

# **Mechanisms of gas permeation through microporous membranes - A review**

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## **ABSTRACT**

A review is presented for various gas transport mechanisms through microporous membranes of both polymeric and inorganic materials. Different transport modes manifest depending on the pore size and the flow regime, which is a function of pressure, temperature, and the interaction between gas molecules and the pore walls. For microporous membranes whose pores are small and the internal surface area huge, the surface diffusion becomes a significant factor. If the pores become even smaller, then the transport mechanism will be more of an activated diffusion type. When conditions are right capillary condensation will take place to create an enormous capillary pressure gradient, which will greatly enhance the permeation flux. At the same time the capillary condensate of the heavier component may block the membrane pores denying the passage of the lighter gas molecules. All of these phenomena will influence the separation of mixtures.

## **1. INTRODUCTION**

Although gas membrane separation has a long history of more than 100 years (1), the industrial applications took place only recently within the last 15 years and they are growing at a rapid pace. The largest industrial gas separation utilizes the traditional cryogenic technique (low temperature distillation) to separate oxygen and nitrogen from air. It is a well engineered and very economical process. Thus, it appears formidable to be challenged by a new technology. On the other hand, membrane processes are new and still have many drawbacks to be overcome. However, at least on an ad hoc basis or on a niche basis, the young membrane process keeps challenging the well-established cryogenic process and continues to chip away its market share.

The heart of the membrane process is of course the membrane itself. The search of a better membrane has been one of the preoccupation in membrane research. The permeability and the selectivity are two most important parameters in choosing a membrane for a given separation job. The vast majority of industrial membranes consists of polymeric materials. There seems to be an upper bound though in improving these two parameters for any known polymeric materials as the so called limiting lines for selectivity-permeability plots indicate (2). The inorganic membranes are still in

developmental stage but have a lot of potential. A flood of research articles is pouring out in journals dealing with ceramic or other inorganic membranes. Here also the same two parameters mentioned above are critical ones.

Whether it is polymeric or inorganic, it appears that a design is required for the next generation of new membrane materials in stead of the traditional trial and error approach. In order to design a new membrane structure and material, it is imperative to understand what the permeation mechanisms are. What are the relevant variables in membrane separations, how are they interdependent, and what are the important parameters in designing a new membrane? To be specific, is it better to have more free volume or less free volume in a polymeric membrane? Thus, is it more advantageous to lower or to elevate the glass transition temperature? What kind of functional groups would enhance the permeation and separation of a given system? How small the pores should be in a ceramic membrane? Do the dead end pores promote or hamper the separations? In order to help answer some of these questions, we have to understand how different species of molecules are transported through various porous membranes.

There are some excellent overviews and overall discussions of gas transport in porous membranes published recently (3-12). It is the aim of this paper to review briefly the status of this field and summarize various transport mechanisms.

## **2. POROUS MEMBRANES**

### **2.1 Pore size in capillary models**

Regardless the membrane materials, a question arises whether or not there are pores in a given membrane. How large the pores must be to be called pores? These questions are somewhat semantic. All ceramic membranes are porous and many polymeric membranes contain also pores. It is known that some polymeric membranes are thought to be nonporous or solid. But even these membranes have the free volume or at least the interstitial spaces. When a membrane is modeled mathematically, it is convenient to define a pore diameter, which corresponds to the average diameter of the cylindrical capillaries that represent the actual porous medium. As the pore size approaches the molecular dimension, all of the concepts associated with the conventional pores become hazy and even disappear. Then it is not necessary to discuss pores at all.

Therefore, the determinations and measurements of pore size distribution became very important topics of study. Many recent articles deal with this aspect (11-19).

### **2.2 Inorganic membranes**

There has been a flurry of activity for the study of ceramic and other inorganic membranes in the past decade. One of the primary motivations to turn to ceramic materials was to manufacture high temperature resistant membranes for industrial applications. The ceramic membranes are also attractive for constructing a membrane reactor, which can be used in shifting equilibrium limited reactions. Many papers deal

with the methods of synthesis and characterization of inorganic membranes (20-32), while others are concerned about permeation and separation (33-40).

