1970

Crystallinity and density in permeation of carbon dioxide and water vapor through polymers

Kook-Wha Koh

University of Iowa

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CRYSTALLINITY AND DENSITY IN PERMEATION OF CARBON DIOXIDE

AND WATER VAPOR THROUGH POLYMERS

by

Kook-Wha Koh

A dissertation submitted in partial fulfilment of the requirement for the degree of Doctor of Philosophy in the Department of Chemical Engineering in the Graduate College of The University of Iowa

January, 1970

Thesis supervisor: Professor James O. Osburn
This is to certify that the Ph.D thesis of

Kook-Wha Koh

with a major in Chemical Engineering
has been approved by the Examining Committee as satisfactory for the thesis requirement for the Ph.D. degree at the convocation of
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NOMENCLATURE

\[ A = \frac{\langle D(\vec{r})C, \vec{l}(\vec{r}) \rangle}{\langle D(\vec{r}) \rangle} \]

- \( A, A_c, A_t \): Areas from p. 87
- \( a \): Constant defined in Eq. (35)
- \( a_0, a_3 \): Constants defined in Eq. (54)
- \( a \lambda \): Constant defined in Eq. (52)
- \( B \): Constant defined in Eq. (56)
- \( b \): Weight of specimen and wire in liquid, g
- \( C \): Concentration, g-mole/cc
- \( C_1 \): Concentration at surface 1, g-mole/cc
- \( C_2 \): Concentration at surface 2, g-mole/cc
- \( c = d_c - d_a, g/cc \)
- \( D \): Diffusion coefficient, sq. cm/sec
- \( d \): Density, g/cc
- \( \hat{e} \): Unit vector
- \( F \): Contribution of polymer to \( P \) in Eq. (31)
- \( f \): Defined in p. 11
- \( G \): Contribution of gas to \( P \) in Eq. (31)
- \( g \): Weight of specimen without wire in air, g
- \( H \): Defined in Eq. (16)
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<td>h</td>
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<td>J</td>
<td>Permeation flux, g-mole/(sq. cm)(sec)</td>
</tr>
<tr>
<td>K</td>
<td>Constant defined in Eq. (30)</td>
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<tr>
<td>k(s)</td>
<td>Function defined in Eq. (17)</td>
</tr>
<tr>
<td>k</td>
<td>Constant integer defined in Eq. (52)</td>
</tr>
<tr>
<td>λ</td>
<td>Direction cosine, equals to cos θ</td>
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<tr>
<td>l₀</td>
<td>The thickness of membrane, cm or mil</td>
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<tr>
<td>n</td>
<td>Constant defined in Eq. (30)</td>
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<tr>
<td>P</td>
<td>Permeability constant, (STD cc)(cm)/(sq. cm)(sec)(cm Hg)</td>
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<td>Permeability constant of region 1</td>
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$q^+$ q in the region, $s \geq -\ln(\frac{X_a}{b})$

$q^-$ q in the region, $s \leq -\ln(\frac{X_a}{b})$

$\mathbf{r}$ Position vector, $(x_1, x_2, x_3)$

$S$ Solubility, $(g$-mol$)/(cm)(cc)$

$\mathbf{s}$ Position vector

$t$ Time, second or hour

$u$ Defined in Eq. (10)

$V$ Volume of the system, cc

$X$ Volume fraction

$x_1, x_2, x_3$ Spatial coordinates in the Cartesian system

Greek letters

$L_1, L_2$ Constants defined in Eq. (48)

$L, \beta, \gamma$ Parameters defined in Eq. (12)

$\gamma_0$ Contribution of interaction to $P$ in Eq. (31)

$\xi$ Crystallinity

$\lambda$ Constant integer defined in Eq. (52)

$\theta$ Diffraction angle

$\tau$ Constant defined in Eq. (29)
NOMENCLATURE (Cont'd)

\( \psi_{(1)}, \psi_{(2)}, \psi_{(3)} \) Characteristic functions of probability defined in Eq. (12)

\[ \phi = \ln D - \langle \ln D \rangle \]

\[ \Phi = (d - d_a)/(d_c - d_a) \]

