Analysis of mass transfer across membranes with chemical reaction

Bert C. Wong
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ANALYSIS OF MASS TRANSFER ACROSS MEMBRANES
WITH CHEMICAL REACTION.

IOWA STATE UNIVERSITY, PH.D., 1978
Analysis of mass transfer across membranes with chemical reaction

by

Bert C. Wong

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Co-majors: Biomedical Engineering
Chemical Engineering

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For the Major Department
Signature was redacted for privacy.
For the Graduate College

Iowa State University
Ames, Iowa
1978
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NOMENCLATURE

A \quad \text{species penetrating the membrane}
\noalign{\smallskip}
a_1, a_0 \quad \text{constants of integration}
\noalign{\smallskip}
B \quad \text{product of chemical reaction}
\noalign{\smallskip}
b_0, b_1 \quad \text{constants of integration}
\noalign{\smallskip}
C \quad \text{concentration; kg/m}^3
\noalign{\smallskip}
C^+ \quad \frac{C}{C_{Ao}}; \text{dimensionless}
\noalign{\smallskip}
D \quad \text{diffusivity; m}^2/s
\noalign{\smallskip}
d_0 \quad k \frac{\Delta}{D \cdot C_{Ao}}; \text{dimensionless zeroth-order reaction rate}
\noalign{\smallskip}
E_1, E_2 \quad \text{estrone, estradiol or their concentrations (g/cm}^3)\)
\noalign{\smallskip}
f \quad \text{friction factor}
\noalign{\smallskip}
h^+ \quad U_A \delta/v; \text{dimensionless half-width of channel}
\noalign{\smallskip}
K \quad \text{overall mass transfer coefficient; m/s}
\noalign{\smallskip}
k \quad \text{reaction rate constants; 1/min}
\noalign{\smallskip}
k'' \quad \text{filtration constant; dimensionless}
\noalign{\smallskip}
q \quad \text{blood flow rate; ml/min}
\noalign{\smallskip}
Re \quad 4 \delta U/v; \text{Reynolds number (dimensionless)}
\noalign{\smallskip}
S \quad \text{transformed dimensionless space variable, see Eq. 88}
\noalign{\smallskip}
Sc \quad \nu/D; \text{Schmidt number (dimensionless)}
\noalign{\smallskip}
t \quad \text{time; min}
\noalign{\smallskip}
U, U^*, U_\tau \quad \text{velocity, average, frictional; m/s}
\noalign{\smallskip}
\bar{U}, \bar{U}' \quad U/U, U/U_\tau; \text{dimensionless}
\noalign{\smallskip}
V \quad \text{blood volume, ml}
\noalign{\smallskip}
X \quad \text{distance downstream, m}
\( X^+ = \frac{D}{\delta <U>} \frac{X}{\delta} \); dimensionless residence time

\( y \) distance from center line of channel

\textbf{Greek}

\( \alpha \) intensity of turbulence

\( \beta = \frac{k_1}{D_m} \); Thiele's modulus; dimensionless

\( \gamma \) solubility

\( \delta \) half-width of channel; m

\( \Delta \) thickness of membrane; m

\( \eta \) \( y/\delta \); dimensionless

\( \nu \) kinematic viscosity; \( m^2/s \)

\textbf{Superscripts}

\( F \) of the fetus

\( K \) of the kidney

\( M \) of the mother

\textbf{Subscripts}

\( I \) in the feed stream

\( II \) in the extract stream

\( I \) in

\( m \) in the membrane

\( o \) out
INTRODUCTION

Transport of matter across membranes is vital in many ways to the survival of all living things. Oxygenation of blood in the lungs, uptake of drugs and nutrients in the intestines of animals and the delivery of water and minerals in plants are prime examples. Without membranes, none of these systems mentioned above could survive in integrity. Therefore, it is of little surprise that many pioneers in the field of transport phenomena in membranes were life scientists.

In 1877, Pfeffer observed that membranes allow the passage of water but not of solutes (after Tuwiner, 1962). Along with subsequent experimentation, the concepts of semi-permeability and selectivity evolved. In the 1870's, little was known about the physics and chemistry involved in osmosis. About a decade later, mathematical expressions were available for predicting this osmotic pressure from the solute concentration. However, it was not until the 1920's that the thermodynamics of osmosis was more completely understood. Soon after that, interest in membrane phenomena was no longer restricted to osmosis but had already branched out into other phenomena, a popular one of which was the maintenance of bioelectric potentials in the neuromuscular systems of higher animals.

In the 1940's, developments in nonequilibrium thermodynamics made it possible to explain some membrane phenomena. Perhaps the most important idea in the development was that of the continuous generation of entropy in processes which are not in equilibrium. Forces and fluxes are conjugated in the entropy production rate expression. The second most important idea is that of coupling, which asserts that flows are related to all
the driving forces, e.g., pressure gradients, concentration gradients, temperature gradients, which help to explain why a concentration gradient can give rise to a hydrostatic pressure gradient or an electrical potential difference. However, coupling is not without constraints. It is governed by Curie's principle which says that the tensorial rank of the flow must be equal to that of the force, or that they should differ by a multiple of two. Persons desiring a more thorough discussion of this should consult a textbook in irreversible thermodynamics (e.g., Katchalsky and Curran, 1965).

Even before the observation of osmosis in natural membrane, experiments had been performed with certain artificial membranes, and similar results were noted. This quickly led to the design of separation equipment in which synthetic membranes were used as the separating agent. The first apparatus of this type is the dialyzer designed by Thomas Graham (see Tuwiner, 1962) which was used to separate a solution into its components. This demonstrates how science and technology advanced independently. In the early twentieth century, von Scherwin patented a series of electroosmotic processes and by the 1930's, electrodecantation was perfected, so that membrane-based creaming of latex was economically feasible (Bier, 1971). Since then, scientists and engineers have continued to study the properties of various artificial membranes in the hope of being able to fabricate materials which have desirable properties for use in large scale industrial separation processes. Significant progress has been made, and many kinds of polymeric membranes are now commercially
available. With the amount of research effort being made, many more should soon reach the market.

Progress in the utilization of membranes in large scale separation process is not as great as that in the development of membranes, partly due to the greater capital cost involved. Nevertheless, the advancement has been impressive. For example, sea water desalination by electrodialysis and waste water recovery by reverse osmosis are processes in which the membrane plays an important role. These processes are already in the operational stage and the economics have been proven profitable.

Although reverse osmosis and electrodialysis are perhaps the most popular among membrane processes, membranes are certainly not limited to be a functional constituent in these processes. Separation of gases and other chemicals by membrane are likely to compete favorably with conventional schemes. Manufacture of foods and drugs is also an instance where membranes can be applied and have advantages over traditional processes. Here, selective membranes can be used to impede the entrance of undesirable substances from the feed into the product and thus minimize contamination. This is, of course, a major function of membranes in biological systems. In many instances it is desirable that the species to be separated undergo one or more reactions before becoming the final product. In biological systems, this actually occurs quite often, for example, in the transport of estrogens in the placenta. These hormones are reacted in the placental tissue (which can be thought of as a membrane) before reaching the blood on either side. Such reactions may be of activation or deactivation. In processing drugs, particularly those which are extracted from
animals and plants, these reactions are frequently necessary for stabilization, so that the drugs would not lose their potency too soon after leaving the factory.

Despite the advantages that membrane processes offer, few, if any, industrial processes used in food and drug manufacture use membranes for separation purposes. This can be attributed to the fact that the mass transfer characteristics of such processes are not well known, particularly when the membrane separating two components contain enzymes or catalysts which cause the permeable species to react, although irreversible thermodynamics tells what is possible and what can be expected in some cases. Knowledge of this kind would also aid in the interpretation of biological transport data, especially when two flowing streams are separated by a layer of tissue, such as the placenta.

Objectives of the Present Study

As of now, mass transfer across a membrane separating two compartments has only been analyzed by assuming negligible resistance in one or more phases. Recently, doubt has been cast upon these assumptions (Tang and Hwang, 1976). In the design and scale-up of membrane separation processes, it is often useful to know a priori the parameters that would critically affect performance. Furthermore, in many industrial operations, continuous processes have been proven to be more profitable than batch operations. Therefore, it is the first objective of this study to delineate the parameters controlling the mass transfer in systems where a membrane separates two laminar fluid streams—feed and extract. Simple
diffusion is to be studied first. The results are then used as a basis for comparison with those obtained when the effect of a chemical reaction is taken into account.

Mammalian placenta resembles the kind of system to be studied in this project. For example, in the transport of oxygen from maternal blood to fetal blood, oxygen is consumed by the placental tissue, which acts as a barrier between the two bloodstreams. The transport of hormones such as estrogens is more complicated. Although much is known about the physiology and biochemistry of estrogens, the reasons why they are distributed the way they are are unclear. Moreover, there is a very limited number of methods for detecting fetal or placental malfunctioning in utero, and the reliability of these has not yet been generally agreed upon. Understanding mass transfer across membranes (the placenta in this case) may lead to answers to the above problems. It may also enable the further development of noninvasive fetal and/or placental function testing. The application of the results of the previously mentioned analysis to biological systems (the sheep placenta, in particular) is the second objective.

In industry, continuous flow process equipment often operates under the condition that all the fluid streams are turbulent. Mass transfer rates are usually greatly enhanced. It is of interest to study the effect of turbulence on membrane processes, especially when a reaction takes place in the membrane. Therefore, the third objective of this study is to extend the analysis of mass transfer across membranes to turbulent flow conditions.
Membrane, Membrane Technology and Membrane Separation Processes

A membrane, according to Lakshminarayanaiah (1969), is a phase which is generally heterogeneous in structure, and which acts as a barrier to the flow of molecules and ions present in the fluids which are in contact with its two surfaces. Membranes can be divided into two kinds according to their origin: natural and artificial. Natural membrane ordinarily refers to membranes in living systems while artificial ones are the ones which are not biological in nature. Structurally, the natural membrane (of cells) consists of two protein layers sandwiching a layer of hydrophobic lipid. Such arrangement is quite universal in cell membranes, but this universality is lacking in artificially fabricated membranes.

Synthetic membranes can be further classified into two types: ion-exchange and nonion-exchange. The latter is distinguished from the former by the absence of fixed ionic groups. Pores are postulated to exist in these membranes. If these pores are large, the membrane is not semipermeable. If the membrane is capable of excluding some species which have sizes comparable to that of the permeating species, that membrane is permselective.

With a membrane separating two solutions having different chemical potentials (functions of composition), electrical potential, hydrostatic pressure, and temperature, one or more of the cross-coupling phenomena can be observed: osmosis, electroosmosis, membrane potential, electro-
dialysis, streaming current (streaming potential), reverse osmosis, thermoosmosis, thermal diffusion, diffusion-thermal effect, and thermal diffusion potential.

For successful operation of membrane systems, the suitable membranes must be available. Enormous research efforts have been made in the fabrication of membranes. A review of the materials and method for preparing membranes is outside the scope of this study. The interested reader is referred to Lakshminarayanaiah (1969) which also discusses much of the physics and chemistry pertaining to membrane phenomena.

As mentioned previously, reverse osmosis is probably the most common membrane process. It has been used in waste water recovery, salt removal, enzyme processing, and blood serum protein separation (see Flinn, 1970; Bier, 1971; Lacey and Loeb, 1972). More recently, reverse osmosis has been used in the concentration of antibiotics (Datta et al., 1977). The economics of some of these processes are sound, while some uncertainty exists in the rest.

