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The process of separation involves several fundamental physical phenomena, as the constituents in the feed stream pass over the membrane, into it, through it, and finally leave the membrane on the other side.

Thus, the basic processes of permeation and diffusion, with the attendant surface phenomena, will be treated.

1 PERMEATION AND DIFFUSION

Permeation is a phenomenon in which a certain species or component is passing through another substance, usually but not necessarily by means of diffusion. The term “diffusion” specifically refers to molecular diffusion, while permeation stands for a much more general phenomenon of mass transmission. In fact, permeation is a phenomenological definition. Thus the term encompasses a variety of transport mechanisms. A number of different kinds of driving forces can cause permeation. To name a few, the concentration gradient, pressure gradient, electric potential gradient, or even the temperature gradient may produce permeation. Depending on the specific permeation mechanisms the flow process may be called diffusion, osmosis, electrodialysis, electro-osmosis dialysis, reverse osmosis, ultrafiltration, electrophoresis, and so forth. These various phenomena will be discussed separately in Chapter III.

Nevertheless, it is necessary to define a quantity to express the overall degree of permeation in general, regardless of the actual transport mechanism. Even in the case where the actual permeation mechanism is known to be diffusion, the general definition of permeability may be more useful than the molecular diffusivity. To calculate diffusivity, the actual concentrations of diffusing
species in the membrane should be known. But these being impossible to
measure experimentally, one therefore has to rely on the assumption that an
equilibrium state exists at the membrane surface. This is, of course, undesirable,
and frequently the assumption is subject to criticism.

A direct approach, that is, defining a phenomenological permeability, is not
only practical but also a realistic way of expressing the overall degree of
permeation through membranes. Permeability is defined in terms of concentra-
tions or pressures, which exist outside of the membrane itself and thus are
measurable experimentally.

![Diagram](image)

**Fig. 2.1** Concentration profile across the membrane.

Referring to Fig. 2.1, the following equations can be written:

\[
F = Q_1 S \frac{\Gamma_1 - \Gamma_2}{l} \quad (2.1)
\]

or

\[
F = Q_p S \frac{P_1 - P_2}{l} . \quad (2.2)
\]

These equations* may be used regardless of the actual permeation mechanism.
As a matter of fact, the detailed mechanisms do not need to be known for the
measurements and for the calculation of permeabilities by the above equations.

If the actual permeation mechanism is diffusion, Fick's first law can be used
for a slow process. (See Eq. 3.13 for the general case.) For the same steady-state

*Symbols are defined in the Nomenclature List at the end of Chapter III.
permeation flux \( F \),

\[
F = DS \frac{C_1 - C_2}{l}.
\]  

(2.3)

Here, \( C \) represents the actual concentration within the membrane; however, \( \Gamma \) and \( P \) in Eqs. 2.1 and 2.2 represent the concentration and pressure, respectively, of bulk fluid outside of the membrane. Equation 2.3 is good in theory but not useful in practice when the concentrations in the membrane are unknown.

When permeation is due to other phenomena, we can similarly rewrite Eq. 2.3 in terms of new variables. However, this requires a model of the actual transport mechanism. As in the case of diffusion, we may be more specific with respect to permeation phenomena, but we must also accept the fact that these equations will be model dependent. For example, the permeation of gases through a microporous membrane is understood as the sum of Knudsen flow and surface flow. If we want to express the flow equation based on these phenomena, we have to agree upon a model of surface flow, which can describe the observed experimental results. There are many different models, sometimes conflicting with each other, therefore resulting in many different flow equations. Thus, a flow coefficient based on one model cannot be compared with a flow coefficient based on another model. However, if we choose to use the permeability equation, either (2.1) or (2.2), the problem does not exist.

There is one necessary precaution when we use the phenomenological permeability; that is, the phenomenological permeability is not a property of the membrane. Rather, it is a phenomenological quantity that depends on the experimental conditions under which the process is conducted. This overall permeability is a measure of permeation through not only the membrane but also the boundary layers on either side of the membrane, if there are any. Because the bulk concentrations or pressures are used in the equation, what goes on in the boundary regions is already included in the permeability. The boundary layer resistances can be analyzed and separated from the total permeability by a study of the membrane-thickness effect on permeability as discussed below.

A study of the thickness effect on permeability reveals explicity how the permeability and diffusivity are related. A hypothetical concentration profile and a schematic view across the membrane are shown in Fig. 2.1. It is assumed that both sides of the membrane are covered by thin layers of immobile fluid, which would give an extra resistance to permeation. The mass transfer through such a system consists of the following stepwise processes:

1. Diffusion through the boundary layer
2. Sorption into the membrane
3. Diffusion through the membrane
4. Desorption out of the membrane
5. Diffusion through the boundary layer

Each step represents a resistance to the gas transport of different magnitude. For practical purposes, however, the resistances of some steps are negligible in comparison with those of others. In the case of gas-phase permeation, processes 1 and 5 are not involved, and the resistances due to the steps 2 and 4 may even be negligible. However, for liquid-phase permeation, a large boundary resistance may result from steps 1, 2, 4, and 5. The presence of these boundary resistances reduces the available driving force for diffusion inside the membrane.