Subscripts

- \( a \) Quantity of amorphous region
- \( c \) Quantity of crystalline region
- \( i \) \( i \)-component of quantity in the Cartesian coordinate system
- \( \ell \) \( \ell \)-component of quantity in the Cartesian coordinate system

Superscripts

- \( (e) \) Effective quantity

Operators

- \( \langle \rangle \) Averaging operator
- \( (\cdot)_i \) \( i \)-th component of the gradient of a quantity
- \( (\cdot)_{i_1 i_2} \) The Laplacian differential operator of a quantity
INTRODUCTION

When we consider the transport of gases and vapors through plastic membranes we have assumed that there are no cracks, pores or other gross defects. The transport of matter usually is considered to take place by the following process: solution (condensation, then mixing) of gas or vapor into the surface layers, migration through the bulk material by activated diffusion to the opposite surface, and evaporation from that surface into the gaseous phase.

Transport of penetrants within a plastic membrane is affected by a number of factors, including the physical and chemical properties of the penetrant as well as the experimental conditions. Significant properties are polarity and condensibility of gases, gas collision diameter. The structure of the polymer also affects the permeation. We can divide the structure into two parts: physical structure and chemical structure. The physical structure includes pre-existing holes, their size, numbers and their distribution in the polymer, and crystallinity. The chemical structure expresses the skeletal chain configuration, molecular weight, chemical modification of polymer; the introduction of methyl or polar side groups, esterification of presence of double bonds in the main polymer chain, etc.

The gas transport through plastic membranes is of interest for many diverse fields of physics and chemistry. An important objective of
studies on the permeability of polymers has been to try to relate permeability to polymer structure. In general, the physical properties of polymeric substances are far less quantitatively defined than those of other substances. The melting point, density, clarity, crystallinity, and etc., if ever specified, are given in terms of ranges.

Polymers can be divided into two categories, those which are wholly amorphous and those which are partly crystalline. Some polymers are wholly amorphous under all conditions; the polymers which are partly crystalline may of course be amorphous under certain conditions (above their melting point, or if quickly quenched from their molten condition). A crystalline region in a polymer is a region of high molecular order and (usually) tight molecular packing. Thus, when gases, vapors or liquids penetrate through polymer matrix they are confined to the non-crystalline (amorphous) region between crystallites. The presence of crystallites within a medium lowers the overall rate of transport. In the absence of capillaries or voids within the plastic membrane, the higher the amount of crystallinity, the lower are both the diffusion and solubility coefficients and, hence, the permeability (16, 17, 18, 19). However, the value of the diffusion coefficient usually is not directly proportional to the amorphous content, as is the solubility, but has a more complex dependence on it.

Despite endless efforts of many investigators to clarify the relationship of permeability on crystallinity, the result is far from our expectations. This is due to the physical properties of
polymeric substances. During the last fifteen years many investigators have shown quantitatively that permeability dependence on crystallinity can be explained by assuming that the plastic medium is homogeneous; however, a few investigators (2, 4) have assumed that the plastic medium is heterogeneous, and the type of flow through the heterogeneous system is analogous to current flow through a medium containing particles whose dielectric constant is nearly zero. Van Amerongen (1) in 1947 demonstrated for the first time how the onset of crystallization reduced diffusion, solubility, and permeability constants for gutta percha. After his demonstration a number of investigations have shown that a semicrystalline polymer has a lower permeability than the corresponding amorphous polymer does. Klute (2, 4) investigated the system of water vapor and polyethylene; Lasoski and co-workers (3) also studied water vapor and polyethylene; Alter (5) extended the work to include oxygen, nitrogen, and carbon dioxide in polyethylene; and Michaels and co-workers (6) measured helium, argon, ethane permeation in polyethylene. All of them suggested empirical equations for permeability dependence on crystallinity, even though there are somewhat different interpretations of the structural factors of the crystalline region.