Electrodialytic processes using ion-exchange membranes have also been proved to be profitable. Salt can be produced inexpensively by electrically concentrating sea water (Nishiwaki, 1972). Desalination of sea water is another process where ion-exchange membranes are employed. Table 1 summarizes the industrial processes using ion-exchange membranes and the scale of use of such equipment. The authors who prepared this table have also investigated the possibility of reacting the species transferred to produce acidic salts (Nishiwaki et al., 1971).
Table 1. Typical application of ion-exchange membranes (Nishiwaki et al., 1971)

<table>
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<tr>
<th>Purpose</th>
<th>Method</th>
<th>Scale of use</th>
</tr>
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<tbody>
<tr>
<td>Production of salt from sea water</td>
<td>Electrodialysis (concentration)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Production of potable water from sea water</td>
<td>Electrodialysis (desalination)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Treatment of radioactive waste</td>
<td>Electrodialysis (demineralization, concentration)</td>
<td>Pilot plant</td>
</tr>
<tr>
<td>Refining of blood serum and vaccine</td>
<td>Electrodialysis (demineralization)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Treatment of dairy products</td>
<td>Electrodialysis (demineralization)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Purification of amino acids</td>
<td>Electrodialysis (demineralization)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Deacidification of fruit juices</td>
<td>Electrodialysis (deacidification)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Treatment of sugar juices</td>
<td>Electrodialysis (demineralization)</td>
<td>Pilot plant</td>
</tr>
<tr>
<td>Purification of organic matter</td>
<td>Electrodialysis (demineralization)</td>
<td>Commercial</td>
</tr>
<tr>
<td>Recovery of waste acid</td>
<td>Dialysis</td>
<td>Commercial</td>
</tr>
<tr>
<td>Refining processes of nickel and copper</td>
<td>Dialysis</td>
<td>Commercial</td>
</tr>
</tbody>
</table>

Table 1 may give the impression that membrane separation processes have a rather long history. On the contrary, they do not. Most of them were not in operation until the 1960's. Realizing this fact, a group of scientists and engineers collaborated in writing a book on this subject (Meares, 1976). Presented in it are more recent developments, some
fundamental principles and certain novel processes. The most noteworthy and perhaps most pertinent of these is the contribution by Thomas and Caplan (1976) who have been active in membrane processes for a number of years. They summarized the membrane research that they carried out with their colleagues. Their main concern was to model nonion-exchange membranes in which enzymes had been insolubilized. The kinetics, thermodynamics and mass transfer across such membranes were discussed. A list of methods for immobilizing enzymes on different types of membrane were included along with a list telling which method to use when dealing with a certain kind of enzyme. However, no reference was made to the mass transfer outside the membrane to which its counterpart inside the membrane must be conjugated.

Mass Transfer

Mass transfer in flowing fluid streams has been studied extensively for many years. A comprehensive review of the development in the last few decades is not feasible if not impossible. In general, the research on this subject can be classified into two categories: laminar and turbulent. Within each category, the type of flow can be subdivided into open-channel, pipe, and channel flow, and flow around submerged objects.

The primary tools used in many of these studies are the equations of motion and of continuity of the species under consideration. In some instances, the equation of energy is also used. These equations are listed in detail in Bird et al. (1960). Investigators have solved these equations for systems with certain prescribed geometry and boundary
conditions. A collection of solutions has been gathered by Crank (1964), and those to some of the analogous heat transfer problems have been published by Carslaw and Jaeger (1959). Because of the similarity between heat and mass transfer, developments in heat transfer should not be overlooked.

In an effort to enhance the rate of mass transfer, the effects of chemical reactions are often included in the analysis. These chemical reactions can be homogeneous or heterogeneous (see Chapter 17 of Bird et al., 1960). Often accompanying reactions and diffusion is the liberation or consumption of heat which creates a space-dependency of physical properties. The effects of this temperature inhomogeneity have been considered recently by Yih (1977) for a falling film reactor.

Mass Transfer in Laminar Flow in Pipes and Channels

Mass transfer is one step more difficult to analyze than momentum transfer because of the effects of the velocity profile. Fortunately, this problem is not insurmountable when one has laminar flow. In pipes and channels, and even in falling films, the velocity profiles are well-described. The equation of continuity of a species can often be reduced to a linear partial differential equation (PDE) with variable coefficients. This kind of equation is often solved by a series expansion method, a quasi-numerical method (numerical solution of the characteristic equation), a finite difference approximation, or a finite element approach. Although analytical methods are generally more desirable than numerical
ones, problems with nonlinearity and boundary conditions often limit their applicability.

The solutions to the equations of continuity and momentum that are presented in textbooks (e.g., Bird et al., 1960; Skelland, 1974) often assume one of the two velocity distributions: parabolic or plug flow (flat), and one of the following sets of boundary conditions: axisymmetric concentration (or temperature) distribution and either constant mass (heat) flux or constant concentration (temperature) at the wall. These assumptions are not unreasonable as long as the pipe or channel wall is not significantly permeable to the species under consideration. However, if the converse is true, the analysis should be amended accordingly to accommodate such occurrence. Colton et al. (1971) assumed the mass flux at the wall to be proportional to the local concentration and reduced the partial differential equation to a Sturm-Liouville problem. Numerical results were also given. While this approach is an improvement over the previously mentioned ones, its applicability is restricted to cases where the concentration on the other side of the wall remains constant, and where the material constituting the wall is homogeneous, isotropic, and of a prescribed geometry. The solution would not apply if a reaction leading to the consumption or generation of the pertinent substance occurs at the fluid-solid interface or in the wall itself. One may note the similarity between the assumption by Colton et al. and that used in solving heat transfer problems for flow around submerged objects.

When pipe or channel walls are permeable, mass fluxes in the wall and in the fluid must be equal at the interface. This enters the problem as a
boundary condition. Instead of one PDE, two need to be solved—one for
the fluid stream and one for the wall. Besides the continuity of flux,
the concentrations (temperature) are usually assumed to be at equilibrium
or continuous at the interface. Problems of this sort are called "con­
jugated boundary value problems." Some fifteen years ago, Hatton and
Quarmby (1963) noted that the effect of axially varying boundary condi­
tions in heat transfer could be significant, and Colton and coworkers
(1971) in essence took one step further, but neither group went far
enough to solve a conjugated problem. Luikov et al. (1971) recognized the
inadequacy of the methods used by Colton (the third kind boundary condi­
tion) and solved the energy equation with the conjugated boundary condi­
tions. They concluded that the rate of heat transfer was dependent on the
ratio of the thermal conductivities of the fluid and the solid. Later,
Luikov (1974) suggested that this ratio be included in the design of
equipment. More recently, Sakakibara and Endoh (1977) examined the same
problem and obtained solutions for turbulent flow in channels.

The methods used by Hatton and Quarmby (1963), Luikov and coworkers
(1971, 1974), and Sakakibara and Endoh (1977) are quite similar. First,
the energy equation was solved with constant temperature at the wall for
the flowing fluid. Then Duhamel's theorem was applied. Hatton and Quarm­
by assumed arbitrary wall temperature distribution functions (linear and
sinusoidal) while both Luikov et al. and Sakakibara and Endoh solved the
conduction equation for the wall as well.

In analyses of mass transfer between two fluids (particularly of
nonelectrolytes) separated by a membrane it has often been assumed that
the bulk of the resistance resides in the membrane (see Lakshminarayanaiah, 1969) so that computation can be simplified. However, it has recently been proven experimentally that this is not the case (Thorman et al., 1975; Tang and Hwang, 1976). Therefore, the resistances in both fluid phases should not be neglected in studying mass transfer in these systems, which means that the fluxes must be coupled at the two membrane surfaces. This further complicates the analysis because the equation of continuity has to be solved for three phases. Solutions to this kind of problem have not yet appeared in the literature.

Biomedical Applications

Application of engineering principles and methods of analysis in medicine has resulted in great advances in health care in the modern world. Heart-lung machines used in open heart surgery and dialyzers for patients with chronic kidney diseases would not have evolved in design had it not been the collaboration of biomedical and engineering scientists. An introduction to the subject of biomedical applications of transport phenomena can be found in Seagrave (1971) and of mechanical aspects in Young (1972). A review of the development up to 1970 is in Middleman (1974). Lightfoot (1974) and Lih (1975) presented more in-depth treat­ments of this subject.

In studying a particular organ or tissues thereof, models are often useful. Since it is one of the objectives of this study to learn about the mass transfer in the placenta, a survey of the work done in this area is therefore appropriate.
The first model of the placenta was apparently developed by Lamport (1954) for studying the exchange of respiratory gases between the mother and the fetus. Differential equations were set up and solved with experimental data available at that time. The conclusion was that the diffusion constant (analogous to the mass transfer coefficient) had to be 11% higher in cocurrent flows than in countercurrent flow if the same amount of oxygen was to be transported.

Wilkin (1958) presented a detailed analysis of transport between the two streams separated by the placenta, the results of which have been cited by many researchers. Metcalfe et al. (1965) investigated the transfer of carbon monoxide and nitrous oxide in the artificially perfused sheep placenta. With the effects of shunting of both uterine and umbilical blood accounted for, they arrived at the conclusion that the placenta contained a mixture of cocurrent and countercurrent units. Meschia et al. (1967) used the idea developed by Wilkin, studied the placental diffusion of various molecules and ion, and found that tritiated water and antipyrine transport was limited by the blood flow rates, while the diffusion of urea was limited by membrane permeability. Faber (1969), using the same principles, analyzed the efficiency of transport of materials for a number of flow patterns, and reported that both maldistribution of permeability and flow ratios decreased the effectiveness and efficiency of the placenta. Rankin and Peterson (1969) determined that 36% of the uterine blood and 23% of the umbilical blood did not enter the area of exchange in the placenta. By perfusing the fetal side of the goat placenta, they came up with data that showed uterine and umbilical flows were either counter-
current in nature with wide distribution of flow ratios, or cocurrent with moderate distribution. All of the above models have been reviewed by Middleman (1974).

Guilbeau et al. (1972) presented what amounted to a distributed parameter model, and calculated the axial partial pressure profiles of oxygen in the uterine blood by considering the maternal blood as flowing cocurrently like an annulus around the fetal capillary. They did this for both steady and unsteady state, with and without the inclusion of the axial dispersion term, and concluded that axial dispersion is, indeed, negligible.

Longo et al. (1972) applied the resistances-in-series concept in studying the various factors affecting placental oxygen transport. The resistances they considered were in: diffusion from maternal red cell through the plasma to the membrane, and diffusion across the membrane, and diffusion from the plasma to the fetal red cell. Power et al. (1972) also used the same idea in the construction of a model simulating placental CO$_2$ transport.

Ramberg et al. (1973) developed a model for studying the transplacental transport of calcium. They used a multiple pool model, and obtained experimental data which suggested the presence of two placental pods, one involved in the transfer from mother to fetus, and the other, vice versa. The technique used in this analysis was to find inverse Laplace transform of the product of a transfer function and an input function, and use that to determine the response.
Guilbeau and Reneau (1973) considered the placenta as consisting of a mixture of cocurrent and countercurrent exchange units, and analyzed it using a distributed-lumped parameter model. When they calculated the response of such systems to sinusoidal maternal blood input (to the placenta), they were able to show significant decreases in fetal oxygen partial pressure in a matter of a few fetal blood residence times, and claimed that this would be a satisfactory explanation for the frequent occurrence of fetal asphyxia during labor.

It is frequently true that dynamic testing (transient analysis) may yield more information in a shorter period of time than steady-state tests. In clinical situations, it is often desirable to disturb the patient as little and as few times as possible, therefore, a model of the placenta allowing for dynamic testing may be more effective and efficient. Nagey et al. (1976) presented a simplified model of the maternal circulation. On assuming that the time taken for placental transport was short compared to the reaction time, he calculated the "estrogen response" to an acute injection of dehydroepiandrosterone (DHEA) into the plasma. Because of the assumptions made in developing the model, they were not able to distinguish some of the "rate constants" they used.

Most of the models discussed so far are either steady or quasi-steady state in nature, with assumptions of particular flow pattern. These models have the advantages that if they are to be tested, only a few measurements are required per run, and that the mathematics are usually relatively simple. This is probably one of the reasons why steady state models are more readily accepted by the clinical sector.
It is interesting to note that placental modeling has a short history and general acceptance has been lacking. This may partly be due to the inadequate communication among scientists. It is also interesting to note that in the area of placental transport of estrogen which is an important phenomena (in that it is used as an indicator of fetal well-being) in pregnancy, nothing has been done to simulate the process until recently.

