

A THEORY FOR MOLECULAR TRANSPORT PHENOMENA
THROUGH THIN MEMBRANES

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I. Introduction

A. Brief Historical Background of Transport Theory.

The earliest physical scientist to understand and apply the now traditional mathematical description of molecular transport phenomena was Adolf Fick in the mid-1800's.¹ Nearly fifty years earlier, however, the mathematician Jean Baptiste Joseph Fourier² had studied extensively the heat transport phenomena through solids and as a part of his work had derived the same relations for one-dimensional heat transport that Fick later recognized as describing the one-dimensional molecular transport phenomena (i. e. Fick's first and second laws). The Fourier derivations of these laws were independent of the uncertain hypotheses on the fundamental nature of heat and were based primarily on the empirical facts known from the experiments carried out in the late 1700's and early 1800's. That these same experiments led many to regard the fundamental nature of heat as molecular (caloric) was incidental to the Fourier derivations but important in understanding why the same relations were eventually recognized as describing molecular transport a half a century later by Fick.

Even without knowledge concerning the fundamental nature of heat, Fourier knew that the motion of heat, described by his equations, was different from the laws of uniform and accelerating motion set down by Galileo³ nearly two centuries before him and that none of the mechanical

theories of Galileo and Newton applied to the observed motion of heat. The motion of heat, Fourier claimed, was a special order of phenomena that could not be accounted for by the principles of motion and equilibrium.

Nearly a century after Fourier, A. Einstein⁴, in the early 1900's, wrote several papers on the theory of Brownian motion that provided the first insight into the fundamental nature of the motion of a diffusion-transported quantity. The single distinguishing characteristic of Brownian motion is that it is a non-directional motion - completely random. Since Galileo's (and Newton's) laws of motion describe directional motion (a vector quantity), Fourier's claim is correct in that the observed motion of heat is a special order of phenomena. This uniqueness of random motion becomes apparent if one, for example, compares the relation of the distance that a particle travels with the travel time for the three types of motion. The time-dependence changes from the second power to the first power and then to the one half power of the time for accelerating motion, uniform motion and random motion (the corresponding coefficients of the motions reflect this fact in their dimensions also). The distance in the random motion case is the root-mean-square distance since for random motion it is equally probable that the particle will move in a positive or negative direction from the starting point and hence would have an average distance that was independent of the time, i. e. zero.

Einstein also pointed out that the observation time is an important factor in the observed randomness of Brownian motion. For if the observation time is set immediately after the start of the motion then the history of the particle becomes important in determining its motion, and the motion of a given particle can not be considered independently of the motion of the other particles in the system. The history of the particle is composed of a series of interactions with the other particles in the system and the motion of the particle at the observation time is determined by the vector summation of the forces encountered in these past interactions. Each of these interactions obeys the fundamental laws of motion of Galileo and Newton for large particles. The fact that Brownian motion appears random, then, is a result of the "long" time duration between observations. If one were to shorten the time duration so that, for example, two observations of the particle were made before the particle interacted with another particle, the motion of the particle during the interval would be described by the fundamental laws of motion. Alternatively, Galileo chose a single (macroscopic) particle system to study the laws of motion.

In the case where these interactions are simple, the transport can be described by a single parameter that depends on the properties of the diffusing particle (called the solute) and the properties of the other particles of the system. The system of interest here contains solute

particles diffusing within a membrane. The interactions are considered simple if they are elastic or inelastic particle collisions that do not result in a chemical change in the particles. If the properties of the membrane are homogeneous throughout the membrane, then the parameter is independent of the location of the solute in the membrane. This parameter is called the diffusion coefficient of the particular solute in the membrane and it is relatively insensitive to the properties of the solute for liquid membranes whereas for solid membranes it is quite sensitive to the shape and size of the solute.

One interpretation of the diffusion coefficient is that it is proportional to the probability that a particle at one surface of the membrane has of being transported to the other surface of the membrane in a unit* time for a unit membrane. That is, from Fick's first law:

$$\frac{dn}{C} = \frac{A dt D}{L} = D \text{ for } A = L = dt = \text{unity}$$

where dn = the number of particles transported, C = the concentration of particles at the surface, L = the membrane thickness, A = the membrane area, dt = the time for transport of dn , and D = the diffusion coefficient. The quantity dn/C is proportional to the probability. The actual number of particles transported across the unit membrane per unit time at steady-state (a quantity that is proportional to the steady-state permeability coefficient) is then the product of the diffusion coefficient and the

*The cgs system of units is used throughout the thesis unless otherwise specified.

concentration of particles at the surface. The relationship between the particle concentration at the surface to the particle concentration in the surrounding medium (where both concentrations are expressed in number / cm^3) can be determined for the case of equilibrium at the surface. This relationship is useful in relating the diffusion and the solubility coefficients to the permeability coefficient, as is discussed further in part B.

I.

B. The Concept of the Solute Solubility Coefficient in a Membrane.

In part A of this section it has been pointed out that the diffusion coefficient in a given membrane can be thought of as being proportional to the steady-state probability of a solute particle, already in the membrane but at one of the surfaces, diffusing to the other surface of a unit membrane per unit time. In addition, the magnitude of this parameter depends on the frequency of the interactions but under certain conditions is independent of the tenacity of the interactions between the solute particle and the particles composing the membrane. D is independent of the tenacity of the interaction when the solute particle has sufficient energy to insure that the interaction is not inelastic. In general for a large number of solute particles the fraction having energies exceeding the threshold energy for an inelastic collision (the threshold energy is commonly called the molar heat of activation for diffusion, ΔH_D) is given by the Boltzmann factor, $\exp(-\Delta H_D / RT)$. When this factor is equal to one then D depends only on the interaction frequency. D then is equal to $D_0 \exp(-\Delta H_D / RT)$ where D_0 depends on the interaction frequency but not on the tenacity of the interaction.

In this sense one can think of the solute-membrane interaction as defining two quite different properties: the frequency of the interaction determining the magnitude of D_0 (and hence the upper bound on the diffusion

coefficient D), and the tenacity of the interaction determining the solubility coefficient, S . It is clear that these two properties of the solute-membrane interaction are closely entwined and that their separation may be artificial and unrealistic. The separation of these two properties, however, is conceptually convenient and is quite probably valid as a first approximation for most systems of interest. The relationship between S and the tenacity of the solute-membrane interaction will be developed in the remainder of this section.

If the interactions are elastic, then energy will be transferred to and from the solute particle in accordance with the laws of conservation of energy and momentum. Since no energy is lost in these interactions the total energy of the particles in the phase is constant with time. A similar result is obtained under equilibrium conditions if the collisions are inelastic. That is, consider that the solute particle collides with a low energy particle composing the membrane. If the collision is inelastic then the particles stick together. Momentum is conserved but a quantity of energy corresponding to the "bond energy" holding the particles together is given up in succeeding collisions with particles of lower energy (this transfer of energy is commonly observed as an evolution of heat in the phase). For a large number of solute particles in the membrane, at equilibrium just as many pairs are being formed as are being broken down. The net result is that the

energy of the phase at equilibrium is constant with time.

If, however, solute particles are allowed to enter the membrane from another phase where the inelastic interaction is different, then for a large number of solute particles entering there will be a change in the total energy of the membrane. Consider a single solute particle of average energy (determined by the temperature of the system - both phases being at the same temperature) entering the membrane from the adjacent phase. Very soon after the solute particle enters the phase (probably at the interface), it collides inelastically with a membrane particle of low energy. The resulting pair yields to the phase by succeeding interactions with low energy particles an amount of energy equivalent to the bond energy. Since the presence of additional solute particles in the membrane affects only negligibly the probability for a solute particle to collide with a membrane particle, there is no change* upon addition of more solute

*Cases where this probability changes due to a solute-solute particle interaction are classically treated as nonideal behavior. In this case the solute concentration is replaced by the solute activity where the activity coefficient indicates the deviation from ideal behavior, i. e. where only solute-membrane interactions are important. Nonideal behavior is discussed later in this part of Section I.

particles in the fraction of solute particles in the membrane that exist as pairs. The average heat energy given to the membrane per single solute particle entering the membrane is therefore the product of the fraction of particles existing as pairs in the membrane, F_1 , times the bond energy, E_{s1} .

In the case that the solute particle enters as a pair, coupled with a particle of the adjacent phase, the average energy given to the membrane as observable heat is the product of F_1 and the difference in the bond energies of the solute pairs, i. e. $E_{s1} - E_{s2}$ where E_{s2} is the bond energy of the solute particle-adjacent phase particle pair.

In the case that the solute particles enter as both pairs and singles, then the total heat evolved in the membrane per solute particle is the sum of two products, i. e. $(E_{s1} - E_{s2}) F_2 F_1 + E_{s1}(1 - F_2) F_1$ where F_2 is the fraction of solute particles in solute particle-adjacent phase particle pairs in the adjacent phase. This expression for the energy assumes that all solute particle-adjacent phase particle pairs are destroyed in the membrane. This quantity of heat calculated for a mole of solute particles is the standard state partial molal heat of solution, $\Delta\bar{H}^\circ$. From similar considerations for the entropy change in this model when a mole of solute particles enters the membrane one can find the standard

state partial molal entropy change, $\Delta\bar{S}^\circ$. Having related the tenacity of the particle interactions at the molecular level to the macroscopic quantities $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ (proof of the model used in this relation awaits attack by the methods of statistical mechanics), it is now convenient to continue the discussion at the macroscopic level in terms of classical thermodynamics and chemical kinetics.

Under equilibrium conditions the partition coefficient of a solute between two phases is given by the Nernst distribution law for a system in heterogeneous equilibrium. This relationship has been derived for dilute ideal liquid solutions⁵ and has been found to be a function of the temperature given by $\exp(-\Delta\bar{G}^\circ/RT)$ where $\Delta\bar{G}^\circ$ is the change in the standard state Gibbs free energy for the transfer of one mole of solute from phase α to phase β (sometimes called the standard state chemical potential or the standard state partial molal Gibbs free energy). The partition coefficient, defined as the ratio of the solute mole fraction in β to the solute mole fraction in α , and the solubility coefficient of the solute in the membrane, defined as the ratio of the solute concentration (in m moles/ml (M)) in the membrane to the solute concentration in the adjacent phase, can be related if the solute

sorption process occurring in the membrane is similar to a solution process.

$$(1) \quad S = \frac{C_1^p}{C_1^m} \approx \frac{N_1^p/N_0^p (10^3 d_0^p/M_0^p)}{N_1^m/N_0^m (10^3 d_0^m/M_0^m)} \quad \text{for dilute solutions, } N \approx N_0$$

where

$$(2) \quad \frac{N_1^p/N_0^p}{N_1^m/N_0^m} \approx \exp(-\Delta \bar{G}^0 / RT) = \exp(\Delta \bar{S}^0 / R) \cdot \exp(-\Delta \bar{H}^0 / RT).$$

Substituting (2) into (1),

$$(3) \quad S = \frac{C_1^p}{C_1^m} = (d_0^p/d_0^m)(M_0^m/M_0^p) \exp(\Delta \bar{S}^0 / R) \cdot \exp(-\Delta \bar{H}^0 / RT) = S_0 \exp(-\Delta \bar{H}^0 / RT).$$

For the nonideal case, the solubility coefficient, S, is defined as the ratio of the solute activity in the membrane to the solute activity in the surrounding medium. In this case the concentrations given in (3) must be multiplied by their corresponding activity coefficients, f,

$$(4) \quad S = \frac{f_1^{\beta} C_1^{\beta}}{f_1^{\alpha} C_1^{\alpha}} = S_o \exp (-\Delta \bar{H}^o / RT) .$$

A description of the symbols used in (1) through (4) is given below:

S = the solute solubility coefficient in the membrane, in

$$\frac{\text{m moles/ml (M/M)}}{\text{m moles/ml}}$$

$$S_o = (d_o^{\beta} / d_o^{\alpha}) (M_o^{\alpha} / M_o^{\beta}) \exp (\Delta \bar{S}^o / R)$$

$$\frac{N_1^{\beta} / N_o^{\beta}}{N_1^{\alpha} / N_o^{\alpha}} \cong \frac{N_1^{\beta} / N^{\beta}}{N_1^{\alpha} / N^{\alpha}} = \text{the solute partition coefficient}$$

between phases α and β .

