MEDARRAY, INC.

# Membrane Gas Exchange

**Using Hollow Fiber Membranes to Separate Gases from Liquid and Gaseous Streams**

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Membranes have emerged as an attractive approach to separating materials in many industries, from medical to chemical to water. When formed into hollow fiber tubes, membranes deliver highly efficient operation in a small footprint. The advantages are numerous: low energy requirements, simplicity of operation, and high specificity. This paper explains the principles behind membrane transport and identifies applications where hollow fiber membranes, and dense membranes in particular, are valuable.

*A membrane is a layer of material that allows one substance to pass through it while blocking another, in the presence of a driving force.*

## What is a Membrane?

A membrane is a layer of material that allows one substance to pass through it while blocking another. This selectivity may be based on particle size, phase of material (liquid vs. gas), or solubility. Additionally, the separation occurs in the presence of a driving force, such as a difference in pressure, temperature or concentration between one side of the membrane and the other.

### Types of Hollow Fiber Membranes

*Dense Membranes:* A dense membrane is solid material, without pores or voids. Examples include polymers (such as silicone), metals (such as palladium), and ceramics. Dense membranes allow substances to pass through them by a process of solution and diffusion, in which the substance dissolves into the membrane and passes through it to the other side.

*Porous Membranes:* A porous membrane has pores, or holes, of a particular size or range of sizes. These membranes separate on the basis of size exclusion: substances larger than the pores do not pass through, while those smaller than the pores do.

*Asymmetric Membranes:* An asymmetric membrane is comprised of a single material, often porous, that has differing characteristics (such as pore size) from one side to the other. This feature allows "tighter" selectivity to occur at the surface and less restriction as a material passes through the membrane matrix.

*Composite Membranes:* Composite membranes are made up of more than one material, often a thin selective layer of a dense material applied to a porous support layer. Generally, the goal is to make the selective layer as thin as possible and the support layer as porous as possible to improve the transfer of the permeating substance.

## Selectivity and Transfer in Dense Membranes

*Permeation of a gas through a dense membrane is directly proportional to the solubility and rate of diffusion of the gas. Mass transport depends on the amount of surface area of the membrane and its thickness*

As a representative dense polymeric membrane, silicone (polydimethyl siloxane, or PDMS), is among the most gas permeable materials available. Gases permeate silicone by a solution/diffusion mechanism, whereby the rate of gas permeation is directly proportional to the product of solubility of the gas, and the rate of diffusion of the dissolved gas in silicone.

The *permeability coefficient* is a parameter defined as the transport flux of a gas (rate of gas permeation per unit area), per unit transmembrane driving force, per unit membrane thickness.

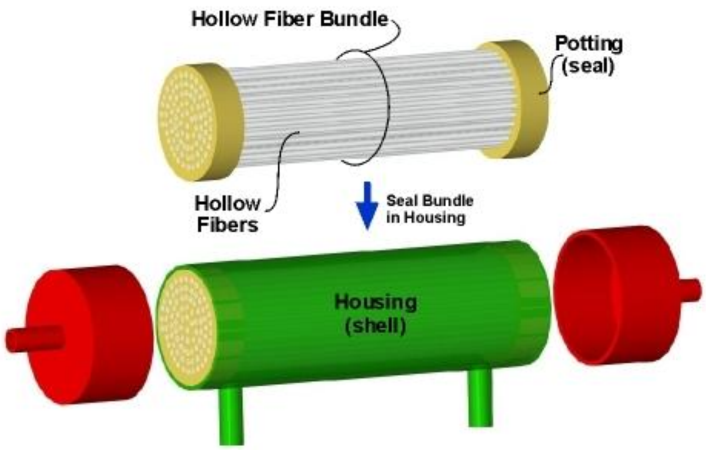
Because silicone is dense (and not porous) liquids cannot grossly transfer through the membrane, enabling its use in liquid contacting applications with all compatible liquids regardless of surface tension. Moreover, the dense membrane also provides a means for separating gases due to the permeability difference between gases in silicone.

## Construction of Hollow Fiber Modules

Hollow fibers are typically packaged in *membrane modules* in which thousands of hollow fibers are bundled in a very compact volume and sealed or *potted* within a housing as shown in the figure below. Consequently, the sum of the surface area of each individual hollow fiber constitutes the total membrane area for the module, and it becomes apparent how it is possible to achieve high membrane surface densities with hollow fibers.

