
The Separation of Gases by Membranes

A. Keith Fritzsche and James E. Kurz

INTRODUCTION

The study of gas transport in membranes has been actively pursued for over 100 years. This extensive research resulted in the development of good theories on single gas transport in polymers and other membranes. The practical use of membranes to separate gas mixtures is, however, much more recent. One well-known application has been the separation of uranium isotopes for nuclear weapon production. With few exceptions, no new, large scale applications were introduced until the late 1970's when polymer membranes were developed of sufficient permeability and selectivity to enable their economical industrial use. Since this development is so recent, gas separations by membranes are still less well-known and their use less widespread than other membrane applications such as reverse osmosis, ultrafiltration and microfiltration. In excellent reviews on gas transport in polymers as recent as 1983, no mention was made of the important developments of the last few years. For this reason, this chapter will concentrate on the more recent aspects of gas separation by membranes. Naturally, many of the examples cited will be from our own experience, but the general underlying principles are applicable to many membrane based gas separating systems.

A Short History

Membranes for the separation of gas mixtures are of two very different kinds: one a microporous membrane, the other nonporous. Microporous membranes were the first to be studied and the basic law governing their selectivity was discovered by Graham.¹ When pore size of a microporous membrane is small compared to the mean-free-path of the gas molecules, permeate will be enriched in the gas of the lower molecular weight. Since molecular weight ratios of most gases are not very large and since the selectivity is proportional to the square

root of this ratio, not only practical but theoretical enrichments achievable by this method necessarily will be small. In order to have an efficient separation of a gas mixture, many separation stages are required. On the other hand, since this method of separation is based strictly on mass ratios and not chemical differences, it is the only membrane based method capable of separating isotopes of a given compound. This is the reason it was chosen as a method to enrich uranium in the fissionable isotope of mass 235 in the development of the atomic bomb in World War II. This separation method inherently is very expensive—it requires a large amount of hardware for a given amount of processed gas, the membrane specifications are stringent (high porosity, small pore size), and the energy requirements are high. The large scale utilization of such a process has been feasible only because economic considerations are not of prime importance in this application.

The other membrane-based gas separation method utilizes non-porous membranes. In permeating through the membrane, the gases are separated due to differences in their diffusivity and solubility in the membrane matrix (normally an organic polymer). Molecular size will play a role in such separations but so will the chemical nature of the gas. Thus, conceptually very efficient separations should be possible this way. As polymer science developed, many polymers were tested for gas permeabilities and indeed some with very good selectivities were found. For example, many polymers are much more permeable to polar gases (H_2O , CO_2 , H_2S , SO_2) than to nonpolar gases (O_2 , N_2 , CH_4). The gases of smallest molecular size (He , H_2) permeate more readily through polymers than larger molecules (CH_4 , C_2H_6).² Still it took many years to bring this basic knowledge to practical utilization. The major problem was to make membranes that would be both highly selective and allow high transmembrane gas fluxes, otherwise membrane areas required would be so large as to make the technique uneconomical. The same problem had faced desalination membranes. In the latter case, the solution appeared in the form of the Loeb-Sourirajan membrane,³ a membrane with an asymmetric cross-section, the top thin part being the selective layer and the remainder a porous, nonselective mechanical support. Still, utilization of this technology in gas separations was not a trivial matter. Asymmetric cellulose acetate reverse osmosis membranes have to be kept wet at all times. Since most gas streams are essentially dry, ways had to be found to make good dry membranes. When cellulose acetate membranes are allowed to dry, they lose their separating power due to morphological changes caused by the large interfacial forces involved. Various interesting approaches were suggested to make dry membranes: for example, casting very thin films on a liquid surface, and then supporting them on a porous substrate.⁴ Such techniques proved to be too cumbersome to be easily scalable to industrial production. The significant start toward practical, economical gas separating membranes was the development of methods of drying cellulose acetate membranes in a controlled manner. It was found that dry asymmetric membranes are obtained with good permeabilities and good selectivities in many gas separations (e.g., H_2/CH_4 , CO_2/CH_4 , $\text{H}_2\text{O}/\text{CH}_4$) when the wet membranes are either freeze dried⁵ or solvent exchanged.⁶ Some inherent limitations of cellulose acetate membranes are their sensitivity to liquid water and plasticizing gases and their limited temperature and pressure resistance. A second breakthrough came in the form of composite membranes introduced by Monsanto Company.⁷ These membranes are highly

unusual in that unlike classical composites, it is not the top layer but the one below in combination with the top layer that is responsible for the membrane's selectivity. The membrane consists of a polysulfone hollow fiber having a small number of surface imperfections which make it quite non-selective. By coating with a highly permeable, non-selective polymer such as silicone, the flux through the imperfections is diminished sufficiently to make the remainder of the membrane matrix dominant in gas transport. Thus, selectivities approaching those inherent to polysulfone are achieved. Also, permeabilities of the membrane are high due to their small effective thickness which can be controlled in the membrane formation process. This new technology makes it possible to fabricate thin membranes which initially are not perfect as the effect of imperfections essentially is eliminated by the coating. With the exception of some short lived projects,^{8,9} Monsanto now operating as a separate subsidiary, Permea Inc., was the first to commercialize gas separation membranes on a relatively large scale. This apparently was an incentive to move dry cellulose acetate membranes to the marketplace and these are being marketed today by a number of companies including Dow, Separex, Envirogenics, W.R. Grace and others. The cellulose acetate membranes are made as hollow fibers or as flat sheets which are used in spiral wound modules. Other membranes, including immobilized liquid membranes and facilitated transport, were reviewed by Matson, et al¹⁰ in 1983.

Since 1983, newer systems for hydrogen separations have appeared. Ube Industries, Ltd. announced the development of a polyimide resin in hollow fiber membrane form for H_2/C_1 separations.^{11,12} Commercial production of this membrane and the engineering of skid mounted units were to begin in the fall of 1985.¹³

Systems for air separations appeared in this same time period. Asahi Glass Company, Ltd. started the production of a membrane system which is reported to upgrade the oxygen content in air to 40%.¹⁴ The flat sheet membrane is a fluoropolymer based composite mounted in a plate and frame unit. Air is supplied at atmospheric pressure and the permeate enriched in O_2 is recovered under vacuum. Signal's UOP Fluid Systems Division offers a similar system. Their Spiragas® (trademark of Signal Company) membrane for oxygen enrichment, is an ultrathin silicone on a porous polysulfone backing in a spiral wound permeator.^{15,16} Dow Chemical Company more recently announced the sale of the Generon® (trademark of The Dow Chemical Company) air separation system to provide 95% N_2 for blanketing applications.¹⁷ The hollow fiber membrane used in this system is made from a polyolefin. Finally, Monsanto announced the development of a new membrane based on crosslinked polyphenylene oxide¹⁸ which is expected to find initial application in air as well as hydrogen and carbon dioxide separations. More details of these systems will be given later in this chapter.

THEORY OF GAS TRANSPORT IN MEMBRANES

Porous Membranes

The separation of gases by microporous membranes depends on the ratio of pore size to the mean free path which is given by:

$$\lambda = \frac{3\mu}{2P} \left[\frac{\pi RT}{2M} \right]^{\frac{1}{2}} \quad (1)$$

where M = molecular weight
 P = pressure
 μ = viscosity
 R = the universal gas constant
 T = temperature

Gases at 20°C and 1 atmosphere have a mean-free-path of 1000 to 2000 Å. If pore size is large relative to the mean-free-path, flow (mols per unit time and area) will be given by Poiseuille's Law.¹⁹

$$Q = \frac{d^2(p_1^2 - p_2^2)}{64 \ell \mu RT} \quad (2)$$

where p_1 & p_2 = the pressures on the high and low pressure sides of the membrane
 d = pore diameter
 ℓ = pore length

In such flow, energy exchange among molecules will occur within the pore, and no separation is obtained. If, however, pores are substantially smaller than the mean-free-path, Knudsen flow prevails:

$$Q = \frac{4d(p_1 - p_2)}{3\ell(2\pi MRT)^{\frac{1}{2}}} \quad (3)$$

As this flow is molecular weight dependent, separation is expected. Ideal separation occurs when downstream pressure is negligibly small. Thus, for a gas mixture:

$$Q_1 = \frac{kp_1x}{M_1^{\frac{1}{2}}} \quad (4)$$

$$Q_2 = \frac{kp_1(1-x)}{M_2^{\frac{1}{2}}} \quad (5)$$

where k is a combination of all constants in Equation 3 excluding M, and x is the mol fraction of gas 1 in the feed, separation factor is defined as:

$$\alpha = \frac{Q_1/Q_2}{x/(1-x)} \quad \text{and equals} \quad \left[\frac{M_2}{M_1} \right]^{\frac{1}{2}}$$

The ideal separation factor for $U^{235}F_6/U^{238}F_6$ is 1.0043. In real separations, the ideal separation factor will not be attained because of various adverse factors including back-diffusion, non-ideal membranes, concentration polarization at the feed surface and surface flow phenomena. Since the actual selectivities obtainable are so small, it is clear that a very large number of stages will be required for efficient separations. For a membrane cascade with undiffused gas recycled to a previous stage, a minimum number of stages will be obtained at total reflux (no product taken out). It can be shown²⁰ that this number is given by:

$$N = \frac{\ln \left[\frac{y_D / (1 - y_D)}{x_B / (1 - x_B)} \right]}{\ln a} \quad (6)$$

where y & x = the mol fractions of gas 1 in the permeated and non-permeated streams respectively

B = bottom stage

D = top stage

a = stage separation factor given as:

$$a = \frac{y/(1-y)}{x/(1-x)}$$

In actual use, the number of stages obviously will be greater since reflux is not total. Available information indicates that U.S. gas diffusion plants for U^{235} production utilize 10,276 stages. Total membrane area for a given separation is given by²¹:

$$S = \frac{3.914 \Delta U l}{(\alpha - 1)^2 \sigma d} \left(\frac{MRT}{d} \right)^{\frac{1}{2}} \cdot \frac{1}{p_2 (1 - p_r)^3} \quad (7)$$

where σ = membrane porosity

p_r = p_2/p_1

ΔU = separative capacity given by:

$$\Delta U = \frac{1}{2} L (\alpha - 1)^2 = 0.48L (1 - p_r)^2 (\alpha - 1)^2 \quad (8)$$

where L = total molar flow rate through the membrane.