**Turbulent Flow**

As the Reynolds number based on the hydraulic radius increases to about 2000, sinusoidal waves begin to appear, and the stability of the flow is greatly determined by the physical conditions of the flow field. When the critical Reynolds number is reached, laminar shear flow gives way to turbulence. Many process equipment operate under this condition. Transport of momentum and mass are mainly achieved by eddy circulation instead of molecular collision. Determination of the velocity profile requires the knowledge of the eddy viscosity function, which is not always available. Empirical and semi-empirical eddy viscosity functions have been proposed by many investigators. The interested reader is referred to Chapter 14 of Brodkey (1967), who offers a good condensed description of various theories and methods involved.

It is customary to divide the turbulent flow field into three regions: the laminar sublayer, buffer zone, and the turbulent core. In the laminar sublayer, diffusion of mass, heat, and momentum is by molecular means; in the turbulent core, by eddy circulation. The mechanism of diffusion in the buffer zone is a mixture of the two. Velocity profile of
fluids in turbulent flow is generally conformant to the universal velocity profile (UVP); universal because velocity is only a function of the distance from the wall. The velocity distributions given by different authors may be slightly different, but the forms and the arguments in arriving at their results are quite similar (Levich, 1962; Davies, 1972; see also Bird et al., 1960; Brodkey, 1967; and Mizushina and Ogino, 1970). A large number of models concerning turbulence have been proposed. Some of the better ones have been reviewed by Solbrig and Gidaspaw (1968).

Since it is not the primary purpose of this study to model turbulence, and reviews of the literature pertaining to this subject can be found in textbooks and elsewhere (e.g., Solbrig and Gidaspaw, 1968; Mizushina and Ogino, 1970), such a review is omitted here. Perhaps it is sufficient to mention that the arbitrariness in dividing the turbulent flow field has caused considerable discomfort among some investigators. Attempts have been made to reduce the arbitrariness but such approaches are of limited utilization (Deissler, 1955).

Mass transfer between turbulent flows separated by a membrane has all the difficulty stated in the previous section in addition to that caused by eddy circulations. The conjugated heat transfer problem solved by Sakakibara and Endoh (1977) was for turbulent flow using an eddy diffusivity model proposed by Mizushina and Ogino (1970). Solutions were presented for two cases: (1) the temperature of the pipe wall not in contact with the fluid is constant; and (2) the flux there is constant. The limitation of these results are apparent, but nevertheless, this is a more
realistic representation of the actual situation than, say, either constant temperature or flux at the fluid-solid interface.
MASS TRANSFER IN LAMINAR FLOW

Statement of the Problem

Mass transfer between parallel flowing streams separated by membranes is studied by examining the characteristics of the system shown in Figure 1, where a newtonian fluid flows cocurrently down the rectangular channels. The geometry and the flow configuration are chosen to keep the analysis simple without loss of generality and because they have been used in some industrial separation process equipment. Chemical species A, to which the membrane is permeable,diffuses from stream I to stream II. Initially (at X = 0), stream II is free of the solute A while stream I contains a small amount of it. The heat of mixing is assumed negligible and thus the temperature of the entire system can be considered uniform. The viscosity of the fluid can be taken as constant (at least in laminar flow). Other assumptions regarding the system are:

1. Rates of transfer are low.
2. Axial diffusion is negligible for high Peclet numbers.
3. Mass transfer occurs after flow is fully developed.
4. Diffusion occurs only as a result of the existence of a concentration gradient in A, all coupling effects are ignored.
5. The membrane is permeable to A but not to other solutes in both streams.
6. In the limit as the volume approaches zero, the membrane can be considered to be a homogeneous phase with finite effective diffusivity and solubility (partition coefficient).
Figure 1. Diagrammatic representation of the system in this study.
7. Concentrations at interfaces are always in equilibrium with those in the adjacent phase, and are related by the partition coefficient.

8. Dimensions of the channels are equal, and the width of the membrane is small compared to the width of the channel.

The velocity profile for the flow in either stream can be obtained by integrating the steady-state Navier-Stokes equation and applying the no slip and zero shear (at the center-line) boundary conditions. The result is

\[ U = -\frac{\partial P}{\partial X} \frac{\delta^2}{\mu L} [1 - (\frac{Y}{\delta})^2] \]

where

\[ P = P + \rho g X \]

In terms of dimensionless variables,

\[ U^* = \frac{U}{<U>} = \frac{3}{2} (1 - \eta^2) \]

(1)

where

\[ <U> = \frac{1}{\delta} \int_0^\delta U \, dy \] and \[ \eta = \frac{Y}{\delta} \]

With the aforelisted assumptions, the conservation equations of species A are:

For stream I \[ U \frac{\partial C_I}{\partial X} = D \frac{\partial^2 C_I}{\partial y_I^2} \]

(2)

For the membrane \[ \frac{\partial^2 C_m}{\partial X^2} + \frac{\partial^2 C_m}{\partial y_m^2} = 0 \]

(3)

For stream II \[ U \frac{\partial C_{II}}{\partial X} = D \frac{\partial^2 C_{II}}{\partial y_2^2} \]

(4)
The boundary conditions to be satisfied are:

\[
\text{at } y_1 = \delta \quad C_I = \frac{1}{\beta} C_m \quad (5) \\
D \frac{\partial C_1}{\partial y_1} = D_m \frac{\partial C_m}{\partial y_m} \quad (6)
\]

\[
\text{at } y_m = \Delta \quad \frac{1}{\beta} C_m = C_{II} \quad (7) \\
D_m \frac{\partial C_m}{\partial y_m} = D \frac{\partial C_{II}}{\partial y_2} \quad (8)
\]

together with the initial conditions

\[
\text{at } X = 0 \quad C_I = C_0 \quad (9) \\
C_{II} = 0 \quad (10)
\]

Using an order of magnitude estimation, the first term in Equation (3) can be dropped. By defining variables

\[
\eta_1 = \frac{y_1}{\delta} \\
\eta_2 = \frac{y_2}{\delta} \\
\eta_m = \frac{y_m}{\Delta} \\
x^* = \frac{D}{\delta \langle U \rangle} X \\
C_I^* = \frac{C_I}{C_0} \\
C_{II}^* = \frac{C_{II}}{C_0} \\
C_m^* = \frac{C_m}{C_0}
\]
The equation can be cast into dimensionless form. The differential equations become

\[ U^* \frac{\partial^2 C^*_I}{\partial x^2} = \frac{\partial^2 C^*_I}{\partial \eta^2} \]  
\[ \frac{\partial^2 C_m}{\partial \eta^2} = 0 \]  
\[ U^* \frac{\partial^2 C^*_II}{\partial x^2} = \frac{\partial^2 C^*_II}{\partial \eta^2} \]

The boundary conditions are then:

at \( \eta_1 = 1 \) \( C^*_I = \frac{1}{\beta_m} C^*_m \) 
\[ \frac{\partial C^*_I}{\partial \eta_I} = \frac{D_m \delta}{\Delta} \frac{\partial C^*_m}{\partial \eta_m} \] 

at \( \eta_m = 1 \) \( C^*_II = \frac{\beta^2}{\beta_m} C^*_m \) 
\[ \frac{\partial C^*_II}{\partial \eta_{II}} = \frac{D_m \delta}{\Delta} \frac{\partial C^*_m}{\partial \eta_m} \]

Initial conditions simplify into

at \( x^* = 0 \) \( C^*_I = 1 \) 
\[ C^*_II = 0 \]

The significance of the "naturally occurring" dimensionless groups \( \frac{D_m \delta}{\Delta} \) and \( \beta \) is to be examined.
Methods of Solution

Due to the nature of the boundary conditions, separation of variables cannot be applied directly in solving Equations 12-14. Purely analytical solutions are out of the question. Quasi-numerical methods are, however, useful in some cases. The methods proposed by Luikov et al. (1971) and Sakakibara and Endoh (1977) are of the latter kind. To use these methods Equations 12 and 14 are to be solved with a fixed boundary condition at the interfaces using the method of separation of variables. For the analogous heat transfer problem, solution to such a PDE is given by

\[ \theta = \sum_{m=0}^{\infty} A_{m} R_{m}(\eta) \exp\left(-\frac{16 G z}{\lambda_{m}^{2} X^{*}}\right) \]  

(21)

where

- \( \theta \) = dimensionless temperature
- \( \lambda_{m} \) = mth eigenvalue
- \( G z \) = Graetz number
- \( X^{*} = X/L \)
- \( R_{m} \) = eigenfunction
- \( A_{m} \) = expansion coefficient
- \( L \) = length of the plate

At the interface, Sakakibara assumed that

\[ \theta = 1 + \tau_{0} + \tau_{1} \xi + \ldots \]  

(22)

where \( \tau \)'s are coefficients, and \( \xi \) is a dummy variable to be defined later.

Using the Duhamel's theorem, the interfacial variation in temperature can be accounted for by writing
for the interface. Conduction in the pipe wall is then analyzed, and expressions for temperature and flux at the interface determined. These are all very complicated functions of $X^*$, but can be used to calculate the coefficients in Equation 22. Finally, by applying the other boundary conditions, the temperature profile and thus the heat flux, bulk temperature, and the Nusselt number can be determined. Notice that this is a long and tedious process. Results have been only presented for two particular cases by Sakakibara and Endoh (1977): constant temperature and constant flux on the side of the wall not in contact with the working fluid. This is an improvement over the solutions to heat and mass transfer problems in textbooks (e.g., Bird et al., 1960; Eckert and Drake, 1972; Skelland, 1974). The complexity involved greatly limits its application in cases where the boundary conditions are slightly different. If this approach is to be used to solve the problem at hand, difficulty would be encountered when the solutions are forced to fit the coupled-conjugated boundary conditions. Calculation of the eigenvalues, eigenfunctions and the expansion coefficients is a time consuming step and it is only the beginning.

Quasi-numerical methods are generally more accurate and therefore more desirable as a tool for solving PDEs. However, the number of iterations sometimes required in calculating the eigenvalues makes finite-difference approximation a sound alternative. Frequently finite difference formulation is more straightforward than the corresponding manipula-
tion of analytical expressions. The complexity of the quasi-numerical method has already been discussed. One should appreciate the difficulty in using this method to study the system of concern—the amount of manipulation is at least doubled. Therefore, the finite-difference method is used in this study.

Equations 12-14 can be represented by finite difference equations and can be made to satisfy the boundary conditions 15-20. Furthermore, Equation 13 can simply be integrated to give

$$C_m^* = a + b_n$$

so that the value of $C_m^*$ at one surface of the membrane together with the initial slope enables one to calculate that at the other surface. Equations 12 and 14, when transformed into finite difference equations using the Crank-Nicholson method, take the following form:

Equation 12

$$U_1 \frac{C_{i+1,j+1} - C_{i,j}}{k} = \frac{1}{2} \left( \frac{C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j+1}}{h^2} \right) + \frac{C_{i+1,j+1} - 2C_{i,j} + C_{i-1,j}}{h^2}$$

Equation 14

$$U_1 \frac{C_{i+1,j+1} - C_{i,j}}{k} = \frac{1}{2} \left( \frac{C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j+1}}{h^2} \right) + \frac{C_{i+1,j+1} - 2C_{i,j} + C_{i-1,j}}{h^2}$$

The boundary conditions
When a second order Lagrange polynomial is used to evaluate the gradient near the membrane, the flux expressions become

\[
\frac{3C_{\bar{I}i,N+1} - 4C_{\bar{I}i,N} + C_{\bar{I}i,N-1}}{(\Delta h)} = b
\]

\[
- \frac{3C_{\bar{I}i,1} - 4C_{\bar{I}i,2} + C_{\bar{I}i,3}}{(\Delta h)} = b
\]

The initial conditions remain unchanged.

