein, (7) which is given as

$$D = \frac{R_G T}{N_f} = \left(\frac{R_G T}{N}\right)\left(\frac{1}{6\pi\eta r}\right) \tag{13}$$

Svedberg checked this equation with a gold sol, and found a value of r of 1.33 mu. This agreed within the limits of experimental error size determined by a nuclear method.

Also, there is the simple relation between diffusivity and Brownian Movement of

$$2Dt = \bar{\Delta}^2 \tag{14}$$

This relation is more difficult to use, and finds its chief value theoretically.

Osmosis.

Van't Hoff (40) first pointed out the analogy between osmosis and the gas law, and gave the relation

$$P_0 V = n R_G T = \frac{g}{M} R_G T \tag{15}$$

However, this relation is true only where the dilution is large enough to grant as approximate ideal solution. If the volume, V, is designated as that of the solvent alone, a better agreement is obtained.

For the case of electrolytes, it is necessary to introduce the ionization factor, or else the relation becomes untenable. (10) Thus, the value of i may be determined from freezing point lowering and boiling point raising data.

$$P_0 V = i n R_G T = \left(i \frac{g}{M}\right)\left(R_G T\right) \tag{16}$$

However, it is useless for the case of non-electrolytes.

Further considerations from a thermodynamic standpoint yield equations of greater value.[10] The change in free energy of a system is given as

$$dF_a = V dp \tag{17}$$

and

$$F = \int V dp = \int_{p}^{p_0} \frac{R_G T}{p} dp \tag{18}$$

integrating between the limits of P and P_0

$$F_0 - F = \Delta F = R_G T \ln\left(\frac{p_0}{p}\right) \tag{19}$$

The work done in removing one mole of solvent from the solution through a diaphragm by applying a force infinitesimally greater than osmotic pressure is equivalent to PV'. Since there is little change in V' when the solvent is added back to the solution, no work is done against the atmosphere. Therefore,

$$P_0 V' = \Delta F \tag{20}$$

Combining (19) and (20)

$$P_0 V' = R_G T \ln\left(\frac{p_0}{p}\right) \tag{21}$$

It must be noted here that a mole of solvent refers to enough solvent to form one mole of vapor at the temperature T.

Equation (21) agrees very well with experimental results, even at high concentrations.

In certain cases it may be desirable to express Equation (21) in terms of concentrations. This may be accomplished by the aid of Raoult's law which is given as

$$p = p_0(1-x) \qquad (22)$$

Rewriting and taking the logarithm of both sides

$$\frac{p_0}{p} = \frac{1}{(1-x)}\ ;\ \ln\left(\frac{p_0}{p}\right) = \ln\left(\frac{1}{1-x}\right) = -\ln(1-x) \qquad (23)$$

Substituting (23) and (21)

$$P_0 V' = R_G T[-\ln(1-x)] \qquad (24)$$

which upon expansion yields

$$P_0 V' = R_G T(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 + \cdots) \qquad (25)$$

However, Equation (25) demands a knowledge of the degree of association or dissociation of a solvent, and therefore is limited. It appears that the best relation to use is Equation (21) which is modified to include empirical relations between vapor pressure and concentration, ie.,

$$P_0 V' = R_G T \ln\left(\frac{p_0}{p}\right) = R_G T \ln \frac{f(c_0, t_0)}{f(c, t)} \qquad (26)$$

Debye and Huckel,(29) with the same reasoning employed in their theory of solutions, arrived at

$$P_0 = \sigma n k T + \varphi(n) \qquad (27)$$

This equation adds a corrective value due to the electrostatic forces between ions, which is expressed as $\phi(m)$.

All of the expressions thus far indicate the equilibrium osmotic pressure and make no consideration of the time required to reach such a value. Ostwald has proved that the osmotic pressure attained with two different semipermeable membranes must be identical. It is evident that the rate of attainment varies in each different membrane according to membrane permeability.

It has been shown that osmotic pressure may be expressed as a function of concentration and temperature. The osmotic rate, however, is a function of concentration, membrane properties, thickness, and temperature.

Membrane Theory.

The complete function of the permeable membrane is not yet understood. There have been many theories advanced, but only a few retained on the basis that they offer an explanation for a certain group of conditions. These are as follows:

Sieve Theory. Traube[34] conceived permeable membranes to be molecular sieves, through which progressively larger particles diffused with increasing difficulty. However, the theory is not adequate since a slightly permeable membrane may be more permeable to the same molecule than a highly permeable membrane. For example, a gelatin-tannate membrane is quite permeable to both sodium chloride and sodium sulfate. However, while a gelatin-tannate-barium sulfate membrane is permeable to sodium chloride, it is impermeable to sodium sulfate.

Solution Theory. L'Hermite[18] advanced the theory that a membrane is permeable to only those substances which dissolve in it. This theory appears to hold fairly well for organic membranes such as rubber, but fails in cases where no solubility can take place.

Sorption Theory. Tinker[33] proposed one of the most interesting theories. He assumed that the membrane particles were spherical, and that the solvent was sorbed on these spheres. Figure 3 illustrates this theory

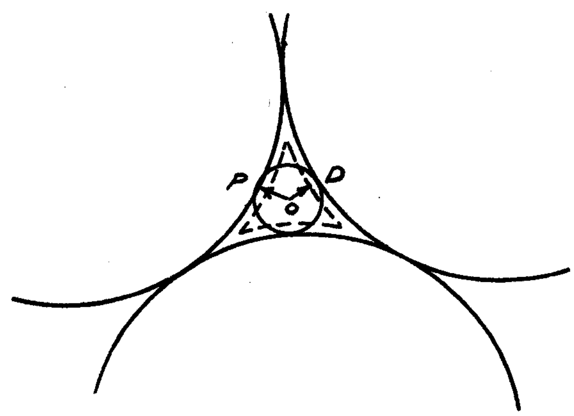


Figure 3

Thus, the pore radius would be OP for a weakly sorbed solvent, and OD for a strongly sorbed solvent. Thereby, the size of the particle passing is limited by solvent sorption and membrane particle size. Tinker assumes that a semipermeable membrane is one in which all of the solvent in the membrane is sorbed, and permeable when membrane swelling takes place.

However, the theory fails to furnish a working basis for estimating permeability, since variations in concentration also vary solvent sorption. It is useful in the explanation of certain permeability phenomena.

There are a few generalizations that can be made concerning permeability.[30] The following factors have a direct bearing:

(1) The type of membrane material, and its method of manufacture.

(2) The solvent nature; the degree of association of solute affects the final membrane.

(3) The relative proportions of solvents, if two or more are employed. Thus, a membrane made in a standard way and soaked in a 75 per cent alcohol and 25 per cent water solution will have a higher permeability than one soaked in a solution of lower alcohol content.

(4) The concentration of the solute; the lower the concentration the higher the permeability.

(5) The presence of non-solvent agents such as glycerol; these tend to increase the permeability.

(6) The rate of drying; the faster the rate the higher the permeability.

(7) The swelling agents; these tend to increase permeability.

Generally, the more permeable membrane exhibits the largest degree of swelling in the solvent. Thus, swelling agents such as zinc chloride solutions may be used to increase permeability. It is evident that at some point, permeability does not increase with swelling due to increased thickness of the membrane.

The following table shows the variation of permeability with swelling. This illustrates the large variation of permeability with the alcohol-water soaking ratio. It may be observed that permeability is not linear with either the degree of swelling or the Alcohol Number.

TABLE III

Alcohol No.	Wt. Wet / Wt. Dry	Time of Penetration
95	5.19	12 min.
90	1.47	70 "
80	1.24	10 hrs.
70	1.18	6 days

Note: The solute for the above was methylene blue.

The relation between the ratio of solvents used has been designated as the Alcohol Index. This simply indicates the per cent alcohol used in the solvent.

The following table illustrates the effect of the Alcohol Index on the permeability of a cellulose nitrate film.

TABLE IV

Alcohol Index	% NaCl Diffused in 10 minutes	% Sucrose Diffused in 30 minutes
10	35	3
15	38	6
20	40	9
30	42	13
40	43	15

Traube found that precipitated membranes are impermeable to ions which are included in the membrane substance or which would form an insoluble compound with one of the ions of the precipitate membrane. Thus, copper ferricyanide is impermeable to both copper and ferricyanide ions.

For the case of organic membranes, the general solution theory appears to be the most valuable index to permeability. Thus, copper oleate, sulfur, naphthalene, and camphor in pyridine solutions dialyzed through rubber, while lithium chloride, silver nitrate, and

(30)
sucrose do not.

Thus, it is seen that the case of permeability is complicated, at the present, beyond comprehensive estimation. It is evident that in some cases dialysis by hydro-diffusion, in others by solution. Further, in many cases chemical interaction between membrane and solution components is of prime importance, whereas, in others this action is of negligable order. There are, however, two points evident. There must exist an affinity between solvent and membrane in order to establish a diffusion path. This is most important for solutes of negligible vapor pressures. Solutes with appreciable vapor pressure may be transferred through a vapor path. Secondly, there must not exist a chemical condition in the membrane which prohibits the diffusion of the solute.

Membrane Equilibrium.

Whenever substances which permeate a membrane are separated from pure solvent by a membrane, the final result of dialysis will be an equalization of solute concentration on both sides of the membrane. The diffusivity of the cation and the anion are seldom identical. Consequently, in a dissociated solution, the faster ion tends to precede the slower one. However, electrical neutrality cannot be obtained thereby. Thus, the faster ion is retarded by the slower, or the slower ion diffuses more rapidly. It is obvious that there must exist a potential across the membrane, which is a measure of the force exerted by the faster ion in requiring the slower ion to accompany it. This process has been quantitatively treated by Nernst, and is given below in detail.

Consider the salt M_mA_a, where $n =$ valence of M. The valence of A is, therefore, (nm/a). Consequently, the dilute solutions, for each mole of M, there are a/m moles of A. Now if nF Faraday's of current are passed through the cell, the electrical work is given by

$$EnF = W_e \tag{28}$$

The passage of this current causes the transfer of N_c or $u/u\ v$ moles of cation, and $N_a(a/m)$ or $(v/u+v)(a/m)$ moles of anion. Thus, the work done in the cation transfer is given by

$$W_c = N_c R_G T \ln\left(\frac{C_M^-}{C_M^+}\right) = \left(\frac{u}{u+v}\right) R_G T \ln\left(\frac{C_M^-}{C_M^+}\right) \tag{29}$$

and that of the anions by

$$W_a = \left(\frac{a}{m}\right) N_a R_G T \ln\left(\frac{C_A^+}{C_A^-}\right) = \left(\frac{a}{m}\right)\left(\frac{v}{u+v}\right) R_G T \ln\left(\frac{C_A^+}{C_A^-}\right) \tag{30}$$

The sum of these two is therefore equal to the electrical work. Equating

$$EnF = W_c + W_a = \left[N_c \ln\left(\frac{C_M^-}{C_M^+}\right) + \left(\frac{a}{m}\right) N_a \ln\left(\frac{C_A^+}{C_A^-}\right)\right] R_G T \tag{31}$$

but

$$C_A = \frac{a}{m} C_M \tag{32}$$

Substitution of (32) in (31) yields

$$E_d = \left(\frac{(a/m)v - u}{u+v}\right)\left(\frac{R_G T}{nF}\right) \ln\left(\frac{C_M^+}{C_M^-}\right) \tag{33}$$

In the future, the above potential shall be termed the diffusion potential. It is to be noted that the sign of the charge on each side of a dialyzer is predicted by the above equation. If $v < u$, the dilute side is negative; when $v = u$, $E_d = 0$; when $u < v$, the dilute side becomes positively charged. This is important in subsequent considerations of electrokinetics.

For the case where the solute contains an ion which will not pass through the dialyzer membrane, and one or more that will, the following analysis of Donnan[6] applies.

Consider the following dialytic cell, where R^- is either a large negative ion, or a negatively charged colloid, impermeable to the membrane. Let MA be an electrolyte permeable to the membrane.

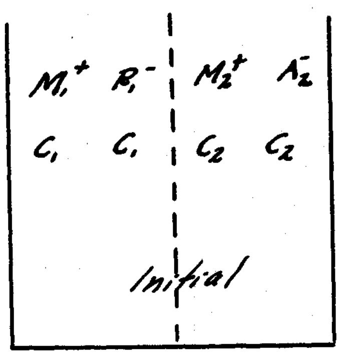


Figure 4

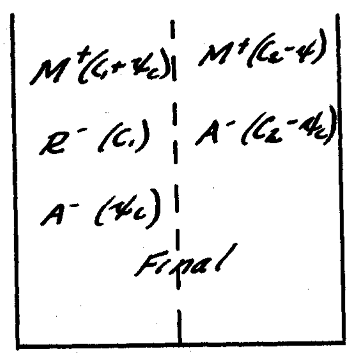


Figure 5

The equilibrium condition is represented by Figure 5. At the equilibrium, if n moles of M and n moles of A are isothermally and reversibly transferred from (1) to (2), the net work is zero, since the free energy of the system is not changed. Therefore,

$$(nRT)\ln\left(\frac{M_2^+}{M_1^+}\right) + (nRT)\ln\left(\frac{A_2^-}{A_1^-}\right) = 0 \tag{34}$$

Thus it is seen that at equilibrium

$$[M_1^+][A_1^-] = [M_2^+][A_2^-] \tag{35}$$

Whence

$$(C_1 + \psi_c)(\psi_c) = (C_2 - \psi_c)^2$$

$$\text{and} \qquad \psi_c = \frac{C_2^2}{C_1 + 2C_2} \tag{36}$$

From this it is seen that if $C_1 = 0$, $x = \frac{1}{2}C_2$ which corresponds to the case where all ions are diffusible. The value of the above equation lies in that it indicates the true driving force to be employed where non-diffusible ions are present.

The presence of the non-diffusible ion causes a potential to be set up across the membrane at equilibrium. This is given by Gibbs and Donnan as

$$E_m = \left(\frac{RT}{2nF}\right) \ln\left(1 + \frac{C_1}{\psi}\right) = \left(\frac{RT}{2nF}\right) \ln\left(\frac{C_1}{C_2} + 1\right) \tag{37}$$

This potential shall be termed as the membrane potential. Its variation with concentration is illustrated in Figure 6 according to Loeb.[(19)] The non-diffusible component was the negatively charged gelatin micelle. While the above material illustrates the final conditions, it yields no insight into the kinetics of the transfer through membranes.

Membrane Electrokinetics.

A study of electrokinetics is of interest with regard to the rate of osmosis, and in the endeavor to establish a valid concept of the membrane action during dialysis.

Apparently, it is a universal law of nature that there always exists a potential difference at the interface of unlike substances. This potential is divisible into two parts, for the case of fluid-solid interfaces. One layer of charges appears to be firmly held to the solid, while the other exists in the fluid and is therefore mobile. The movement of the mobile electrical layer passed the rigid one is responsible for phenomena which have been termed electrokinetic.

Figure 7 illustrates the electrical layer as conceived by Helmholtz.(16)

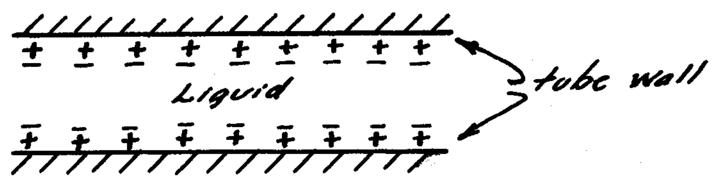


Figure 7

A later, and probably more accurate picture is that of Guoy and Freundlich.(11) Their assumption of a diffuse layer has met with more general approval. Figure 8 illustrates this concept.

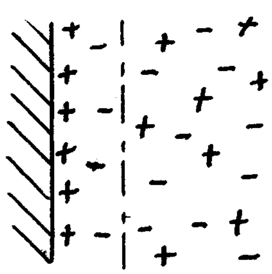


Figure 8

From the concept of the rigid and mobile electrical layers, it is obvious that the total potential between the solid and the bulk of the fluid may be further subdivided. The Nernst, or so-called thermodynamic potential designates the total potential between the solid and the liquid bulk, or

$$E_t = \epsilon_o - \epsilon_L \tag{38}$$

The second potential is that existing between the limit of the rigid layer and the liquid bulk. This is designated as the Zeta (ζ) potential, and may be expressed as

$$\zeta = \epsilon_r - \epsilon_L \tag{39}$$

or

$$\zeta = \epsilon_r - \epsilon_o + E_t \tag{40}$$

The above relations are diagramatically illustrated by Figure 9.

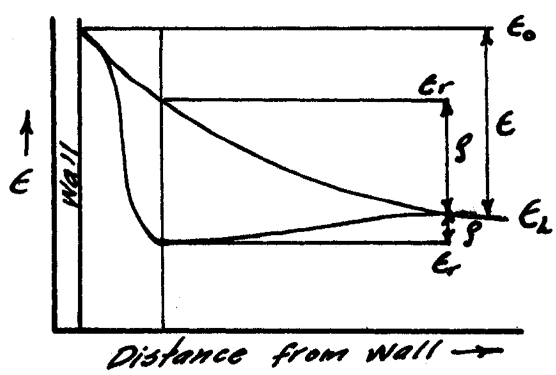


Figure 9

The various electrokinetic phenomena are given below:

<u>Electroosmosis:</u> When an electrical potential is applied across a capillary filled with a fluid, a flow of fluid will take place through the capillary, the direction of which depends upon the potential polarity and the charge of the capillary relative to the fluid.

<u>Streaming Potential:</u> This is the reverse of electroosmosis. Thus, when a fluid is forced through a capillary, a potential will be set up across the capillary in opposition to the flow.

<u>Electrophoresis:</u> A substance suspended in a fluid will migrate upon the imposition of an electrical potential across the fluid.

<u>Sedimentation Potential:</u> This is the reverse of electrophoresis.

Thus, if a suspended material is allowed to settle, a potential is set up across the fluid medium.

Of these, only electroosmosis and streaming potential have a direct bearing upon dialysis. The development of the relations governing them are therefore developed as follows.

Consider the diagram in Figure 10.

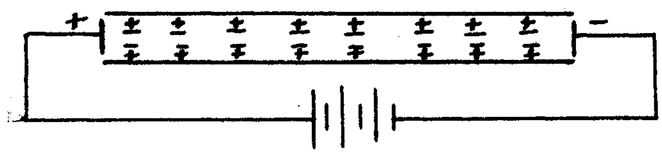


Figure 10

The volumetric rate of flow is given by

$$Q_E = \pi r^2 U \qquad (41)$$

Now for a given flow rate, the electrical forces must just balance the hydrodynamic frictional forces, or

$$F_e = F_f \qquad (42)$$

but

$$P = f/A \qquad (43)$$

If A = 1 sq. cm., P is numerically equal to F

The velocity gradient is given by

$$\frac{dU}{ds} = \frac{U}{\delta} \qquad (44)$$

but

$$\frac{dU}{ds}\eta = F_f = \eta U/\delta \qquad (45)$$

substituting (41) in (45)

$$F_f = \frac{\eta O_E}{\pi r^2 \delta} \tag{46}$$

Also,

$$H = \frac{E}{l} \tag{47}$$

Therefore,

$$F_c = H q_p \tag{48}$$

Combining (46) and(48)

$$H q_p = \frac{\eta O_E}{\pi r^2 \delta} \tag{49}$$

If the double layer is considered as a condenser, its capacity is then

$$C = \frac{D_o A}{4\pi d} \tag{50}$$

but

$$C = \frac{q_p}{E} A \tag{51}$$

Substituting (51) in (50),

$$\frac{q}{E} = \frac{D}{4\pi d} \qquad E = \rho \quad d = \delta \tag{52}$$

Substituting (52) in (49),

$$\frac{H \rho D_o}{4} = \frac{\eta O_E}{r^2} \tag{53}$$

$$O_E = \frac{\rho r^2 H D_o}{4\eta}$$

but,

$$H = E/l \tag{54}$$

and therefore

$$O_E = \frac{\rho r^2 E D_0}{4\eta l} \tag{55}$$

Now, consider a bundle of capillaries; then $Q = \Sigma \pi r^2$, but the effective radius is r_{mean}. Then,

$$r^2 = \frac{Q}{\pi} \tag{56}$$

Substituting (56) in (55)

$$O_E = \frac{\rho Q E D_0}{4\pi\eta l} \tag{57}$$

but, $E = I R$ and $R = l/QK$

Thus,

$$E = Il/QK \tag{58}$$

Substituting (58) in (57)

$$O_E = \frac{\rho I D_0}{4\pi\eta K} = \frac{\rho D X}{4\pi\eta} \qquad X = \frac{I}{K} \tag{59}$$

The above seems to be the most applicable form of the equation, and will be employed in subsequent treatment. From Equation (59) it is seen that the volume of the fluid transported is independent of the length and cross-section of the capillaries.

It must be remembered that the Zeta potential varies with the concentration of the solute, and reaches its largest proportions when the fluid concentration is slight. Figure 11 illustrates this variance.

The bearing of electrokinetic phenomena is primarily to the osmose. Thus, the diffusion potential set up across the membrane causes normal osmosis either to be accelerated, or retarded. Also, as osmosis proceedes, streaming potential is set up opposite to the diffusion potential. The four possible conditions which may affect the rate of osmosis according to Bartell (2) are given in Figure 12.

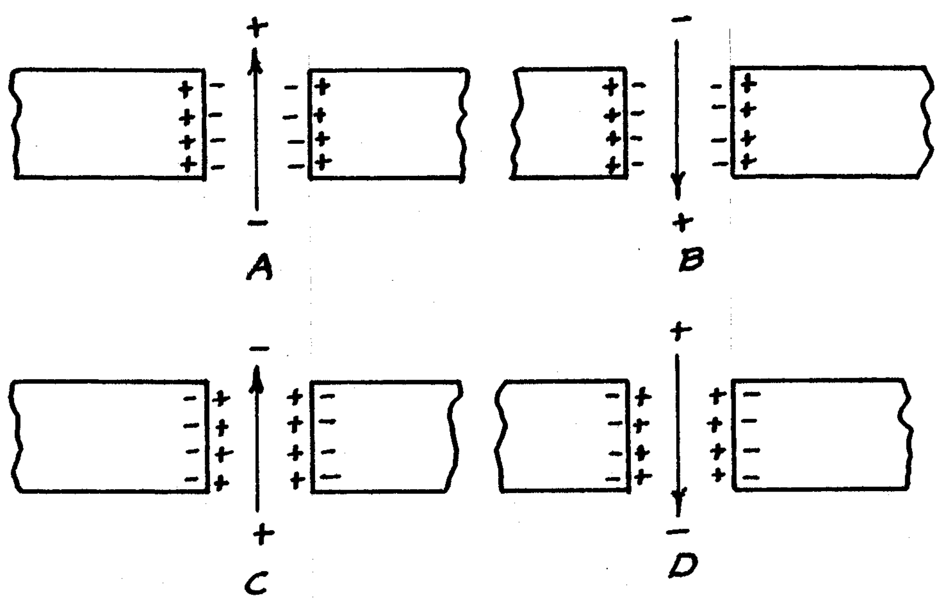


Figure 12

It is assumed that the membrane selectively adsorbs on its surface the cation or anion, depending upon the system, which is balanced by a mobile opposite charge. When the diffusion potential is considered, the manner in which the membrane electrical properties affect osmosis is obvious.

The charge on the solid may be accorded to one of the following (14) processes:

(1) Direct ionization of the material composing the micelle.

(2) Adsorption of an ion by a micelle.

(3) Electrification by contact.

While none of the material thus far presented even approximates a complete concept of membrane action during dialysis, it at least yields an insight into some of the effects.

Dialyzer Kinetics.

Since Graham's discovery of the dialyzer its use has been confined almost entirely to laboratory work where economic considerations are not of primary importance. Consequently, there has been little work on the kinetics of dialysis.

The work of Bethe and Terada[3] is the most complete published theory. It is given as follows.

