8 GAS SEPARATION

Introduction and History

Gas separation has become a major industrial application of membrane technology only during the past 20 years, but the study of gas separation has a long history. Systematic studies began with Thomas Graham who, over a period of 20 years, measured the permeation rates of all the gases then known through every diaphragm available to him [1]. This was no small task because his experiments had to start with synthesis of the gas. Graham gave the first description of the solution-diffusion model, and his work on porous membranes led to Graham's law of diffusion. Through the remainder of the nineteenth and the early twentieth centuries, the ability of gases to permeate membranes selectively had no industrial or commercial use. The concept of the perfectly selective membrane was, however, used as a theoretical tool to develop physical and chemical theories, such as Maxwell's kinetic theory of gases.

From 1943 to 1945, Graham's law of diffusion was exploited for the first time, to separate $U^{235}F_6$ from $U^{238}F_6$ as part of the Manhattan project. Finely microporous metal membranes were used. The separation plant, constructed in Knoxville, Tennessee, represented the first large-scale use of gas separation membranes and remained the world's largest membrane separation plant for the next 40 years. However, this application was unique and so secret that it had essentially no impact on the long-term development of gas separation.

In the 1940s to 1950s, Barrer [2], van Amerongen [3], Stern [4], Meares [5] and others laid the foundation of the modern theories of gas permeation. The solution-diffusion model of gas permeation developed then is still the accepted model for gas transport through membranes. However, despite the availability of interesting polymer materials, membrane fabrication technology was not sufficiently advanced at that time to make useful gas separation membrane systems from these polymers.

The development of high-flux anisotropic membranes and large-surface-area membrane modules for reverse osmosis applications in the late 1960s and early 1970s provided the basis for modern membrane gas separation technology. The first company to establish a commercial presence was Monsanto, which

launched its hydrogen-separating Prism® membrane in 1980 [6]. Monsanto had the advantage of being a large chemical company with ample opportunities to test pilot- and demonstration-scale systems in its own plants before launching the product. The economics were compelling, especially for the separation of hydrogen from ammonia-plant purge-gas streams. Within a few years, Prism systems were installed in many such plants [7].

Monsanto's success encouraged other companies to advance their own membrane technologies. By the mid-1980s, Cynara, Separex and Grace Membrane Systems were producing membrane plants to remove carbon dioxide from methane in natural gas. This application, although hindered by low natural gas prices in the 1990s, has grown significantly over the years. At about the same time, Dow launched Generon®, the first commercial membrane system for nitrogen separation from air. Initially, membrane-produced nitrogen was cost-competitive in only a few niche areas, but the development by Dow, Ube and Du Pont/Air Liquide of materials with improved selectivities has since made membrane separation much more competitive. This application of membranes has expanded very rapidly and is expected to capture more than one-half of the market for nitrogen separation systems within the next few years. To date, approximately 10 000 nitrogen systems
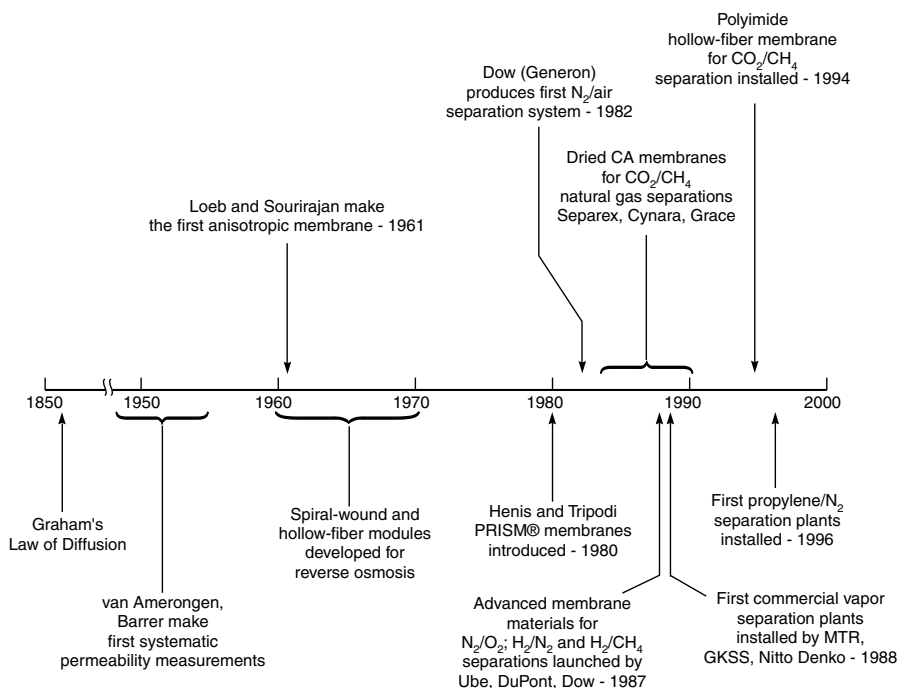

Figure 8.1   Milestones in the development of gas separation

have been installed worldwide. Gas separation membranes are also being used for a wide variety of other, smaller applications ranging from dehydration of air and natural gas to organic vapor removal from air and nitrogen streams. Application of the technology is expanding rapidly and further growth is likely to continue for the next 10 years or so. Figure 8.1 provides a summary of the development of gas separation technology.

Theoretical Background

Both porous and dense membranes can be used as selective gas separation barriers; Figure 8.2 illustrates the mechanism of gas permeation. Three types of porous membranes, differing in pore size, are shown. If the pores are relatively large—from 0.1 to 10 μm—gases permeate the membrane by convective flow, and no separation occurs. If the pores are smaller than 0.1 μm, then the pore diameter is the same size as or smaller than the mean free path of the gas molecules. Diffusion through such pores is governed by Knudsen diffusion, and the transport rate of any gas is inversely proportional to the square root of its molecular weight. This relationship is called Graham's law of diffusion. Finally, if the membrane pores are extremely small, of the order 5–20 Å, then gases are separated by molecular sieving. Transport through this type of membrane is complex and includes both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores (surface diffusion). These very small-pore membranes have not been used on a large scale, but ceramic and ultramicroporous
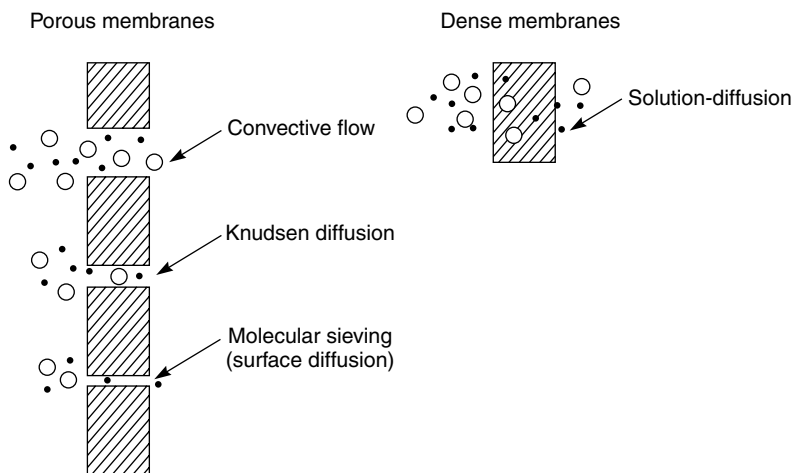

Figure 8.2 Mechanisms for permeation of gases through porous and dense gas separation membranes

glass membranes with extraordinarily high selectivities for similar molecules have been prepared in the laboratory.

Although these microporous membranes are topics of considerable research interest, all current commercial gas separations are based on the dense polymer membrane shown in Figure 8.2. Separation through dense polymer films occurs by a solution-diffusion mechanism.

In Chapter 2 [Equation (2.59)], it was shown that gas transport through dense polymer membranes is governed by the expression

$$J_i = \frac{D_i K_i^G (p_{i_o} - p_{i_\ell})}{\ell} \tag{8.1}$$

where J_i is the flux of component i (g/cm$^2 \cdot$ s), p_{i_o} and p_{i_ℓ} are the partial pressure of the component i on either side of the membrane, ℓ is the membrane thickness, D_i is the permeate diffusion coefficient, and K_i^G is the Henry's law sorption coefficient (g/cm$^3 \cdot$ pressure). In gas permeation it is much easier to measure the volume flux through the membrane than the mass flux and so Equation (8.1) is usually recast as

$$j_i = \frac{D_i K_i (p_{i_o} - p_{i_\ell})}{\ell} \tag{8.2}$$

where j_i is the volume (molar) flux expressed as [cm^3(STP) of component i]/cm$^2 \cdot$ s and K_i is a sorption coefficient with units [cm^3(STP) of component i/cm^3 of polymer]·pressure. The product $D_i K_i$ can be written as $\mathcal{P}_i$, which is called the membrane permeability, and is a measure of the membrane's ability to permeate gas.[1] A measure of the ability of a membrane to separate two gases, i and j, is the ratio of their permeabilities, α_{ij}, called the membrane selectivity

$$\alpha_{ij} = \frac{\mathcal{P}_i}{\mathcal{P}_j} \tag{8.3}$$

The relationship between polymer structure and membrane permeation was discussed in detail in Chapter 2 and is revisited only briefly here. Permeability can be expressed as the product $D_i K_i$ of two terms. The diffusion coefficient, D_i, reflects the mobility of the individual molecules in the membrane material; the gas sorption coefficient, K_i, reflects the number of molecules dissolved in the membrane material. Thus, Equation (8.3) can also be written as

$$\alpha_{ij} = \left[\frac{D_i}{D_j} \right] \left[\frac{K_i}{K_j} \right] \tag{8.4}$$

---

[1]The permeability of gases through membranes is most commonly measured in Barrer, defined as 10^{-10} cm^3(STP)/cm$^2 \cdot$ s $\cdot$ cmHg and named after R.M. Barrer, a pioneer in gas permeability measurements. The term $j_i/(p_{i_o} - p_{i_\ell})$, best called the pressure-normalized flux or permeance, is often measured in terms of gas permeation units (gpu), where 1 gpu is defined as 10^{-6} cm^3(STP)/cm$^2 \cdot$ s $\cdot$ cmHg. Occasional academic purists insist on writing permeability in terms of mol $\cdot$ m/m$^2 \cdot$ s $\cdot$ Pa (1 Barrer = 0.33×10^{-15} mol $\cdot$ m/m$^2 \cdot$ s $\cdot$ Pa), but fortunately this has not caught on.

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients of the two gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of the two gases. In all polymer materials, the diffusion coefficient decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity always favors the passage of small molecules over large
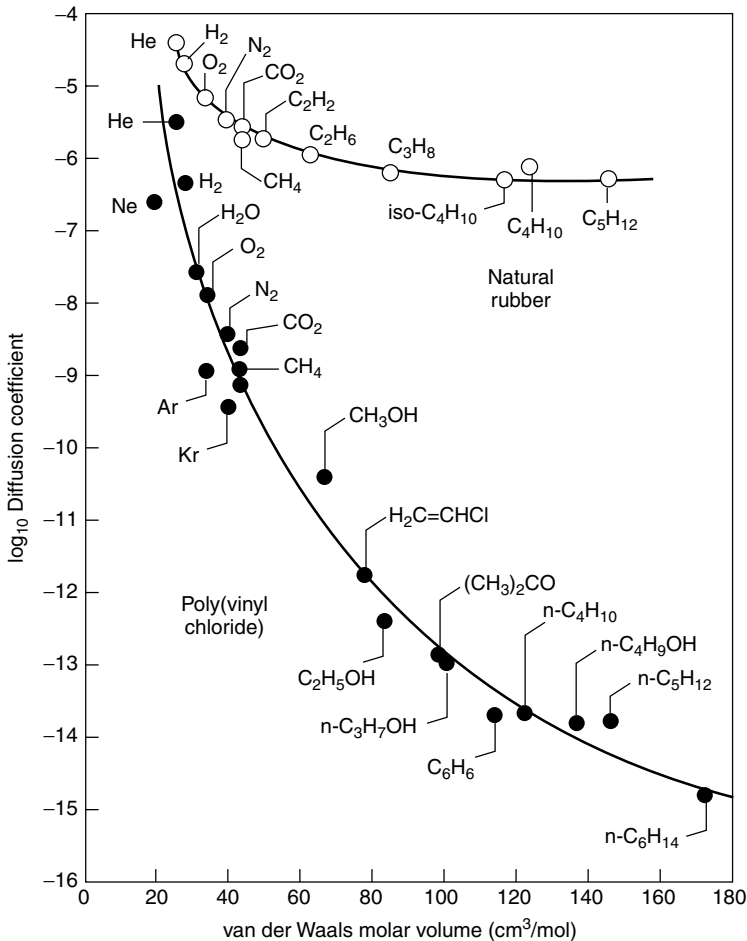

Figure 8.3 Diffusion coefficient as a function of molar volume for a variety of permeants in natural rubber and in poly(vinyl chloride), a glassy polymer. This type of plot was first drawn by Gruen [8], and has been used by many others since

ones. However, the magnitude of the mobility selectivity term depends greatly on whether the membrane material is above or below its glass transition temperature (T_g). If the material is below the glass transition temperature, the polymer chains are essentially fixed and do not rotate. The material is then called a glassy polymer and is tough and rigid. Above the glass transition temperature, the segments of the polymer chains have sufficient thermal energy to allow limited rotation around the chain backbone. This motion changes the mechanical properties of the polymer dramatically, and it becomes a rubber. The relative mobility of gases, as characterized by their diffusion coefficients, differs significantly in rubbers and glasses, as illustrated in Figure 8.3 [8]. Diffusion coefficients in glassy materials decrease much more rapidly with increasing permeate size than diffusion coefficients in rubbers. For example, the mobility selectivity of natural rubber for nitrogen over pentane is approximately 10. The mobility selectivity of poly(vinyl chloride), a rigid, glassy polymer, for nitrogen over pentane is more than 100 000.

The second factor affecting the overall membrane selectivity is the sorption or solubility selectivity. The sorption coefficient of gases and vapors, which is a measure of the energy required for the permeant to be sorbed by the polymer, increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient also increases with molecular diameter, because large molecules are normally more condensable than smaller ones. The gas sorption coefficient can, therefore, be plotted against boiling point or molar volume as shown in Figure 8.4 [9]. As the figure shows, sorption selectivity favors larger, more condensable molecules, such as hydrocarbon vapors, over permanent gases, such as oxygen and nitrogen. However, the difference between the sorption coefficients of permeants in rubbery and glassy polymers is far less marked than the difference in the diffusion coefficients.

It follows from the discussion above that the balance between the mobility selectivity term and the sorption selectivity term in Equation (8.4) [10] is different for glassy and rubbery polymers. This difference is illustrated by the data in Figure 8.5. In glassy polymers, the mobility term is usually dominant, permeability falls with increasing permeate size, and small molecules permeate preferentially. Therefore, when used to separate organic vapors from nitrogen, glassy membranes preferentially permeate nitrogen. In rubbery polymers, the sorption selectivity term is usually dominant, permeability increases with increasing permeate size, and larger molecules permeate preferentially. Therefore, when used to separate organic vapor from nitrogen, rubbery membranes preferentially permeate the organic vapor. The separation properties of polymer membranes for a number of the most important gas separation applications have been summarized by Robeson [11]. A review of structure/property relations has been give by Stern [12]. Properties of some representative and widely used membrane materials are summarized in Table 8.1.