A similar set of equations have been solved by Tang and Hwang (1976) when they studied mass transfer of dissolved gases through tabular membranes. Of course in their case, cylindrical coordinates were used. Moreover, they neglected the resistance in one side of the membrane, thus simplifying the calculation procedure. However, their approach cannot be used here since the resistance to mass transfer is not negligible in either stream.

The strategy used in solving the equations is as follows:

1. Solve Equation 25 by assuming a value of \(a\).
2. Obtain \(b\) by using Equation 29.
3. Calculate \(C_{\bar{I}I}\) at the interface using Equation 28.
4. Solve Equation 26 and evaluate \(a\) base on the solution to this equation (use Equation 30).
5. Compare the b's. If the ratio of the two b's is equal to 1.0±10^{-6}, then the set of equations is considered solved and boundary conditions are assumed met.

Mass Transfer with Chemical Reaction in the Membrane

When mass transfer across the membrane is accompanied by chemical reaction, mass transfer rates are often enhanced. If the reaction takes place in the membrane phase only, then the problem at hand is not much different from the one just stated. Continuity equations for species A for both streams (Equations 12 and 14) remain unchanged while Equation 13 is modified slightly and it becomes

\[ \frac{\partial^2 C^*_m}{\partial n^2_m} + f(C^*_m) = 0 \]  

(31)

where \( f(C^*_m) \) is the dimensionless rate of generation of A by chemical reaction. The kind of reactions of interest here are the ones mediated by enzymes. It must be emphasized here that membranes carrying insolubilized enzymes cannot physically be homogeneous, therefore Michaelis-Menten kinetics cannot be expected to hold. However, it can be used to approximate the rate of consumption locally. This assumption has also been used by Thomas and Caplan (1976).

The rate expression for a Michaelis-Menten reaction can be written in simple terms as

\[ r_A = -\frac{k_1 C_A}{1+k_2 C_A} \]

(32)
Written in dimensionless form

\[ f(C^*) = \frac{\Delta^2 r_A}{D} = -\frac{k_1 C_m}{1 + k_2 C_m} \frac{\Delta^2}{DC_A} \]  (33)

**First and pseudo-first order reactions**

Equation 32 is a nonlinear expression and substitution into Equation 31 yields a nonlinear ordinary differential equation (ODE), which can only be solved numerically. In many cases when the substrate concentration is very low such that \( k_2 C_m \ll 1 \), the reaction approaches one which is first order in \( A \), i.e.,

\[ f(C^*) = -\frac{k_1 \Delta^2}{D} C^*_m \]  (34)

When this is substituted into Equation 31, the following ODE is obtained

\[ \frac{d^2 C^*_m}{d\eta^2_m} = -\frac{k_1 \Delta^2}{D} C^*_m = 0 \]  (35)

which can be integrated to give

\[ C^*_m = a_1 \cosh(\gamma \eta_m) + b_1 \sinh(\gamma \eta_m) \]  (36)

The bracketed quantity in Equation 35 is like the Damkohler number in flow reactors. It is the ratio of the rate of consumption by reaction to that of diffusion of \( A \). \( \gamma \) in Equation is the Thiele modulus (Thomas and Caplan, 1976) and is given by

\[ \gamma^2 = \frac{k_1 \Delta^2}{D} \]  (37)

To investigate the effect of a first order reaction in the membrane, Equations 12 and 14 are solved in conjunction with Equation 37. The boundary conditions are written in the following way
at \( \eta_1 = 1 \) \( C_i^* = \frac{1}{\beta_m} a_1 \) \( (27) \)

at \( \eta_m = 1 \) \( C_{II}^* = \frac{\beta_2}{\beta_m} (a_1 \cosh \gamma + b_1 \sinh \gamma) \) \( (38) \)

and

\[
\frac{3C_{II, N+1}^* - 4C_{II, N}^* + C_{II, N-1}^*}{(\partial h)} - \frac{D_m \delta_{II}}{D_{II}} \gamma b_1 = 0 \] \( (39) \)

\[
\frac{3C_{II, 1}^* - 4C_{II, 2}^* + C_{II, 3}^*}{(\partial h)} - \frac{D_m \delta_{II}}{D_{II}} \gamma (a_1 \sinh \gamma + b_1 \cosh \gamma) = 0 \] \( (40) \)

The strategy used here is similar to that used earlier. The only difference is that Equation 40 is used as the criterion for convergence.

In studying chemical reactions, it is sometimes desirable to pursue the fate of the product(s) of the reaction as well. That is, if the following reaction takes place in the membrane, what is to become of B?

\[
A \stackrel{k_1}{\longrightarrow} B
\]

To answer this, conservation equations for B must be written for the two streams and the membrane. Assumption No. 5 stated in an earlier section has to be relaxed to allow B to diffuse out of the membrane. Solubility of B in stream II and in the membrane can be defined relative to that in stream I. These conservation equations are:

for stream I \( U^+ \frac{\partial B^*_I}{\partial x^+} = D_{Bm} \frac{\partial^2 B^*_I}{\partial \eta_1^2} \) \( (41) \)

for stream II \( U^+ \frac{\partial B^*_II}{\partial x^+} = D_{Bm} \frac{\partial^2 B^*_II}{\partial \eta_2^2} \) \( (42) \)
and for the membrane

$$\frac{\partial^2 B^*}{\partial x^2} = \frac{\partial^2 B^*}{\partial n^2} + \frac{k_1}{D_{Bm}} C_m = 0 \quad (43)$$

When the rate of reaction is low, i.e., $B$ is generated slowly, Equation 43 can be simplified by assuming that locally $\frac{\partial B^*}{\partial x^+}$ is nearly linear and so

$$\frac{\partial^2 B^*}{\partial x^+^2} \approx 0. \quad \text{The result is}$$

$$\frac{d^2 B^*}{d n^2} + \frac{D_{Am}}{D_{Bm}} \gamma^2 C_m = 0 \quad (44)$$

which can be integrated to give

$$B^* = \frac{D_{Am}}{D_{Bm}} (a_1 \cosh n + b_1 \sinh n) + c_1 n + d_1 \quad (45)$$

Equations 41 and 42 can be solved with the following conditions:

at $x^+ = 0$ \quad $B^*_I = B^*_I = 0 \quad (46)$

at $n_1 = 1$ \quad $B^*_I = \frac{1}{\gamma n_m} \left( \frac{D_{Am}}{D_{Bm}} a_1 + d_1 \right) \quad (47)$

$$\frac{\partial B^*_I}{\partial n_1} - \frac{D_{Bm}}{D_{BI}} \left( \frac{D_{Am}}{D_{Bm}} b_1 + c_1 \right) = 0 \quad (48)$$

at $n_m = 1$ \quad $B^*_II = \frac{\beta^B_B}{\beta^B_m} \left( \frac{D_{Am}}{D_{Bm}} (a_1 \cosh n + b_1 \sinh n) + c_1 + d_1 \right) \quad (49)$

and

$$\frac{\partial B^*_II}{\partial n_{II}} - \frac{D_{Bm}}{D_{BII}} \left( \frac{\gamma D_{Am}}{D_{Bm}} (a_1 \sinh n + b_1 \cosh n) + c_1 \right) = 0 \quad (50)$$
The method of solution of Equations 41 and 42 is the same as that
stated previously.

Zeroth and pseudo-zeroth order reaction

In the other end of the spectrum, suppose the concentration of A is
such that \( k_{2}C_{m} >> 1 \), the reaction would become pseudo-zeroth order.

Placental uptake and consumption of oxygen can be thought of as an exam­
ple where the diffusing agent is consumed at a relatively constant rate.

The conservation equation now becomes

\[
\frac{d^{2}C^{*}}{d\eta^{2}_{m}} - \frac{k_{o}}{D_{m}C_{ao}} = 0
\]

(51)

Once again, \( \frac{k_{o}}{D_{m}C_{ao}} \) can be interpreted the same way as \( \gamma^{2} \) for a first or
pseudo-first order reaction. Equation 51 can be integrated directly to
give

\[
C^{*} = a_{o} + b_{o} \eta_{m} + \frac{k_{o}}{D_{m}C_{ao}} \frac{\eta^{2}_{m}}{2}
\]

(52)

Since the reaction occurs in the membrane only, Equations 12 and 14
are still applicable to the flowing streams. They are now to be solved
with these boundary conditions:

at \( \eta_{l} = 1 \)

\[
C^{*}_{l} = \frac{1}{\delta_{m}} a_{o}
\]

(53)

\[
\frac{3C^{*}_{l}}{3\eta_{l}} - D_{l} \frac{\delta}{\delta \eta_{l}} b_{o} = 0
\]

(54)
To keep track of the products, conservation principles must be applied. Equations 41 and 42 are still valid while Equation 44 has to be modified corresponding to account for a zeroth order reaction. The following equation is appropriate:

\[ B^*_m = \frac{D_{Am}}{D_{Bm}} (c_o + d_o \eta_m - \frac{D_{Am} \Delta^2}{D_{Bm} D_{Am} C_{Ao}} \eta_m^2) \]  

Therefore, boundary conditions for Equations 41 and 42 are then:

at \( \eta = 1 \):

\[ B^*_I = \frac{1}{\beta^B_m} c_o \]  

and

\[ \frac{\partial B^*_I}{\partial \eta_I} - \frac{D_m \delta}{D_I \Delta} d_o = 0 \]  

at \( \eta = 1 \):

\[ B^*_II = \frac{\beta^B_m}{\beta^B_m} (c_o + d_o - \frac{1}{2} \frac{D_{Am} \Delta^2}{D_{Bm} D_{Am} C_{Ao}}) \]  

and

\[ \frac{\partial B^*_II}{\partial \eta_{II}} - \frac{D_m \delta}{D_{II} \Delta} (d_o - \frac{D_{Am} \Delta^2}{D_{Bm} D_{Am} C_{Ao}}) = 0 \]  

Equations 56 and 61 are used as criteria for convergence for the reactant A and for the product B, respectively.

Seemingly, this procedure can be extrapolated to higher order reactions. But one should realize that any reaction of order higher than one
would make the conservation equation for the membrane a nonlinear ODE. This often renders integration useless or requires additional conditions. Therefore, these reactions are not considered here.
APPLICATION OF RESULTS OF MASS TRANSFER ACROSS MEMBRANES
IN THE PLACENTAL TRANSPORT OF HORMONES

During pregnancy in most mammals, the urinary estrogen increases significantly except in cases of abortion and other abnormalities. It was suspected by early researchers that the maternal ovaries were responsible for the overproduction of estrogen. With experimental evidence now available it is generally accepted that the fetus and the placenta synthesize most of the extra estrogens. The complementary functions of the enzymes in these places constitute the fetal placental unit (FPU). The term was coined by physiologists after understanding the distribution of enzymes essential for steroidogenesis and for recycling of steroids. A brief summary of this is in Table 2.

A substrate for fetoplacental synthesis of estrogen has been identified to be dehydroepiandrosterone, the structure of which and the sequence of reactions leading to its formation are shown in Figure 2. Since the C21 - C19 reaction takes place primarily in the fetus, and aromatization occurs in the placenta, dehydroepiandrosterone has been used as an agent for testing fetal well-being by Pupkin et al. (1976).

In blood, estrogens can exist in two forms, free and conjugated. "Conjugated" means metabolized—be it sulfated or otherwise—and should not be confused with the usage in boundary value problems presented previously. Research in the biochemistry of estrogens has shown that estrone (E₁) is converted to estradiol (E₂) in the placenta and vice versa in placental tissue and sulfatase action is high there. The interconver-
Table 2. Enzymatic activities in the fetoplacental unit (from Diczfalusy, 1974)

Distribution of enzyme activities between the fetal and placental compartments

<table>
<thead>
<tr>
<th>Fetus</th>
<th>Placenta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cholesterol synthesizing enzymes</td>
<td>--</td>
</tr>
<tr>
<td>Hydroxylases</td>
<td>--</td>
</tr>
<tr>
<td>Sulphokinases</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>Sulphatases</td>
</tr>
<tr>
<td>--</td>
<td>3-HO-steroid DHG</td>
</tr>
</tbody>
</table>

Role of placenta in fetoplacental steroidogenesis

<table>
<thead>
<tr>
<th>Acetate to cholesterol</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cholesterol to C-21</td>
<td>Yes</td>
</tr>
<tr>
<td>C-21 to C-19</td>
<td>Very limited</td>
</tr>
<tr>
<td>Aromatisation</td>
<td>Yes</td>
</tr>
<tr>
<td>16-hydroxylation</td>
<td>No</td>
</tr>
</tbody>
</table>

ion and deconjugation are perhaps the FPU's method for recycling estrogens—less energy is required for recycling than for synthesis from acetate.

