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Gas Separation Membranes

Polymeric and Inorganic

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Preface

Over the last decade, there have been growing interests in the advancement and applications of membrane-based gas separation technology to tackle various global issues and challenges. Tremendous progress has been made in the development of gas separation membranes based on both inorganic and polymeric materials for applications in a wide range of industrial sectors. Interestingly, new polymers and copolymers as well as advanced materials such as metal organic frameworks (MOF) and composite materials such as polymer inclusion membranes (PIM) have been introduced. Tremendous efforts have also been made to design and fabricate asymmetric membranes based on these emerging materials. Inorganic materials, particularly those in the nano-sized range, have been incorporated in polymeric membranes to prepare mixed matrix membranes (MMMs) with higher selectivity and permeability to surpass the Robeson upper boundary limits.

In this contribution, the authors give a contemporary and comprehensive review of the progress made in the field of gas separation membranes and membrane gas separation processes. This book covers innovative designs and inventions of new materials for polymeric and inorganic membrane preparation. It also emphasizes the recent advances made for the characterizations of membranes (atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction, electron spin resonance (ESR), and positron annihilation spectroscopy). Recent progresses in membrane module and system design are also included. Likely future R&D directions relevant to the development of gas separation membranes and gas separation processes are also highlighted. Since such a contribution is unprecedented, it is the main intention of the authors to promote this book as a small dictionary to cover a broad range of subjects related to gas separation membranes which include material, theory, preparation, characterization, membrane module, and system design and applications.

The book consists of the following chapters:

Chapter 1 briefly introduces the membrane gas separation processes. The process is outlined and compared with other gas separation processes to highlight the advantages and limitations of membrane gas separation processes.

Chapter 2 deals with the fundamental theory of gas transport through the membrane. Transport equations for porous and nonporous membranes are provided and discussed. Gas transport through rubbery and glassy polymers is distinguished and the transport models for the mixed matrix membrane are outlined.

Chapter 3 delivers the most important information where the membranes developed from different materials, including organic and inorganic, and the mixture of organic and inorganic materials in the composite MMMs are summarized. Carbon-based membranes are also outlined in this chapter. Developments and preparations of MOFs and membranes based on inorganic materials such as zeolites, silica, and metals are also described in this chapter.

Chapter 4 summarizes methods to prepare membrane materials and membranes. Membrane preparation method based on conventional phase inversion technique, hollow fiber spinning, and membrane surface modification by coating and other methods are presented thoroughly in this chapter.

Chapter 5 is a relatively short chapter. Various membrane modules, such as plate and frame, spiral wound, tubular, capillary, and hollow fiber, are briefly outlined and their advantages and disadvantages are shown. The concept of membrane contactors is also included in this chapter.

Chapter 6 includes various applications of membrane gas separation processes. The chapter also deals with membrane separation processes that are related to membrane gas separation, such as pervaporation and membrane distillation. The hybrid processes of membrane gas separation and other separation processes are also outlined in this chapter.

Finally, Chapter 7 summarizes membrane characterization methods which include macroscopic and spectrophotometric methods. Advanced characterization methods such as positron annihilation are also included in this chapter.

The authors believe that readers in universities, research institutions, and industry who are engaged in research on membranes for gas separation processes will benefit from the scientific knowledge contained in this book. It is therefore the authors' wish and ultimate goal to render general yet significant contributions to the further development of membrane science and technology particularly in membrane-based gas separation.

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Chapter 1

Introduction

1.1 Membrane Separation Processes

Membrane separation technology is based on the interaction of specific gases with the membrane material by a physical or chemical interaction. Membrane processes are considered to be visible and effective technologies for the separation of gaseous mixtures at the industrial scale due to their high efficiency, simple operation, and low cost. Membrane processes encompass a wide range of applications in fluid separation and are now considered a new and emerging separation technology for industrial applications. For several important separation processes, membrane technology has now reached its initial stage of maturity.

As a general definition, a membrane is regarded as a selective barrier between two phases. A membrane is usually a solid film, and occasionally a fluid film, of a small but observable thickness. It is characterized by flux and selectivity properties that provide functional transport across the barrier. The driving force for transport across the membrane is the chemical potential gradient, and the physical structure of the membrane determines the flux. The difference in flux between individual penetrant components determines membrane selectivity. In other words, membrane separation is a technology which selectively separates (fractionates) materials via pores and/or minute gaps in the molecular arrangement of a continuous structure. Membrane separations are often classified by pore size and by the separation driving force. Such classifications include: Microfiltration (MF), Ultrafiltration (UF), Ion-Exchange (IE), and Reverse Osmosis (RO).

1.2 Membrane-Based Gas Separation

Membrane-based gas separation can refer to any of a number of techniques used to separate gases, either to give multiple products or to purify a single product. A gas conforms to the shape of a container in which it is held and acquires a uniform density inside the container, even in the presence of *gravity* and regardless of the amount of substance in the container. If not confined to a container, gases, also known as vapors, will disperse into *space*. The *atoms* or *molecules* of matter in a gaseous state move freely among each other, and are, in most instances, packed more loosely than the molecules of the same substance in the *solid* or *liquid* state.