Non-Porous Membranes

As mentioned earlier, the mechanism of gas separation by non-porous membranes basically is different from the one in microporous membranes. Gas molecules actually dissolve and diffuse in the dense membrane matrix. Differences in permeability, therefore, will result not only from diffusivity (mobility) differences of the various gas species but also from differences in physico-chemical interactions of these species within the polymer, determining the amount of gas that can be accommodated per unit volume of the matrix.

Rubbery Polymers. For polymers above their glass transition temperatures, T_g , the permeation behavior is relatively simple phenomenologically. Solubility of the gas in the polymer, as in liquids, follows Henry's law,

$$C = S \cdot p \quad (9)$$

where C is the equilibrium sorption at partial pressure p , and S is Henry's solubility constant for the particular polymer-gas pair. Gas concentration in the polymer thus is related linearly to the external partial pressure. Both positive and negative deviations from this simple relationship have been observed at high gas pressures. Gas flux through the membrane normally is found to follow Fick's first law.

$$Q = -D \frac{dC}{dx} \quad (10)$$

where D is the diffusivity, defined by this equation, and C is the local concentration of gas in the membrane. The diffusivity normally is concentration independent with some deviations in the case of very soluble gases. Integration over the membranes thickness, ℓ , yields:

$$Q = D \frac{C_1 - C_2}{\ell} \quad (11)$$

where C_1 and C_2 are gas concentrations at the high and low pressure faces of the membrane, respectively, and ℓ is the thickness. Substituting Equation 9 into 11 yields:

$$Q = DS \frac{p_1 - p_2}{\ell} = P \frac{p_1 - p_2}{\ell} \quad (12)$$

where p_1 and p_2 are the external partial pressures of the gas on the high and low pressure side of the membrane and P is the permeability defined by this equation. It is, therefore, given by:

$$P = DS \quad (13)$$

Both P and D (and thus S) can be determined in a single experiment, measuring the "time lag" for pressure increase on the low pressure side of the membrane after high pressure had been applied the other side of the membrane. This time lag, obtained by extrapolating the linear portion of the pressure vs time function back to the time axis (Figure 10.1),²² is given by:

$$\theta = \frac{\ell^2}{6D} \quad (14)$$

The permeability is given by the slope of the function, and solubility can be calculated by dividing the permeability by diffusivity. For most permanent gases, the permeability coefficient P will be pressure independent for all practical purposes. However, for some gases with high boiling points at temperatures lower than the critical temperature, permeability increases with pressure, reflect-

ing an increase in the solubility constant. The effects of temperature on diffusivity and solubility of gas normally are of opposite signs, i.e., diffusivity increasing and solubility decreasing with increasing temperature. The effect of temperature on permeability is, therefore, a composite of these effects. Under most normally encountered conditions, the effect on diffusivity predominates, and permeability increases with temperature. However, below some temperature solubility can become so high as to reverse the effect. These effects are summarized in Figure 10.2.²³ The effect of temperature on gas selectivity of membranes has not been studied very thoroughly. As a rule of thumb, temperature will have a greater effect on the permeability of the gas with the higher diffusion activation energy, i.e., the less permeable gas. Therefore, it is the usual observation that selectivity decreases with increasing temperature.

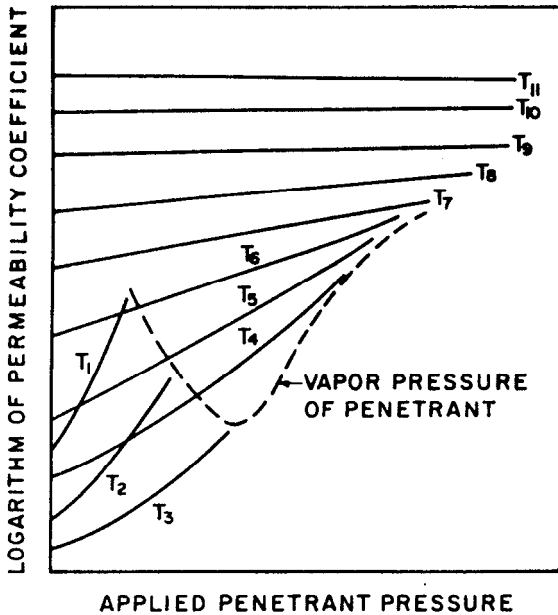


Figure 10.1: Typical result of transient permeation experiment.²³

Glassy Polymers

Some rubbery polymers are among the most permeable polymers known. Contrary to popular belief, however, it is not true that rubbery polymers as a family are more permeable than glassy polymers. In fact, the most permeable polymers reported to date have quite high glass transition temperatures.²⁴ An important deficiency of rubbery polymers is their low modulus. Therefore, they will not form thin, self-supporting, pressure resistant membranes. For this reason, most recent interest has been in using glassy polymers to make gas separating membranes. It was found that the solubility of gases in (and hence permeability of) crystalline polymers is extremely low. Therefore, the most practically

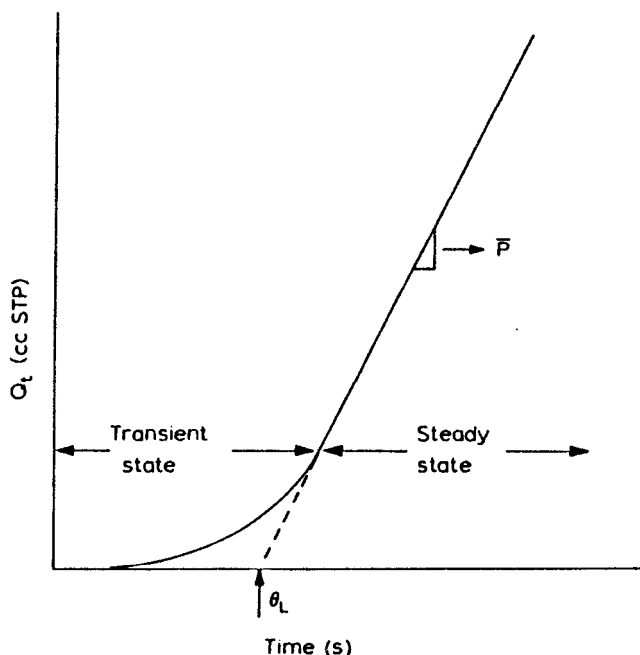


Figure 10.2: Pressure and temperature dependence of permeability.²⁴

interesting polymers are amorphous with high glass transition temperatures. Unlike rubbery polymers, sorption of gases in glassy polymers does not follow Henry's law, and a typical sorption isotherm is convex to the pressure axis, as shown in Figure 10.3.²² This was shown to be the case with a large number of polymers and many gases. One theory that has gained wide popularity in explaining this behavior and a broad range of other experimental data is the dual sorption theory.^{22,25,26} It postulates the existence of two types of sorption sites in the glassy polymer. One accommodates mobile gas molecules following Henry's law. The other consists of Langmuir type sites with much less mobile sorbed species. The Langmuir sites have been associated with fixed voids or excess free volume in the glassy state and correlated with the abrupt change in slope of the specific volume vs temperature curve as one passes the glass transition temperature, Figure 10.4.²⁵ The two sorbed gas populations are in rapid equilibrium throughout the membranes. This behavior is described by the following equation:

$$C = C_D + C_H = Sp + \frac{C'_H \cdot bp}{1 + bp} \quad (15)$$

- where C_D = solubility in the Henry type sites
- C_H = solubility in the Langmuir type sites
- C_H = hole saturation constant
- b = hole affinity constant

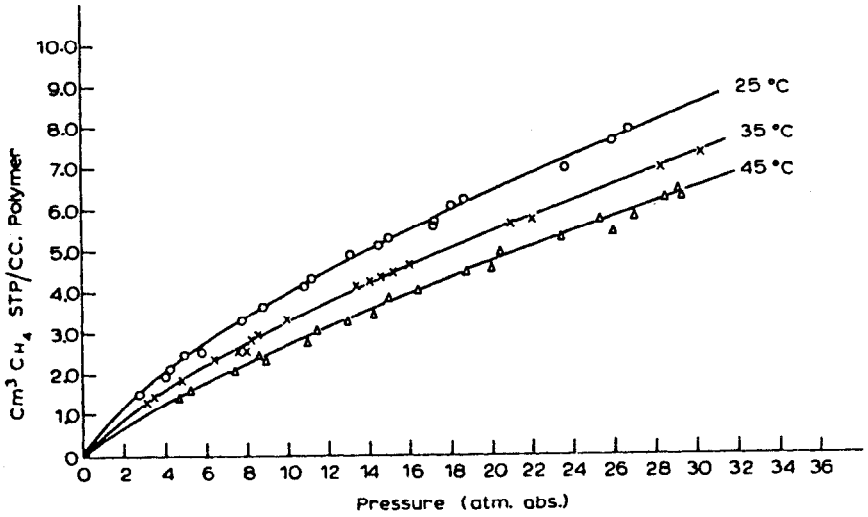


Figure 10.3: Solubility of methane in polystyrene.²³

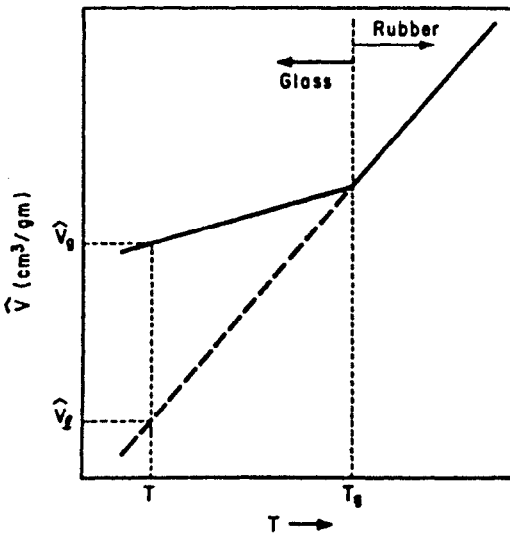


Figure 10.4: Specific volume dependence on temperature in the region of the glass transition.²⁶