Calculating the selectivity of a membrane using Equation (8.3) and using the permeabilities listed in Table 8.1 must be done with caution. Permeabilities in
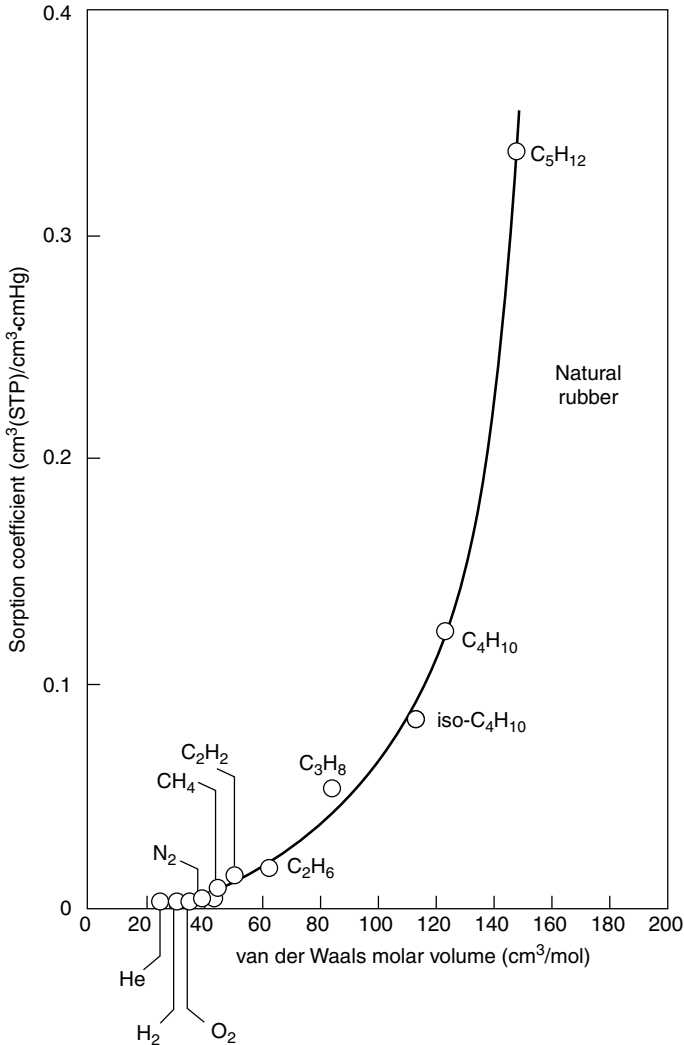
Figure 8.4 Gas sorption coefficient as a function of molar volume for natural rubber membranes. Larger permeants are more condensable and have higher sorption coefficients [9]

Table 8.1 are measured with pure gases; the selectivity obtained from the ratio of pure gas permeabilities gives the ideal membrane selectivity, an intrinsic property of the membrane material. However, practical gas separation processes are performed with gas mixtures. If the gases in a mixture do not interact strongly with the membrane material, the pure gas intrinsic selectivity and the mixed
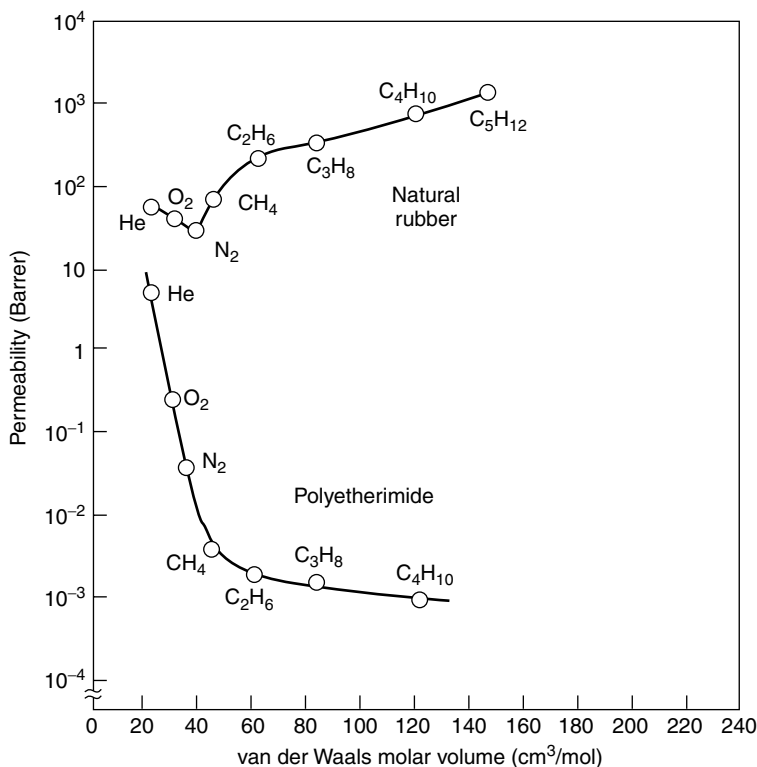
Figure 8.5 Permeability as a function of molar volume for a rubbery and a glassy polymer, illustrating the different balance between sorption and diffusion in these polymer types. The natural rubber membrane is highly permeable; permeability increases rapidly with increasing permeant size because sorption dominates. The glassy polyetherimide membrane is much less permeable; the permeability decreases with increasing permeant size because diffusion dominates [10]. Reprinted from R.D. Behling, K. Ohlrogge, K.-V. Peinemann and E. Kyburz, The Separation of Hydrocarbons from Waste Vapor Streams, in *Membrane Separations in Chemical Engineering*, A.E. Fouda, J.D. Hazlett, T. Matsuura and J. Johnson (eds), AIChE Symposium Series Number 272, Vol. 85, p. 68 (1989). Reproduced by permission of the American Institute of Chemical Engineers. Copyright © 1989 AIChE. All rights reserved

gas selectivity will be equal. This is usually the case for mixtures of oxygen and nitrogen, for example. In many other cases, such as a carbon dioxide and methane mixture, one of the components (carbon dioxide) is sufficiently sorbed by the membrane to affect the permeability of the other component (methane). The selectivity measured with a gas mixture may then be one-half or less of the selectivity calculated from pure gas measurements. Pure gas selectivities are much more commonly reported in the literature than gas mixture data because

Table 8.1 Permeabilities {Barrer [10^{-10} cm^3(STP) $\cdot$ cm/cm^2 $\cdot$ s $\cdot$ cmHg]} measured with pure gases, at the temperatures given, of widely used polymers

Gas	Rubbers		Glasses		
	Silicone rubber at 25 °C ($T_g - 129$ °C)	Natural rubber at 30 °C ($T_g - 73$ °C)	Cellulose acetate at 25 °C (T_g 40 − 124 °C)	Polysulfone at 35 °C (T_g 186 °C)	Polyimide (Ube Industries) at 60 °C ($T_g > 250$ °C)
H_2	550	41	24	14	50
He	300	31	33	13	40
O_2	500	23	1.6	1.4	3
N_2	250	9.4	0.33	0.25	0.6
CO_2	2700	153	10	5.6	13
CH_4	800	30	0.36	0.25	0.4
C_2H_6	2100	—	0.20	—	0.08
C_3H_8	3400	168	0.13	—	0.015
C_4H_{10}	7500	—	0.10	—	—

they are easier to measure. Neglecting the difference between these two values, however, has led a number of workers to seriously overestimate the ability of a membrane to separate a target gas mixture. Figure 8.6 [13] shows some data for the separation of methane and carbon dioxide with cellulose acetate membranes. The calculated pure gas selectivity is very good, but in gas mixtures enough carbon dioxide dissolves in the membrane to increase the methane permeability far above the pure gas methane permeability value. As a result the selectivities measured with gas mixtures are much lower than those calculated from pure gas data.

Membrane Materials and Structure

Metal Membranes

Although almost all industrial gas separation processes use polymeric membranes, interest in metal membranes continues, mostly for the high-temperature membrane reactor applications discussed in Chapter 13 and for the preparation of pure hydrogen for fuel cells. For completeness, the background to these membranes is described briefly here. The study of gas permeation through metals began with Graham's observation of hydrogen permeation through palladium. Pure palladium absorbs 600 times its volume of hydrogen at room temperature and is measurably permeable to the gas. Hydrogen permeates a number of other metals including tantalum, niobium, vanadium, nickel, iron, copper, cobalt and platinum [14]. In most cases, the metal membrane must be operated at high temperatures (>300 °C) to obtain useful permeation rates and to prevent embrittlement and cracking of
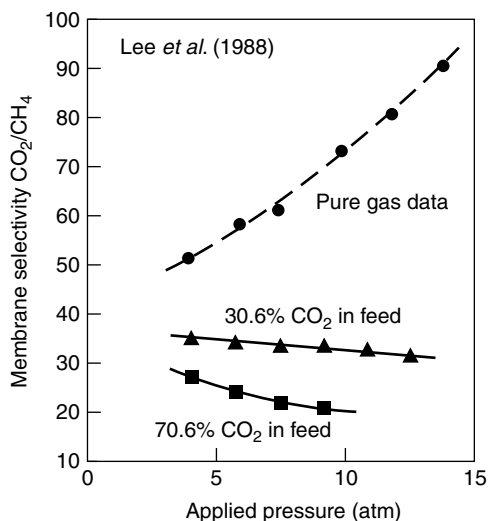
Figure 8.6 The difference between selectivities calculated from pure gas measurements and selectivities measured with gas mixtures can be large. Data of Lee *et al.* [13] for carbon dioxide/methane with cellulose acetate films. Reprinted from S.Y. Lee, B.S. Minhas and M.D. Donohue, Effect of Gas Composition and Pressure on Permeation through Cellulose Acetate Membranes, in *New Membrane Materials and Processes for Separation*, K.K. Sirkar and D.R. Lloyd (eds), AIChE Symposium Series Number 261, Vol. 84, p. 93 (1988). Reproduced with permission of the American Institute of Chemical Engineers. Copyright © 1988 AIChE. All rights reserved

the metal by sorbed hydrogen. Poisoning of the membrane surface by oxidation or sulfur deposition from trace amounts of hydrogen sulfide also occurs. A breakthrough in metal permeation studies occurred in the 1960s when Hunter at Johnson Matthey discovered that palladium/silver alloy membranes showed no hydrogen embrittlement even when used to permeate hydrogen at room temperature [15]. Although most work on gas permeation through membranes has focused on hydrogen, oxygen-permeable metal membranes are also known; however, the permeabilities are low.

Hydrogen-permeable metal membranes are extraordinarily selective, being extremely permeable to hydrogen but essentially impermeable to all other gases. The gas transport mechanism is the key to this high selectivity. Hydrogen permeation through a metal membrane is believed to follow the multistep process illustrated in Figure 8.7 [16]. Hydrogen molecules from the feed gas are sorbed on the membrane surface, where they dissociate into hydrogen atoms. Each individual hydrogen atom loses its electron to the metal lattice and diffuses through the lattice as an ion. Hydrogen atoms emerging at the permeate side of the membrane reassociate to form hydrogen molecules, then desorb, completing the permeation
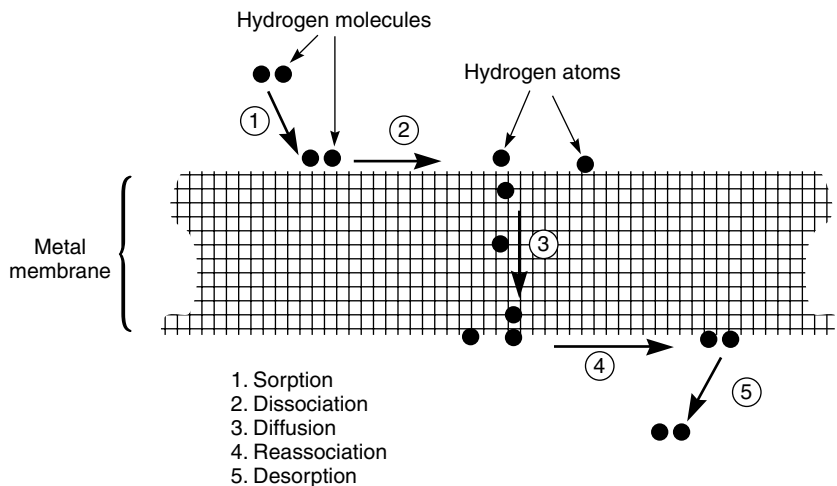
Figure 8.7 Mechanism of permeation of hydrogen through metal membranes

process. Only hydrogen is transported through the membrane by this mechanism; all other gases are excluded.

If the sorption and dissociation of hydrogen molecules is a rapid process, then the hydrogen atoms on the membrane surface are in equilibrium with the gas phase. The concentration, c, of hydrogen atoms on the metal surface is given by Sievert's law:

$$c = Kp^{1/2} \tag{8.5}$$

where K is Sievert's constant and p is the hydrogen pressure in the gas phase. At high temperatures ($>300\ °C$), the surface sorption and dissociation processes are fast, and the rate-controlling step is diffusion of atomic hydrogen through the metal lattice. This is supported by the data of Holleck and others, who have observed that the hydrogen flux through the metal membrane is proportional to the difference of the square roots of the hydrogen pressures on either side of the membrane. At lower temperatures, however, the sorption and dissociation of hydrogen on the membrane surface become the rate-controlling steps, and the permeation characteristics of the membrane deviate from Sievert's law predictions.

Palladium-alloy membranes were studied extensively during the 1950s and 1960s, and this work led to the installation by Union Carbide of a full-scale demonstration plant to separate hydrogen from a refinery off-gas stream containing methane, ethane, carbon monoxide and hydrogen sulfide [17]. The plant could produce 99.9 % or better pure hydrogen in a single pass through the membrane. The plant operated with 25-μm-thick membranes, at a temperature of 370 °C and a feed pressure of 450 psi. The high cost of the membranes and

the need to operate at high temperatures to obtain useful fluxes made the process uncompetitive with other hydrogen recovery technologies. In the 1970s and early 1980s, Johnson Matthey built a number of systems to produce on-site hydrogen by separation of hydrogen/carbon dioxide mixtures made by reforming methanol [18]. This was not a commercial success, but the company still produces small systems using palladium–silver alloy membranes to generate ultrapure hydrogen from 99.9 % hydrogen for the electronics industry.

Recently, attempts have been made to reduce the cost of palladium metal membranes by preparing composite membranes. In these membranes a thin selective palladium layer is deposited onto a microporous ceramic, polymer or base metal layer [19–21]. The palladium layer is applied by electrolysis coating, vacuum sputtering or chemical vapor deposition. This work is still at the bench scale.

Polymeric Membranes

Most gas separation processes require that the selective membrane layer be extremely thin to achieve economical fluxes. Typical membrane thicknesses are less than 0.5 μm and often less than 0.1 μm. Early gas separation membranes [22] were adapted from the cellulose acetate membranes produced for reverse osmosis by the Loeb–Sourirajan phase separation process. These membranes are produced by precipitation in water; the water must be removed before the membranes can be used to separate gases. However, the capillary forces generated as the liquid evaporates cause collapse of the finely microporous substrate of the cellulose acetate membrane, destroying its usefulness. This problem has been overcome by a solvent exchange process in which the water is first exchanged for an alcohol, then for hexane. The surface tension forces generated as liquid hexane is evaporated are much reduced, and a dry membrane is produced. Membranes produced by this method have been widely used by Grace (now GMS, a division of Kvaerner) and Separex (now a division of UOP) to separate carbon dioxide from methane in natural gas.

Experience has shown that gas separation membranes are far more sensitive to minor defects, such as pinholes in the selective membrane layer, than membranes used in reverse osmosis or ultrafiltration. Even a single small membrane defect can dramatically decrease the selectivity of gas separation membranes, especially with relatively selective membranes such as those used to separate hydrogen from nitrogen. For example, a good polymeric hydrogen/nitrogen separating membrane has a selectivity of more than 100. A small defect that allows as little as 1 % of the permeating gas to pass unseparated doubles the nitrogen flux and halves the membrane selectivity. The sensitivity of gas separation membranes to defects posed a serious problem to early developers. Generation of a few defects is very difficult to avoid during membrane preparation and module formation.