The most important characteristics of gases include:

1. *High compressibility*: External forces can compress a gas and decrease its volume; removing the external force allows the gas volume to increase.
2. *Thermal expandability*: When a gas sample is heated, its volume increases, and when it is cooled its volume decreases.
3. *Low viscosity*: Gases flow much easier than liquids.
4. *Low density*: Gas densities are on the order of grams per liter, whereas liquids and solids are grams per cubic cm—1,000 times greater.
5. *Infinite miscibility*: Gases mix in any proportion, such as in air, and in any combination.

Important variables that describe a gas are pressure (P), temperature (T), and volume (V).

In gas mixtures, the gas behavior depends on the number, not the identity, of gas molecules. The ideal gas equation applies to each gas individually and to the mixture as a whole. Beside these properties, all molecules in gas mixtures behave exactly the same way.

Membrane technology has received significant attention from various industrial sectors and academics in their research because the technology offers the most relevant means of reducing environmental problems and costs. The gas separation membrane field is highly competitive both between companies developing membrane technologies and with other gas separation technology developers. Benny D. Freeman [1] says “Membranes will have a large role to play in important environmental and energy-related processes such as the cost-effective purification of hydrogen and methane.”

Membranes are employed in:

- the separation of *nitrogen* or *oxygen* from air;
- separation of *hydrogen* from gases like *nitrogen* and *methane*;
- recovery of hydrogen from product streams of *ammonia* plants;
- recovery of hydrogen in *oil refinery* processes;
- separation of methane from the other components of *biogas*;
- *enrichment of air by oxygen* for medical or metallurgical purposes;
- enrichment of ullage by nitrogen in *inerting systems* designed to prevent fuel tank explosions;
- removal of *water vapor* from *natural gas* and other gases;

- removal of CO_2 from natural gas;
- removal of H_2S from natural gas;
- removal of *volatile* organic liquids (VOL) from air of exhaust streams.

Inorganic membranes are increasingly being explored to separate gas mixtures. Such membranes usually have much higher gas fluxes as compared to polymeric membranes. Furthermore, inorganic membranes are well-known to be more thermally and chemically stable than polymeric membranes.

1.2.1 Historical Background

In the middle of the eighteenth century, Nollet [2] discovered that a pig's bladder passes preferentially ethanol when it was brought into contact on one side with a water–ethanol mixture and on the other side with pure water. This was the first recorded study of membrane phenomena and the discovery of osmosis phenomena. Graham [3] systematically studied on mass transport in semipermeable membranes during diffusion of gases through different media and reported that natural rubber exhibits different permeabilities to different gases. Fick [4] interpreted diffusion in liquids as a function of concentration gradients and derived the Law of Mass Diffusion. Table 1.1 shows briefly the main events related to the development of gas separation membranes.

1.2.2 Scientific and Commercial Development of Membrane Processes

After the invention of a cellulose acetate high-flux asymmetric membrane by Loeb and Sourirajan for RO in 1962, and its application for gas separation that followed, intense development activities were started to produce high-performance membranes economically. Although gas separation membranes have been known for more than a century, only during the last 30 years have membranes been used on an industrial scale for gas separation (GS). Membrane-based GS has grown exponentially since the first industrial application of Prism membranes by Permea (Monsanto) for hydrogen separation from the purge gas stream of ammonia plants. The use of synthetic membranes commercially by industrial gas suppliers, petroleum producers, chemical companies, and refineries began in the early 1980s. Figure 1.1 shows the major events of industrial membrane gas separation that have occurred in the last 30 years.

The largest membrane plant for natural gas processing (CO_2 – CH_4 separation) installed in Pakistan in 1995 with spiral wound modules is included in Fig. 1.1, which is a clear example of the easy scale-up of membrane technology [50]. Table 1.2 shows the commercial applications and current major suppliers of membrane gas separation.