The major objectives of present work has been the following:

The first, to discover the permeability dependence on crystallinity in polyethylene, polypropylene, nylon 6, and cellulose acetate under the theoretical assumption that the system is heterogeneous, with the following considerations. One is that the permeability constant depends only on the degree of crystallinity. Then the
permeability constants should be about the same at a fixed point of crystallinity regardless of the kind of polymers. If the above assumption is not true, it means the permeability constant depends on other factors besides the degree of crystallinity. A different approach is based on the assumption that the permeability depends not only on the degree of crystallinity but also on crystallite shape and its size and distribution. If at a certain point of crystallinity, for example 50% crystallinity, the size and distribution of crystallinity are the same, then the permeability constant should be the same at that point regardless of kind of polymers. If the above assumption is not true, it means at that point the size and distribution of crystallite are different for different polymers, even if the degree of crystallinity is the same. Therefore, a third assumption is that the permeability constant depends not only on the physical properties but also on the chemical properties of the polymer.

The second objective is development of an equation for the effective permeability coefficient in the heterogeneous system, based on that of Prager (15), as a function of concentration and position.

The third objective is to derive correlations between crystallinity and density, and between density and permeability.

The fourth, to compare the Lasoski and Cobbs' equation (3)

$$P = P_a \chi_a^2$$

with the equation derived for my heterogeneous system model, in predicting the permeability dependence on crystallinity.
The fifth, to study the perm-selectivity of permeability in polymers.

The sixth, to compare the gas permeability coefficients by two methods; method A(38) is the upstream pressure is under the atmosphere and as the amount of transmitted gas increases with time, the mercury level in the calibrated capillary falls and the mercury height as a function of time can be obtained. Method B(43) is the transmission of gases under superatmospheric pressure through polymer films in a cell has been determined. The permeability coefficient is calculated from the rate of change of volume of permeated gas. The steady-state transmission rate is measured by the rate which a short column of mercury moved through a section of calibrated glass capillary tubing which is vibrated to prevent the mercury from sticking.
A. Permeability Dependence on Crystallinity

The problem of permeation in the inhomogeneous media has received relatively little attention, although the mathematically analogous problem of the dielectric behavior of heterogeneous media has been extensively discussed.

De Vries (7) treated mathematically the flow of current in a medium comprising a dilute suspensions and regular lattices of uniform particles. He derived the analytical equation for dielectric permeability. Maxwell (8), Burger (9) and Eucken (10) treated a system which was a dilute suspension of spheres and ellipsoids. Rayleigh (11), Runge (12), Barrer and Petropoulos (13) treated other shapes of particles suspended in the continuum. Barrer (20) has derived the diffusion coefficient for steady state as a function of concentration and position in a heterogeneous system. Brown (14) and Prager (15) attempted to treat the heterogeneous system by statistical methods.

Prager, especially, suggested methods for the calculation of an effective diffusion coefficient for inhomogeneous media. The equation for the effective diffusion coefficient is in the form of an infinite series involving a correlation between diffusion coefficients at n different points. He also has derived the approximate expressions
involving two-point correlations. It is assumed that the crystalline regions are dispersed randomly in a continuum of amorphous material and that the system is isotropic. The crystalline region is in the form of spheres of different sizes. A sphere consists of several lamellae as shown Figs. 1 and 2. It is also assumed that transport of gases and vapors among the lamellae is negligible, that solubility is directly proportional to the amorphous volume fraction, $X_a$, and that there is a complex dependence of diffusion on the amorphous content.

In a homogeneous membrane when Henry's law is obeyed, the steady state permeation flux of matter can be expressed as

$$J = D S \left( \frac{P_1 - P_2}{\lambda_0} \right)$$

(1)

or

$$P = D S = \frac{J \lambda_0}{(P_1 - P_2)}$$

(2)

$D$ is diffusion coefficient, $S$ is solubility coefficient, $\lambda_0$ is the thickness of membrane, $P_1$ and $P_2$ are partial pressure of gases and vapors at surface 1, and 2, respectively, $P$ is permeability constant.

In a heterogeneous system the actual permeability constant varies from point to point in a random manner as diffusion and solubility constants vary point to point.