From 1978 to 1980, Henis and Tripodi [6,23], then at Monsanto, devised an ingenious solution to the membrane defect problem; their approach is illustrated in Figure 8.8. The Monsanto group made Loeb–Sourirajan hollow fiber membranes
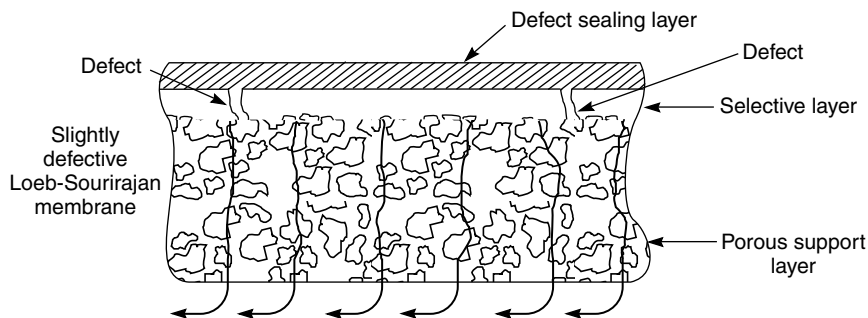
Figure 8.8 The technique devised by Henis and Tripodi [23] to seal defects in their selective polysulfone Loeb–Sourirajan membrane

(principally from polysulfone), then coated the membranes with a thin layer of silicone rubber. Silicone rubber is extremely permeable compared to polysulfone but has a much lower selectivity; thus, the silicone rubber coating did not significantly change the selectivity or flux through the defect-free portions of the polysulfone membrane. However, the coating plugged membrane defects in the polysulfone membrane and eliminated convective flow through these defects. The silicone rubber layer also protected the membrane during handling. The development of silicone rubber-coated anisotropic membranes was a critical step in the production by Monsanto of the first successful gas separation membrane for hydrogen/nitrogen separations.

Another type of gas separation membrane is the multilayer composite structure shown in Figure 8.9. In this membrane, a finely microporous support membrane is overcoated with a thin layer of the selective polymer, which is a different material from the support. Additional layers of very permeable materials such as silicone rubber may also be applied to protect the selective layer and to seal any defects. In general it has been difficult to make composite membranes with
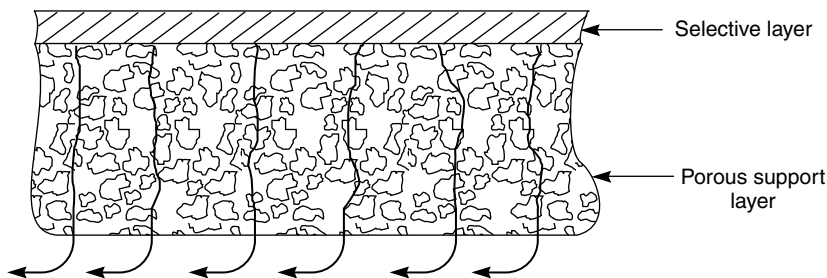

Figure 8.9 Two-layer composite membrane formed by coating a thin layer of a selective polymer on a microporous support that provides mechanical strength

glassy selective layers as thin and high-flux as good-quality Loeb–Sourirajan membranes. However, composites are the best way to form membranes from rubbery selective materials; the microporous support layer can be a tough glassy material to provide strength. Rubbery composite membranes of this type can withstand pressure differentials of 1500 psi or more.

Ceramic and Zeolite Membranes

During the last few years, ceramic- and zeolite-based membranes have begun to be used for a few commercial separations. These membranes are all multilayer composite structures formed by coating a thin selective ceramic or zeolite layer onto a microporous ceramic support. Ceramic membranes are prepared by the sol–gel technique described in Chapter 3; zeolite membranes are prepared by direct crystallization, in which the thin zeolite layer is crystallized at high pressure and temperature directly onto the microporous support [24,25].

Both Mitsui [26] and Sulzer [27] have commercialized these membranes for dehydration of alcohols by pervaporation or vapor/vapor permeation. The membranes are made in tubular form. Extraordinarily high selectivities have been reported for these membranes, and their ceramic nature allows operation at high temperatures, so fluxes are high. These advantages are, however, offset by the costs of the membrane modules, currently in excess of US$3000/m^2 of membrane.

Mixed-matrix Membranes

The ceramic and zeolite membranes described above have been shown to have exceptional selectivities for a number of important separations. However, the membranes are not easy to make and consequently are prohibitively expensive for many separations. One solution to this problem is to prepare membranes from materials consisting of zeolite particles dispersed in a polymer matrix. These membranes are expected to combine the selectivity of zeolite membranes with the low cost and ease of manufacture of polymer membranes. Such membranes are called mixed-matrix membranes.

Mixed-matrix membranes have been a subject of research interest for more than 15 years [28–33]. The concept is illustrated in Figure 8.10. At relatively low loadings of zeolite particles, permeation occurs by a combination of diffusion through the polymer phase and diffusion through the permeable zeolite particles. The relative permeation rates through the two phases are determined by their permeabilities. At low loadings of zeolite, the effect of the permeable zeolite particles on permeation can be expressed mathematically by the expression shown below, first developed by Maxwell in the 1870s [34].

$$P = P_c \left[\frac{P_d + 2P_c - 2\Phi(P_c - P_d)}{P_d + 2P_c + \Phi(P_c - P_d)} \right] \tag{8.6}$$

(a) Diffusion below the percolation   (b) Diffusion above the percolation
     threshold   threshold
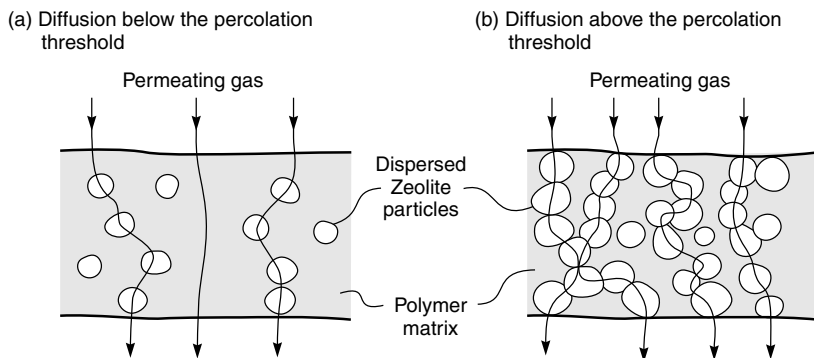

Figure 8.10 Gas permeation through mixed-matrix membranes containing different amounts of dispersed zeolite particles

where P is the overall permeability of the mixed-matrix material, Φ is the volume fraction of the dispersed zeolite phase, P_c is the permeability of the continuous polymer phase, and P_d is the permeability of the dispersed zeolite phase.

At low loadings of dispersed zeolite, individual particles can be considered to be well separated. At higher loadings, some small islands of interconnected particles form; at even higher loadings, these islands grow and connect to form extended pathways. At loadings above a certain critical value, continuous channels form within the membrane, and almost all the zeolite particles are connected to the channels. This is called the percolation threshold. At this particle loading, the Maxwell equation is no longer used to calculate the membrane permeability. The percolation threshold is believed to be achieved at particle loadings of about 30 vol %.

Figure 8.11, adapted from a plot by Robeson *et al.* [35], shows a calculated plot of permeation of a model gas through zeolite-filled polymer membranes in which the zeolite phase is 1000 times more permeable than the polymer phase. At low zeolite particle loadings, the average particle is only in contact with one or two other particles, and a modest increase in average permeability occurs following the Maxwell model. At particle loadings of 25–30 vol % the situation is different—most particles touch two or more particles, and most of the permeating gas can diffuse through interconnected zeolite channels. The percolation threshold has been reached, and the Maxwell model no longer applies. Gas permeation is then best described as permeation through two interpenetrating, continuous phases. At very high zeolite loadings, the mixed-matrix membrane may be best described as a continuous zeolite phase containing dispersed particles of polymer. The Maxwell model may then again apply, with the continuous and the dispersed phases in Equation (8.6) reversed.

The figure also shows that the highly permeable zeolite only has a large effect on polymer permeability when the percolation threshold is reached. That is, useful
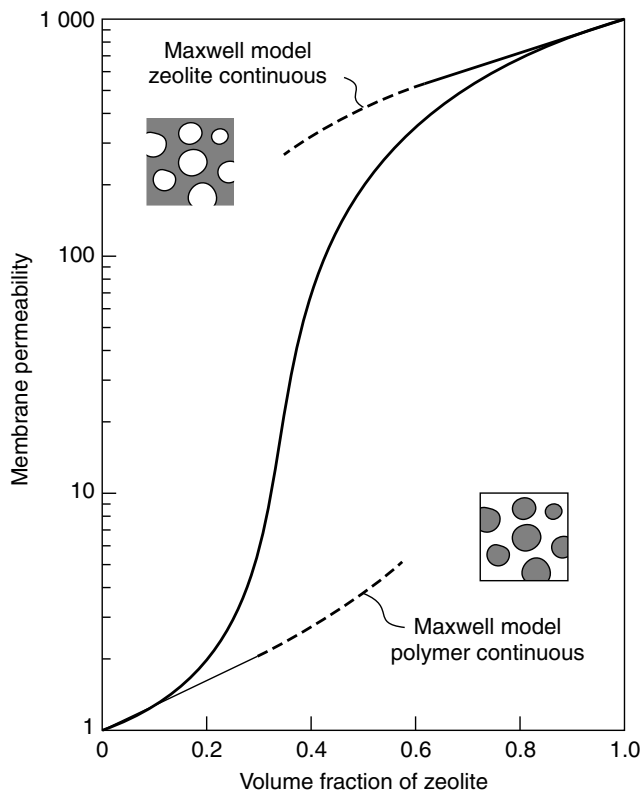
Figure 8.11   Change in membrane permeabilities for mixed-matrix membranes containing different volume fractions of zeolite. Adapted from Robeson *et al*. [35]

membranes must contain more than 30 vol % zeolite. This observation is borne out by the limited experimental data available.

Despite the great deal of recent research on mixed-matrix membranes, the results to date have been modest. Two general approaches have been used. The first, investigated by Koros [31–33] and Smolders [29], is to use the expected difference in the diffusion coefficients of gases in the zeolite particles. Koros, in particular, has focused on zeolites with small aperture sizes, for example, Zeolite 4A, with an effective aperture size of 3.8–4.0 Å, which has been used to separate oxygen (Lennard-Jones (LJ) diameter 3.47 Å) from nitrogen (LJ diameter 3.8 Å). The oxygen/nitrogen selectivity of the Zeolite 4A membrane has been calculated to be 37, with an oxygen permeability of 0.8 Barrer—an exceptional membrane. To maximize the effect of the zeolite in his mixed-matrix membrane, Koros used relatively low-permeability polymers, such as Matrimid® and other polyimides, or poly(vinyl acetate).

The second type of zeolite mixed-matrix membrane relies on relative sorption of different permeants to obtain an improved separation. For example, Smolders *et al.* [28] at the University of Twente, and Peinemann at GKSS, Geesthacht [30], showed that silicalite-silicone rubber mixed-matrix membranes had exceptional selectivities for the permeation of ethanol (kinetic diameter 4.5 Å) over water (kinetic diameter 2.6 Å). These zeolites separate by virtue of their higher sorption of ethanol compared to water on the hydrophobic silicalite surface. Differences in diffusion coefficients favor permeation of water, but this effect is overcome by the sorption effect. The net result is a more than seven-fold increase in the relative permeability of ethanol over water, compared to pure silicone rubber membranes. Because the aperture diameter of the silicalite particles is relatively large, permeabilities through the zeolite phase are also high, allowing rubbery, relatively high-permeability polymers to be used as the matrix phase.

Membrane Modules

Gas separation membranes are formed into spiral-wound or hollow fiber modules. Particulate matter, oil mist, and other potentially fouling materials can be completely and economically removed from gas streams by good-quality coalescing filters, so membrane fouling is generally more easily controlled in gas separation than with liquid separations. Therefore, the choice of module design is usually decided by cost and membrane flux. The hollow fiber membranes used in gas separation applications are often very fine, with lumen diameters of 50–200 μm. However, the pressure drop required on the lumen side of the membrane for these small-diameter fibers can become enough to seriously affect membrane performance. In the production of nitrogen from air, the membrane pressure-normalized fluxes are relatively low, from 1 to 2 gpu, and parasitic pressure drops are not a problem. However, in the separation of hydrogen from nitrogen or methane or carbon dioxide from natural gas, pressure-normalized fluxes are higher, and hollow fine fiber modules can develop excessive permeate-side pressure drops. The solution is to use capillary fibers or spiral-wound modules for this type of application. Nonetheless, these disadvantages of hollow fiber membranes may be partially offset by their lower cost per square meter of membrane. These factors are summarized for some important gas separation applications in Table 8.2.

Process Design

The three factors that determine the performance of a membrane gas separation system are illustrated in Figure 8.12. The role of membrane selectivity is obvious; not so obvious are the importance of the ratio of feed pressure (p_o) to permeate pressure (p_ℓ) across the membrane, usually called the pressure ratio, φ, and defined as

$$\varphi = \frac{p_o}{p_\ell} \tag{8.7}$$

Table 8.2   Module designs used for various gas separation applications

Application	Typical membrane material	Selectivity (α)	Average pressure-normalized flux $[10^{-6}\ \mathrm{cm^3(STP)/cm^2 \cdot s \cdot cmHg}]$	Module design commonly used
O_2/N_2	Polyimide	6–7	1–2	Hollow fiber
H_2/N_2	Polysulfone	100	10–20	Hollow fiber
CO_2/CH_4	Cellulose acetate	15–20	2–5	Spiral or hollow fiber
VOC/N_2	Silicone rubber	10–30	100	Spiral
H_2O/Air	Polyimide	>200	5	Capillary —bore-side feed

and of the membrane stage-cut, θ, which is the fraction of the feed gas that permeates the membrane, defined as

$$\theta = \frac{\text{permeate flow}}{\text{feed flow}} \tag{8.8}$$

Pressure Ratio

The importance of pressure ratio in the separation of gas mixtures can be illustrated by considering the separation of a gas mixture with component concentrations of n_{i_o} and n_{j_o} at a feed pressure p_o. A flow of component i across the membrane can only occur if the partial pressure of i on the feed side of the membrane $(n_{i_o}p_o)$ is greater than the partial pressure of i on the permeate side of the membrane $(n_{i_\ell}p_\ell)$, that is,

$$n_{i_o}p_{i_o} > n_{i_\ell}p_\ell \tag{8.9}$$

It follows that the maximum separation achieved by the membrane can be expressed as

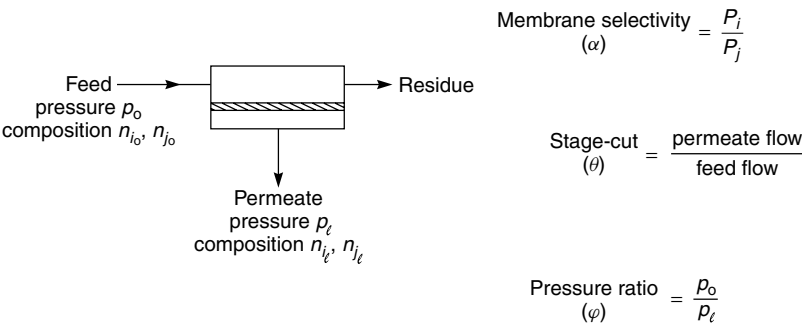$$\frac{n_{i_\ell}}{n_{i_o}} \leq \frac{p_o}{p_\ell} \tag{8.10}$$

Figure 8.12   Parameters affecting the performance of membrane gas separation systems