Table 1.1 Events in development of gas separation membranes

Scientist (year)	Events
Nollet (1752) [2]	Discovered that a pig's bladder passes preferentially ethanol when it was brought in contact on one side with a water–ethanol mixture and on the other side with pure water. This was the first recorded study of membrane phenomena and the discovery of osmosis phenomena
Graham (1829) [3]	Performed the first recorded experiment on the transport of gases and vapors in polymeric membranes
Fick (1855) [4]	Proposed a quantitative description of material transport through boundary layers
Graham (1866) [3]	Systematically studied on mass transport in semipermeable membranes during diffusion of gases through different media and reported that the natural rubber exhibits different permeabilities to different gases. Graham's Law of Mass Diffusion was proposed
Lord Rayleigh (1900) [5]	Determined relative permeabilities of oxygen, argon, and nitrogen in rubber
Benchohd (1907) [6]	Prepared nitrocellulose membranes with graded pore size structure. Defined the relationship between bubble point and temperature, surface tension, and pore radius
Knudsen (1908) [7]	Defined Knudsen diffusion
Shakespear (1917–1920) [8–10]	Found temperature dependency of gas permeability that is independent of partial pressure difference across membranes
Daynes (1920) [11]	Developed time lag method to determine diffusion and solubility coefficient
Barree (1939) [12]	Applied Arrhenius equation for permeabilities and diffusivities
Barrer and Strachan (1955) [13]	Studied the diffusion and the adsorption of permanent gases through compressed carbon powders
Loeb and Sourirajan (1962, 1964) [14, 15]	Developed RO membrane based on cellulose acetate, which provided high fluxes at moderate hydrostatic pressures. Found dried RO membrane can be used for gas separation
Vieth and Sladek (1965) [16]	Proposed models for sorption and diffusion in glassy polymers
Stern et al. (1969) [17]	First to systematically study the transport of gases in high polymers at elevated temperatures
Cynara and Separex Company (1982–1983) [18]	Developed cellulose acetate membranes for the separation of CO ₂
Henis and Tripodi (1980) (Monsanto, Inc.) [19]	The first major product Monsanto Prism A [®] membrane for hydrogen separation
Gies (1986) [20]	All-silica zeolite deca-dodecasil 3R (DD3R)
Paul and Kemp (1973) [21]	First reported MMMs for gas separation
Permea PRISM membrane (1980) [22]	First commercialized gas separation membrane
Kulprathipanja et al. (1988) [23, 24]	Mixed matrix systems of polymer/adsorbent might yield superior separation performance to that of pure polymeric system
Robeson (1991) [25]	Proposed upper bound between gas permeability and selectivity
Iijima (1991) [26]	Discovery of carbon nanotubes (CNTs)

(continued)

Table 1.1 (continued)

Scientist (year)	Events
Suda and Haraya (1997) [27]	Prepared carbon molecular sieve (CMS) membrane, prepared from pyrolyzation of polyimide, and permeabilities of different gases were studied ($H_2 > He > CO_2 > O_2 > N_2$)
McKeown (1998) [28]	Polymers of intrinsic microporosity (PIMS)
Yang et al. (1999) [29]	Proposed gas separation by zeolite membranes on the basis of different adsorption properties
Caro et al. (2000) [30]	Proposed gas separation by zeolite membranes on the basis of differences in the molecular size and shape
Mahajan and Koros (2002) [31–33]	Application of 4A zeolite in polymers for MMMs membrane preparation
Skoulidas et al. (2002) [34]	Made simulations for both self- and transport diffusivities of light gases such as H_2 and CH_4 in carbon nanotubes and zeolite
Ackerman et al. (2003) [35]	Made simulations for Ar and Ne transport through CNTs
Hinds et al. (2004) [36]	Tried to incorporate aligned CNTs into the polymer matrix and proposed the potential of the nanotubes' inner cores to act as a channel for gas transport
McKeown et al. (2005) [37]	PIMS are excellent performers for gas separation
Chen and Sholl (2006) [38]	Predicted selectivity and flux of CH_4 – H_2 separation using single-walled carbon nanotubes as membranes
Gonzo et al. (2006) [39]	Applied Maxwell equation to the performance of mixed matrix membranes (MMMs)
Cong et al. (2007) [40]	Used BPO _{ap} membranes using both pristine single-wall CNTs (SWNTs) and multi-wall CNTs (MWNTs). Composite membranes increased in CO_2 permeability compared to the corresponding pure-polymer membrane
Husain and Koros (2007) [41]	Increased hydrophobicity of the zeolite surface by capping surface hydroxyls with hydrophobic organic chains via Grignard-type reactions (MMMs preparation)
Himeno et al. (2007) [42]	α -alumina surface coated with DDR zeolite for gas separation
Bergh et al. (2008) [43]	Separation and permeation characteristics of a DDR zeolite membrane (gas separation)
Yoo, Lai, and Jeong group (2009) [44]	The first MOF membranes were reported
Li et al. (2010) [45]	SAPO-34 zeolite membranes for CO_2 – CH_4 separation
Aroon et al. (2010) [46]	Fabricated PI/Raw-MWCNTs and PI/Chitosan functionalized MWCNTs (PI/C-f-MWCNTs) MMMs membranes for gas permeation
Mustafa et al. (2010) [47]	Fabricated MMMs consisting of functionalized carbon nanotubes (CNTs) and polyethersulfone (PES) for biogas purification. The PES-modified carbon nanotubes membranes had increased permeability and CO_2 – CH_4 selectivity
Betard et al. (2012) [48]	Metal–organic framework (MOF) membrane by stepwise deposition of reactants
Li et al. [49]	Reported the first mixed matrix composite membrane made of commercially available poly(amide-b-ethylene oxide) (Pebax®1657, Arkema)

