1.04 Introduction

The objective of this chapter is to provide the beginning researcher or practitioner a comprehensive introduction to mass transport in polymeric membranes that will help in digesting and perhaps extending the vast literature that has developed over the past half-century and continues to grow rapidly. The scope is limited to systems where transport occurs by a solution-diffusion mechanism; this implies that the membrane has no pores or is fully dense. Of course, useful membranes are generally complex structures, but the type of interest here has at least a dense skin that controls the transport at a molecular level.

A common feature of all membranes processes is the transfer of one or more species from an upstream fluid phase through the membrane to a downstream fluid phase; the fluid phases may be gases, vapors, or liquids. In the solution-diffusion process, the species being transported molecularly dissolve in the polymer membrane, diffuse through the polymer segments, and then leave the membrane at the downstream surface to enter the fluid phase there. The polymer is an active participant in both the solution and diffusion processes. The sorption is a thermodynamic process while the transport is a kinetic process, and in each the polymer comprising the membrane has to be considered one of the components. In many porous membranes, the membrane material is not an active participant and only its pore structure matters, not its molecular structure. In the following sections the relationships that describe penetrant diffusion in polymers will be described; these can vary from very simple to complex depending on levels of approximation that are permissible. Then the various sorption or solution relationships that can be operative will be described for the different polymeric states that find use as membranes. The solution and diffusion relationships are then combined in various forms for describing the permeation and permselectivity of species through membranes. These relationships are first developed for binary systems, that is, the membrane and one penetrant. In most membrane processes, there are two or more penetrants since the purpose is to separate these species. In some cases, the simple binary relationships give an adequate description even for multiple penetrants if the penetrants permeate more or less independently. However, penetrant–penetrant interactions in both sorption and diffusion
can occur; thus, the reader is introduced to the considerably more complex ternary relationships.

There are a number of books [1–8] and review articles [9–16] that the interested reader can consult for more details and a further introduction to the literature on membrane processes.

1.04.2 Diffusion in Polymers

Quite often discussion of diffusion in polymers begins with the following simple relation between the flux of penetrant and the gradient of its concentration:

\[
\text{Flux} = -D \frac{dC}{dz}
\]  

(1)

where \( D \) is the diffusion coefficient. This version of Fick’s law seems intuitive in its similarity to Fourier’s law for heat conduction or Ohm’s law for electrical current flow. In may cases, this is an entirely appropriate description of mass transport, but there are cases where the inherent assumptions implicit in Equation (1) are not met so it is useful to go back to more rigorous beginnings and understand when the simple version is adequate and when it is not.

1.04.2.1 Binary Systems: Fick’s Law

The diffusive flux of a species in a mixture must be expressed relative to some frame of reference. There are several ways to deal with this but an easily understandable one is to use a fixed frame of reference or stationary coordinates; this is particularly appropriate for membranes since this means relative to the membrane itself. The following are two fully equivalent forms of Fick’s law of binary diffusion in three-dimensional (vector) form [17]:

\[
\begin{align*}
    n_i &= \bar{w}_i (n_1 + n_2) - \rho D_{12} \nabla \bar{w}_i \\
    N_i &= x_i (N_1 + N_2) - CD_{12} \nabla x_i
\end{align*}
\]  

(2)  

(3)

where \( n_i \) is the mass flux of species \( i \) relative to stationary coordinates, \( N_i \) the molar flux, \( \bar{w}_i \) the mass fraction of \( i \), \( x_i \) the mole fraction, \( \rho \) the mass density of the mixture, \( C \) its molar density, and \( D_{12} \) the binary diffusion coefficient. Either version can be converted to the other by simple definitions. Corresponding relations can be written for component 2 by interchanging the subscripts realizing that \( D_{12} = D_{21} \). These forms look similar to Equation (1) except for the terms \( \bar{w}_i (n_1 + n_2) \) or \( x_i (N_1 + N_2) \) that are necessary to express what the diffusion fluxes are relative to as will become clearer below. Equation (3) turns out to be more convenient for mixtures of gases since at constant pressure and temperature, the total molar density, \( C \), is a constant; for ideal gases \( C = RT/p \), where \( p \) is the total pressure. Equation (2) is more convenient for liquids since the mass density, \( \rho_i \) of such a mixture is more likely to be nearly constant than \( C \). So how are these relations adapted to diffusion of a penetrant in a membrane?