In sheep, the metabolism of estrogens has been extensively studied. The system is simple; only two estrogens, estrone and estradiol (and their sulfates), are involved. Recently, radioimmunoassays for estrogens in fetal blood reveal that there is a much greater concentration of E₂ in the fetal blood than there is in the maternal blood; furthermore, the ratio of
the concentration of $E_2$ to that of $E_1$ is also higher in the fetus (W. C. Wagner, Department of Veterinary Anatomy and Physiology, University of Illinois, Champagne, Illinois, personal communication). The data in Table 3 have been kindly provided by Professor Wagner.

As of now, there is no satisfactory explanation for what has been observed experimentally. Active transport is possible but unlikely. Therefore, the following model of placental estrogen transport is proposed.

The model of fetal and placental circulation is diagrammatically depicted in Figure 3. It is understood that this is an oversimplification of the real system. The actual flow pattern in the placenta as well as
Table 3. Daily concentrations of various estrogens in a sheep (in pg/ml) from about 10 days prior to parturition

<table>
<thead>
<tr>
<th>Day</th>
<th>$E_1$</th>
<th>$E_2^\beta$</th>
<th>$E_2^\alpha$</th>
<th>$E_1SO_4$</th>
<th>$E_2SO_4$</th>
<th>$E_1SO_4$</th>
<th>$E_2SO_4$</th>
<th>$E_1$</th>
<th>$E_2^\beta$</th>
<th>$E_2^\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Umbilical artery</td>
<td>Umbilical vein</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Jugular vein</td>
<td>Uterine vein</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>357</td>
<td>16</td>
<td>76</td>
<td>5624</td>
<td>174</td>
<td>18377</td>
<td>255</td>
<td>42</td>
<td>68</td>
<td>4190</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
<td>20</td>
<td>44</td>
<td>4125</td>
<td>156</td>
<td>26201</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>117</td>
<td>-</td>
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Jugular vein

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<sup>a</sup>Labor.
those in other tissue organs are too complicated for analysis, assumption of one flow configuration over another makes little difference as far as analysis is concerned because of the deviations from ideality that one may encounter. It is therefore justified to choose the simplest model which can represent the system satisfactorily. In this model, all flow streams are considered laminar. The placenta is nothing but a membrane which separates the fetal blood from the maternal blood, and contains the necessary enzymes for estrogen synthesis and interconversion. Other assumptions are:

1. Maternal kidney is the only significant site for elimination of estrogens, and the rate of filtration is proportional to the concentration of the estrogen concerned.

2. Interconversion occurs only in the placenta.

3. Rate of synthesis of estrogens by the maternal and fetal gonads are negligible compared to that by the FPU.

4. All the reactions can be considered pseudo-first order. These reactions are:

\[ E_2^\beta + E_1 \xrightarrow{k_2} E_2^\alpha \]

\[ \text{AND}^1 \rightarrow E_2^\beta \]

Terqui (1972) has demonstrated that in sheep \( E_2^\beta \) is converted to \( E_2^\alpha \), its stereoisomer, and \( E_1 \) and most of the reactant ends up as \( E_2^\alpha \), only about 20% is converted to \( E_1 \), so \( k_3 \) is at least 4\( k_2 \). The results shown in \(^1\)17-androstenedione—see Figure 2.
Table 3 show that the majority of E₂ in the sheep is E₂α in its conjugated form. Interconversion is unlikely until the sulfate groups have been removed from the molecules. Therefore, the sequence of reactions to be considered is:

\[ \frac{k_3}{k_2} E_1 S \rightarrow E_1 + \frac{1}{k_2} E_2 \alpha \]  \hspace{1cm} (62)

It should be noted that the amount of E₁S in the fetal side is about 1/4 of that of E₂S, and the concentration of E₁S does not change appreciably on a day to day basis. If the sulfatase activity is high, then the reversible part of the chain of the reaction that controls the rate. If it can be considered that \( k_2 \ll k_3 \), the only important reaction reduces to

\[ E_1 \rightarrow E_2 \alpha \]  \hspace{1cm} (63)

Under normal conditions, the rate at which AND is synthesized is quite constant. If the conversion from AND to estrogens occurs in the placenta, E₂ can be expected to be generated four times more rapidly than E₁.

Writing the conservation equations for E₂ for the blood streams,

\[ V^M \frac{dE^M_2}{dt} = -q^M (E^M_{21} - E^M_{2o}) - q^M (k''E^M_{21}) \]  \hspace{1cm} (64)

and

\[ V^F \frac{dE^F_2}{dt} = -q^F (E^F_{21} - E^F_{2o}) \]  \hspace{1cm} (65)

where \( V \) = volume of blood and \( F \) and \( M \) refer to the fetal and maternal compartments respectively.

At steady state, the maternal estrogen concentrations are related by
Equation 63 shows that at steady state,

\[ E_{2i}^F = E_{2o}^F \]

which is not substantiated by experimental data. This implies that estrogens are generated elsewhere in the fetus. To account for this generation, Equation 65 must be modified to

\[ VF \frac{dE_2^F}{dt} = -q^F(E_{2i}^F - E_{2o}^F) + R_{E_2} \]

so that at steady state,
So long as no long term accumulation of $E_2$ occurs, the amount produced by the fetus should be matched by that eliminated in the kidney. Therefore

$$R_{E_2} = q^K (k''_E E_{2o}^M) (1 + \frac{k''_q}{q^M})$$

(69)

where $E_{2o}^M$ concentration in the uterine vein if only the $E_2$ synthesized by the fetus is eliminated, as opposed to $E_{2o}^M$ which includes the quantity obtained from interconversion.

Treating the placenta as two well-mixed reactors separated by a membrane, and performing a mass balance for each compartment, one obtains

$$q^M (E_{21}^M - E_{2o}^M) = k_m^M (E_{2o}^M - E_{2o}^F) + k_{m1}^M (E_{1o}^F - E_{1o}^M)$$

(69)

$$q^F (E_{21}^F - E_{2o}^F) = k_m^F (E_{2o}^F - E_{2o}^M) - k_{m1}^F (E_{1o}^F - E_{1o}^M)$$

(70)

where the $k_m$'s are mass transfer coefficients multiplied by their respective areas available for exchange. $k_m$'s are included because some of the $E_1$ must be transported as $E_2$. Substitution into previous equations yields

$$M \frac{dE_{2o}^M}{dt} = -k_m^M (E_{2o}^M - E_{2o}^F) - q^K (1 + \frac{k''_q}{q^M}) E_{2o}^M + k_{m1}^M (E_{1o}^F - E_{1o}^M)$$

(71)

and

$$F \frac{dE_{2o}^F}{dt} = -k_m^F (E_{2o}^F - E_{2o}^M) + R_{E_2} + k_{m1}^F (E_{1o}^F - E_{1o}^M)$$

(72)

Since a small percentage of maternal blood is in the placenta,

$$E_{2o}^M \approx E_{2o}^F$$

(73)
whereas about 60% of the blood of the fetus is there,

\[ E_2^F = 0.6E_2^{2o} + 0.4E_2^{2i} \]  

(74)

Further substitution yields

\[
\frac{dE_2^M}{dt} = - \frac{k_m^M}{V^M(1 + \frac{k''q^M}{q^M})} (E_2^M - E_2^{2o}) - \frac{qk''}{V^M} E_2^M + \frac{k_m^M}{V^M(1 + \frac{k''q^M}{q^M})} (E_1^{0o} - E_1^{0o})
\]

(75)

\[
\frac{dE_2^F}{dt} = - \frac{k_m^F}{V^F} (E_2^F - E_2^{2o}) + \frac{qk''}{V^F} (1 + \frac{k''q^M}{q^M}) E_2^{2o} + \frac{k_m^F}{V^F} (E_1^{0o} - E_1^{0o})
\]

(76)

These are two coupled first order ODE describing the fate of \( E_2 \) in both the fetal and maternal blood streams. These can be solved upon knowing the parameters, some of which are disguised in the literature as something else. For example, \( q^M \) is equivalent to the metabolic clearance rate. This has been determined experimentally by Challis et al. (1974) for a 138-day pregnant sheep to be \( 2.624 \pm 0.237 \) l/min. This value is actually for estrone, but considering that \( E_1 \) and \( E_2 \) probably look alike to the kidneys, assuming the same MCR for \( E_1 \) and \( E_2 \) probably would not cause severe errors. Uterine blood flow rate in the same sheep has also been determined by the same group to be \( 0.395 \) l/min. The umbilical blood flow rate can be estimated by multiplying the fetal body weight by \( 199 \pm 20 \) ml/kg-min (Faber and Green, 1972) while the utero-placental blood flow rate is also in this neighborhood (Caton, 1972). The blood volumes can also be estimated from the respective body weights (Swenson, 1977). The \( k_m \)'s have not been determined, however. When the results of the analysis
in the previous section are applied here, some interesting results are obtained. This will be the topic of discussion in a later section.
MASS TRANSFER ACROSS A MEMBRANE WITH TURBULENT FLOW

Development of an Eddy Viscosity Function

In the area of turbulent flow, analysis of heat and mass transfer are complicated by the eddy viscosity which cannot be easily determined without resorting to some kind of empiricism. Frequently, more than one parameter in the model has to be determined experimentally. As mentioned earlier, the turbulent flow field is usually divided into three regions. Since the predominant mechanism of transport in different regions is not the same, one often develops velocity profiles which are valid in one particular region and not in others. Furthermore, it is often true that experimental measurements are more accurate in regions far away from the wall, hypotheses leading to velocity distribution close to the wall are, in essence, never tested.

In analysis, it would be convenient if a continuous eddy viscosity distribution function is available. Such a function would simplify the analysis and would reduce the arbitrariness in trichotomizing the flow field. The following is aimed at deriving a function of this nature with only one parameter. The expression

\[
\frac{\varepsilon}{\nu h^+} = 0.07 (1 - \eta^8)
\]

(77)

where

\[ h^+ \]

will be defined later.

fits well the data obtained by Reichardt (1951) for flow between parallel plates and the result by other investigators for pipe flow (see Mizushina and Ogino, 1970). A comparison of these can be seen in Figure 4.
Figure 4. Eddy viscosity function.
To obtain the velocity profile, Equation 77 is substituted into the equation of motion. It is more convenient to define a parameter $\alpha$ where

$$\alpha = 0.07R^+$$  \hspace{1cm} (78)

and $\alpha$ can be thought of as a parameter characterizing the intensity of turbulence. Equation 77 becomes

$$\frac{e}{\nu} = \alpha(1 - \eta^8)$$  \hspace{1cm} (79)

The equation of motion becomes

$$\frac{3}{2n} [(1 + \alpha(1 - \eta^8)) \frac{\partial u}{\partial \eta}] = \frac{10p}{\rho a x} \left( \frac{\delta^2}{\nu} \right)$$  \hspace{1cm} (80)

For steady flow, $\frac{\partial p}{\partial x} = \text{constant}$; $\frac{\partial p}{\partial x}$ can be replaced by $\frac{T_0}{\delta}$. The friction velocity is

$$U_* = \left( \frac{T_0}{\rho} \right)^{1/2}$$  \hspace{1cm} (81)

By defining $\bar{U} = \frac{U}{U_*}$ and rearranging, Equation 65 becomes

$$\frac{d}{d\eta} [(1 + \alpha(1 - \eta^8)) \frac{d\bar{U}}{d\eta}] = - \frac{U_* \delta}{\nu}$$  \hspace{1cm} (82)

which can be integrated using the no-slip and axisymmetry boundary conditions to give

$$\bar{U} = - \frac{h^+}{2\alpha} \left( \frac{1}{2k^3} \right) \frac{1}{2} \ln \left[ \left( \frac{x-k}{x-k}(1-k) \right) + \tan^{-1} \left( \frac{x}{k} \right) - \tan^{-1} \left( \frac{1}{k} \right) \right]$$  \hspace{1cm} (83)

where

$$h^+ = \frac{U_* \delta}{\nu}$$

$$x = \eta^2$$

$$k = \left( \frac{1+\alpha}{\alpha} \right)^{1/4}$$

Since $\alpha$ is often much larger than one, $k$ is for all purposes unity.
In calculating the velocity distribution, $\alpha$ has to be determined a priori. This may seem to be an impossible task at first glance, but $\alpha$ is related somewhat to the Reynolds number by

$$Re = 4h^+ \frac{1}{b} Ud\eta$$

(84)

The result of this will be shown in a later section. It should be cautioned at this point that Equation 79 is based on the experimental data of Reichardt and these data are only accurate far enough away from the channel wall. Therefore, the velocity profile given by Equation 83 may not be expected to hold in the immediate vicinity of the wall.