Sorption behavior at low and high pressure is consistent with the model: At low pressures ($bp < 1$), Equation 15 reduces to:

$$C = (S + C'_H b) p \quad (16)$$

a modified Henry-like behavior. At high pressure ($bp \gg 1$), Equation 15 becomes:

$$C = Sp + C'_H \quad (17)$$

indicating saturation of the Langmuir sites. Thus, C is a linear function of p at both low and high pressure with a nonlinear region in between. This corresponds well with the results as shown in Figure 10.3. These mathematical relations allow the determination of the various dual sorption parameters. Thus, from the pressure dependence of C at high pressures (Equation 17), S and C'_H can be determined from the slope and intercept, respectively. Writing the Langmuir part of the sorption equation:

$$C'_H = \frac{C'_H bp}{1 + bp} \quad (18)$$

rearranging to

$$p/C'_H = 1/C'_H b + p/C'_H \quad (19)$$

and plotting p/C'_H vs p , one can determine C'_H and b (C'_H is obtained as the difference between total sorption and Sp).

Total solubility of gases in glassy polymers is higher than in rubbers, which is consistent with the apparent existence of an additional sorption site in such polymers. The temperature dependence of Henry's law constant

$$S = S_o e^{-\Delta H_D/RT} \quad (20)$$

and the dependence of the Langmuir constant:

$$b = b_o e^{\Delta H_H/RT} \quad (21)$$

enable the determination of the sorption enthalpies into the various sites. It was found that the Henry-type sorption enthalpy, ΔH_D , is of the same order as that in rubbers, whereas the enthalpy for sorption in Langmuir sites, ΔH_H is appreciably higher. This accounts for the empirical finding that gas sorption in glassy polymers is substantially more exothermic than in rubbers, and it is explained in dual sorption theory by the sorption of gas into preexisting sites rather than sites that need to be formed by polymer molecular reorientations (as in rubbers).

While the permeability of most rubbery polymers to most gases is pressure independent, the permeability of glassy polymers usually is observed to decline with increasing pressure. This is accounted for by the dual sorption theory if one assumes that both the Henry and Langmuir type sites contribute to per-

meability.²⁵ Thus, a modified one dimensional Fick's law is:

$$Q = -D_D \frac{dC}{dx} - D_H \frac{dC}{dx} \quad (22)$$

where D_D and D_H are the diffusivities of gas molecules associated with the Henry and Langmuir environments respectively. Solution of this equation yields

$$P = S D_D \left[1 + \frac{FK}{1+bp} \right] \quad (23)$$

where $F = D_H/D_D$ and $K = C_H' b/S$.

The time lag also takes on a more complicated form:

$$\theta = \frac{l^2}{6D} [1 + f(K, F, bp)] \quad (24)$$

where the function f is too complex to reproduce here.

For very high values of bp , such as at high pressures, when Langmuir sites are saturated and thus do not participate in transport, Equation 23 reduces to the simple Henry form.¹³

At low pressure, the following limiting forms are obtained:

$$P = S D_D + b C_H' D_H \quad (25)$$

$$\theta = \frac{l^2}{6D} \frac{(1+K)}{(1+FK)} \quad (26)$$

These relationships were demonstrated for many gases in various polymers. In spite of its wide acceptance and success in representing a large amount of experimental data, the dual sorption theory has come under attack recently. One reason is that it has never been demonstrated conclusively that two sorbed gas molecule populations actually exist in polymers. An alternate model was suggested—the matrix model.²⁷ In this model, it is assumed that only a single population of sorbed gas molecules exists and that the gas changes the properties of the polymer matrix over the entire pressure–concentration range in a continuous manner. Mathematical expressions were developed to describe the dependence of solubility, apparent diffusivity, permeability and time lag on gas concentration. These are at least as successful as dual sorption expressions in describing experimental data. Thus, the concentration dependent solubility constant is given by:

$$S = \frac{S_0}{1 - \alpha C} \quad (27)$$

where C is the equilibrium concentration of gas in the matrix and α is a constant. The concentration dependent diffusivity is given by:

$$D = D_0 (1 + \beta C) \quad (28)$$

β , the "interaction parameter" is positive for a plasticizing gas and negative if the gas has antiplasticizing effect. By solving Fick's first law with the appropriate expression for the diffusivity, one obtains the concentration dependent permeability as:

$$P = D_0 S_0 \frac{(1 + \beta C)}{(1 + \alpha C)} \quad (29)$$

The expression for the concentration dependent time lag is:

$$\theta = \frac{l^2}{6D} \frac{10 + 15\beta C + 16\beta^2 C^2}{10(1 + \beta C)^3} \quad (30)$$

The fit of these expressions to experimental results is very good. At low pressure regimes, the fit was shown to be even better than that of dual sorption expressions. Except for these regimes, the two models seem to do equally well in describing sorption and permeability data. Concentration dependent diffusivity and permeability have been considered before mainly for vapors. The new aspect of the matrix model is that it broadens these effects to fixed gases. The important difference between the matrix and dual sorption models is in the physical picture they convey of gas transport and interaction with the polymer. Additional experimental evidence will be needed to determine the preference of these different physical representations.

The theories described above, though successful at correlating many experimental data, are phenomenological in nature. Attempts have been made also to explain gas diffusion in polymers on a molecular basis. One of the more recent theories is that by Pace and Dadyner²⁸ which elaborates on earlier theories of Brandt²⁹ and DiBenedetto.³⁰ Gas molecules are viewed as being trapped in channels formed from polymer chains over short distances. Longitudinal diffusion along these channels is very rapid with low activation energy. The true activation energy for diffusion is that associated with transverse diffusion out of the molecular cage which depends on polymer chain reorientation. The theory provides an expression for the activation energy for diffusion based on first principles. The expression predicts an apparent activation energy (that obtained from an Arrhenius plot) which is independent of temperature above and below T_g , with the value above T_g higher than below. This general behavior is indeed observed experimentally. The theory also derived an expression for the diffusion constant; however, it contains a parameter, the mean-square-jump displacement of the diffusant, which cannot be determined as yet.

ENGINEERING ASPECTS

The efficiency of a gas separation process can be described by essentially two parameters: the purity of the product gas and the fraction of that gas in the feed recovered as product (the recovery). These parameters in turn will be determined by the membrane's intrinsic properties—its permeability and selectivity and by operating factors such as total and partial pressures on the feed and

permeate sides, feed flow rate and pressure drop on either side of the membrane. These factors will determine the membrane area and compression energy necessary for a given separation, and only with all these parameters can an economic evaluation of the process be made.

The basic engineering analysis of gas separations by membranes was made by Weller and Steiner^{31,32} long before good, practical membranes were developed, but it is still useful as a good approximation. Assuming a binary gas feed and laminar flow on both high and low pressure sides of the membrane, permeate composition at any point will be determined by the transport rate of the two gases at that point:

$$-dn_A = P_A dA \left[p_1 \frac{n_A}{n_A + n_B} - p_2 \frac{dn_A}{dn_A + dn_B} \right] \quad (31)$$

$$-dn_B = P_B dA \left[p_1 \frac{n_B}{n_A + n_B} - p_2 \frac{dn_B}{dn_A + dn_B} \right] \quad (32)$$

where P_A & P_B = the membrane's permeability to gases A and B respectively,

p_1 & p_2 = total pressures on the high and low pressure side respectively,

n_A & n_B = the numbers of mols of gases A and B flowing per unit time on the high pressure side, and

dn_A & dn_B = permeation rates.

An analytical solution to these equations giving the molar ratio of component B leaving and entering the membrane stage is:²⁹

$$\ln \frac{n_B^f}{n_B^o} = R \ln \frac{t^o - B/A}{t^f - B/A} + U \ln \frac{t^o - \alpha + C}{t^f - \alpha + C} + T \ln \frac{t^o - C}{t^f - C} \quad (33)$$

where $\alpha = P_A/P_B$

$A = [(1 - \alpha)p_2/p_1 + \alpha] / 2$

$B = -AC + \alpha/2$

$C = -[(1 - \alpha)p_2/p_1 - 1] / 2$

$R = 1/(2A - 1)$

$U = [\alpha(A - 1) + C] / (2A - 1) (\alpha/2 - C)$

$T = 1/(1 - A - B/C)$

$t = -Ai + [A^2i^2 + 2Bi + C^2]^{1/2}$

$i = n_A/n_B$

Once n_B^f (rate of gas B leaving the high pressure side) has been determined, bore composition can be calculated by mass balance:

$$y = \frac{n_A^o - n_A^f}{n_A^o - n_A^f + n_B^o - n_B^f} \quad (34)$$

where y is the mol fraction of gas A in the permeate, o and f denote entering and leaving, respectively. The recovery of gas A will be given by:

$$\frac{n_A^o - n_A^f}{n_A^o}$$

Obviously, the higher the recovery the lower the purity of the permeated gas. In the special case of zero recovery or complete mixing (and therefore, constant shell and bore compositions along the membranes), an especially simple expression is obtained by dividing Equation 31 and 32:

$$\frac{y}{1-y} = \alpha \frac{p_1 x - p_2 y}{p_1(1-x) - p_2(1-y)} \quad (35)$$

where y = the mol fraction of gas A in the permeate
 x = the mol fraction of gas A on the high pressure side
 α = the separation factor P_A/P_B