N_1^{β} = the number of moles of solute in phase β .

N_o^{β} = the number of moles of solvent in phase β .

N^{β} = the total number of moles in phase β .

f_1^{β} = the activity coefficient of the solute in phase β .

M_o^{β} = the g -molecular weight of the solvent in phase β .

d_o^{β} = the density of the solvent in phase β , in g/ml.

(By substituting α for β in the above, a similar description of the quantities applies to phase α .)

$\bar{\Delta G}^\circ$ = the standard state chemical potential.

$\bar{\Delta H}^\circ$ = the heat solution of a mole of solute dissolving in phase β
from phase α .

$\bar{\Delta S}^\circ$ = the change in the standard state entropy per mole of
solute transferred from α to β .

R = the gas constant.

T = the absolute temperature.

If molecular transport is occurring across the membrane, however, the system is not at equilibrium and at best approaches a steady-state condition where the concentration in the membrane is independent of time but is a function of the distance from the surfaces of the membrane. The concentration at any point within the membrane can be described at any time by the Fourier relation in terms of the concentrations at the surfaces of the membrane. The relationship between the concentration at the surface to the concentration in the adjacent phase is in general most difficult to determine.

The usual assumption made is that the time required for the surface to reach equilibrium with the adjacent phase (phase α) is negligible compared to the time for the concentration inside the membrane to reach a steady state. The solute concentration at the surface of the membrane can then be determined from the equilibrium result (3), if the equilibrium solubility coefficient, S,

and the solute concentration in the adjacent phase are known.

This is a special application of (3) since the derivation of (3) assumes that the surface to volume ratio is small so that surface effects are negligible, i. e. (3) is true for the bulk phase, but may not be true at the surface. In general one can expect that the concentration at the surface of the membrane will be different at equilibrium from the concentration in the bulk phase. This difference results from the continuous change in properties as one moves through the interfacial region separating the membrane and the adjacent phase, and can be expected to be independent of whether the phases are ideal.

The solubility coefficient at the surface using (3) can then be expected to differ from the solubility coefficient in the bulk phase. Since the solubility coefficient determined from the permeability measurements is the surface solubility coefficient whereas the solubility coefficient determined directly is the bulk phase solubility coefficient, one can not expect that the two coefficients will generally agree.

These two coefficients can, however, be determined directly for a given solute-membrane system by measuring the equilibrium solute concentrations in the two phases (the bulk phase of the membrane and the adjacent phase) for a wide range of membrane

surface area-to-volume ratios. Then by extrapolating the plot of the solubility coefficient (using (3)) versus the membrane surface area-to-volume ratio to zero membrane surface area-to-volume ratio, the intercept is the solubility coefficient for the bulk phase. Extrapolation of the plot of the solubility coefficient (using (3)) versus the membrane volume-to-surface area ratio to zero membrane volume-to-surface area ratio gives the surface solubility coefficient as the intercept. If this series of measurements is repeated at different temperatures, the heats of solution for the surface and the bulk phase can also be found (from $\ln S$ vs. $\frac{1}{T}$ - see (3)). In addition, if the surface solubility coefficient found above is compared with the surface solubility coefficient determined from the permeability measurements, the nonideality of the system can be investigated from (4).

Unless one of the activity coefficients in (4) is known or can be assumed to be unity, only the ratio of the activity coefficients can be determined from the comparison of the extrapolated value with the permeability value of the surface solubility coefficient. The case where one of the activity coefficients can be assumed to be unity is particularly useful: as an illustration consider the permanent gas-membrane system at low pressures where the gas obeys the ideal gas law.

For these systems (4) becomes

$$(5) \quad S = \frac{f_1^{\beta} C_1^{\beta}}{C_1^{\alpha}} = (10^3 d_0^{\beta} / M_0^{\beta}) RT \exp (\Delta \bar{S}^{\circ} / R) \cdot \exp (-\Delta \bar{H}^{\circ} / RT)$$

$$S = S_0 \exp (-\Delta \bar{H}^{\circ} / RT) \quad \text{where } C_1^{\alpha} = P_1^{\alpha} / RT^* \quad \text{and } P_1^{\alpha} = \text{the pressure of 1 in } \alpha, \text{ in atm.}$$

If P_1^{α} is corrected to some standard temperature, e. g. 273 °K, then S_0 in (5) is independent of temperature (i. e. in each case it is proportional to 273 °K). The activity coefficient f_1^{β} in (5) can be found by comparing the extrapolated surface solubility coefficient with the surface solubility coefficient found from the permeability measurements. For example, in several permanent gas-rubber systems the solubility coefficient measured directly, using fine snippings of rubber, agrees well with S determined from the permeability measurements.⁶ This indicates that f_1^{β} approaches unity for these systems (assuming that S determined by using the

*The use of concentration in (5) for the gas phase rather than the more commonly used pressure has been chosen so that a consistent set of units may be developed for the permeability (K), diffusion (D) and solubility (S) coefficients for all solute-membrane systems. The units are: for K and D, cm²/sec. and for S, M/M. If the pressure is used, (5) is Henry's law.

fine snippings of rubber approaches the extrapolated surface solubility coefficient). This completes the discussion of the non-ideal case; for the remainder of the thesis the discussion of the solubility coefficient will be restricted to the ideal case given by (3).

It is also worthwhile to derive an expression for S at the surface of the membrane starting from a kinetic theory viewpoint and to compare the results with the equilibrium thermodynamic results given above. S in the membrane is determined by the processes of sorption and desorption that occur at the surface of the membrane. In order to find the relationship between S and the surface processes, one needs an expression for the concentration in the membrane as a function of time. Since the rate of sorption is proportional to the number of solute particles that strike the surface of the membrane per unit time it will be proportional to the concentration of the solute, C_0 , in the adjacent phase. By similar reasoning the rate of desorption is proportional to the concentration at the surface of the membrane. In the case of finding S for the bulk phase, the concentration throughout the membrane is uniform; the surface concentration may in reality be different from the interior concentration even for equilibrium conditions as was pointed out earlier. For simplicity the surface and interior concentrations can be assumed equal here since it will not affect the sought-for result.

The resulting expression for the solute concentration in the membrane $C(x, t)$ is,

$$(6) \quad AL \frac{dC(x, t)}{dt} = AK_1 C_0 - AK_2 C(x, t) \quad \begin{array}{l} 0 \leq x \leq L \\ t > 0 \end{array}$$

where C_0 = the solute concentration in phase α ,
in Molarity
 K_1 = the sorption rate coefficient, in cm/sec.
 K_2 = the desorption rate coefficient, in cm/sec.
 L = the membrane thickness, in cm,
 A = the membrane area in contact with α ,
where AL is the volume of the membrane.

For $t \geq t_e$, the time needed for equilibrium,

$$(7) \quad \frac{dC(x, t)}{dt} = 0$$

and (6) can be rewritten in terms of the equilibrium solubility coefficient, S (see (3) where $C_1^\beta = C(x, t_e)$ and $C_1^\alpha = C_0$),

$$(8) \quad S = \frac{C(x, t_e)}{C_0} = \frac{K_1}{K_2}, \quad 0 \leq x \leq L$$

In the derivation of (8), $C(x, t)$ is assumed to be independent of x in the range $(0, L)$ implying that diffusion within the membrane is rapid. In the case where the diffusion in the membrane is so slow as to be negligible, (6), (7) and (8) are valid only at the surfaces, i. e. at $x = 0$ and at $x = L$. The latter is the model assumed in the traditional description in order to obtain a relationship between the concentration at the surface of the membrane and the concentration in the adjacent phase. The boundary condition at $x = 0$ is given by specializing (6) and at $x = L$ the concentration is commonly held at zero. From (6)

$$(9) \quad A l \frac{dC(0, t)}{dt} = A K_1 C_0 - A K_2 C(0, t)$$

where l = the "thickness" of the surface at $x = 0$.

$C(0, t)$ = the solute concentration at $x = 0$ at time t .

For $t \geq t_s$, the time needed for the surface concentration to reach equilibrium,

$$(10) \quad \frac{dC(0, t)}{dt} = 0$$

and (9) can be rewritten in terms of the equilibrium solubility, S ,

$$(11) \quad S = \frac{C(0, t_s)}{C_0} = \frac{K_1}{K_2} \cdot$$

This case, where the diffusion in the membrane is slow, will be developed more fully in Section II. Equation (11) will be used there to determine $C(0, t)$ for $t \geq t_s$ with the assumption that $t_s \sim 0$. The case where diffusion is not so slow as to be neglected in (9) will be treated in Section III. This latter case becomes important when the solute-membrane interaction becomes tenacious, i. e. K_2 becomes small in (9), and/or when the membrane is thin enough that the diffusion term ($-DC_x(0, t)$) can not be neglected from (9) (or from the boundary condition at $x = L$). The role of the membrane thickness L in determining the magnitude of $C_x(x, t)$ in the diffusion term can be seen most easily in the case of steady-state diffusion where for a given concentration difference across the membrane, $C_x(x, t)$ increases in proportion to an increase in $1/L$.

An expression of the form of (11) can also be derived starting from the Langmuir premises for monomolecular adsorption to a surface. These are that the surface is assumed to be composed of distinct and equivalent adsorption sites, each of which can adsorb only one solute particle. When equilibrium is attained between the surface and the adjacent phase a certain fraction of the surface

will be covered with a monomolecular layer. The magnitude of this fraction depends on the solute concentration in the adjacent phase. If the concentration at the surface for an infinite solute concentration in the adjacent phase is defined as the saturation concentration for the surface (this may or may not correspond to complete coverage of the surface depending on the particular solute and surface of interest), then the fraction, θ , covered at some finite solute concentration in the adjacent phase is

$$(12) \quad \theta = \frac{C(0, t_g)}{C_s(0, t_g)}$$

where $C(0, t_g)$ = the equilibrium solute concentration in the membrane at $x = 0$ for some finite concentration in the adjacent phase, C_0 , expressed in Molarity.

$C_s(0, t_g)$ = the saturation concentration in the membrane at $x = 0$, in Molarity.

t_g = the time for equilibrium between the surface and the adjacent phase.

The rate of desorption is proportional to the fraction of the surface covered, whereas the rate of adsorption is proportional to the uncovered fraction of the surface, $(1 - \theta)$, and to the number of solute particles that strike the surface per unit time, i. e.

proportional to the solute concentration in the surrounding medium.

At equilibrium the rate of desorption equals the rate of adsorption

so that

$$(13) \quad K_1' (1-\theta) A C_o = K_2' \theta A$$

where C_o = the solute concentration in the adjacent phase,
expressed as Molarity .

K_1' = the adsorption rate coefficient, in cm/sec.

K_2' = the desorption rate coefficient, in $\frac{\text{m moles}}{\text{cm}^2 \text{ sec}}$.