**Simple Diffusion Across Membranes**

The general formulation of the problem here is almost identical to that for laminar flow. All the assumptions stated earlier concerning the membrane and the two fluid streams also apply here except, of course, that the flows are now turbulent. The membrane is further assumed to have strong enough mechanical properties to withstand the high shear stresses imposed on it by the fluids.

The conservation equation for species A in stream I can be written as

$$\frac{U^+}{\eta^+} \frac{\partial c_I^+}{\partial x^+} = \frac{\partial}{\partial \eta_I^+} \left[ (1 + \frac{\varepsilon_D}{D}) \frac{\partial c_I^+}{\partial \eta_I^+} \right]$$

(85)

where $\varepsilon_D$ is the eddy mass diffusivity. Here, $\varepsilon_D$ is taken to be

$$\frac{\varepsilon_D}{D} = \frac{\varepsilon}{\nu} Sc = aSc(1 - \eta^5)$$

(86)

and this is supposed to hold for the entire range of $\eta$. Similarly, for stream II, the following relation applies:
For the membrane, Equation 13 is assumed to hold

$$\frac{\partial^2 c^+}{\partial \eta_m^2} = 0$$  \hspace{1cm} (13)

To study the effect of turbulence, Equations 85, 87 and 13 are solved simultaneously with the conditions stated by Equations 15-20. Again, the finite difference method is employed. Due to the steep gradients of velocity and concentration near the wall, much smaller grid spacing is required in order that accuracy of the approximation is not jeopardized. Since it is not economical to have very fine grids, some kind of manipulation of variables is called for. The transformation is performed on $\eta$ in a way which was proposed by Solbrig and Gidaspaw (1968) and used by Mendez and Sandall (1974) in their study of a falling film reactor, namely

$$S = \frac{\int_{\eta}^{1} \frac{d\eta}{1 + \epsilon_{m}/D}}{\int_{0}^{1} \frac{d\eta}{1 + \epsilon_{m}/D}}$$  \hspace{1cm} (88)

The effect of this transformation is that much finer spacing is obtained near the wall and slightly larger grids closer to the center of the channel where gradients are almost nonexistent. Some results can be seen in Figure 5.

Defining

$$S_o = \int_{0}^{1} \frac{d\eta}{1 + \epsilon_{m}/D}$$  \hspace{1cm} (89)

Equations 85 and 87 can be very conveniently written as
Figure 5. Relationship between $S$ and $\eta$. 
The subscripts I and II have been omitted from the S's in the above expressions, but they are understood to be there. Crank-Nicholson formulation of Equations 85 and 87 is straightforward.

Besides investigating the effects of turbulence on simple diffusion the presence of chemical reactions in the membrane is also considered. The reactions considered are of zeroth and first order in the transported component, A.

It may be appropriate to point out here that the quantities $U^+, C^+_I, C^+_II$ are all time-smoothed. One should be warned of using these quantities in cases where there is a homogeneous even-order reaction in the stream.
RESULTS AND DISCUSSION

Simple Diffusion in Laminar Flow

When Equations 12 and 14 are solved with the boundary conditions 15-20 through Crank-Nicholson approximation procedure, the concentration of A at various points in space can be determined. The concentration, as expected, depends on the solubility parameters as well as the diffusivity ratio. If the variable \( X^+ \) can be thought of as an average residence time, then the longer the fluid stays in the equipment, the more exchange takes place. The concentration profiles of the two streams for a wide range of values of \( \frac{D_m \delta}{D \delta} \) are shown in Figure 6. It can be seen that as \( X^+ \) increases, the concentration profiles flatten and eventually disappear, and it can be shown easily that \( C^+ \) takes on the value 0.5 asymptotically for cases where the solubility of A in both streams is equal, and \( C^+ \) reaches \( \frac{1}{1+\beta^2} \) as \( X^+ \) approaches infinity for unequal solubilities.

It is seldom convenient to report concentration profiles, so bulk concentrations are frequently used as indicators of the progress of operation. The bulk concentration (or the mixing cup concentration) is defined as

\[
C_{\text{bulk}}^+ = \frac{\int_0^1 C^+ U d\eta}{\int_0^1 U d\eta} = \int_0^1 C^+ U^+ d\eta
\]

A plot of \( C_{\text{bulk}}^+ \) vs. \( X^+ \) is in Figure 7. That the bulk concentrations approach 0.5 for large \( X^+ \) can be seen more clearly. Also note that the sum of the bulk concentrations is always 1.000000, showing that the principle of conservation of mass is not violated.
Figure 6a. Effect of $\frac{D_m \delta}{D \Delta}$ on concentration profile—simple diffusion in laminar flow.

$\beta_m = 2.0$

$\beta_2 = 1.0$
Figure 6b. Local Sherwood number—simple diffusion in laminar flow.
Figure 7. Effect of $\frac{D_m \delta}{D \Delta}$ on bulk concentrations—simple diffusion in laminar flow.

$\beta_m = 2.0$

$\beta_2 = 1.0$
As \( \frac{D_m \delta}{D \Delta} \) increases, the asymptotic concentration is approached more quickly. However, the difference is slight for resistance ratios greater than 5. This is due to the fact that when the resistances in the fluid streams are large compared to that in the membrane, the rate of mass transfer is limited by how fast \( \text{A} \) can diffuse to and from the interfaces. Mathematically, it is the solution to Equations 12 and 14 with the boundary conditions:

at \( \eta_1 = 1 \quad C^+_I = 0.5 \) \hspace{1cm} (93)

at \( \eta_m = 1 \quad C^+_II = 0.5 \) \hspace{1cm} (94)

Such solution is of course independent of \( D_m \) and hence the resistance ratio. Conditions 93-94 are nearly met for \( \frac{D_m \delta}{D \Delta} > 5 \). As this ratio decreases, the resistance in the membrane dominates, and large differences in bulk concentrations at large \( \lambda^+ \) can be resulted. In gas separation, Tang and Hwang (1976) have shown that liquid side resistance controls the mass transfer rate. Lakshminarayanaiah (1969), in discussing the diffusion of nonelectrolytes across membranes, stated that the bulk of the resistance to mass transfer resides in the membrane. The results of the present analysis show that the resistance in the liquid phases as well as in the membrane can be important, and the determining parameter is \( \frac{D_m \delta}{D \Delta} \).

In analysis for design purposes, neglecting the resistance in one or more phases frequently eases the mathematics. However, one should exercise caution when making such decisions.

The local Sherwood number can be defined as
Unlike the local bulk concentration, the local Sherwood number is totally insensitive to the resistance ratio (see Figure 6b). This is not surprising since the Sherwood number is a measure of the reciprocal of the resistance in the liquid phase, and is therefore a function only of the properties of the fluid and is independent of those of the membrane. The Sherwood number would change only if something like a homogeneous or heterogeneous chemical reaction occurs in the liquid phase.

If the resistances to mass transfer can be considered to be in series, then an overall mass transfer coefficient can be defined

\[ K = \frac{1}{\left(\frac{1}{k_{LI}} \right) + \left(\frac{\Delta}{D_m} \right) + \left(\frac{1}{k_{LII}} \right)} \]  

(96)

Inasmuch as \( k_{LI} = k_{LII} \), Equation 99 can be cast into the form

\[ K = \frac{D_m}{\Delta} \left(1 + \frac{2}{Sh} \frac{D_m \delta}{D \Delta} \right) \]  

(97)

It can easily be shown that as \( \frac{D_m \delta}{D \Delta} \) becomes large,

\[ K \approx \frac{Sh D}{2 \delta} \]

signifying that the process is controlled by mass transfer in the liquid streams. On the other hand, if the resistance ratio is low

\[ K \approx \frac{D_m}{\delta} \]

meaning that the membrane controls the rate of diffusion.
Effects of Solubilities

As stated earlier, the effects of the solubility of A in the membrane and in stream II are to be investigated. The results are shown in Figures 8 and 9. From Figure 8, it can be seen that the membrane solubility does not have great effect on the progress of transport unless $\beta_m$ approaches zero. The reason here is that diffusion across the membrane is not hindered as long as a steep enough concentration gradient can exist within it. The solubility parameter, $\beta_m$, dictates how steep that concentration gradient can be. So long as this limit is not reached, the effects of solubility are minimal. As the dominant resistance shifts from the liquid to the membrane phase, the effects of solubility are more pronounced because the maximum allowable concentration gradient in the membrane is approached more easily (compare Figure 8a with 8b).

The solubility of A in stream II has effects which are different from those of $\beta_m$. Here, the saturation point is changed resulting in great differences in the bulk concentration vs. $X^+$ plots. Once again, the bulk concentrations in the two streams add up to 1.00, showing that the total mass of A is conserved.

Combination of Solubilities and Resistance Ratios

It appears that any combination of $\beta_m$, $\beta_2$, and $\frac{D_m}{D} \frac{\delta}{\Delta}$ should yield results which would comply with the law of conservation of mass. This is only true when $\frac{D_m}{D} \frac{\delta}{\Delta}$ for both liquids concerned are equal. If they are not, then $\beta_2$ must differ from unity. Specifically,
Figure 8a. Effect of membrane solubility on bulk concentrations—simple diffusion in laminar flow.
Figure 8b. Effect of membrane solubility on bulk concentrations—simple diffusion in laminar flow.

\[ \frac{D_m \delta}{D \Delta} = 1.0 \]
Figure 9. Effect of solubility of A in stream II—simple diffusion in laminar flow.
However, if a consuming chemical reaction is present, this restriction can be lifted.