That is, the separation achieved can never exceed the pressure ratio φ, no matter how selective the membrane:

$$\frac{n_{i_\ell}}{n_{i_o}} \leq \varphi \tag{8.11}$$

The relationship between pressure ratio and membrane selectivity can be derived from the Fick's law expression for the fluxes of components i and j

$$j_i = \frac{\mathcal{P}_i(p_{i_o} - p_{i_\ell})}{\ell} \tag{8.12}$$

and

$$j_j = \frac{\mathcal{P}_j(p_{j_o} - p_{j_\ell})}{\ell} \tag{8.13}$$

The total gas pressures on the feed and permeate side are the sum of the partial pressures. For the feed side

$$p_o = p_{i_o} + p_{j_o} \tag{8.14}$$

and for the permeate side

$$p_\ell = p_{i_\ell} + p_{j_\ell} \tag{8.15}$$

The volume fractions of components i and j on the feed and permeate side are also related to partial pressures. For the feed side

$$n_{i_o} = \frac{p_{i_o}}{p_o} \quad n_{j_o} = \frac{p_{j_o}}{p_o} \tag{8.16}$$

and for the permeate side

$$n_{i_\ell} = \frac{p_{i_\ell}}{p_\ell} \quad n_{j_\ell} = \frac{p_{j_\ell}}{p_\ell} \tag{8.17}$$

while from mass balance considerations

$$\frac{j_i}{j_j} = \frac{n_{i_\ell}}{n_{j_\ell}} = \frac{n_{i_\ell}}{1 - n_{i_\ell}} = \frac{1 - n_{j_\ell}}{n_{j_\ell}} \tag{8.18}$$

Combining Equations (8.14–8.18) yields an expression linking the concentration of component i on the feed and permeate sides of the membrane

$$n_{i_\ell} = \frac{\varphi}{2}\left[n_{i_o} + \frac{1}{\varphi} + \frac{1}{\alpha - 1} - \sqrt{\left(n_{i_o} + \frac{1}{\varphi} + \frac{1}{\alpha - 1}\right)^2 - \frac{4\alpha n_{i_o}}{(\alpha - 1)\varphi}}\right] \tag{8.19}$$

This somewhat complex expression breaks down into two limiting cases depending on the relative magnitudes of the pressure ratio and the membrane selectivity. First, if the membrane selectivity (α) is very much larger than the pressure ratio (φ), that is,

$$\alpha \gg \varphi \tag{8.20}$$

then Equation (8.20) becomes

$$n_{i_\ell} = n_{i_o}\varphi \tag{8.21}$$

This is called the pressure-ratio-limited region, in which the performance is determined only by the pressure ratio across the membrane and is independent of the membrane selectivity. If the membrane selectivity (α) is very much smaller than the pressure ratio (φ), that is,

$$\alpha \ll \varphi \tag{8.22}$$

then Equation (8.19) becomes

$$n_{i_\ell} = \frac{\alpha n_{i_o}}{1 - n_{i_o}(1 - \alpha)} \tag{8.23}$$

This is called the membrane-selectivity-limited region, in which the membrane performance is determined only by the membrane selectivity and is independent of the pressure ratio. There is, of course, an intermediate region between these two limiting cases, in which both the pressure ratio and the membrane selectivity affect the membrane system performance. These three regions are illustrated in Figure 8.13, in which the calculated permeate concentration (n_{i_ℓ}) is plotted versus pressure ratio (φ) for a membrane with a selectivity of 30 [36]. At a pressure ratio of 1, feed pressure equal to the permeate pressure, no separation is achieved by the membrane. As the difference between the feed and permeate pressure increases,
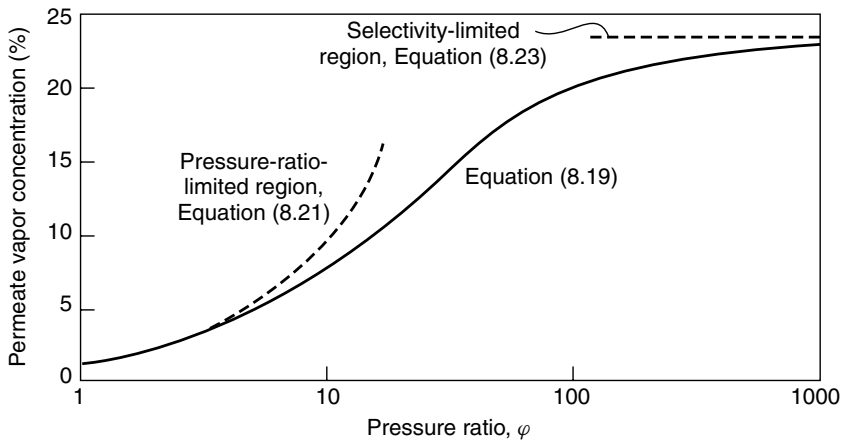

Figure 8.13   Calculated permeate vapor concentration for a vapor-permeable membrane with a vapor/nitrogen selectivity of 30 as a function of pressure ratio. The feed vapor concentration is 1 %. Below pressure ratios of about 10, separation is limited by the pressure ratio across the membrane. At pressure ratios above about 100, separation is limited by the membrane selectivity [36]

the concentration of the more permeable component in the permeate gas begins to increase, first according to Equation (8.21) and then, when the pressure ratio and membrane selectivity are comparable, according to Equation (8.19). At very high pressure ratios, that is, when the pressure ratio is four to five times higher than the membrane selectivity, the membrane enters the membrane-selectivity-controlled region. In this region the permeate concentration reaches the limiting value given by Equation (8.23).

The relationship between pressure ratio and selectivity is important because of the practical limitation to the pressure ratio achievable in gas separation systems. Compressing the feed stream to very high pressure or drawing a very hard vacuum on the permeate side of the membrane to achieve large pressure ratios both require large amounts of energy and expensive pumps. As a result, typical practical pressure ratios are in the range 5–20.

Because the attainable pressure ratio in most gas separation applications is limited, the benefit of very highly selective membranes is often less than might be expected. For example, as shown in Figure 8.14, if the pressure ratio is 20, then increasing the membrane selectivity from 10 to 20 will significantly improve system performance. However, a much smaller incremental improvement results from increasing the selectivity from 20 to 40. Increases in selectivity above 100 will produce negligible improvements. A selectivity of 100 is five times the pressure ratio of 20, placing the system in the pressure-ratio-limited region.
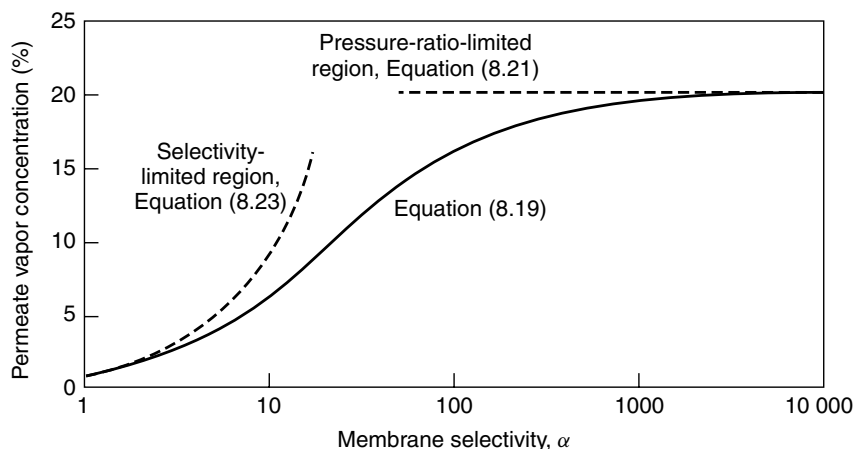

Figure 8.14 Calculated permeate vapor concentration as a function of selectivity. The feed vapor concentration is 1 %; the pressure ratio is fixed at 20. Below a vapor/nitrogen selectivity of about 10, separation is limited by the low membrane selectivity; at selectivities above about 100, separation is limited by the low pressure ratio across the membrane [36]

Stage-cut

Another factor that affects membrane system design is the degree of separation required. The usual target of a gas separation system is to produce a residue stream essentially stripped of the permeable component and a small, highly concentrated permeate stream. These two requirements cannot be met simultaneously; a trade-off must be made between removal from the feed gas and enrichment in the permeate. The system attribute that characterizes this trade-off is called the stage-cut. The effect of stage-cut on system performance is illustrated in Figure 8.15.

In the example calculation shown in Figure 8.15, the feed gas contains 50 % of a permeable gas (i) and 50 % of a relatively impermeable gas (j). Under the assumed operating conditions of this system (pressure ratio 20, membrane selectivity 20), it is possible at zero stage-cut to produce a permeate stream containing 94.8 % of component i. But the permeate stream is tiny and the residue stream is still very close to the feed gas concentration of 50 %. As the fraction of the feed gas permeating the membrane is increased by increasing the membrane area, the concentration of the permeable component in the residue and permeate streams falls. At a stage-cut of 25 %, the permeate gas concentration has fallen from 94.8 % (its maximum value) to 93.1 %. The residue stream concentration of permeable gas is then 35.5 %. Increasing the fraction of the feed gas that permeates the membrane to 50 % by adding more membrane area produces a residue
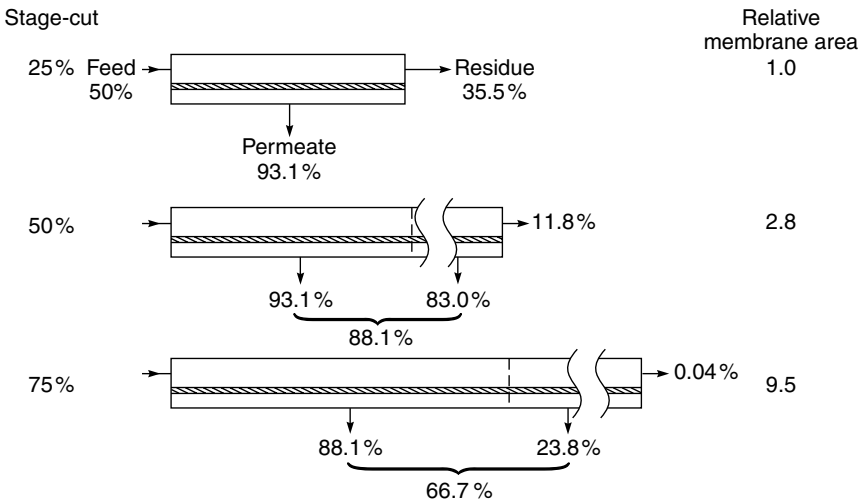

Figure 8.15 The effect of stage-cut on the separation of a 50/50 feed gas mixture (pressure ratio, 20; membrane selectivity, 20). At low stage-cuts a concentrated permeate product, but only modest removal from the residue, can be obtained. At high stage-cuts almost complete removal is obtained, but the permeate product is only slightly more enriched than the original feed

stream containing 11.8 % of the permeable gas. However, the gas permeating the added membrane area only contains 83.0 % of the permeable component, so the average concentration of permeable component in the permeate stream is reduced from 93.1 to 88.1 %. If the fraction of the feed gas that permeates the membrane is increased to 75 % by adding even more membrane area, the concentration of the permeable component in the residue stream is reduced to only 0.04 %. However, the gas permeating the added membrane area only contains 23.8 % of the permeable component, *less than the original feed gas*. The average concentration of the permeable component in the feed gas is, therefore, reduced to 66.7 %. This means that one-half of the less permeable component has been lost to the permeate stream.

The calculations shown in Figure 8.15 illustrate the trade-off between recovery and purity. A single-stage membrane process can be designed for either maximum recovery or maximum purity, but not both. The calculations also show that membranes can produce very pure residue gas streams enriched in the less permeable component, although at low recoveries. However, the enrichment of the more permeable component in the permeate can never be more than the membrane selectivity, so a membrane with low selectivity produces an only slightly enriched permeate. This is why membranes with an oxygen/nitrogen selectivity of 4–6 can produce very pure nitrogen (>99.5 %) from air on the residue side of the membrane, but the same membranes cannot produce better than 50–60 % oxygen on the permeate side. If the more permeable component must be pure, very selective membranes are required or multistage or recycle membrane systems must be used.

Finally, the calculations in Figure 8.15 show that increasing the stage-cut to produce a pure residue stream requires a disproportionate increase in membrane area. As the feed gas is stripped of the more permeable component, the average permeation rate through the membrane falls. In the example shown, this means that permeating the first 25 % of the feed gas requires a relative membrane area of 1, permeating the next 25 % requires a membrane area increment of 1.8, and permeating the next 25 % requires an increment of 6.7.

Multistep and Multistage System Designs

Because the membrane selectivity and pressure ratio achievable in a commercial membrane system are limited, a one-stage membrane system may not provide the separation desired. The problem is illustrated in Figure 8.16. The target of the process is 90 % removal of a volatile organic compound (VOC), which is the permeable component, from the feed gas, which contains 1 vol % of this component. This calculation and those that immediately follow assume a feed gas mixture VOC and nitrogen. Rubbery membranes such as silicone rubber permeate the VOC preferentially because of its greater condensability and hence solubility in the membrane. In this calculation, the pressure ratio is fixed at 20
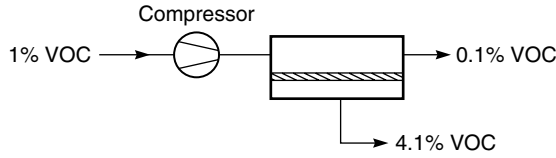
Figure 8.16 A one-stage vapor separation operation. The performance of this system was calculated from a crossflow model using a vapor/nitrogen selectivity of 20 and a pressure ratio of 20

by compressing the feed gas, and the permeate is maintained at atmospheric pressure. The membrane VOC/nitrogen selectivity is assumed to be 20.

Figure 8.16 shows that when 90 % of the VOC in the feed stream is removed, the permeate stream will contain approximately 4 % of the permeable component. In many cases, 90 % removal of VOC from the feed stream is insufficient to allow the residue gas to be discharged, and enrichment of the component in the permeate is insufficient also.

If the main problem is insufficient VOC removal from the feed stream, a two-step system as shown in Figure 8.17 can be used. In a two-step system, the residue stream from the first membrane unit is passed to a second unit, where the VOC concentration is reduced by a further factor of 10, from 0.1 to 0.01 %. Because the concentration of VOC in the feed to the second membrane unit is low, the permeate stream is relatively dilute and is recirculated to the feed stream.

A multistep design of this type can achieve almost complete removal of the permeable component from the feed stream to the membrane unit. However, greater removal of the permeable component is achieved at the expense of increases in membrane area and power consumption by the compressor. As a rule of thumb, the membrane area required to remove the last 9 % of a component from the feed equals the membrane area required to remove the first 90 %.

Sometimes, 90 % removal of the permeable component from the feed stream is acceptable for the discharge stream from the membrane unit, but a higher
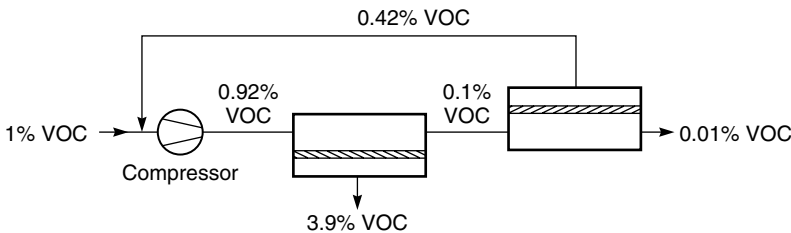

Figure 8.17 A two-step system to achieve 99 % vapor removal from the feed stream. Selectivity, 20; pressure ratio, 20
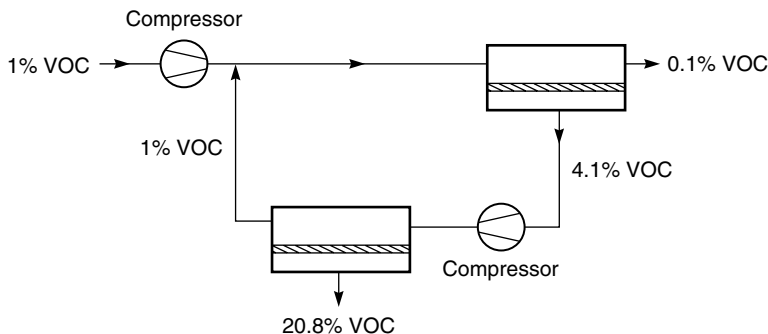
Figure 8.18 A two-stage system to produce a highly concentrated permeate stream. Selectivity, 20; pressure ratio, 20

concentration is needed to make the permeate gas usable. In this situation, a two-stage system of the type shown in Figure 8.18 is used. In a two-stage design, the permeate from the first membrane unit is recompressed and sent to a second membrane unit, where a further separation is performed. The final permeate is then twice enriched. In the most efficient two-stage design, the residue stream from the second stage is reduced to about the same concentration as the original feed gas, with which it is mixed. In the example shown in Figure 8.18, the permeate stream, concentrated a further five-fold, leaves the system at a concentration of 21 %. Because the volume of gas treated by the second-stage membrane unit is much smaller than in the first stage, the membrane area of the second stage is relatively small. Thus, incorporation of a second stage only increases the overall membrane area and power requirements by approximately 15–20 %.