First, it is useful to let the membrane component be identified with the subscript \( m \) and the penetrant with the subscript \( 1 \); this is particularly useful for the cases when there are other penetrants as we can identify them as 2, 3, etc. In some cases, the binary form of Fick’s law can be used when there are more than two components but not always. Second, since diffusion through membranes is almost always unidirectional (e.g., the \( z \)-direction), Equations (2) and (3) can be written without vector notation as done for Equation (1). Third, for all practical cases in steady state, the membrane itself is stationary so the flux of this component is zero. Finally, it is important to recognize that for polymeric membranes, molar concentrations and terms like \( x_i \) or \( C \) in Equation (3) are at best ill-defined and at worst not meaningful since the molecular weight of the polymer may not be unique or may even be infinite. The earliest thermodynamic treatments of polymer mixtures revealed that mole fractions were not an appropriate way to express compositions in such systems [18]. Thus, Equation (2) provides a more useful form of Fick’s first law for membrane systems. With the simplifications noted above, it becomes

\[
n_1 = -\frac{\rho D_{1m} d\bar{w}_1}{1 - \bar{w}_1} = \frac{\rho D_{1m} d\bar{w}_1}{\bar{w}_m} \frac{d\bar{w}_1}{dz}
\]  

(4)

This still does not quite look like the simple form of Equation (1). First, there is the \((1 - \bar{w}_1) = \bar{w}_m\) term which arises because of frame of reference considerations or a convection term. As shown later, it is necessary to include this term in some cases; however, when the content of penetrant in the membrane is very small, \( \bar{w}_1 \ll 1 \), then \( \bar{w}_m \equiv 1 \). In addition, when the mass density of the membrane–penetrant mixture, \( \rho \), is constant (this will surely be the case when \( \bar{w}_1 \ll 1 \)), then Equation (4) reduces to

\[
n_1 = -D_{1m} \frac{d\rho_1}{dz}
\]  

(5)

where \( \rho_1 \) is the mass concentration of species 1 and \( n_1 \) is the mass flux. Dividing both sides by the molecular weight of 1 leads to
\[ N_i = -D_{im} \frac{dC_i}{dz} \quad (6) \]

where \( C_i \) is the molar concentration of \( i \) and \( N_i \) is its molar flux; in this simple form the flux and concentration can be written in any units so long as they are consistent. Equation (6) is identical to the familiar Equation (1) noting that \( D = D_{im} \). It is clear what assumptions are behind Equations (1) and (6) and why it is necessary to be careful about these details in order to have \( D_{im} \) be the same quantity through all these different forms.

Of course, for all membrane separations there is always more than one penetrant so the question is how to formulate a proper diffusion law for a ternary or multicomponent mixture. Fortunately, in many cases it is adequate to use a version of Equations (5) or (6) applied to each component \( i \). This amounts to assuming that each component diffuses as if the other were not present; however, there are several ways such a simplification can fail. A most common situation is when the presence of component \( j \) affects the diffusion coefficient for component \( i \), that is, \( D_{im} = f(C_j) \) or plasticization occurs. Another complication is when the penetrant concentrations are not small enough to use the approximation \( w_m \approx 1 \). A further complication is when the flux of one species is dependent on the gradient of concentration of other species. It is truly difficult to correctly and accurately sort out all these potential interactions. The next section gives a logical starting framework to deal with these effects.

### 1.04.2.2 Ternary Systems: Maxwell–Stefan Equations

In some simple cases, ad hoc generalizations of Equations (2) or (3) to multicomponent mixtures have been suggested [17]; however, in general, this approach is not sufficient and leads to obvious problems [16]. A more sound approach is to begin with the Maxwell–Stefan equations that were originally developed to describe multicomponent diffusion in gas mixtures at low density and can be derived from kinetic theory [17, 19]. These equations have been extended with good success to dense gases, liquids, and polymers [17]; many review papers and books have discussed uses of these equations [17, 20]. A general form of the one-dimensional Maxwell–Stefan equations for isothermal multicomponent mixtures can be written as

\[ d_i = \sum_{j \neq i} \frac{x_i x_j}{D_{ij}} (v_i - v_j) \quad (7) \]