Fick's law of diffusion at steady state in a homogeneous system is

$$D C_{i,1,1} = 0$$

(3)

Here is used a very valuable abbreviation, the Cartesian Convention Summation. Comma indicates differentiation with respect to the
Fig. 1.
Schematic Picture of Heterogeneous System.
Fig. 2.
Schematic Picture of Crystalline System,
Consisting of Several Lamellae.
corresponding position coordinate.

The diffusion flux of matter can be expressed as

$$D = \frac{J \cdot S}{C_1 - C_2}$$  \hspace{1cm} (4)$$

In a heterogeneous system the corresponding equation is

$$(D C_{i1})_{i1} = 0$$  \hspace{1cm} (5)$$

with boundary conditions

$$C(0, x_2, x_3) = C_1 \text{ and } C(l, x_2, x_3) = C_2$$  \hspace{1cm} (6)$$

In the present work Prager's effective diffusion coefficient equation is used for derivation of permeability in heterogeneous system and the precise derivations of equations are in Appendix II.

If the actual diffusion coefficient $D$ and concentration is known as a function of position $\vec{r} = (x_1, x_2, x_3)$, the flux vector can be calculated by the following equation

$$J_i(\vec{r}) = -D(\vec{r}) \cdot C_{i1}$$  \hspace{1cm} (7)$$

and its average is

$$\langle J_i \rangle = \frac{1}{V} \int_V J_i(\vec{r}) \, d\vec{r}$$  \hspace{1cm} (8)$$

Substitution of $\langle J_i \rangle$ for $J$ in equation (4) would then give the effective diffusion coefficient. The difficulty is that it is very difficult to find out explicitly the distribution of $D$ and $C$ as a function of position.

Barrer (20) and others suggested that the concentration dependence of the diffusion coefficient can be represented by an exponential equation, and Barrer also suggested many shapes of concentration and
position dependence of diffusion coefficient.

Prager (15) suggested exact and approximate mathematical methods for calculation of an effective diffusion coefficient when $D$ is a function of concentration and position in a heterogeneous medium. An exact effective diffusion coefficient is obtained in the form of an infinite series involving correlations between diffusion coefficients at $n$ different points and an approximate one is obtained in the form of an approximate expression involving only two-point correlations.

In the present work only two points, $\mathbf{r}$, $\mathbf{r} + \mathbf{s}$, are considered. The relationship between two points, $\mathbf{r}$, $\mathbf{r} + \mathbf{s}$ can be given as

$$ f(s) = D(\mathbf{r}) \phi(r + s) $$

$$ \phi(r + s) = \ln D(r + s) - \langle \ln D \rangle $$

After Eq. (5) is written at a point $\mathbf{r} + \mathbf{s}$, multiply by $D(\mathbf{r})$ and take an average over $\mathbf{r}$.

$$ \left< D(\mathbf{r}) D(\mathbf{r} + \mathbf{s}) C_{ij}(\mathbf{r} + \mathbf{s}) \right>,_i = 0 $$

or

$$ \left< e^{\ln D(\mathbf{r})} e^{\ln D(\mathbf{r} + \mathbf{s})} C_{ij}(\mathbf{r} + \mathbf{s}) \right>,_i = 0 $$

or

$$ \left< e^{\ln D(\mathbf{r})} - \langle \ln D \rangle e^{\ln D(\mathbf{r} + \mathbf{s})} - \langle \ln D \rangle C_{ij}(\mathbf{r} + \mathbf{s}) \right>,_i $$

$$ \times e^2 \langle \ln D \rangle = 0 $$
or
\[ \langle e^{\phi(\vec{r})} \phi(\vec{r} + \vec{s}) C_{1}(\vec{r} + \vec{s}) \rangle, \hat{s} = 0 \]
or
\[ \langle e^{u + v} \rangle, \hat{s} = 0 \] (9)

where
\[ u = \phi(\vec{r}) \]
\[ v = \phi(\vec{r} + \vec{s}) \]
\[ w = C_{1}(\vec{r} + \vec{s}) \] (10)

