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PERMEABILITY AS A PHENOMENOLOGICAL COEFFICIENT

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## I. INTRODUCTION

With the advent of gaseous diffusion as a large scale separation process and the promising developments in water purification by reverse osmosis, membrane permeation has become rather popular as a separation and purification process. A wide variety of membranes is used in many different types of unit operations and research experiments. Invariably, one encounters the term "permeability."

Permeability is, at least historically, a natural definition to express the degree of permeation of a component through a certain material, usually in the form of a membrane. In many cases, the basic mechanism of permeation is molecular diffusion. In others, some other mechanisms such as hydrodynamic flow, capillary action or electrokinetic flow are the cause of permeation. For simple cases, the use of a diffusivity is obvious and sufficient in expressing the permeation rate. However, in general, the complexity and multiplicity of permeation mechanisms call for a quantity which tells the overall degree of permeation, that is, permeability. Another factor, which adds to the complexity of the term permeability, is the fact that it is used in so many different disciplines and research fields. It seems, at times, that there is hardly any communication among investigators in different fields of study. Numerous publications report all sorts of permeability data in the literature. However, it is impossible to make valid comparisons of the data and utilize them without a proper reference to basic definitions.

## II. VARIOUS DEFINITIONS OF PERMEABILITIES

### A. Molecular Diffusivity

If the permeation is due to molecular diffusion alone, then permeability is equivalent to diffusivity, which is a property of a given system. Provided that the concentrations of the diffusing species in the membrane are known, Fick's first law is adequate to describe such a system:

$$F = DA \frac{C_1 - C_2}{L} \quad [1]$$

### B. Overall Permeability

Frequently, however, the actual concentrations at the very surface or the inside of the membrane are not known, or are very difficult to measure experimentally. This requires a new definition of a phenomenological coefficient, namely permeability, in terms of measurable quantities, that is, outside concentrations or pressures:

$$F = Q_2 A \frac{\Gamma_1 - \Gamma_2}{L} \quad [2]$$

or

$$F = Q_3 A \frac{P_1 - P_2}{L} \quad [3]$$

Here,  $\Gamma$  represents the concentration of bulk fluid outside of the membrane while  $C$  represents the concentration within the membrane.

The permeability definitions given by Equations [2] and [3] may be used regardless of the actual transport mechanism. In fact, the mechanism does not need to be known for the measurements and for the calculation of permeabilities by these equations.

If the permeation mechanism is not solely due to diffusion, the following definition results, using the actual concentrations:

$$F = Q_4 A \frac{C_1 - C_2}{L} \quad [4]$$

This permeability will have the same units as those of diffusivity, but it should never be called or confused with true diffusivity. One may call it "effective diffusivity."

In the case of a porous membrane, another permeability is defined (1) to take porosity into account:

$$F = Q_5 A \epsilon \frac{\Gamma_1 - \Gamma_2}{L} \quad [5]$$

### C. Darcy's Law of Permeability

Darcy's Law is widely used in the petroleum industry and in soil mechanics. Here, the flow coefficient is divided by the viscosity of the fluid in order to isolate the properties of the porous medium in its permeability (2).

$$F = \frac{Q_6 A}{\mu} \frac{P_1 - P_2}{L} \quad [6]$$

### D. Comparison

By any means, the definitions given above are not exhaustive. One can make countless combinations of units in the expression of permeability. For instance mass flow rate may be used as well as volume flow rate, or inches instead of centimeters for the thickness of the membrane, etc. However, these are considered as mere unit conversions.

On the other hand, the interconversion between the above given permeabilities may or may not be so simple. Sometimes it can be meaningless. For example, the gas phase permeation through a porous membrane may be expressed by any of the permeabilities defined by Equations [2], [3], [5] and [6]. And yet, the liquid phase permeability through a nonporous membrane can hardly be expressed by those given in Equations [3], [5] and [6]. Even though it could, one can find no physical meanings attached to the permeability.

Summing up, permeability is a phenomenological quantity; hence, it depends upon the system and the experimental conditions. It is, in general, not a property of the membrane as diffusivity is. Depending on the structure of the membrane or mechanism of permeation, one can also define special permeabilities as shown in the next section.