where the \( D_{ij} \) are multicomponent diffusion coefficients [17], \( x_i \) is the mole fraction of \( i \) in the mixture, and \( v_j \) is the velocity of \( j \) in the \( z \)-direction relative to stationary coordinates. The term \( d_i \) is a generalized force (in the \( z \)-direction) for component \( i \) that causes it to diffuse relative to other species. Its general form is

\[ CRT \left[ d_i = C_i \left( \frac{d\mu_i^m}{dz} - \frac{1}{C_0} \frac{dp_i}{dz} \right) \right] \quad (8) \]

where

\[ \frac{d\mu_i^m}{dz} = RT \frac{d \ln a_i^m}{dz} + \bar{p} \frac{dp_{\bar{m}}}{dz} \quad (9) \]

where \( C \) is the molar density of the mixture, \( C_i \) is the molar concentration of \( i \) (note \( x_i = C_i / C \)), \( \mu_i^m \) is the chemical potential of \( i \) in the membrane, \( a_i^m \) in the activity of \( i \) in the membrane, and \( p_m \) is the pressure in the membrane. For nonporous-supported membranes, the pressure throughout the membrane is constant (see References 14, 16, and 21–30) so for the cases of interest here, \( \frac{dp_{\bar{m}}}{dz} = 0 \). As a result, Equation (7) simplifies to

\[ \sum_{j \neq i} \frac{x_i x_j}{D_{ij}} (v_i - v_j) = x_i \frac{d \ln a_i^m}{dz} \quad (10) \]

The pressure that drives many membrane transport processes does not enter the picture by the flux law but comes in via the boundary conditions used in the integration of these equations.

Equation (10) can be expressed in forms more useful for describing diffusion in membranes. In steady state, the velocity or flux of the membrane material is zero relative to stationary coordinates, that is, \( v_m = n_m = 0 \). Penetrant velocities can be converted to fluxes via

\[ n_i = w_i \rho v_i \quad (11) \]

where \( \rho \) is the mass density of the membrane-penetrants mixture. As noted earlier, use of mole fractions is not useful for membrane systems; this issue can be resolved by converting to volume or mass fractions as discussed in recent papers [16, 31, 32]. Mass fractions and fluxes will be used here, and the conversion can be accomplished by the following:

\[ x_i = \frac{M_i}{M} w_i \quad M = \left[ \sum_{i} \frac{w_i}{M_i} \right]^{-1} \quad (12) \]

where \( M_i \) is the molecular weight of \( i \) and \( M \) is the number average molecular weight of the mixture. It could be said that \( M \) is ill-defined because of the
ambiguity of the molecular weight of the membrane material; however, this potential complication appears to be resolved by redefining the diffusion coefficients. In the end, these diffusion coefficients must be determined experimentally. For a ternary system, Equation (10) requires three independent coefficients: \( D_{1m}, D_{2m}, \) and \( D_{12}. \) With the conversion to mass fractions, it becomes useful to redefine the diffusion coefficients in the following way:

\[
D_{ij} = \frac{M_i}{M} \frac{D_{ij}}{\rho_i} 
\]

since they always appear in these combinations [16, 31]; similar redefinitions in terms involving molar volumes are needed when expressing Equation (10) in terms of volume fractions [32]. With the above simplifications, the Maxwell–Stefan equations for the 1–2–m ternary can be reduced to the following equations (after considerable algebra):

\[ n_1 + \left( \frac{w_1 n_1 - w_2 n_1}{w_m} \right) \frac{D_{1m}}{D_{12}} = -\rho \frac{w_1 D_{1m} \ln n_1}{w_m} \frac{\partial}{\partial x} \]

\[ n_2 + \left( \frac{w_2 n_1 - w_2 n_1}{w_m} \right) \frac{M_2 D_{2m} M_1 D_{12}}{M_1 D_{12}} = -\rho \frac{w_2 D_{2m} \ln n_2}{w_m} \frac{\partial}{\partial x} \]

The \( w_m = 1 - w_1 - w_2 \) in the denominator of the right-hand terms in each of the two equations reflects convection or frame of reference considerations inherently included in the Maxwell–Stefan equations. Alternate forms of Equations (14) and (15) can be written in terms of gradients of concentration or weight fractions by making use of the definition

\[ D_{im} = D_{im} \frac{\partial \ln n_i}{\partial \ln \gamma_i} \]

to get

\[ n_1 + \left( \frac{w_1 n_1 - w_2 n_1}{w_m} \right) \frac{D_{1m}}{D_{12}} = -\rho \frac{D_{1m} \ln n_1}{w_m} \frac{\partial}{\partial x} \]

\[ n_2 + \left( \frac{w_2 n_2 - w_2 n_1}{w_m} \right) \frac{M_2 D_{2m} M_1 D_{12}}{M_1 D_{12}} = -\rho \frac{D_{2m} \ln n_2}{w_m} \frac{\partial}{\partial x} \]