Multistage/multistep combinations of two-step and two-stage processes can be designed but are seldom used in commercial systems—their complexity makes them uncompetitive with alternative separation technologies. More commonly some form of recycle design is used.

Recycle Designs

A simple recycle design, sometimes called a two-and-one-half-stage system, proposed by Wijmans [37] is shown in Figure 8.19. In this design, the permeate from the first membrane stage is recompressed and sent to a two-step second stage, where a portion of the gas permeates and is removed as enriched product. The remaining gas passes to another membrane stage, which brings the gas concentration close to the original feed value. The permeate from this stage is mixed with the first-stage permeate, forming a recycle loop. By controlling the relative size of the two second stages any desired concentration of the more permeable component can be achieved in the product. In the example shown, the permeable
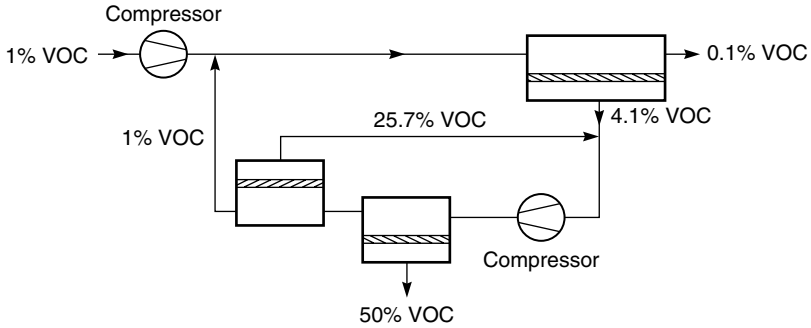
Figure 8.19 Two-and-one-half-stage system: by forming a recycle loop around the second stage, a small, very concentrated product stream is created. Selectivity, 20; pressure ratio, 20 [37]

component is concentrated to 50 % in the permeate. The increased performance is achieved at the expense of a slightly larger second-stage compressor and more membrane area. Normally, however, this design is preferable to a more complex three-stage system.

Figure 8.20 shows another type of recycle design in which a recycle loop increases the concentration of the permeable component to the point at which it can be removed by a second process, most commonly condensation [38]. The feed stream entering the recycle loop contains 1 % of the permeable component as in Figures 8.16–8.19. After compression to 20 atm, the feed gas passes through a condenser at 30 °C, but the VOC content is still below the condensation concentration at this temperature. The membrane unit separates the gas into a VOC-depleted residue stream and a vapor-enriched permeate stream, which is recirculated to the front of the compressor. Because the bulk of the vapor is recirculated, the concentration of vapor in the loop increases rapidly until the pressurized gas entering the condenser exceeds the vapor dew point of 6.1 %. At
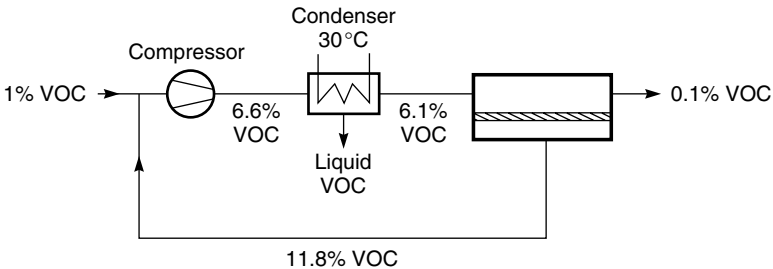

Figure 8.20 Recycle system design using one membrane stage, preceded by a compressor and condenser: feed stream, 1 % vapor in nitrogen; selectivity, 20; pressure ratio, 20

this point, the system is at steady state; the mass of VOC entering the recirculation loop is equal to the mass discharged in the residue stream plus the mass removed as liquid condensate.

Recycle designs of this type are limited to applications in which the components of the gas mixture, if sufficiently concentrated, can be separated from the gas by some other technique. With organic vapors, condensation is often possible; adsorption, chemical scrubbing or absorption can also be used. The process shown in Figure 8.20 is used to separate VOCs from nitrogen and air or to separate propane, butane, pentane and higher hydrocarbons from natural gas (methane).

Applications

The membrane gas separation industry is still growing and changing. Most of the large industrial gas companies now have membrane affiliates: Air Products (Permea), MG (Generon), Air Liquide (Medal) and Praxair (IMS). The affiliates focus mainly on producing membrane systems to separate nitrogen from air, but also produce some hydrogen separation systems. Another group of companies, UOP (Separex), Natco (Cynara), Kvaerner (GMS) and ABB Lummus Global (MTR), produces membrane systems for natural gas separations. A third group of smaller independents are focusing on the new applications, including vapor separation, air dehydration and oxygen enrichment. The final size and form of this industry are still unknown. The following section covers the major current applications. Overview articles on the main gas separation applications can be found in Paul and Yampol'skii [39], in Koros and Fleming [40] and elsewhere [41].

Hydrogen Separations

The first large-scale commercial application of membrane gas separation was the separation of hydrogen from nitrogen in ammonia purge gas streams. The process, launched in 1980 by Monsanto, was followed by a number of similar applications, such as hydrogen/methane separation in refinery off-gases and hydrogen/carbon monoxide adjustment in oxo-chemical synthesis plants [7]. Hydrogen is a small, noncondensable gas, which is highly permeable compared to all other gases. This is particularly true with the glassy polymers primarily used to make hydrogen-selective membranes; fluxes and selectivities of hydrogen through some of these materials are shown in Table 8.3. With fluxes and selectivities as high as these, it is easy to understand why hydrogen separation was the first gas separation process developed. Early hydrogen membrane gas separation plants used polysulfone or cellulose acetate membranes, but now a variety of specifically synthesized materials, such as polyimides (Ube, Praxair), polyaramide (Medal) or brominated polysulfone (Permea), are used.

Table 8.3   Hydrogen separation membranes

Membrane (developer)	Selectivity			Hydrogen pressure-normalized flux [10^{-6} cm^3(STP)/ cm$^2 \cdot$ s $\cdot$ cmHg]
	H$_2$/CO	H$_2$/CH$_4$	H$_2$/N$_2$	
Polyaramide (Medal)	100	>200	>200	—
Polysulfone (Permea)	40	80	80	100
Cellulose acetate (Separex)	30–40	60–80	60–80	200
Polyimide (Ube)	50	100–200	100–200	80–200
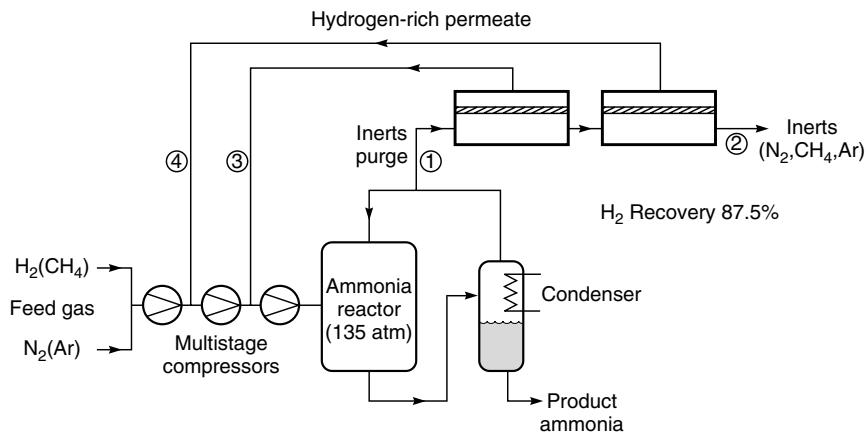
	Stream Composition (%)			
	Membrane Feed ①	Membrane Vent ②	High-Pressure Permeate ③	Low-Pressure Permeate ④
Hydrogen	62	21	87.3	84.8
Nitrogen	21	44	7.1	8.4
Methane	11	23	36	4.3
Argon	6	13	2.0	2.5
Pressure (atm)	135	132	70	28
Flow (scfm)	2000	740	830	430

Figure 8.21   Simplified flow schematic of the PRISM® membrane system to recover hydrogen from an ammonia reactor purge stream. A two-step membrane system is used to reduce permeate compression costs

A typical membrane system flow scheme for recovery of hydrogen from an ammonia plant purge gas stream is shown in Figure 8.21. A photograph of such a system is shown in Figure 8.22. During the production of ammonia from nitrogen and hydrogen, argon enters the high-pressure ammonia reactor as an impurity with the nitrogen stream and methane enters the reactor as an impurity with the hydrogen. Ammonia produced in the reactor is removed by condensation, so the argon and methane impurities accumulate until they represent as much as 15 % of the gas in the reactor. To control the concentration of these components, the reactor must be continuously purged. The hydrogen lost with this purge gas can represent 2–4 % of the total hydrogen consumed. These plants are very large, so recovery of the hydrogen for recycle to the ammonia reactor is economically worthwhile.

In the process shown in Figure 8.21, a two-step membrane design is used to reduce the cost of recompressing the hydrogen permeate stream to the very high
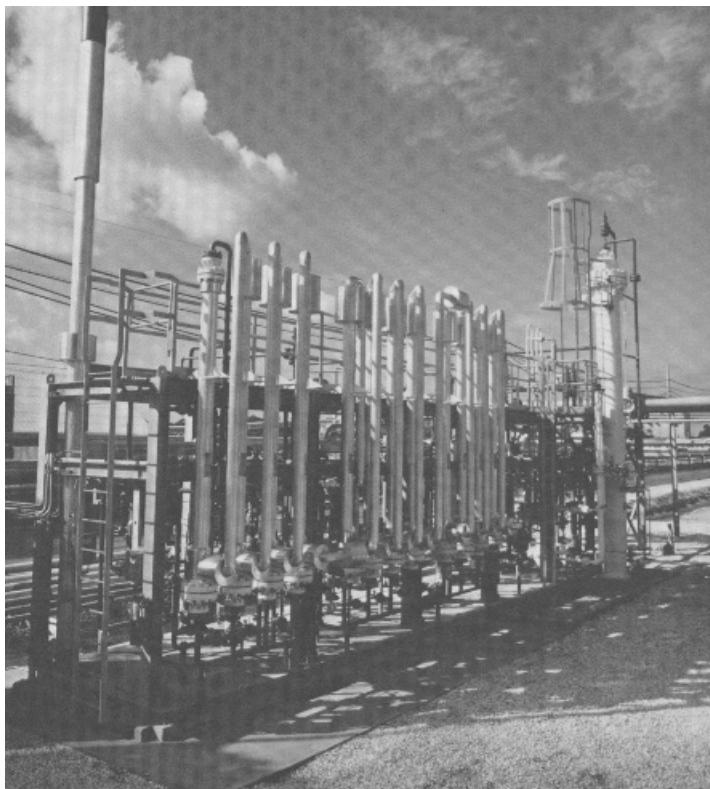

Figure 8.22 Photograph of an Air Products and Chemicals, Inc. PRISM® membrane system installed at an ammonia plant. The modules are mounted vertically

pressures of ammonia reactors. In the first step, the feed gas is maintained at the reactor pressure of 135 atm, and the permeate is maintained at 70 atm, giving a pressure ratio of 1.9. The hydrogen concentration in the feed to this first step is about 45 %, high enough that even at this low pressure ratio the permeate contains about 90 % hydrogen. However, by the time the feed gas hydrogen concentration has fallen to 30 %, the hydrogen concentration in the permeate is no longer high enough for recycle to the reactor. This remaining hydrogen is recovered in a second membrane step operated at a lower permeate pressure
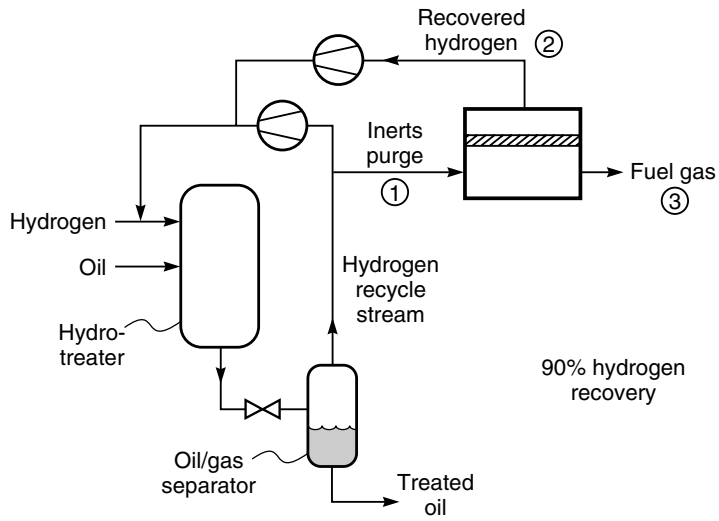
	Stream Composition		
	Untreated Purge ①	Recovered Hydrogen ②	Treated Purge ③
Hydrogen	82	96.5	34.8
Methane	12	2.6	43.3
Ethane	4.6	0.7	17.1
Propane	1.2	0.2	4.8
Pressure (psig)	1800	450	1450
Flow (MMscfd)	18.9	14.5	4.4

Figure 8.23 Hydrogen recovery from a hydrotreater used to lower the molecular weight of a refinery oil stream. Permea polysulfone membranes (PRISM®) are used [42]

of 28 atm and a pressure ratio of 4.7. The increased pressure ratio increases the hydrogen concentration in the permeate significantly. By dividing the process into two steps operating at different pressure ratios, maximum hydrogen recovery is achieved at minimum recompression costs.

A second major application of hydrogen-selective membranes is recovery of hydrogen from waste gases produced in various refinery operations [7,42,43]. A typical separation—treatment of the high-pressure purge gas from a hydrotreater—is shown in Figure 8.23. The hydrogen separation process is designed to recycle the hydrogen to the hydrotreater. As in the case of the ammonia plant, there is a trade-off between the concentration of hydrogen in the permeate and the permeate pressure and subsequent cost of recompression. In the example shown, a permeate of 96.5 % hydrogen is considered adequate at a pressure ratio of 3.9.

Another example of the use of highly hydrogen-selective membranes in the petrochemical industry is the separation of hydrogen from carbon monoxide/hydrogen mixtures to obtain the correct ratio of components for subsequent synthesis operations.

Oxygen/Nitrogen Separation

By far the largest gas separation process in current use is the production of nitrogen from air. The first membranes used for this process were based on poly(4-methyl-1-pentene) (TPX) and ethyl cellulose. These polymer materials have oxygen/nitrogen selectivities of 4; the economics of the process were marginal. The second-generation materials now used have selectivities of 6–7, providing very favorable economics, especially for small plants producing 5–500 scfm of nitrogen. In this range, membranes are the low-cost process, and most new small nitrogen plants use membrane systems.