## III. PERMEABILITIES FOR MICROPOROUS MEMBRANES

In this section, the permeabilities and diffusivities for flow

in microporous membranes are discussed in order to illustrate how the theoretical interpretations and modeling of the flow mechanisms affect the definition of permeability. It is also possible to establish interrelationships between different flow coefficients. This would resolve the difficulty arising in the comparison of reported permeability data in the literature.

A survey of the literature on gas permeation at low surface coverage reveals little uniformity in the presentation of the gas and surface permeability data. Hence, the following discussions will be limited to the Knudsen regime for gas phase flow and to the region of low surface coverage for surface flow.

Gas phase flow in the Knudsen regime occurs where the mean free path of the molecules is greater than the diameter of the pore. Under these conditions, the gas molecules are transported with little intermolecular collisions, but collide mainly with the pore walls. Although the gas phase flow is then well described by the Knudsen law, it becomes difficult to represent a porous medium by a geometrical model in order to directly apply Knudsen's work. However, a number of models (4,5,6) have been proposed as a basis for calculating the Knudsen diffusivity,  $D_k$ , for various porous media. Such models try to take into account factors of tortuosity, porosity, etc.

In addition, several theoretical interpretations (7,8,9,10,11, 12,13) have evolved from the considerable evidence supporting the existence of transport by surface flow in porous media. Since a surface diffusivity,  $D_s$ , is then often calculated for the many corresponding models, it should be emphasized that these surface diffusivities are only valid for a particular model and are often in a range where they are strongly dependent on surface coverage. Therefore both the model and amount of surface coverage must be considered when comparing reported surface diffusivities. The results discussed here are all in the region of low surface coverage.

Unfortunately, the experimental results of permeation are expressed as either diffusivities or permeabilities, with permeabilities being expressed in both units of  $\text{cm}^2/\text{sec}$  and  $(\text{std.cc}) (\text{cm})/(\text{sec})(\text{cm}^2)(\text{cmHg})$ . It should also be noted that the definition of "permeability" is usually the same as the definition of "permeability coefficient," and this is also the case with "diffusivity" and "diffusivity coefficient."

It is therefore pertinent to review these basic definitions used in the study of permeation of gases through porous media, to establish a relationship between them, and then to outline a method of calculating "diffusivities" from "permeability data." Since it is beyond the scope of the present discussion to perform a comprehensive evaluation of the proposed theories in gas diffusion, only some of the reported experimental results are considered in order to illustrate the relationship between "permeabilities" and "diffusivities" in the region of Knudsen flow and low surface coverage.

#### A. Gas Phase

The permeability of gases and vapors through microporous media is usually considered to be the sum of gas phase flow,  $F$ , and surface flow,  $F_s$ . Using the concept that the two flow processes take place in parallel, the steady state flow (4,10) is:

$$F = F_g + F_s \quad [7]$$

Applying the analogy of Fick's first law of diffusion, the steady state flow rate can be expressed by

$$F = -D_t A \frac{dC_t}{dx} \quad [8]$$

and similarly for the gas phase

$$F_g = -D_g A \frac{dC_g}{dx} \quad [9]$$

Since the gas phase flow is in the Knudsen regime, a Knudsen diffusivity,  $D_K$  is often calculated for a given geometrical model and is defined by (14):

$$F_g = -D_K A' \frac{dC'_g}{dx} \quad [10]$$

Knudsen showed that if a straight cylindrical capillary is very long relative to its deameter, the following expression (4,5,6,14) is obtained for the Knudsen diffusivity in the Knudsen flow region:

$$D_K = \frac{4r}{3} \sqrt{\frac{2RT}{\pi M}} \quad [11]$$

It should be noted that the following relationships exist for the straight cylindrical capillary model:

$$A' = \epsilon A \quad [12]$$

$$C'_g = \frac{C_g}{\epsilon} \quad [13]$$

in which  $\epsilon$  is the porosity of porous medium. When Equations [12] and [13] are substituted into Equation [10]:

$$F_g = -D_K A \frac{dC_g}{dx} \quad [14]$$

and  $D_K = D_G$ , if the straight cylindrical capillary model represents the actual porous medium. However, usually this is not the case and Equation [11] is modified by more complicated models where Equations [12] and [13] are not applicable. In general, Equation [10] then becomes (10,15):

$$F_g = -D_K A G_1 \frac{dC_g}{dx} \quad [15]$$

where  $G_1$  is a dimensionless geometrical factor.