### 2.3 Polymeric membranes

Many research papers are being published for polymeric membranes also concerning similar aspects. A report is made on the study of membrane surface by an atomic force microscopy (41). Some highly permeable polymers are thought to possess interconnected micropores (42), while other glassy polymers have very narrow free volume spaces so that the kinetic diameter of the permeating molecules may be an important factor in determining the selectivity (43, 44). For polymeric membranes the most popular model is still the free volume concept successfully applied to rubbery polymers by Fujita (45, 46). Later on other investigators extended this notion to glassy polymers (47-51). Another idea used quite successfully together with the free volume theory is the so-called dual sorption model to represent the adsorption sites within the polymer membrane. A new composite membrane is being experimented by mixing adsorbent or zeolite into polymeric membranes (52, 53).

There is a wealth of literature in the field of molecular modeling by utilizing the knowledge of quantum mechanical computations of molecular dynamics. This approach seems to hold the future, however, it has not reached a level to yield any practical applications to membrane field yet.

## 3. TRANSPORT OF FLUIDS IN POROUS MEMBRANES

### 3.1 Phenomenological expressions

When gas molecules permeate through a porous membrane the mechanism of particular transport mode is determined by not only the physical properties of gas and pores but also by the operating conditions. In some cases more than one transport mechanism will prevail. In still other cases the exact transport means are not known. Therefore it is necessary to define the gas permeation equation on a phenomenological basis and define the phenomenological permeability coefficient.

$$F = QA \left( \frac{p_h - p_l}{l} \right) \quad (1)$$

Here  $F$  is permeation rate,  $Q$  is permeability,  $A$  is membrane area,  $p_h$  is upstream pressure,  $p_l$  is downstream pressure, and  $l$  is membrane thickness. It is well known that the permeability is the product of membrane solubility,  $S$ , and diffusivity,  $D$ :

$$Q = SD \quad (2)$$

Some authors call this solution-diffusion model but it is not based on a flow mechanism, therefore, it should be recognized as a phenomenological definition. The above equations may be used to any membrane systems regardless the membrane structure or operating conditions. In other words, whether the membrane is porous or not, these equations apply equally well to define those phenomenological coefficients.

### 3.2 Poiseuille and Knudsen flow

A continuum regime can be assumed when most gas molecules suffer intermolecular collisions rather than wall-to-wall collisions and molecular chaos prevails. The equation of continuity holds and the flow of gases,  $F_p$ , can be described by the Poiseuille equation:

$$F_p = \frac{\pi r^4}{8\mu RT} \left( \frac{p_h + p_l}{2} \right) \left( \frac{p_h - p_l}{l} \right) \quad (3)$$

Here  $r$  is radius of pore,  $\mu$  is gas viscosity,  $R$  is gas constant, and  $T$  is temperature. This continuum condition is met when the mean free path

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 p} \quad (4)$$

is much smaller than the pore radius  $r \gg \lambda$ . Here,  $k$  is the Boltzmann constant,  $d$  is the collision diameter of gas molecules, and  $p$  is pressure.

In the reverse situation, when  $r \ll \lambda$ , the continuum concept breaks down and rarefied gas condition will set in. This means that the intermolecular collisions become far less frequent compared to wall-to-wall collisions. This may happen even at a relatively high pressure. Then molecular chaos disappears and free molecular behavior rules. The flow rate of gas,  $F_{kn}$ , through such a fine pore obeys the Knudsen equation:

$$F_{kn} = \frac{8\pi r^3}{3\sqrt{2}\pi MRT} \left( \frac{p_h - p_l}{l} \right) \quad (5)$$

Here, the molecular weight of gas,  $M$ , enters into the picture due to the free molecular nature of the flow regime.