Here, it is assumed \( \phi(\vec{r}), \phi(\vec{r} + \vec{s}), C_{1}(\vec{r} + \vec{s}) \) are jointly distributed. In order to reduce three random variables, \( u = \phi(\vec{r}), v = \phi(\vec{r} + \vec{s}), w = C_{1}(\vec{r} + \vec{s}) \), with a joint probability density

\[ p_{uvw}^{(3)}(u, v, w) \]

reduced to the two-variable distributions, \( p_{uv}^{(2)}(u, v), p_{vw}^{(2)}(v, w) \), let us consider the following two approximations:

1. A joint probability density, \( p_{uvw}^{(3)}(u, v, w) \) must reduce to

\[ p_{vw}^{(2)}(v, w) \cdot p_{u}^{(1)}(u), \]

if any variable, for example, \( u \) is independent, where \( p_{u}^{(1)}(u) \) is the single-variable distribution for \( u \).

2. If \( p_{uvw}^{(3)}(u, v, w) \) is intergrated with respect to any variable, for example, \( u \), the result must be \( p_{vw}^{(2)}(v, w) \).

Thus, the superposition approximation (21, 22, 23)
which is not reasonable our standards, since, although it satisfies condition (1), it does not satisfy (2).

In terms of characteristic functions as the Fourier transform of the probability density functions,

\[
\psi_{uvw}^{(3)}(\alpha, \beta, \gamma) = \int \exp \left[ i(\alpha u + \beta v + \gamma w) \right] p_{uvw}^{(3)}(u, v, w) du dv dw
\]

\[
\psi_{uv}^{(2)}(\alpha, \beta) = \int \exp \left[ i(\alpha u + \beta v) \right] p_{uv}^{(2)}(u, v) du dv
\]

\[
\psi_{u}^{(1)}(\alpha) = \int \exp \left[ iu\alpha \right] p_{u}^{(1)}(u) du
\]  

(12)

both approximations (1) and (2) can be satisfied more easily than in terms of the distribution functions themselves,

1. If \( u \) is independent of both \( v \) and \( w \), then

\[
\psi_{uvw}^{(3)}(\alpha, \beta, \gamma) = \psi_{uv}^{(2)}(\beta, \gamma) \psi_{u}^{(1)}(\alpha)
\]

2. \( \psi_{uvw}^{(3)}(\alpha, \beta, 0) = \psi_{uv}^{(2)}(\alpha, \beta) \), etc.

Thus, we get the approximation

\[
\psi_{uvw}^{(3)}(\alpha, \beta, \gamma) = \frac{\psi_{uv}^{(2)}(\beta, \gamma) \psi_{uv}^{(2)}(\alpha, \beta) \psi_{u}^{(1)}(\alpha)}{\psi_{u}^{(1)}(\alpha) \psi_{v}^{(1)}(\beta) \psi_{w}^{(1)}(\gamma)}
\]  

(13)

By using Eqs. (12) and (13), Eq. (9) can be expressed as

\[
\exp^{u + v w} = -i(\frac{\partial \psi_{uvw}^{(3)}}{\partial \gamma})\alpha = \beta = -i, \gamma = 0
\]

\[
\exp^{u + v} \left[ (\exp^{u} / \exp^{v}) + (\exp^{v} / \exp^{u}) - (\exp^{v}) \right]
\]  

(14)

Substituting Eq. (10) into Eq. (14)
\[ \langle e^{\phi(\vec{r}) + \phi(\vec{r} + \vec{s})} C_{*1}(\vec{r} + \vec{s}) \rangle \]

\[ = \langle D(\vec{r}) D(\vec{r} + \vec{s}) (e^{-2 \langle \ln D \rangle}) \rangle \times \]

\[ \left[ \frac{\langle D(\vec{r}) C_{*1}(\vec{r} + \vec{s}) \rangle}{\langle D(\vec{r}) \rangle} + \frac{\langle D(\vec{r} + \vec{s}) C_{*1}(\vec{r} + \vec{s}) \rangle}{\langle D(\vec{r} + \vec{s}) \rangle} - \langle C_{*1}(\vec{r} + \vec{s}) \rangle \right] \]