Using the definition of overall permeability given by Eq. 2.1, the steady-state flow equation is written as

\[ F = Q'S \frac{\Gamma_1 - \Gamma_2}{l} \]  \hspace{1cm} (2.4)

If the diffusivity of the membrane is independent of concentration, the same steady-state flow rate for the inside of the membrane can also be expressed by

\[ F = DS \frac{C_1 - C_2}{l} \]  \hspace{1cm} (2.5)

Here Fick's first law is used. For the sake of simplicity, the second term in the more rigorous Eq. 3.13 is neglected. Should diffusivity be concentration dependent, an average diffusivity can be used:

\[ F = \bar{D}S \frac{C_1 - C_2}{l} \]  \hspace{1cm} (2.6)

where

\[ \bar{D} = \int_{C_2}^{C_1} \frac{D}{C_1 - C_2} dC \]  \hspace{1cm} (2.7)

Because it is very difficult to separate steps 2 and 4 from steps 1 and 5 experimentally, it is convenient to lump the resistances of steps 1 and 2 in one group, and steps 4 and 5 in another. Then one can write the flow equation for one side of the membrane:

\[ F = S \frac{\Gamma_1 - \Gamma_1^*}{r_1} \]  \hspace{1cm} (2.8)

and for the other side:

\[ F = S \frac{\Gamma_2^* - \Gamma_1}{r_2} \]  \hspace{1cm} (2.9)
where \( r_1 \) and \( r_2 \) are film resistances including resistances of sorption and desorption if they exist. The fictitious quantities, \( \Gamma^*_1 \) and \( \Gamma^*_2 \), are the concentrations that would have produced the inside concentrations \( C_1 \) and \( C_2 \), respectively, under equilibrium conditions. If a linear isotherm (Henry's law) is applicable,

\[
C_1 = S_m \Gamma^*_1, \\
C_2 = S_m \Gamma^*_2.
\]  

(2.10)

Combining Eqs. 2.8 to 2.11 with Eq. 2.5, and solving for \( F \), yields

\[
F = \frac{S D S_m (\Gamma_1 - \Gamma_2)}{D S_m (r_1 + r_2) + l}.
\]  

(2.12)

Comparing Eq. 2.12 with Eq. 2.4, the following is obvious:

\[
Q' = \frac{D S_m l}{D S_m (r_1 + r_2) + l}.
\]  

(2.13)

This equation tells exactly how the observed permeability changes as the thickness of a membrane varies. Also, it shows that the film resistance could be significant when the diffusivity of the membrane is large, or when the thickness of the membrane is small. If there is no such film present, then the film resistance simply becomes zero, and the observed permeability reduces to the familiar form:

\[
Q' = D S_m.
\]  

(2.14)

This equation has been used widely in many systems. However, it is clear from Eq. 2.13 that Eq. 2.14 holds only in a special case. Furthermore, Eq. 2.13 illustrates the fact that permeability is a phenomenological coefficient rather than a property of a given system, as given in Eq. 2.14. A change of an outside condition, such as film resistance or membrane thickness, alters the value of permeability. Therefore, in general, a comparison of two permeabilities for the same system but at different experimental conditions may not be meaningful.

The analysis of the thickness effect can be easily achieved by inverting Eq. 2.13:

\[
\frac{1}{Q'} = \frac{1}{D S_m} + (r_1 + r_2) \frac{1}{l}.
\]  

(2.15)
When the inverse permeability is plotted against the inverse thickness, a straight line will result. From the intercept, the limiting value of permeability at infinite thickness will be obtained. The slope of the straight line gives the resistances of the boundary layer. A special example of the above analysis will be given in Chapter X for the dissolved oxygen permeation through a silicone rubber membrane.

2 NONEQUILIBRIUM THERMODYNAMICS

The phenomena of mass transmission across membranes are irreversible processes. Furthermore, a number of different driving forces can cause mass permeation through membranes, as mentioned in the previous section. Therefore, in order to discuss the general theory of membrane permeation, perhaps the best approach would be to start with the phenomenological theories of nonequilibrium thermodynamics.