Rearranging (13),

$$(14) \quad K_1' C_o = \frac{K_2' C(0, t_s)}{C_s(0, t_s)} \left[1 + \frac{C(0, t_s)}{C_s(0, t_s)} + \left(\frac{C(0, t_s)}{C_s(0, t_s)} \right)^2 + \dots \right]$$

In the case of dilute solutions in the adjacent phase where $C(0, t_s) \ll$

$C_s(0, t_s)$, (14) simplifies to

$$(15) \quad \frac{C(0, t_s)}{C_o} = \frac{K_1}{K_2}$$

where $K_1 = K_1'$, in cm/sec.

$K_2 = \frac{K_2'}{C_s(0, t_s)}$, in cm/sec.

Equation (15) is of the same form as (11) so that for dilute solute concentrations the expression for the solute solubility coefficient in the membrane, S , is independent of whether the membrane surface is composed of distinct adsorption sites that limit the coverage to a monomolecular layer or the surface is nonspecific in its sorption properties. Since a nonspecific sorption process is a solution process, the assumption made earlier to qualify the use of the Nernst distribution law in the case of solid membranes is seen to be valid for Langmuir-type adsorption as well as solution processes at the surface provided the solute concentration is dilute.

In Section III the intent has been to modify the traditional description considered in Section II where the surface processes alone determine the surface concentration in the membrane to a description where the diffusion process also determines the surface concentration. In both of these descriptions the time for the surface concentration to reach equilibrium is assumed negligible compared to the time for steady-state diffusion through the membrane. In some cases, however, it is conceivable that this assumption would not be valid. The ultrathin biological cell membrane might be an example of such a system. To describe this case is, however, more difficult, since the boundary conditions of the corresponding initial-boundary value problem contains derivatives x and t . The problem

is of continued interest, however, since its solution leads to a generalized expression for molecular transport phenomena that is applicable to all isothermal, chemically unreactive systems with a particular application to systems of ultra thin membranes.

In general, one can consider that the modification presented in Section III is the result of an increase in the concentration gradient across the membrane as the membrane thickness is decreased (the concentration difference across the membrane remaining constant). For a thick membrane the time for steady-state diffusion across the membrane is long and the concentration gradient across the membrane is small in comparison with the desorption term. For this system the traditional description considered in Section II is adequate. As the membrane thickness decreases, however, the concentration gradient increases and the time for steady-state diffusion decreases. For the system where the concentration gradient has increased sufficiently so that the diffusion term is no longer negligible with respect to the desorption term but where the time for steady-state diffusion is still long compared to the time for the surface concentration to reach equilibrium, the description of Section III is adequate.

One can also consider that the modification presented in Section III is the result of an alteration in the solute-membrane interaction characterized by a decrease in the desorption rate coefficient

(or by an increase in the diffusion coefficient). The description of Section II is then adequate for systems where this decrease is small so that the desorption term is still large compared to the diffusion term. The description of Section III is adequate (in addition to the systems covered by the traditional description) for systems where the solute-membrane interaction is tenacious enough that the desorption term is of the same order as or smaller than the diffusion term.

II. Limiting Diffusion Process in Transport.

The case of limiting diffusion is the usual representation chosen to describe the transport process through a membrane. The differential equation describing the process is the one-dimensional Fourier relation (Fick's second law):

$$(1a) \quad C_t(x, t) = D C_{xx}(x, t) \quad 0 < x < L, t > 0$$

where the subscripts indicate the corresponding partial differentiation,

$$\text{i. e. } C_{xx}(x, t) = (\partial^2 C(x, t) / \partial x^2)_t, \text{ etc.}$$

D = the diffusion coefficient of the solute in the membrane, in cm^2/sec .

$C(x, t)$ = the solute concentration at x in the membrane at time t , in

m moles/ml (M).

For a membrane of thickness L located between two infinite baths of concentration C_0 and zero for all time, the boundary conditions chosen for the problem are those where the diffusion term and the time for the concentration at the surface to reach equilibrium are negligible, i. e.

$$\begin{aligned} (1b) \quad C(0, t) &= SC_0 && \text{from I - (11)} \\ C(L, t) &= 0 && t > 0 \end{aligned}$$

where S = the solubility coefficient of the solute in the membrane, in M/M .

Initially the solute concentration in the membrane is zero, i. e.,

$$(1c) \quad C(x, 0) = 0 \quad , \quad 0 < x < L$$

Equation (1) is the inhomogeneous initial-boundary value problem that represents the transport problem where diffusion is considered the limiting process, i. e. the diffusion term is negligible compared with $K_2 C(0, t)$ as discussed in section I-B, equation I-(9).

In order to solve this problem it is convenient to express the solution, $C(x, t)$, as the sum of two solutions $U(x, t)$ and $W(x, t)$ where one of the solutions is the solution of the homogeneous problem corresponding to (1).

Let

$$(2) \quad C(x, t) = U(x, t) + W(x, t) .$$

Then

$$\text{D. E.} \quad U_t(x, t) - D U_{xx}(x, t) = - (W_t(x, t) - D W_{xx}(x, t))$$

$$(3) \quad \text{B. C.} \quad U(0, t) = S C_0 - W(0, t)$$

$$U(L, t) = - W(L, t)$$

$$\text{I. C.} \quad U(x, 0) = -W(x, 0)$$

where D. E. = differential equation

B. C. = boundary conditions

I. C. = initial condition .

If one chooses $W(x, t)$ such that (3) is homogeneous in $U(x, t)$,

$$- W(L, t) = 0$$

$$(4) \quad S C_0 - W(0, t) = 0$$

$$W_t(x, t) - D W_{xx}(x, t) = 0 .$$

$$(5) \quad \text{Try} \quad W(x, t) = \alpha x + \beta$$

$$\text{then} \quad W(0, t) = \beta = S C_0$$

$$\text{and} \quad W(L, t) = 0 = \alpha L + \beta$$

$$\text{so} \quad \alpha = \frac{-\beta}{L} = \frac{-S C_0}{L}$$

and

$$(6) \quad W(x, t) = W(x) = SC_0 \left(1 - \frac{x}{L} \right).$$

Then (3) becomes,

$$(7) \quad \begin{aligned} \text{D. E.} \quad & U_t(x, t) - DU_{xx}(x, t) = 0 \\ \text{B. C.} \quad & U(0, t) = 0 \\ & U(L, t) = 0 \\ \text{I. C.} \quad & U(x, 0) = SC_0 \left(\frac{x}{L} - 1 \right). \end{aligned}$$

Looking for solutions of (7) that are separable, i. e. of the form,

$$(8) \quad U(x, t) = X(x) T(t)$$

equation (7) becomes,

$$(9) \quad XT' - DX''T = 0$$

or

$$\frac{X''}{X} = \frac{T'}{T} = -\lambda \quad \text{where } -\lambda \text{ is a constant and the}$$

primed quantities are differential quantities, i. e. $T' = \frac{dT(t)}{dt}$
and $X'' = \frac{d^2X(x)}{dx^2}$.

Equation (9) can be set equal to a constant since the left-hand side is a function of x only and is independent of t , and the right-hand side is a function of t only and is independent of x , therefore both sides of the equation must be independent of both x and t or equal to some constant, e. g. $-\lambda$.

Equation (9) can be written as two separate ordinary differential equations.

$$(10) \quad X'' + \lambda X = 0$$

and

$$(11) \quad T' + D\lambda T = 0$$

The general solutions of (10) and (11) are, respectively,

$$(12) \quad X = \bar{P} \cos \sqrt{\lambda} x + \bar{Q} \sin \sqrt{\lambda} x$$

and

where \bar{P} , \bar{Q} and T_0 are

$$(13) \quad T = T_0 e^{-\lambda Dt}$$

arbitrary constants.

The general solution of the differential equation (D. E.)

of (7) is then,

$$(14) \quad U(x, t) = X(x) T(t) = e^{-\lambda Dt} \left[P \cos \sqrt{\lambda} x + Q \sin \sqrt{\lambda} x \right]$$

$$\text{where } P = T_0 \bar{P}$$

$$\text{and } Q = T_0 \bar{Q}$$

The values of P and Q can be determined from the boundary conditions (B. C.) of (7). Substituting (14) into the B. C. of (7),

$$(15) \quad P \cos \sqrt{\lambda} \cdot 0 + Q \sin \sqrt{\lambda} \cdot 0 = 0$$

$$\text{and } P \cos \sqrt{\lambda} L + Q \sin \sqrt{\lambda} L = 0$$

Non-trivial values of P and Q exist only if the determinant of their coefficients is zero, i. e.

$$(16) \quad \begin{vmatrix} 1 & 0 \\ \cos \sqrt{\lambda} L & \sin \sqrt{\lambda} L \end{vmatrix} = 0$$

or if

$$(17) \quad \sin \sqrt{\lambda} L = 0 .$$

The λ 's for which (17) holds are the eigenvalues of the problem and can be shown to be

$$(18) \quad \lambda_n = \left(\frac{n\pi}{L} \right)^2 \quad \text{where } n = 1, 2, \dots$$

The eigenfunctions corresponding to the λ_n 's can be found by first determining P and Q from (15) for the λ_n 's and then substituting these values of P and Q into (14).

From (15),

$$P = 0$$

and Q is arbitrary so that the general solutions for the D. E.

and B. C. of (7) from (14) are then,

$$(19) \quad U_n(x, t) = Q_n e^{-\lambda_n D t} \sin \sqrt{\lambda_n} x. \quad n = 1, 2, \dots$$

By selecting a particular linear combination of the solutions given in (19), the remaining condition of the initial-boundary value problem in (7) can be satisfied*, i. e. it is required that the Q_n 's in (19) be such that,

*This was the noted discovery made by Fourier, that one could generally represent a given function by an infinite series, of sines and cosines. Euler attempted this feat unsuccessfully a few years earlier in the 1790's.

$$(20) \quad U(x,0) = SC_0 \left(\frac{x}{L} - 1 \right) = \sum_{n=1}^{\infty} Q_n \sin \frac{n\pi x}{L} .$$

Since the infinite series in (20) is composed of a set of orthogonal functions⁷, the coefficients Q_n can be evaluated from (21).

$$(21) \quad Q_n = \frac{\int_0^L SC_0 \left(\frac{x}{L} - 1 \right) \sin \frac{n\pi x}{L} dx}{\int_0^L \sin^2 \frac{n\pi x}{L} dx} = \frac{2}{L} \int_0^L SC_0 \left(\frac{x}{L} \sin \frac{n\pi x}{L} - \sin \frac{n\pi x}{L} \right) dx$$

Equation (21) simplifies with the use of (17) to,

$$(22) \quad Q_n = \frac{-2SC_0}{n\pi} .$$

From (19), (20) and (22) the solution of the initial-boundary value problem in (7) is

$$(23) \quad U(x,t) = \sum_{n=1}^{\infty} \frac{-2SC_0}{n\pi} \sin \frac{n\pi x}{L} e^{\frac{-n^2\pi^2 Dt}{L^2}} .$$

From (2), (6) and (23) the solution of the initial-boundary value problem in (1) is

$$(24) \quad C(x,t) = SC_0 \left(1 - \frac{x}{L} \right) - \sum_{n=1}^{\infty} \frac{2SC_0}{n\pi} \sin \frac{n\pi x}{L} e^{\frac{-n^2\pi^2 Dt}{L^2}} .$$

Equation (24) describes the solute concentration distribution inside the membrane and can be used to find the flux out of the membrane at $x=L$ (the downstream surface of the membrane). The number of m moles of solute that have diffused into the downstream chamber after time t can be found by integrating the flux out of the membrane at $x=L$ over the time t , i. e.

$$(25) \quad n_d(t) = - \int_0^t A D C_x(L, t) dt + B$$

where $n_d(t)$ = the number of m moles of solute in the downstream chamber after time t .