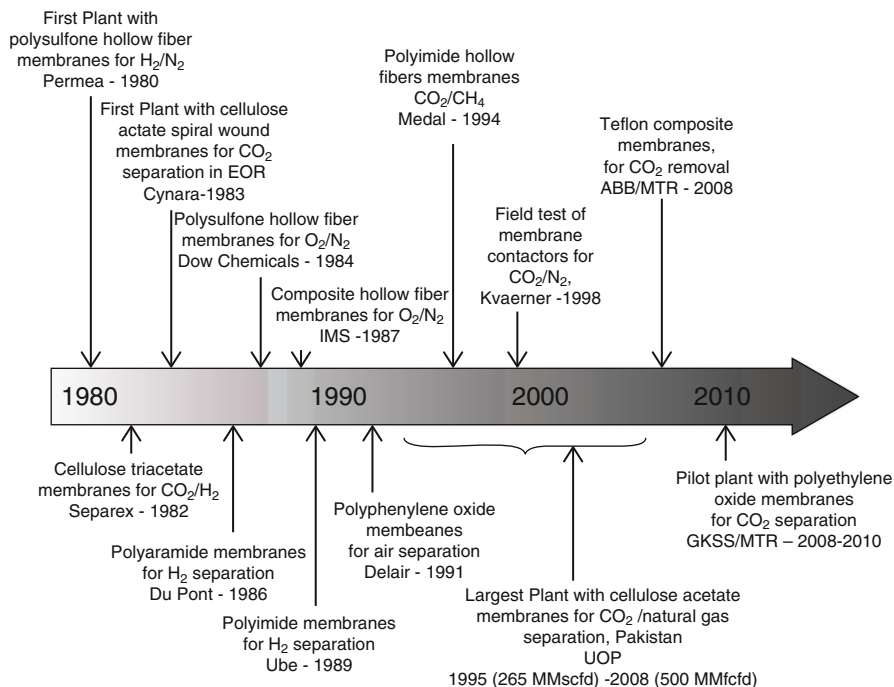


Fig. 1.1 Milestones in the industrial application of membrane gas separation systems

Table 1.2 Commercial applications and current major suppliers of membrane gas separation

Gas separation	Application	Supplier
O_2-N_2	Nitrogen generation Oxygen enrichment	Permea (Air Products) Generon (IGS), IMS (Praxair), Medal (Air Liquid), Parker Gas Separation, Ube
H_2 -hydrocarbons	Refinery hydrogen recovery	Air Products, Air Liquid Praxair, Ube
H_2-CO_2	Syngas ratio adjustment	As above
H_2-N_2	Ammonia Purge gas	As above
CO_2-CH_4	Acid gas treatment enhanced oil recovery landfill gas upgrading	Cynara (NATCO), Kvaerner, Air Products, Ube, UOP (Separex)
H_2S -hydrocarbon	Sour gas treating	As above
H_2O -hydrocarbon	Natural gas dehydration	Kvaerner, Air Products
H_2O -air	Air dehydration	Air Products, Parker Balxston Ultratroc, Praxair
Hydrocarbons-air	Pollution control hydrocarbon recovery	Borsig, MTR, GMT, NKK
Hydrocarbons from process streams	Organic solvent recovery Monomer recovery	Borsig, MTR, GMT, SIHI

1.3 Advantages of Membrane Processes

There are many significant advantages of using membranes for industrial processes. In 2002, an ad hoc committee at the International Conference on Membranes and Membrane Processes (ICOM 2002) prepared a report on membrane technology perspectives and needs. The following advantages to membrane processes are listed.

1. Do not involve phase changes or chemical additives.
2. Simple in concept and operation.
3. Modular and easy to scale up.
4. Greater efficiency for raw materials use and potential for recycling of by-products.
5. Equipment size may be decreased.

Furthermore another advantage for membrane devices for gas separation is that they usually operate under continuous steady-state conditions.

Baldus and Tillmman [51] described simple rules for gas separation by membranes to be favorable:

1. When moderate purity recovery is sufficient.
2. When the components to be separated are a considerable amount.
3. When the feed gas is available at the necessary pressure, or when the residue stream is needed at high pressure.
4. When the feed gas contains no substances harmful to the membrane.
5. When a membrane with sufficient selectivity is available.

The choice of membrane material for GS applications is based on specific physical and chemical properties, since a material should be tailored in an advanced way to separate particular gas mixtures. Membrane material should be robust (i.e., long-term and stable) for GS process.

The GS properties of membranes depend upon [52]:

1. Material (permeability, separation factors).
2. Membrane structure and thickness (permeance).
3. Membrane configuration (e.g., flat, hollow fiber).
4. Module and system design.

There are, however, some practical problems or weaknesses with membranes [52]. Membrane performance generally decreases with time. This decrease can be caused by concentration polarization and fouling. Concentration polarization occurs because of limited permeation of certain species. These species will become higher in concentration directly adjacent to the membrane, reducing permeate transport. The magnitude of this effect depends on the type of species used and the flow setup. However, concentration polarization is not a very severe problem for gas separation membranes. Fouling is due to the adsorbed species to the membrane surface as well as inside the pores. This fouling limits or even blocks the permeation of the gas species. Notable fouling species of gas separation membranes are sulfur-containing

compounds such as H_2S and SO_2 . To mitigate the effects of fouling, membranes can be cleaned by heating and purging with non-adsorbing gases. Small particles can best be removed from the feed flow using a filter.

Membrane deterioration may also be caused by compaction, i.e., a reduction in pore size due to pressurization. This phenomenon occurs with polymeric membranes and is usually irreversible. Most often the pore size does not return to its original value when pressure is decreased.