If, in addition, bore pressure is zero, $p_2 = 0$, the selectivity and the mol fractions show the simple relation:

$$\frac{y/(1-x)}{x/(1-y)} = \alpha \quad (36)$$

Equation 35 clearly shows that product purity is directly related to membrane selectivity. Solving the quadratic Equation 35 for y yields:

$$y = \frac{-B + [B^2 + 4(1-\alpha) \alpha(p_1/p_2)x]^{\frac{1}{2}}}{2(1-\alpha)} \quad (37)$$

where $B = (\alpha - 1)(p_1/p_2)x + p_1/p_2 + \alpha - 1$

Thus, an increase in total pressure ratio p_1/p_2 will improve purity for a given α . The various effects of pressure ratio and membrane selectivity are shown in Figure 10.5.³³ It will be observed that under certain conditions the pressure ratio is of even greater importance than intrinsic selectivity. Thus, with a feed gas relatively poor in the more permeable component, and an α of about 40, further increase in selectivity has little effect on product purity, whereas an increase in

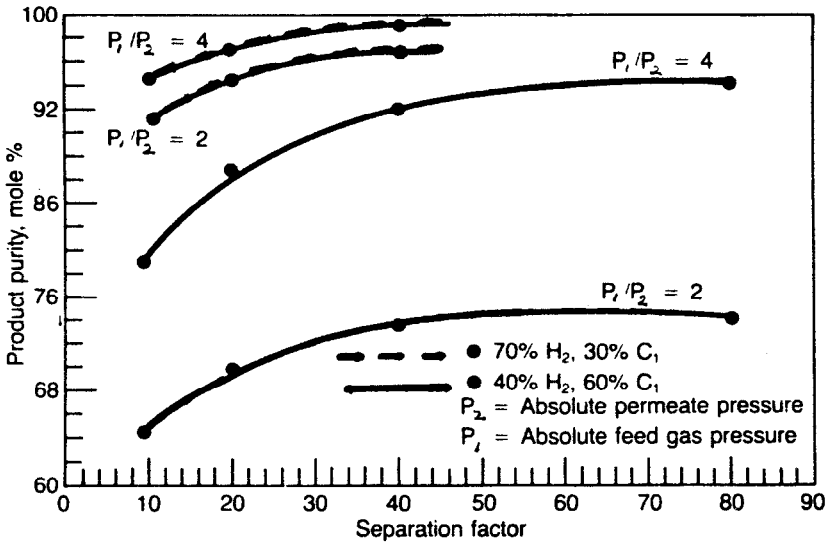


Figure 10.5: Product purity as a function of feed composition and membrane selectivity.³³

pressure ratio has a substantial effect over the whole selectivity range. The effect of pressure ratio is much smaller if the feed gas is already rich in the more permeable component. It is seen that with any feed composition the effect of membrane selectivity on product purity reaches a plateau above some α value. Therefore, research effort to develop super-selective membranes always should be considered with this trend in mind.

One of the main determinants of process economics is the membrane area required for a given separation. The exact solution, obtainable by numerical methods, is:

$$S = \frac{n_B^o}{p_B} \int_{if}^{i^o} \frac{\text{antiln} [n_B(i)/n_B^o] di}{[f(i)-1] [p_1(1/(i+1)) - p_2(1/(f(i)+1))]} \quad (38)$$

where $i = n_A/n_B$
 $f(i) = Ai - C + [A^2i^2 + 2Bi + C^2]^{1/2}$ (see Equation 33)

A good approximation for the area can be obtained by averaging the solutions of Equation 35 for inlet and outlet compositions. Thus, a permeate mol fraction at the inlet, y^o , can be determined from:

$$\frac{y^o}{1-y^o} = \alpha \frac{p_1 x^o - p_2 y^o}{p_1 (1-x^o) - p_2 (1-y^o)} \quad (39)$$

(x^o is the mol fraction of gas A at the feed inlet). If it is desired to obtain Δn_A mols of gas A per unit time, a corresponding area will be:

$$S^o = \frac{\Delta n_A}{p_A(p_1x^o - p_2y^o)} \quad (40)$$

A similar expression can be written for the stage outlet, and the average of the two areas is taken as the approximate required area. The area is thus seen to be inversely proportional to fast gas permeability and partial pressure differential.

It should be realized that the membrane contributes only a part (sometimes a small part) of total capital cost of the separation system. Compressors, pre-treatment facilities and mounting may amount to more than membrane cost. Pretreatment to remove contaminants harmful to the specific membrane can be especially costly. It is, therefore, desirable to have membranes that are highly environmentally resistant or that can be operated under conditions (e.g., high temperature) in which the solubility of the contaminants in the membrane is low. Compression may be a major factor in system operating cost. Therefore, membranes with high permeabilities are desired to minimize the need for high driving force and to minimize membrane area. If membrane selectivity is too low, multistaging will be necessary. As a rule, this will increase both capital and operating cost due to the additional membrane area required and the recompression between the stages.

Gas separation by membranes will always have to compete with other separation processes such as cryogenics, absorption and adsorption systems. Membranes usually are less competitive in very large scale operations where the fast gas is less than about 20% of the feed gas, unless the slow gas is the desired product. Membranes also are not usually the method of choice when extremely pure product gas is required. Membranes do, however, have distinct advantages in small to medium scale operations, in situations where gas is available at pressure, in situations where high recovery is paramount, and in applications where simplicity and minimal maintenance are of prime importance (such as in remote locations). Membranes are very well suited for applications in which the non-permeate is the product of interest, since it is obtained at pressure. Examples are acid gas removal from natural gas and gas dehydration.

PREPARATION OF MEMBRANES FOR GAS SEPARATION

Permea's (Monsanto) Composite Membrane

Membranes to be used in practical gas separations have to satisfy many requirements; they have to exhibit high fluxes so as not to demand excessive membrane areas for large volume gas processing. They must have good selectivities in order to offer product gas streams of high purity. They must be able to withstand the high gas pressures often encountered in natural and industrial streams. They must withstand reasonable concentrations of contaminants often accompanying the gases of interest (e.g., H_2O , H_2S , hydrocarbons).

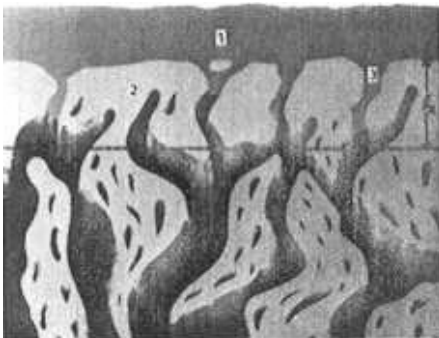
It was the combination of these stringent requirements which impeded the development of useful gas separating membranes for so many years. Obviously,

one of the most difficult requirements is the achievement of high permeability and high selectivity simultaneously. A similar problem had hampered the development of reverse osmosis membranes. It was solved brilliantly in the asymmetric Loeb-Sourirajan membrane, having a thin selective layer supported by a much thicker porous, non-selective matrix. In this membrane, the fact was exploited that whereas permeability is thickness dependent, selectivity—being a ratio of permeabilities—is not. The problem with gas separation membranes is even more severe. Reverse osmosis membranes can show good salt rejection even if slightly porous, by virtue of electrostatic interactions (non-availability of free water to solvate ions inside small pores). Most common gases are of very small effective diameters (2 to 5 Å) and mechanisms such as the above to increase selectivity are not available. Also, permeabilities of gases in polymer matrices are usually very low,

$$10^{-12} - 10^{-8} \frac{\text{Sec} - \text{cm}}{\text{cm}^2 - \text{sec} - \text{cmHg}}$$

Therefore, membranes for gas separation are extremely sensitive to the existence of even a relatively few small imperfections, due to the very high permeability of such holes relative to the imperfection-free areas. The solution developed by Monsanto is unique in that it circumvented the need to make a perfect membrane by devising a special coating procedure.³⁴ On coating the membrane with a thin layer of a highly permeable, non-selective polymer, the permeability through the holes is reduced sufficiently to make the permeation through the matrix predominant (Figure 10.6). Performance close to that expected from intrinsic (dense film) properties is thus achieved. The materials presently used in Permea's (a Monsanto Company) commercial membranes are a polysulfone as the matrix and a silicone rubber as a coating. However, the method is general and any matrix-coating combination with the appropriate permeability ratio can be used. A numerical example will illustrate the utility of such membranes in the separations of CO_2 from CH_4 .