A = the area of the membrane.

B = the constant of integration.

Differentiating (24) with respect to x , substituting into (25) and integrating (25) with respect to t ,

$$(26) \quad n_d(t) = ASC_0D \left[\frac{t}{L} - \sum_{n=1}^{\infty} \frac{2L}{n^2\pi^2 D} \cos \frac{n\pi L}{L} e^{-\frac{n^2\pi^2 Dt}{L^2}} \right] + B.$$

The constant of integration, B , can be found at $t=0$ since $n_d(0) = 0$.

$$(27) \quad 0 = - ASC_0D \sum_{n=1}^{\infty} \frac{2L}{n^2\pi^2 D} \cos n\pi + B$$

Substituting (27) into (26) and replacing $\cos n\pi$ by $(-1)^n$, the total number of m moles that have diffused into the downstream chamber after time t is given by (28).

$$(28) \quad n_d(t) = ASC_oD \left[\frac{t}{L} + \sum_{n=1}^{\infty} \frac{2L(-1)^n}{n^2\pi^2 D} \left(1 - e^{-\frac{n^2\pi^2 Dt}{L^2}} \right) \right]$$

The relationship between the steady-state differential permeability coefficient (K) (henceforth referred to as the permeability coefficient) and the solubility (S) and diffusion (D) coefficients from (28) is

$$(29) \quad K = \frac{L}{AC_o} \left(\frac{dn_d(t)}{dt} \right)_{t \rightarrow \infty} = SD$$

The expression for the time-lag of the system as first found by Daynes⁸ and later by Barrer⁹ can also be found from (28). The time-lag is the time-axis intercept of the plot of $n_d(t)$ versus t extrapolated from the linear steady-state portion of the curve (see fig. 1), i. e.

$$(30) \quad 0 = ASC_oD \left[\frac{t_1}{L} + \frac{2L}{\pi^2 D} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \right]$$

$$0 = \frac{t_1}{L} + \frac{2L}{\pi^2 D} \left(-\frac{\pi^2}{12} \right)$$

$$t_1 = \frac{L^2}{6D}$$

where t_1 = the time-lag (the time-axis intercept), in sec.

L = the membrane thickness, in cm.

D = the diffusion coefficient of the solute in the
membrane, in cm^2/sec .

The relation between the time-lag and the time for steady-state is given by (31) where the time* corresponding to the root-mean-square distance being set equal to L is commonly taken as the time for steady-state, i. e.

$$(31) \quad T = \frac{L^2}{2D} = 3t_1 \quad \text{where } T = \text{the time for steady-state,} \\ \text{in sec.}$$

From (28) one can see that the error in using (31) to determine $\frac{dn_d(t)}{dt}$ as t approaches infinity is about 1 percent and therefore valid to determine K for most problems.

It should be noted that while the error in K obtained at T is only about 1 percent or less from the K found as t approaches infinity, experimentally T is not uniquely determined and hence in an experiment is not precisely known. The time-lag, t_1 , is uniquely determined and by proper choice of the experiment can be precisely known. The time-lag

*The derivation of the relationship between the time and the root-mean-square distance travelled by a particle has been given by Einstein. ⁴

measured for a system, however, is dependent on the boundary conditions of the problem; the result in (30) is correct for the boundary conditions given in (1). A somewhat different result will be obtained in Section III where other boundary conditions are chosen. By measuring the permeability coefficient and the time-lag of the system one can obtain two of the three experimental parameters of the system directly, i. e. K and D , and the third parameter, S , indirectly using (29). Hence from the two measurements the two fundamental parameters, D and S , are determined.

In many systems, e. g. using thin membranes and gas solutes, the time-lag is extremely short (in some cases of the order of a few seconds or less). Using the method of Dayne's to obtain the time-lag from the short-time data, then requires either a long extrapolation of the data to the time-axis or a detection system capable of making measurements in the first few seconds of the experiment and at few-second intervals thereafter. In general the detection systems available for diffusion studies are not responsive enough to measure the time-lag for thin membranes from the short-time data and the long extrapolation of the more leisurely obtained data to the time-axis introduces large errors in the measurement of the time-lag.

From (28) one can define the integral permeability coefficient, \bar{K} . This quantity is useful in finding the time-lag (and hence the solubility and diffusion coefficients) from the long-time data.

$$(32) \quad \bar{K} = \frac{L}{AC_0} \frac{n_d(t)}{t} = SD \left[1 + \sum_{n=1}^{\infty} \frac{2L^2(-1)^n}{t\pi^2 Dn^2} \left(1 - e^{-\frac{n^2\pi^2 Dt}{L^2}} \right) \right]$$

Taking the logarithms (natural) of both sides,

$$(33) \quad \ln \bar{K} = \ln SD + \ln \left[1 + \frac{2L^2}{tD\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n (1 - e^{-\frac{n^2\pi^2 Dt}{L^2}})}{n^2} \right]$$

For t large ($t \gg \frac{2L^2}{D}$), the last term in (33) can be simplified, yielding

$$(34) \quad \ln \bar{K} = \ln SD + \frac{2L^2}{D\pi^2 t} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2}$$

or

$$(35) \quad \ln \bar{K} = \ln K - \frac{t_1}{t}$$

Therefore if one plots $\ln \bar{K}$ versus $1/t$, the intercept at $1/t = 0$ is the logarithm of the permeability coefficient, K , defined by (29) and the slope as $1/t$ approaches zero is the negative of the time-lag, t_1 , defined by (30) (see fig. 2). It should be noted that in using either the Dayne's extrapolation of the short-time data or the above method for the long-time data to find small values of t_1 , the start of the experiment must be well defined. In the case where t_1 is large this condition still applies but violations on the order of, for example, a few seconds or so

are negligible. For the case of thin membranes these same violations could be astronomical in comparison with t_1 .

The form of (32) suggests that one might be able to find a slope having S separated from D as one of its factors. If one differentiates (32) with respect to t and looks at times large compared to t_1 ,

$$(36) \quad \frac{d\bar{K}}{dt} = \sum_{n=1}^{\infty} \frac{2S(-1)^{n+1} L^2}{t^2 \pi^2 n^2} = \frac{SL^2}{6t^2}$$

Multiplying both sides by $-t^2$, (36) can be rewritten as

$$(37) \quad \frac{d\bar{K}}{d(1/t)_0} = \frac{-SL^2}{6}$$

Therefore if one plots \bar{K} versus $1/t$, the slope of the plot for $1/t$ approaching zero contains the solubility coefficient, S , as a factor, independent of the other parameters K and D . One notes from (32) that the intercept at $1/t = 0$ is K for the plot \bar{K} versus $1/t$.

In concluding this section, it should be iterated that the boundary conditions used here are the same as used traditionally by Fourier (in heat conduction), Fick and others. Subsequent to their work numerous permanent gas-membrane (particularly rubber) permeability measurements have been made verifying the adequacy of these B. C. for the description of the molecular transport in many systems. In addition, some of these systems have been shown

independently to obey Henry's law (essentially the form of the B. C. at $x = 0$ in (1b)). There are, however, many systems other than these permanent gas-membrane systems which are not adequately described by the relations of this section. It is the transport in some of these systems that the modification developed in Section III attempts to describe.

III. A General Expression Considering Both the Solute-Membrane Interaction and the Diffusion Processes in Transport.

The case to be considered here is a generalization of the problem considered in Section II in that the diffusion term is included in each of the boundary conditions. The results of Section II are adequate to describe molecular transport systems where this term is negligible. By including the diffusion term the results have wider applicability, particularly to thin membrane and tenacious solute-membrane interaction systems. As in Section II, the time for the concentration at the surface to reach equilibrium is assumed to be negligible in comparison with the time for steady-state diffusion through the membrane.

The differential equation describing the process is the one-dimensional Fourier relation:

$$(1a) \quad C_t(x, t) = D C_{xx}(x, t) \quad 0 < x < L, \quad t > 0$$

where the quantities are the same as defined in II -(1).

For a membrane of thickness L located between two infinite baths of concentration C_0 and zero for all time, the boundary conditions chosen include separate terms for sorption, desorption and diffusion at $x = 0$ and terms for desorption and diffusion at $x = L$ (there is no sorption term at $x = L$ since the adjacent bath is maintained at zero concentration for all time). Subtracting the diffusion term ($-D C_x(x, t)$) from the boundary

condition at $x = 0$ (I -(9)) and adding it to the boundary condition at $x = L$, the boundary conditions are (assuming I -(10)),

$$(1b) \quad DC_x(0,t) - K_2C(0,t) + N = 0$$

and

$$t > 0$$

$$DC_x(L,t) - K_2'C(L,t) = 0$$

where

$$N = K_1C_0 = \text{constant.}$$

K_1 = the sorption rate coefficient at $x = 0$.

K_2 = the desorption rate coefficient at $x = 0$.

K_2' = the desorption rate coefficient at $x = L$.

$$C_x(0,t) = (\partial C(x,t)/\partial x)_t \text{ at } x = 0.$$

$$C_x(L,t) = (\partial C(x,t)/\partial x)_t \text{ at } x = L.$$

Initially the solute concentration in the membrane is zero, i.e.

$$(1c) \quad C(x,0) = 0 \quad . \quad 0 < x < L$$

The method of solution of the initial-boundary value problem given in (1) is similar to that used in Section II and will be somewhat abbreviated to avoid excessive repetition.

Let

$$(2) \quad C(x, t) = U(x, t) + W(x, t)$$

where $W(x, t)$ is chosen such that the initial-boundary value problem for $U(x, t)$ is homogeneous.

Try

$$(3) \quad W(x, t) = \alpha x + \beta$$

For

$$\alpha = \frac{K_2' N}{K_2 D - K_2' D - K_2 K_2' L}$$

and

$$\beta = \frac{N(D - K_2' L)}{K_2 D - K_2' D - K_2 K_2' L}$$

or in a more convenient form,

$$(4) \quad W(x) = \bar{A}(x - L) - \bar{B}$$

$$\text{where } \bar{A} = \frac{NK_2'}{K_2 D - K_2' D - K_2 K_2' L}$$

$$\text{and } \bar{B} = \frac{-ND}{K_2 D - K_2' D - K_2 K_2' L}$$

The homogeneous initial-boundary value problem in terms of $U(x, t)$ is

$$(5) \quad \begin{array}{ll} \text{D. E.} & U_t(x, t) = D U_{xx}(x, t) \\ \text{B. C.} & DU_x(0, t) - K_2 U(0, t) = 0 \\ & DU_x(L, t) - K_2' U(L, t) = 0 \\ \text{I. C.} & U(x, 0) = \bar{A}(L - x) + \bar{B}. \end{array}$$

By solving this homogeneous problem for $U(x, t)$ and remembering (2) where $W(x, t)$ is given by (4), the solution to (1), $C(x, t)$, can be found.