Effects of a First-Order Reaction

When a first-order reaction occurs within the membrane, the concentration profile in the membrane becomes slightly skewed due to the hyperbolic trigonometric terms, namely,

\[ C_m^+ = a_1 \cosh \eta_m + b_1 \sinh \eta_m \]  

The concentration profiles for the case where \( \gamma^2 = 1 \) are shown in Figure 10. The concentration profile for simple diffusion is included for comparison. Profiles shown in this figure are for \( \frac{D_m \delta}{\Lambda} = 5 \). The concentration gradients are steeper at \( \eta_m = 0 \) and reach a minimum at \( \eta_m = 1 \). This can be seen more clearly when the reaction rate is high. The result of this is a difference in the local Sherwood numbers in the two streams, namely, \( S_{h_1} > S_{h_II} \). It is quite obvious that not all the \( A \) that diffuses out of I reaches II unconverted. It can be shown that the fluxes at two sides of the membrane for any chosen \( X^+ \) are related by

\[ J \bigg|_{\eta_m = 0} = J \bigg|_{\eta_m = 1} + \Delta \int_0^1 k \cdot C_m^+ d\eta_m \]  

which is a particular case of an expression which is true throughout the membrane.
Figure 10. Concentration profiles in the stream when a first-order reaction is present in the membrane ($\gamma^2 = 1.00$).
The underlying principle in arriving at Equations 98 and 99 is simply that of mass balance. A more elegant derivation of 99 can be found in Thomas and Caplan (1976). It can also be noted from Figure 11 that instead of the increased transport from stream I, the local Sherwood number actually decreased slightly. The decrease is in such a manner that it is almost insensitive to the rate of reaction. This is attributable to the fact that when mass transfer is limited by the liquid film, increasing the demand (as in chemical reactions) in another phase would not ease the transport out of the source. The Sherwood number for \( \frac{D_m}{D} \) = 1.0 remains virtually unchanged with or without the reaction, however, small increases (<1%) can be noted at high reaction rates. At \( \frac{D_m}{D} \) = 0.5, increases in \( Sh_I \) are very slightly more noticeable. These observations tend to imply that as the value of \( \frac{D_m}{D} \) decreases, a reaction (of any order) in the membrane would decrease the relative resistance in the stream I. This is understandable as \( \frac{D_m}{D} \rightarrow 0 \), there is plenty of A in stream I awaiting entry into the membrane. A reaction in the membrane increases the demand of A, and thus eases the diffusion in stream I.

The effects of reaction rates on bulk concentrations are shown in Figure 12a,b,c. From Figure 12a and 12c, it can be seen that these effects are more profound for \( \frac{D_m}{D} = 5 \) than for \( \frac{D_m}{D} = 1 \). This is because the reaction rate in the former case is higher than that in the latter.
Figure 11. Effect of a first order reaction on the local Sherwood number of stream I.
$\gamma^2 = 0.00$

$0.01, 0.10, 1.00$

$\frac{D_m \delta}{D \Delta} = 5.0$
Figure 12a. Effect of a first-order reaction inside the membrane on $c_{i,bulk}^+$. 

$$\frac{D_m \delta}{D \Delta} = 5.0$$
Figure 12b. Effect of a first-order reaction inside the membrane on $c_{II\text{bulk}}^+$.

\[
\frac{D_m}{D} \frac{\delta}{\Delta} = 5.0
\]
Figure 12c. Effect of a first-order reaction within the membrane.
Provided that the parameters $\delta$, $D$, $\Delta$, and $\gamma^2$ are unchanged, $k_1$ in the Figure 12a case is five times that in Figure 12c.

The effect of membrane solubility is not very important when $B_m < 1$. The reaction rate is of course slowed down, and at low reaction rates, the effect of the reaction can be neglected altogether.

Fate of the Reaction Product

Equation 44 has been solved with boundary conditions 46-50 for \( \frac{D_{Am}}{D_{Bm}} = 1 \). The primary reason for choosing this value for the ratio is that the arithmetic is simplified. Before discussing the results, it should be pointed out that certain combinations of the parameters

\[
\frac{D_{Am}}{D_{Bm}}, \frac{D_{Am} \Delta}{D_{Bm} \Delta'}, \frac{D_{Am} \Delta'}{D_{Bm} \Delta''}, \frac{D_{Am} \Delta''}{D_{Bm} \Delta'''}
\]

are forbidden by the law of conservation of mass. For example, if

\[
\frac{D_{Am}}{D_{Bm}} = 1; D_{AI} = D_{AII} = D_{A} \text{ and } D_{BI} = D_{BII} = D_{B}
\]

then $D_A$ must be equal to $D_B$.

Returning to the distribution of the product of the reaction, recall that the concentration profiles of A in the membrane are skewed so that the magnitude of the gradient decreases monotonically as $\eta_m$ increases. The concentration profile of the product B is like a distorted arc. The slope is steeper closer to stream I, as depicted in Figure 13. The bulk
concentration in the two streams are also different as a result of this.  

\( c_{BIIbulk}^+ \) is always higher than \( c_{BIIbulk}^+ \). The difference is most marked for intermediate contact times (as much as 40%), and diminishes to about 1% for large contact times.

Zeroth or Pseudo-Zeroth Order Reaction

The effects of a slow zeroth order reaction are similar to those of a first order. The concentration profiles are parabolic with the quadratic form proportional to the rate of reaction. From Equation 52, it can be seen that \( b_0 \) must be negative. But since \( \frac{k_o \Delta^2}{D_m C_{Ao}} \) is always positive, differentiation of this equation shows quite explicitly that the gradients are steeper closer to stream I. As can be seen from Figure 14, the bulk concentration of the reactant as a function of \( x^+ \) for \( \frac{k_o \Delta^2}{D_m C_{Ao}} = 0.01 \) is

Figure 13. Concentration profiles in the membrane with a first-order reaction.
Figure 14. Effect of a zeroth-order reaction within the membrane.

\[ \frac{D_m \delta}{\bar{D} \Delta} = 5.0 \]

\[ \beta_m = 2.0 \]

\[ \beta_2 = 1.0 \]
almost identical to that for a first-order reaction with \( \frac{k \Delta^2}{D_m} = 0.01 \).

However, as the reaction rate increases, the influence of a zeroth-order reaction is much more eminent than that of a first-order reaction. The reason is clear. The rate of consumption of reactant in a first-order reaction is proportional to its local concentration while this is not so in a zeroth-order reaction. The result of this difference is that even at very low concentrations, the demand of A in the membrane remains unchanged in the latter case, and the reaction would progress until the supply of A is totally depleted.

At high rates of reaction, the reactant is consumed very rapidly. It is not long until the concentration gradients at the two membrane interfaces take on opposite signs. At this point, the amount of A transported to stream II is being recalled. Soon after this, the concentration of A in stream II becomes negative; the solution then becomes nonphysical. Notice that this happens more readily when the dominant resistance to mass transfer is in the liquid phase.

Mathematically, the pertinent equations can be solved, but the results do not make physical sense when \( c^+_{Am} < 0 \). The conservation of A in the membrane now becomes a moving boundary problem because reaction can no longer occur when the reactant is depleted. This moving boundary problem is a simple one. When the concentration in the membrane reaches zero, the concentration of A in the extract stream is so low that it can be neglected, so that only one moving boundary needs attending to. This is the reactant front, which recedes to \( \eta_m = 0 \) as \( X^+ \) reaches infinity. The criterion for convergence here is that the flux of A at the front is zero.
Algebraically, the concentration of A in the membrane (>0) can still be described by

\[ C_m^+ = a_0 + b_0 \eta_m + \frac{k_o \Delta^2}{2D_cA_o} \eta_m^2 \]  

(100)

which is equal to zero at

\[ \eta_m^* = -\frac{b_o}{d} - \left(\frac{b_o}{d}\right)^2 - \left(\frac{2a_o}{d}\right) \]  

(101)

where \( d = \frac{k_o \Delta^2}{D_cA_o} \). Iteration is continued until an \( a_o \) is chosen such that

\[ |b_o + d\eta_m^*| \leq 10^{-6} \]  

(102)

This converges very slowly. However, this has been used in the calculation for \( \frac{k_o \Delta^2}{D_cA_o} = 1.00 \).

Application of Previous Analysis to Placental Estrogen Transport

For a 175 kg ewe with an approximately 2 kg fetus, using the following estimates

\[ k_o^q^K = 2.624 \quad \text{ (1/min)} \]
\[ q^F = q^M = 0.395 \quad \text{ (1/min)} \]
\[ V^M = 10 \quad \text{(1)} \]
\[ V^F = 0.2 \quad \text{(1)} \]

Equations 75 and 76 can be rewritten as

\[ \frac{dE^M_2}{dt} = \frac{1}{764} \left[ -k_{m2}^M (E^M_{2o} - E^F_{2o}) - 20.6E^M_{2o} + k_{m1}^M (E^F_{1o} - E^M_{1o}) \right] \]  

(75a)
Examination of the above two equations immediately indicates that the fetal side would be more sensitive to disturbances mainly due to its small volume.

Inasmuch as the two flow rates are taken to be equal, results from the analysis of mass transfer in laminar flow can be applied here. Estrogens are quite hydrophobic, so the solubilities in the placenta (membrane phase) would be expected to be somewhat higher than those in the blood streams. It is also reasonable to assume that the solubility of all estrogens in the blood streams are equal. $E_2$ can be analyzed as an inert material passing from the fetal side of the placenta to the maternal side for as long as the amount consumed by the placenta is small, so that $k_{m2}^F = k_{m2}^M = k_{m2}$. As far as $E_1$ is concerned, it can be treated as a reactant diffusing through the placenta while being converted there to $E_2$ in a first-order reaction. Recall that in this case

$$k_{m1}^F > k_{m1}^M$$

because $E_1$ is more concentrated in the fetal side. Upon subtracting Equation 93a from 94a, one has

$$\frac{dE_2^F}{dt} = 5[-k_{m2}^F(E_2^F - E_2^M) + \frac{20.6E_2^M}{E_2^M} + k_{m2}^F(E_1^F - E_1^M)]$$

(76a)

The level of estrone is usually quite steady and its difference in blood streams is often well-maintained. Suppose the assumptions made in the
derivation of equation are valid, then it is easy to show that if \( E_{20}^F \approx E_{20}^M \), then

\[
\frac{d(E_{20}^F - E_{20}^M)}{dt} > 0
\]

This shows that if initially \( E_{20}^F \approx E_{20}^M \), the difference would increase until a steady state is reached. Of course, this has to be true if estrogens synthesized by the fetus can be eliminated. Equations 93a and 94a can also be divided by the concentration of \( E_1 \) in their respective blood streams to give

\[
\frac{d(E_{20}^M/E_{10}^M)}{dt} = \frac{1}{T_3.4} \left[ -k \frac{E_{20}^M}{E_{10}^M} - \frac{E_{20}^F}{E_{10}^M} - 20.6 \frac{E_{20}^M}{E_{10}^M} + k_m (\rho - 1) \right] \tag{104}
\]

and

\[
\frac{d(E_{20}^F/E_{10}^F)}{dt} = 5 \left[ -k \frac{E_{20}^F}{E_{10}^F} - \frac{1}{\rho} \frac{E_{20}^M}{E_{10}^F} + 20.6 \frac{1}{\rho} \frac{E_{20}^M}{E_{10}^F} + k_m (1 - \frac{1}{\rho}) \right] \tag{105}
\]

where

\[
\rho = \frac{E_{10}^M}{E_{10}^F}
\]

It is not difficult to show that if the L.H.S. of equation is equal to zero, and \( E_{20}^M \approx E_{20}^M \), then

\[
\frac{d(E_{20}^F/E_{10}^F)}{dt} > 0
\]

When both equations are simultaneously taken to steady state, it can be shown that
\[
\frac{E^F_{20}}{E^F_{10}} = \frac{1}{\rho} \left(1 + \frac{20.6}{k_{m2}}\right) \frac{E^M_{20}}{E^M_{10}} - \frac{(\rho - 1)}{\rho} \frac{k_{m1}}{k_{m2}}
\]  

(106)

The second term on the R.H.S. is usually small and therefore can be neglected. As long as

\[1 + \frac{20.6}{k_{m2}} > \rho\]

then

\[\frac{E^F_{20}}{E^F_{10}} > \frac{E^M_{20}}{E^M_{10}}\]

The value of \(k_{m2}\) can be estimated from Equation 103 and the data in Table 3, and it is of the order of 1/4-1/10. \(\rho\) is usually between 4-8. With these values, the ratio of the level of \(E_2\) to that of \(E_1\) in the fetal blood would be expected to be higher than that in the maternal circulation, which is in agreement with experimental data.