Equations (17) and (18) can be solved simultaneously to get independent equations for \( n_1 \) and \( n_2, \) but this adds great complexity [9]. Indeed, this complexity is why the more rigorous Maxwell–Stefan formulation is used so infrequently in the membrane literature. Importantly, Equations (17) and (18) reduce to Fick’s law, Equation (4), where there is component 2 present and likewise, in some cases, where \( w_2 \) and \( n_2 \) are small.

### 1.04.3 Sorption of Gases and Vapors in Polymers

Knowledge about the equilibrium sorption of gases or vapors in polymers is essential for understanding the process of permeation by the solution-diffusion mechanism. Thus, considerable effort has been devoted to measuring and interpreting the sorption isotherms for small molecules in rubbery, glassy, and semi-crystalline polymers [4–9, 33–38]. The limiting cases described below are useful for understanding the possibilities. In a subsequent section these models are used to set the boundary conditions for permeation of gas and vapors in polymers.

#### 1.04.3.1 Rubbery Polymers

Consider an amorphous polymer membrane above its glass transition temperature, \( T_g, \) surrounded by a vapor of component 1 at a partial pressure \( p_1. \) If the saturation vapor pressure of 1 is \( p_1^s, \) then its activity in the vapor phase is \( a_1 = p_1/p_1^s. \) The Flory–Huggins thermodynamic model for mixing small molecules of molar volume \( V_m \) with large polymer molecules of molar volume \( V_g \) combines an estimate for the entropy of mixing with a measure of the enthalpy of mixing, expressed in terms of an interaction parameter \( \chi, \) to give the following expression for the equilibrium sorption [18]:

\[ \ln a_1 = \ln \phi_1 + (1 - \phi_1) \phi_m + \chi \phi_m \]

where the \( \phi_i \) are volume fractions. Figure 1 shows example calculations, using Equation (19), of the amount of sorption of penetrant 1, expressed as \( \phi_1, \) in the membrane at equilibrium versus its activity in the vapor phase for several values of the dimensionless interaction parameter, \( \chi. \) At low activity, the extent of sorption is proportional to \( p_1; \) however, the isotherm shows upward curvature at higher activities. The degree of curvature increases with the extent of sorption as the interaction parameter decreases or becomes more favorable for mixing. If the interaction parameter depends on the amount of vapor sorbed, the shape will be altered somewhat but the upward curvature remains a generally expected shape for simple systems where sorption can be modeled as a nearly random mixing process.

In the limit of low activities or small extents of sorption, a linear approximation to the sorption
isotherm provides an adequate description; that is, Henry's law applies,

$$C = Sp_1$$

where $C$ is the concentration of gas or vapor in the membrane in equilibrium with the gas phase at partial pressure $p_1$, and $S$ is a solubility coefficient. This limiting case of the Flory–Huggins type of isotherm is normally used to analyze the behavior of gases in polymers above their glass transition temperatures.

Figure 2 shows that sorption of CO$_2$ gas at 35 °C in crosslinked butyl rubber [33] is well described by Henry's law up to at least 20 atm. Since the critical temperature of CO$_2$ is about 31 °C, it is not possible to define an activity relative to the liquid state, but simple extrapolation of the vapor pressure curve to 35 °C allows one to see that CO$_2$ at 20 atm has an effective activity of less than 0.3. If the measurements in Figure 2 were extended to pressures two to three times this level, curvature similar to that in Figure 1 would probably be seen. For less soluble gases, such as O$_2$, N$_2$, and argon, Henry's law behavior is assured over a very wide range of pressures. Consequently, it may be said that linear isotherms are characteristic of gas sorption in rubbery polymers.

The solubility coefficient $S$ increases with the condensability of the gas and generally can be correlated with the boiling point, the critical temperature, or other measures of the cohesive forces between the gas molecules [8, 9].