Assuming that the driving force across a membrane is the difference in concentration, one may write

$$dC_2 = K(C_1 - C_2)\,d\theta \qquad C_1 > C_2 \tag{60}$$

If the volume of the rich solution is large compared to that of the dilute solution, then C_1 may be regarded as constant, and integration yields

$$\frac{C_2}{C_1} = 1 - \frac{1}{e^{K\theta}} \tag{61}$$

However, this condition is seldom realized. If a material balance is written across the septum, or

$$V_1(C_1' - C_1) = V_2 C_2 \tag{62}$$

a relation of C_1 in terms of C_2 may be obtained. Thus,

$$C_1 = C_1' - \frac{V_2}{V_1} C_2 \tag{63}$$

Substituting (63) in (60), we obtain

$$dC_2 = K\left[C_1' - C_2\left(\frac{V_2+V_1}{V_1}\right)\right]d\theta \tag{64}$$

which upon integration gives

$$\frac{C_2}{C_1'\left(\frac{V_1}{V_1+V_2}\right)} = 1 - \frac{1}{e^{K\left(\frac{V_1+V_2}{V_1}\right)\theta}} \tag{65}$$

Correlation was found by Terada for sugar and sodium chloride, but failed elsewhere.

For the case of steady state dialysis as employed in the rayon industry, Lee[17] gives the following relation for the calculation of the capacity of the dialyzer.

$$\frac{q}{\theta} = \Gamma A\left(\frac{\Delta_1 - \Delta_2}{\ln\frac{\Delta_1}{\Delta_2}}\right) \tag{66}$$

This relation was apparently intended to hold from the top to the bottom of a plate.

Thus, it is seen that there has been little work in an effort quantitatively to evaluate dialysis. Possibly this may be attributed to the limits found by their relations and a failure to account the total variables involved.

Dialyzers.

Probably the most convenient type of a dialyzer for laboratory purification of a sol is that described by Neidle.[22] This is illustrated in Figure 13. This has the advantage of assuring the highest concentration difference possible. This dialyzer requires the membrane to be in tubular form, but could be modified to employ sheet membranes.

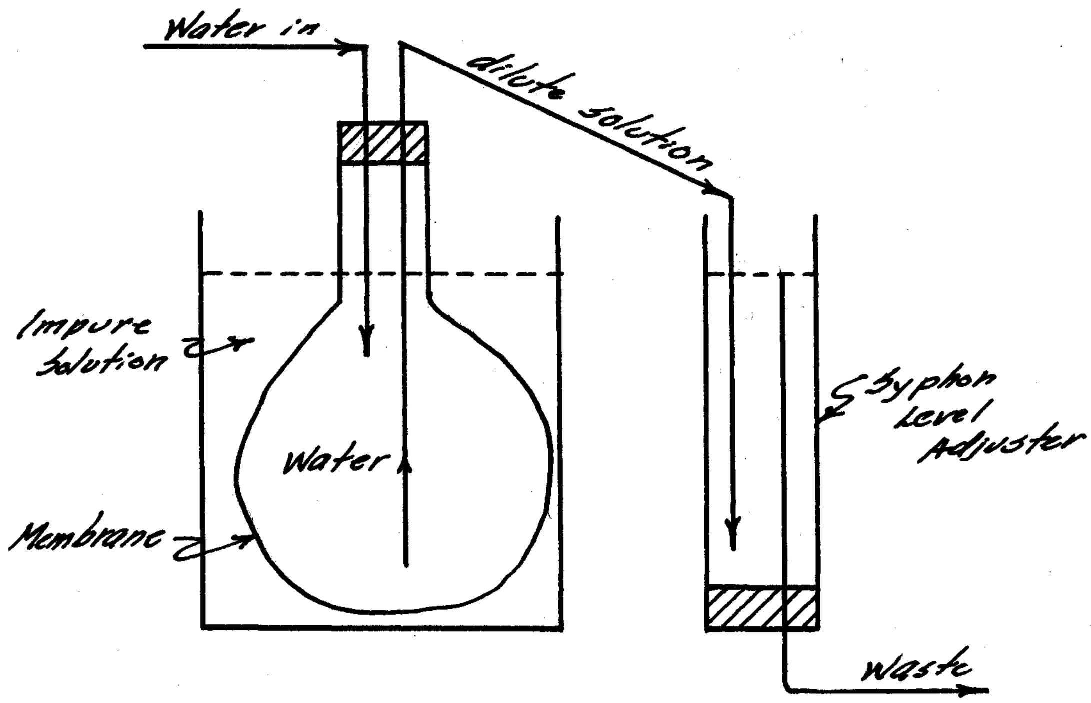


Figure 13

There are four different types of commercial dialyzers. These are listed below and discussed accordingly.

Griffin Dialyzer. This consists of a rectangular tank, the tank being divided into a series of compartments. Into each compartment is introduced a frame which supports a permeable membrane on either side. The dilute liquor is contained in the annular space between the frame and tank while the concentrated liquor is held in the frame. The connections between frames and compartments are external to the tank. The flow is counter-current, the frames and compartments being in series.[(37)] The advantages of this cell are its simplicity and ruggedness. The disadvantages are

(1) Too large a ratio of volume to area.

(2) Short circuiting of the liquors.

(3) Bulkiness of the dialyzer.

(4) Lack of membrane support.

(5) Excessive hydrostştic pressure strains.

(6) Necessity of a thick membrane.

(7) Inability to withdraw one plate from the circuit.

This dilyzer was never used widely for obvious reasons.

Heibig Dialyzers. This dialyzer is of the filter press type. It consists of a series of identical metal plates bolted together. Dilute and concentrated liquors flow through alternate plates counter-currently. Connection between plates is facilitated by channels bored in the metal plates. The feature of this dialyzer lies in its baffle arrangement. This was developed in an effort to obtain better transfer of material without increasing flow rates. The patent claims a 10-15 per cent increase of transfer rate per unit area over other types.[(38)] No specification is made concerning the type or membrane employed. The advantages of this dialyzer are

(1) Compactness of design.

(2) Good membrane support.

(3) A long liquid path.

(4) Structural sturdiness.

(5) Thorough mixing.

Its disadvantages are

(1) High initial cost.

(2) Low flow resistance.

(3) The dead space tends to counteract the advantages of the baffles.

(4) Inability to short circuit one plate.

(5) Inability to determine membrane rupture.

(6) Inability to repair one plate without cessation of operation.

This dialyzer appears to be fairly good, and apparently found some use in Europe.

Cerini Dialyzer. This dialyzer is of the plate and tank type. The liquors are in counter-current flow. The plates are arranged as a bank of four or more in parallel connected in series with another such bank. Separating each bank is a large baffle which necessitates the back and forth traverse of the rich liquor. The rich liquor surrounds the plates, while the dilute liquor flows inside them. The entire system is enclosed by a rectangular tank.

One of the features of this dialyzer is the plate etructure. The membranes are fastened on the frame edges by sewing and by metal clamps. The support is furnished by a knit metal fillet disposed on the inside of the frame. The dialyzer's advantages are

(1) Relatively low initial cost.

(2) Simplicity of structure.

(3) Ability to determine membrane rupture.

(4) Ability to withdraw one plate from the system without cessation of operation.

Its disadvantages are

(1) Tendency for the liquors to short circuit across the plates.

(2) Necessity of a strong membrane.

(3) Slow transfer rates.

(4) Difficulty of replacing membranes.

(5) Loss of full counter current operation.

This dialyzer is widely employed in the rayon industry, in spite of its slow rate of transfer.(36) Apparently, the ruggedness of the membranes and the ability to remove a single plate from service outweighs other disadvantages.

Asahi Dialyzer. This dialyzer is of the plate and frame type, and consists of a series of frames with membranes inserted between them, the dialyzer being clamped together by hand screw wheels.

Its feature is a system whereby the pressure differentials across the membranes are neutralized by two pumps or hydraulic heads for the concentrated liquor, and two for the dilute liquor.(39) This system facilitates the use of much thinner membranes, thereby securing a faster transfer rate. Its advantages are

(1) Pressure equalization.

(2) The use of thin membranes.

(3) Fast transfer rates.

(4) Small floor space.

Its disadvantages are

(1) Difficulty of operation.

(2) High initial cost.

(3) Membrane fragilness.

(4) Inability to withdraw a single plate from the system.

(5) Inability to determine membrane rupture.

(6) Necessity of cessation of service to repair one plate.

The Asahi dialyzer has the largest capacity per unit area and floor space of any dialyzer manufactured. It is widely used, but its use is limited by the time required to replace a single plate.

Table V illustrates some of the properties of the Cerini and the Asahi dialyzers.

TABLE V

Name	Type	Dimensions	No. Plates	Total Area	Capacity	Capacity / Area
Cerini	Plate & Tank	10'x 5'x 4'	25	3,460 ft.^{2}	23.8#/hr.	0.00238
Asahi	Plate & Frame	6'x 17$\frac{3}{4}$'x?	60	5,240 ft.^{2}	83.2#/hr.	0.01590

Thus, the great advantage of the Asahi dialyzer over the Cerini is apparent. However, the time required to change the membranes of an Asahi dialyzer is two hours. This may be facilitated in the Cerini unit without cessation of operation. The life of the Asahi parchment is about one month, while the life of the Cerini membrane is seven to twelve months.(42)

In summary, it may be said that dialysis may be readily and effectively applied if suitable equipment and membranes can be developed. The process is fully auto-active, and is rather delicate. The rate of transfer across a membrane is affected by the concentration driving force, the resistance of the septum, the nature of the septum and solute, and the inherent electrical properties of the membrane-solution interfaces.

The equipment employed at the present is bulky, inefficient, expensive, and troublesome to operate. The membranes of the frame and tank type are heavy and inefficient, The plate and frame type employing balanced pressures is difficult to operate.

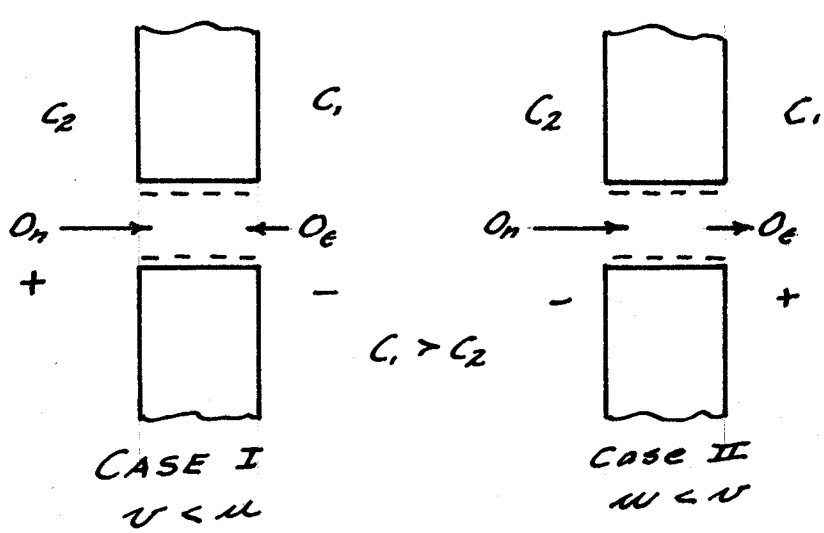
It is hoped that an investigation of the mechanism of dialysis may lead to the development of more efficient equipment, and therefore a more widespread employment.

III THEORETICAL

It is now necessary to relate the various factors affecting the rate of dialysis. The Section of this thesis, entitled Historical, has indicated the complexity, and lack of complete understanding of the process. Consequently, it becomes necessary to make certain assumptions that appear feasible, and to analyze certain of the factors, thereby establishing a first approximation.

Electrokinetic Negligibility: The effect of the membrane electrical properties is a primary and otherwise complex consideration. It may be seen from Figure 11, page 25, that in the range of relatively high concentrations, the Zeta potential approaches negligible proportions. Consequently, in concentrated solutions of the usual range, electrokinetic effects may be assumed to be negligible or constant, thereby facilitating the induction of a transfer coefficient.

It has been found that most aqueous solutions are electronegative with respect to membranes. From this, the following concept of the effect of electrokinetic phenomena for electrolytes is set up. Consider the following diagram.



Where $v < u$, the dilute solution will become positive relative to the concentrated solution. In this case, the diffusion potential will be augmented by the streaming potential. Thus, the total potential is

$$E_a = E_D + E_s$$

The electroosmosis, O_e, is given by

$$O_e = \frac{Q \rho E D}{4\pi \eta l}$$

and works in opposition to normal osmosis. Thus,

$$O_a = O_n - O_e = \alpha A \int_0^\theta \Delta \, d\theta - \frac{Q \rho D (E_D + E_s)}{4\pi \eta l}$$

Where $u < v$, the dilute solution will become negative relative to the concentrated solution. Thus, the diffusion potential will be decreased by the streaming potential. Therefore,

$$O_a = O_n - O_e \; ; \; E_a = E_D - E_s$$

However, here electroosmosis works to increase with the normal osmosis. Thus,

$$E_a = E_D - E_s \; ; \qquad O_a = O_n + O_e = \gamma A \int_0^\theta \Delta \, d\theta + \frac{Q \rho D (E_D - E_s)}{4\pi \eta l}$$

From the above, several conclusions may be drawn, which are as follows.

(1) Where $u = v$, $E_d = 0$, and a potential will be set up in opposition to normal osmosis.

(2) Where $v < u$, the actual osmose will be less than the normal osmose.

(3) Where $u < v$, the actual osmose will be greater than the normal osmose.

(4) Where $E_d = E_s$, osmosis will proceed at the normal rate.

(5) Where the Zeta potential is negligible, osmosis will proceed at the normal rate.

(6) When the dilute side is negative, the effect of the Zeta potential is diminished by the streaming potential.

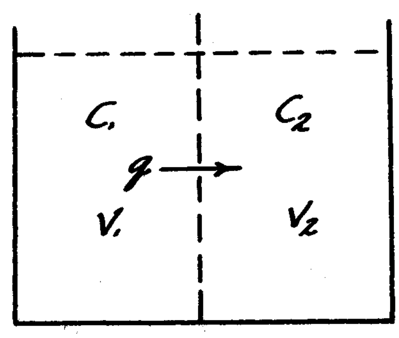
From the above considerations, it may be assumed that usually the electrokinetic effect is small relative to normal action, and therefore may be neglected as a first approximation. The following relations are developed as the first approximation, and are therefore subject to the assumptions stated for each case.

CASE I - UNSTEADY STATE - OSMOSE NEGLIGIBLE

A. ASSUMPTIONS:

(1) The amount of osmose passing the membrane is negligible.
(2) The electrokinetic effects are negligible.
(3) The concentrated and dilute solutions remain constant in
(4) Stirring has a negligible effect on the rate of transfer.
(5) Perfect mixing of the solutions throughout each phase.

B. DIAGRAM:



C. DEVELOPMENT:

By analogy to diffusion, the following differential relation may be written for solute transfer across a membrane.

$$\frac{dq}{d\theta} = kA\frac{dC}{dt} \qquad (1)$$

Since the membrane is relatively thin, and because the diffusion path is in the form of a fine pore, the concentration gradient may be considered to be linear with membrane thickness. Therefore, combining the ratio k/t into a new constant K, Equation (1) becomes

$$\frac{dq}{d\theta} = KA(C_1 - C_2) \qquad (2)$$

It is now necessary to relate q and C_2 in terms of C_1. By material balances, it follows that

$$q = V_1(C_1' - C_1) \qquad C_2 = \frac{V_1}{V_2}(C_1' - C_1) + C_2'$$
$$q = V_2(C_2 - C_2') \quad \text{or} \quad C_2 = \psi(C_1' - C_1) + C_2' \tag{3}$$

Also, atany time

$$dq = -V_1 dC_1 \tag{4}$$

Substituting Equations (3) and (4) in (2), one obtains

$$-\frac{V_1 dC_1}{d\theta} = KA\left[C_1(1+\psi) - \psi C_1' - C_2'\right] \tag{5}$$

which is separable to

$$\int_{C_1'}^{C_1} \frac{dC_1}{[C_1(1+\psi) - \psi C_1' - C_2']} = -\frac{KA}{V_1}\int_0^\theta d\theta \tag{6}$$

Integration of (6) between the limits of C_1' to C_1, and 0 to θ yields the following equation upon simplification.

$$\ln\left[\frac{C_1(1+\psi) - \psi C_1' - C_2'}{(C_1' - C_2')}\right] = -\frac{KA}{V_1}(1+\psi)\theta \tag{7}$$

However, the form of the equation is bulky, and will therefore be further simplified by the introduction of the new constants

$$J = (1+\psi) = \left(1 + \frac{V_1}{V_2}\right) = \left(\frac{V_1 + V_2}{V_2}\right) \tag{8}$$

$$\Delta_0 = (C_1' - C_2') \tag{9}$$

Introduction of (8) and (9) into (7) yields

$$\ln\left[\frac{J(C_1 - C_1')}{\Delta_0} + 1\right] = -\frac{KAJ}{V_1}\theta \tag{10}$$

In case it is desired to know the concentration C_1 after any period of time, Equation (10) may be solved to give

$$C_1 = -\frac{\Delta_0}{J}\left[1 - e^{\frac{-KAJ}{V_1}\theta}\right] - C_1' \tag{11}$$

To solve directly for the quantity of material transposed, it is only necessary to substitute in (11) one of the material balances from (3). Thus

$$q = \frac{V_1\Delta_0}{J}\left[1 - e^{\frac{-KAJ}{V_1}\theta}\right] - 2C_1' \tag{12}$$

It is necessary that the concentration limits be kept in mind. For the case in which the solute is permeable to the membrane, the limit of dialysis is where $C_1 - C_2 = 0$, or where

$$q = \frac{\Delta_0 V_1}{J} \tag{13}$$

If one component of the system is non-diffusible, the limits as set down by Donnan must be employed. Thus, at equilibrium

$$[M_1^+][A_1^-] = [M_2^+][A_2^-]$$

and

$$\left(C_1' + \frac{q}{V_1}\right)\left(\frac{q}{V_1}\right) = \left(C_2' - \frac{q}{V_2}\right)^2 \tag{14}$$

Solving (14) for q

$$q = \frac{\frac{C_1'}{V_1} + \frac{2(C_2')^2}{V_2} \pm \left[\left(\frac{C_1'}{V_1} + \frac{2(C_2')^2}{V_2}\right)^2 - 4\left(\frac{C_1}{V_1^2} - \frac{1}{V_2^2}\right)(C_2')^2\right]^{1/2}}{2\left(\frac{C_1}{V_1^2} - \frac{1}{V_2^2}\right)} \qquad (15)$$

However, where $V_1 = V_2$, the solution simplifies to

$$C_{1_A} = \frac{(C_2')^2}{C_1' + 2C_2'} = \frac{(C_2')^2}{\Delta_0 + 3C_2'} \qquad (16)$$

In order to verify this development, it is only necessary to plot

$$\ln\left[\frac{J(C_1 - C_2)}{\Delta_0} + 1\right] \quad vs. \quad \theta$$

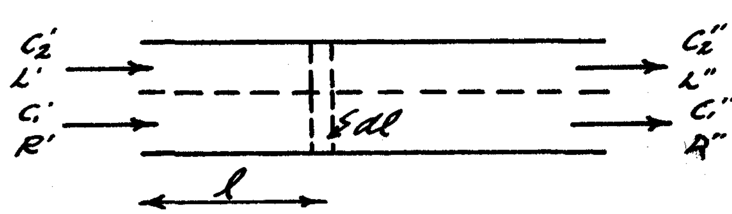
The slope of the line is $-KAJ/V_1$, from which K may be computed. Should the value of K be variable, a rectification as a function of C is recomended.

CASE II - PARALLEL FLOW - STEADY STATE - OSMOSE NEGLIGIBLE

A. ASSUMPTIONS:

The same assumptions apply here as in Case I.

B. DIAGRAM:



C. DEVELOPMENT:

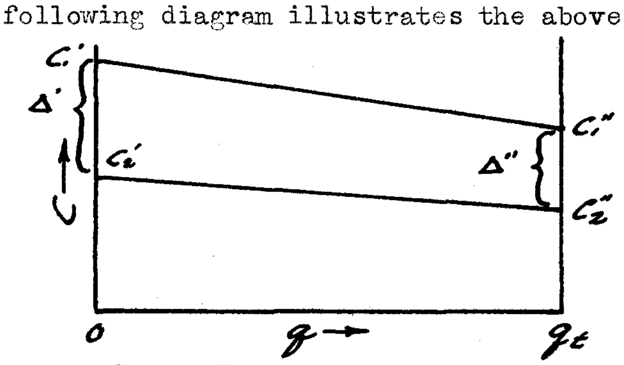
Consider a differential section of the membrane at any point of distance l from the concentrated liquor inlet. The value of area, dA is also equivalent to h(dl). Across this differential area, the rate of transfer is given by

$$\frac{q}{\theta} = K \Delta dA \tag{1}$$

However, since the quantity transferred varies with the area, the following differential equation may be written, where the value of K has the same dimensions and is of identical magnitude as in (1).

$$\frac{dq}{dA} = K \Delta \theta = \frac{dq}{h\,dl} \tag{2}$$

Since all of the solute lost by the rich liquor must be gained by the lean liquor, then both C_1 and C_2 must be linear in the dialysate, or q. The following diagram illustrates the above principle.



From the diagram, it may be seen that

$$\frac{d\Delta}{dq} = \frac{\Delta_1' - \Delta_2''}{q_t} \tag{3}$$

The substitution of Equation (3) in (2) gives

$$\frac{q_t\, d\Delta}{(\Delta' - \Delta'')\, h\,dl} = K \Delta \theta \tag{4}$$

Separating (4)

$$\int_{\Delta'}^{\Delta''} \frac{d\Delta}{\Delta} = \frac{K\theta h(\Delta' - \Delta'')}{q_t} \int_0^{l} dl$$

Integrating and rearranging the above yields

$$\frac{q}{\theta} = Khl \frac{\Delta' - \Delta''}{\ln \frac{\Delta'}{\Delta''}} \qquad (5)$$

which is the familiar form of the log mean.

It now becomes necessary to evaluate Δ' and Δ'' in terms of the flow rates and the quantity of material transferred. Obviously,

$$\Delta' = C_1' - C_2'' \qquad (6)$$

To obtain Δ'', a material balance will be employed. Thus,

$$q = C_1' R\theta - C_1'' R\theta = C_2'' L\theta - C_2' L\theta \qquad (7)$$

and,

$$C_1'' = C_1 - \frac{q}{R\theta} \qquad (8)$$

$$C_2'' = C_2' + \frac{q}{L\theta} \qquad (9)$$

Consequently, from (6), (8) and (9)

$$(\Delta' - \Delta'') = \frac{q}{\theta}\left(\frac{1}{R} + \frac{1}{L}\right) \qquad (10)$$

Also, from (6) and (10)

$$(\Delta' - \Delta'') = \frac{q}{\theta}\left(\frac{1}{R} + \frac{1}{L}\right) \qquad (11)$$

Solving for $\frac{\Delta'}{\Delta''}$ from (6) and (10), we get

$$\frac{\Delta'}{\Delta''} = \frac{\Delta'}{\Delta' - \frac{q}{\theta}\left(\frac{1}{R} + \frac{1}{L}\right)} \tag{12}$$

Substituting (11) and (12) in (5), and solving for l, we obtain a more directly applicable relation, which is

$$l = \frac{\ln\left[\frac{\Delta'}{\Delta' - \frac{q}{\theta}\left(\frac{1}{R}+\frac{1}{L}\right)}\right]}{Kh\left(\frac{1}{R} + \frac{1}{L}\right)} \tag{13}$$

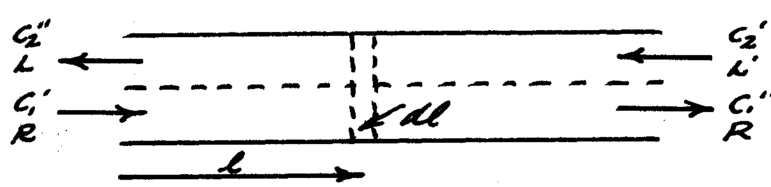
Thus, by the aid of Equation (13) it is possible to solve directly for the length of the flow path required to effect a given transfer of solute for a definite condition of flow rates and plate height, in any period of time. However, it must be recalled that usually the largest mean driving force is attained by means of counter-current flow. However, it is evident that a case may exist where the reverse could be true. In a case where the lean liquor flow rate is very high, C_2 may be assumed negligible, and therefore the driving force becomes equivalent to the rich liquor concentration.