Assuming that the solution $U(x, t)$ of (5) is separable, i. e.

$$(6) \quad U(x, t) = X(x) T(t)$$

the differential equation (D. E.) in (5) becomes,

$$(7) \quad XT' - D X'' T = 0$$

Dividing by XT and rearranging, and equating to the constant $-\lambda$ by the usual arguments (see Section II),

$$(8) \quad \frac{X''}{X} = \frac{T'}{DT} = -\lambda$$

The two ordinary differential equations in (8) have the general solutions

$$(9) \quad X(x) = \bar{P} \cos \sqrt{\lambda} x + \bar{Q} \sin \sqrt{\lambda} x$$

$$(10) \quad T(t) = T_0 e^{-\lambda Dt}$$

Solving (9) for the boundary conditions (B. C.) given in (5), i. e.

$$(11) \quad DX_x(0) - K_2 X(0) = 0$$

and

$$DX_x(L) - K_2' X(L) = 0$$

yields

$$(12) \quad \sqrt{\lambda} D \bar{Q} - K_2 \bar{P} = 0$$

$$(13) \quad \bar{Q} (D\sqrt{\lambda} \cos\sqrt{\lambda} L - K_2' \sin\sqrt{\lambda} L) + \bar{P} (-D\sqrt{\lambda} \sin\sqrt{\lambda} L - K_2' \cos\sqrt{\lambda} L) = 0$$

For a non-trivial solution of (12) and (13) the determinant of the coefficients of \bar{P} and \bar{Q} must equal zero.

$$(14) \quad \begin{vmatrix} -K_2 & \sqrt{\lambda} D \\ -(D\sqrt{\lambda} \sin\sqrt{\lambda} L + K_2' \cos\sqrt{\lambda} L) & (\sqrt{\lambda} D \cos\sqrt{\lambda} L - K_2' \sin\sqrt{\lambda} L) \end{vmatrix} = 0$$

Solving (14) and rearranging,

$$(15) \quad \tan \sqrt{\lambda} L = \frac{\sqrt{\lambda} D (K_2 - K_2')}{(K_2 K_2' + D^2 \lambda)}$$

For $K_2' = K_2$, (15) simplifies to,

$$(16) \quad \sin \sqrt{\lambda} L = 0$$

and $\lambda_n = \left(\frac{n\pi}{L}\right)^2, \quad n = 1, 2, \dots$

For $K_2' \neq K_2$, the two sides of (15) can be set equal to two functions of $\sqrt{\lambda}$, i. e.

$$(17) \quad y_1 = \tan \sqrt{\lambda} L$$

$$y_2 = \frac{D (K_2 - K_2') \sqrt{\lambda}}{(K_2 K_2' + D^2 \lambda)}$$

One can then solve for $\sqrt{\lambda}_n$ graphically by plotting y_1 and y_2 versus $\sqrt{\lambda}$. The abscissae of the intersections of y_1 and y_2 mark the eigenvalues λ_n . In the treatment presented here, however, only the case of $K_2 = K_2'$ will be considered. Since (16) determines the eigenvalues when the

relationship between \bar{P} and \bar{Q} is given by (12) (or by (13), the eigenfunctions that satisfy the B. C. of (5) are

$$(18) \quad X_n(x) = P_n \left(\cos \sqrt{\lambda_n} x + \frac{K_2}{\sqrt{\lambda_n} D} \sin \sqrt{\lambda_n} x \right), \quad n = 1, 2, \dots$$

The solutions that satisfy the D. E. and the B. C. of (5) are then (from (6), (10) and (18)),

$$(19) \quad U_n(x, t) = X_n(x) T_n(t) = P_n \left(\cos \sqrt{\lambda_n} x + \frac{K_2}{\sqrt{\lambda_n} D} \sin \sqrt{\lambda_n} x \right) e^{-\lambda_n D t} \quad n = 1, 2, \dots$$

where T_0 and \bar{P}_n have been incorporated into the arbitrary constant P_n .

The general solution of the initial-boundary value problem (5) can then be found by taking a suitable linear combination of the solutions given in (19) such that this combination satisfies the initial conditions (I. C.) of (5). The general solution of (5) then takes the form of the infinite series given in (20).

$$(20) \quad U(x, t) = \sum_{n=1}^{\infty} P_n \left(\cos \sqrt{\lambda_n} x + \frac{K_2}{\sqrt{\lambda_n} D} \sin \sqrt{\lambda_n} x \right) e^{-\lambda_n D t}$$

For (20) to satisfy the I. C. of (5), (21) must hold for $0 < x < L$,

$$(21) \quad U(x, 0) = \bar{A}(L - x) + \bar{B} = \sum_{n=1}^{\infty} P_n \left(\cos \sqrt{\lambda_n} x + \frac{K_2}{\sqrt{\lambda_n} D} \sin \sqrt{\lambda_n} x \right).$$

Since the infinite series is composed of orthogonal functions, the P_n 's in the series can be determined by multiplying both sides of (21) by

$\left(\cos \sqrt{\lambda_m} x + \frac{K_2}{\sqrt{\lambda_m} D} \sin \sqrt{\lambda_m} x \right)$ and integrating over the range of x from 0 to L .

For $m \neq n$, the corresponding terms in the series vanish by orthogonality arguments⁷ (this is easily verified directly by integration) so that the following expression for the P_n 's can be written where $m=n$.

$$(22) \quad P_n = \frac{\int_0^L (\bar{A}(L-x) + \bar{B}) \left(\cos \sqrt{\lambda_n} x + \frac{K_2}{\sqrt{\lambda_n} D} \sin \sqrt{\lambda_n} x \right) dx}{\int_0^L \left(\cos \sqrt{\lambda_n} x + \frac{K_2}{\sqrt{\lambda_n} D} \sin \sqrt{\lambda_n} x \right)^2 dx} \quad n = 1, 2, \dots$$

Evaluating the integrals in (22),

$$(23) \quad P_n = \frac{((1 - \cos n\pi)(K_2(\bar{A}L + \bar{B}) + \bar{A}D) + \bar{A}LK_2 \cos n\pi)}{L(\lambda_n D^2 + K_2^2)} \quad n = 1, 2, \dots$$

or representing the even terms in (23) by $n = 2m$ and the odd terms in (23) by $n = 2m-1$,

$$(24) \quad P_{2m} = \frac{2\bar{A}K_2D}{(\lambda_{2m}D^2 + K_2^2)} \quad m = 1, 2, \dots$$

$$P_{2m-1} = \frac{(\bar{A}LK_2 + 2\bar{B}K_2 + 2\bar{A}D) 2D}{L(\lambda_{2m-1}D^2 + K_2^2)}$$

Substituting (24) into (20), the general solution for the initial-boundary value problem given in (5) is

$$(25) \quad U(x,t) = \sum_{m=1}^{\infty} \left[\frac{2D(\bar{A}LK_2 + 2\bar{B}K_2 + 2\bar{A}D)}{L(\lambda_{2m-1}D^2 + K_2^2)} \left(\cos \frac{(2m-1)\pi x}{L} + \frac{K_2L}{(2m-1)\pi D} \sin \frac{(2m-1)\pi x}{L} \right) \exp(-\lambda_{2m-1}Dt) + \frac{2\bar{A}K_2D}{(\lambda_{2m}D^2 + K_2^2)} \left(\cos \frac{2m\pi x}{L} + \frac{K_2L}{2m\pi D} \sin \frac{2m\pi x}{L} \right) \exp(-\lambda_{2m}Dt) \right]$$

The general solution to the initial-boundary value problem given in (1) can then be found from (2), (4) and (25),

$$(26) \quad C(x,t) = \bar{A}(x - L) - \bar{B} + \sum_{m=1}^{\infty} \left[\frac{2D(\bar{A}K_2 + 2\bar{B}K_2 + 2\bar{A}D)}{L(\lambda_{2m-1}^2 D^2 + K_2^2)} \left(\cos \frac{(2m-1)\pi x}{L} + \frac{K_2 L}{(2m-1)\pi D} \sin \frac{(2m-1)\pi x}{L} \right) \exp(-\lambda_{2m-1}^2 Dt) + \frac{2\bar{A}K_2 D}{(\lambda_{2m}^2 D^2 + K_2^2)} \left(\cos \frac{2m\pi x}{L} + \frac{K_2 L}{2m\pi D} \sin \frac{2m\pi x}{L} \right) \exp(-\lambda_{2m}^2 Dt) \right]$$

The total number of m moles that have diffused into the downstream chamber after time t , $n_d(t)$, can be found by integrating the flux out of the membrane at the downstream surface over t , i.e.

$$(27) \quad n_d(t) = - \int_0^t ADC_x(L,t) dt + B$$

The integration constant, B , in (27) can be evaluated at $t = 0$ since $n_d(0) = 0$. Substituting for \bar{A} and \bar{B} (from (4)) in the integrated form of (27), and remembering that K_2 is assumed equal to K_2' in this treatment and that $N = K_1 C_0$ where C_0 is constant for all time, the expression for $n_d(t)$ can be written as,

$$(28) \quad n_d(t) = AC_0 S \left[\frac{Dt}{L} + \sum_{n=1}^{\infty} \frac{(-1)^n 2K_2^2 (1 - e^{-\lambda_n^2 Lt})}{\lambda_n L (\lambda_n^2 D^2 + K_2^2)} \right]$$

where $S = \frac{K_1}{K_2}$ = the solubility coefficient (from I -(11)).

The expression for $n_d(t)$ derived in the previous section (II -(28)) is a limiting form of (28) derived above where the diffusion term is negligible with respect to the desorption term, i. e. $\frac{D}{L} \ll K_2$. If the term $\lambda_n D^2$ is neglected in (28) then (28) is identical with II -(28).

Many similarities appear also in the results derived from (28) above and the results derived from II-(28) in the previous section. For example, the permeability coefficient predicted from (28),

$$(29) \quad K = \frac{L}{AC_0} \left(\frac{dn_d(t)}{dt} \right)_{t \rightarrow \infty} = S D$$

is identical with the permeability coefficient predicted in the previous section, II -(29). The expression for the time-lag can be derived from (28),

$$0 = AC_0 S D \left[\frac{t_1}{L} + \sum_{n=1}^{\infty} \frac{(-1)^n 2K_2^2 L}{n^2 \pi^2 D \left(\frac{n^2 \pi^2 D}{L^2} + K_2^2 \right)} \right]$$

$$t_1 = \frac{2K_2^2 L^2}{\pi^2 D} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^2 \left(\frac{n^2 \pi^2 D^2}{L^2} + K_2^2 \right)}$$

$$t_1 = \frac{2K_2^2 L^2}{\pi^2 D} \left[\frac{\pi^2}{12K_2^2} + \frac{\pi^2 D}{2LK_2^3 \sinh \frac{K_2 L}{D}} - \frac{\pi^2 D^2}{2K_2^4 L^2} \right]$$

$$(30) \quad t_1 = \frac{L^2}{6D} + \frac{L}{K_2 \sinh K_2 L/D} - \frac{D}{K_2^2}$$

The time-lag expression derived in the previous section, II -(30),

is seen to be a limiting form of (30) derived above, i. e. where

$\frac{D}{L} \ll K_2$. Intuitively, the time-lag should decrease with decreasing membrane thickness and continuously approach zero for L approaching zero. Using l'Hospital's rule¹⁰ for evaluating the limit of 0/0, the limit of t_1 given in (30) as L approaches zero is,

$$(31) \quad \lim_{L \rightarrow 0} t_1 = \lim_{L \rightarrow 0} \left(\frac{L}{K_2 \sinh K_2 L/D} - \frac{D}{K_2} \right) = \left(\frac{1}{\frac{K_2}{D} \cosh 0} - \frac{D}{K_2} \right) = 0$$

At large L, (30) simplifies to

$$(32) \quad t_1 = \frac{L^2}{6D} - \frac{D}{K_2^2}$$

so that a plot of t_1 versus L^2 approaches the straight line having a slope of $\frac{1}{6D}$ and a $L = 0$ intercept of $-\frac{D}{K_2^2}$ as L becomes large (see fig. 3). Therefore, D and K_2 can easily be obtained experimentally by measuring t_1 at a few membrane thicknesses in the range where t_1 versus L^2 is linear. If the permeability coefficient, K, is also measured, then all of the fundamental parameters, i. e. D, K_2 and K_1 , can be found for the solute-membrane system using (29) where $S = K_1/K_2$.