PM COMPOSITE – SCHEMATIC



PM COMPOSITE – ELECTRICAL CIRCUIT ANALOG

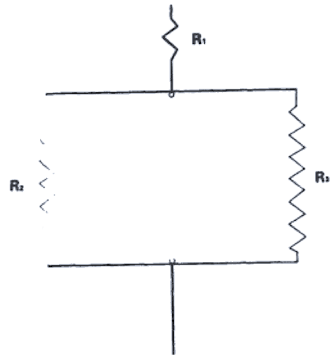


Figure 10.6: Schematic representation of Monsanto's composite membrane. Cross-sectional view on left, electrical circuit analog on right.³⁴

Assume a polysulfone fiber with an effective thickness of 1000 Å and a surface porosity of 10^{-6} (ratio of pore area to total area). The fiber is coated with a silicone at a thickness of 1 μm. The intrinsic permeabilities of polysulfone and silicone are:

$$\begin{array}{ll} \text{PCO}_2 \text{ (polysulfone)} = 6 \times 10^{-10} & \frac{\text{Scc - cm}}{\text{cm}^2\text{-sec-cmHg}} \\ \text{PCH}_4 \text{ (polysulfone)} = 0.2 \times 10^{-10} & \frac{\text{Scc - cm}}{\text{cm}^2\text{-sec-cmHg}} \\ \text{PCO}_2 \text{ (silicone)} = 3500 \times 10^{-10} & \frac{\text{Scc - cm}}{\text{cm}^2\text{-sec-cmHg}} \\ \text{PCH}_4 \text{ (silicone)} = 800 \times 10^{-10} & \frac{\text{Scc - cm}}{\text{cm}^2\text{-sec-cmHg}} \end{array}$$

Remembering that the permeability term P/ℓ (where ℓ is the effective membrane thickness) is reciprocal resistance, the total CO_2 resistance of the membrane will be:

$$\left(\frac{P}{\ell}\right)_{\text{CO}_2} = \left[\left(\frac{P_{\text{CO}_2}}{\ell}\right)_{\text{Si}}^{-1} + \left[\frac{(\text{PCO}_2)_{\text{Si}} \times \text{porosity} + (\text{PCO}_2)_{\text{PS}}}{\ell_{\text{PS}}} \right]^{-1} \right]^{-1}$$

thus

$$\begin{aligned} (P/\ell)_{\text{CO}_2} &= \left[\left(\frac{3500 \cdot 10^{-10}}{10^{-4}} \right)^{-1} + \left(\frac{3500 \cdot 10^{-10} \cdot 10^{-6} + 6 \cdot 10^{-10}}{10^{-5}} \right)^{-1} \right]^{-1} \\ &= 61 \cdot 10^{-6} \frac{\text{Scc}}{\text{cm}^2\text{-sec-cmHg}} \end{aligned}$$

Similarly for methane

$$\begin{aligned} (P/\ell)_{\text{CH}_4} &= \left[\left(\frac{800 \cdot 10^{-10}}{10^{-4}} \right)^{-1} + \left(\frac{800 \cdot 10^{-10} \cdot 10^{-6} + 0.2 \cdot 10^{-10}}{10^{-5}} \right)^{-1} \right]^{-1} \\ &= 1.99 \cdot 10^{-6} \frac{\text{Scc}}{\text{cm}^2\text{-sec-cmHg}} \end{aligned}$$

the separation factor,

$$\alpha = \frac{(P/\ell)_{\text{CO}_2}}{(P/\ell)_{\text{CH}_4}} = 30.6$$

is essentially identical to the intrinsic (dense film) separation factor of ~ 30 .

The uncoated membrane has a much lower selectivity: assuming cylindrical pores, the molar Knudsen flow through the pores will be given by:

$$Q = \frac{4d}{3\ell} \frac{P_1 - P_2}{(2\pi MRT)^{\frac{1}{2}}}$$

- where d = Pore diameter
 l = Pore length
 M = Molecular weight
 R = Gas constant
 T = Absolute temperature

If the pressure differential is 1 atmosphere, CO_2 flow through the pores in our example will be:

$$112 \times 10^{-6} \frac{\text{cc STP}}{\text{cm}^2 \text{ membrane area-sec-atm}}$$

methane flux will be

$$186 \times 10^{-6} \frac{\text{cc}}{\text{cm}^2 - \text{sec} - \text{atm}}$$

The corresponding fluxes through the polysulfone matrix will be

$$\text{for } \text{CO}_2: \frac{6 \times 10^{-10}}{1000 \times 10^{-8}} \times 76 = 4560 \times 10^{-6} \frac{\text{cc}}{\text{cm}^2 - \text{sec} - \text{atm}}$$

and for methane

$$\frac{0.2 \cdot 10^{-10}}{1000 \cdot 10^{-8}} 76 = 152 \times 10^{-6} \frac{\text{cc}}{\text{cm}^2 - \text{sec} - \text{atm}}$$

Adding reciprocal permeabilities as resistances, overall selectivity will be

$$\alpha \text{ CO}_2/\text{CH}_4 = \frac{4672}{338} = 13.8$$

The coating thus eliminates the detrimental effect of the imperfections without affecting the flux in any major way.

It can be shown that the coating technique will give an almost constant performance over a wide range of surface porosity (Figure 10.7). Only at relatively high porosity (10^{-3} or higher) will flux of the slower gas through the plugged pores become large enough to adversely affect the selectivity. Also, the technique is not very sensitive to coating thickness and only at thicknesses of $1 \mu\text{m}$ or greater will the coating contribute significantly to the total resistance (thus lowering selectivity). It is this flexibility and the freedom from very stringent and expensive process control which makes this technology so attractive.

A number of advantages of this kind of composite membrane are noteworthy. It is not sensitive to water and, therefore, feed streams do not have to be dry. Its temperature resistance is good and, therefore, operation at elevated temperatures is a simple and inexpensive way to minimize the effect of contaminants and to increase permeability. The pressure rating is excellent, and the

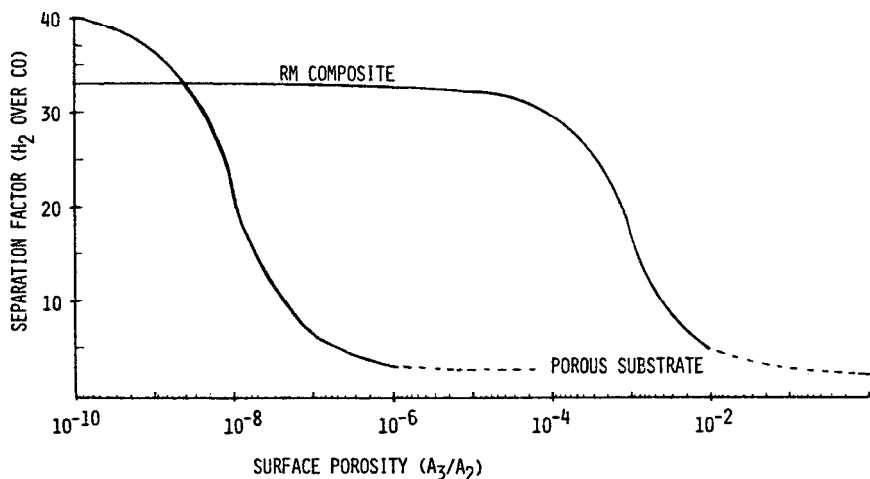


Figure 10.7: Effect of surface porosity on the separation factor (H_2/CO) for a porous substrate and Monsanto's composite membrane.³⁴

membranes perform well for extended periods in high pressure feeds such as those encountered in ammonia plants.

The composite membranes were made into successful systems thanks to various additional developments, including appropriate chemical and pressure resistant module seals^{35,36} and shell design. These membranes were first used in house and by now have found numerous applications throughout the world.

Dry Cellulose Acetate Membranes

As stated previously, asymmetric cellulose acetate reverse osmosis membranes are kept wet at all times. Uncontrolled drying brings about a loss of selectivity. This results from the large interfacial forces developing during drying of the small pores of this hydrophilic polymer. Such uncontrolled drying can occur on exposing a wet membrane to a gas stream. Therefore, techniques had to be found to dry cellulose acetate in a controlled manner before the membranes could be used to separate gases. In 1968, it was suggested that drying by solvent exchange could lead to a good gas separating membrane.^{6,37} The procedure called for soaking the wet membrane in isopropanol for half an hour followed by toluene for several hours. Water is thus removed by dissolution in the alcohol and all polar solvent is removed before exposure to air. It was soon learned that surfactant treatment or freeze drying would achieve a similar result.^{38,39}

Thus, a freeze dried membrane showed a He permeability of

$$3 - 10 \times 10^{-5} \frac{\text{cc}}{\text{cm}^2 - \text{sec} - \text{cmHg}}$$

and α He/N₂ selectivity of 34–46 vs 97 for the dense film. Apparently, a small number of defects were present in the membrane. Improvements in the drying procedure were then developed such as carrying out the solvent exchange at low temperature.⁴⁰ For example, a membrane treated at 0°C with n-butanol followed by n-heptane showed (P/l) He of

$$280 \times 10^{-6} \frac{\text{cc}}{\text{cm}^2 \text{ sec} - \text{cmHg}}$$

and a He/CH₄ of 62. Heat treatment at 95°C following the drying was found to be beneficial, increasing He/CH₄ selectivity to 75.

Cellulose acetate membranes have been suggested for hydrogen recovery, CO₂/CH₄ separations, gas dehydration and for nitrogen enrichment.^{41–43}

Composite Polyimide Membranes

Ube Industry, Ltd. introduced a polyimide membrane which is reported to be made from a condensation polymer of biphenyltetracarboxylic anhydride and an aromatic diamine such as 4,4'-diaminodiphenyl ether or a mixture of two diamines.^{44–46} The comparison in Table 10.1 indicates the intrinsic permeabilities for H₂ in these polyimides are similar to polysulfone, and the H₂/CO selectivities are two times greater. Likewise the O₂/N₂ selectivities are twice those of polysulfone, but the O₂ permeabilities are only one-half the polysulfone values. These polyimide materials are good candidates for gas separation membranes owing to their high selectivities, high insolubilities, and high strengths and glass transition temperatures.^{45,46}

Asymmetric membranes are made from solution in the form of a hollow fiber, but the process used to form a thin, pore free dense layer on these hollow fibers is not disclosed.^{45,46} However, US patent 4,440,643¹² describes a unique process for producing pore-free polyimide composite membranes. An asymmetric polyimide porous substrate is prepared from solution. When fully imidized, the substrate is insoluble. The substrate can now be coated with a polyamic acid from dilute solution (~1%). When fully imidized, the resultant polyimide coating becomes the separating layer. This process allows use of the same or different polyimides for the substrate and the separating membrane. While the examples in the reference describe preparation of flat sheet membranes, this process could be used to prepare hollow fiber membranes.