CASE III <u>COUNTER CURRENT FLOW</u> - <u>STEADY STATE</u> - <u>OSMOSE NEGLIGIBLE</u>

A. <u>ASSUMPTIONS:</u>

The same assumptions apply here as in Case I.

B. <u>DIAGRAM:</u>



C. DEVELOPMENT:

A consideration similar to Case II yields a similar relation, which is

$$\frac{q}{\theta} = k h l \frac{\Delta' - \Delta''}{\ln \frac{\Delta'}{\Delta''}} \tag{1}$$

However, the values of Δ are not the same, and must be considered as follows. From Equations (8) and (9) of Case II

$$C_1'' = C_1' - \frac{q}{R\theta} \tag{2}$$

$$C_2'' = C_2' + \frac{q}{L\theta} \tag{3}$$

and therefore,

$$\Delta' = C_1' - C_2'' = (C_1' - C_2') - \frac{q}{L\theta} = \Delta_0 - \frac{q}{L\theta} \tag{4}$$

$$\Delta'' = C_1'' - C_2' = (C_1' - C_2') - \frac{q}{R\theta} = \Delta_0 - \frac{q}{R\theta} \tag{5}$$

Subtracting (4) from (5) we obtain

$$\Delta' - \Delta'' = \frac{q}{\theta}\left(\frac{1}{R} + \frac{1}{L}\right) \tag{6}$$

and dividing (4) by (5)

$$\frac{\Delta'}{\Delta''} = \frac{\Delta_0 - \frac{q}{L\theta}}{\Delta_0 - \frac{q}{R\theta}} \tag{7}$$

Substituting (6) and (7) in (1) and solving for l yields

$$l = \frac{\ln\left[\frac{\Delta_0 - \frac{q}{L\theta}}{\Delta_0 - \frac{q}{R\theta}}\right]}{k h \left(\frac{1}{R} + \frac{1}{L}\right)} \tag{8}$$

The above three cases do not consider osmose. It is well known that osmotic pressure reaches large proportions. Since the membranes are porous, it is evident that there must be some osmosis. For large concentrations, the relation of osmosis to solute transfer may become appreciable.

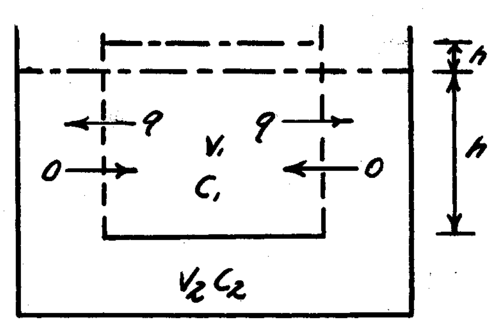
If osmosis is considered, the relations governing transfer are complicated by its induction. The six cases of interest are therefore developed in the following material. It must be recalled that these are also subject to the same end conditions as defined by concentration equivalence and the Donnan equilibrium.

CASE IV UNSTEADY STATE - OSMOSE NOT NEGLIGIBLE - OSMOSE RETAINED IN CONCENTRATED CELL - C_2 NEGLIGIBLE

A. ASSUMPTIONS:

(1) The dilute concentration is negligible.
(2) The transfer area is limited by the level of V_2.
(3) Osmosis is appreciable relative to solute transfer.
(4) The small hydrostatic head between V_1 and V_2 is negligible.
(5) The electrokinetic effects are negligible.
(6) The solutions are of uniform concentration.
(7) The osmose is pure solvent.
(8) Stirring has a negligible effect on the rate of transfer.

B. DIAGRAM



C. DEVELOPMENT:

By analogy to Case I,

$$\frac{dq}{d\theta} = kA(C_1 - C_2) = kAC_1 \tag{1}$$

However, it is necessary that osmosis be included. It has been shown that the rate of flow through fine pores is streamline, and therefore $dO/d\theta \propto P$. Further, we have seen that osmotic pressure is proportional to concentration. Therefore, the following relation may be written.

$$\frac{dO}{d\theta} = \gamma A(C_1 - C_2) = \gamma AC_1 \tag{2}$$

Dividing (1) by (2) yields

$$\frac{dq}{dO} = \frac{k}{\gamma} = \frac{q}{\theta} = \frac{1}{\varphi} \tag{3}$$

Equation (3) is extremely important, and will be discussed in detail later. Since dO is measured by increments in V_1, it will be convenient for the moment to write (3) as

$$\frac{dq}{dV_1} = \frac{k}{\gamma} = \frac{1}{\varphi} \tag{4}$$

Also,

$$dq = -V_1 dC_1 \tag{5}$$

Substituting (5) in (4)

$$-\frac{V_1 dC_1}{dV_1} = \frac{k}{\gamma} = \frac{1}{\varphi} \tag{6}$$

Separating,

$$-\varphi\int_{C_1'}^{C_1} dC_1 = \int_{V_1'}^{V_1'+O=V_1} \frac{dV_1}{V_1} \tag{7}$$

Integrating between the limits of C_1' and C_1 and V_1' and V_1 yields

$$\tau(C_1' - C_1) = \ln\left(\frac{V_1}{V_1'}\right) = \ln\left(\frac{V_1' + q}{V_1'}\right) \tag{8}$$

Since volume equals Ah

$$\tau(C_1' - C_1) = \ln\left(\frac{h_1}{h_1'}\right) \tag{9}$$

Solving for h yields

$$h = h_1' e^{\tau(C_1' - C_1)} \tag{10}$$

It is not possible to test the validity of Equation (10) by a direct plot, since the value of   is not known. However, integration of Equation (4) between the limits of 0 and q, and h_1' and h_1 yields

$$\frac{q}{V_1} = \frac{K}{\gamma} = \frac{1}{\tau} \tag{11}$$

Solving (11) for

$$\tau = \frac{V_1}{q} \tag{12}$$

Employing (12), it is now possible to test Equation (10) by plotting

$$\ln\left(\frac{h_1}{h_1'}\right) \text{ vs } (C_1' - C_1)$$

The slope of the line is τ, and the values of K and γ are solved for by the use of (11). However, Equation (10) is only an expression of osmose in terms of concentration. It can serve only to verify the general assumptions. It is desirable to determine the relation governing the time required to accomplish a given separation. The following development holds for the latter.

At any time,

$$C_1 = \frac{V_1 C_1' - q}{V_1 + \gamma q} \tag{13}$$

Substituting (13) in (10)

$$\frac{dq}{d\theta} = KA\left(\frac{V_1 C_1' - q}{V_1 + \gamma q}\right) \tag{14}$$

Separating the variables and establishing limits yields

$$V_1 \int_0^q \frac{dq}{V_1 C_1' - q} + \gamma \int_0^q \frac{q\,dq}{V_1 C_1' - q} = KA \int_0^\theta d\theta \tag{15}$$

Integration and simplification of (15) gives

$$(\gamma C_1' - 1)\left[V_1 \ln\left(1 - \frac{q}{V_1 C_1'}\right)\right] - \gamma q = KA\theta \tag{16}$$

Equation (16) is useful in determining the time required for a given separation. To solve for q when the time is specified, the method of iteration is suggested.

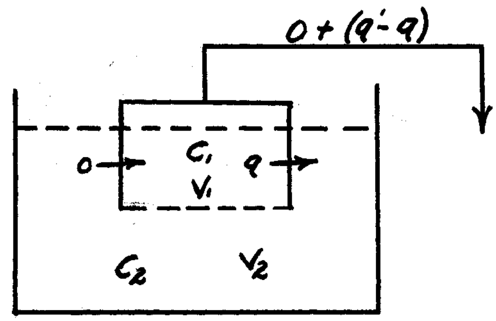
CASE V - UNSTEADY STATE - C_2 NEGLIGIBLE
OSMOSE NOT NEGLIGIBLE - OSMOSE WITHDRAWN

Note: This case is of value only for the determination of the constants K and γ, and for the verification of assumptions.

A. ASSUMPTIONS:

Same as Case 4

B. DIAGRAM:



C. DEVELOPMENT:

By analogy to Case 4, Equations (1) and (2) are applicable. Thus,

$$\frac{dq}{d\theta} = kA(C_1 - C_2) = kAC_1 \tag{1}$$

$$\frac{dO}{d\theta} = \gamma A(C_1 - C_2) = \gamma AC_1 \tag{2}$$

Equation (1) is valid only when there is no other transfer of solute from the cell other than by diffusion through the membrane. However, solute is also removed by the osmose. Let q' represent the total solute removed from the cell by diffusion and by osmosis. Then

$$\frac{dq'}{d\theta} = kAC_1 + \frac{dO}{d\theta}C_1 \tag{3}$$

Substituting (2) in (3),

$$\frac{dq'}{d\theta} = kAC_1 + \gamma AC_1^2 = AC_1(k + \gamma C_1) \tag{4}$$

At any instant,

$$dq' = -V_1 dC_1 \tag{5}$$

Substitution of (5) in (4) yields

$$-\frac{V_1\,dC_1}{d\theta} = AC_1(K+\gamma C_1) \tag{6}$$

Separating the variables yields

$$\int_{C_0}^{C_1}\frac{dC_1}{AC_1(K+\gamma C_1)} = -\frac{A}{V_1}\int_0^{\theta} d\theta$$

Integration between the limits of C_o and C_1, and 0 and θ gives

$$\ln\left(\frac{C_1}{C_0}\right)\left(\frac{K/\gamma + C_0}{K/\gamma + C_1}\right) = -\frac{KA\theta}{V_1} \tag{7}$$

after simplification.

The chief value of equation (7) lies in its use for the determination of K and γ. From Equation (3), Case 4,

$$\frac{K}{\gamma} = \frac{q}{O} \tag{8}$$

Substituting (8) in (7)

$$\ln\left(\frac{C_1}{C_0}\right)\left(\frac{q/O + C_0}{q/O + C_1}\right) = -\frac{KA\theta}{V_1} \tag{9}$$

In order to determine K from some data, it is only necessary to plot

$$\log\left(\frac{C_1}{C_0}\right)\left(\frac{q/O + C_0}{q/O + C_1}\right) \text{ vs } \theta$$

Thus, the slope of the line, m, will be equivalent to $\frac{KA}{2.303\,V_1}$, from which

$$K = \frac{2.303\,V_1\,m}{A} \tag{10}$$

From (8)

$$\gamma = K\frac{\Theta}{q} = \frac{2.303\, V_1 m}{q} \times \Theta \qquad (11)$$

In case it is desired to determine the concentration after any period of time for any system, Equation (7) may be solved for C_1. Thus,

$$C_1 = \frac{C_0 K e^{-\frac{KA\theta}{V_1}}}{K + \gamma C_0\left(1 - e^{-\frac{KA\theta}{V_1}}\right)} \qquad (12)$$

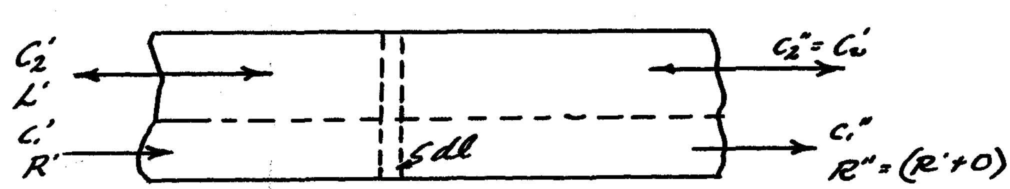
The solutions for this case are very useful in obtaining the values of K and γ employing small scale equipment.

CASE VI STEADY STATE - OSMOSE NOT NEGLIGIBLE - PARALLEL AND COUNTER CURRENT FLOW - C_2 NEGLIGIBLE

A. ASSUMPTIONS:

(1) The volume of flow of the lean liquor is large relative to that of the rich liquor.
(2) The value of C_2 is negligible at all points.
(3) Osmose is appreciable relative to solute transfer.
(4) The electrokinetic effects are negligible.
(5) The osmose is pure solvent.
(6) The solutions are uniform.
(7) The rate of flow has a negligible effect on the rate of transfer.

B. DIAGRAM:



C. DEVELOPMENT:

By analogy to Equation (2) Case II

$$\frac{dq}{dA} = \frac{dq}{h\,dl} = K\theta\Delta = K\theta C_1 \qquad (1)$$

By a material balance through any flow distance l,

$$q = C_1'R\theta - C_1(R\theta + O) \qquad (2)$$

from which it follows that

$$C_1 = \frac{C_1'R\theta - q}{R\theta + rq} \qquad (3)$$

Substituting (3) in (1), and separating variables gives

$$R\theta\int_0^q \frac{dq}{C_1'R\theta - q} + r\int_0^q \frac{q\,dq}{C_1'R\theta - q} = K\theta h\int_0^l dl \qquad (4)$$

Integration of (4) between the limits of 0 and q, and 0 and l yields

$$(rC_1' - 1)\left[R\theta \ln\left(1 - \frac{q}{C_1'R\theta}\right)\right] - rq = K\theta h l \qquad (5)$$

It must be recalled that this relation is applicable to both parallel and countercurrent flow under the assumptions made. It is useful in the calculation of the length of path required to accomplish a given solute transfer under specific conditions of flow and concentration.

When it is desired to recover a solute which has been polluted, it is advantageous to do so with the highest possible concentration of the exuding pure liquor. In such case, it is obvious that the lean liquor concentration cannot be considered negligible. Also, since such solutes are evidently highly diffusable, it appears that neither can osmose be considered negligible. The following developments apply to the conditions stated above.

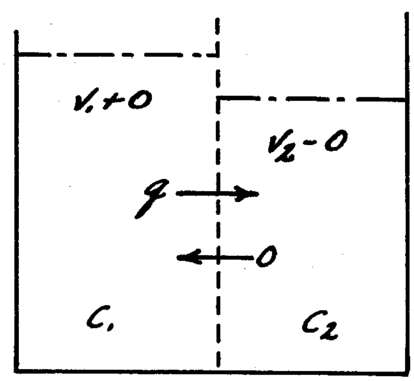
CASE VII UNSTEADY STATE - C_2 NOT NEGLIGIBLE

OSMOSE NOT NEGLIGIBLE

A. ASSUMPTIONS:

(1) The solutions are uniform throughout.
(2) Stirring has a negligible effect on the rate of transfer.
(3) The electrokinetic effects are negligible
(4) The osmose is pure solvent.

B. DIAGRAM:



C. DEVELOPMENT:

By analogy to Case I, Equation (2),

$$\frac{dq}{d\theta} = KA(C_1 - C_2) \qquad (1)$$

In order to integrate the above relation, it is necessary that

C_1 and C_2 be expressed in terms of q
C_1 and q be expressed in terms C_2
C_2 and q be expressed in terms of C_1

This may be accomplished by writing the following material balances over any period of time

$$q = C_1'V_1' - C_1(V_1'+O) = q' - C_1(V_1+O) \qquad (2)$$

$$q = (V_2'-O)C_2 - V_2'C_2' \qquad (3)$$

From these, any of the above conditions may be fulfilled. For this purpose, it is most advantageous to solve as follows.

$$C_1 = \frac{q'-q}{V_1+O} \qquad (4)$$

$$C_2 = \frac{q}{V_2-O} \quad \text{when } C_2'=0 \qquad (5)$$

Subtracting (4) from (5) and expanding yields

$$C_1 - C_2 = \frac{V_2 q' - q(V_2 + Tq + V_1)}{V_1 V_2 + Tq(V_2 - V_1) - T^2 q^2} \qquad (6)$$

Substituting (6) in (1)

$$\frac{dq}{d\theta} = KA\left(\frac{V_2 q' - q(V_2 + Tq + V_1)}{V_1 V_2 + Tq(V_2 - V_1) - T^2 q^2}\right) \qquad (7)$$

For the purpose of simplification, it is desireable to introduce new constants in place of the constant groups. Thus

$$a = V_1 V_2 \qquad (8)$$

$$b = T(V_2 - V_1) \qquad (9)$$

$$i = V_2 q' \tag{10}$$

$$j = (V_2 + r q' + V_1) \tag{11}$$

Substitution of (8), (9), (10), and (11) in (7), and separating the variables yields

$$a\int_0^q \frac{dq}{i - jq} + b\int_0^q \frac{q\,dq}{i - jq} - r^2\int_0^q \frac{q^2\,dq}{i - jq} = KA\int_0^\theta d\theta \tag{12}$$

Integration of (12) between the limits of 0 and q, and 0 and θ by the method of substitution results in

$$\frac{1}{j}(h)\ln\left(1 - \frac{jq}{i}\right) - qsi + \tfrac{1}{2}r^2q^2 = KA\theta \tag{13}$$

$$s = \left(1 + \frac{r^2}{j}\right)$$

$$h = \left(\frac{bi}{j} - a + \frac{r^2 i^2}{j^2}\right)$$

The above relation specifies the time required to attain a definite separation in a specific cialyzer. In case it is desired to solve for the quantity of solute transferred in a finite time, Equation (13) may be further simplified and solved by the method of iteration. In case it is desirable, Equation (12) may be integrated by approximate methods with facility.

$$C_2 = \frac{Q - q + C_2' L\theta}{L\theta - O'' + O} \tag{5}$$

From Equation (3), Case IV, it may be seen that

$$O = \frac{\gamma}{K} q = \Upsilon q \tag{6}$$

Substituting (6) in (4) and (5)

$$C_1 = \frac{C_1' R\theta - q}{R\theta + \Upsilon q} \tag{7}$$

$$C_2 = \frac{Q - q + C_2' L\theta}{L\theta - \Upsilon(Q - q)} \tag{8}$$

Subtracting (7) from (8)

$$C_1 - C_2 = \Delta = \frac{C_1' R\theta - q}{R\theta + \Upsilon q} - \frac{Q - q + C_2' L\theta}{L\theta - \Upsilon(Q - q)} \tag{9}$$

The following substitutions are then made for groups of constants:

$$B = C_1' R\theta \tag{10}$$

$$S = R\theta \tag{11}$$

$$G = L\theta - \Upsilon Q \tag{12}$$

$$F = Q + C_2' L\theta \tag{13}$$

Substituting (10), (11), (12), and (13) in (9) yields upon expansion

$$C_1 - C_2 = \Delta = \frac{BG - CF + q[C - G + \Upsilon(B-F)]}{CG + \Upsilon q(G+C) + \Upsilon^2 q^2} \quad (14)$$

$$= \frac{X + Yq}{\psi + \phi q + \Upsilon^2 q^2}$$

where

$$X = BG - CF \quad (15)$$

$$Y = C - G + \Upsilon(B-F) \quad (16)$$

$$\psi = CG \quad (17)$$

$$\phi = \Upsilon(G+C) \quad (18)$$

The variables of (14) may be separated, and thus

$$\psi\int_0^q \frac{dq}{X+Yq} + \phi\int_0^q \frac{q\,dq}{X+Yq} + \Upsilon^2\int_0^q \frac{q^2 dq}{X+Yq} = K\theta\int_0^A dA \quad (19)$$

Integration between the limits of 0 and q, and 0 and Θ yields upon expansion and simplification

$$\left[\ln\left(1+\frac{Y}{X}q\right)\right]\left[\frac{\psi}{Y} + \frac{\phi X}{Y^2} + \frac{\Upsilon^2 X^2}{Y^3}\right] + \frac{q}{Y}\left(\phi + \Upsilon^2\frac{X}{Y}\right) + \frac{\Upsilon^2}{2Y}q^2 = KA\theta \quad (20)$$

Further simplification is of advantage when it is desired to solve for q, where l is given. Further simplification is of no advantage where it is desired to solve for the length of path required to accomplish a given separation. The simplification is as follows.

Let

$$Z = \frac{Y}{X} \qquad (21)$$

$$M = \frac{\psi}{Y} + \frac{\phi}{Z} + \frac{\varphi^2}{Z^2 Y} \qquad (22)$$

$$W = (\phi - \varphi^2)\frac{1}{Y} \qquad (23)$$

$$S = \frac{\varphi^2}{2Y} \qquad (24)$$

Substitution of Equations (21) through (24) in (20), after the apprrpriate simplification and expansion yields

$$[\ln(1+Zq)][M] + Wq + Sq^2 = KA\theta \qquad (25)$$

This equation may be more readily solved by iteration, although it is doubtful if any advantage is gained if one is solving for the time required to accomplish a given separation. It is to be noted that approximate methods of integration of Equation (19) may be applied with facility, thereby yielding a numerical answer to a specific design problem.

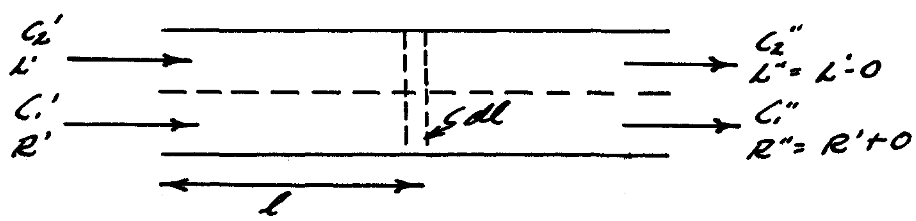
CASE IX STEADY STATE - PARALLEL FLOW

OSMOSE AND C_2 ARE NOT NEGLIGIBLE

A. ASSUMPTIONS:

The assumptions in Case V apply here.

B. DIAGRAM:



C. DEVELOPMENT:

By analogy to Case II, Equation (2),

$$\frac{dq}{dA} = K\theta\Delta = \frac{dq}{h\,dl} = K\theta(C_1 - C_2) \quad (1)$$

It is desirable to solve (1) in terms of the quantity transferred and the length of path required. Therefore, over any distance l from the rich liquor inlet, the following material balances may be written.

$$q = C_1'R\theta - C_1(R\theta + O) \quad (2)$$

$$q = C_2(L\theta - O) - C_2'L\theta \quad (3)$$

Solving for C_1 and C_2

$$C_1 = \frac{C_1'R\theta - q}{R\theta + O} \quad (4)$$

$$C_2 = \frac{q - C_2' L\theta}{L\theta - O} \qquad (5)$$

From Equation (3), Case IV,

$$O = \frac{\gamma}{K} q = \Upsilon q \qquad (6)$$

Substituting (6) in (4) and (5)

$$C_1 = \frac{C_1' R\theta - q}{R\theta + \Upsilon q} \qquad (7)$$

$$C_2 = \frac{C_2' L\theta + q}{L\theta - T q} \qquad (8)$$

Let

$$G'' = L\theta \qquad (9)$$

$$F'' = C_2' L\theta \qquad (10)$$

Substituting (9), (10), and Equations (10) and (11) from Case VIII in (7) and (8), and subtracting (8) from (7) yields

$$\Delta = C_1 \cdot C_2 = \frac{B' - q}{S' + \Upsilon q} - \frac{F'' + q}{G'' + T q} \qquad (11)$$

Simplifying and substituting the following

$$X' = B' G'' - F'' S' \qquad (12)$$

$$Y' = -S' - G'' - T(B' + F'') \qquad (13)$$

$$\phi = S G'' \qquad (14)$$

$$\phi' = \gamma(6'' - 5') \tag{15}$$

yields

$$\Delta = C_1 - C_2 = \frac{X' + Y'q}{\psi' + \phi' q - \gamma^2 q^2} \tag{16}$$

Substituting in (1), and separating variables

$$\psi' \int_0^q \frac{dq}{X' + Y'q} + \phi' \int_0^q \frac{q\,dq}{X' + Y'q} - \gamma^2 \int_0^q \frac{q^2\,dq}{X' + Y'q} = K\theta \int_0^A dA \tag{17}$$

Integrating between the limits of q = 0 and q, and 0 and l gives

$$\left[\ln\left(1 + \frac{Y'}{X'}q\right)\right]\left[\frac{\psi'}{Y'} + \frac{\phi X'}{Y'^2} - \frac{\gamma^2 \overline{X'^2}}{Y'^3}\right] + \frac{q}{Y'}\left(\phi + \gamma^2 \frac{X'}{Y'}\right) - \frac{\gamma^2 q^2}{2Y'} = K\theta A \tag{18}$$

Further simplification is as follows.