If the mean free path is comparable to the pore radius, a transition from viscous flow to free molecular flow will occur. This is called slip flow, and the equation is:

$$F_{sl} = \frac{\pi r^3}{2M\bar{v}} \left( \frac{p_h - p_l}{l} \right) \quad (6)$$

where the mean speed of gas molecules is given by

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}} \quad (7)$$

All of the above equations are valid for a single cylindrical capillary, which represents a typical pore in the membrane. Also these expressions are good only for a pure species of gas. For real pores, some geometric parameters may enter into the equations such as porosity and tortuosity.

For a mixture of gases, each component will obey its own equation separately for free molecular flow thus yielding separation of species by membrane permeation. However, the separation factor is not very large to be practical, because it is given by a ratio of the inverse square root of molecular weights. For a continuum, an average viscosity is used in the Poiseuille equation, therefore no separation takes place in this regime of flow. Neither of the above flow mechanisms will result in much of separations.

### 3.3 Surface diffusion

When a membrane contains micropores, the internal surface area is so large that the interaction between gas molecules and the pore walls can not be neglected. The adsorbed gas molecules on the pore walls can migrate through the porous membrane due to its own

gradient of surface concentration. This phenomenon is referred as the surface diffusion or surface flow. It is a significant portion of gas permeation through a microporous membrane (22, 42,54-60). A Fick's law can be written for this two dimensional diffusion:

$$F_s = D_s \left( \frac{C_{sh} - C_{sl}}{l} \right) \quad (8)$$

Here,  $F_s$  is the surface diffusion flux,  $D_s$  is the surface diffusivity,  $C_{sh}$  and  $C_{sl}$  represent the surface concentrations of high pressure side and low pressure sides, respectively. Based upon the local equilibrium concept, it has been shown that the surface diffusion can be combined with the Knudsen flow in parallel (59).

$$F = F_{kn} + F_s \quad (9)$$

The amount of adsorption depends on pressure, temperature, and the interaction forces between the gas molecules and the pore walls. The amount of adsorption at a given temperature is expressed in terms of adsorption isotherm. There are many adsorption isotherms covering from monolayer to multilayer adsorption (11). Each one enables to express the surface concentration as a function of bulk phase (gas phase) pressure.

Based upon the statistical mechanical theory, the surface diffusivity and concentrations can be evaluated as a function of temperature and pressure of gas phase (55). After combining Eqs.(1), (5), (8), and (9), it is possible to express the overall permeability term as a function of temperature and pressure:

$$Q\sqrt{MT} = A + B \text{Exp} \left( \frac{\Delta}{T} \right) \quad (10)$$

Here,  $A$ ,  $B$ , and  $\Delta$  are parameters that have to be determined for a specific system. The constant  $A$  represents the Knudsen flow term and the second term is for the surface diffusion. The values of  $B$  and  $\Delta$  are well correlated to the Lennard-Jones parameters and in turn to the critical properties (58). The surface diffusion depends strongly on the gas solid interactions. How closely a given gas-membrane system is depicted by a model interaction potential will determine the accuracy of agreement between the experimental and theoretical permeabilities. However these parameters of the interaction potentials between gases and membrane materials are not readily available.

Another approach was taken based on the statistical mechanics using the Boltzmann equation (60). Without distinguishing gas or surface phases, the total flow rate was calculated for gas molecules under a potential field in a narrow slit. The results show that the total flux increases considerably compared with the case in which there is no potential field. This extra flow can be interpreted as the surface diffusion.

### 3.4 Activated diffusion

When the pore size becomes smaller and smaller to approach the molecular dimensions, the ordinary methods of surface diffusion run into a difficulty. The pore space is so narrow that no clear cut distinction can be made between the gas phase molecules which are under a potential field and surface adsorbed molecules. Since the pore walls are so close together the interaction potentials overlap each other considerably (3,11) creating a much stronger potential for the trapped gas molecules. As a result, the gas molecules are

strongly attracted to these pores but they have to travel these narrow and long passages. Since the interaction potential is so amplified the gas molecules have to overcome large activation energy barriers. This would be the situation for zeolites or molecular sieves.