Since the Knudsen diffusivity is a constant and is defined by the geometry of the model, it can be related to the effective gas diffusivity by (8,15):

$$D_g = G_1 D_K \quad [16]$$

Thus, the calculations of  $D_K$  will depend on the model selected while  $D_g$  can be determined directly from the appropriate experimental data.

When the outside concentrations or the pressures are used instead of the concentrations within the porous membrane, the following permeabilities are defined: for total flow,

$$F = -Q_t A \frac{dP}{dx} \quad [17]$$

or

$$F = -K_t A \frac{dP}{dx} \quad [18]$$

and similarly for the gas phase flow,

$$F_g = -Q_g A \frac{dP}{dx} \quad [19]$$

or

$$F_g = -K_g A \frac{dP}{dx} \quad [20]$$

When  $F_g$  is taken to be Knudsen flow, it can be expressed (10) as:

$$F_g = - \frac{A G_2}{\sqrt{2\pi MRT}} \frac{dP}{dx} \quad [21]$$

Therefore, the gas phase permeability,  $Q_g$ , for the Knudsen regime can be obtained by

$$Q_g = \frac{G_2}{\sqrt{2\pi MRT}} \quad [22]$$

### B. Adsorbed Phase

Applying Fick's diffusion equation for two-dimensional steady state flow, the flow rate for the adsorbed phase in terms of surface concentration per unit area,  $C'_s$ , becomes (5):

$$F_s = -W D_s \frac{dC'_s}{dx} \quad [23]$$



where  $\underline{D}_s$  is the surface diffusivity, and is assumed to be constant for the region of low surface coverage. In order to obtain Equation [23] in terms of measurable quantities, it is transformed into three-dimensional units. The surface concentration,  $C'_s$ , is expressed as concentration per unit volume of porous medium by using the surface area per unit volume of the porous medium,  $S_v$ , such that:

$$C_s = C'_s S_v \quad [24]$$

Combining Equations [23] and [24], the following three-dimensional expression is obtained:

$$F_s = -D_s \left( \frac{W}{S_v} \right) \frac{dC_s}{dx} \quad [25]$$

In order to obtain the same form as Equation [8], the macroscopic cross sectional area,  $A$ , is included in Equation [25] so that:

$$F_s = -A D_s \left( \frac{W}{AS_v} \right) \frac{dC_s}{dx} \quad [26]$$

If the quantity  $\left( \frac{W}{AS_v} \right)$  is represented by a geometric factor  $\underline{G}_3$ , then:

$$F_s = -A \underline{G}_3 D_s \frac{dC_s}{dx} \quad [27]$$

An "apparent" surface diffusivity,  $\underline{D}'_s$ , is often defined as (8):

$$F_s = -A \underline{D}'_s \frac{dC_s}{dx} \quad [28]$$

and is related to  $\underline{D}_s$  by:

$$\underline{D}'_s = \underline{G}_3 \underline{D}_s \quad [29]$$

Calculation of the true surface diffusivity,  $\underline{D}_s$ , can only be done by assuming a model and cannot, therefore, be explicit as also previously shown in the calculation of the Knudsen diffusivity,  $\underline{D}_K$ , from the effective gas diffusivity  $\underline{D}$ . If, for an example, the straight cylindrical capillary model<sup>8</sup> is again considered, then:

$$W = A S_v \quad [30]$$

yielding  $\underline{G}_3 = 1$ . Equation [27] becomes:

$$F_s = -A \underline{D}_s \frac{dC_s}{dx} \quad [31]$$

and  $\underline{D}_s$  is equal to  $\underline{D}'_s$  for this particular model.

In consideration of the above definitions, it is necessary that all authors clearly define all their reported diffusivities and corresponding models if the Knudsen diffusivity,  $\underline{D}_K$ , and actual surface diffusivity  $\underline{D}_s$ , are calculated.