Let

$$Z' = \frac{Y'}{X'} \tag{19}$$

$$M' = \frac{\psi'}{Y'} + \frac{\phi'}{2YZ'} - \frac{\gamma^2}{Z^2 Y'} \tag{20}$$

$$W' = \frac{1}{Y'}\left(\phi' + \gamma^2 \frac{X'}{Y'}\right) \tag{21}$$

$$Z'' = \frac{\gamma^2}{2Y'} \tag{22}$$

Substitution of Equations (19) through (22) in (18) and simplifying

$$M'[\ln(1 + Z'q)] + W'q - Z''q^2 = K\theta A \tag{23}$$

The above relation may therefore be readily solved by iteration for values of q when l and other parameters are known.

IV EXPERIMENTAL

The experimental work consisted of an effort to verify the concepts of the dialytic process as developed in the preceeding section. It was also desired to determine the transfer coefficients for several solutes and membranes.

Procedure.

The section of the thesis, entitled Literature Review, did not indicate that the quantity of osmose was large relative to the solute transfer. Consequently, an unsteady state apparatus in which the dilute concentration was held negligible was constructed. This apparatus is illustrated in Plate I, and corresponds to Case I.

The membrane employed was clear cellophane. This was the product of the Dennison Manufacturing Company of Farmingham, Massachusetts. It was not treated to make it water-impervious. Its thickness was 0.0021 centimeters, the variance being 0.0001 centimeter as a maximum. The cellophane was made into a tube, the joint being sealed with rubber cement. This tube was then slipped over the bakelite support and fastened onto the support with insulated copper wire, thereby insuring a water tight seal. The rate of solvent flow was 2.96 liters per hour. The stirrer operated at position number I. The stirring of the concentrated liquid was accomplished by saturated air bubbling through the cell. The rate was 200 bubbles per minute. The operation proceeded smoothly, but it was observed that there was a continual increase in the rich volume. The data taken at intervals were as follows:

(1) Time
(2) 1 c.c. sample of C_1
(3) 25 c.c. sample of C_2
(4) Air bubble rate
(5) Dilute liquor quantity
(6) Temperature

At the beginning and the end of the run, the rich volume was measured.

It was observed in the above experiments that osmose amounted to roughly 50 per cent of the original volume over five hours. Therefore, it was evident that osmose could not be neglected.

An attempt to measure the rate of osmose by withdrawing the osmose through a tube with suction failed. A siphon was then employed, Dreft being introduced at the exit in an effort to reduce surface tension effects. This also failed to yield reproducable results.

The failure in the above two cases may be attributed to surface tension interference and to membrane flexure. The force required to produce a drop on the end of a capillary was equivalent to about 2-4 m.m. head of water. Further, small increases in pressure caused the membrane to flex, thereby distorting the osmose results.

It then appeared that it was necessary to construct a steady state piece of equipment employing balanced pressures. This equipment was to operate until equilibrium was reached. Then the value of K and were to be determined as follows:

$$K = \frac{q}{\theta A(C_1 - C_2)}$$

and

$$\gamma = \frac{O}{\theta A(C_1 - C_2)}$$

Thus, over a period of time, with a known input of rich liquor, the two constants could be determined. The pressure on both sides of the membrane were adjusted until identical. At this condition,

$$H_2 = H_1 \frac{\rho_1}{\rho_2}$$

where H_1 and H_2 represent the height of the liquor levels of the concentrated and dilute liquors, respectively. ρ_1 and ρ_2 represent the density of the rich and dilute solutions. After the apparatus had come into equilibrium, a measured quantity of the rich solution was introduced and permitted to pass through the system. The data taken were as follows:

(1) Time at start of flow
(2) Temperature
(3) Inlet volume of solution
(4) Outlet volume of solution
(5) Concentration of dilute liquor
(6) Concentration of rich liquor

This piece of equipment is illustrated in Plate II. The results from it were very poor. It was possible to reproduce fairly well the values of K, but not those of γ.

The failure of the above equipment can be attributed to membrane flexure alone. Thus, it became evident that the membrane must be supported, and that it be under some slight positive pressure to hold it against the support.

An experimental dialyzer was then constructed which facilitated these requirements. This dialyzer is illustrated by Plate III. The top and bottom frames were of $\frac{3}{4}$ inch bakelite. The rich volume container was a tenite plate. The support was a $\frac{1}{4}$ inch mesh screen made of galvanized iron. This was fastened to the bottom bakelite frame.

The apparatus was held together by four bolts.

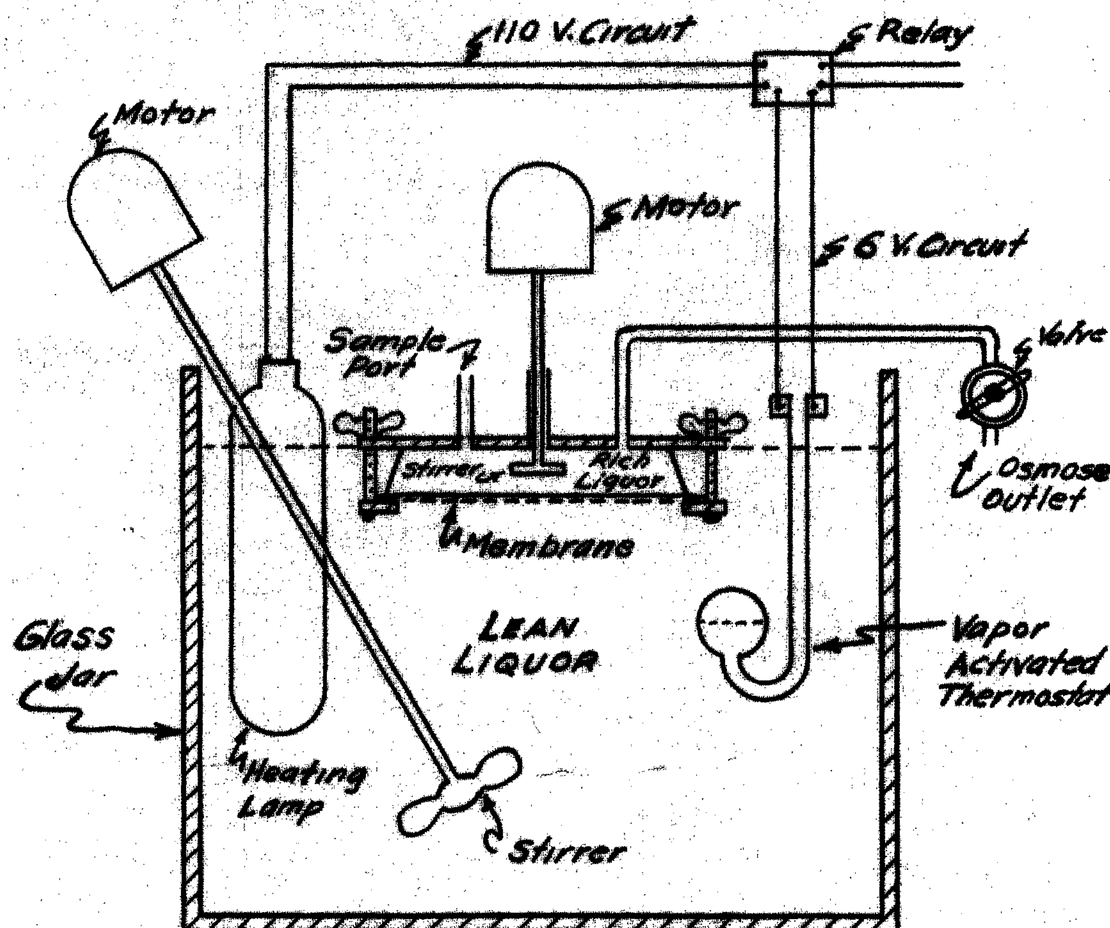
The procedure for a run is given as follows. The dilute liquor container was filled with distilled water. The thermostat was introduced, and the liquid stirred while it came up to temperature. The membrane was soaked in distilled water for $\frac{1}{2}$ hour. The top frame and the plate were purged of impurities and placed on a rack up-end down. Both the osmose and sampling tubes were closed. The rich liquor was then poured in the plate until its level was flush with the plate edge. The membrane was slid on in such a manner as to prevent air entering. The rubber washer was then placed on the periphery of the plate. The lower frame was placed on the washer and bolted in place. The apparatus was then inverted, and liquid run in until the system was completely filled. The apparatus was next introduced into the dilute liquor bath and the osmose lead and stirrer connected. It was then tested for leaks and run for 10-15 minutes to insure uniformity, operation smoothness, and to allow the membrane to come into equilibrium. The dilute liquor stirrer operated at position III, while the concentrated liquor stirrer operated at position I. The data taken during a run over a period of time were as follows:

(1) The osmose volume
(2) A 1 c.c. sample of the rich liquor
(3) A 25 c.c. sample of the lean liquor
(4) The temperature
(5) The time

At the beginning of the run the dilute liquor volume was measured. At the end of the run the rich liquor volume was measured.

Analytical Procedure.

Chlorides. All Chlorides were titrated with silver nitrate



EXPERIMENTAL DIALYZER

FOR DIRECT DETERMINATION OF K & γ

-MATERIALS-

DIALYZER PAN - TENITE

DIALYZER FRAME - BAKELITE

MEMBRANE SUPPORT - ZINC COATED WIRE

CONNECTIONS - GLASS

SPECIFICATIONS

MEMBRANE DIA. - 14.4 cm.

FRAME DIA. - 19.6 cm.

DIALYZER VOL. - 330-60 CC.

JAR VOL. - 16-18 LITERS

TEMP. CONTROL - ±0.25 °C.

solutions. The indicator was a 0.1 per cent alcoholic solution of dichlorfluorescein. The 1 c.c. samples were diluted by the addition of 25 c.c. of water. Two samples of 10 c.c. each were then titrated. The 25 c.c. samples were titrated directly using 10 c.c. portions. The concentrations were calculated by

$$C_1 = N_{AgNO_3} \times CC._{AgNO_3} \times 0.15198$$

$$C_2 = N_{AgNO_3} \times CC._{AgNO_3} \times 0.005484$$

Sulfates. All sulfates were analyzed by taking to dryness in an oven. The samples were dried for 24 hours at 120° C. and drying continued until constant weight was reached.

Sugars. Sugar was analyzed by refractive indices. Their values were read with an Abbe' Refractometer. The sugar concentration was determined by reference to the Chemical Rubber Handbook of Physics and Chemistry, 21st Edition, page 1629. A constant correction value of 0.0025 was found for the refractometer.

Calcium. Calcium was determined by titration with 0.2610 Normal Na_2CO_3 solution. The pH of the 1 c.c. sample diluted to 26 c.c. was adjusted just basic to methyl orange. An excess, 10 c.c., of Na_2CO_3 was added, and the precipitate filtered off. The precipitate was thoroughly washed, and the filtrate was then titrated with nitric acid, with methyl orange as an indicator. C_1 and C_0 were found by

$$C_1 = \left[10 - (0.7605 \times C.C._{HNO_3})\right] \times 0.03762$$

TABLE I

Membrane: Cellophane
Thickness: 0.0021 cm.
Solute: Sodium Chloride
Membrane not supported

Temperature; 21°C.
Rich Volume: 322 c.c.
Lean Volume: 11,667 c.c.
Apparatus No. III

Run No. 4

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	0 c.c.
0.000	0.1506	0.001124	0.000000	0.000	0.00
0.500	0.1130	0.001755	0.000631	7.325	40.30
1.000	0.0902	0.002195	0.000440	5.080	20.80
1.500	0.0708	0.002630	0.000435	5.010	15.30
2.500	0.0483	0.003000	0.000370	4.245	20.60
4.917	0.0138	0.003370	0.000370	4.230	15.60

mean q/0 = 0.2465

q/0 gm./c.c.^{2}	C_1 cor't.	C_1/C' cor't.	q/0 C_1 cor't.	$\frac{q/0 + C'}{q/0 + C_1}$	$\left(\frac{q/0 + C'}{q/0 + C_1}\right)\left(C_1/C'\right)$
0.0000	0.1495	1.000	0.3960	1.000	1.000
0.1816	0.1112	0.750	0.3577	1.107	0.831
0.2422	0.0880	0.588	0.3345	1.183	0.696
0.3275	0.0682	0.463	0.3147	1.257	0.583
0.2060	0.0453	0.303	0.2918	1.356	0.411
0.2720	0.0104	0.070	0.2569	1.540	0.108

m = 0.1540
K = 0.613
γ = 2.458

TABLE II

Membrane: Cellophane
Thickness: 0.0021 cm.
Solute: Sodium Chloride
Membrane not supported

Temperature: 21.5° C.
Rich Volume: 334 c.c.
Lean Volume: 12,150 c.c.
Apparatus No. III

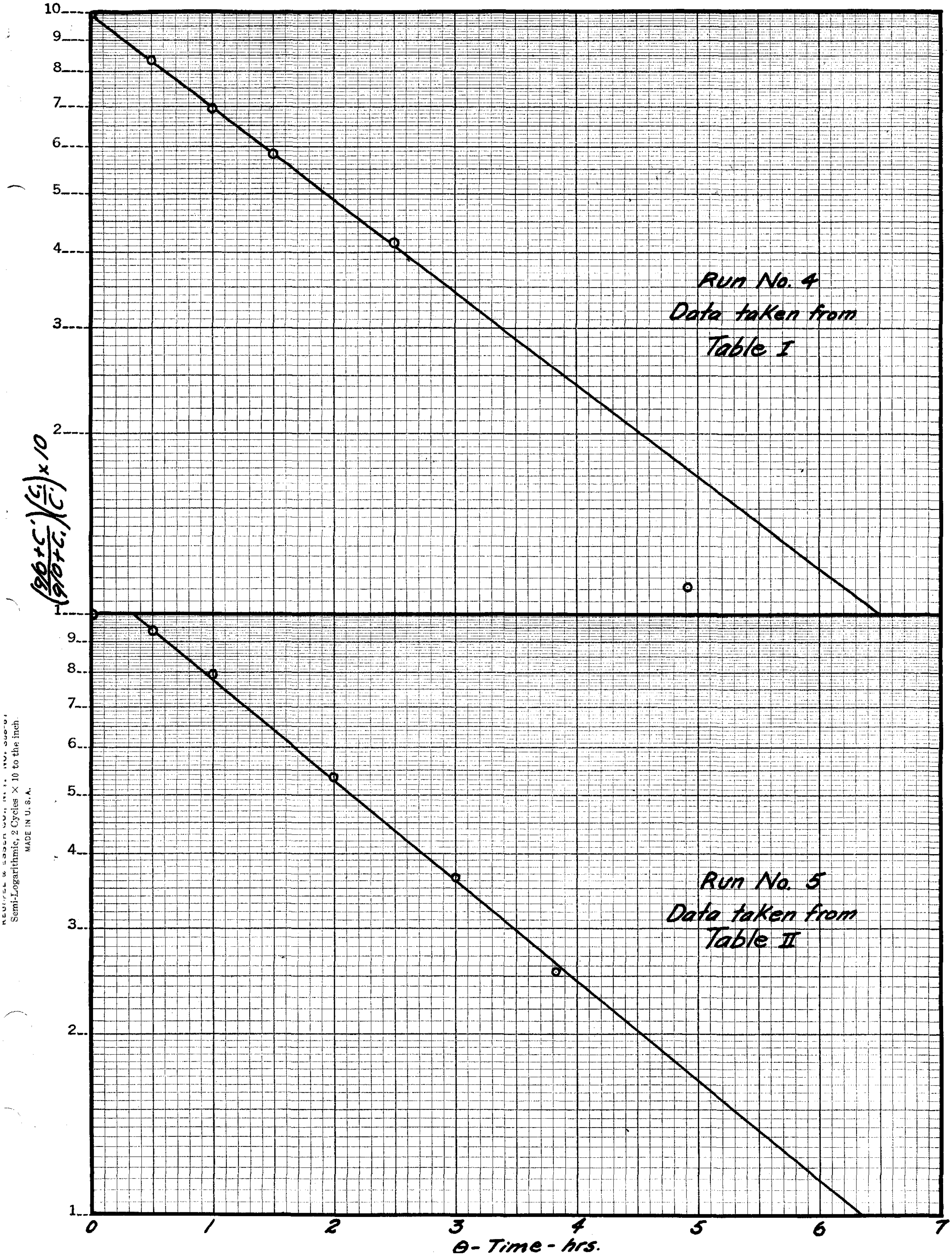
Run No. 5

Θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	0 c.c.
0.000	0.2085	0.002400	0.000000	0.00	0.00
0.500	0.1606	0.003230	0.000830	10.02	21.40
1.000	0.1268	0.003880	0.000650	7.83	19.00
2.000	0.0788	0.004630	0.000750	9.00	31.10
3.000	0.0515	0.004980	0.000350	4.18	21.50
3.833	0.0359	0.005200	0.000220	2.63	13.60

q/0 gm./c.c.	C_1 cor't.	C_1/C' Cor't.	q/0 C_1 cor't.	$\frac{q/0 + C'}{q/0 + C_1}$	$\left(\frac{q/0 + C'}{q/0 + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2061	1.000	0.5179	1.000	1.000
0.4690	0.1574	0.763	0.4692	1.235	0.943
0.4120	0.1229	0.597	0.4347	1.332	0.795
0.2890	0.0742	0.359	0.3860	1.502	0.540
0.1950	0.0465	0.225	0.3583	1.618	0.364
0.1940	0.0307	0.149	0.3425	1.690	0.252

Mean q/0 = 0.3118

m = 0.1540
K = 0.634
γ = 2.410



Run No. 4
Data taken from
Table I
Run No. 5
Data taken from
Table II
θ - Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch
MADE IN U.S.A.

TABLE III

Membrane: Cellophane, HS
Thickness: 0.00907 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 20.5° C.
Rich Volume: 363 c.c.
Lean Volume: 16,168 c.c.
Apparatus No. IX

Run No. 8

Θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2297	0.0003215	0.0000000	0.00	0.00
0.500	0.1746	0.0005845	0.0002630	4.25	12.75
1.000	0.1675	0.0008480	0.0002635	4.23	11.10
1.500	0.1650	0.0011100	0.0002620	4.20	10.50
2.000	0.1502	0.0012560	0.0001460	2.34	9.73
3.000	0.1298	0.0017230	0.0004670	7.47	16.93
4.000	0.1110	0.0020210	0.0002980	4.76	13.00
6.000	0.0838	0.0025520	0.0005310	8.46	22.40
7.000	0.0743	0.0028050	0.0002530	4.03	8.38
8.000	0.0657	0.0029520	0.0001470	2.34	8.20
9.000	0.0578	0.0030900	0.0001380	2.18	7.00

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ Corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2294	1.000	0.5912	1.000	1.000
0.3330	0.1740	0.759	0.5388	1.103	0.838
0.3810	0.1667	0.727	0.5285	1.118	0.813
0.4000	0.1639	0.714	0.5257	1.124	0.803
0.2410	0.1489	0.650	0.5107	1.143	0.743
0.4400	0.1281	0.558	0.4899	1.207	0.673
0.3660	0.1090	0.476	0.4709	1.256	0.598
0.3775	0.0812	0.354	0.4430	1.332	0.472
0.4820	0.0715	0.312	0.4333	1.364	0.426
0.2860	0.0628	0.274	0.4246	1.391	0.381
0.3120	0.0547	0.238	0.4165	1.419	0.338

Mean q/O = 0.3618

m = 0.043
K = 0.221
γ = 0.611

TABLE IV

Membrane: Cellophane, 4F
Thickness: 0.00997 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 21.3° C.
Rich Volume: 380 c.c.
Lean Volume: 15,905 c.c.
Apparatus No. IX

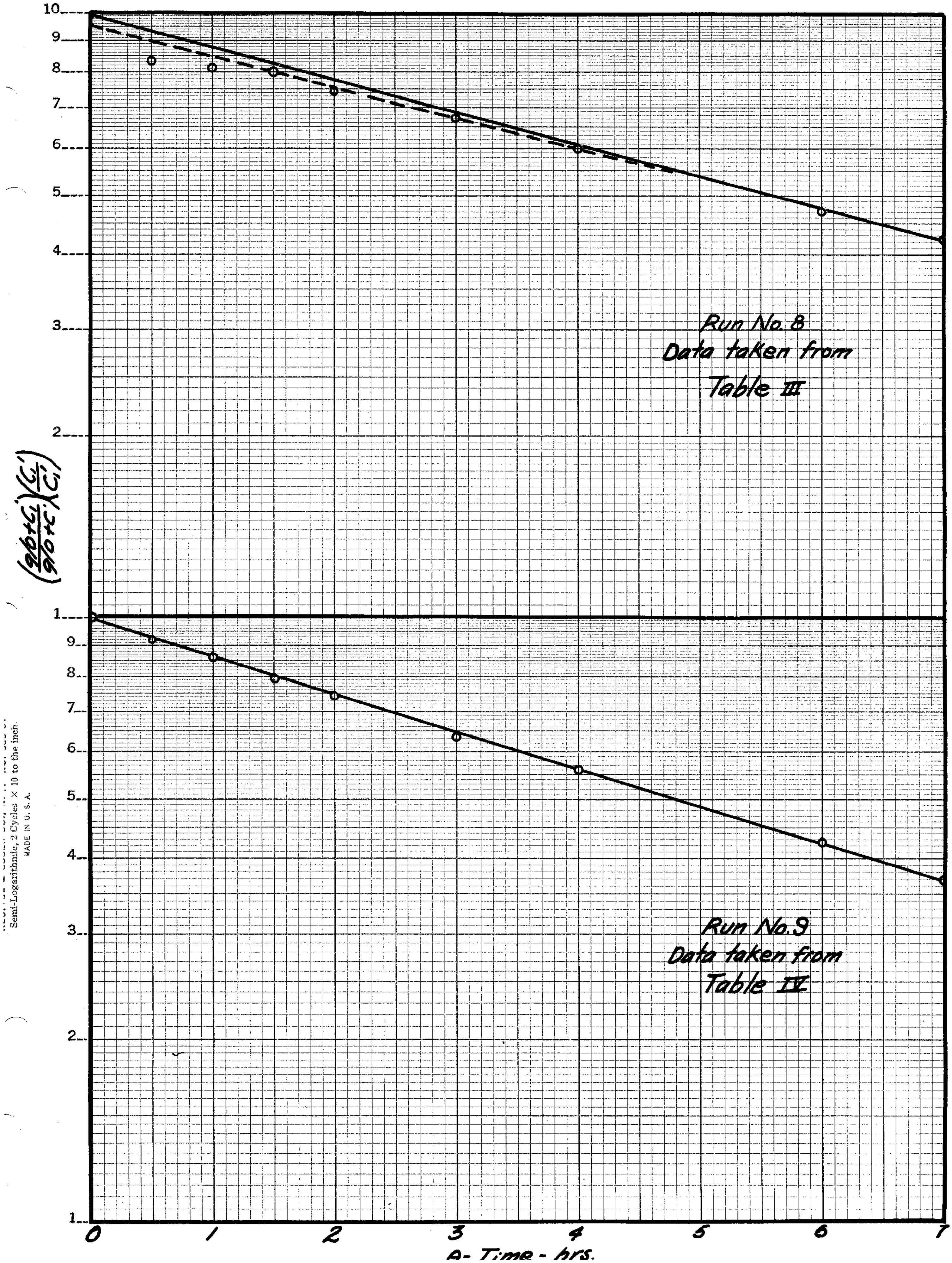
Run No. 9

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2010	0.000468	0.000000	0.00	0.00
0.500	0.1795	0.000790	0.000323	5.13	13.96
1.000	0.1620	0.001092	0.000302	4.89	12.24
1.517	0.1460	0.001360	0.000268	4.25	9.84
2.000	0.1328	0.001613	0.000253	4.00	10.85
3.000	0.1093	0.002045	0.000432	6.81	19.59
4.000	0.0944	0.002402	0.000357	5.63	13.50
6.000	0.0684	0.002935	0.000533	8.40	22.10
7.000	0.0585	0.003160	0.000225	3.55	9.90

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2005	1.000	0.5845	1.000	1.000
0.3680	0.1787	0.892	0.5627	1.038	0.926
0.3990	0.1609	0.802	0.5449	1.072	0.860
0.4320	0.1446	0.720	0.5286	1.105	0.795
0.3690	0.1312	0.654	0.5152	1.135	0.742
0.3480	0.1073	0.535	0.4913	1.190	0.638
0.4170	0.0920	0.458	0.4760	1.227	0.563
0.3800	0.0655	0.326	0.4495	1.299	0.424
0.3590	0.0553	0.276	0.4293	1.363	0.376

Mean q/O = 0.3840

m = 0.0617
K = 0.3310
γ = 0.8620



Run No. 8
Data taken from
Table III
Run No. 9
Data taken from
Table IV
A- Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U. S. A.