Other practical considerations come into play when making choices to get the optimal membrane system design. One of them is the effect of the thermal stresses on structural integrity. If temperature variation occurs, several parts of the system may experience different degrees of expansion. If there is no room to accommodate these differences in expansion, the system can be seriously damaged. Beside this, the pressure drop over a membrane unit (not the membrane itself) is directly proportional to the module length. To reduce the pressure drop, it would be advantageous to apply shorter modules; however, shorter modules will require more seals.

Another issue to be considered is the ease in starting up and shutting down the unit. A system design needs to accommodate these effects.

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Chapter 2

Fundamentals of Gas Permeation Through Membranes

2.1 Gas Permeation Through Membranes

Gas permeation is a technique for fractionating gas mixtures by using nonporous polymer membranes having a selective permeability to gas according to a dissolution–diffusion mechanism. The membrane gas separation process is driven by a pressure difference across the membrane. The membrane may be either in the form of a flat sheet or a hollow fiber. In general, hollow fibers are preferred as they achieve a higher effective membrane area within a given module volume.

2.1.1 Technical Terms Used in Gas Permeation Membrane Science

To understand the fundamentals of membrane gas separation, one should be familiar with some laws, processes or words that are commonly used.

Graham's law (Thomas Graham in 1848): Graham's law states that the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight. This formula can be written as:

$$Rate_A / Rate_B = (M_B / M_A)^{1/2} \quad (2.1)$$

where $Rate_A$ is the rate of diffusion of the first gas (volume or number of moles per unit time), $Rate_B$ is the rate of diffusion for the second gas, M_A is the molar mass of gas A, and M_B is the molar mass of gas B.

Fick's first law: Fick's first law relates the diffusive flux to the concentration under the assumption of steady state. It postulates that the flux goes from regions of high

concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative).

Fick's second law: Fick's second law predicts how diffusion causes the concentration to change with time.

Henry's law: Henry's law is one of the gas laws formulated by William Henry in 1803. It states that at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

Diffusion: Diffusion is the process by which molecules spread from areas of high concentration, to areas of low concentration. When the molecules are even throughout a space, that space is said to be in "EQUILIBRIUM". There are three main types of diffusion through a membrane: Knudsen diffusion, molecular sieving/molecular diffusion, and solution diffusion (Fig. 2.1).

Knudsen diffusion: Knudsen diffusion may take place in a microporous inorganic membrane or through pinholes in dense polymeric membranes. It is a means of diffusion that occurs in a long pore with a narrow diameter (2–50 nm) because molecules frequently collide with the pore wall. This mode of transport is important when the mean free path of the gas molecules is greater than the pore size. In such situations the collisions of the molecules with the pore wall are more frequent than the collision between molecules. Separation selectivities with these mechanisms are proportional to the ratio of the inverse square root of the molecular weights. This mechanism is often prominent in macroporous and mesoporous membranes [1].

Molecular diffusion: In molecular diffusion, the mean free path of the gas molecules is smaller than the pore size and diffusion occurs primarily through molecule-molecule collisions. In molecular diffusion, the driving force is the composition gradients. If pressure gradient is applied in such pore regimes, bulk (laminar) flow occurs, as given by Poiseuille's equation. Such transport is often referred to as *Poiseuille flow* or viscous flow [1].

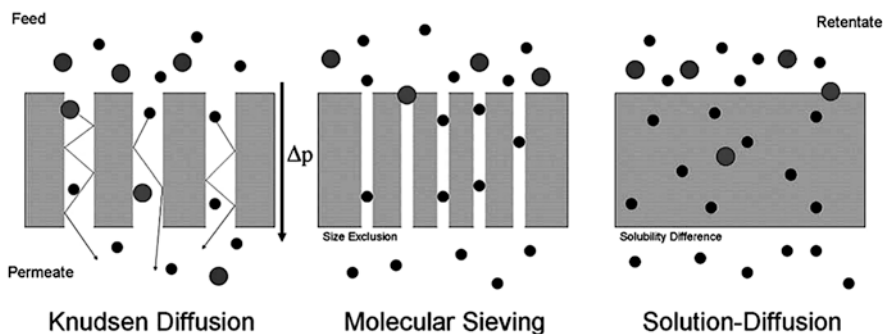


Fig. 2.1 Schematic representation of three of the different possible mechanisms for membrane gas diffusion—Knudsen diffusion, molecular sieving, and solution diffusion/surface diffusion

Surface diffusion/solution diffusion: This diffusion occurs when the permeating species shows a strong affinity for the membrane surface and adsorb along the pore walls. In this mechanism, separation occurs due to the differences in the amount of adsorption of the permeating species. Surface diffusion often occurs in parallel with other transport mechanisms such as Knudsen diffusion.

Configurational or micropore diffusion: This type of diffusion may be considered surface diffusion in the limit where the pore size becomes comparable to the molecular size. In this mechanism, diffusion is perceived as an “activated” process and separation is a strong function of molecular shape and size, pore size, and interactions between the pore wall and gas molecules. This process mainly works in microporous zeolite/zeolitic membranes and carbon molecular sieves.

Concentration gradient: Concentration gradient is the difference between concentrations in a space.

Pores: Pores are miniature openings or passageways in the membrane. Table 2.1 shows the classification of pore sizes in membranes.