In some cases t_1 may be too short to be conveniently measured from the short-time data by the Dayne's method. However, as in the previous section, (28) can be used to derive an expression for the integral permeability coefficient which is useful to obtain t_1 from the long-time data.

$$(33) \quad \bar{K} = \frac{1}{AC_0} n_d(t)/t = SD \left[1 + \sum_{n=1}^{\infty} \frac{(-1)^n 2K_2^2 L^2 (1 - e^{-\frac{n^2 \pi^2 Dt}{L^2}})}{t \pi^2 L n^2 (\frac{n^2 \pi^2 D^2}{L^2} + K_2^2)} \right]$$

Taking logarithms of both sides,

$$(34) \quad \ln \bar{K} = \ln K + \ln \left[1 + \frac{2K_2^2 L^2}{t \pi^2 D} \sum_{n=1}^{\infty} \frac{(-1)^n (1 - e^{-\frac{n^2 \pi^2 Dt}{L^2}})}{n^2 (\frac{n^2 \pi^2 D^2}{L^2} + K_2^2)} \right]$$

for $1/t \rightarrow 0$,

$$(35) \quad \ln \bar{K} = \ln K - \frac{t_1}{t}$$

where t_1 is given by (30).

Equation (35) above is similar to the equation II -(35) derived in the previous section except that the expression for t_1 is more general. Experimentally, t_1 can be obtained from the slope of the plot $\ln \bar{K}$ versus $1/t$ as $1/t$ approaches zero (see fig. 2). The intercept is again $\ln K$. The condition that the start of the experiment be well-

defined commented on in Section II also must be observed here.

The result II -(37) where the solubility coefficient, S, is proportional to the slope of the plot \bar{K} versus $1/t$ as $1/t$ approaches 0 is seen to be a limiting result of the more general expression derived from (33).

$$(36) \quad \frac{d\bar{K}}{d(1/t)_0} = \frac{2SK_2^2L}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2 \frac{(n^2 \pi^2 D^2 + K_2^2)}{L^2}} = \frac{-SL^2}{6} - \frac{SDL}{K_2 \sinh K_2 L/D} + \frac{SD^2}{K_2^2}$$

In general (36) indicates that the slope of the plot \bar{K} versus $1/t$ is not independent of K(i. e. S D) and D, but that only in the limiting description of Section II is the slope independent of K and D. A similar complication of the limiting t_1 expression (II -(30)) was shown above to occur in the more general case (30). The same approach to the problem for t_1 is valid here in obtaining the fundamental parameters D, K_1 and K_2 from the slope of the plot \bar{K} versus $1/t$ (36).

At large L, (36) simplifies to

$$(37) \quad - \frac{d\bar{K}}{d(1/t)_0} = \frac{SL^2}{6} - \frac{SD^2}{K_2^2}$$

so that a plot of $-\frac{d\bar{K}}{d(1/t)_0}$ versus L^2 approaches the straight line having a slope $S/6$ and a $L = 0$ intercept of $-\frac{SD^2}{K_2^2}$ as L becomes large (see fig. 4). S and the ratio D/K_2 can be obtained by measuring

the permeability of the system of interest at a few membrane thicknesses in the range where $\frac{-d\bar{K}}{d(1/t)_0}$ versus L^2 is linear. If the permeability coefficient, K , is also measured then all of the fundamental parameters, D , K_2 and K_1 , can be found for the system using (29). The ratio of K to S gives D , which, substituted into the ratio D/K_2 , gives K_2 . The product of K_2 and S is K_1 .

Rearranging (36), remembering that $K = SD$,

$$(38) \quad \frac{-d\bar{K}}{d(1/t)_0} = K \left[\frac{L^2}{6D} + \frac{L}{K_2 \sinh K_2 L/D} - \frac{D}{K_2^2} \right] = K t_1 .$$

From (38) the relationship between K , t_1 and the slope as $1/t$ approaches zero of the plot \bar{K} versus $1/t$ becomes clear. In all of the methods described thus far for obtaining the fundamental parameters of the system of interest it has been necessary to have either t_1 and K or $\frac{-d\bar{K}}{d(1/t)_0}$ and K . Once either pair was known the fundamental parameters of the system could be determined (one may have to know t_1 or $\frac{-d\bar{K}}{d(1/t)_0}$ for a few thicknesses). Since in general all three of the quantities in (38) can be obtained from the same experiment, (38) then provides a valuable check on these three quantities and their use in the calculation of the fundamental parameters.

From the experimental side, one may raise the legitimate query as to the ease with which a system may be classified in terms

of the traditional description of Section II, the more general description of Section III, or some description more sophisticated than either presented here (perhaps accounting for both the x and t derivatives in the boundary conditions or for a chemical reaction occurring within the membrane). In the concluding paragraphs some similarities and differences between the results of sections II and III are developed that are diagnostic for decisions on whether the limiting description of Section II is adequate and on whether a more elaborate description than the descriptions of Sections II and III is required for the system of interest. These decisions can be made on the basis of a single experiment (with one exception that requires two experiments). If two experiments using membranes of different thicknesses are carried out then one can also decide if the description of Section III is adequate.

In the discussion of the time-lag, t_1 , and the time for steady-state, T , given in Section II it was pointed out that t_1 in principle can be precisely determined from experiment. If T were also exactly determined then by comparing T with t_1 , one could determine the adequacy of the traditional description on the basis of a single experiment using II -(31). Minor deviations only from II -(31) would indicate that the traditional description was adequate. Since, however, T can not be determined exactly from experiment, it is not a useful

experimental quantity and one is motivated to look for another quantity precisely defined by a single experiment that can be compared with t_I . One quantity that is useful in this respect is the time needed for the plot of the differential permeability coefficient, K' , versus time of the experiment to reach an inflection point, t_I . At t_I the curvature of the plot changes from positive to negative (see fig. 5).

This point can be obtained directly from the permeability data if the permeability apparatus is of the flow type where the downstream chamber is continuously flushed out with a solvent stream and the measurements made are solute concentration in this stream as a function of time, i. e. $\frac{dn_d(t)}{dt}$. These measurements are proportional to the differential permeability coefficient, K' . If the permeability apparatus is of the no flow type where the solute concentration is allowed to build up in the downstream chamber with time and the measurements made are of this concentration as a function of time, i. e. $n_d(t)$ for a unit downstream chamber volume, then in order to obtain t_I the slope of this data, i. e. $\frac{dn_d(t)}{dt}$, must be found as a function of time. The time coordinate corresponding to the inflection point of the slope versus time plot is t_I .

The experimental point t_I has two disadvantages which should be noted: One, pointed out above, is that for the no flow apparatus where t_I can be obtained directly t_I must be calculated indirectly from

the data and for the flow apparatus where t_1 can be obtained directly t_1 must be calculated indirectly from the data. The second is that t_1 must be obtained from the short-time data and is therefore subjected to the same detector-response limitations elaborated on in Section II in connection with obtaining t_1 from the short-time data.

The inflection-point-time, t_p , however, appears to be the only point that is uniquely determined by experiment (in addition to t_1). These two points therefore are the only experimental quantities that can be precisely determined and compared with their theoretical values.* The experimental uniqueness of t_p and t_1 compared with the

*This last statement is not strictly correct since one could always make a theoretical calculation for any time, e. g. 10^4 seconds, and then by accurately measuring $n_d(10^4)$ or $\frac{dn_d(10^4)}{dt}$ for the system of interest one could make a comparison between experiment and theory. By comparing several points one could with some work determine the fundamental parameters D , K_1 and K_2 if the description of Section III was adequate (or determine D and S if the traditional description was adequate). If constant values of these parameters could not be found then one could conclude that some more sophisticated description was needed. In general this method is arduous and is better reserved as a last-resort method in the case that suitable values of t_p and t_1 can not be obtained.

other points centers about some "discontinuous" or limiting experimental result. The "discontinuous" result applies in the case of t_I and is the change in sign of the curvature of an experimental plot. The limiting result applies in the case of t_I as t_I is related to the steady-state portion of an experimental curve (traditionally by a Dayne's extrapolation, and in the methods of Sections II and III by a slope).

In order to investigate the relationship between t_I and t_I , an expression for K' must be derived from (28) and then the condition for t_I , i. e. $\frac{d^2 K'}{dt^2} = 0$, must be applied.

The differential permeability coefficient is defined as

$$(39) \quad K' = \frac{L}{AC_0} \left(\frac{dn_d(t)}{dt} \right) = \frac{LAC_0 S}{AC_0} \left[\frac{D}{L} + \sum_{n=1}^{\infty} \frac{(-1)^n 2K_2^2 D e^{-\lambda_n D t}}{L(\lambda_n D^2 + K_2^2)} \right]$$

(Note the similarity but not identity of the first equation in (39) to II -(29), the definition of the steady-state differential permeability coefficient, K).

Rearranging and substituting $\lambda_n = \frac{n^2 \pi^2}{L^2}$ into (39),

$$(40) \quad K' = SD \left[1 + \frac{2K_2^2 L^2}{\pi^2 D^2} \sum_{n=1}^{\infty} \frac{(-1)^n e^{-\frac{n^2 \pi^2 D t}{L^2}}}{(n^2 + K_2^2 L^2 / \pi^2 D^2)} \right]$$

Differentiating (40) twice with respect to t and equating to zero,

$$(41) \quad d^2K^*/dt^2 = 0 = \frac{SD2K_2L^2}{\pi^2 D^2} (\pi^2 D/L^2)^2 \sum_{n=1}^{\infty} \frac{(-1)^n n^4 e^{-\frac{n^2 \pi^2 D t_1}{L^2}}}{(n^2 + K_2^2 L^2 / \pi^2 D^2)}$$

Let $a = \frac{\pi^2 D t_1}{L^2}$ and $c = \frac{K_2 L}{\pi D}$, then the condition for t_1 , (41),

becomes

$$(42) \quad 0 = \sum_{n=1}^{\infty} \frac{(-1)^n n^4 e^{-an^2}}{(n^2 + c^2)} .$$

Where the condition (42) holds for some functional relationship between a and c, i. e. each value of c defines a single value of a for a and c both greater than zero. The author has not yet been able to find tables for this series; hence it has not proved possible to uncover the relationship between a and c. It is hoped that in the near future the series can be solved numerically for various values of a and c using an electronic computer. For the purposes of this discussion it is sufficient to designate the relationship by $a = f(c)$ where f is a function determined by (42).

Experimentally, one can obtain numerical values for t_1 and t_2 so that the ratio of t_2 to t_1 is also a number, R, for a given system. If this ratio is written as a function of a and c where f(c) is eventually substituted for a in the expression, then R can be shown to be a function of c alone.

From (30)

$$t_1 = \frac{L^2}{6D} + \frac{L}{K_2 \sinh K_2 L/D} - \frac{D}{K_2^2} = \frac{L^2}{6D} + \frac{L^2}{D\pi c \sinh \pi c} - \frac{L^2}{D\pi^2 c^2}$$

$$t_1 = \frac{\pi^2 t_I}{a} \left[\frac{1}{6} + \frac{1}{\pi c \sinh \pi c} - \frac{1}{\pi^2 c^2} \right]$$

$$(43) \quad R(c) = t_1/t_I = \frac{\pi^2}{f(c)} \left[\frac{1}{6} + \frac{1}{\pi c \sinh \pi c} - \frac{1}{\pi^2 c^2} \right]$$

where $a = f(c)$ and c are defined between (41) and (42).