TABLE V

Membrane: Fiber Paper, 4F
Thickness: 0.009975 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 25° C.
Rich Volume: 384 c.c.
Lean Volume: 16,450 c.c.
Apparatus No. IX

Run No. 10

Θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.1885	0.000780	0.000000	0.00	0.00
0.500	0.1741	0.001060	0.000280	4.60	13.50
1.250	0.1482	0.001482	0.000422	6.92	17.75
1.750	0.1333	0.001742	0.000260	4.26	11.25
2.250	0.1211	0.001978	0.000236	3.86	10.50
3.250	0.1018	0.002390	0.000412	6.72	16.79
4.250	0.0848	0.002712	0.000322	5.25	13.92
5.500	0.0674	0.003080	0.000368	5.99	14.55
8.250	0.0441	0.003575	0.000495	8.05	21.92
9.250	0.0378	0.003740	0.000165	2.68	6.69

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.1875	1.000	0.5698	1.000	1.000
0.3500	0.1730	0.923	0.5553	1.026	0.947
0.3890	0.1467	0.782	0.5290	1.077	0.842
0.3790	0.1316	0.702	0.5139	1.108	0.778
0.3680	0.1191	0.636	0.5014	1.136	0.722
0.3990	0.0994	0.530	0.4817	1.182	0.627
0.3770	0.0821	0.438	0.4644	1.227	0.538
0.4120	0.0643	0.343	0.4466	1.277	0.438
0.3670	0.0405	0.216	0.4228	1.348	0.292
0.4000	0.0341	0.182	0.4164	1.368	0.249

Mean q/O = 0.3823

m = 0.0660
K = 0.3580
γ = 0.9410

TABLE VI

Membrane: Fiber Paper, 4F
Thickness: 0.009975 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 35° C.
Rich Volume: 389 c.c.
Lean Volume: 16,450 c.c.
Apparatus No. IX

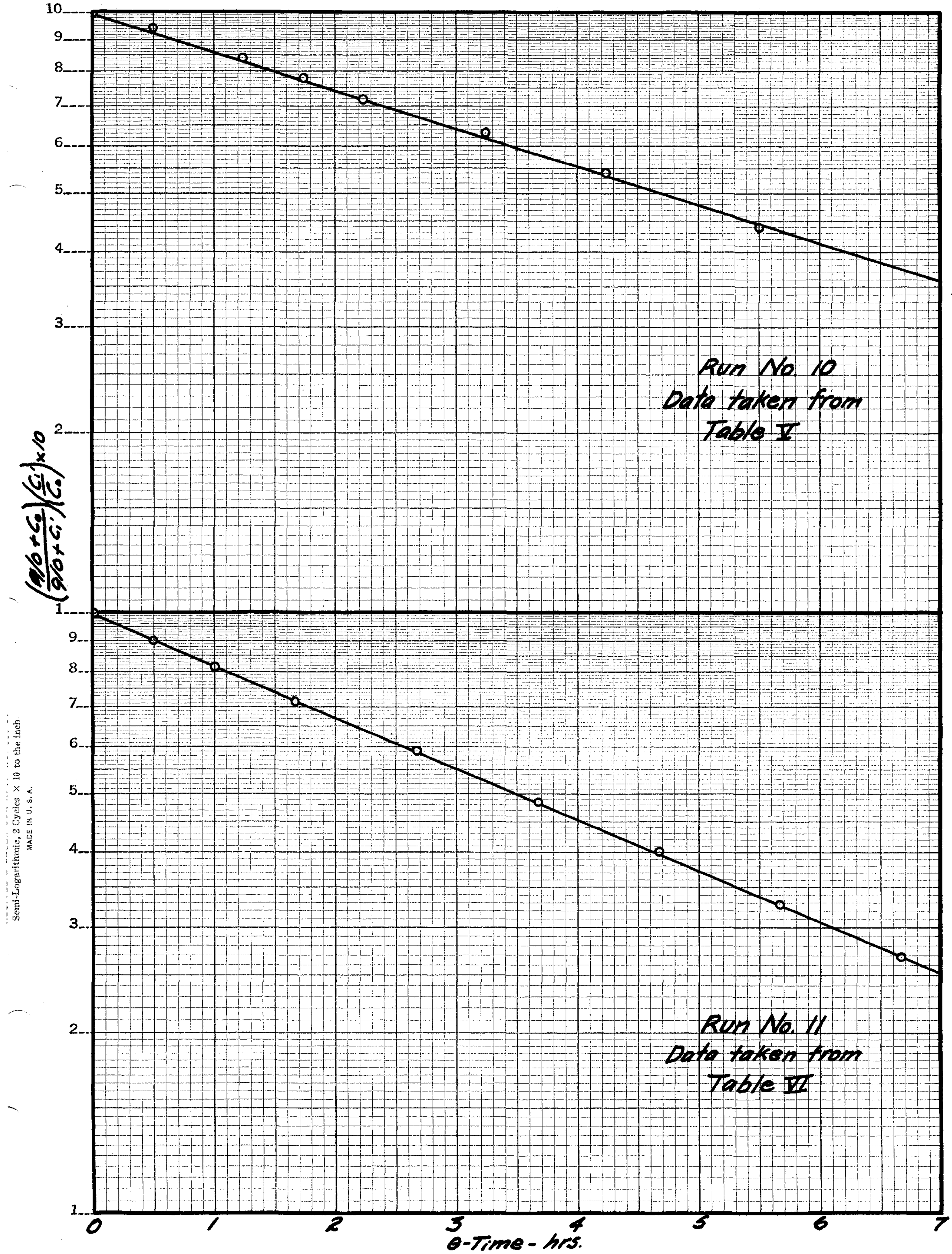
Run No. 11

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2396	0.000675	0.000000	0.00	0.00
0.500	0.2032	0.001210	0.000535	8.78	22.10
1.000	0.1766	0.001646	0.000436	7.15	19.20
1.667	0.1475	0.002172	0.000526	8.61	20.95
2.667	0.1152	0.002790	0.000678	10.10	26.08
3.667	0.0910	0.003272	0.000428	7.87	19.47
4.667	0.0735	0.003642	0.000369	6.01	17.55
5.667	0.0593	0.003924	0.000283	4.60	12.30

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2389	1.000	0.6228	1.000	1.000
0.3970	0.2020	0.845	0.5859	1.062	0.897
0.3720	0.1750	0.732	0.5589	1.115	0.814
0.4110	0.1453	0.608	0.5292	1.177	0.716
0.3870	0.1124	0.471	0.4963	1.254	0.591
0.403	0.0877	0.367	0.4716	1.320	0.485
0.343	0.0699	0.292	0.4538	1.372	0.401
0.374	0.0554	0.232	0.4393	1.419	0.329

Mean q/O = 0.3839

m = 0.0855
K = 0.4700
γ = 1.2250



Run No. 10
Data taken from
Table V
Run No. 11
Data taken from
Table VI
θ-Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U. S. A.

TABLE VII

Membrane: Fiber Paper
Thickness: 0.009975
Solute: Sodium Chloride
Membrane supported

Temperature: 44.8° C.
Rich Volume: 384 c.c.
Lean Volume: 16,450 c.c.
Apparatus No. IX

Run No. 12

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2453	0.0004675	0.000000	0.00	0.00
0.500	0.2140	0.0010520	0.000584	9.59	29.10
1.008	0.1718	0.0015680	0.000416	6.82	26.60
1.500	0.1460	0.0018710	0.000303	4.96	19.60
2.750	0.1019	0.0028280	0.000957	15.62	38.10
3.750	0.0762	0.0033080	0.000480	7.34	21.78
4.766	0.0587	0.0036620	0.000354	5.77	16.15

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2448	1.000	0.6188	1.000	1.000
0.3290	0.2129	0.870	0.5869	1.054	0.927
0.2570	0.1702	0.697	0.5442	1.137	0.793
0.2530	0.1441	0.589	0.5181	1.183	0.690
0.4100	0.0991	0.405	0.4731	1.307	0.530
0.3370	0.0729	0.298	0.4469	1.385	0.413
0.3570	0.0550	0.225	0.4290	1.442	0.325

Mean q/O = 0.3740

m = 0.1024
K = 0.5560
γ = 1.4870

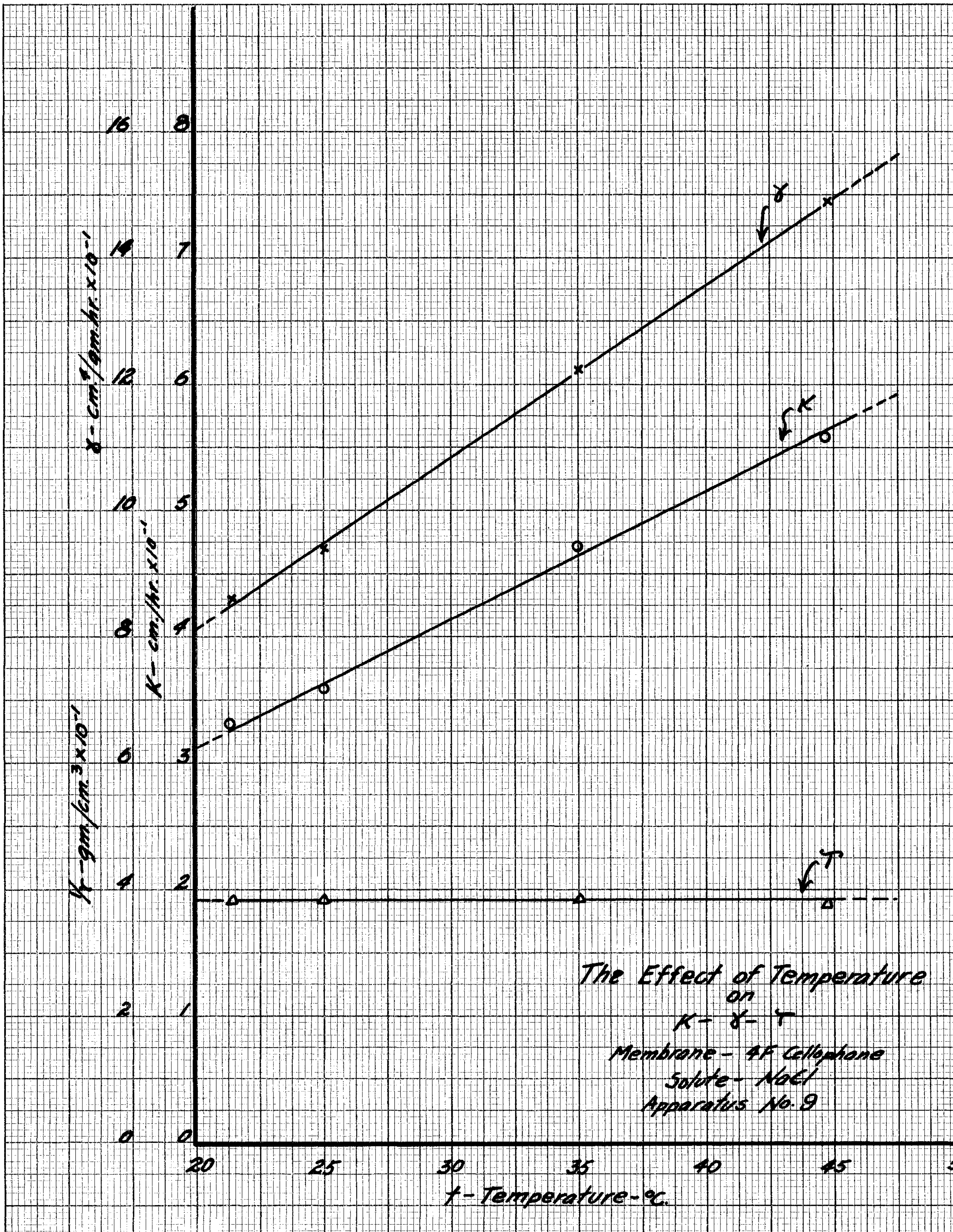

γ - cm.⁴/gm. hr. x 10⁻¹
K - cm./hr. x 10⁻¹
Υ - gm./cm.³ x 10⁻¹
16
14
12
10
8
6
4
2
0
8
7
6
5
4
3
2
1
0
20
25
30
35
40
45
5
t - Temperature - °C.
γ
K
Υ
The Effect of Temperature
on
K - γ - Υ
Membrane - 4F Cellophane
Solute - NaCl
Apparatus No. 9

TABLE VIII

Membrane: Cellophane, S.S.
Thickness: 0.00777 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 25° C.
Rich Volume: 379 c.c.
Lean Volume: 17,991 c.c.
Apparatus No. IX

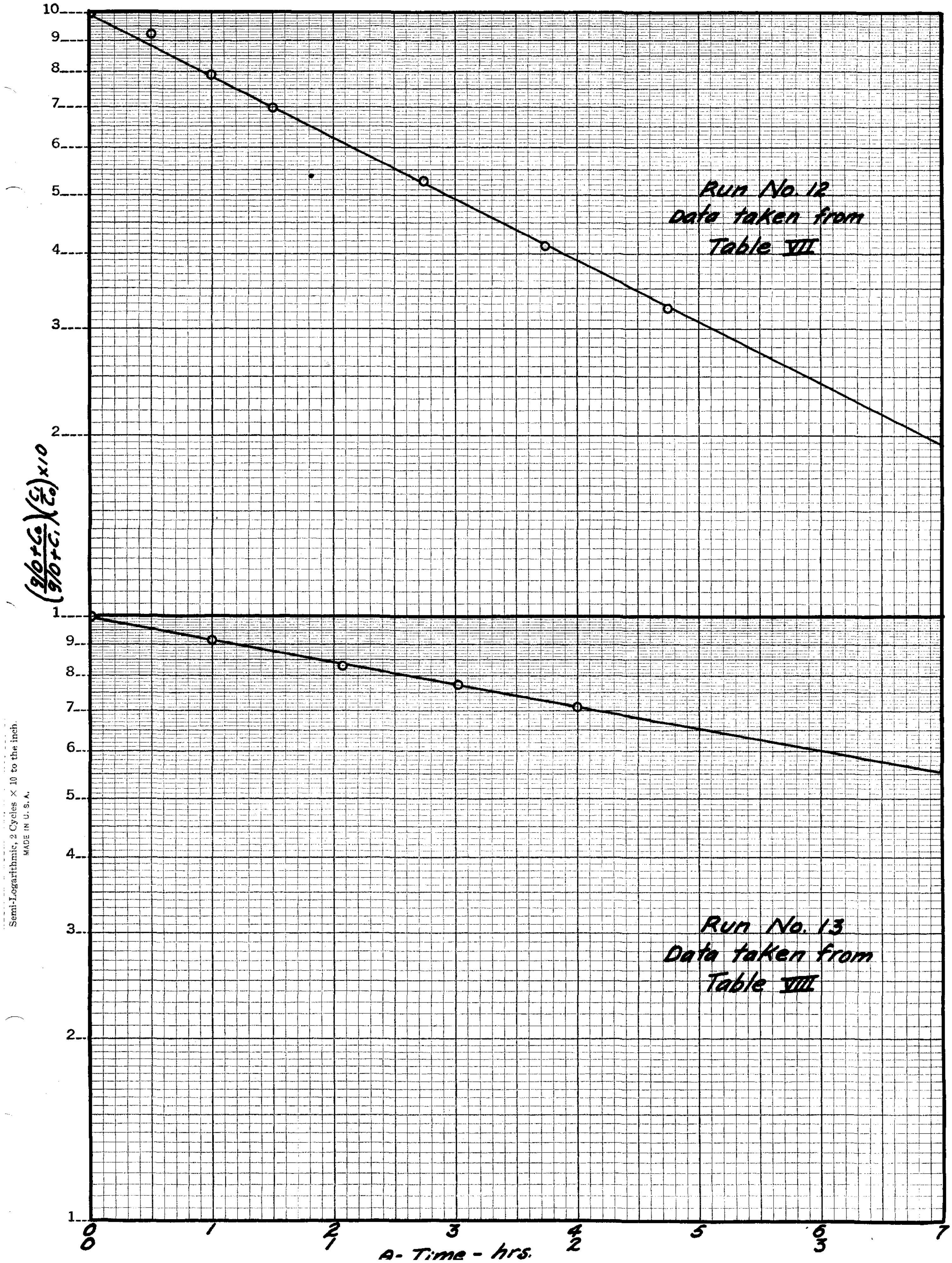
Run No. 13

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2132	0.000308	0.000000	0.00	0.00
0.500	0.1928	0.000679	0.000371	6.67	9.25
1.033	0.1706	0.000989	0.000310	5.56	7.82
1.516	0.1558	0.001340	0.000351	6.28	6.87
2.000	0.1432	0.001613	0.000273	4.88	4.50

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2129	1.000	1.0709	1.000	1.000
0.7210	0.1921	0.903	1.0501	1.020	0.920
0.7110	0.1696	0.797	1.0276	1.043	0.831
0.9150	0.1545	0.726	1.0125	1.058	0.768
1.0850	0.1416	0.664	0.9996	1.071	0.711

Mean q/O = 0.8580

m = 0.0740
K = 0.3960
γ = 0.4630



Run No. 12
Data taken from
Table VII
Run No. 13
Data taken from
Table VIII
A- Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U. S. A.

TABLE IX

Membrane: Cellophane, 2 3/4HS
Thickness: 0.00907 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 25^{0} C.
Rich Volume: 372 c.c.
Lean Volume: 18,416 c.c.
Apparatus No. IX

Run No. 14

θ hrs.	C_1 gm./c.c.	C_1 gm./c.c.	$V_1\ C_1$ gms.	O c.c.	C_{1av} gm./c.c.	OC_{1av} gms.
0.000	0.2036	0.0000	0.00	0.00	------	-----
0.500	0.1837	0.0199	7.40	11.98	0.1967	2.355
1.000	0.1670	0.0167	6.21	11.10	0.1754	1.948
1.500	0.1526	0.0144	5.35	9.90	0.1598	1.427
2.500	0.1270	0.0256	9.52	18.50	0.1398	2.585
5.117	0.0802	0.0468	17.50	32.20	0.1036	3.335

q 1.102 gms.	q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ gm./c.c.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.000	0.000	0.2032	1.000	0.6600	1.000	1.000
5.55	0.463	0.1831	0.903	0.6399	1.032	0.933
4.80	0.443	0.1661	0.819	0.6229	1.059	0.866
4.33	0.481	0.1515	0.747	0.6083	1.086	0.810
7.63	0.413	0.1255	0.618	0.5823	1.133	0.700
15.60	0.484	0.0783	0.385	0.5351	1.233	0.475

Mean q/O = 0.4568

m = 0.0615
K = 0.3230
γ = 0.7070

TABLE X

Membrane: Cellophane
Thickness: 0.0021 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 25° C.
Rich Volume: 341 c.c.
Lean Volume: 18,040 c.c.
Apparatus No. IX

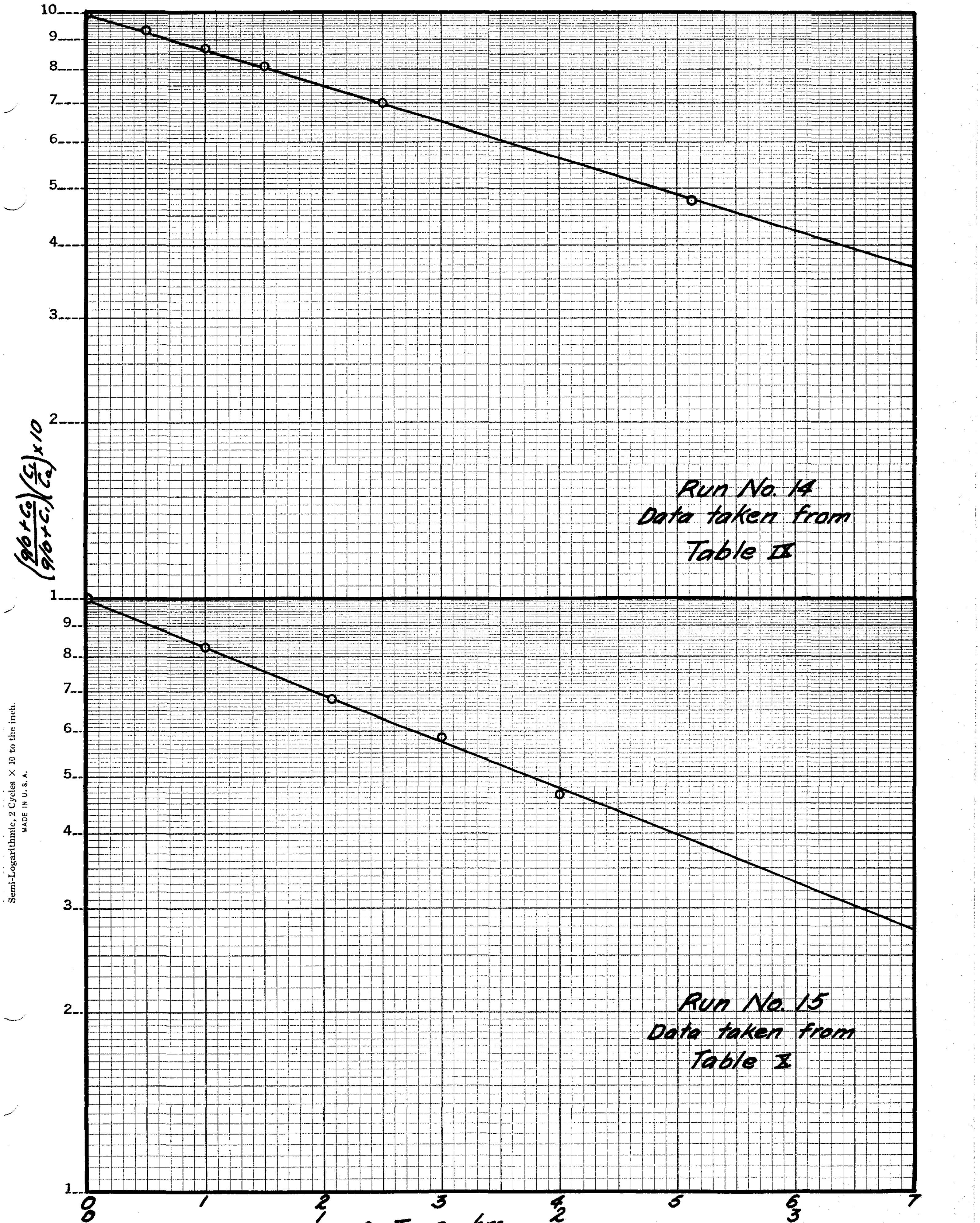
Run No. 15

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2007	0.000395	0.000000	0.00	0.00
0.500	0.1548	0.001090	0.000696	12.51	30.40
1.033	0.1197	0.001638	0.000548	9.85	24.80
1.500	0.0994	0.002050	0.000412	7.39	16.60
2.000	0.0769	0.002360	0.000310	5.56	14.60

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\left(\frac{q/O + C'}{q/O + C_1}\right)$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2003	1.000	0.6096	1.000	1.000
0.4120	0.1537	0.766	0.5630	1.082	0.830
0.3980	0.1181	0.590	0.5274	1.156	0.682
0.4450	0.0973	0.485	0.5066	1.203	0.583
0.3820	0.0745	0.372	0.4838	1.259	0.468

Mean q/O = 0.4093

m = 0.1862
K = 0.8970
γ = 2.1950



Run No. 14
Data taken from
Table IX
Run No. 15
Data taken from
Table X
θ - Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U. S. A.