For such a membrane the predominant factor is the molecular size of the gases. For small molecules (or for large pores) with a weak interaction potential, the diffusivity would be high. But as the gas molecules become bigger (or for small pores) with a strong potential, the diffusivity will decrease. In such a case the diffusivity depends primarily on the kinetic diameter of gas (40). The activated diffusion is treated much the same as the surface diffusion (31,35,39). The diffusivity is expressed in an Arrhenius form as a function of an activation energy,  $E_a$ , and a preexponential factor,  $D_0$ :

$$D = D_0 \text{Exp}\left(\frac{-E_a}{RT}\right) \quad (11)$$

### 3.5 Capillary condensation

When the interaction potential between gas molecules and pore walls become large, a condensation may take place even before the thermodynamic saturation point is reached. This phenomenon is called capillary condensation and the lowered condensation pressure can be estimated by the Kelvin equation:

$$\frac{RT}{\rho} \ln \frac{p_t}{p_0} = -J\gamma + (p_t - p_0) \quad (12)$$

where  $\rho$  is the density of capillary condensate,  $p_t$  is the capillary condensation pressure, which is less than the saturated vapor pressure,  $p_0$ ,  $J$  is the mean curvature, and  $\gamma$  is the surface tension. The capillary condensation will occur for any small pores to produce the high surface curvature of condensate whenever the pressure and temperature conditions are met in the pores.

When capillary condensation takes place a tremendous capillary pressure can develop within pores, which creates an added driving force. A suddenly increased flux is observed when it happens. At the same time if the entire pores are filled with the condensate, the flow mechanism would follow the Poiseuille equation for a liquid. Altogether there are six different modes of flow including surface diffusion and partial blockage of pores (61,62). Another interesting aspect of capillary condensate flow involves a hysteresis in permeability measurements similar to the one in the adsorption-desorption cycle (62,63). As newer membranes contain smaller pores the capillary condensation flow becomes more important mechanism for gas separations (35,61-65). When a mixture of condensable vapor and non-condensable gas flows through a microporous membrane an infinite separation factor may be achieved due to the blockage of pores by the capillary condensate (65).

### 3.6 Dual-mode sorption model

According to the "dual-mode sorption" model, there are two types of sorptions taking place in a membrane: one is Henry's law type and the other is Langmuir type of monolayer adsorption. The total adsorption,  $C_a$ , is given by a sum of the two:

$$C_a = C_d + C_h = k_d P + \frac{c_h b p}{1 + b p} \quad (13)$$

where the subscripts  $d$  and  $h$  denote the dense region (Henry's law region) and holes (Langmuir adsorption region), respectively, and  $k_d, c_h, b$  are constants. Combining this expression with Eqs.(1) and (2) yields:

$$Q = k_d D_d + \frac{c_h b}{1 + b p} D_h \quad (14)$$

where  $D_d$  and  $D_h$  represent the diffusivities for Henry and Langmuir types, respectively. Generally speaking a glassy polymer consists of a dense region and micro-voids. The dense region is responsible for the Henry's law type sorption and the micro-voids (holes) possess the Langmuir adsorption sites. Details of this approach can be found in the literature (48-51).

### 3.7 Dusty-gas model

As seen in the above discussions the gas transport mechanism varies widely depending on the structure, morphology, and materials of the membrane. Also the operating conditions such as pressure and temperature can alter the flow scheme. There is a universal theory developed by Mason and his associates (66-69), which covers simultaneously all of these mechanisms but less utilized by membrane community due to its complexity. This is called "dusty-gas model." It encompasses even nonideal liquid transport as well as ordinary diffusion through a solid. The presentation of equations will be omitted here since they are rather involved. Instead it is referred to the above mentioned references. It should be noted that there is a recent revisit to this theory by Datta and his coworkers (4) for the readers in membrane community.