There are three basic principles in nonequilibrium thermodynamics. The first law states that any driving forces can create any fluxes of nonequilibrium processes. The fluxes and forces are linearly related as follows:

\[ J_i = \sum_j L_{ij} X_j, \]  

(2.16)

The second law states that the phenomenological coefficients satisfy the Onsager reciprocal relationships:

\[ L_{ij} = L_{ji}. \]  

(2.17)

The third law specifies that the rate of lost work or entropy production multiplied by the temperature due to any irreversible processes can be expressed as the sum of products of conjugated fluxes and forces:

\[ \phi = T \frac{d \Delta S}{dt} = \sum_i J_i X_i. \]  

(2.18)

There are some exceptions to the above principles. The first one is the so-called Curie theorem: "For an isotropic system, fluxes and forces of different tensorial character (not rank) do not couple." The second one concerns the Onsager reciprocal relations. When an external field \( |B| \) is present, Eq. 2.17 is slightly modified to read

\[ L_{ij} (|B|) = L_{ji} (-|B|), \]  

(2.19)

where \( |B| \) may be an external magnetic field or the angular velocity of rotation.
for systems with Coriolis forces.

The linear law, Eq. 2.16, is just a generalization of the well-known laws of Fick, Fourier, Poiseuille, Ohm, or D'Arcy, which are linear relationships only between conjugated fluxes and forces. The generalized equation covers these existing laws, and all of the coupling phenomena. Such are the Dufour effect, Soret effect, electro-osmosis, electrophoresis, sedimentation potential, streaming potential, and the Donnan equilibrium. The Onsager reciprocal relationships are very valuable in studies of the coupled phenomena. They provide the symmetric results between a pair of coupled phenomena. For example, Saxén's relation in electrokinetic phenomena can be derived from this reciprocal equation [1].

The study of nonequilibrium thermodynamics is a phenomenological theory. It does not offer any explanation of how materials permeate through membranes. The actual mechanisms of transport cannot be unveiled by the result of a thermodynamic study. As in the case of classical equilibrium thermodynamics, nonequilibrium thermodynamics only tells the limits of certain phenomena. It describes a system by macroscopic variables. It is especially useful for the study of systems in which couplings take place between two or more processes.

In membrane permeation, nonequilibrium thermodynamics is of no value if there is only one kind of driving force that causes one type of flux. However, this phenomenological study is very helpful when there are two or more driving forces generating two or more fluxes and coupled phenomena between them.

As an example, let us consider the electrokinetic phenomena. A porous membrane separates an isothermal system of multicomponents carrying electrical charges into two compartments. From conservation of mass, energy, and charge, and utilizing the Gibbs equation, the entropy production rate is obtained from the following equation [2]:

$$\phi = T \frac{dS}{dt} = J \Delta P + I \Delta E. \quad (2.20)$$

This equation corresponds to Eq. 2.16. We can write the linear phenomenological equations for fluxes and forces from Eq. 2.17:

$$I = L_{11} \Delta E + L_{12} \Delta P, \quad (2.21)$$

$$J = L_{21} \Delta E + L_{22} \Delta P. \quad (2.22)$$

Equation 2.21 tells us that both the electrical potential and the pressure gradient can cause the electric current. Likewise, Eq. 2.22 tells us that both the electric potential and the pressure gradient are responsible for the bulk volume flow. From the Onsager reciprocal relationship, Eq. 2.18,
\[ L_{12} = L_{21}. \]  
(2.23)

The above equations are basic laws of nonequilibrium thermodynamics for our system. Now, let us see how these equations describe the various electrokinetic phenomena.

First, the streaming potential or mechanolectric effect is an electric potential buildup across the membrane due to a pressure difference when there is no electric current. From Eq. 2.21:

\[ \left( \frac{\Delta E}{\Delta P} \right)_{I=0} = -\frac{L_{21}}{L_{11}}. \]  
(2.24)

Second, the electro-osmosis or electroendosmosis is defined as the bulk volume flow due to the electric current when the pressure drop across the membrane is zero. From Eqs. 2.21 and 2.22:

\[ \left( \frac{J}{I_{\Delta P=0}} \right) = \frac{L_{21}}{L_{11}}. \]  
(2.25)

Third, the electro-osmotic pressure is the pressure buildup across the membrane due to an electrical potential difference when there is no mass flow. From Eq. 2.22:

\[ \left( \frac{\Delta P}{\Delta E} \right)_{J=0} = -\frac{L_{21}}{L_{22}}. \]  
(2.26)

Fourth, the streaming current is an electric current caused by a bulk flow of material across the membrane when there is no electrical potential drop. From Eqs. 2.21 and 22:

\[ \left( \frac{I}{I_{\Delta E=0}} \right) = \frac{L_{12}}{L_{22}}. \]  
(2.27)

Using the Onsager reciprocal relationship, Eq. 2.23, we can combine Eqs. 2.24 to 2.27 into the following two equations:

\[ \left( \frac{\Delta E}{\Delta P} \right)_{J=0} = -\left( \frac{J}{I_{\Delta P=0}} \right), \]  
(2.28)

\[ \left( \frac{\Delta P}{\Delta E} \right)_{J=0} = -\left( \frac{I}{J_{\Delta E=0}} \right). \]  
(2.29)
The above equations are known as Saxén's relations [1], and these have been verified experimentally [3].

References