Table 8.4 lists the permeabilities and selectivities of some of the materials that are used or have been used for this separation. There is a strong inverse relationship between flux and selectivity. Membranes with selectivities of 6–7 typically have 1 % of the permeability of membranes with selectivities of 2–3. This selectivity/permeability trade-off is very apparent in the plot of selectivity as a function of oxygen permeability shown in Figure 8.24, prepared by Robeson [11]. This plot shows data for a large number of membrane materials reported in the literature. A wide range of selectivity/permeability combinations are provided by different membrane materials; for gas separation applications only the most permeable polymers at a particular selectivity are of interest. The line linking these polymers is called the upper bound, beyond which no better material is currently known. The relative positions of the upper bound in 1991 and in 1980 show the progress that has been made in producing polymers specifically tailored for this separation. Development of better materials is a continuing research topic at the

Table 8.4   Permeabilities and selectivities of polymers of interest in air separation

| Polymer	Oxygen permeability (Barrer)	Nitrogen permeability (Barrer)	Oxygen/ nitrogen selectivity
Poly(1-trimethylsilyl-1-propyne) (PTMSP)	7600	5400	1.4
Teflon AF 2400	1300	760	1.7
Silicone rubber	600	280	2.2
Poly(4-methyl-1-pentene) (TPX)	30	7.1	4.2
Poly(phenylene oxide) (PPO)	16.8	3.8	4.4
Ethyl cellulose	11.2	3.3	3.4
6FDA-DAF (polyimide)	7.9	1.3	6.2
Polysulfone	1.1	0.18	6.2
Polyaramide	3.1	0.46	6.8
Tetrabromo *bis* polycarbonate	1.4	0.18	7.5
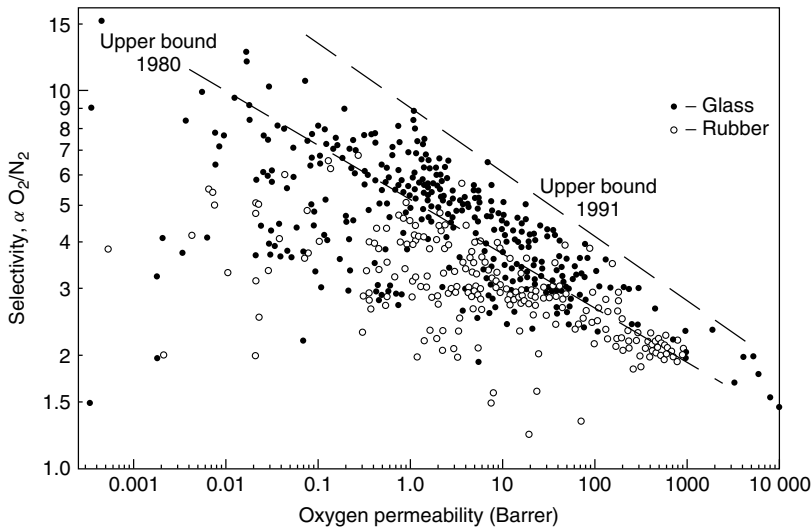
Figure 8.24   Oxygen/nitrogen selectivity as a function of oxygen permeability. This plot by Robeson [11] shows the wide range of combination of selectivity and permeability achieved by current materials. Reprinted from *J. Membr. Sci.* **62**, L.M. Robeson, Correlation of Separation Factor Versus Permeability for Polymeric Membranes, p. 165. Copyright 1991, with permission from Elsevier

major gas separation companies and in some universities, so further but slower movement of the upper bound may be seen in the future.

High oxygen/nitrogen selectivity is required for an economical nitrogen production process. The effect of improved membrane selectivities on the efficiency of nitrogen production from air is illustrated in Figure 8.25. This figure shows the
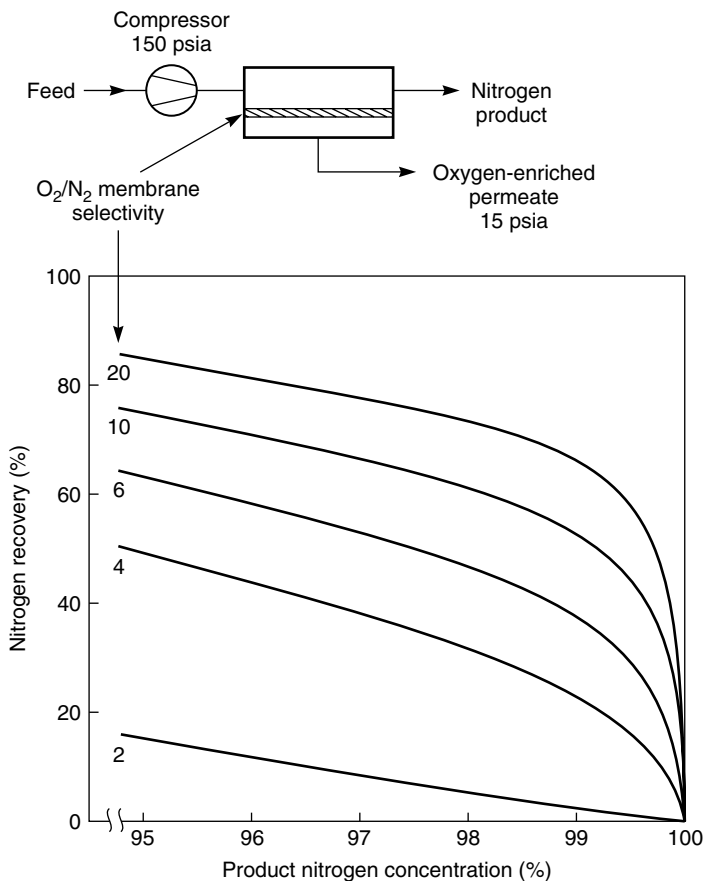
Figure 8.25 Nitrogen recovery as a function of product nitrogen concentration for membranes with selectivities between 2 and 20

trade-off between the fraction of nitrogen in the feed gas recovered as nitrogen product gas as a function of the nitrogen concentration in the product gas. All oxygen-selective membranes, even membranes with an oxygen/nitrogen selectivity as low as 2, can produce better than 99 % nitrogen, albeit at very low recoveries. The figure also shows the significant improvement in efficiency that results from an increase in oxygen/nitrogen selectivity from 2 to 20.

The first nitrogen production systems used membranes made from TPX with a selectivity of about 4. These membranes were incorporated in one-stage designs to produce 95 % nitrogen used to render flammable-liquid storage tanks inert. As the membranes improved, more complex process designs, of the type shown in Figure 8.26, were used to produce purer gas containing >99 % nitrogen. The
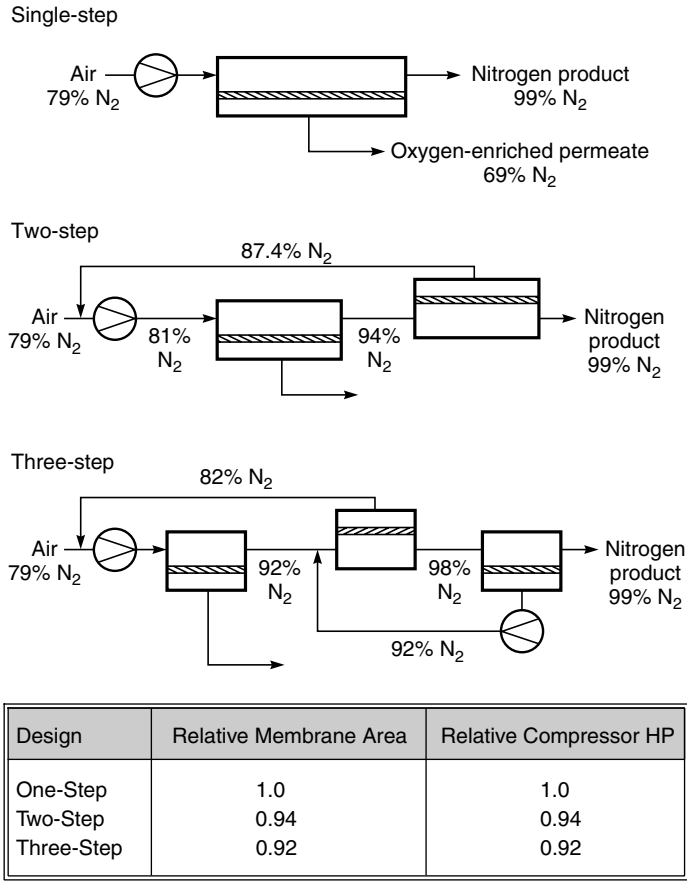
Single-step

Air ———⊙—→ [▓▓▓▓▓▓▓▓] ———→ Nitrogen product
79% N$_2$ 99% N$_2$
                            └———→ Oxygen-enriched permeate
                                    69% N$_2$

Two-step

                    87.4% N$_2$
          ┌————————————————————┐
Air ——⊙——→   [▓▓▓▓▓▓] →   [▓▓▓▓▓▓] ——→ Nitrogen
79% N$_2$ 81%   94%   product
          N$_2$ └———→   N$_2$ 99% N$_2$

Three-step

                82% N$_2$
          ┌————————————————┐
Air ——⊙——→ [▓▓▓▓]   [▓▓▓▓]   [▓▓▓▓] ——→ Nitrogen
79% N$_2$ 92% ↑   98%   product
                N$_2$ N$_2$ ⊙   99% N$_2$
              └———→   92% N$_2$

Design	Relative Membrane Area	Relative Compressor HP
One-Step	1.0	1.0
Two-Step	0.94	0.94
Three-Step	0.92	0.92

Figure 8.26 Single-, two- and three-step designs for nitrogen production from air

first improvement was the two-step process. As oxygen is removed from the air passing through the membrane modules, the concentration in the permeating gas falls. At some point the oxygen concentration in the permeate gas is less than the concentration in normal ambient feed air. Mixing this oxygen-depleted gas permeate with the incoming air then becomes worthwhile. The improvement will be most marked when the system is used to produce high-quality nitrogen containing less than 1 % oxygen. In the example shown in Figure 8.26, the second-step permeate gas contains 12.5 % oxygen, and recycling this gas to the incoming feed air reduces the membrane area and compressor load by about 6 %. This relatively small saving is worthwhile because it is achieved at essentially no cost by making a simple piping change to the system. In the two-step design, the 12.5 % oxygen permeate recycle stream is mixed with ambient air containing 21 % oxygen. A

more efficient design would be to combine the recycle and feed gas where the feed gas has approximately the same concentration. This is the objective of the three-step process shown in Figure 8.26. This design saves a further 2 % in membrane area and some compressor power, but now two compressors are needed. Three-step processes are, therefore, generally limited to large systems in which the energy and membrane area savings compensate for the extra complexity and higher maintenance cost of a second compressor. A discussion of factors affecting the design of nitrogen plants is given by Prasad *et al.* [44,45].

Membrane nitrogen production systems are now very competitive with alternative technologies. The competitive range of the various methods of obtaining nitrogen is shown in Figure 8.27. Very small nitrogen users generally purchase gas cylinders or delivered liquid nitrogen, but once consumption exceeds 5000 scfd of nitrogen, membranes become the low-cost process. This is particularly true if the required nitrogen purity is between 95 % and 99 % nitrogen. Membrane systems can still be used if high quality nitrogen (up to 99.9 %) is required, but the cost of the system increases significantly. Very large nitrogen users—above 10 MMscfd of gas—generally use pipeline gas or on-site cryogenic systems. Pressure swing adsorption (PSA) systems are also sometimes used in the 1–10 MMscfd range.

A membrane process to separate nitrogen from air inevitably produces oxygen-enriched air as a by-product. Sometimes this by-product gas, containing about 35 % oxygen, can be used beneficially, but usually it is vented. A market for oxygen or oxygen-enriched air exists, but because oxygen is produced as the permeate gas stream it is much more difficult to produce high-purity oxygen than
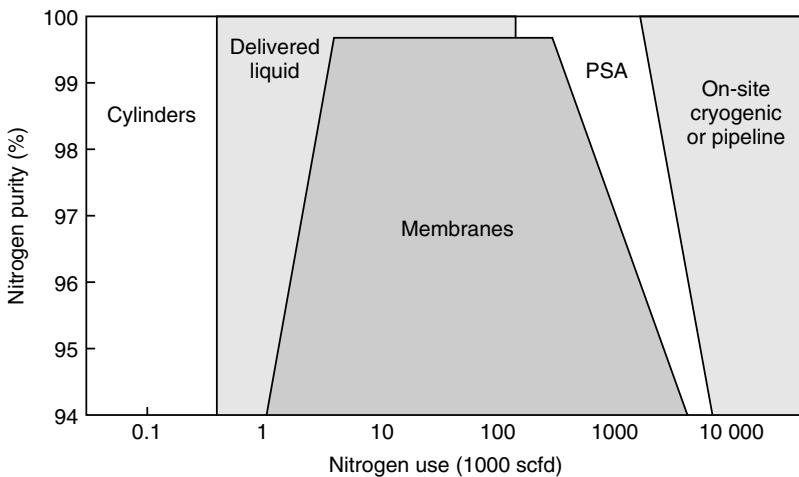

Figure 8.27 Approximate competitive range of current membrane nitrogen production systems. Many site-specific factors can affect the actual system selection
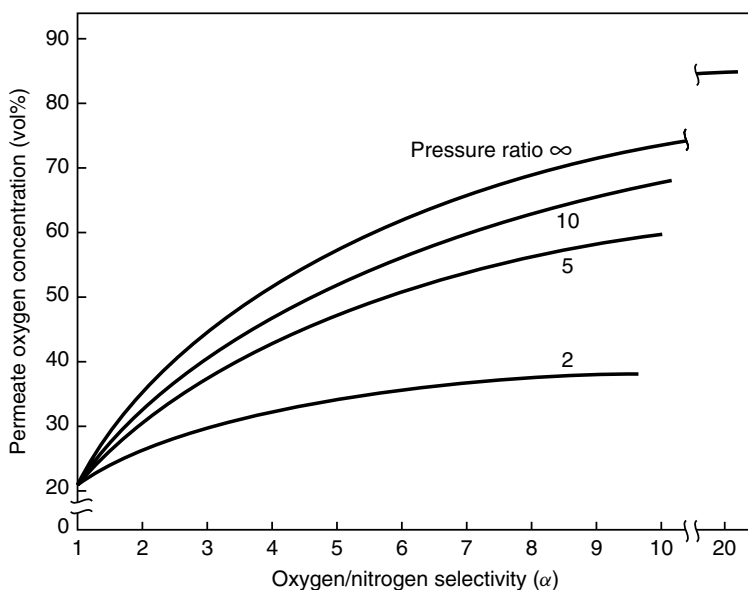
Figure 8.28   The maximum possible oxygen concentration in the permeate from a one-step membrane process with membranes of various selectivities (assumes zero stage-cut). Even the best current membrane materials, with a selectivity of 8, only produce 68 % oxygen in the permeate at an infinite pressure ratio

high-purity nitrogen with membrane systems. Figure 8.28 shows the maximum permeate oxygen concentration that can be produced by a one-step membrane process using membranes of various selectivities. Even at zero stage-cut and an infinite pressure ratio, the best currently available membrane, with an oxygen/nitrogen selectivity of 8, can only produce 68 % oxygen. At useful stage-cuts and achievable pressure ratios this concentration falls. These constraints limit membrane systems to the production of oxygen-enriched air in the 30–50 % oxygen range.

Oxygen-enriched air is used in the chemical industry, in refineries, and in various fermentation and biological digestion processes, but it must be produced very cheaply for these applications. The competitive technology is pure oxygen produced cryogenically then diluted with atmospheric air. The quantity of pure oxygen that must be blended with air to produce the desired oxygen enrichment determines the cost. This means that in membrane systems producing oxygen-enriched air, only the fraction of the oxygen above 21 % can be counted as a credit. This fraction is called the equivalent pure oxygen (EPO_2) basis.

A comparison of the cost of oxygen-enriched air produced by membranes and by cryogenic separation shows that current membranes are generally uncompetitive. The only exception is for very small users in isolated locations, where the

logistics of transporting liquid oxygen to the site increase the oxygen cost to US$80–100/ton.