A recent report⁴⁹ indicates the permeabilities of the composite hollow fiber membranes made by Ube may be considerably lower than those of polysulfone when compared at the same temperature. The Japanese literature suggests higher permeabilities than given by Reference 49. It is not known which is the case for the membranes actually used in the separators. The polyimides are reported to be capable of sustained, higher temperature operation to give permeabilities comparable to those of polysulfone while still retaining adequate selectivity.^{45,46}

The cited references indicate the hollow fibers are assembled and installed in a module of a design very similar to that employed by Permea. The success of sustained, high temperature operation, which may be needed for permeability, will depend on the development of heat resistant end seal materials. The materials must not only withstand high temperatures, but also survive the effects of

Table 10.1: Intrinsic Permeabilities and Ideal Separation Factors for Selected Polymers

<u>Polymer (Reference)</u>				<u>H₂/CO</u>	<u>H₂/CH₄</u>	<u>H₂/N₂</u>	<u>CO₂/CH₄</u> ^(b)	<u>O₂/N₂</u>
Polysulfone ^(c) (7, 47)	13	6	1	40	60	72	25-30	6
Polyimide (44, 46)	9	-	0.5	76	~200	~200	-	11
Poly(4-methyl pentene-1) (48)	136	93	32	-	-	17	-	4
Crosslinked PPO (18)	22	9	2.3	37	55	56	22	6
Silicone Rubber (51)	550	271	501	-	0.7	2	0.3	2
Cellulose Acetate (64)	12	6	1	40	60	70	30	5.5

(a) Units are cm³ (STP)-cm/cm² sec cmHg at temperatures of 25°-35°C.

(b) Low pressure (<20 atm). The separation factor of this pair varies with pressure.

(c) Product of Union Carbide Corp.

temperature cycling and stream contaminants to prevent failure by cracking.

Polyolefin Membranes for Air Separation

The membrane is made from a polyolefin. Based on work Dow did for the Federal Aviation Agency and reported performance capabilities, it is believed that poly(4-methylpentene-1) is used.¹⁷ A comparison of the intrinsic permeabilities of this polymer with polysulfone and polyimide is given in Table 10.1. Poly(4-methylpentene-1) is highly permeable, but it has low selectivities as indicated by the O₂/N₂ pair data and the α of 17 for H₂/N₂. While the melting point of this crystalline polymer is high, 235°C, the glass transition temperature⁵⁰ is much lower than polysulfone or polyimide necessitating operation of a membrane system at temperatures close to ambient to maintain the best selectivities.

The membrane is made in hollow fiber form. It is melt spun to nominal dimensions of 40 μm outside diameter and 30 μm inside diameter to give a wall thickness of about 5 μm . The wall thickness of a melt spun membrane is much thicker than the effective separating layer of an asymmetric membrane which is on the order of 0.1 μm . However, the permeability of the polyolefin is high and the small dimensions allow use of a very large membrane area in a compact unit which together compensate for the large membrane thickness. A disadvantage of small dimension fiber is the large pressure drop in the bore side due to capillary flow which limits the length of the fiber in the separating unit and therefore the area. This effect is accommodated by appropriate module design. This membrane is well suited for air separations, but the low selectivities will prevent its application to hydrogen in carbon dioxide separations.

Other Membranes

Signal's UOP Fluid Systems Division Spiragas (a trademark of Signal Co.) membrane is prepared from an ultrathin silicone material on a porous polysulfone flat sheet. A spiral wound module is prepared from this membrane. Silicones, typically, have very high permeabilities and low selectivities.^{2,51} For this reason, Spiragas is sold for oxygen enrichment applications rather than a system to produce nitrogen of greater than 95% purity.

The Asahi Glass membrane also is reported to be a composite based on a fluoropolymer. Flat sheets are assembled into a plate and frame module design rather than spiral wound.

Monsanto announced the development of a crosslinked polyphenylene oxide membrane early in 1985.¹⁸ While the intrinsic permeabilities of this material are lower than polyphenylene oxide, they are higher than those of polysulfone, Table 10.1. The membrane is made by brominating PPO followed by base crosslinking. The transport properties of this material can be manipulated by altering the bromine content and degree of substitution in the ring or methyl groups. The bromine on the methyl group reacts readily with bases affording the opportunity for crosslinking and further transport property modification. This material is spun into hollow fiber membranes using Monsanto technology. Typically, the fiber is treated with aqueous ammonia followed by coating with a silicone rubber.^{7,18} The membrane is reported to be more resistant to stream contaminants and due to the higher permeabilities is more productive than polysulfone.

Membrane Testing and Evaluation

Since gas separation by membranes is a relatively recent development, it is still quite common to base selectivity determinations on pure gas tests. This will sometimes give a reasonable estimate of membrane performance but can often lead to erroneous results. The reason is that in many cases one gas in a mixture will influence the transport of the other gases. Usually selectivity measured with mixtures will be lower than that obtained from pure gas measurements.

Also from the discussion in Chapter 1, it is clear that membrane performance will be strongly influenced by testing conditions, i.e., pressure and temperature. Therefore, it is most advisable in evaluating membranes to test them under conditions as close as possible to actual operating conditions.

Future

Present day membranes are capable of separating mainly inherently "fast" gases (e.g., H_2 , CO_2) from inherently "slow" gases (e.g., N_2 , CH_4). Current technology is not sufficiently refined to efficiently separate different traditionally slow gases (such as N_2 from CH_4 , hydrocarbons from each other). Such separations can, in principle, be achieved by facilitated transport. In this process, imitating the function of biological membranes, the membrane contains a compound interacting specifically with only one of the feed constituents. With appropriate binding constants and binding kinetics, very efficient separations can be obtained. To date most work in this area has been confined to liquid membranes (thin liquid films, liquid in liquid microcapsules or liquid impregnated solid films). Transport facilitation was demonstrated for O_2 , N_2 , CO_2 , H_2S and ethylene (extensive work was done on ion transport in liquids). The most practically advanced facilitated gas transport system has been the ethylene/ethane separation studied at Amoco.⁵² This separation, based on aqueous silver ion, was scaled up to pilot plant size. Technical problems that have not yet been solved in these systems are associated mainly with the need for water in the membrane and hence in the feed streams. It is difficult to prevent the membrane from drying at all times, especially at high pressure differentials. Once such problems are solved in an economical way, new, previously impractical gas separations should become possible.

APPLICATIONS OF GAS SEPARATING MEMBRANES

Within a relatively short period after their commercialization, membranes for gas separation have been utilized in a wide variety of applications. Among these applications are recovery of hydrogen from purge streams such as encountered in ammonia plants, retrofit chemical plants and from hydroprocessors in refineries. Membrane systems have been introduced into oil fields for CO_2 recovery from well-head gas in enhanced oil recovery, and they have been used to separate oxygen from nitrogen in air. Also, they have been utilized in combination with other recovery systems, such as cryogenic and adsorption, to both reduce cost and increase efficiency.

These applications will be discussed in detail in the remainder of this chapter. The cross section of a PRISM[®] (trademark of Monsanto Co.) separator is

shown in Figure 10.8. It is a simple, sturdy structure providing feed inlet and outlet for permeate and non-permeate. Feed and permeate flow is countercurrent and the fibers have one end plugged near the non-permeate outlet.

Hydrogen Recovery

Wasted hydrogen from the inert purge of reactors can be recovered by membrane separator systems. This hydrogen had normally been either flared or burned for fuel, and its chemical value was lost. The ammonia purge gas recovery system was developed at the Monsanto ammonia plants in Luling, Louisiana.⁵³ Figure 10.9 shows a two-stage pressure operation which maximizes recovery while minimizing recompression costs. Systems can now be designed with hydrogen recoveries as high as 95% at a purity of 88%. Operation at differential pressures up to 1,650 psi has been demonstrated.

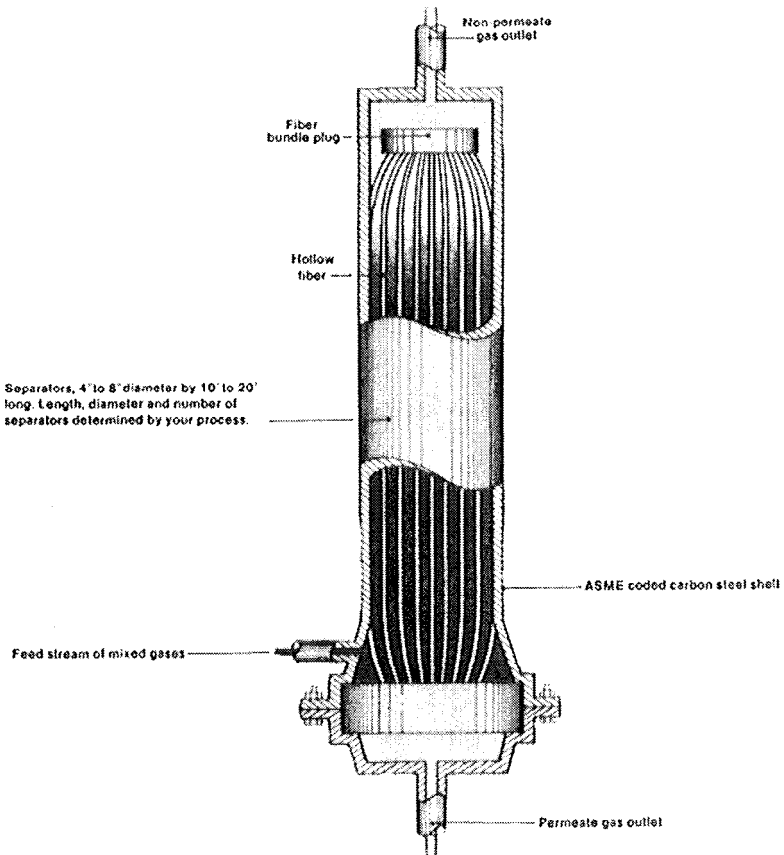


Figure 10.8: PRISM[®] separator.