Microporous membrane: A thin, porous film or hollow fiber having pores ranging from 0.01 to 10 μm

Capillary condensation: Capillary condensation is one form of surface flow where one of the gases condensable. The pores are completely filled by the condensed gas at certain critical relative pressures, especially in mesopores and small macropores. Due to the formation of menisci at both ends of the pore, transport can take place through hydrodynamic flow driven by a capillary pressure difference between the two ends. This mechanism of gas transport can be thought of as the ultimate limit of the process of adsorption as pressure is increased. In theory, capillary condensation can be used to achieve very high selectivities because the formation of the liquid layer of the condensable gas will block and prevent the flow of the non-condensable gas.

Free volume: The free-volume in a polymer is the space not occupied by polymer molecules. The occupied volume is generally taken to include the van der Waals volume multiplied by a factor (typically 2.2) to take into account that even for a perfect crystal at absolute zero, there is a limit to the packing density achievable. On this basis, fractional free volume, f_v , can be calculated as [2].

$$f_v = (V - 1.3V_w) / V \quad (2.2)$$

Table 2.1 IUPAC (International Union of Pure and Applied Chemistry) classification of pores as a function of their size

Microporous		Mesopores	Macropores
<2 nm			
Ultra-micropores	Super-micropores	2–50 nm	>50 nm
<0.7 nm	>0.7 nm		

where V is the specific volume of the polymer (i.e., reciprocal of density) and V_w is the specific van der Waals volume. This equation is widely used in the membrane literature. However, it should be noted that in other contexts the occupied volume is taken also to include the effects of molecular vibrations, and in such cases is temperature dependent.

Selectivity: This term means that the membrane lets in some compounds while keeping others out. For example, a cell membrane can keep out ions while letting in small hydrophobic compounds. The best measure of the ability of the membrane to separate two gases, A and B , is the ratio of their permeabilities, $\alpha_{A/B}$, also called the membrane selectivity.

Mean free path: The motion of a molecule in a gas is complicated. Besides colliding with the walls of the confinement vessel, the molecules collide with each other. The mean free path is the average distance travelled by a molecule between collisions with another molecule. The mean free path of a molecule is related to its size; the larger its size the shorter its mean free path.

Kinetic diameter: Kinetic diameter of a gaseous molecule can be calculated by following equations based on ideal gas laws. Table 2.2 shows the molecular weight and kinetic diameter (\AA) of a few gases encountered in membrane gas separation.

$$l = 1 / \pi d^2 n \quad (2.3)$$

where l is the mean free path length of the molecule, d is the kinetic diameter of the molecule and n is number of molecules per unit volume.

Molecular sieve: Molecular sieve is a material with very small holes of precise and uniform size. These holes are small enough to block large molecules while allowing small molecules to pass. Many molecular sieves are used as desiccants. Some examples include activated charcoal and silica gel. According to IUPAC notation, microporous materials have pore diameters of less than 2 nm (20 \AA) and macroporous materials have pore diameters of greater than 50 nm (500 \AA); the mesoporous category thus lies in the middle with pore diameters between 2 and 50 nm (20–500 \AA) [3].

Molecular sieve effect: With respect to porous solids, the surface associated with pores communicating with the outside space may be called the *internal surface*. Because the accessibility of pores may depend on the size of the fluid molecules, the extent of the internal surface may depend on the size of the molecules comprising

Table 2.2 Molecular weight and kinetic diameter (\AA) of gases encountered in membrane gas separation

Molecule	Molecular weight	Kinetic diameter (\AA)
CO ₂	44	3.3
O ₂	32	3.46
N ₂	28	3.64
H ₂ O	18	2.65
CH ₄	16	3.8
H ₂	2	2.89

the fluid, and may be different for the various components of a fluid mixture. This effect is known as the molecular sieve effect.

Glass transition temperature: The glass transition temperature is a function of chain flexibility. The glass transition occurs when there is enough vibrational (thermal) energy in the system to create sufficient free-volume to permit sequences of 6–10 main-chain carbons to move together as a unit. At this point, the mechanical behavior of the polymer changes from rigid and brittle to tough and leathery—the behavior we define as “plastic behavior”. Actually, the glass transition temperature is more important in plastics applications than the melting point, because it tells us a lot about how the polymer behaves under ambient conditions. The melting temperature is often referred to as the “first-order transition”—that is where the polymer changes state from solid to liquid. Technically, only crystalline polymers have a true melting point, the temperature at which the crystallites melt and the total mass of plastic becomes amorphous. Amorphous polymers do not have a true melting point; however, they do have a first-order transition where their mechanical behavior transitions from a rubbery nature to a viscous rubbery flow [4].

2.1.2 Membrane Separation Principles

Membrane separation methods can be divided into classes according to their separation characteristics: (i) separation by sieving action; (ii) separation due to a difference in affinity and diffusivity; (iii) separation due to a difference in charge of molecules; (iv) carrier-facilitated transport; and (v) the process of (time-)controlled release by diffusion.

Gas is made to pass through the membrane by applying a pressure difference on either side of the membrane. This pressure difference causes a difference in dissolved gas concentration between the two faces of the membrane and, hence, a diffusion gas flows through the membrane. Gas permeation through the membrane occurs with the following three steps:

1. Absorption of the permeating species into the polymer.
2. Diffusion through the polymer.
3. Desorption of the permeating species from the polymer surface and removal.