### 1.04.3.2 Glassy Polymers

It is well established that the shape of gas sorption isotherms in glassy polymers, that is, polymers below their $T_g$ values, stands in marked contrast to the forms described above for rubbery polymers. The sorption of CO$_2$ in poly(phenylene oxide) (PPO) at 35 °C shown in Figure 3 clearly illustrates this [39]. The isotherms for glassy polymers are far from linear, and the curvature has the opposite sense to that seen in Figure 1. Such isotherms can be well...
described by a model that is an additive combination of Henry’s law and a Langmuir isotherm, that is,
\[
C = k_d + \frac{C'_{11}b_p}{1 + b_p} \tag{21}
\]
where \(k_d\), \(C'_{11}\) and \(b\) are parameters of the model. This form implies that there are two mechanisms of sorption in glassy polymers [9, 36–41]. Many alternatives to this model and its implied mechanistic aspects have been suggested over the years [40–55]; however, this so-called dual sorption model continues to be widely used for describing sorption in glassy polymers.

Generally, gases are more soluble in glassy polymers than rubbery ones [9] as may be seen in Figure 3 by comparing the sorption of CO\(_2\) in PPO versus that in butyl rubber; the dashed line is reproduced from Figure 2. Studies have shown that the \(k_d\) parameter from the dual sorption model, obtained from sorption data below \(T_g\), varies smoothly with temperature through the glass transition forming a continuous connection with data above \(T_g\), where simple Henry’s law behavior, that is, Equation (20), is observed [38]. This, plus other observations, provide strong evidence that the Henry’s law term in Equation (21) is physically a manifestation of the same solubility mechanism operative for gases in rubbery polymers or organic liquids. Thus, it follows that the Langmuir term in Equation (21) stems from the nonequilibrium character of the glassy state, and this is supported by considerable evidence [9, 55–61]. Additional evidence for this can be seen by examining the Langmuir capacity term \(C'_{11}\) for one gas, CO\(_2\), measured at a single temperature, 35 °C, in a wide range of glassy polymers; Figure 4 shows that \(C'_{11}\) plotted versus the polymer glass transition temperature provides a remarkable correlation [56]. It has been suggested [55] that the Langmuir term arises from packing of gases like CO\(_2\) into the unrelaxed volume of the glass \(V_g - V_l\) with a liquid-like density. The unrelaxed volume at any temperature \(T\) may be estimated from thermal expansion coefficients above and below \(T_g\); that is,
\[
\frac{V_g - V_l}{V_g} = (\alpha_l - \alpha_g) (T_g - T) \tag{22}
\]

Since \((\alpha_l - \alpha_g)\) values are quite similar for most polymers, it follows from this picture that \(C'_{11}\) should be proportional to \((T_g - T)\), as seen in Figure 4. The support for this interpretation of the Langmuir mode is the quantitative agreement shown by numerous sets of experimental observations, including Figure 4 [57]. From the above, it should be clear that sorption in glassy polymers will depend on the material’s prior history as supported by many observations [60, 61]. The unrelaxed volume of the glass may decrease with aging time, especially at temperatures just below \(T_g\), leading to decreased sorption [60]. On the other hand, sorption of gases or vapors in the polymer may lead to an increased unrelaxed volume upon desorption that in turn leads to increased sorption in subsequent experiments [61]. These effects of conditioning are sometimes manifested as hysteresis between sorption and desorption observations [4].

Sorption of large enough amounts of gases and vapors in any polymer causes plasticization; one manifestation of this is a reduction in the glass transition temperature. Because of this, the sorption isotherm under certain conditions may exhibit the characteristic glassy-type shape (see PPO data in Figure 3) at low pressures and then revert to the characteristic rubbery-type shape (shown by butyl rubber in Figures 2 and 3) at high pressures [62]. This can be seen for glassy polymers whose \(T_g\) values are not much higher than the temperature of sorption
and whose $T_g$ values are lowered by plasticization as gas or vapor is sorbed such that the original glass becomes a rubber within the range of pressure over which the isotherm is measured. Figure 5 shows an example of this for sorption of CO$_2$ in a polystyrene containing 3 wt.% of the lubricant, mineral oil [62].