   Development of better membranes for producing oxygen-enriched air has been, and continues to be, an area of research because of the potential application of the gas in combustion processes. When methane, oil, and other fuels are burned with air, a large amount of nitrogen passes as an inert diluent through the burners and is discarded as hot exhaust gas. If oxygen-enriched air were used, the energy lost with the hot exhaust gas would decrease considerably. Use of oxygen-enriched air also improves the efficiency of diesel engines [46]. The useful energy that can be extracted from the same amount of fuel increases significantly even if air is enriched only from 25 to 35 % oxygen. But to make this process worthwhile, the fuel savings achieved must offset the cost of the oxygen-enriched air used. Calculations show that the process would be cost-effective for some applications at an EPO_2 cost as high as US$60/ton and, for many applications, at an EPO_2 cost of US$30–40/ton. Bhide and Stern [47] have published an interesting
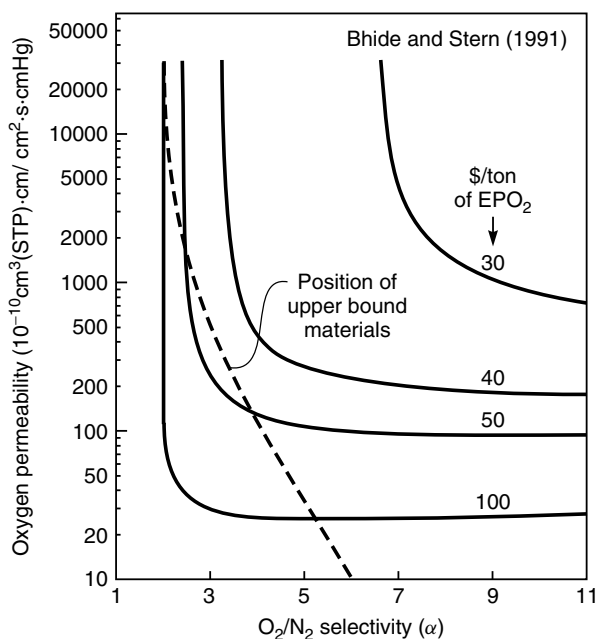

Figure 8.29 Cost of oxygen-enriched air produced by membrane separation on an EPO_2 basis as a function of the oxygen permeability and oxygen/nitrogen selectivity of the membrane. The performance of today's best membranes is represented by the upper bound performance line from Robeson's plot (Figure 8.24) [35,47]. Reprinted from *J. Membr. Sci.* **62**, B.O. Bhide and S.A. Stern, A New Evaluation of Membrane Processes for the Oxygen-enrichment of Air, p. 87. Copyright 1991, with permission from Elsevier

analysis of this problem, the results of which are shown in Figure 8.29. The figure shows the cost of oxygen-enriched air produced by a membrane process for membranes of various permeabilities and selectivities. The assumptions were optimistic–low-cost membrane modules (US$54/m^2) and membranes with extremely thin selective separating layers (1000 Å). Also shown in Figure 8.29 is the portion of the upper-bound curve obtained from the permeability/selectivity trade-off plot shown in Figure 8.24. As the figure shows, a number of materials at the upper-bound limit, with oxygen/nitrogen selectivities of 3–4 and permeabilities of 50–500, are within striking distance of the US$30–40/ton target. Production of these very high-performance membrane modules is at the outer limit of current technology but improvements in the technology could open up new, very large applications of membranes in the future.

Natural Gas Separations

US production of natural gas is about 20 trillion scf/year; total worldwide production is about 40 trillion scf/year. All of this gas requires some treatment, and approximately 20 % of the gas requires extensive treatment before it can be delivered to the pipeline. As a result, several billion dollars' worth of natural gas separation equipment is installed annually worldwide. The current membrane market share is about 2 %, essentially all for carbon dioxide removal. However, this fraction is expected to increase because applications of membranes to other separations in the natural gas processing industry are under development [48].

Raw natural gas varies substantially in composition from source to source. Methane is always the major component, typically 75–90 % of the total. Natural gas also contains significant amounts of ethane, some propane and butane, and 1–3 % of other higher hydrocarbons. In addition, the gas contains undesirable impurities: water, carbon dioxide, nitrogen and hydrogen sulfide. Although raw natural gas has a wide range of compositions, the composition of gas delivered to the pipeline is tightly controlled. Typical US natural gas specifications are shown in Table 8.5. The opportunity for membranes lies in the processing of gas to meet these specifications.

Table 8.5 Composition of natural gas required for delivery to the US national pipeline grid

Component	Specification
CO_2	<2 %
H_2O	<120 ppm
H_2S	<4 ppm
C_{3+}	950–1050 Btu/scf
Content	Dew point, −20 °C
Total inerts (N_2, CO_2, He, etc.)	<4 %

Natural gas is usually produced from the well and transported to the gas processing plant at high pressure, in the range 500–1500 psi. To minimize recompression costs, the membrane process must remove impurities from the gas into the permeate stream, leaving the methane, ethane, and other hydrocarbons in the high-pressure residue gas. This requirement determines the type of membranes that can be used for this separation. Figure 8.30 is a graphical representation of the factors of molecular size and condensability that affect selection of membranes for natural gas separations.

As Figure 8.30 shows, water is small and condensable; therefore, it is easily separated from methane by both rubbery and glassy polymer membranes. Both rubbery and glassy membranes can also separate carbon dioxide and hydrogen sulfide from natural gas. However, in practice carbon dioxide is best separated by glassy membranes (utilizing size selectivity) [49,50], whereas hydrogen sulfide, which is larger and more condensable than carbon dioxide, is best separated by rubbery membranes (utilizing sorption selectivity) [51,52]. Nitrogen can be separated from methane by glassy membranes, but the difference in size is small, so the separations achieved are small. Finally, propane and other hydrocarbons, because of their condensability, are best separated from methane with rubbery sorption-selective membranes. Table 8.6 shows typical membrane materials and the selectivities that can be obtained with good-quality membranes.
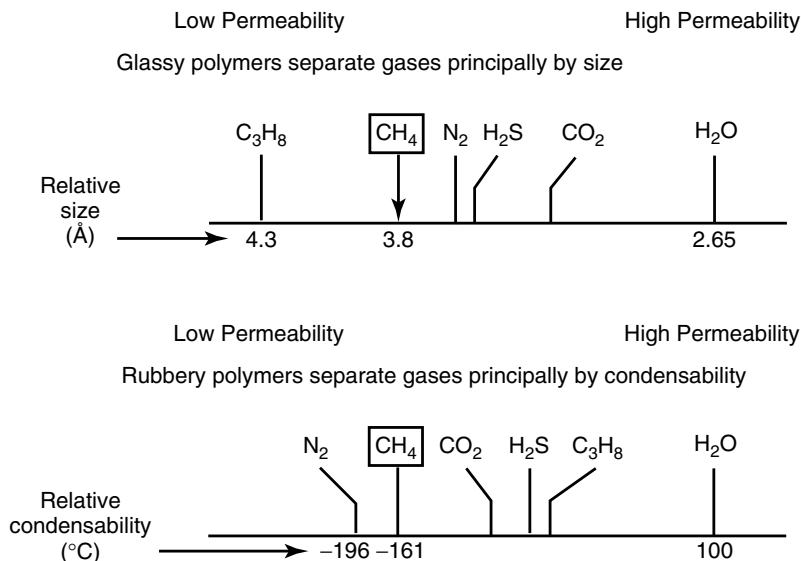

Figure 8.30   The relative size and condensability (boiling point) of the principal components of natural gas. Glassy membranes generally separate by differences in size; rubbery membranes separate by differences in condensability

Table 8.6 Membrane materials and selectivities for separation of impurities from natural gas

Component to be permeated	Category of preferred polymer material	Typical polymer used	Typical selectivity over methane
CO_2	Glass	Cellulose acetate, polyimide	10–20
H_2S	Rubber	Ether-amide block copolymer	20–40
N_2	Glass	Polyimide, perfluoro polymers	2–3
H_2O	Rubber or glass	Many	>200
Butane	Rubber	Silicone rubber	7–10

Carbon Dioxide Separation

Removal of carbon dioxide is the only membrane-based natural gas separation process currently practiced on a large scale—more than 200 plants have been installed, some very large. Most were installed by Grace (now Kvaerner-GMS), Separex (UOP) and Cynara and all use cellulose acetate membranes in hollow fiber or spiral-wound module form. More recently, hollow fiber polyaramide (Medal) membranes have been introduced because of their higher selectivity.

The designs of two typical carbon dioxide removal plants are illustrated in Figure 8.31. One-stage plants, which are simple, contain no rotating equipment, and require minimal maintenance, are preferred for small gas flows. In such plants methane loss to the permeate is often 10–15 %. If there is no fuel use for this gas, it must be flared, which represents a significant revenue loss. Nonetheless, for gas wells producing 1–2 MMscfd, one-stage membrane units with their low capital and operating costs may still be the optimum treatment method.

As the natural gas stream increases in size, the methane loss from a one-stage system becomes prohibitive. Often the permeate gas is recompressed and passed through a second membrane stage. This second stage reduces the methane loss to a few percent. However, the recompression cost is considerable, and the membrane system may no longer compete with amine absorption, the alternative technology. In general, membrane systems have proved to be most competitive for gas streams below 30 MMscfd containing high concentrations of carbon dioxide. Spillman [48] and McKee *et al*. [53] have reviewed the competitive position of membrane systems for this application. Currently the market for membrane carbon dioxide gas separation systems can be summarized as follows:

1. Very small systems (less than 5 MMscfd). At this flow rate, membrane units are very attractive. Often the permeate is flared or used as fuel, so the system is a simple bank of membrane modules.

2. Small systems (5–30 MMscfd). Two-stage membrane systems are used to reduce methane loss. In this gas flow range, amine and membrane systems
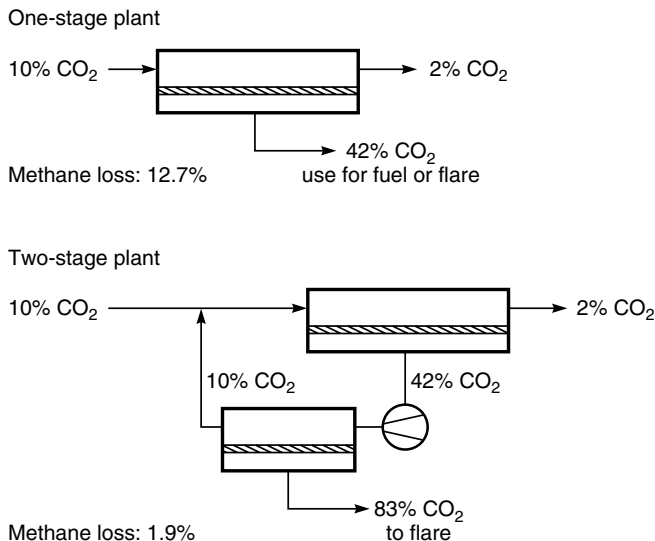
Figure 8.31 Flow scheme of one-stage and two-stage membrane separation plants to remove carbon dioxide from natural gas. Because the one-stage design has no moving parts, it is very competitive with other technologies especially if there is a use for the low-pressure permeate gas. Two-stage processes are more expensive because a large compressor is required to compress the permeate gas. However, the loss of methane with the fuel gas is much reduced

    compete; the choice between the two technologies depends on site-specific factors.

3. Medium to large systems (greater than 30 MMscfd). In general, membrane systems are too expensive to compete head-to-head with amine plants. However, a number of large membrane systems have been installed on offshore platforms, at carbon dioxide flood operations, or where site-specific factors particularly favor membrane technology. As membranes improve, their market share is increasing.

    In principle, the combination of membranes for bulk removal of the carbon dioxide with amine units as polishing systems offers a low-cost alternative to all-amine plants for many streams. However, this approach has not been generally used because the savings in capital cost are largely offset by the increased complexity of the plant, which now contains two separation processes. The one exception has been in carbon dioxide flood enhanced oil-recovery projects [49,54], in which carbon dioxide is injected into an oil formation to lower the viscosity of the oil. Water, oil and gas are removed from the formation; the carbon dioxide is separated from the gas produced and reinjected. In these projects,
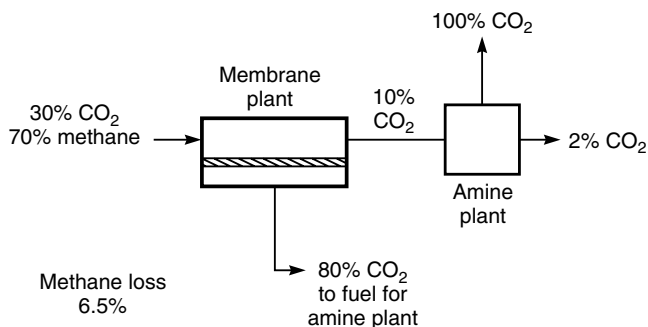
Figure 8.32   A typical membrane/amine plant for the treatment of associated natural gas produced in carbon dioxide/enhanced oil projects. The membrane permeate gas is often used as a fuel for the amine absorption plant

the composition and volume of the gas changes significantly over the lifetime of the project. The modular nature of membrane units allows easy retrofitting to an existing amine plant, allowing the performance of the plant to be adjusted to meet the changing separation needs. Also, the capital cost of the separation system can be spread more evenly over the project lifetime. An example of a membrane/amine plant design is shown in Figure 8.32. In this design, the membrane unit removes two-thirds of the carbon dioxide, and the amine plant removes the remainder. The combined plant is usually significantly less expensive than an all-amine or all-membrane plant.

Dehydration

All natural gas must be dried before entering the national distribution pipeline to control corrosion of the pipeline and to prevent formation of solid hydrocarbon/water hydrates that can choke valves. Currently glycol dehydrators are widely used; approximately 50 000 units are in service in the United States. However, glycol dehydrators are not well suited for use on small gas streams or on offshore platforms, increasingly common sources of natural gas. In addition, these units coextract benzene, a known carcinogen and trace contaminant in natural gas, and release the benzene to the atmosphere. The Environmental Protection Agency (EPA) has announced its intention to require benzene emission control systems to be fitted to large glycol units.

   Membrane processes offer an alternative approach to natural gas dehydration and are being developed by a number of companies. Membranes with intrinsic selectivities for water from methane of more than 500 are easily obtained, but because of concentration polarization effects, actual selectivities are typically about 200. Two possible process designs are shown in Figure 8.33. In the first
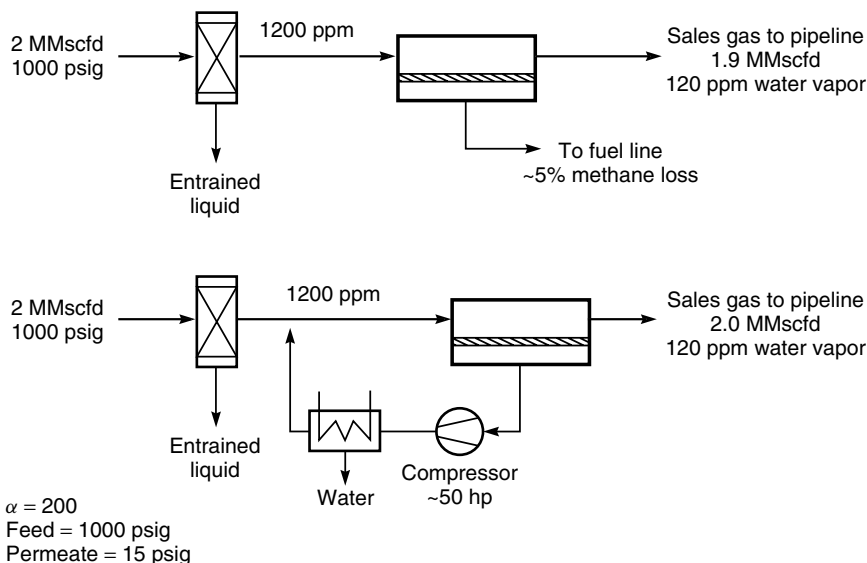
Figure 8.33 Dehydration of natural gas is easily performed by membranes but high cost may limit its scope to niche applications

design, a small one-stage system removes 90 % of the water in the feed gas, producing a low-pressure permeate gas representing 5–6 % of the initial gas flow. This gas contains the removed water. If the gas can be used as low-pressure fuel at the site, this design is economical and competitive with glycol dehydration. In the second design, the wet, low-pressure permeate gas is recompressed and cooled, so the water vapor condenses and is removed as liquid water. The natural gas that permeates the membrane is then recovered. However, if the permeate gas must be recompressed, as in the second design, the capital cost of the system approximately doubles, and membranes are then only competitive in special situations where glycol dehydration is not possible.