The gas permeation is affected by:

1. Solubility and diffusivity of the small molecule in the polymer.
2. Chain packing and side group complexity, polarity, crystallinity, orientation, fillers, humidity and plasticization.

Permeance: The state or quality of a material or membrane that causes it to allow liquids or gases to pass through it. The productivity of a gas separation membrane is expressed in terms of its permeance the amount of permeate that passes through a certain membrane area in a given time for a particular pressure difference.

Values of permeance are often quoted in units of GPU [1 GPU = 10^{-6} cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹].

Permeability: Permeance multiplied by the thickness of the membrane gives permeability P (sometimes called permeability coefficient). It is a characteristic of the material. In principle, permeability is independent of membrane thickness for a homogeneous membrane, but in practice values can depend both on thickness of the membrane and on its history. Values of permeability are often quoted in units of Barrer [1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ = 3.35×10^{-16} mol m m⁻² s⁻¹ Pa⁻¹]. Permeability measurements are frequently made on thick (20–100 μm) homogeneous membranes, but for practical application a very thin active layer (<1 μm) is desired in order to increase the permeance. For a suitable polymer, a so-called phase inversion process may be used to generate asymmetric membranes with a thin, dense surface layer and a highly porous sublayer. Alternatively, a thin separating layer may be coated onto a porous substrate, giving a composite membrane [2].

The gas permeability of the membrane can be measured also by means of two chamber cell [5], which is discussed in detail in Chap. 7.

Different mechanisms may be involved in the transport of gases across membranes depending on their physical properties such as porous, non-porous, glassy, and rubbery.

2.1.3 Gas Permeation Through Porous Membranes

For gas separation, the selectivity and permeability of the membrane material determines the efficiency of the gas separation process. Based on flux and selectivity, a membrane can be classified broadly in two classes: (1) porous and (2) nonporous.

A porous membrane is a rigid, highly voided structure with randomly distributed interconnected pores. The separation of materials by porous membrane is mainly a function of the permeant character and membrane properties, such as the molecular size of the membrane polymer, pore size, and pore size distribution. A porous membrane is very similar in its structure and function to a conventional filter. In general, only those molecules that differ considerably in size can be separated effectively by microporous membranes. Porous membranes for gas separation do exhibit very high levels of flux but inherit low selectivity values. Microporous membranes are characterized by the average pore diameter d , the membrane porosity, and tortuosity of the membrane. Porous membranes can be utilized for gas separation. The pore diameter must be smaller than the mean free path of gas molecules. Under normal condition (100 kPa, 300 K) diameter is about 50 nm. The gas flux through the pore is proportional to the molecule's velocity, i.e., inversely proportional to the square root of the molecule mass (Knudsen diffusion). Flux through a porous membrane is much higher than through a nonporous one, 3–5 orders of magnitude. Separation efficiency is moderate—hydrogen passes four times faster than oxygen.

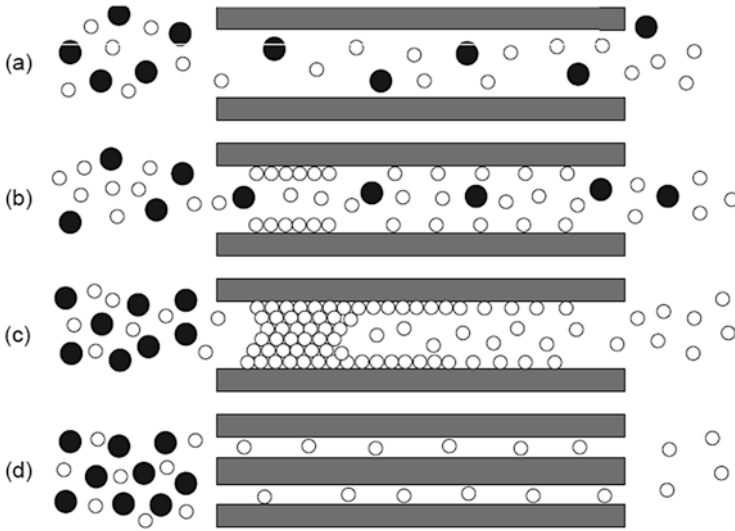


Fig. 2.2 Four types of diffusion mechanism

Four types of diffusion mechanism can be utilized to effect separation by porous membranes (see Fig. 2.2) [6].

The four diffusion mechanisms above are:

1. Knudsen (or free molecule) diffusion.
2. Surface diffusion.
3. Capillary condensation.
4. Molecular sieving.

In some cases, molecules can move through the membranes by more than one mechanism. Knudsen diffusion gives relatively low separation selectivity compared to surface diffusion and capillary condensation. Shape selective separation or molecular sieving can yield high selectivities. The separation factor of these mechanisms depends strongly on the pore size distribution, temperature, pressure and interaction between gases being separated, and the membrane surfaces.