Between 1979 and 1985, forty-five PRISM[®] separator recovery systems have been successfully implemented on ammonia purges around the world. As a result of hydrogen recovery, an incremental ammonia production of 3 to 5% can be achieved. Alternatively, at constant ammonia production energy savings amount to 0.6 to 0.9M̄ BTU/ton ammonia. For a typical 1,150 ton/day plant, these improvements translate into \$3M̄/year energy savings.

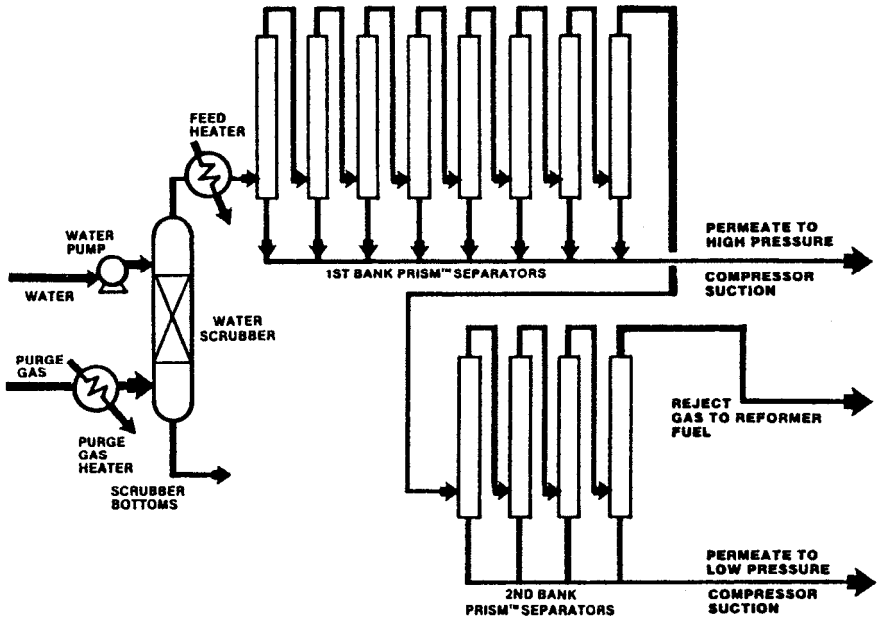


Figure 10.9: Hydrogen recovery from ammonia plant purge.⁵³

Prior to entering the hollow fiber PRISM[®] separators, the feed gas is passed through a water scrubber. This serves a dual purpose of recovering ammonia and extending the fiber life. The ammonia scrubber pretreatment alone contributed about \$200,000/year to the equipment payback in recovered ammonia.⁵⁴ Typically, the recovered hydrogen is recycled back to the ammonia synthesis compressor. However, if a source of high purity hydrogen is needed within the complex, some or all of the gas from the first bank of separators can be used for that application. If higher purity hydrogen is desired, the permeate from the first bank can be processed by an additional PRISM[®] separator to produce, for example, 99% hydrogen.

In methanol synthesis purge recovery, a water scrubber is also used with a similar purpose, and it too pays for itself in recovered methanol. The methanol/water mixture is simply sent to the existing crude methanol distillation column. Hydrogen recovered from this purge can result in energy savings or if additional carbon oxide is available, it can be used to obtain increased methanol production. PRISM[®] separators have operated on stoichiometric as well as non-

stoichiometric $H_2/(CO)_x$ ratio methanol plants at 75° and differential pressures up to 1,000 psi.

As a major user of expensive and often scarce hydrogen, hydrocrackers are also prime candidates for hydrogen use optimization. This enables not only the conservation of hydrogen by purge recovery, but also high-pressure loop modifications to adjust hydrogen partial pressure in the reactor. A simplified process flow diagram of a typical hydrocracker is shown in Figure 10.10. The oil and hydrogen feed (including recycle hydrogen) are charged to the reactors at the desired space velocity. The effluent liquid and vapor pass through a heat exchanger to a high-pressure separator, where the recycle gas is separated from the liquid. The recycle gas is returned to the reactor inlet by a recycle compressor. The liquid is let down in pressure, and hydrogen and light hydrocarbon gas are released in a low pressure separator. The liquid product from the low pressure flash is sent to fractionation. In the reactor, hydrogen partial pressure is reduced by consumption through chemical reaction, by dissolved hydrogen being carried out in the product, and by the formation of light hydrocarbons which dilute the remaining hydrogen. There are several ways of maintaining reactor hydrogen partial pressure within the desired range. The most common involve the addition to the high pressure loop of either a purge or an oil absorber. Hydrocarbons, which dilute the reactor hydrogen, can be removed by purging a part of the gas stream coming from the high-pressure separator. A purge, however, is not selective; for every mol of hydrocarbon purged, typically four mols of hydrogen are lost. Because of the expense of replacing this lost hydrogen, high-pressure purge rates are usually kept to a minimum.

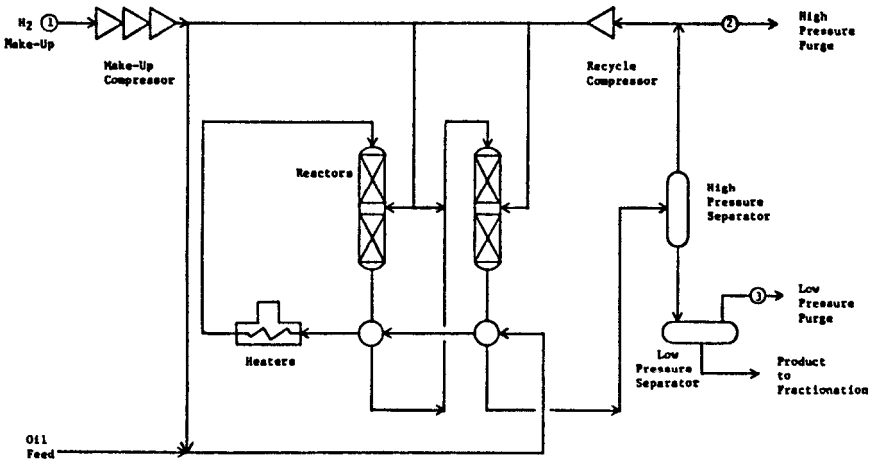


Figure 10.10: Hydrocracker.⁵⁵

The most common alternative to the high pressure purge is oil scrubbing. This involves an absorber vessel in the high-pressure loop, a low-pressure flash drum, and a high pressure pump to return the lean oil to the absorber. The

principal advantage this system has over purging is hydrogen conservation. The oil scrubber flash-drum offgas typically contains one mol of hydrogen per mol of hydrocarbon; thus absorbers lose only about 25% as much hydrocarbon as high-pressure purges. The main disadvantage of the absorber systems is their cost. High operating pressures makes the mechanical components expensive, and pump power requirements often exceed 1000 kW.

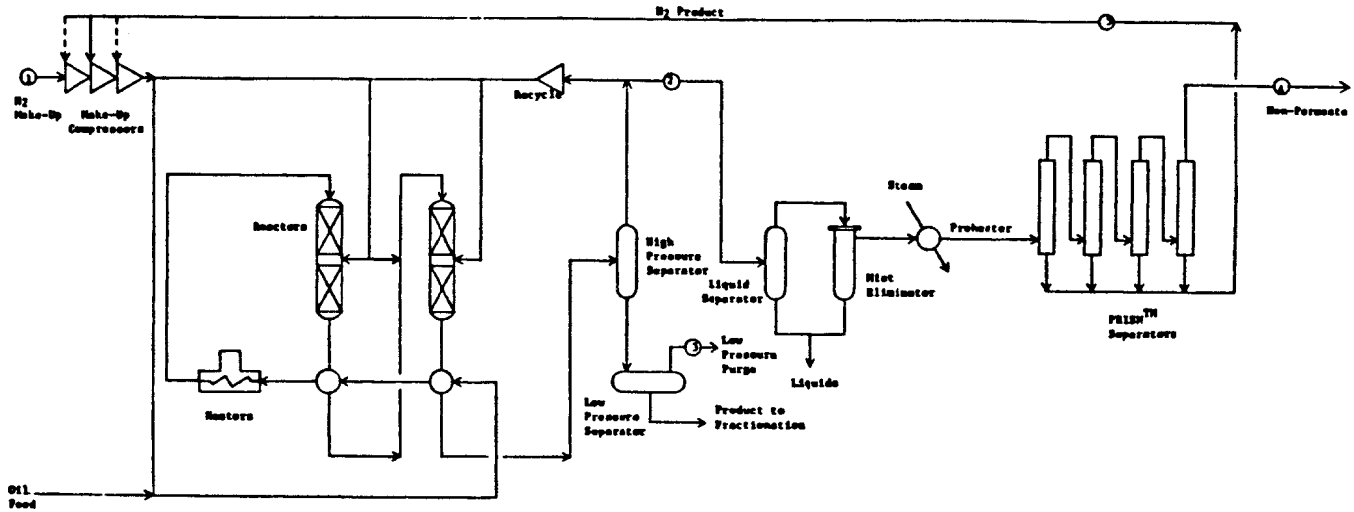
The addition of a PRISM[®] separator to the recycle loop will effectively remove gases such as methane from the process. A simple flow diagram of a hydrocracker with the addition of the PRISM[®] separators is shown in Figure 10.11. A recycle gas slip stream is fed to a liquid separator, where any entrained liquids and mist are removed. The gas is then heated to 150° to 180°F (339° to 355°K) prior to entering the PRISM[®] separators. Hydrogen which permeates the fibers is recovered and returned to the make-up compressor. With about 90% of the hydrogen removed, the non-permeate is primarily hydrocarbons and can be used as fuel gas. Because of the low hydrogen content of the non-permeate, three to four mols of hydrocarbon are rejected for each mol of hydrogen lost. By comparison, simple purges lose 12 to 15 times as much hydrogen.⁵⁵

Other refinery applications in which PRISM[®] separators have been successfully used are naphtha hydrotreaters, middle distillate hydrotreaters, cat crackers, and toluene hydrodealkylation.^{56,57}

The Ube system was designed to be capable of handling the applications described above for PRISM[®] separators. Compared at the same temperature, it is reported that the permeabilities of the Ube composite polyimide hollow fiber membranes may be substantially lower than those of polysulfone,⁴⁹ but with two times the selectivities. The lower permeabilities are overcome in two ways. The Ube module contains 9000 (m²/m³) membrane area per unit volume compared with 4000 (m²/m³) in a PRISM[®] separator. Since the separator units are approximately the same size (from Permea, Inc. and Ube product brochures), the Ube membrane must be smaller in diameter than is the PRISM[®] separator membrane in order to increase the unit membrane area. In transporting large volumes of H₂, small diameter hollow fiber membranes often lead to a large bore pressure drop on the permeate side. The pressure drop is due to flow of gas in a long capillary and is inversely proportional to the inside radius of the hollow fiber to the fourth power, i.e., Poiseuille's law. Pressure buildup on the permeate side of the membrane results in a reduction of the differential partial pressure driving force with attendant reductions in product recovery and purity. Thus, fiber dimensions are important in designing a system for a given separation. In practice, the Ube module most likely will not function as if the unit membrane area is more than twice that of a PRISM[®] separator due to differences in fiber dimensions. The penalty, however, will depend greatly on operating conditions.