Equation (43) is readily amenable to evaluation and tabulation using an electronic computer once the fundamental relationship between a and c , $a = f(c)$, is known. Once this table has been constructed an experimental value of R can then be compared with the table in order to find c for the given system. If c is known then a can be found from $a = f(c)$. Using the experimental value of t_1 and a one can determine

D ($D = \frac{aL^2}{\pi^2 t_1}$). Substituting this value of D and the known value of c into the definition of c , K_2 can be found ($K_2 = \frac{cD\pi}{L}$).

The remaining fundamental parameter of the system, K_1 , can be found from (29), where $S = \frac{K_1}{K_2}$, by substituting in the values of D and K_2 found above and the measured permeability coefficient, K .

In order to determine if the description of Section III is adequate, a second experiment using a different thickness of the membrane must be carried out. A favorable comparison of the parameters determined

in the two experiments would indicate that the description of Section III is adequate for the system of interest.

In the limiting description of Section II, K_1 and K_2 are not independently determined so that there is one less fundamental parameter to describe the system, i. e. only D and S. In this case the assumption is made that $K_2 \gg \frac{D}{L}$ (see II -(1)) so that c is much greater than 1 and the condition for t_1 , (42), simplifies to

$$(44) \quad 0 = \sum_{n=1}^{\infty} (-1)^n n^4 e^{-an^2} .$$

The value of a in (44) can be determined and is the same for all experimental systems where the traditional description of Section II is adequate. Using an approximation to a, $a \approx .906$; the equation between (41) and (42) relating t_1 to a; and the limiting form of t_1 given by II -(30), the ratio of t_1 to t_I is

$$(45) \quad t_1/t_I = \frac{\pi^2}{(6)(.906)} = 1.82 .$$

Comparison of the experimental ratio with (45) then indicates the adequacy of the traditional description for the experimental system of interest. The fundamental parameters of D and S can be obtained from

II -(29) and II -(30) in the case that the experimental ratio is sufficiently close to 1.82.

From (42) one notes that the other extreme value of c , i. e. where c approaches zero for $K_2 \ll \frac{D}{L}$, the series is negative for all positive values of a and approaches zero as a approaches zero. In the limit as c approaches zero then t_I also approaches zero. Therefore all the experimental systems that can be adequately described by the results of Sections II and III have ratios of t_I to t_I that are less than or equal to the limiting ratio of (45) of approximately 1.82. Any system having a ratio greater than 1.82 would therefore require a description more sophisticated than those presented here. There may be other descriptions besides those of Sections II and III that have ratios less than or equal to 1.82. For a decision concerning these, two experiments are necessary and an unknown description is concluded to be required in the case that neither the description of Section II nor Section III is found to be adequate.

The method using the ratio t_I to t_I is the most elegant method described here for obtaining the fundamental parameters of the system of interest. At most only two experiments are required to determine the fundamental parameters of the system or to know that a more sophisticated description is needed. Its applicability, however, is hampered by the same restriction that has here been removed from the

measurement of t_1 , namely, the necessity of using the short-time data to obtain t_1 .

In the case that t_1 (and possibly t_I) is not experimentally available from the short-time data, the ratio of t_1 to t_I method can not be used and another approach must be tried using the long-time data. At this point, (38) is particularly helpful since if (38) does not hold, then one knows that a more sophisticated description than either of those given here is required for the system of interest. If (38) does hold then one must attempt to evaluate the fundamental parameters, D , K_1 and K_2 , before making a decision on the adequacy of the descriptions of Section II or III.

From one experiment the two fundamental parameters, D and S , can be determined using , for example, t_1 and K . To show that the traditional description is adequate, however, requires that a second experiment using a different membrane thickness be conducted. If the parameters agree then the traditional description is adequate.

To obtain the fundamental parameters, D , K_1 and K_2 , one could measure t_1 using membranes thick enough that the plot of t_1 versus L^2 is linear according to the discussion following (32). It is conceivable that this may not be experimentally possible (e. g. the necessary thicknesses are not available or t_1 is too large to be measured conveniently with the thick membranes, possibly $t_1 > 10^6$

seconds). In this case the last-resort method described earlier could be used (see footnote on page 55).

To summarize, the main issue of the thesis is to derive a more general relationship than the traditional description to describe the molecular transport phenomena through membranes. This increased generality is achieved by accounting for both the surface (sorption and desorption) and diffusion processes in determining the solute concentrations at the surfaces of the membrane. The traditional description determines the concentration at the surface from considerations of the surface processes only. The difference between these two considerations is seen by comparing II-(1b) with III-(1b). The more general description of Section III is particularly applicable to thin membrane and/or tenacious solute-membrane interaction systems.

In Sections II and III some attention is given to the experimental problem of determining the fundamental parameters of a given system. Measurement of the experimental times t_1 and t_I (see fig's 1, 2 and 5), when possible, provides valuable diagnostic information about the system (see discussion following III-(43)) and is the most elegant technique presented here for the determination of the fundamental parameters.

Section I defines an approach to the general problem of molecular transport through membranes and sets the limits of complexity of the phenomena considered here (e.g. no chemical reactions and a diffusion coefficient that is independent of the distance from the surface of the membrane).

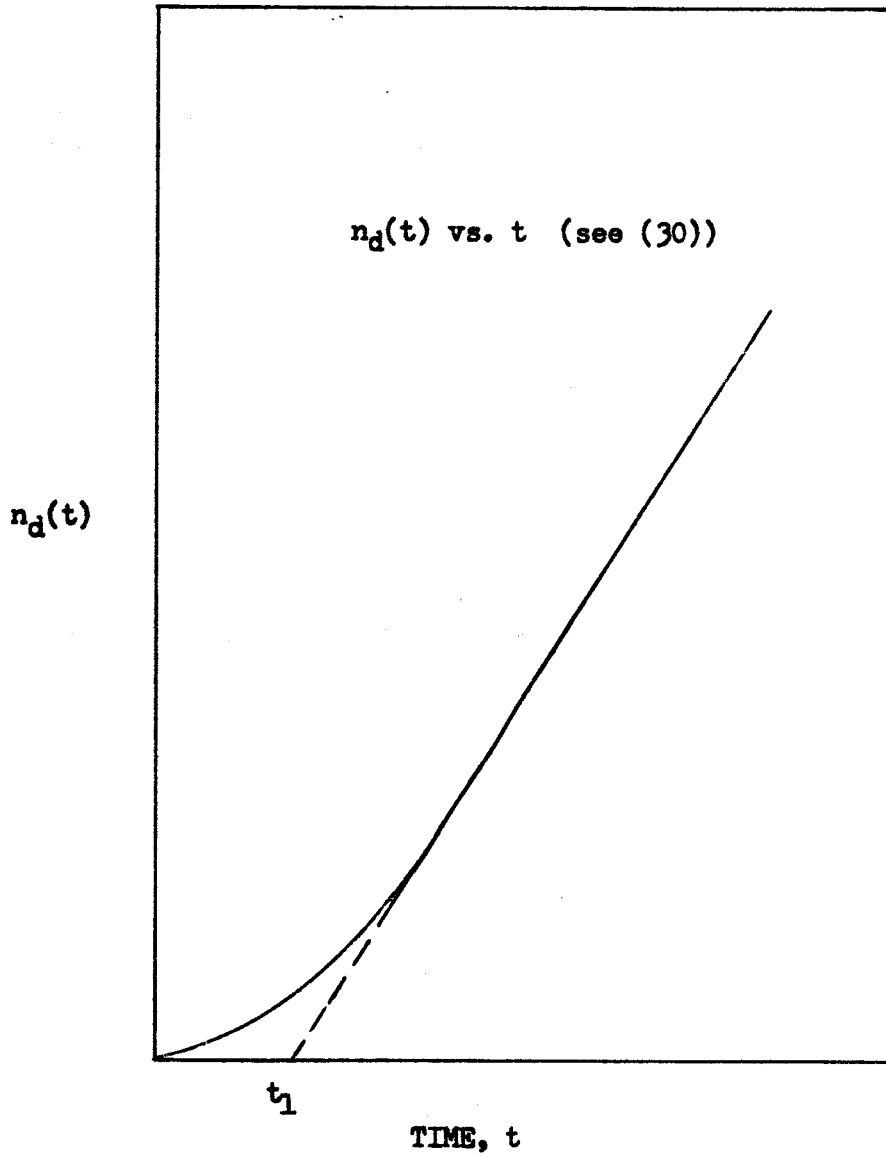


FIGURE 1 Obtaining the time-lag by extrapolation from the linear portion of the permeability curve.

$n_d(t)$ = the number of m moles of solute that have passed through the membrane in time t .

t_1 = the time-lag.

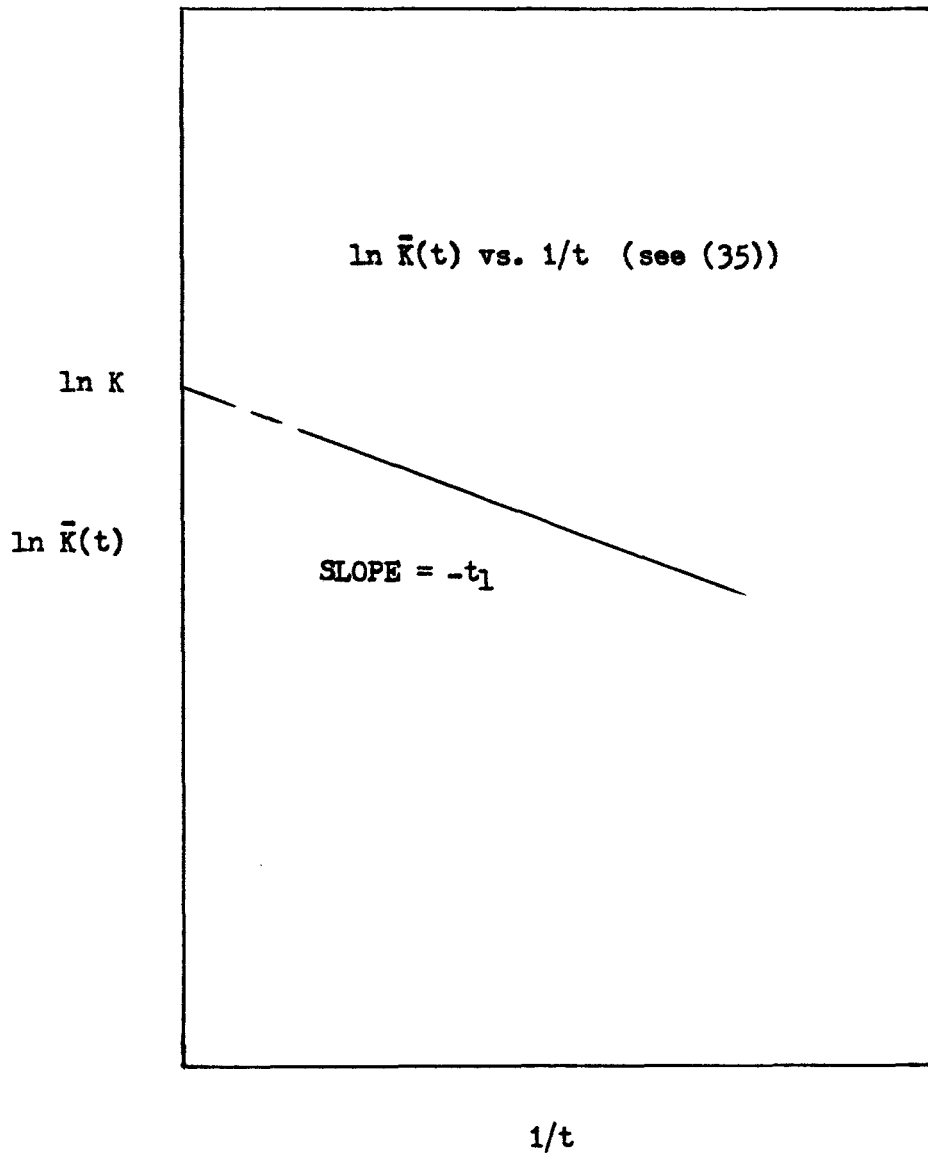


FIGURE 2 Obtaining the time-lag from the long time data.