Membrane modules will typically have an inlet and an outlet port in "communication" with the inside of all the hollow fibers (also known as *tube side*) which are manifolded at both ends of the fiber bundle. Similarly the membrane modules will have one or more ports in fluid communication to the outside of the hollow fibers or the *shell side*.

*Hollow fiber membrane modules contain high membrane surface area densities, in some cases reaching 10,000 $m^2$ per $m^3$*




Therefore the rate of gas transfer across the membrane is proportional to the gas permeability coefficient, the membrane surface area, the trans-membrane gas partial pressure difference, and inversely proportional to the membrane thickness. Thus gas transfer across a membrane increases with increased gas permeability coefficient, increased surface area, increased transmembrane gas partial pressure and decreased membrane thickness.

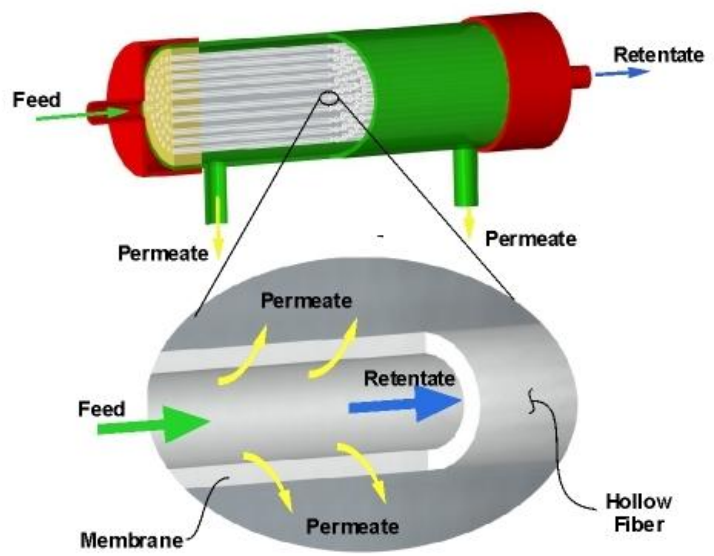
## Hollow Fiber Operation within a Module

Configuring membranes into hollow fibers enables the packaging large amounts of membrane surface area in very compact volumes. Moreover, hollow fibers constitute a self supported, inherently stable membrane structure that can tolerate high pressure differences between the inside and outside of the hollow fiber.

Depending on the type of material, membrane modules can be used for liquid contacting and gas separation applications. The side of the hollow fibers (shell or tube) in which a gas or liquid should flow will depend on the specific application for the membrane module, and is selected to maximize membrane module performance.

*Gases permeate through a dense membrane at differing rates, which allows their separation*

For example, as shown in the figure below, in gas separation a *feed* mixture of gases enters the membrane module through the inlet port to the tube side and flows through the inside of the hollow fibers. The gas species in the mixture with higher permeability will transfer at a greater rate across the walls of hollow fibers leaving behind the less permeable species. The transferred gas is referred to as the *permeate*. In the shell side, a vacuum can be applied or a *sweep* gas (or liquid) can flow therein to carry away the permeate. Exiting the outlet of the tube side is the *retentate* which constitutes a gas mixture with a higher concentration of the less permeable gas species.




**Gas Separation**. Although the permeability ratio for two gases in a binary gas mixture provides a gross estimate for the ratio of permeate flow for the two gases, actual measurements show that the interaction of a gas mixture on the membrane can affect permeation rates. Moreover feed and permeate pressures can also affect permeation rates as the membrane structure can change under pressure. The **separation factor** is a membrane property that is useful in determining permeation rates for mixtures of gases under certain operating conditions.

## Liquid Contacting Applications

*Dense membranes do not have pores to clog, which allows their use in liquid contacting applications*

Liquid contacting is the use of membrane modules for the transfer of gases to and from liquids. Dense membranes do not have pores to clog, and do not leak (or "wet") as porous membranes can do.

This feature makes dense membranes very useful in removing dissolved gases from liquids. Oxygen and carbon dioxide dissolved in water, for example, can adversely affect many processes. Delivering process water with very low levels of dissolved gases leads to longer equipment life, reduced maintenance, and improved performance. Certain membranes, such as silicone, can even be used in contact with low surface tension liquids.