### 1.04.3.3 Semi-Crystalline Polymers

In most cases, penetrants do not dissolve in the crystalline regions of semi-crystalline polymers [63]. The reason for this is that usually the crystal is significantly more dense than the amorphous phase; thus, there is much less free volume to accommodate insertion of penetrants. However, there are some exceptions where the crystals are similar in density as the amorphous phase in which case there is evidence for solubility in the crystal phase [64–66]. If there is no solubility in the crystalline regions, then sorption is modulated by the extent of crystallinity [63]. The shape of the sorption isotherm is dictated by whether the amorphous phase is above or below its $T_g$.

### 1.04.3.4 Sorption of Gas or Vapor Mixtures

For membrane separation processes the feed contains two or more types of gases. In the simplest of cases when the extent of sorption by all species is quite small, the individual components sorb as if the others are not present. However, there can be interactions between the penetrants or between one or more of the penetrants and the membrane polymer that cause more complex behavior; in these cases, mixed gas sorption data may be needed [67, 68]. The most typical case is where one component is sorbed to a rather considerable extent plasticizing the polymer and, thereby, altering the sorption behavior of other components. In glassy polymers, there may be competitive sorption effects that can be described by an extension of the dual sorption model [69].

### 1.04.4 Permeation of Gases and Vapors in Polymers

To understand or describe the permeation of small molecules through polymer membranes by the solution-diffusion mechanisms requires combining the results in Sections 1.04.3 and 1.04.4 using only appropriate assumptions so that the details of interest can be captured. Permeation involves transferring components from an upstream fluid phase into the membrane, diffusion through the membrane, and then transferring these components to a downstream fluid phase. Basically, the sorption behavior discussed in Section 1.04.3 defines the boundary conditions for the diffusion in the membrane discussed in Section 1.04.2. In nearly all cases the surfaces of the membrane are in equilibrium with the fluid phase to which they are adjacent. Permeability coefficients are based on the driving force difference between the upstream and downstream fluid phases while diffusion coefficients are based on the driving force difference between the two surfaces but within the membrane phase.

#### 1.04.4.1 Rubber Polymers

First, we consider the steady-state permeation of simple gases in rubbery polymers where Equations (20) and (6) adequately describe the sorption and diffusion processes. Assuming $D_{lm}$ is not concentration dependent, Equation (6) can be integrated across the membrane to get

$$N_i = D_{lm} \frac{C_{10} - C_{1\ell}}{\ell} \quad (23)$$

where $\ell$ is the membrane thickness, $C_{10}$ and $C_{1\ell}$ are the concentrations of $i$ in the membrane at the upstream ($z = 0$) and downstream ($z = \ell$) surfaces, respectively. From Equation (20), $C_{10} = S_i p_{10}$ and $C_{1\ell} = S_i p_{1\ell}$, where $p_{10}$ and $p_{1\ell}$ are the partial...
pressures of 1 in the upstream and downstream fluid phases, respectively. Thus, Equation (23) becomes

\[ N_1 = D_{1m} \frac{S_1 p_{10} - S_1 p_{1t}}{\ell} = D_{1m} S_1 \frac{\Delta p_1}{\ell} \]  

(24)

where \( \Delta p_1 = p_{10} - p_{1t} \). The permeability coefficient \( p_1 \), in general, is defined by

\[ p_1 = \frac{\ell N_1}{\Delta p_1} \]  

(25)

but is given by the product \( D_{1m} S_1 \) in this case.

If a second gas 2 is also permeating but the concentrations of both 1 and 2 are small enough that \( D_{im} \) and \( S_i \) are the same as if the other gas were not present, then the permeation in the mixed gas case can be described by the pure gas coefficients. An often-used measure of the selectivity of this permeation process is the ratio of the permeability coefficients:

\[ \frac{p_1}{p_2} = \left( \frac{D_{1m}}{D_{2m}} \right) \left( \frac{S_1}{S_2} \right) \]  

(26)

that is the product of diffusion and solubility selectivity components.

Transient permeation experiments are often used to obtain the \( P, D, \) and \( S \) coefficients. In this experiment, the membrane is degassed from both sides until no sorbed gas remains. At time \( t = 0 \), a certain fixed pressure is imposed at the upstream surface of the membrane while the total amount of gas that has exited the downstream membrane surface until time \( t, Q_n \) is measured. The result will look like the graph of \( Q_n \) versus \( t \) shown in Figure 6. Eventually, a steady state is reached where the flux is given by \((1/A)(dQ_n/dt)_n\), where \( A \) is the membrane area.