Dew Point Adjustment, C₃₊ Recovery

Dew Point Adjustment, C_{3+} Recovery

Natural gas usually contains varying amounts of ethane, propane, butane, and higher hydrocarbons. The gas is often close to its saturation point with respect to some of these hydrocarbons, which means liquids will condense from the gas at cold spots in the pipeline transmission system. To avoid the problems caused by condensation of liquids, the dew point of US natural gas is lowered to about $-20\,^\circ$C before delivery to the pipeline by removing portions of the propane and butane and higher hydrocarbons. For safety reasons the Btu rating of the pipeline gas is also usually controlled within a narrow range, typically

950–1050 Btu per cubic foot. Because the Btu values of ethane, propane and pentane are higher than that of methane, natural gas that contains significant amounts of these hydrocarbons may have an excessive Btu value, requiring their removal. Of equal importance, these higher hydrocarbons are generally more valuable as recovered liquids than their fuel value in the gas. For all of these reasons almost all natural gas is treated to control the C_{3+} hydrocarbon content.

The current technology used to separate the higher hydrocarbons from natural gas streams is condensation, shown schematically in Figure 8.34. The natural gas stream is cooled by refrigeration or expansion to between $-20\,°C$ and $-40\,°C$. The condensed liquids, which include the higher hydrocarbons and water, are separated from the gas streams and subjected to fractional distillation to recover the individual components. Because refrigeration is capital-intensive and uses large amounts of energy, there is considerable interest in alternative techniques, such as membrane gas separation.

A typical flow diagram of a membrane system for C_{3+} liquids recovery is also shown in Figure 8.34. The natural gas is fed to modules containing a higher-hydrocarbon-selective membrane, which removes the higher hydrocarbons as the permeate stream. This stream is recompressed and cooled by a cold-water exchanger to condense higher hydrocarbons. The non-condensed bleed

Current technology
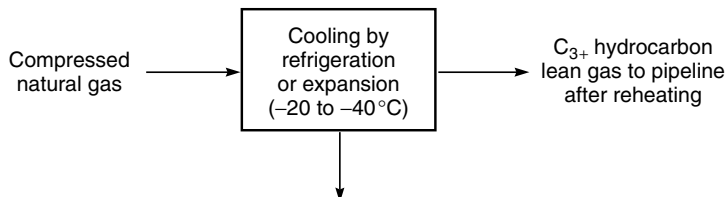
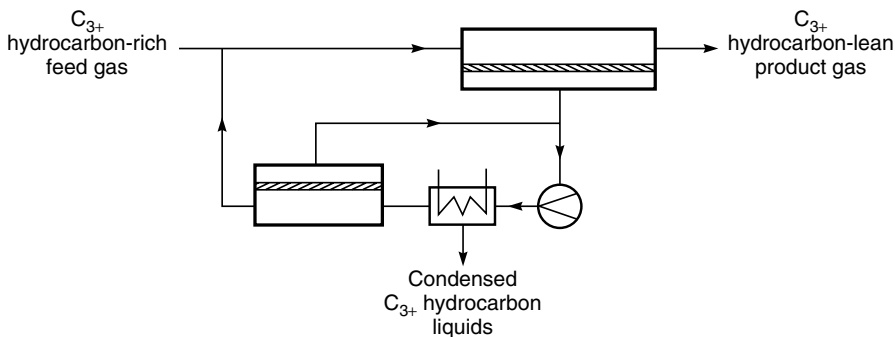Membrane system using C_{3+} hydrocarbon-selective membranes

Figure 8.34 Recovery of C_{3+} hydrocarbons from natural gas

stream from the condenser to the inlet will normally still contain more heavy hydrocarbons than the raw gas, so prior to returning the gas to the feed stream, the condenser bleed stream is passed through a second set of membrane modules. The permeate streams from the two sets of modules are combined, creating a recirculation loop around the condenser, which continuously concentrates the higher hydrocarbons [37].

The competitiveness of membrane systems in this application is very sensitive to the selectivity of the membranes for propane, butane and higher hydrocarbons over methane. If the membranes are very selective (propane/methane selectivity of 5–7, butane/methane selectivity of 10–15), the permeate stream from the main set of modules will be small and concentrated, minimizing the cost of the recompressor. Currently, silicone rubber membranes are being considered for this application, but other, more selective materials have been reported [55].
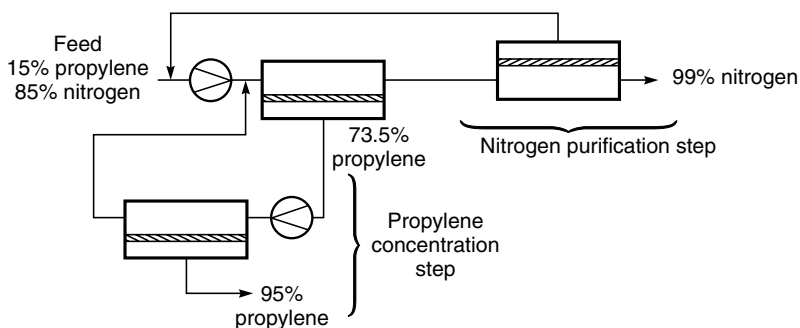
Vapor/Gas Separations

In the separation of vapor/gas mixtures, rubbery polymers, such as silicone rubber, can be used to permeate the more condensable vapor, or glassy polymers can be used to permeate the smaller gas. Although glassy, gas-permeable membranes have been proposed for a few applications, most installed plants use vapor-permeable membranes, often in conjunction with a second process such as condensation [36,38] or absorption [56]. The first plants, installed in the early 1990s, were used to recover vapors from gasoline terminal vent gases or chlorofluorocarbon (CFC) vapors from the vents of industrial refrigeration plants. More recently, membranes have begun to be used to recover hydrocarbons and processing solvents from petrochemical plant purge gas. Some of these streams are quite large and discharge vapors with a recovery value of US$1–2 million/year.

One of the most successful petrochemical applications is treatment of resin degassing vent gas in polyolefin plants [57,58]. Olefin monomer, catalyst, solvents, and other co-reactants are fed at high pressure into the polymerization reactor. The polymer product (resin) is removed from the reactor and separated from excess monomer in a flash separation step. The recovered monomer is recycled to the reactor. Residual monomer is removed from the resin by stripping with nitrogen. The composition of this degassing vent stream varies greatly, but it usually contains 20–50 % of mixed hydrocarbon monomers in nitrogen. The monomer content represents about 1 % of the hydrocarbon feedstock entering the plant. This amount might seem small, but because polyolefin plants are large operations, the recovery value of the stream can be significant.

Several membrane designs can be used; two are shown in Figure 8.35 [59]. The two-step, two-stage system shown in Figure 8.35(a) achieves the target separation by linking several membrane units together, each unit performing a partial separation. The first unit removes a portion of the propylene from the feed gas to produce a concentrated permeate. The residue gas from this step is then sent to a

(a) Multi-stage membrane separation system design

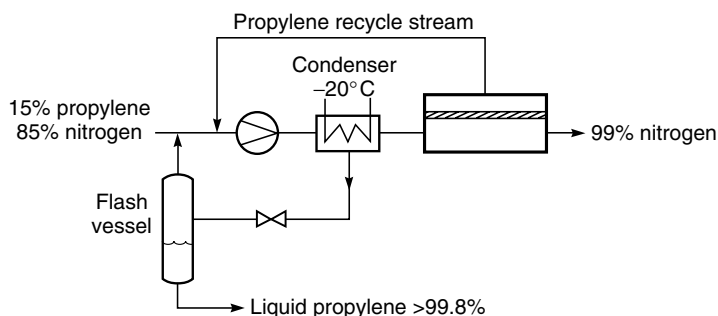

(b) Hybrid compression-condenser-membrane Design

Figure 8.35   Vapor separation process designs able to achieve high vapor recovery and high-purity product streams

second membrane unit which produces a nitrogen gas stream containing less than 1 % propylene. The permeate from this second step is only partially enriched in propylene, so it is mixed with the incoming feed gas.

To increase the propylene concentration in the permeate gas from the first step, a second-stage membrane unit is used. The permeate gas from the first stage is compressed and then passed through the second stage to produce a final permeate stream containing 95 % propylene. The partially depleted second stage residue stream is recycled back to the feed. By linking together the three membrane separation units, the target recovery for both propylene and nitrogen can be achieved.

A number of multistep vapor separation systems of the type shown in Figure 8.35(a) have been installed. These systems have the advantage of operating at ambient temperatures and having as the main rotating equipment gas compressors with which petrochemical plant operators are very familiar.

However, if very good removal of the nitrogen from the recycle gas is required, the hybrid process combining condensation and membrane separation shown in Figure 8.35(b) is preferred. In this design, the compressed feed gas is sent to a condenser. On cooling the feed gas, a portion of the propylene content is removed as a condensed liquid. The remaining, uncondensed propylene is removed by the membrane separation system to produce a 99 % nitrogen stream. The permeate gas is recycled to the incoming feed gas from the purge bin.

Because the gas sent to the membrane stage is cooled, the solubility of propylene in the membrane is enhanced, and the selectivity of the membrane unit is increased. The propylene condensate contains some dissolved nitrogen so the liquid is flashed at low pressure to remove this gas, producing a better than 99.5 % pure hydrocarbon product. A photograph of a propylene/nitrogen vent gas treatment system is shown in Figure 8.36.

Vapor/Vapor Separations

A final group of separations likely to develop into a major application area for membranes is vapor/vapor separations, such as ethylene (bp $-103.9\,^{\circ}$C) from

Figure 8.36 Photograph of a membrane unit used to recover nitrogen and propylene from a polypropylene plant vent gas

ethane (bp $-88.9\,^{\circ}$C), propylene (bp $-47.2\,^{\circ}$C) from propane (bp $-42.8\,^{\circ}$C), and *n*-butane (bp $-0.6\,^{\circ}$C) from isobutane (bp $-10\,^{\circ}$C). These close-boiling mixtures are separated on a very large scale in the synthesis of ethylene and propylene, the two largest-volume organic chemical feedstocks, and in the synthesis of isobutane in refineries to produce high-octane gasoline. Because the mixtures are close-boiling, large towers and high reflux ratios are required to achieve good separations.

If membranes are to be used for these separations, highly selective materials must be developed. Several groups have measured the selectivities of polymeric membranes for ethylene/ethane and propylene/propane mixtures. Burns and Koros have reviewed these results [60]. The data should be treated with caution. Some authors report selectivities based on the ratio of the permeabilities of the pure gases; others use a hard vacuum or a sweep gas on the permeate side of the membrane. Both procedures produce unrealistically high selectivities. In an industrial plant, the feed gas will be at 100–150 psig and a temperature sufficient to maintain the gas in the vapor phase; the permeate gas will be at a pressure of 10–20 psig. Under these operating conditions, plasticization and loss of selectivity occur with even the most rigid polymer membranes, so selectivities are usually low. Because of these problems, this application might be one for which the benefits of ceramic or carbon fiber membranes can justify their high cost. Caro *et al.* have recently reviewed the ceramic membrane literature [24].

Dehydration of Air

The final application of gas separation membranes is dehydration of compressed air. The competitive processes are condensation or solid desiccants, both of which are established, low-cost technologies. Membranes with water/air selectivities of more than 500 are known, although actual selectivities obtained in membrane modules are less because of concentration polarization effects. Nonetheless, existing membranes are more than adequate for this separation. The problem inhibiting their application is the loss of compressed feed air through the membrane. Compressed air is typically supplied at about 7 atm (105 psi), so the pressure ratio across the membrane is about 7. Because air dehydration membranes have a selectivity of more than 200, these membranes are completely pressure-ratio-limited. Based on Equation (8.10), this means that the permeate gas cannot be more than seven times more concentrated than the feed. The result is that a significant fraction of the feed gas must permeate the membrane to carry away the permeate water vapor. Typically 15–20 % of the pressurized feed gas permeates the membrane, which affects the productivity of the compressor significantly. Counterflow-sweep designs of the type discussed in Chapter 4 are widely used to reduce permeant loss. For this reason, membrane air dehydration systems have not found a wide market except where the reliability and simplicity of the membrane design compared to adsorbents or cooling are particularly attractive.

Conclusions and Future Directions

The application of membranes to gas separation problems has grown rapidly since the installation of the first industrial plants in the early 1980s. The current status of membrane gas separation processes is summarized in Table 8.7, in which the processes are divided into four groups. The first group consists of the established processes: nitrogen production from air, hydrogen recovery and air drying. These processes represent more than 80 % of the current gas separation membrane market. All have been used on a large commercial scale for 10 years, and dramatic improvements in membrane selectivity, flux and process designs have been made during that time. For example, today's hollow fine fiber nitrogen production module generates more than 10 times the amount of nitrogen, with better quality and at a lower energy consumption, than the modules produced in the early 1980s. However, the technology has now reached a point at which, barring a completely unexpected breakthrough, further changes in productivity are likely to be the result of a number of small incremental changes.

Developing processes are the second group of applications. These include carbon dioxide separation from natural gas, organic vapor separation from air and nitrogen, and recovery of light hydrocarbons from refinery and petrochemical plant purge gases. All of these processes are performed on a commercial scale, and in total several hundred plants have been installed. Significant expansion in these applications, driven by the development of better membranes and process designs, is occurring. For example, carbon dioxide removal from natural gas has been practiced using cellulose acetate membranes for more than 15 years. Introduction of more selective and higher-flux membranes has begun and, in time, is likely to make membrane processes much more competitive with amine absorption. The application of silicone rubber vapor separation membranes in petrochemical and refinery applications is currently growing.

The 'to be developed' membrane processes represent the future expansion of gas separation technology. Natural gas treatment processes, including dehydration, natural gas liquids (C_{3+} hydrocarbons) recovery, and hydrogen sulfide removal, are currently being studied at the field testing and early commercial stage by several companies. The market is very large, but the fraction that membranes will ultimately capture is unknown. The production of oxygen-enriched air is another large potential application for membranes. The market size depends completely on the properties of the membranes that can be produced. Improvements of a factor of two in flux at current oxygen/nitrogen selectivities would probably produce a limited membrane market; improvements by a factor of five to ten would make the use of oxygen-enriched air in natural gas combustion processes attractive. In this case the market could be very large indeed. The final application listed in Table 8.7 is the separation of organic vapor mixtures using membranes in competition, or perhaps in combination, with distillation.

Table 8.7   Status of membrane gas separation processes

Process	Application	Comments
Established processes		
Oxygen/nitrogen	Nitrogen from air	Processes are all well developed. Only incremental improvements in performance expected
Hydrogen/methane; hydrogen/nitrogen; hydrogen/carbon monoxide	Hydrogen recovery; ammonia plants and refineries	
Water/air	Drying compressed air	
Developing processes		
VOC/air	Air pollution control applications	Several applications being developed. Significant growth expected as the process becomes accepted
Light hydrocarbons from nitrogen or hydrogen	Reactor purge gas, petrochemical process streams, refinery waste gas	Application is expanding rapidly
Carbon dioxide/methane	Carbon dioxide from natural gas	Many plants installed but better membranes are required to change market economics significantly
To-be-developed processes		
C_{3+} hydrocarbons/methane	NGL recovery from natural gas	Field trials and demonstration system tests under way. Potential market is large
Hydrogen sulfide, water/methane	Natural gas treatment	Niche applications, difficult for membranes to compete with existing technology
Oxygen/nitrogen	Oxygen enriched air	Requires better membranes to become commercial. Size of ultimate market will depend on properties of membranes developed. Could be very large
Organic vapor mixtures	Separation of organic mixtures in refineries and petrochemical plants	Requires better membranes and modules. Potential size of application is large

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