Adding gases to liquids can be desirable as well. Applications such as carbonating liquid (adding carbon dioxide) or oxygenating blood during surgery can be performed with certain membranes. In life sciences, conditioning the liquid media in cell culture can be done in a closed loop using membranes. This can avoid subjecting sensitive cells to higher shear stress from impellers or bubble rupture, and reduce foaming.

Water vapor can also permeate through certain membranes, allowing for either humidification or dehumidification of an enclosed space.

## Pervaporation

Pervaporation is a membrane separation process that typically uses a vacuum to facilitate the transfer of a vaporizing compound through a dense membrane. It is most often used to separate liquids that have similar boiling points but different rates of transfer through the membrane material.

## Gas Separation Applications

Gas separation is accomplished by dense membranes due to the differences among gases in their ability to permeate through the membrane material, not based on their molecular sizes. The driving force of the gas transfer is the partial pressure differential of each gas across the membrane.

Volatile organic compounds (VOC's) in air or liquid streams pose a challenge for separation approaches. Recovering and recycling such compounds and solvents may be desirable economically, as many have significant market value or may be reused in the process. Decreased discharge and lower consumption of chemicals reduces operating costs. In addition, increasingly stringent regulatory requirements make recovery of VOC's more and more important.

Dense membranes can be used in the separation and recovery of VOC's due to the unique characteristics of the material. Certain VOC's permeate the membrane very well, and can be effectively removed from the feed stream. In a pervaporation system, the VOC vapors are permeated from the feed stream; in a vapor recovery system, a vacuum or an inert sweep gas is used to create the driving force across the membrane.

## For More Information

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## Will a Silicone Membrane Work in Your Application?

Consult the table below to identify the gases you are interested in separating or concentrating, by estimating the separation factor. Using the Silicone Permeability Coefficient, calculate the ratio of the higher figure to the lower; depending on the application, silicone membrane may deliver desirable results with separation factors as low as 2.

### *Example 1: Hydrogen Sulfide and Methane*

| | | |
|---|---|---|
| Hydrogen Sulfide Coefficient | 10000 | |
| Methane Coefficient | 950 | |
| Ratio | 10000/950 = 10.5 | Excellent candidates for separation |

### *Example 2: Hexane and Butane*

| | | |
|---|---|---|
| Hexane Coefficient | 9400 | |
| Butane Coefficient | 9000 | |
| Ratio | 9400/9000 = 1.04 | Unlikely candidates for separation |

| GAS NAME | FORMULA | SILICONE PERMEABILITY COEFFICIENT (Barrer)* |
|---|---|---|
| Acetone | $C_3H_6O$ | 5860 |
| Ammonia | $NH_3$ | 5900 |
| Argon | Ar | 600 |
| Benzene | $C_6H_6$ | 10800 |
| Butane | n-$C_4H_{10}$ | 9000 |
| Carbon dioxide | $CO_2$ | 3250 |
| Carbon disulfide | $CS_2$ | 90000 |
| Carbon monoxide | CO | 340 |
| Ethane | $C_2H_6$ | 2500 |
| Ethylene | $C_2H_4$ | 1350 |
| Helium | He | 350 |
| Hexane | n-$C_6H_{14}$ | 9400 |
| Hydrogen | $H_2$ | 650 |
| Hydrogen sulfide | $H_2S$ | 10000 |
| Methane | $CH_4$ | 950 |
| Methanol | $CH_3OH$ | 13900 |
| Nitric oxide | NO | 600 |
| Nitrogen | $N_2$ | 280 |
| Nitrogen dioxide | $NO_2$ | 7500 |
| Nitrous oxide | $N_2O$ | 4350 |
| Octane | n-$C_8H_{18}$ | 8600 |
| Oxygen | $O_2$ | 600 |
| Pentane | n-$C_5H_{12}$ | 20000 |
| Propane | $C_3H_8$ | 4100 |
| Sulfur dioxide | $SO_2$ | 15000 |
| Toluene | $C_7H_8$ | 9130 |
| Water vapor | $H_2O$ | 36000 |

*1 Barrer = $10^{-10}$ $cm^3$ (STP)· cm /$cm^2$ · s · cm-Hg