Knudsen (or free molecule) diffusion: The Knudsen number (Kn) is defined as the ratio of the mean free path of the gas molecules (average distance between collisions) (λ) and a representative physical length scale (e.g., the pore radius), (r).

$$K_n = \lambda / r \quad (2.4)$$

The mean free path is given by

$$\lambda = (\eta / P) \left\{ (\pi k_B T / 2M) \right\}^{1/2} \quad (2.5)$$

where η is the viscosity of the gas, k_B the Boltzmann constant, T the temperature, M the molecular weight, and P the pressure.

If the pore radius is used as the representative physical length scale, the mean free path lengths are substantially higher than the pore radius when the Knudsen number is larger than 10. The result is that mainly the lighter molecules permeate through the pores. Selectivity is limited and can be calculated with the square root of the ratio of the molar masses of the gases involved. The smaller the K_n , the larger the pores become (relative to the mean free path of the gas molecules). For Knudsen numbers < 1 the dominant transport mechanism is *viscous flow*, which is non-selective. When K_n is inbetween, the permeation of gas through porous membrane consists of Knudsen diffusion and Poiseuille flow [7].

For the Knudsen flow, the molar flow rate of gas, G_{Kn} , through a pore with a radius of r is given by

$$G_{Kn} = (8r(P_1 - P_2)) / (3L(2\pi MRT)^{1/2}) \quad (2.6)$$

where P_1 and P_2 are pressures on high pressure and low pressure side of the membrane, and L is the pore length.

For the viscous flow, the molar flow rate of gas, G_{vis} , is given by

$$G_{vis} = r_2 (P_1 - P_2) / 16L\mu RT \quad (2.7)$$

where μ is the gas viscosity.

Knudsen separation can be achieved with membranes having pore sizes smaller than 50 nm. Table 2.3 presents the ideal separation factors of various pairs of gases based on Knudsen flow. However, the actual separation factor is found to be smaller. This is attributed to back diffusion, to non-separative diffusion, concentration polarization on the feed or on the permeate side, and the occurrence of viscous flow (in large pores).

Surface diffusion (Fig. 2.2b) can occur in parallel with Knudsen diffusion. Gas molecules are adsorbed on the pore walls of the membrane and migrate along the surface. Surface diffusion increases the permeability of the components adsorbing more strongly to the membrane pores. At the same time, the effective pore diameter is reduced. Consequently, transport of non adsorbing components is reduced and selectivity is increased. This positive contribution of surface diffusion only works for certain temperature ranges and pore diameters.

Table 2.3 Calculated separation factors based on Knudsen flow of selected binary gas mixtures

Gas pair	Separation factor
H ₂ /N ₂	3.73
H ₂ /CO	3.73
H ₂ /H ₂ S	4.11
H ₂ /CO ₂	4.67
H ₂ /SO ₂	5.64
N ₂ /O ₂	1.07
O ₂ /CO ₂	1.17

Capillary condensation (Fig. 2.2c) occurs if a condensed phase (partially) fills the membrane pores. If the pores are completely filled with condensed phase, only the species soluble in the condensed phase can permeate through the membrane. Fluxes and selectivities are generally high for capillary condensation. The appearance of capillary condensation, however, strongly depends on gas composition, pore size, and uniformity of pore sizes.

Molecular sieving (Fig. 2.2d) occurs when pore sizes become sufficiently small (3.0–5.2 Å), leading to the separation of molecules that differ in kinetic diameter: the pore size becomes so small, that only the smaller gas molecules can permeate through the membrane.

There are several ways to prepare porous polymeric membranes, such as solution casting, sintering, stretching, track etching, and phase separation. The final morphology of the membrane obtained will vary greatly, depending on the properties of the materials and process conditions utilized.

Various mechanisms have been distinguished to describe the transport in membranes: transport through bulk material (dense membranes); Knudsen diffusion in narrow pores; viscous flow in wide pores or surface diffusion along pore walls.

2.1.4 Gas Permeation Through Nonporous Membranes

In dense polymeric membranes, solution diffusion is widely accepted to be the main mechanism of transport [1]. This mechanism is generally considered to be a three-step process. In the first step the gas molecules are adsorbed by the membrane surface on the upstream end. This is followed by the diffusion of the gas molecules through the polymer matrix. In the final step the gas molecules evaporate on the down-end stream.

Sir Thomas Graham [8] proposed the transport of gases in dense, nonporous polymers based on the solution-diffusion mechanism. Under the driving force of a pressure difference across a membrane, penetrant molecules dissolve in the upstream (or high pressure) face of a membrane, diffuse across the membrane, and desorb from the downstream (or low pressure) face of the membrane. Thus, according to the solution-diffusion model, the permeation of the module is controlled by two major parameters: diffusivity coefficient (D) and solubility coefficient (S) (see Eq. (2.8)). Diffusion is the rate-controlling step in penetrant permeation. The rate-controlling step in diffusion is the creation of gaps in the polymer matrix sufficiently large to accommodate penetrant molecules by thermally stimulated, random local segmental polymer dynamics [9]. The permeation of a gas through the dense polymer (membrane) can be described by using the sorption–diffusion theory [10].

The productivity of a membrane is defined by the permeability of the gas through the membrane. The permeability of a gas A is given by:

$$P_A = D_A S_A \quad (2.8)$$