TABLE XI

Membrane: Parchment
Thickness: 0.0065 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 25° C.
Rich Volume: 315 c.c.
Lean Volume: 18,162 c.c.
Apparatus No. IX

Run No. 16

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2312	0.000298	0.000000	0.00	0.00
0.500	0.1943	0.000746	0.000448	8.13	26.28
1.508	0.1393	0.001468	0.000722	13.05	42.20
2.000	0.1197	0.001748	0.000280	5.05	16.30
3.033	0.0930	0.002217	0.000469	8.47	27.00
3.500	0.0796	0.002385	0.000168	3.03	10.36

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't	$q/O + C_1$ corr't	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2309	1.0000	0.5384	1.000	1.000
0.3092	0.1936	0.8380	0.5015	1.075	0.902
0.3098	0.1379	0.5970	0.4465	1.207	0.720
0.3098	0.1180	0.5120	0.4269	1.262	0.646
0.3140	0.0908	0.3935	0.4002	1.347	0.530
0.2930	0.0772	0.3341	0.3868	1.393	0.466

Mean q/O = 0.3072

$m = 0.0935$
$K = 0.4160$
$\gamma = 1.3560$

TABLE XII

Membrane: Parchment
Thickness: 0.0065 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 30° C.
Rich Volume: 340 c.c.
Lean Volume: 17,865 c.c.
Apparatus No. IX

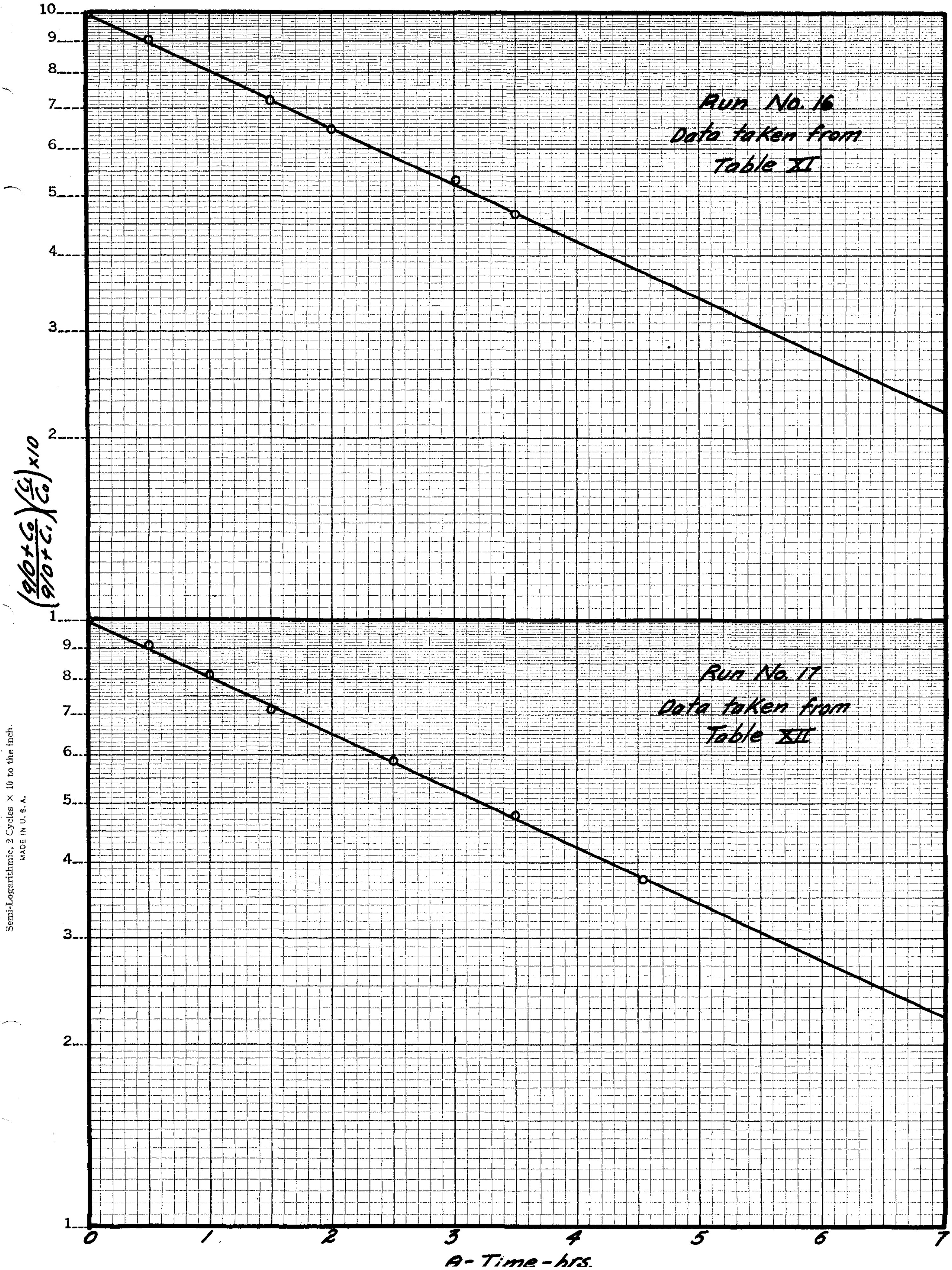
Run No. 17

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.2280	0.000362	0.000000	0.00	0.00
0.500	0.1930	0.000860	0.000498	8.90	30.30
1.000	0.1628	0.001290	0.000430	7.67	25.40
1.500	0.1390	0.001670	0.000380	6.77	22.00
2.500	0.1028	0.002240	0.000570	10.12	34.60
3.500	0.0800	0.002680	0.000440	7.82	25.30
4.550	0.0610	0.003010	0.000330	5.85	19.50

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.000	0.2276	1.000	0.5284	1.000	1.000
0.294	0.1921	0.846	0.4929	1.071	0.907
0.302	0.1613	0.710	0.4621	1.144	0.813
0.307	0.1323	0.583	0.4331	1.221	0.712
0.293	0.1006	0.443	0.4014	1.317	0.584
0.309	0.0773	0.340	0.3781	1.398	0.475
0.300	0.0580	0.255	0.3588	1.473	0.376

Mean q/O = 0.3008

m = .0952
K = 0.452
γ = 1.467



Run No. 16
Data taken from
Table XI
Run No. 17
Data taken from
Table XII
$\left(\frac{9/0+C_0}{9/0+C_1}\right)\left(\frac{C_1}{C_0}\right)\times 10$
A- Time-hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U.S.A.

TABLE XIII

Membrane: Patapar Parchment
Thickness: 0.0065 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 35° C.
Rich Volume: 340 c.c.
Lean Volume: 18,100 c.c.
Apparatus No. IX

Run No. 18

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q' gms.	O c.c.
0.000	0.2290	0.000354	0.000000	0.00	0.00
0.500	0.1875	0.000912	0.000558	10.10	32.30
1.017	0.1537	0.001380	0.000468	8.47	28.50
1.532	0.1268	0.001800	0.000420	7.58	23.60
2.824	0.0810	0.002565	0.000765	13.77	43.50

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.2284	1.000	0.5429	1.000	1.000
0.3130	0.1866	0.816	0.5011	1.082	0.884
0.2975	0.1523	0.667	0.4668	1.163	0.775
0.3210	0.1250	0.547	0.4395	1.236	0.675
0.3165	0.0784	0.343	0.3929	1.382	0.473

Mean q/O = 0.3145

m = 0.1140
K = 0.5470
γ = 1.7400

TABLE XIV

Membrane: Patapar Parchment	Temperature: 40° C.
Thickness: 0.0065 cm.	Rich Volume: 322 c.c.
Solute: Sodium Chloride	Lean Volume: 18,285 c.c.
Membrane supported	Apparatus No. IX

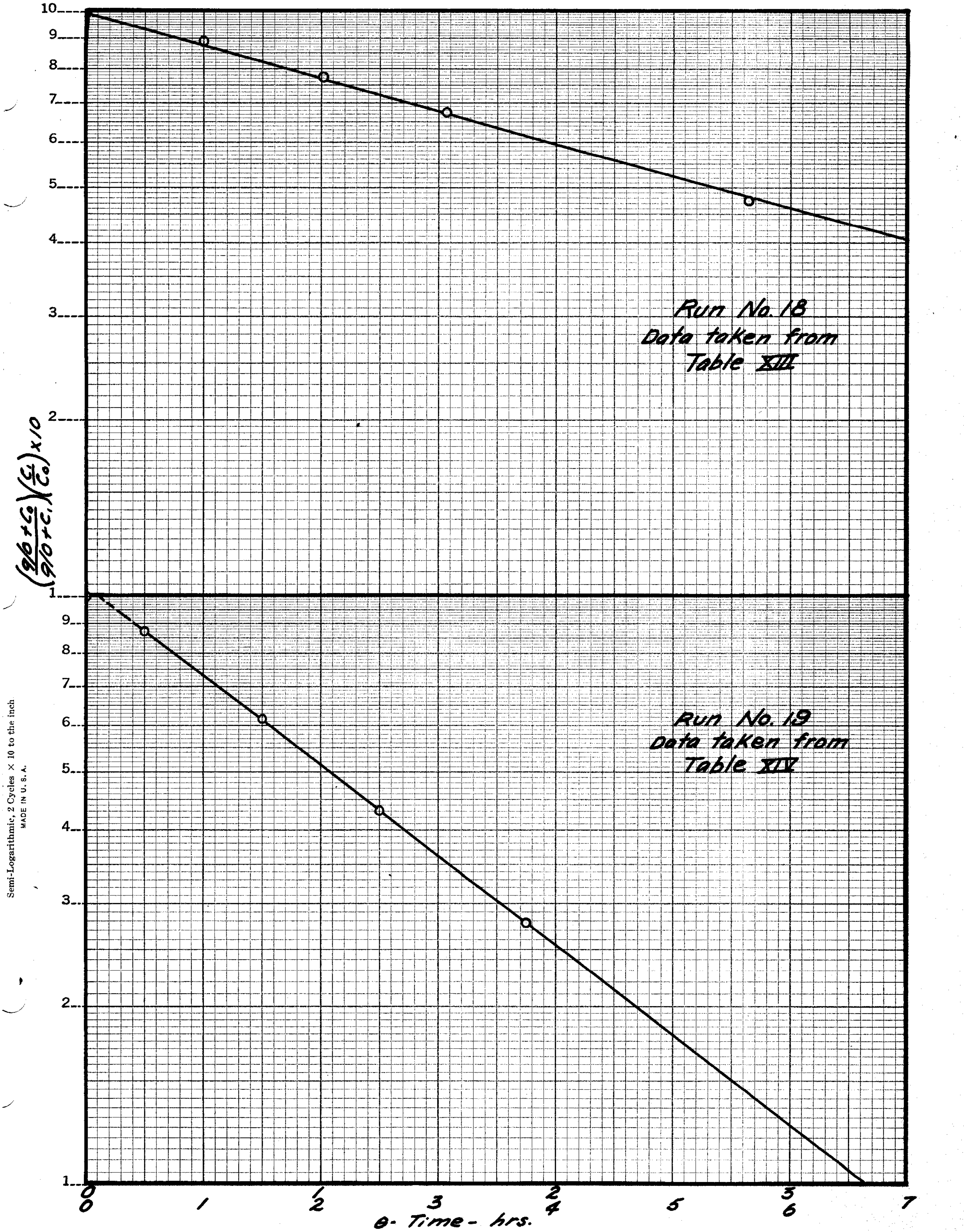
Run No. 19

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.1950	0.000400	0.000000	0.00	0.00
0.500	0.1542	0.000904	0.000504	9.20	30.80
1.500	0.0958	0.001653	0.000749	13.64	43.00
2.500	0.0634	0.002145	0.000492	8.95	28.60
3.750	0.0396	0.002520	0.000375	6.81	23.80

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.1946	1.000	0.4994	1.000	1.000
0.2990	0.1533	0.789	0.4581	1.090	0.872
0.3170	0.0941	0.489	0.3989	1.251	0.613
0.3130	0.0613	0.316	0.3661	1.363	0.430
0.2900	0.0371	0.191	0.3419	1.460	0.278

Mean q/O = 0.3048

m = 0.1428
K = 0.6500
γ = 2.1300



10
9
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7
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3
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1
9
8
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6
5
4
3
2
1
$\left(\frac{9/6+C_0}{9/0+C_1}\right)\left(\frac{C_1}{C_0}\right)\times 10$
Run No. 18
Data taken from
Table XIII
Run No. 19
Data taken from
Table XIV
0 1 2 3 4 5 6 7
0 1 2 3
θ- Time- hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch
MADE IN U. S. A.

TABLE XV

Membrane: Patapar Parchment
Thickness: 0.0065 cm.
Solute: Sodium Chloride
Membrane supported

Temperature: 45° C.
Rich Volume: 315 c.c.
Lean Volume: 18,315 c.c.
Apparatus No. IX

Run No. 20

θ hrs.	C_1 gm./c.c.	C_2 gm./c.c.	C_2 gm./c.c.	q gms.	O c.c.
0.000	0.1918	0.000400	0.000000	0.00	0.00
0.550	0.1437	0.000983	0.000583	10.68	34.50
1.517	0.0885	0.001710	0.000727	13.26	41.70
2.649	0.0524	0.002250	0.000540	9.85	31.20
3.517	0.0364	0.002510	0.000260	4.74	15.00

q/O gm./c.c.	C_1 corr't.	C_1/C' corr't.	$q/O + C_1$ corr't.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.0000	0.1914	1.000	0.5064	1.000	1.000
0.3100	0.1428	0.746	0.4578	1.104	0.850
0.3180	0.0868	0.453	0.4018	1.260	0.571
0.3160	0.0501	0.262	0.3651	1.387	0.362
0.3160	0.0339	0.177	0.3489	1.450	0.257

Mean q/O = 0.3150

m = 0.1670
K = 0.7500
γ = 2.3800

TABLE XVI

Membrane: Patapar Parchment
Thickness: 0.0065 cm.
Solute: Sodium Sulfate
Membrane supported

Temperature: 30°C.
Rich Volume: 333 c.c.
Lean Volume: 18,188 c.c.
Apparatus No. IX

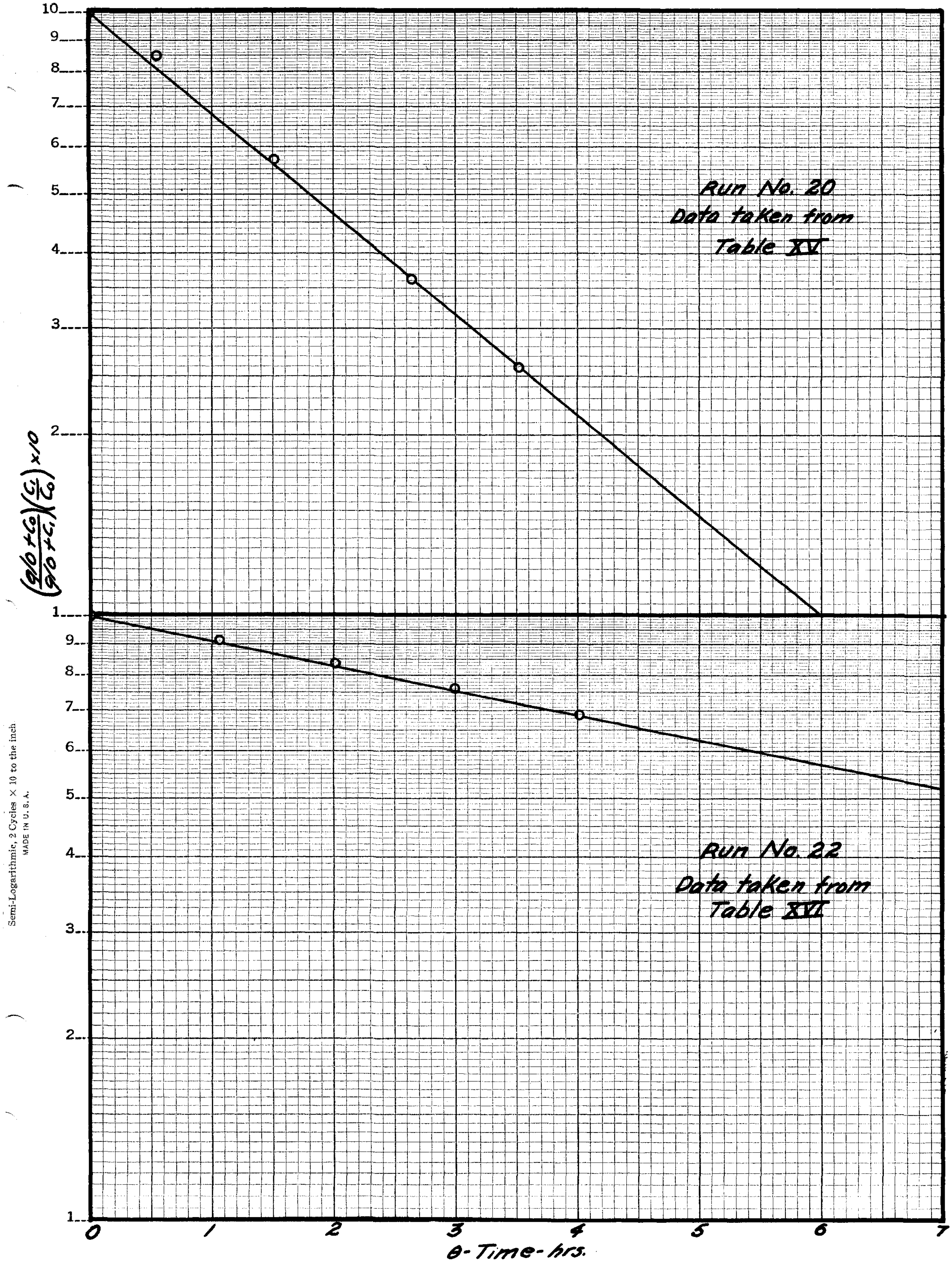
Run No. 22

Θ hrs.	C_1 gm./c.c.	C_1 gm./c.c.	V_1 C_1 gms.	O c.c.	C_o gm./c.c.	OC_o gms.
0.000	0.1534	0.0000	0.00	0.00	------	----
1.067	0.1254	0.0280	9.32	38.60	0.1477	5.70
2.017	0.1055	0.0199	6.63	29.40	0.1232	3.62
3.000	0.0888	0.0167	5.57	26.10	0.1029	2.68
4.016	0.0745	0.0143	4.76	23.10	0.0876	2.02

Θ hrs.	q gms.	q/O gm./c.c.	C_1/C'	$q/O + C_1$ gm./c.c.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.000	0.00	0.0000	1.000	0.2598	1.000	1.000
1.067	3.62	0.0938	0.818	0.2318	1.120	0.915
2.017	3.01	0.1024	0.688	0.2119	1.227	0.844
3.000	2.68	0.1108	0.579	0.1952	1.330	0.770
4.016	2.74	0.1187	0.486	0.1809	1.439	0.700

Mean q/O = 0.1064

m = 0.0387
K = 0.1830
γ = 1.7170



Run No. 20
Data taken from
Table XV
Run No. 22
Data taken from
Table XVI
θ- Time- hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch
MADE IN U. S. A.

TABLE XVII

Membrane: Cellophane
Thickness: 0.0065 cm.
Solute: Sodium Sulfate
Membrane supported

Temperature: 30^{o} C.
Rich Volume: 329 c.c.
Lean Volume: 18,270 c.c.
Apparatus No. IX

Run No. 23

θ hrs.	C_1 gm./c.c.	C_1 gm./c.c.	V_1 C_1 gms.	O c.c.	C_o gm./c.c.	OC_o gms.
0.000	0.1372	0.0000	0.00	0.00	------	----
1.000	0.1017	0.0355	11.67	42.10	0.1246	5.24
2.333	0.0700	0.0317	10.42	42.50	0.0896	3.81
4.000	0.0455	0.0245	8.05	37.90	0.0603	2.29
4.917	0.0362	0.0093	3.06	15.70	0.0441	0.69

θ hrs.	q gms.	q/O gm./c.c.	C_1/C'	$q/O + C_1$ gm./c.c.	$\left(\frac{q/O + C'}{q/O + C_1}\right)$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
0.000	0.00	0.0000	1.000	0.2900	1.000	1.000
1.000	6.43	0.1528	0.741	0.2545	1.138	0.842
2.333	6.61	0.1555	0.510	0.2228	1.272	0.650
4.000	5.76	0.1520	0.332	0.1983	1.462	0.486
4.917	2.37	0.1510	0.254	0.1890	1.534	0.390

Mean q/O = 0.1528

m = 0.0803
K = 0.3730
γ = 2.4400

TABLE XVIII

Membrane: Parchment
Thickness: 0.0065 cm.
Solute: Sucrose
Membrane supported

Temperature: 30° C.
Rich Volume: 338 c.c.
Lean Volume: 18,210 c.c.
Apparatus No. IX

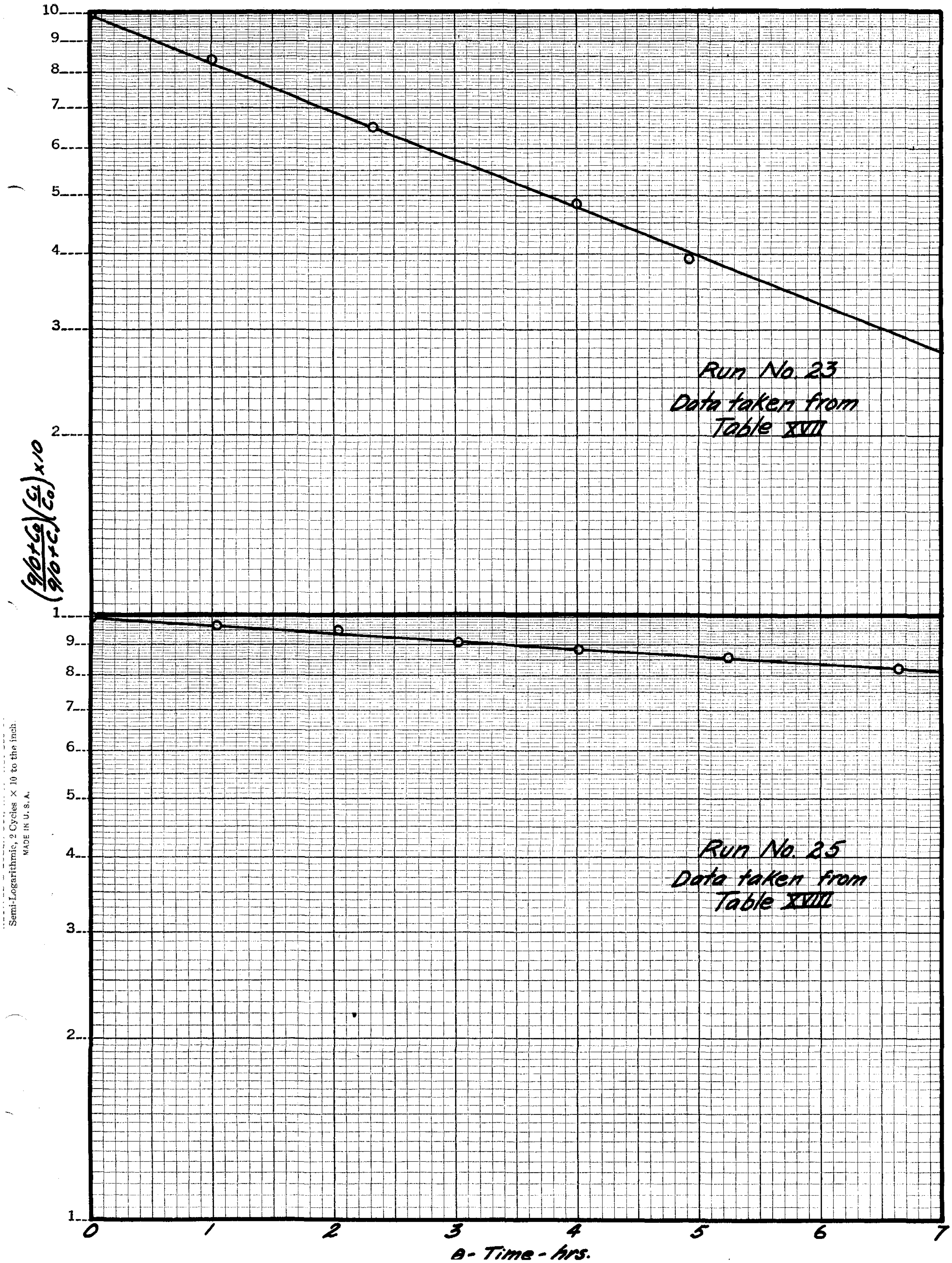
Run No. 25

Θ hrs.	C_1 gm./c.c.	C_1 gm./c.c.	$V_1 \ C_1$ gms.	C_o gm./c.c.	O c.c.
0.000	0.3996	0.0000	0.00	------	0.00
1.042	0.3480	0.0516	17.29	0.3755	34.40
2.042	0.3208	0.0272	9.10	0.3345	29.90
3.033	0.2800	0.0408	13.70	0.3024	26.40
4.016	0.2505	0.0295	9.86	0.2716	24.00
5.260	0.2258	0.0247	8.26	0.2435	27.00
6.677	0.1973	0.0285	9.55	0.2147	26.70

OC_o gms.	q gms.	C_1/C'	$q/O + C_1$ gm./c.c.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
-----	0.00	1.000	0.5090	1.000	1.000
12.90	4.39	0.871	0.4574	1.111	0.968
10.00	0.90	0.804	0.4302	1.182	0.950
7.98	5.72	0.701	0.3894	1.306	0.916
6.49	3.37	0.627	0.3599	1.412	0.883
6.57	1.69	0.565	0.3352	1.518	0.857
5.73	3.25	0.494	0.3067	1.658	0.819

Mean q/O = 0.1094

m = 0.01307
K = 0.0618
γ = 0.5640



Run No. 23
Data taken from
Table XVII
Run No. 25
Data taken from
Table XVIII
θ - Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U. S. A.