The surface permeabilities are defined similarly to the gas phase permeabilities.

$$F_s = -Q_s A \frac{dP}{dx} \quad [32]$$

or

$$F_s = -K_s A \frac{d\Gamma}{dx} \quad [33]$$

### C. Diffusivities from Permeabilities

The actual concentrations in the porous medium are very difficult to measure directly because they are the result of pressures or concentrations existing outside of the membrane. Expressing the equation of state for the gas phase as

$$\Gamma = \frac{P}{zRT} \quad , \quad [34]$$

the following relationships are observed:

$$K_t = zRT Q_t \quad [35]$$

$$K_g = zRT Q_g \quad [36]$$

$$K_s = zRT Q_s \quad [37]$$

#### 1. Effective Gas Diffusivity

The relationship between  $\underline{D}_g$  and  $Q_g$  is obtained from Equations [9] and [19].

$$\underline{D}_g = Q_g \frac{dP}{dC_g} \quad [38]$$

Since  $\underline{C}_g$  is the concentration of transported species in the gas phase per unit volume of the porous medium, it can be related to pressure by:

$$\underline{C}_g = \frac{eP}{zRT} \quad [39]$$

It should be noted that Equation [39] ignores the void volume reduction due to the adsorbed species since the reduction is usually very small at low surface coverage. Taking the derivative of pressure,  $\underline{P}$ , with respect to the concentration,  $\underline{C}_g$  in Equation [39]:

$$\frac{dP}{dC_g} = \frac{zRT}{\epsilon} \quad [40]$$

and substituting into Equation [38], the effective gas diffusivity can be calculated using the following expression:

$$D_g = Q_g \frac{zRT}{\epsilon} \quad [41]$$

## 2. Apparent Surface Diffusivity

The surface permeability is then obtained using Equations [7], [19] and [32]

$$Q_s = Q_t - Q_g \quad [42]$$

The relationship between  $\frac{Q_s}{D_s}$  and  $\frac{D_s'}{D_s}$  is obtained from Equations [28] and [32] for the case where  $\frac{D_s'}{D_s}$  is constant:

$$D_s = Q_s \frac{dP}{dC_s} \quad [43]$$

In order to obtain  $\frac{dP}{dC}$ , the following relationships were developed. Since the adsorption isotherm is generally plotted as  $y$  (in std. cc. of adsorbate per gram of adsorbent) versus pressure, the slope of any given pressure can be defined as:

$$\alpha = \frac{dy}{dP} \quad [44]$$

In the Henry's law region of the isotherm, which should hold at low surface coverage, the slope is constant and thus  $\alpha$  is independent of pressure in this range. Since  $C_s$  is related to  $y$  by:

$$C_s = \rho y \quad [45]$$

Equations [44] and [45] yield:

$$\frac{dP}{dC_s} = \frac{1}{\alpha \rho} \quad [46]$$

Thus, the apparent surface diffusivity can be related to the surface permeability for the Henry's law region by substituting Equation [46] into Equation [43] to obtain:

$$D_s' = Q_s \frac{1}{\alpha \rho} \quad [47]$$

## 3. Total Diffusivity

The total effective diffusivity can be related to the total

permeability by combining Equations [8] and [17] to yield:

$$D_t = Q_t \frac{dP}{dC_t} \quad [48]$$

Since  $C_t$  can be expressed as:

$$C_t = C_g + C_s, \quad [49]$$

the following equation is obtained:

$$\frac{dP}{dC_t} = \frac{1}{\frac{dC_g}{dP} + \frac{dC_s}{dP}} \quad [50]$$

Thus, by combining Equations [40], [46], [48] and [50] the relationship between  $D_t$  and  $Q_t$  is given by:

$$D_t = Q_t \frac{1}{\frac{\epsilon}{zRT} + \alpha \rho} \quad [51]$$

#### D. Comparisons

Utilizing the equations developed in the preceding section, various diffusivities are calculated and listed in Table I from the permeability data of Hwang (10,11) and Huckins (16). The adsorption isotherm data reported by Barrer (4) are used to calculate the diffusivities shown in the table. These values are compared with those reported by Barrer (4). A comparison of the apparent surface diffusivities are slightly higher than those calculated from the data of Hwang and of Huckins. However, this is not surprising since the apparent surface diffusivities reported by Barrer are based on transient state measurements while Hwang's and Huckins' measurements were at steady state. Barrer (17) has shown that surface diffusivities for some alumina-silica and carbon plugs were about twice as large for the transient state cases as compared with the steady-state conditions.