The polyimide membrane is reported to be capable of operating at temperatures up to 150°C compared to upper limits of 100°C for PRISM[®] separators and 60°C for cellulose acetate.⁴⁶ Permeabilities increase with temperature while selectivities normally drop. The second way to overcome the lower permeabilities is to operate the Ube system at higher temperatures than possible with polysulfone or cellulose acetate. Even at the high temperatures, the polyimide selectivity will remain high enough for the abovementioned hydrogen separations. Thus, one expects the Ube system to be competitive with PRISM[®] separators for many hydrogen applications.

Figure 10.11: Hydrocracker with PRISM[®] separators.⁵⁵



The cellulose ester systems have some application in hydrogen separations, but are more limited in capability due to temperature limitations. Operation at higher temperature minimizes the need for stream pretreatment to remove components which may attack the membranes. The PRISM[®] separators and the Ube systems are superior to the cellulose esters in this respect.

Carbon Dioxide Separation

Both hollow fiber and spiral-wound membrane systems have been utilized to recover carbon dioxide in sour gas purification and in enhanced oil recovery.

Removal of hydrogen sulfide (H₂S) and carbon dioxide (CO₂) from natural gas is an ideal application for membranes in that both H₂S and CO₂ permeate through membranes at a much higher rate than methane, enabling a high recovery of the acid gases without significant loss of pressure in the methane pipeline product gases.^{41-43, 58-60}

Membrane gas separation by PRISM[®] separators offers a low cost processing alternative to conventional CO₂ removal processes^{61,62} as shown in Table 10.2.

Once the needed partial pressure driving force is achieved by compressing the feed gas, no further expenditure of energy is necessary to separate the CO₂.⁶³

Separex¹s,⁴¹⁻⁴³ Grace Membrane Systems cellulose ester,⁶⁰ Envirogenics GASEP[®] (trademark of Envirogenics Company)⁶⁴ cellulose triacetate spiral-wound membranes, and Dow cellulose acetate hollow fibers are used to produce a salable product from sour gas streams.

Table 10.2: Product Purity and Recovery

<u>SEPARATORS SYSTEM</u>	<u>HOT POTASSIUM CARBONATE</u>	<u>CRYOGENIC SEPARATION</u>	<u>PRISM[®] SEPARATORS</u>
<u>CO₂ Product Stream</u>			
CO ₂ Recovery %	96.9	93.0	96.9
CO ₂ Purity %	99.8	95.1	95.5
<u>Overall Hydrocarbon Stream</u>			
Hydrocarbon Recovery %	99.5	81.0 ¹	83.5
<u>Hydrocarbon Gas Product</u>			
CO ₂ %	2.0	2.0	2.0
C ₁ Recovery %			78.2
C ₂ Recovery %			90.1
C ₃ ⁺ Recovery %			97.0

¹The recovery is based on CO₂ rejection column being operated for ethane reflection/propane recovery.

For enhanced oil recovery programs utilizing CO₂ injections,⁴⁵ membrane separation technology is also finding increasing application. Carbon dioxide is injected into the well as a miscible flood to remove additional oil from depleted fields. It has been found that CO₂ at concentrations above 90% will solubilize oil absorbed in the substrata, allowing secondary and tertiary recovery. In EOR production, CO₂ injected into the formation eventually reemerges mixed with light hydrocarbon gases associated with crude oil. A membrane system can be used to recover CO₂ for reinjection and recover the light hydrocarbons for sale as pipeline gas.

Goddin⁶³ presented a detailed cost analysis for recovering CO₂ from casing-head gas where bulk removal is effected by membrane separation followed by a conventional gas treating process. His analysis showed that for feed gas containing more than 30% CO₂, the process heat requirements for a membrane separation process are approximately 30 to 40% lower than for a cryogenic process. When compared to an acid gas removal process using DEA as a solvent, the membrane separation process requires only 20 to 25% of the process heat requirement.

There are many wells containing about 40 to 80% CO₂ that could be processed with a membrane system, providing a high purity CO₂ for EOR and a fuel gas by-product.

Membrane gas separators may also be used to separate methane from carbon dioxide formed during the decomposition of organic matter in landfills.⁶⁴ Permea's PRISM[®] gas separators are being used in a Florence, Alabama landfill to upgrade raw to 95% methane purity so that it can be routed to the city gas department.

The Ube system may also be useful for CO₂ separations,⁴⁶ but no data have been reported.

Oxygen/Nitrogen Separation

The U.S. produces approximately 15 millions tons of oxygen from air each year.⁶⁶ Most of this production is accomplished cryogenically, and in large plants the cost is very low. Uses of oxygen in quantities of less than 10 tons per day, however, constitute a substantial share of this market. It is thought that membrane systems could economically enrich air at this smaller plant size.⁶⁷

In many applications, such as inert blankets for combustible materials or chemicals, nitrogen rather than oxygen is the desired separator product. Permea in conjunction with Maritime Protection S.A. (wholly owned subsidiary of Permea Kristiansand, Norway) commercialized a system to provide >95% pure nitrogen aboard ships using PRISM[®] separators.^{68,69} The system can process up to 100,000 scf/d of air and operates at 120° to 150°F and pressures up to 425 psig. At the optimum operating conditions, the system can produce nitrogen at less than 4¢ per normal cubic meter or less than \$1.40 per thousand scfm.^{17,69} More recently, membrane systems are planned to provide nitrogen on offshore platforms and in remote landbased applications. Other possible applications include nitrogen blanketing of food to prevent spoilage and to provide nitrogen for manufacturing plant operations.

Permea has under development a new membrane which has approximately 3 times the permeability of the currently used PRISM[®] separator and the same

selectivity.¹⁸ This membrane system should provide nitrogen at a significantly lower cost thus broadening the applicability of membranes for O₂/N₂ separations.

The Generon Air Separation Membrane System which was introduced by Dow Chemical Company in 1985, also is used to provide 95% nitrogen for blanketing. The cost per unit volume nitrogen produced is similar to that reported by Permea.¹⁷ One major difference is the Generon system uses 75 to 90 psi air with an upper limit of 115 psig whereas Permea prefers to use air at 300 to 600 psi. The Permea system operates over a rather broad temperature range and is quite flexible. The Generon system operates preferably at about 15° to 25°C which requires refrigeration of the feed stream. The choice of system will depend largely on the availability of compressed air and the constraints of a given application. Both systems produce nitrogen with a dew point of about -65°C.

The Asahi Glass system is designed to produce oxygen enriched air of up to 40% for medical applications. The driving force is maintained by a vacuum on the permeate side of the plate and frame system. Air at atmospheric pressure is the feed.

Signal's UOP Fluid Systems Division system also produces oxygen enriched air of 30% O₂ for commercial applications. Japan's Osaka Gas has developed a similar system.¹⁵ Again, air is supplied to the membrane at atmospheric pressure and the driving force is maintained by a vacuum on the permeate side of the membrane. Oxygen enriched air can be supplied at very attractive costs.

Dehydration

A potentially large market for membrane separators exists in dehydration. A hollow fiber membrane separator system is being developed by Permea Inc. to dehydrate water/alcohol mixtures including methanol, ethanol, isopropanol, and/or butanol. The system is not limited to azeotropic mixtures, but it will eventually be used in the dehydration of a wide variety of water/alcohol mixtures.⁷⁰ Although the first system investigated was ethanol/water, the work aims at separating water/organic mixtures in general.⁷¹ One such application is the removal of water from natural gas to bring it to pipeline specifications. The cellulose acetate systems also are useful for natural gas dehydration. A major problem is the loss of CH₄ during dehydration, and it appears that currently available membranes are not suitable in this regard.⁷² More water permeable and more selective systems are required.

Other Separations

Pervaporation is a special case of gas separations in that it is a concentration driven process. The feed mixture is supplied as a liquid to the membrane and the permeate is recovered as a vapor on the low pressure side of the membrane. Pervaporation finds application in dehydration as well as the separation of a variety of liquid mixtures. A discussion of pervaporation is beyond the scope of this review.

Liquid separations including reverse osmosis, ultra and microfiltration are pressure driven membrane processes. Membranes are broadly applied to effect separations in these areas. They are used in the making of potable water, in filtration and concentration in the food industries, in the electronic industries

and find wide application in medicine and health care. As with pervaporation, these membranes also are beyond the scope of this review. The reader is referred to an outstanding, up to date discussion of the membranes which are used for these processes as well as summary of the processes themselves by R.E. Kesting.⁷³

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