TABLE XIX

Membrane: Cellophane
Thickness: 0.0021 cm.
Solute: Sucrose
Membrane supported

Temperature: 30° C.
Rich Volume: 333 c.c.
Lean Volume: 18,000 c.c.
Apparatus No. IX

Run No. 26

Θ hrs.	C_1 gm./c.c.	C_1 gm./c.c.	V_1 C_1 gms.	C_{1av} gm./c.c.	O c.c.
0.000	0.3753	0.0000	0.00	------	0.00
1.000	0.3139	0.0614	20.42	0.3446	41.30
2.000	0.2599	0.0540	17.97	0.2869	37.70
3.000	0.2181	0.0418	13.92	0.2390	30.40
4.000	0.1840	0.0341	11.34	0.2011	27.10
5.000	0.1571	0.0269	8.95	0.1706	22.70
6.000	0.1390	0.0181	6.03	0.1481	18.00

$C_{1av}\Theta$ gms.	q gms.	C_1/C'	$q/O + C_1$ gm./c.c.	$\frac{q/O + C'}{q/O + C_1}$	$\left(\frac{q/O + C'}{q/O + C_1}\right)\left(\frac{C_1}{C'}\right)$
-----	0.00	1.000	0.5746	1.000	1.000
14.24	6.18	0.838	0.5132	1.112	0.933
10.82	7.15	0.694	0.4592	1.252	0.868
7.62	6.66	0.583	0.4174	1.377	0.803
55.45	5.89	0.491	0.3833	1.502	0.737
3.87	5.08	0.418	0.3564	1.612	0.674
2.67	4.36	0.371	0.3383	1.700	0.630

Mean $q/O = 0.1993$

$m = 0.0234$
$K = 0.1101$
$\gamma = 0.5530$

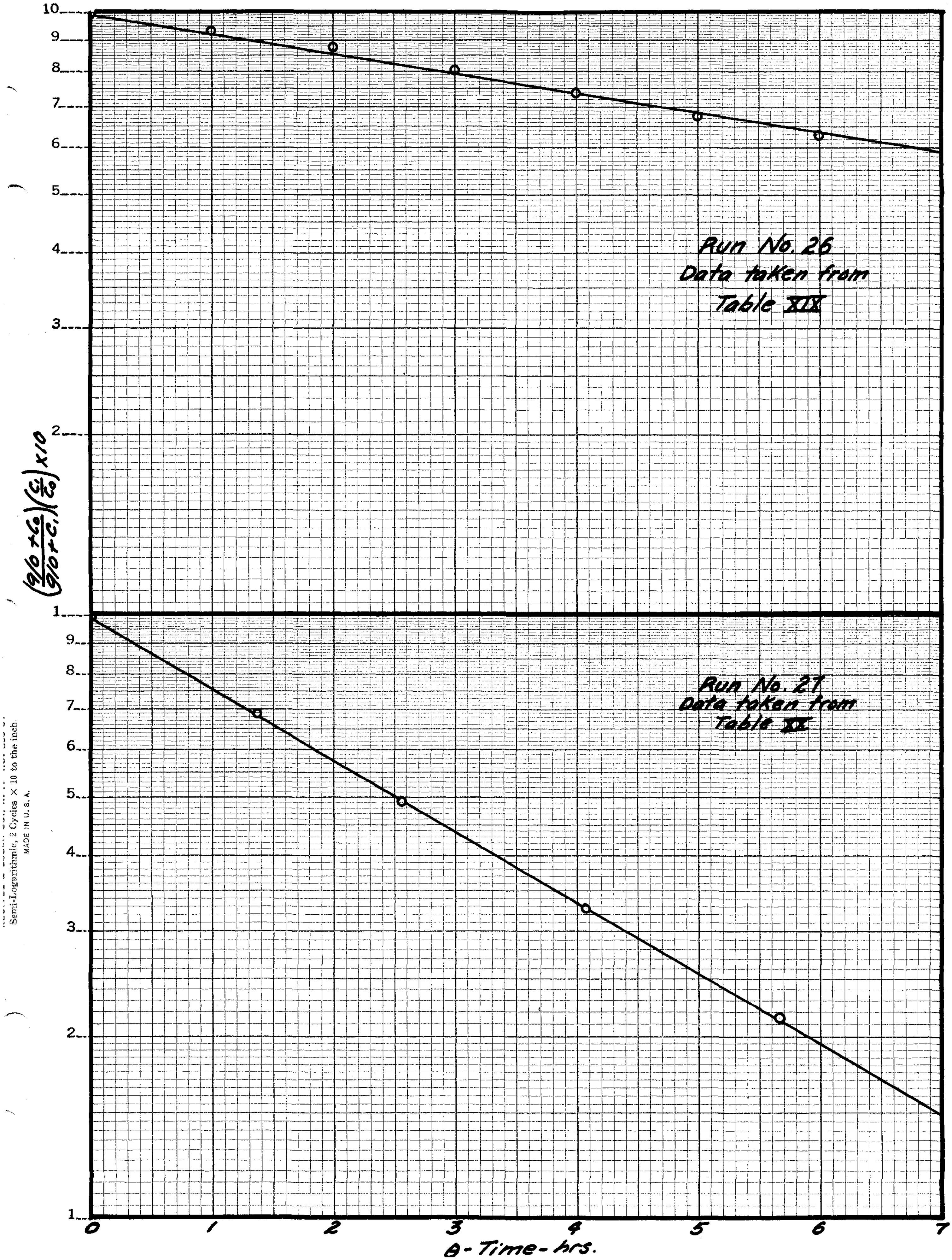

Run No. 26
Data taken from
Table XIX
Run No. 27
Data taken from
Table XX
$\left(\frac{9/10+C_0}{9/10+C_1}\right)\left(\frac{C_1}{C_0}\right) \times 10$
θ - Time - hrs.
Semi-Logarithmic, 2 Cycles × 10 to the inch.
MADE IN U.S.A.

TABLE XX

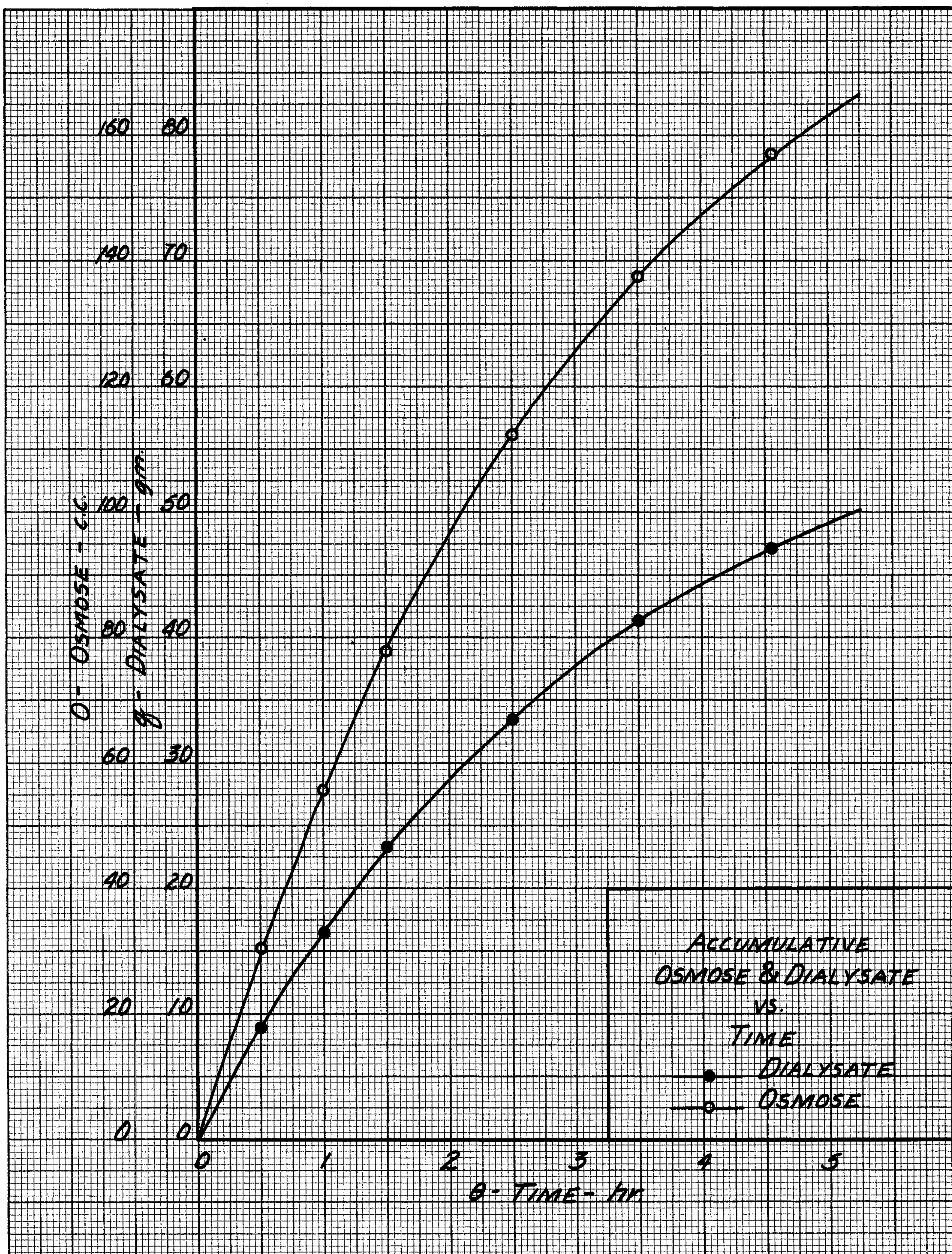
Data Showing Variation of
Dialysate and Osmose with Time

Run No.	Θ hrs.	q gms.	q gms.	O c.c.	O c.c.
17	0.00	0.00	0.00	0.00	0.00
	0.50	8.90	8.90	30.30	30.30
	1.00	7.67	16.57	25.40	55.70
	1.50	6.77	23.34	22.00	77.70
	2.50	10.12	33.46	34.60	112.30
	3.50	7.82	41.28	25.30	137.60
	4.55	5.85	47.13	19.50	157.10

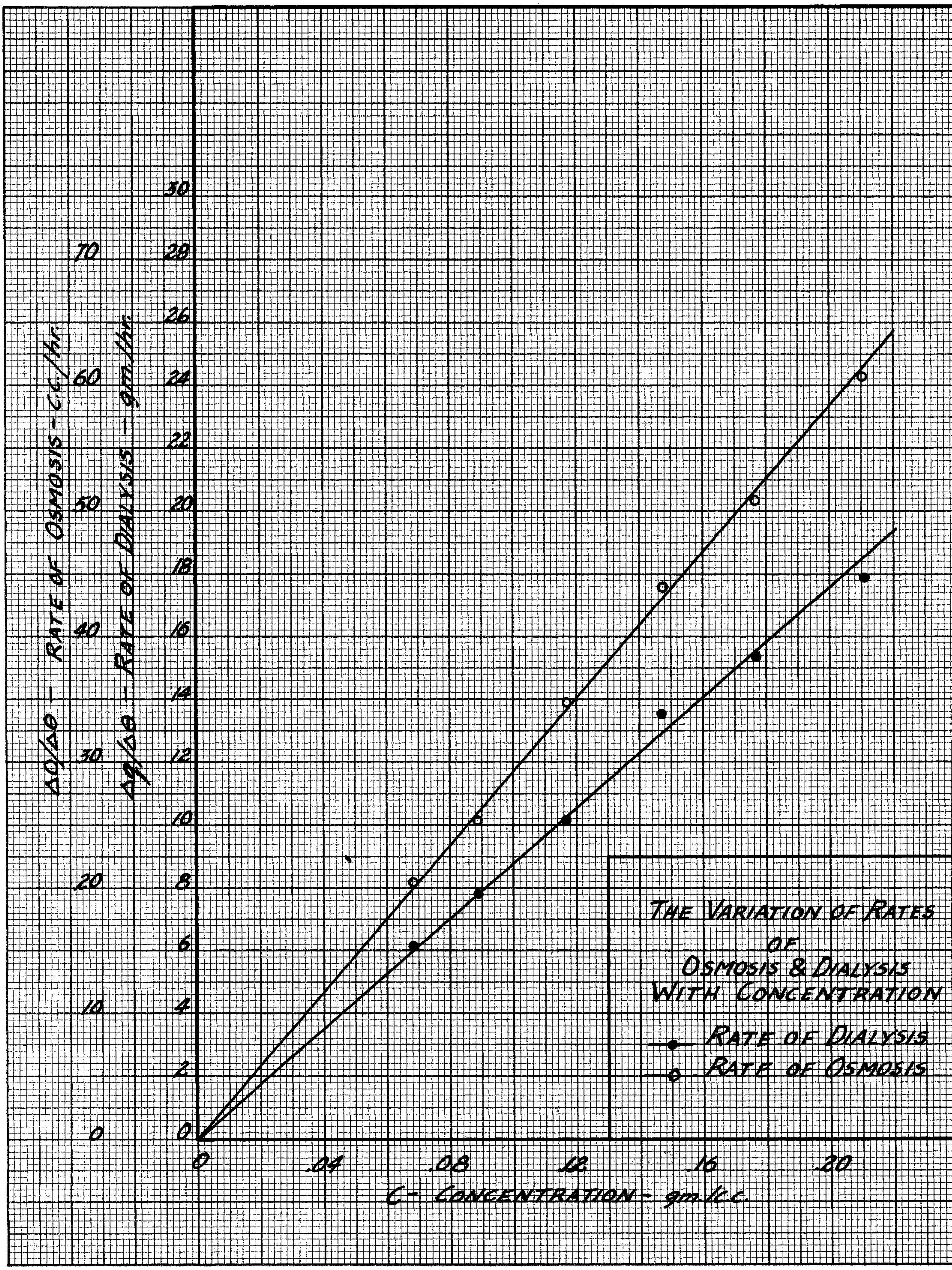
TABLE XXI

Data Showing Variation of
Rate of Dialysis and Osmosis
with Concentration

Run No.	q/Θ gm./hr.	O/Θ c.c./hr.	C_1 gm./c.c.	C_{1av} gm./c.c.	q/O gm./c.c.
17	0.00	0.00	0.2276	------	-----
	17.80	60.60	0.1921	0.2099	0.294
	15.34	50.80	0.1613	0.1767	0.297
	13.54	44.00	0.1323	0.1468	0.300
	10.12	34.60	0.1006	0.1165	0.299
	7.82	25.30	0.0773	0.0890	0.309
	6.14	20.50	0.0580	0.0678	0.300



160
140
120
100
80
60
40
20
0
80
70
60
50
40
30
20
10
0
O - OSMOSE - c.c.
● - DIALYSATE - gm.
0
1
2
3
4
5
θ - TIME - hr.
ACCUMULATIVE
OSMOSE & DIALYSATE
VS.
TIME
DIALYSATE
OSMOSE



Δθ/Δθ - Rate of Osmosis - cc./hr.
Δg/Δθ - Rate of Dialysis - gm./hr.
C - Concentration - gm./cc.
The Variation of Rates of Osmosis & Dialysis with Concentration
Rate of Dialysis
Rate of Osmosis

CALCULATION OF CAPACITY OF A WASTE Na_2SO_4 DIALYZER

Essential Information:

Inlet concentration: 15 lb./ft^3
Rate of flow: 25 ft^3/hr.
Na_2SO_4 to be recovered: 90%

Opereation temperature: 86° F.
Recovery medium: water
Recovery liquor flow rate: 100 ft^3/hr.

It is desired to compute the length of path of a plate and frame type dialyzer to accomplish the above recovery, employing parchment paper as a membrane.

Fundamental Relations:

(1) $$\frac{dq}{2h\,dl} = K\theta(C_1 - C_2)$$

(3) $$C_2 = \frac{Q - q + C_2' L\theta}{L\theta - \Upsilon(Q-q)}$$

(2) $$C_1 = \frac{C_1' R\theta - q}{R\theta + \Upsilon q}$$

(4) $$\Delta = \frac{C_1' R\theta - q}{R\theta + \Upsilon q} - \frac{Q - q + C_2' L\theta}{L\theta - \Upsilon(Q-q)}$$

$$K = 0.006$$
$$\gamma = 0.00083$$
$$\Upsilon = 0.183$$

(1) 0 varies between 0 and 47 ft^3.
(2) q varies between 0 and 338 lbs.
(3) Allot values of q as 50, 100, 150, 200, 250, 300 for graphical integration.

TABLE XXII

Data for Plot of C_1 and C_2 Vs q
Counter-Current Flow

q lb. solute	$C_1R\Theta$ lb.	$C_1R\Theta - q$ lb.	$R\Theta$ ft^3	$R\Theta + \tau q$ ft^3	C_1 $lb./ft^3$
00	375	375	25	25.0	15.0
50		325		31.9	10.2
100		275		38.8	7.1
150		225		45.7	4.9
200		175		52.6	3.3
250		125		59.5	2.1
300		75		66.3	1.1
338		37		71.6	0.5

q lb. solute	Q - q lb.	$\tau(Q-q)$ ft^3	$L\Theta - (Q-q)$ ft^3	C_2 $lb./ft^3$	$C_1 - C_2$ $lb./ft^3$
0	338	46.6	53.4	6.3	8.7
50	288	39.7	60.3	4.8	5.4
100	238	32.8	67.2	3.5	3.6
150	188	25.9	74.1	2.5	2.4
200	138	19.0	81.0	1.7	1.6
250	88	12.1	87.9	1.0	1.1
300	38	5.2	94.8	0.4	0.7
338	0	0.0	100.0	0.0	0.5

TABLE XXIII

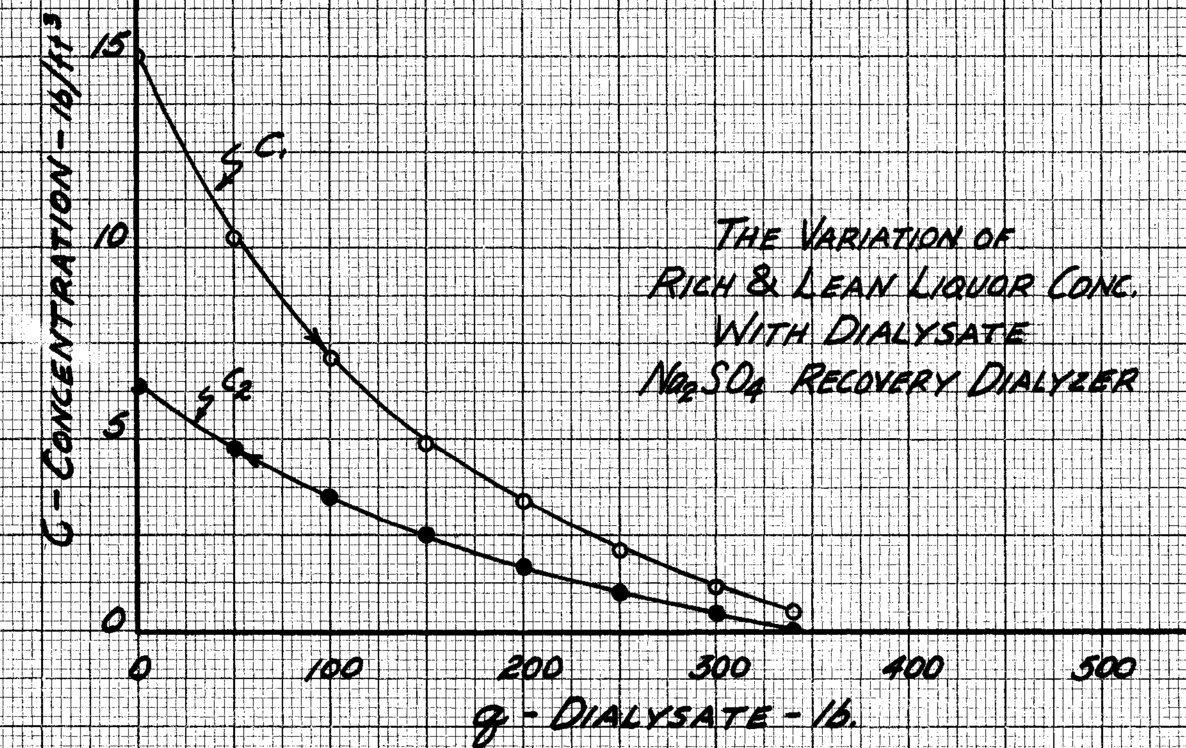
Data for Graphical Integration
from Vs q Plot