The gas permeabilities calculated from the Knudsen flow constant reported by Hwang (10,11) are compared with some values reported by Barrer (17) in Table II. This table also includes a comparison of effective gas diffusivities calculated from Hwang's (10,11) gas permeabilities and the effective gas diffusivities reported by Barrer (4). It should be noted that Barrer's gas diffusivities are based on the conventional assumption of no surface diffusion for helium, which is incorrect. Hwang's gas diffusivities were calculated from a constant which was determined when helium surface diffusion is taken into account. A sample calculation is given in the Appendix.

#### E. Recommendation

The main objective of the foregoing analysis was to clarify a confusing situation existing in the reporting of diffusivity and

Table I

Comparison of calculated and reported diffusivities in the region of low surface coverage for vycor glass.

Gas	Temp. °K	Q <sub>t</sub> x 10 <sup>6</sup> Reported by Hwang Huckins (10,11) (16)	D <sub>g</sub> x 10 <sup>5</sup> Calculated from Hwang's Constant (10,11)	Calculated for Hwang Huckins (10,11) (16)	D <sub>t</sub> x 10 <sup>5</sup> Reported by Barrier <sup>≠</sup> (4)	D <sub>t</sub> x 10 <sup>5</sup> Calculated for Hwang Huckins (10,11) (16)	Adsorption Isotherm Slope α from Barrer(4)
N <sub>2</sub>	273	6.03	125	7.64	-----	26.8	0.0125
"	290	5.78	128	9.95	23.35*	34.5	0.00884
"	323	5.38	136	15.0	30.53	49.7	0.00514
"	343	5.18	140	18.9	34.50	59.9	0.00381
O <sub>2</sub>	273	5.62	117	7.01	-----	25.0	0.0125
"	290	5.40	120	8.87	19.84*	31.3	0.00919
"	323	5.04	127	13.7	26.41	45.6	0.00529
"	343	4.86	131	17.3	31.29	54.8	0.00396
Ar	273	4.97	104	6.54	-----	23.9	0.0114
"	290	4.77	108	8.16	20.00*	29.4	0.00850
"	323	4.46	113	11.7	25.19	40.4	0.00529
"	343	4.31	117	14.2	29.16	47.4	0.00410
H <sub>2</sub>	273	20.4	466	150.	-----	350.	0.00142#
"	298	19.5	487	197.	-----	395.	0.00104#
"	313	19.1	499	233.	-----	423.	0.00086#
CH <sub>4</sub>	273	8.61	165	8.38	-----	25.4	0.0201
"	294	8.06	171	10.9	18.93	34.0	0.0135
"	323	7.47	179	14.3	23.96	46.1	0.00872
"	343	7.14	185	17.7	26.41	56.6	0.00645
C <sub>2</sub> H <sub>6</sub>	294	8.56	125	3.16	3.96*	6.17	0.0901
"	323	7.39	131	5.87	7.02	12.4	0.0375
"	343	6.80	135	8.07	9.00	17.8	0.0235

\* 292°K.

# Adsorption isotherm data from Graham (18).

≠ Obtained by dividing all values in Table 8 of original article (4) by a tortuosity factor of 6.55.

Table II

Comparison of effective gas diffusivities and gas permeabilities for vycor glass at  $T = 292^{\circ}\text{K}$ .

Gas	Data taken from Barrer and Barrie (4)		Data taken from Barrer (17)		Calculated data from a constant given by Hwang (10,11)	
	(b) $D_g \times 10^4$	(c) $Q_g \times 10^5$	(d) $D_g \times 10^4$	(c) $Q_g \times 10^5$	(e) $D_g \times 10^4$	(f) $Q_g \times 10^5$
He	42.8	1.571	---	---	34.09	1.176
Ne	18.7	0.686	---	---	15.18	0.524
H <sub>2</sub>	53.7	1.975	---	---	48.21	1.663
Ar	13.0	0.477	13.5	0.496	10.79	0.372
N <sub>2</sub>	16.0	0.587	16.2	0.595	12.88	0.444
O <sub>2</sub>	14.5	0.532	15.1	0.554	12.05	0.416
Kr <sup>a</sup>	9.33	0.343	9.4	0.345	7.48	0.256
CH <sub>4</sub> <sup>a</sup>	20.2	0.742	21.4	0.786	17.11	0.586
C <sub>2</sub> H <sub>6</sub>	17.2	0.631	---	---	12.45	0.429

Note: Units of  $D_g$  and  $Q_g$  are listed in Nomenclature Section.