The last step is only justified when the diffusion coefficient does not depend on concentration. Equation (27) can be solved [70] using the conditions at the membrane surface described earlier, that is, \( C_1 = 0 \) for all \( z \) at \( t < 0 \), then for \( t > 0 \) \( C_{1i} = \) constant and \( C_{1t} = 0 \). From such a solution, the following important result can be deduced [70]:

\[ \theta = \frac{\ell^2}{6D_{1m}} \]  

(28)

Thus, by the transient permeation experiment one measures \( \theta \) and \( P \) from which \( D_{1m} \) is obtained from Equation (28) and \( S_i \) from \( P_i = D_{1m} S_i \). Of course, \( S_i \) can be also measured directly using sorption experiments. Often, diffusion and solubility coefficients are deduced from transient experiments when the assumptions implicit in the above are not strictly met, for example, a concentration-dependent diffusion coefficient, in which case these coefficients should be considered apparent values; they may still have some utility, however.

For rubbery polymers, highly condensable gases or vapors may no longer follow Henry’s law but follow relations more similar to those in Figure 1. In principle, the same methodology described above can be followed, but certain caveats apply. First, the solubility coefficient is no longer a constant. Second, the diffusion coefficient is most likely not constant due to plasticization. Finally, at high penetrant concentrations, the convective terms seen in Equations (2)–(4) may not be negligible as assumed in Equations (5) and (6).
If one knows $D_{1m}$ as a function of $w_1$, then the integration can be carried out, at least numerically, to calculate the flux as a function of the boundary conditions or the external fluid phase partial pressures, or activities, assuming the sorption isotherm has been measured. More often than not, the situation is that $n_1$ has been measured as a function of the external fluid phase conditions and the issue is to deduce $D_{1m}(w_1)$ from this information. Often one assumes a mathematical form for $D_{1m}(w_1)$ such as

$$D_{1m} - (D_{1m})_0 e^{-a_{w_1}}$$

(30)

and performs the integration in Equation (29), perhaps with some simplifications, and fits the resulting mathematical form to the experimental data to get the model parameters.

However, when there are two or more penetrants, as there always is for separations, this problem grows more complex in several respects. In general, the various components do not sorb or diffuse as if the others were not there as in the case for very slightly soluble gases (e.g., see Equation (26)). Rather, the permeation of the species may be coupled in various ways. At the very least, the diffusion coefficient for one species may depend not only on its own concentration but on the concentration of all the other species as well. In the simplest of these cases, all the diffusion coefficients depend on the total penetrant concentration, that is, $w = w_1 + w_2$ for the case of two penetrants. Such an approach has recently been described, and the reader is referred to Reference 68 for the details.

Coupling at a more subtle level may occur by the flux of one species depending on the gradient of the concentration of another species. These issues, plus the frame of reference terms, are formally considered in the Maxwell–Stefan equations discussed in Section 1.04.2.2. This level of complexity has rarely been used in analyzing membrane processes for understandable reasons. However, a recent paper provides an in-depth experimental study with the results analyzed by the Maxwell–Stefan equations as well as Fick’s law [68]. In this case, the contribution of the extra effects included by the Maxwell–Stefan approach versus Fick’s law was of similar order as the experimental uncertainty. It is premature to judge if this conclusion is general or not.

### 1.04.4.2 Glassy Polymers

Steady-state permeation of a gas through a glassy polymer raises the questions of whether there are two populations of sorbed gas as implied by Equation (21) and, if there are, do they have different levels of mobility. A vast body of literature too numerous to list here has dealt with these questions [9, 57, 72–77]. Within the context of the dual sorption idea, the following model for the flux of a pure gas has been widely used [9, 57, 72, 73]:

$$\text{Flux} = -D_0 \frac{\partial C_0}{\partial z} - D_1 \frac{\partial C_1}{\partial z}$$