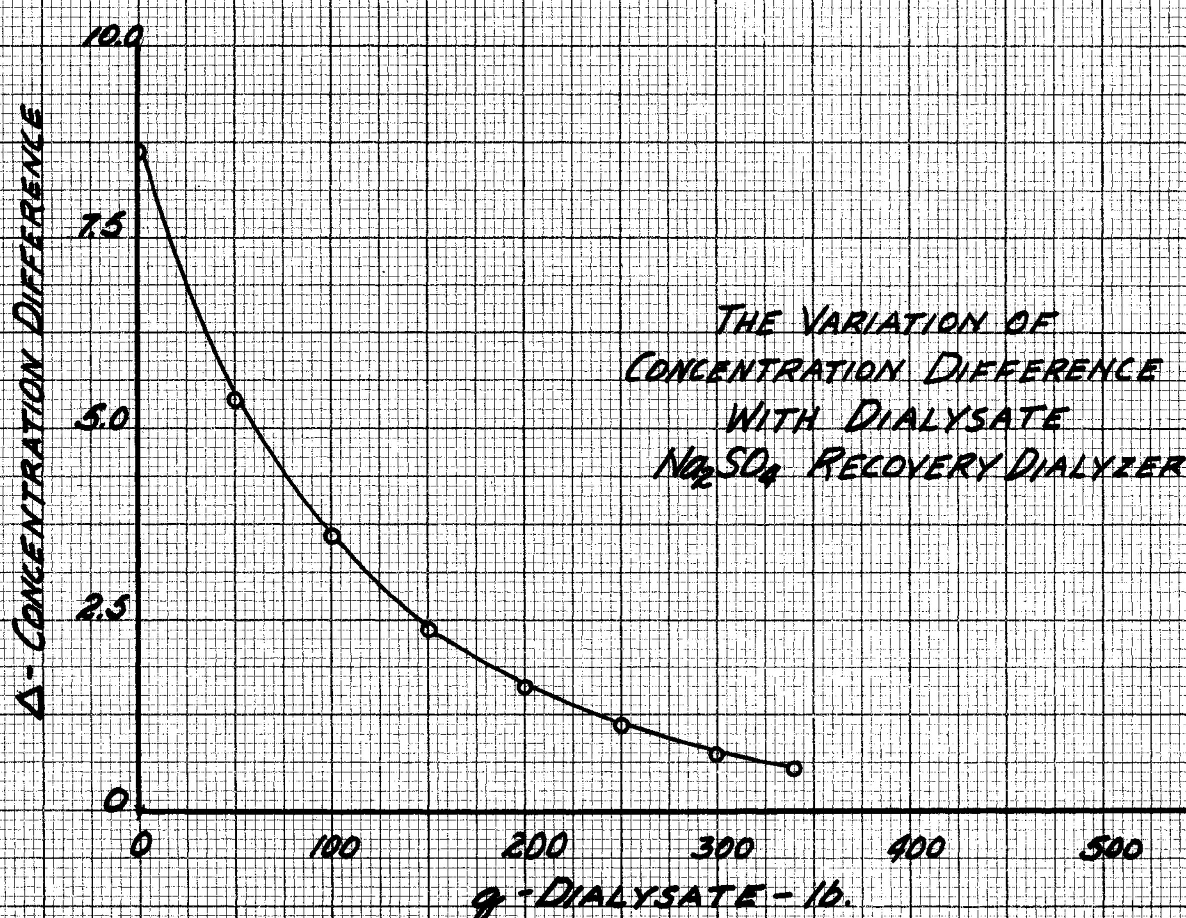
q lb. solute	$C_1 - C_2$	1/K	1/ Θ	1/K Θ
0	8.70	167	0.115	19.2
50	5.30		0.189	31.6
100	3.60		0.278	46.4
150	2.40		0.417	69.5
200	1.70		0.588	98.3
250	1.20		0.833	139.2
300	0.75		1.333	222.5
338	0.50		2.000	334.0

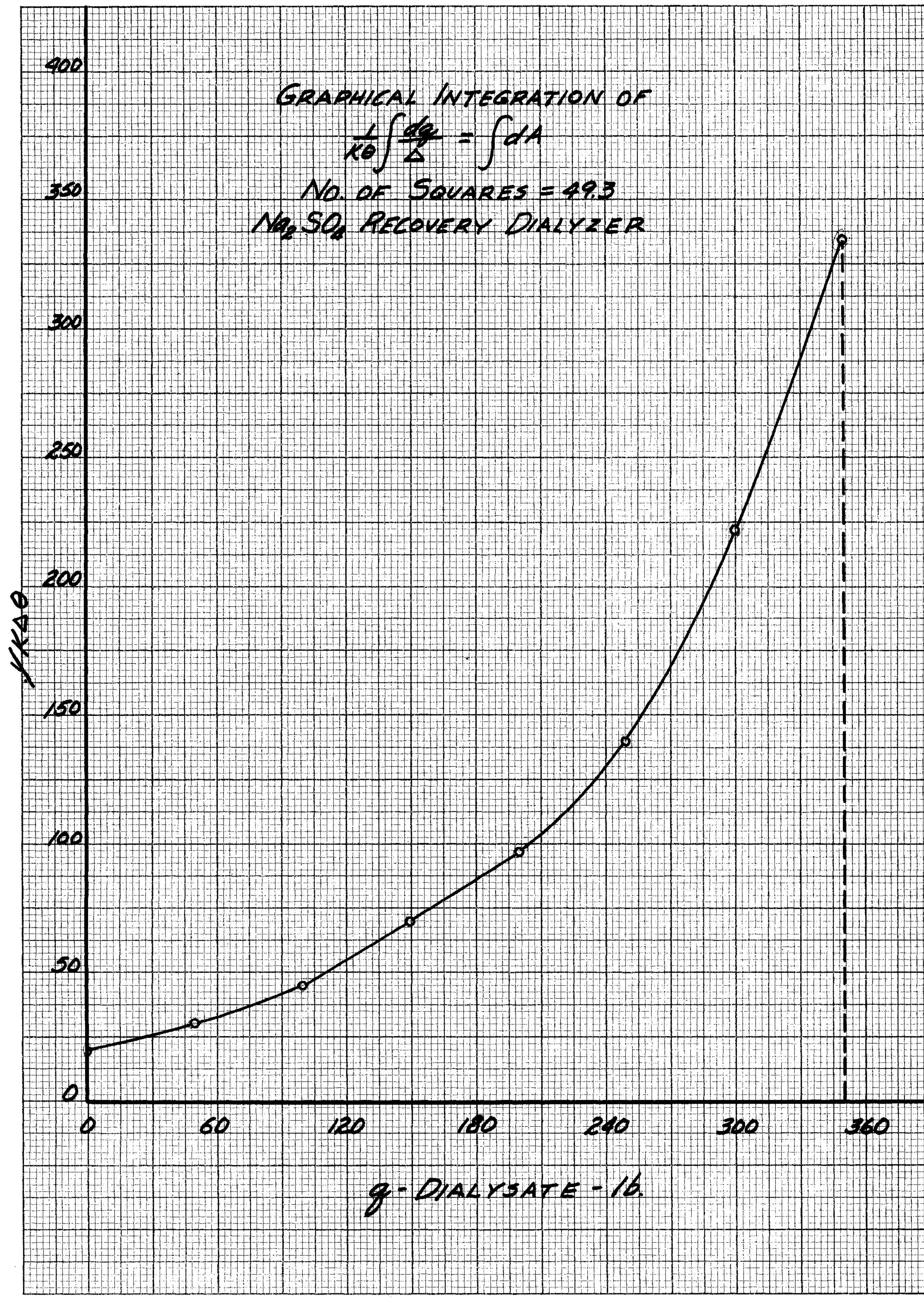
No. of squares = 7.41
Value per square = 5,000

A = 2hl = 7.41   5,000 = 37,050 sq. ft.
Let h = 1 ft.
Then $l = \frac{37,050}{2} = 18,525$ ft.

Assume plates 10 ft^2 (10 passes/plate)
Length per plate = 100 ft.
No. of plates = $\frac{18,525}{100} = 185$


THE VARIATION OF
RICH & LEAN LIQUOR CONC.
WITH DIALYSATE
Na2SO4 RECOVERY DIALYZER
C - CONCENTRATION - lb/ft3
q - DIALYSATE - lb.
C1
C2
0
5
10
15
0
100
200
300
400
500


THE VARIATION OF
CONCENTRATION DIFFERENCE
WITH DIALYSATE
Na2SO4 RECOVERY DIALYZER
Δ - CONCENTRATION DIFFERENCE
q - DIALYSATE - lb.
0
2.5
5.0
7.5
10.0
0
100
200
300
400
500


GRAPHICAL INTEGRATION OF
$\frac{1}{K\theta}\int\frac{dq}{\Delta} = \int dA$
NO. OF SQUARES = 49.3
Na_2SO_4 RECOVERY DIALYZER
1/KΔθ
400
350
300
250
200
150
100
50
0
0
60
120
180
240
300
360
q - DIALYSATE - lb.

V DISCUSSION OF RESULTS

The data from the experimental work were correlated with the relations derived under Case V of Section III. The assumptions made here apply to all other cases where the osmose is not negligible, and therefore should be capable of extrapolation.

Initial Work.

It was found that the rate of osmosis could not be considered negligible with respect to the quantity of solute transferred. Further, the variation of concentration resulting from osmose alone could be from 10 to 50 per cent over a period of five hours, depending upon the solute, membrane and the ratio of liquor volume to membrane area. Consequently, it was evident that the relation

$$dC_2 = K(C_1 - C_2)d\theta$$

could not be correct except where V_2 was very large relative to V_1, or where the salt concentrations were extremely dilute. The evidence that this relation must be in error was verified experimentally.

The relation

$$dq = KA(C_1 - C_2)d\theta$$

was investigated thoroughly. It was initially written as a first approximation, since it postulates that for electrolytes,

$$K = \frac{1}{R} = \frac{1}{r_{unionized}} = \frac{1}{r_{cation} + r_{anion}}$$

An analogy for non-electrolytes may also be drawn to cover association of the molecules. Upon examination of the data it was found that over the range of concentrations of 0.25 to 0.03 gm./c.c. the sum of the resistances of the cations and anions must have been approximately equal to that of the unionized particle. If this were not so a straight line rectification would not occur. Even below this range, the above postulate was nearly true within experimental error. At high concentrations the approximate average experimental error was two per cent, and at low concentrations it was ten per cent.

The experimental dialyzer was operated with C_2 small relative to C_1. Therefore the test was at a maximum, and small differences should have been magnified. The value of K includes membrane thickness, and it was assumed that the concentration gradient through the membrane was linear with thickness. Since membrane thickness varied fivefold, it is apparent that the assumption was valid within experimental error.

From these considerations it appears that the above relation is applicable at high concentrations, and approximately true even at quite low concentrations.

The values of C_1 and C_2 are not altered by the transfer of solute alone, since osmosis is in operation simultaneously. Consequently, it was necessary to include a function of osmose in all relations where it is not negligible. The equation

$$\frac{dO}{d\theta} = \gamma A(C_1 - C_2)$$

was employed initially as a first approximation. The measurement of osmosis could not be executed as accurately as that of concentrations. The average experimental error over the range of concentrations of 0 to 0.30 gm./c.c. was about eight per cent. The total variation was about sixteen per cent. Within this variance range the relation was experimentally verified. The eight per cent error in osmosis would produce only about 1.5 per cent error in concentrations. In view of the error of measurement of concentrations the use of the relation was tenable. While its accuracy was not closely checked it seems not to be entirely correct. The osmotic pressure has been shown not to be directly proportional to concentration for electrolytes. However, it is evident that the high resistance to flow of the membrane offsets the increase in osmotic pressure due to ionization. In several cases where experimental error was less than the average this relation checked within two per cent.

In summation, it may be said that the relation written as a first approximation for the rate of osmose fortunately appeared to be suitable for use in combination with the relation governing the rate of solute transfer, and therefore was employed in all correlations.

The electrokinetic effects set up by the diffusion of the solute and by osmosis were fortunately found to be of a very small order over the investigated range of concentrations. In several of the runs, at low concentrations, there was some evidence that the rate of osmosis receded more rapidly than it normally should. However, as osmosis proceeded, the rate increased until it coincided with the normal rate once more. The effect of this variation on the concentrations, and consequently the rate of dialysis, was of a very small order. Therefore this variation was not considered in the correlation of the data. It has been shown that for cellulose-water interfaces, the rate of osmosis goes through a maximum (above the normal rate) near a concentration of 0.0001 normal solutions of chlorides. This maximum may be as much as 50 per cent greater than the normal osmotic rate. Normal osmosis at this low concentration difference is quite small. Consequently, relative to the total osmose over a wide range of concentrations, the variation is trivial. This is true only for reclamation processes, or where the concentration range is large. For purification processes, it is important provided that osmosis is appreciable at low concentrations.

The effect of the rate of stirring was not noticed. The stirring paddle of the experimental dialyzer was varied twofold, with no evidence of an increase in the rate of dialysis that was not within experimental error. This is in accordance with the consideration that the rate of diffusion through a membrane is only about ten per cent of that in the free liquid state. Therefore, the diffusion resistance of the stagnant liquid at the liquid-solid interface may be considered with respect to the membrane resistance.

It is to be recalled that the osmose as measured was the apparent osmose, or the increase in volume over the original volume. This is not the true amount of osmose, since the solute was also being removed from the dialyzer. The true osmose would therefore be the sum of the apparent osmose and the volume of the solute removed from the dialyzer. It is, however, more convenient in theoretical treatments and in the use of the data to consider the apparent osmose. The osmotic coefficient therefore includes the variation of volume with density changes. This facilitated by the fact that the rate of dialysis and osmosis are linear with concentration, and the variation of density with concentration is nearly linear. This assumption was found to be accurate within the experimental error.

In view of the previous discussion, the assumptions made in the formulation of the first approximation are apparently accurate enough to warrant their employment. This is true, however, for reclamation processes only. These relations are believed to be only roughly accurate at extremely low concentrations. Furthermore, large concentrations of colloids which are sorbed by the membrane will undoubtedly reduce their accuracy. This will be discussed more fully in subsequent work.

The Permeability Coefficient.

The permeability coefficient is the most important factor in relating dialysis and osmosis. The value of Υ is also of interest in that it sets up the mathematical scale for measuring membrane permeability. Thus, for membranes impermeable to the solute but permeable to the solvent, $\Upsilon = \infty$, and where the solvent does not pass but the solvent does, $\Upsilon = 0$. For the materials tested Υ varies between 0.4 and 10 in c.g.s. units.

The value of Υ was found to be constant for any system tested with an average error of less than ten per cent. This error caused a much less error in concentration, and consequently the rate of dialysis. It appears that this valuable constant is applicable and that the relation $O = \Upsilon q$ is tenable. In some of the runs where osmose was large, and very accurate analyses were possible, the average variation of Υ was about 1.6 per cent. This is well within the limit of experimental error. These values were calculated over intervals of time, and therefore the variation is at a maximum. Further, the values of q were determined by increments in the concentration of the dilute solution. This solution was maintained at a very low concentration, and therefore the accuracy of the analytical procedure was inhibited. The runs of sugars and mixed salts were not as accurately analyzed. Since the quantity of solute transferred was determined by difference of these concentrations any small error was magnified. From this, the value of Υ may be considered more valid than the experimental procedure indicated. Certainly it is as accurate as the relations governing osmose and dialysis. The value of Υ is subject to the same considerations as osmose at low concentrations, and similarly may be expected to be only a rough estimate where electrokinetic phenomena are appreciable. However, the relation is suitable for use in reclamation processes.

The Effect of Temperature.

It was found that both K and γ increase linearly with temperature. This is in accordance with the fundemental theory of diffusion, and was to be expected. However, it interesting to note that the rate of increase of the value of K was not the same for parchment paper and cellophane. The equations of the lines are as follows

Parchment Paper:

$$K = 0.019t - 0.106$$

$$\gamma = 0.0653t + 0.61$$

Cellophane:

$$K = 0.01008t + 0.112$$

$$\gamma = 0.0265t + 0.289$$

Thus, it is seen from the tangents that the parchment paper yielded a more rapid increase of K with temperature than did the cellophane.

This is of interest in that it appears to support the sorption theory of permeability. This would indicate that the cellophane tended to sorb solvent more strongly than the parchment paper. Therefore, temperature would have a lesser effect on the rate of dialysis.

The rate of dialysis is given as

$$\frac{dq}{d\theta} = k A (C_1 - C_2)$$

The rate of diffusion is given as

$$\frac{dq}{d\theta} = \frac{D}{t} A_c (C_1 - C_2)$$

Dividing the latter by the former

$$\frac{A_c}{A} = \frac{k t}{D}$$

From this, it is possible to calculate the per cent effective area for any membrane. The following table indicates the porosity values for various systems. This further indicates that the solution-membrane affect the porosity of the membrane which apparently bears out the sorption theory of permeability. The strong sorptive power of cellophane, as illustrated in the following table has also been observed by other investigators. The sorption affects the porosity by as much as 31 per cent.

TABLE VI

S System	Temp. Deg. C.	D $Cm.^2/day$	K Cm./hr.	% Effective Area
NaCl - 4F Cellophane	25	1.27	0.3580	6.75
	30	1.46	0.4130	6.75
NaCl - Parchment	25	1.27	0.4160	4.34
	30	1.46	0.4600	4.92
NaCl - Cellophane	25	1.27	0.8970	3.55
Sugar - Cellophane	30	0.27	0.1101	2.06
Sugar - Parchment	30	0.27	0.0618	3.58

The values of $1/r$ remained essentially constant with temperature variation, there by indicating the validity of the initial differential equations. The following table illustrates the validity of the constant.

TABLE VII

Temp. Deg. C.	Parchment cm./hr.	% Error	4F Cellophane cm./hr.	% Error
21.3	-------	---	0.3840	0.8
25.0	0.3072	1.6	0.3823	0.3
30.0	0.3196	2.4	------	---
35.0	0.3145	0.7	0.3839	0.7
40.0	0.3048	0.8	------	---
45.0	0.3150	0.9	0.3740	1.8
	Mean = 0.3122	Mean = 1.3	Mean = 0.3811	Mean = 0.9

The above average deviations are within experimental error.

Recomendations.

(1) It is evident that solvent sorption plays a large part in the effective porosity of membranes. Consequently, it would be desirable to investigate this property for a series of systems.

(2) It has been shown that certain colloids are strongly sorbed

by the membrane. It would be of value to determine porosity as affected by colloid sorption for a series of systems. Solute concentrations and pH also affect the degree of sorption.

(3) With the knowledge of the degree of sorption it would then be desirable to attempt a correlation between solvent adsorption and the porosity for various systems. Thus, by measuring the adsorptivity and pore size, the values of K could be calculated from diffusion equations and the osmotic pressure.

(4) It would be desirable, as a refinement, to determine the effect of flow velocity upon the values of K and Υ.

(5) The applications of dialysis are limited by the membranes available. It is desirable to develop new membranes having better properties. A good membrane must be strong, and must not be attacked by the solutions. It should be of maximum pore size, limited by the necessity of retaining colloids. The per cent void space should be as large as possible.

(6) It would be desirable to determine the rate of separation of ions from a mixture of ions. Such a process could be utilized to diffuse off a pair of ions in a manner analogous to a continuous distillation column.

(7) By virtue of the specific nature of organic membranes for organic solutions, it would be possible to effect a separation of organic solutions at room temperature. Therefore, it is evident that a study of this process is of value.

(8) It would be of value, for purifying processes to determine the variations of solute transfer and osmosis with the Zeta potential.

VI SUMMARY

Within the past decade, dialyzers have been employed industrially for recovery and purification operations. The small amount of quantitative information available is inadequate for design purposes. Of the previous design relation one facilitates a laborious approximation, while another fails to indicate the quantity of material transferred. Neither of these permit an estimation of the initial and final volume of solutions.

The equations were derived governing nine possible cases. of these, only those including osmosis were found to be valid. It was found that both previous design equations were theoretically incorrect, since the assumption of negligible osmose is not warranted.

Special equipment was constructed and operated for the determination of the dialytic and osmotic transfer coefficients. These values are reported for a range of concentrations and systems. They were found to be constant over the ranges tested, and within the experimental error.

A permeability coefficient was set up varying between zero and infinity, which is of use in the evaluation of membranes. It was found that the dialytic and osmotic coefficients vary linearly with temperature, but do not increase at the same rate. The permeability coefficient is constant for any system over a range of temperatures. No correlation was obtained between the dialytic transfer coefficient and the effective membrane area.

The design relations indicate a distinct advantage of counter-current flow over parallel flow. Counter-current flow is recommended for reclamation processes.

BIBLIOGRAPHY

(1) Bassett, Chem. and Met. Eng., 45, 254, 1938.

(2) Bartell, "Colloid Symposium Monograph", I, 120, 1923.

(3) Bethe and Terada, Z. Physik. Chem., 112, 251, 1924.

(4) Debye and Huckel, Physik. Z., 24, 185, 1923.

(5) Ibid. 305.

(6) Donnan, Z. Elektrochem., 17, 572, 1911.

(7) Einstein, Ann. Physik., (4), 17, 549, 1905.

(8) Fick, Pogg. Ann., 94, 59, 1855.

(9) Findlay, "Osmotic Pressure", Longman and Green Co., 1919.

(10) Getman and Daniels, "Outlines of Theoretical Chemistry", John Wiley and Sons, Inc., N.Y., 1937.

(11) Guoy, Le Journal de Physique et le radium, (4), 9, 457, 1910.

(12) Graham, T., Phil. Trans., B, 144, 177, 1854.

(13) Graham, T., Phil. Trans., B. 156, 183, 1861.

(14) Gortner, "Outlines of Biochemistry", 75 John Wiley and Sons, Inc., N.Y., 1929.

(15) Hartley and Berkely, Phil. Trans., A, 206, 1906.

(16) Helmholtz, Ann. Phys., 7, 337, 1879.

(17) Lee, J.A., Chem. and Met. Eng., 42, 482, 1935.

(18) L'Hermite, Ann. Chem. Phys., 43, 420, 1854.

(19) Loeb, J. Gen. Physiol., 6, 307, 1924.

(20) Morse and Frazer, Pub. No. 198, Carnegie Inst. of Washington.

(21) Nernst, Z. Physik. Chem., 2, 613, 1888.

(22) Niedle, J. Amer. Chem. Soc., 38, 1270, 1916.

(23) Oholm, Z. Elektrochem., 14, 129, 1908.

(24) Oholm, Z. Physik. Chem., 50, 309, 1904.

BIBLIOGRAPHY (Cont.)

(25) Pfeffer, ")smotische Untersuchungen", Leipzig, 1827.

(26) Stephans and Rowe, Soc. Chem. Ind. J., 56, 397T, 1937.

(27) Stephans and Rowe, Soc. Chem. Ind. J., 59, 116M, 1939.

(28) Sutherland, Phil. Mag., 9, 781, 1905.

(29) Taylor, "A Treatise of Physical Chemistry".

(30) Thomas, "Colloid Chemistry", McGraw Hill Book Co., N.Y., 78, 1934.

(31) Ibid., 85.

(32) Thovert, Compt. rend., 150, 270, 1910.

(33) Tinker, Proc. Roy. Soc. London, A, 93, 268, 1916-17.

(34) Traube, Arch. f. Anatomie u. Physiologie, 233, 1928.

(35) U. S. Patent No. 1,719,754 - L. Cerini.

(36) " " " " 1,815,761 - L. Cerini.

(37) " " " " 1,573,703 - F.H. Griffin.

(38) " " " " 1,849,622 - E. Heibig.

(39) " " " " 1,868,955 - S. Tachikawa.

(40) Van't. Hoff, Z. Physik. Chem., 1, 481,1887.

(41) Vierodt, Ann. Phys., (2), 73, 519, 1848.

(42) Vollrath, H.B., Chem. and Met. Eng., 43, 303, 1936.

(43) Weiser, H.B., "Colloid Chemistry", J. Wiley and Sons, N.Y., 1939.

(44) Ibid., 148.

(45) Ibid., 150.

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