Key:

- Krypton and methane data for  $T = 294^{\circ}\text{K}$
- Calculated from Barrer and Barrie (4) who reported a  $K_K$  which is equal to  $(D_g \epsilon)$ , where  $\epsilon = 0.298$
- Calculated from  $D_g$  by Eq. [41],  $Q_g = D_g \left( \frac{\epsilon}{zRT} \right)$
- Reported by Barrer (17) as  $\frac{K}{g}$  \* which is the same as  $Q_g$  for gas phase
- Calculated from  $Q_g$  by Eq. [41],  $D_g = Q_g \left( \frac{zRT}{\epsilon} \right)$
- Calculated from Knudsen flow constant,  $Q_g \sqrt{\frac{MT}{\epsilon}} = 4.02 \times 10^{-4}$  as given by Hwang (10)

permeability data for microporous media. For ease in making comparisons of data it is necessary that authors report permeabilities in one of the forms defined in this section. In addition, if diffusivities are also desired, then the effective gas, apparent surface, and total diffusivities should be calculated, as they are based only on the concept of unhindered parallel flow and are independent of any pore model. Further, the relationship between these diffusivities and any other reported diffusivities should be clearly defined.

#### IV. PERMEABILITIES FOR LIQUID SYSTEMS THROUGH PLASTIC MEMBRANES

The previous section discussed the variation of permeability

with the mechanism of mass transfer within the membrane. Additionally the permeability is also affected by the conditions outside a membrane.

#### A. Relationship between Permeability and Diffusivity

It is generally true that there are always some resistances to permeation at the interfaces between the bulk fluids and the membrane. These may be due to the presence of physical boundary layers near the membrane, to sorption and desorption processes, or both. Therefore, it is possible to propose the following general model for membrane permeation.

A hypothetical concentration profile and a schematic view across the membrane are shown in Figure 1. It is assumed that both sides

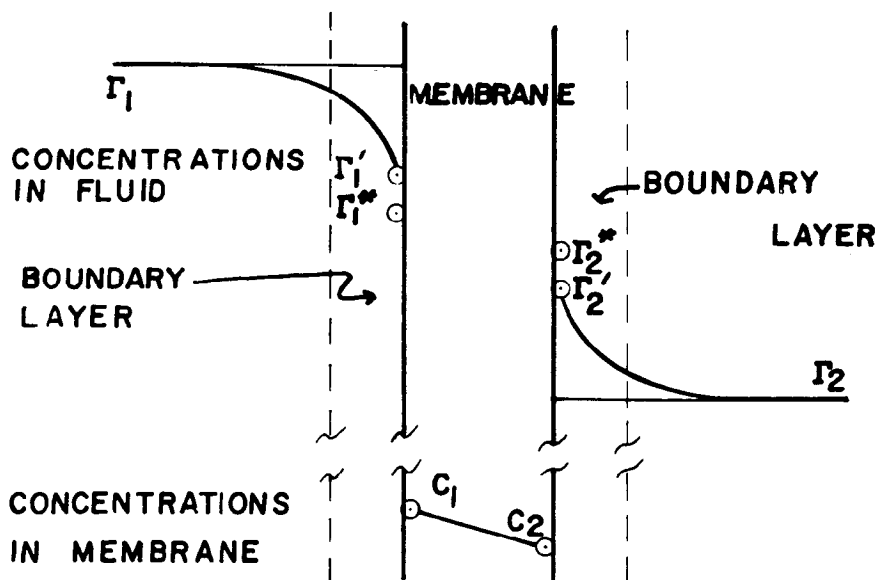


Figure 1. Concentration profile across the membrane.

of the membrane are covered by thin layers of immobile fluid, which would give an extra resistance to permeation. The mass transfer through such a system consists of the following stepwise processes:

1. Diffusion through the boundary layer.
2. Sorption into the membrane.
3. Diffusion through the membrane.
4. Desorption out of the membrane.
5. Diffusion through the boundary layer.