$\bar{K}(t)$ = the integral permeability coefficient at time t .

K = the permeability coefficient.

t_1 = the time-lag.

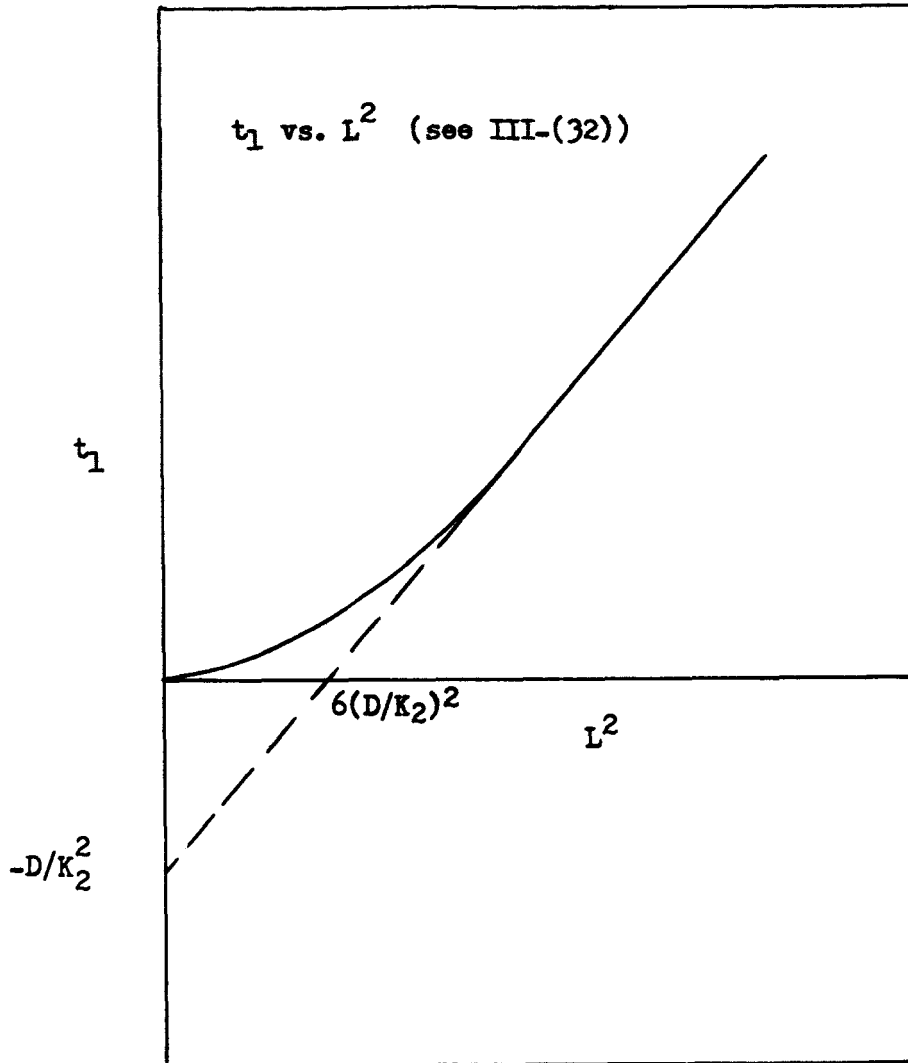


FIGURE 3 Obtaining D and K_2 from measurements of t_1 for different membrane thicknesses.

D = the diffusion coefficient.
 K_2 = the desorption rate coefficient.
 L = the membrane thickness.
 t_1 = the time-lag.

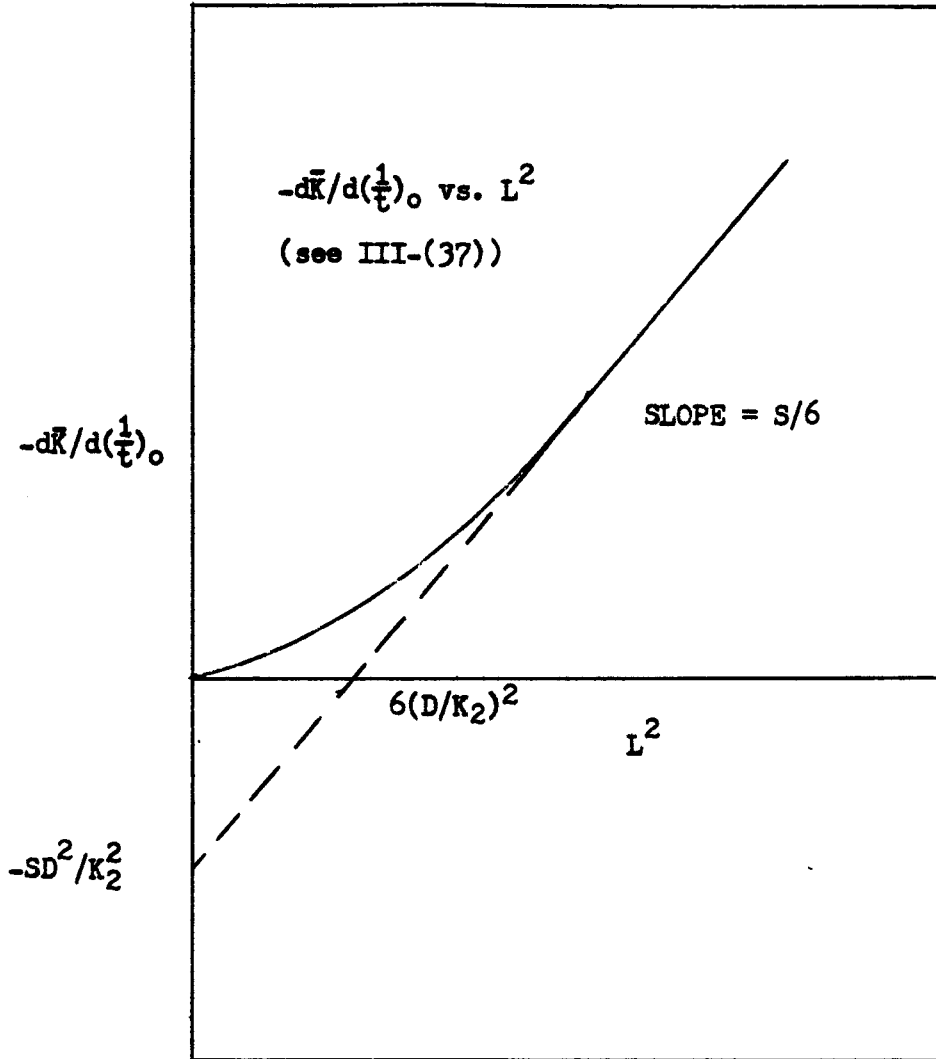


FIGURE 4 Obtaining S and D/K_2 from measurements of the slope as $1/t$ approaches zero, $\bar{dK}/d(\frac{1}{t})_0$, for different membrane thicknesses.

- S = the solubility coefficient.
- D = the diffusion coefficient.
- K_2 = the desorption rate coefficient.
- L = the membrane thickness.

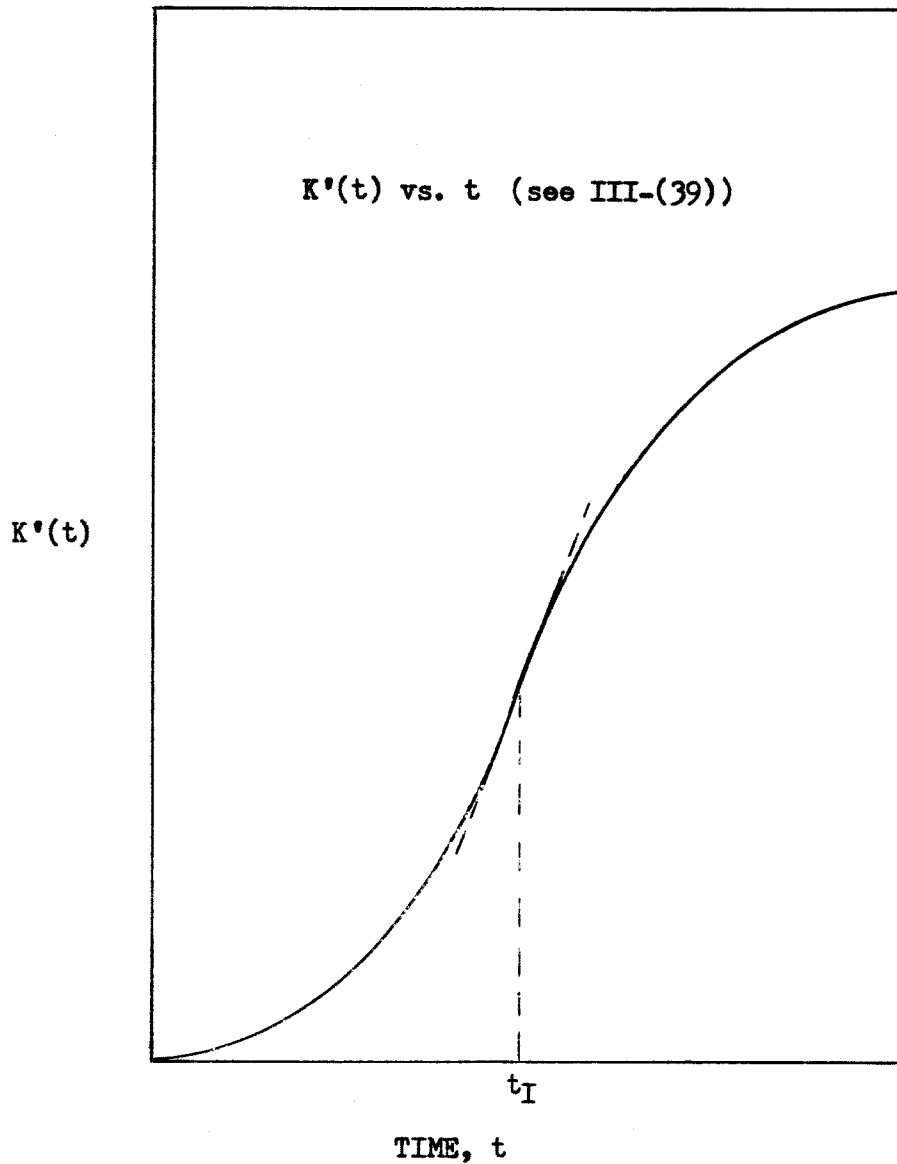


FIGURE 5 Obtaining the inflection-point time from the differential permeability coefficient data.

$K'(t)$ = the differential permeability coefficient at time t .

t_I = the inflection-point time.

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