If \(k_{m2}\), \(k_{m1}^F\) and \(k_{m1}^M\) can be determined and other parameters estimated accurately, Equation 93 can in principle be used to detect functional abnormalities in the placenta. The \(k_m\)'s can be computed from estrogen levels in the fetal and maternal blood. However, this is not advisable in clinical settings because of the inaccessibility and fragility of the fetus. Such procedure may do more harm to the fetus than a small placental malfunctioning. If enough experiments are performed so that the normal range of \(k_m\)'s are well-established in animals, then Equation 93 can be used for function testing at least in the species tested. For example, if a high concentration \(E_2\) solution is infused at a high rate, and if
\( E_2^M \) remains higher in the maternal blood than in the infusate, this shows that \( E_2 \) is converted from something else in the placenta, which is equivalent to saying the activity of the enzyme catalyzing the reaction

\[
E_1 + E_2 \xrightarrow{\alpha} \frac{E_1}{E_2}
\]

is high. Similarly, a dose of \( E_1 \) can be injected into the maternal circulation. If an increase in \( E_2 \) results, then the same information is implied.

Tests of this kind may well supplement the DHEA loading test for fetoplacental well-being proposed by Pupkin et al. (1976) because the latter assumes that the conversion to estrogen occurs in the placenta while Equation 65 says that it is not really possible. There is no question that DHEA is converted to AND in the fetus, but it is very unlikely that all the AND gets aromatized in the placenta; so the DHEA test is mainly a test for fetal but not necessarily placental enzymatic activities. Placental functions therefore can be tested more specifically using the activity of the enzymes in estrogen interconversion as an indicator.

**Turbulent Mass Transfer**

**Velocity distribution resulting from the eddy viscosity function**

Using the eddy viscosity function

\[
\frac{\nu}{\nu} = \alpha(1 - \eta^\delta)
\]  

(79)

the velocity profiles for various values of \( \alpha \) are shown in Figure 15. As can be predicted, at higher intensities of turbulence, \( \alpha \), the velocity profiles are essentially flat. For large values of \( \alpha \), the 1/7-power law
Figure 15. Dependence of velocity profile on $\alpha$. 
is well-approximated, but for small \( \alpha \)'s, the profile obtained by integrating Equation 82 underestimates the dimensionless velocity near the wall. As \( \alpha \) decreases to near zero, the parabolic profile for laminar flow is obtained.

Examination of the universal velocity profile shows that \( \bar{U} \) obtained through Equation 79 is low compared to what has been measured. However, for \( y^+ \) (dimensionless distance from the wall: \( y^+ = h^+(1 - \eta) \)) greater than about 200, the slope of \( \bar{U} \) vs. \( y^+ \) is nearly the same as that in published data (see Bird et al., 1960, Chapter 6). This seems to imply that although Equation 79 describes well the behavior of the eddy kinematic viscosity, it probably does not apply to regions in the vicinity of the wall.

The Reynolds numbers calculated from Equation 84 are overestimates. However, if a correction factor is added to the UVP, the Reynolds number approaches more closely that predicted by Blasius formula from the friction factor. The friction factor here is defined as

\[
f = 2 \left( \frac{1}{\bar{U}} \right)^2
\]

Addition of the correction factor does not have much effect on the velocity profile (relative to the average velocity) particularly for large \( \alpha \)'s because the contribution near the wall is small. The factor must approach zero as \( \eta \to 1 \), and become constant when \( h^+(1 - \eta) \approx 30 \). One such function is

\[
(4.9673 + 0.0057\alpha)\tan^{-1}(h^+(1 - \eta))
\]

Adding the above function to \( \bar{U} \) is like arbitrarily choosing a constant of
integration, as done by Mizushina and Ogino (1970). The justification for this is that it works. Without using this factor, the relationship between $\alpha$ and $Re$ is shown in Figure 16.

Inadequacy of the eddy viscosity function to predict the velocity may have some repercussion on the eddy diffusivity function. However, it is the relative quantities that are used in all calculations, and since it has been demonstrated that the velocity profile relative to the average velocity is fairly well-predicted, the errors caused by using a similar function in mass transfer studies may not be great.

**Simple diffusion in turbulent flow**

As can be expected, mass transfer in the liquid phases is greatly enhanced by the circulating eddies. This can be seen from Figure 18 where the liquid film Sherwood number is plotted versus the dimensionless distance $X^+$. This is due to the very large concentration gradients near the wall at almost all bulk concentrations. The gradients are actually so steep that they appear vertical on a $C_1^+ \text{ vs. } \eta_1$ diagram. Therefore, concentration profiles of both streams are plotted versus $S$, the transform variable in Figure 19. Table 4 is included to ease the interpretation of these graphs. The wall gradients in Figure 24, when multiplied by about 1000, are good approximates of the actual slopes.

The local Sherwood number is also dependent on $\alpha$—it increases with $\alpha$. The bulk concentration, on the other hand, is not very sensitive to the intensity of turbulence. This can be explained by Equation 97, where the overall mass transfer coefficient is defined as
Figure 16. $\alpha$ as a function of $Re$. 
Figure 17. Effect of turbulence on Sh₁—simple diffusion.
\[ \alpha = 25, \text{Sc} = 1 \]
\[
\frac{D_m \delta}{D \Delta} = 5, \beta_m = 2
\]
\[ \beta_2 = 1 \]

Figure 18. Concentration profile of the feed stream in turbulent flow.
$Sc = 1.00$

$\beta_m = 2$

$\beta_{II} = 1$

$\frac{D_m \delta}{D \Delta} = 5$

Figure 19. Effect of the intensity of turbulence—simple diffusion in turbulent flow.
Table 4. Relationship between η and the transform variables

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\[ K = \frac{D_{m}/\Delta}{1 + \frac{2}{Sh} \left( \frac{D_{m} \delta}{D \Delta} \right)} \] (97)

Since \( Sh \) is high in turbulent flow, the contribution by the second term in the denominator is often masked by that of 1, showing that the mass transfer is mainly controlled by diffusion across the membrane, making the rate of transport insensitive to turbulence, as demonstrated in Figure 19.
However, the above statement is not always true. When the Schmidt number is small, particularly when it is near zero, the amount transported by eddies is negligible compared to that by molecular diffusion. This can be seen from the eddy diffusion expression

\[
\frac{\varepsilon_D}{D} = 1 + \alpha Sc(1 - \eta^5)
\]

(72)
as \(Sc \to 0\), \(\frac{\varepsilon_D}{D} \to 1\). The effects of low Schmidt numbers are graphically presented in Figures 20 and 21.

**Effects of a chemical reaction in the membrane**

As discussed earlier, when the dominant resistance resides in the membrane, a chemical reaction greatly increases the mass transfer rate. This is well-demonstrated when the flowing streams are turbulent. The local Sherwood numbers are not changed to any appreciable extent so they will not be plotted, but the changes in bulk concentration versus \(x^+\) are substantial.

**Effects of a first-order reaction**

The effects of a first-order reaction in the membrane on the liquid phase bulk concentrations are shown in Figure 22. Again, at low reaction rates, the local bulk concentrations approach those in simple diffusion. At high rates of reaction, the supply of A in stream I is depleted much more rapidly than in simple diffusion.

The distribution of the reaction product is similar to laminar flow, i.e., the bulk concentration is greater in stream I if the solubility of A in the two liquid streams is equal. See Figure 23.
Figure 20. Local Sherwood numbers for low Schmidt numbers.
Figure 21. Effects of low Schmidt numbers on bulk concentrations.
\[ \beta_m = 2 \]
\[ \beta_{II} = 1.00 \]
\[ \frac{D_m \delta}{D \Delta} = 5 \]

Turbulent flow, \( \alpha = 25 \), \( Sc = 1.00 \)

**Figure 22.** Effect of a first-order chemical reaction in the membrane.
\[ \alpha = 25 \]
\[ Sc = 1.00 \]
\[ \beta_m = 2 \]
\[ \beta_1 = 1 \]
\[ \frac{D_m \delta}{D \Delta} = 5 \]

Figure 23. Distribution of products in turbulent streams, first-order reaction.
Effects of a zeroth-order reaction

The effects are similar to those of a first-order reaction. For large values of \( \frac{k_o \Delta^2}{D_mC_A^0} \), the decrease in bulk concentration in stream I is more severe than that caused by a first-order reaction (see Figure 24). This is because the reaction proceeds with no reference to the local concentration until the reactant has completely been consumed. As far as the reaction product is concerned, it is distributed evenly in the two liquid streams.

In every case, be it simple diffusion or diffusion with chemical reaction in the membrane, the law of conservation of mass is always obeyed, i.e., the sum of the dimensionless concentration of A and B is always unity at every \( X^+ \).
turbulent flow, \( \alpha = 25 \)

\[ Sc = 1.00 \]

\[ \beta_m = 2.0 \]

\[ \beta_{II} = 1.0 \]

\[ \frac{D_m \delta}{D \Delta} = 5.0 \]

**Figure 24.** Effect of a zeroth-order reaction in the membrane.
CONCLUSIONS

A model for studying mass transfer between two cocurrent laminar streams separated by a reactive membrane has been developed. This model can be used in the study of transplacental transport, and the results can be used as guidelines in the design of membrane processes.

Analysis based on this model confirms that, contrary to the general belief, the resistance to mass transfer resides primarily in the fluid streams for nominal values of $\frac{Dm \delta}{D \Delta}$, which has been shown by Tang and Hwang (1976). The effect of the solubility of the penetrant in the membrane is not noticeable unless it is very low compared to that in the feed stream, in which case transmembrane diffusion is greatly hindered. The solubility of the diffusing species in the extract allows the system to proceed toward a different point of equilibrium than if both streams have the same solubility. However, the dimensionless residence time required to effect the same fractional equilibrium remains unchanged. Moreover, the local Sherwood number in the feed stream is insensitive to changes in any of the parameters mentioned above.

When enzymes are insolubilized in the membrane so that the diffusing species is consumed in a first-order reaction, the bulk concentration in the feed stream decreases more rapidly when the reaction rate is high. The local Sherwood number in the feed stream is only very slightly affected, however. The product is distributed so that it is as much as 40% more concentrated on the feed side than on the extract side. This difference diminishes to about 1% at large contact times. If the reaction in one of zeroth- or pseudo-zeroth order, its effects are similar to those
of a first-order reaction at low reaction rates. At intermediate rates, the effects are more noticeable because the reaction progresses independently of the local reactant concentration. At high reaction rates, the rate of consumption exceeds that of diffusion. As the dimensionless residence time increases, the reactants transferred to the extract stream are gradually returned to the membrane so that the reaction can proceed, and it does until the reactant is depleted locally. The product of the chemical reaction is evenly distributed in all cases except when part of the membrane becomes void of the reactant, as in the case of high reaction rates. In that case, the product is richer in the feed stream. Again, the local Sherwood number is not greatly affected because the bulk of the resistance is in the membrane.

Conservation equations written for the circulating estrogen in the placenta indicate that some of the estrogens must be synthesized in the fetus despite current consensus that the synthesis is almost exclusively in the placenta. When the results of the above analysis are applied to the placenta in conjunction with the experimental data available, it can be shown that in sheep, at steady state, the ratio of estradiol to estrone in fetal blood is greater than its counterpart in maternal blood. Some of the equations used in this study can potentially be used to test placental functions.

Extension of the above analysis to turbulent flow shows that the resistance to mass transfer is mainly in the membrane. Increasing the intensity of turbulence as well as the presence of a reaction in the mem-
brane increases the local Sherwood number. Otherwise, the effects of a reaction in the membrane are the same as that in laminar flow.
BIBLIOGRAPHY


ACKNOWLEDGMENTS

I wish to express my gratitude to Professor R. C. Seagrave for his patient guidance and moral support during the course of my graduate study, and to Professors D. L. Carlson, C. E. Glatz, J. D. Stevens, and D. F. Young for serving on my committee. I also wish to thank Professor F. B. Hembrough for teaching me the surgical techniques that are indispensable in obtaining chronic fetal blood samples, and Joyce Feavel for her help in the operating theater.

The Biomedical Engineering Program, the Graduate College, and the Department of Engineering Science and Mechanics have provided me financial assistance for which I am particularly thankful.

Lastly, I would like to thank my parents for their uninterrupted encouragement.