Each step represents a resistance to the gas transport of different magnitudes. For practical purposes, however, the resistances of some steps are negligible in comparison with those of others. In the case of gas-phase permeation, processes 1 and 5 are not involved, and the resistances due to the steps 2 and 4 may even be negligible. However, for liquid phase permeation, a large boundary resistance may result from steps 1, 2, 4 and 5. The presence of these boundary resistances reduces the available driving force for diffusion inside the membrane.

Using the definition of overall permeability given by Equation [2], the steady-state flow equation is written as:

$$F = QA \left( \frac{\Gamma_1 - \Gamma_2}{L} \right). \quad [52]$$

If the diffusivity of the membrane is independent of concentration, the same steady-state flow rate for the inside of the membrane can also be expressed by:

$$F = DA \left( \frac{C_1 - C_2}{L} \right). \quad [53]$$

Should diffusivity be concentration-dependent, an average diffusivity can be used.

$$F = \bar{D}A \left( \frac{C_1 - C_2}{L} \right) \quad [54]$$

where:

$$\bar{D} = \int_{C_2}^{C_1} D dC / (C_1 - C_2) \quad [55]$$

Because it is very difficult to separate steps 2 and 4 from steps 1 and 5 experimentally, it is convenient to lump the resistances of steps 1 and 2 in a group, and steps 4 and 5 in another. Then one can write the flow equation for one side of the membrane:

$$F = A \left( \frac{\Gamma_1 - \Gamma_1^*}{r_1} \right) \quad [56]$$

and for the other side

$$F = A \left( \frac{\Gamma_2^* - \Gamma_2}{r_2} \right) \quad [57]$$

where  $r_1$  and  $r_2$  are film resistances including resistances of sorption and desorption if they exist. The fictitious quantities,  $\Gamma_1^*$  and  $\Gamma_2^*$ , are the concentrations which would have produced the inside concentrations  $C_1$  and  $C_2$  respectively under equilibrium conditions. If a linear isotherm (Henry's Law) is applicable,

$$C_1 = S \Gamma_1^* \quad [58]$$



$$C_2 = S \Gamma_2^* \quad [59]$$

Combining Equations [56], [57], [58] and [59] with Equation [53] and solving for  $\bar{F}$ ,

$$F = \frac{DS(\Gamma_1 + \Gamma_2)}{DS(r_1 + r_2) + L} \quad [60]$$

Comparing Equation [60] with Equation [52], the following is obvious:

$$Q = \frac{DSL}{DS(r_1 + r_2 + L)} \quad [61]$$

This equation tells exactly how the observed permeability changes as the thickness of a membrane varies. Also, it shows that the film resistance could be significant when the diffusivity of the membrane is large, or when the thickness of a membrane is small. If there is no such film present, then the film resistance simply becomes zero, and the observed permeability reduces to the familiar form.

$$Q = DS \quad [62]$$

This equation has been used widely in many systems. However, it is clear from Equation [61] that Equation [62] holds only in a special case. Furthermore, Equation [61] illustrates the fact that permeability is a phenomenological coefficient rather than a property of a given system as a given in Equation [62]. A change of an outside condition, such as film resistance or membrane thickness, alters the value of permeability. Therefore, in general, a comparison of two permeabilities for the same system but at different experimental conditions may not be meaningful.

## B. Dissolved Oxygen Permeation through Membrane

The studies by Yasuda (19,20) and Robb (21) on permeation of oxygen dissolved in water present an interesting comparison of gas phase permeability with the permeability of dissolved oxygen in the aqueous phase. Among many polymer membranes employed, silicone rubber showed a marked difference from other membranes in the magnitude of its permeability. Therefore, the system of silicone rubber membrane and dissolved oxygen would be quite suitable for testing the validity of Equation [61]. There are two reasons for this. First, a stagnant film would exist at the surface of membrane to give the film resistance. Second, the overall permeation rate is so great that such an interface resistance may not be negligible in comparison with the diffusion resistance in the membrane.

### 1. Effect of Thickness

A recent study (22) showed that the observed permeability of dissolved oxygen through a silicone rubber membrane depends on the membrane thickness. In both, steady-state (circles) and unsteady-state (hexagons) measurements, the observed permeability increased with increasing membrane thickness and approached asymptotically a limiting value as shown in Figure 2. The analysis of the experimental data can best be done by plotting the inverse permeability