## 4. SEPARATION OF MIXTURES BY MEMBRANES

Membrane separation is accomplished by virtue of the difference in permeabilities of gas species. Since the permeability is a product of solubility and diffusivity, separation is actually controlled by these two factors independently. This can be shown explicitly through the definition of ideal separation factor. Consider a binary mixture of gases A and B permeates through a membrane. The ideal separation factor  $\alpha^*$ , which is the ratio of two permeabilities, can be expressed by using Eq. (2):

$$\alpha^* = \left( \frac{Q_A}{Q_B} \right) = \left( \frac{S_A}{S_B} \right) \left( \frac{D_A}{D_B} \right) \quad (15)$$

where the subscripts A and B represent each species. The solubility is an equilibrium property while diffusivity is a dynamic property. When a mixture of fast moving and slow moving gas species are introduced into a membrane, the fast species will come out first only if the solubilities are comparable or at least they do not negate the diffusivity advantage. On the other hand when the diffusivities are comparable, the one with a larger

solubility will permeate faster. Therefore there are two ways to promote the gas membrane separation by maximizing the differences in solubility and in diffusivity.

#### 4.1 Sorption difference

For many rubbery polymers the difference in solubility is much greater than the difference in diffusivity in determining the separation factor. Because of the large interstitial spaces between polymer chains, the size of the penetrant molecule does not affect very much the mobility of different species. A similar situation is true for inorganic membranes with large pores when a mixture of non-condensable and condensable gases (or small molecules and large molecules) permeates. The affinity between gas molecules and membrane material also influences the sorption characteristics. Therefore the rule of thumb is that the larger the penetrant molecule is the greater the permeability becomes. Or, the closer (affinity) the gas molecule is to the membrane material the higher the permeability becomes, thus, the better the separation is.

#### 4.2 Mobility difference

For glassy polymeric membranes the overall separation of similar gas molecules is by and large controlled by the mobility difference. The same is true for ultrafine microporous inorganic membranes. In both of these cases, the pore space available for the passage of gas molecules is so narrow that the size of penetrant molecules becomes the overriding factor in determining the mobility. Therefore, the diffusivity ratio will control the extent of separation. In this situation the shape factor of the penetrant molecules becomes also an important variable. For instance the molecules with a side branch might have a difficulty in getting through a narrow pore while similar molecules with a straight chain might be able to go through easily.

#### 4.3 Blocking and sieving

When pores become really tight to accommodate only the smallest molecules, the other large molecules will be denied. This condition creates a sieving effect or blocking effect. Molecular sieve or zeolite membranes fall into this category. As mentioned earlier the capillary condensation can also cause some blocking effect for the non-condensing species. Usually when this happens the separation factor becomes so large that it approaches a perfect separation. This is one of the ideal goals of membrane gas separation by either polymeric or inorganic membranes of the future.

## 5. CONCLUSION

For both polymeric and inorganic membranes with any recognizable pore structure, Poiseuille, Knudsen, slip flow can occur depending primarily on the pore size. When the interaction between the gas molecules and pore walls becomes significant, surface diffusion might take place. As the pore space gets smaller the permeation will be carried out by an activated diffusion. If the pores are even smaller molecular sieving will result. Also a capillary condensation might take place as the pressure and temperature conditions



are met. Free volume and dual-mode sorption models have been quite successful in explaining diffusion of gases through various types of membranes.

From the view point of practical applications, gas separation by membranes will be economical only when the pores are controlled to a right size and possibly introduce a certain functional groups on the pore walls. If a molecular sieving effect takes place it will be even better. For polymeric membranes, glassy polymers would render a better handle to provide a tailor made membranes than rubbery materials. The mobility controlled membranes would have a greater chance in succeeding. In designing the future generation membranes, more sophisticated methods such as molecular modeling based on the quantum mechanical calculations might become necessary.

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