(31)

where two diffusion coefficients and concentrations corresponding to the Henry’s law population ($D =$ dissolved) and the Langmuir population ($H =$ holes) in Equation (21) are used. At first glance, Equation (31) would appear to suggest two parallel and independent pathways of diffusion; however, Barrer [73] has shown that this model is more general. A steady-state analysis of Equations (21) and (31) shows the permeability coefficient, $P$, to be given by [72]

$$P = k_D D_0 \left[ 1 + \frac{FK}{1 + b p_0} \right]$$

(32)

where $F = D_1 / D_0$, $K = C_{1h} / k_D$, and $p_0 =$ upstream pressure of the permeating gas; the downstream pressure has been assumed to be zero. For clarity, subscripts denoting the component have been omitted. Equation (32) indicates that the permeability decreases slightly as $p_0$ increases as has been observed repeatedly for glassy polymers [9, 57, 58]. Figure 7 shows data for CO$_2$ permeation in PPO [39] plotted as suggested by Equation (32); clearly, the experimental
results conform quite well to this theoretical prediction as has been shown repeatedly for glassy polymers when complicating factors like plasticization are not important [9, 57, 58, 74–77]. The parameters of Equation (21) can be deduced by fitting of sorption data while the parameters $D_P$ and $F$ can be obtained by fitting of permeation data to Equation (32); the data in Figure 7 give a value of $F=0.06$ which is typical of most glassy polymers. The implications are that the Langmuir part of the sorption processes in glassy polymers tends to partially trap gas molecules, that is, their mobility is about an order of magnitude less than the gas molecules sorbed by the equilibrium or Henry's law mode.

An analysis of transient permeation has been made for the case when Equations (21) and (31) apply [9, 72] and predicts the time lag $\theta$ to be a complex relation of the form

$$\theta = \frac{\tau}{6D_P}[1 + f(K, F, b_0)]$$

(33)

where the function $f$ is quite involved [72]. This relation predicts that $\theta$ is a decreasing function of $b_0$ as observed experimentally [9, 58]; this is in contrast to the simple equation (28) where $\theta$ is independent of the upstream pressure. Clearly, values of the solubility diffusion and permeability coefficients for glassy polymers computed by the methods outlined in Section 1.04.4.1 are only apparent values and are pressure dependent. Nevertheless, such quantities are useful and widely used in the literature, for example, Equation (26) continues to be used to assess what part of the permeability selectivity (i.e. $P_1/P_2$) is due to solubility versus diffusive selectivity [4, 8].

The above results assume that effects due to plasticization by the sorbed gas are not significant; however, as the concentration of the gas in the polymer increases to high enough levels due to very high pressures or high intrinsic solubility (e.g., highly condensable gases like CO$_2$ or vapors), plasticization inevitably occurs and the above analyses no longer describe the observations. A particularly important example of this involves separation of CO$_2$ or light hydrocarbons from high pressure natural gas [4, 7, 8]. Typically, the permeability of glassy polymers to CO$_2$ will first decrease as the driving pressure increases as expected from Equation (32) and then go through a minimum and rise with further increases in upstream pressure owing to plasticization [14–82]. Formally, one can describe such effects by assigning concentration dependence to the parameters in Equations (21) and (31) [78]; however, this increases the number of parameters and the resulting analyses become very complex and can be devoid of physical meaning as a result. Since glassy polymers are not in equilibrium, the observations also become time dependent [79, 80] and may show hysteresis as the pressure is moved up and down [43].

For gas separations by glassy polymers, pure gas permeation behavior is not always a reliable indicator of mixed gas behavior. As a result, mixed gas measurements for both sorption and permeation may be needed [82]. Even in the absence of plasticization, competitive sorption effects can occur such that the presence of one component affects the transport of the other as shown by theoretical analyses and experiment [83, 84]. These effects can become quite severe in very high free volume polymers [85]. Of course, plasticization complicates the behavior even further [83, 85–87]. An active area of research is the development of membrane materials that are more resistant to plasticization [82, 86–89].

### 1.04.4.3 Semi-Crystalline Polymers

As described in Section 1.04.3.3, the presence of crystallinity in a polymer generally reduces the sorption of penetrants since usually these molecules do not enter the crystals. The effects on permeation can be even more dramatic since the shape of the crystals, in addition to their amount, affects the diffusion process owing to the tortuosity effect. In addition, the presence of crystals may alter the mobility of the penetrant in the amorphous phase. Further discussion of this complex, but important, behavior will not be given here since generally semi-crystalline polymers are not used for membranes owing to their usually lower permeability and issues of processing. The reader can consult a few key references to begin exploring this subject [90–92].

### 1.04.5 Liquid Permeation in Membranes

There are at least two important membrane processes (reverse osmosis [1, 16] and pervaporation [2]) that operate by a solution-diffusion mechanism where the feed is a liquid. Here, the latter is dealt with briefly while the former is analyzed more extensively.