\[ = H(s) e^{-2 \langle \ln D \rangle} k_{*1}(s) \quad (15) \]

where \( H(s) = \langle D(\vec{r}) D(\vec{r} + \vec{s}) \rangle \),

\[ (16) \]

and

\[ k_{*1}(s) = \frac{\langle D(\vec{r}) C_{*1}(\vec{r} + \vec{s}) \rangle}{\langle D(\vec{r}) \rangle} - \frac{\langle D(\vec{r} + \vec{s}) C_{*1}(\vec{r} + \vec{s}) \rangle}{\langle D(\vec{r} + \vec{s}) \rangle} - \langle C_{*1}(\vec{r} + \vec{s}) \rangle \quad (17) \]

Thus

\[ \langle D(\vec{r}) D(\vec{r} + \vec{s}) C_{*1}(\vec{r} + \vec{s}) \rangle_{*1} = (H(s) k_{*1}(s) e^{-2 \langle \ln D \rangle})_{*1} \]

\[ = 0 \]

or

\[ (H(s) k_{*1}(s))_{*1} = 0 \quad (18) \]

Eq. (18) has once again the form of a diffusion equation with \( H(s) \) and \( k(s) \) acting as the diffusion coefficient and the concentration, respectively, and \( H(s) \) depends on the magnitude of \( s \) alone.

To obtain the solution of Eq. (18), first let us find the solution of \( k(s) \) for an isotropic medium in the form of
k(s) = q(s) s \cos \theta \frac{\langle D(\mathbf{r}) C_{\lambda}^{(x)}(\mathbf{r}) \rangle}{\langle D(\mathbf{r}) \rangle} + k(0, 0, 0) \quad (19)

where \( \theta \) is the angle between the \( i \)-direction and the \( \lambda \)-direction to which the main diffusion occurs.

The function \( q(s) \) in Equation (19) is satisfied by the following differential equation.

\[
\frac{d^2 q}{ds^2} + \left( \frac{1}{s} + \frac{d(\ln H)}{ds} \right) \frac{dq}{ds} + \left( \frac{1}{s} \frac{d(\ln H)}{ds} \right) \cdot q = 0
\]

(20)

with boundary conditions

\[
\lim_{s \to \infty} \frac{dq(s)}{ds} = 0
\]

\[
\lim_{s \to \infty} q(s) = 1
\]

\( q(0) \) : finite

Derivation of Eq. (20) is in Appendix II.

If we know \( q(0) \), the effective diffusion coefficient is then obtained from the following equation which from Eq. (17) and Eq. (19) and its derivation is in Appendix II.

\[
D(e) = \frac{\langle D \rangle}{2} - q(0)
\]

(21)

In order to find \( q(0) \) the following system and probability are assumed. The material is isotropic and consists of two regions, amorphous and crystalline, which are randomly dispersed in each other.
The diffusion coefficient \( \overline{D_a} \) prevails in the amorphous region, and \( \overline{D_c} \) in the crystalline region. The term \( p_{12}(s) \) is the probability that of two points a distance \( s \) apart one will lie in region 1 while the other will lie in region 2. Also, define \( X_a \) and \( X_c \) as the volume fraction occupied by amorphous and crystalline region, respectively. The diffusivity, \( \overline{D_c} \), in the crystalline region is zero. Then we can postulate

\[
H(s) = D_a^2 \left[ X_a - \frac{1}{2} p_{12}(s) \right]
\]  

(22)

It is assumed that \( p_{12}(s) \) has the form of

\[
p_{12}(s) = \begin{cases} 
2X_a (1 - e^{-bs}) & s \leq \langle \ln X_a \rangle/b \\
2X_a X_c & s > \langle \ln X_a \rangle/b 
\end{cases}
\]  

(23)

Substituting Eq. (22) into Eq. (20) and then solving for \( q(s) \), the result is

\[
q(0) = \frac{\ln X_a}{2} \cdot \frac{X_a}{X_c + X_a \ln X_a}
\]  

(24)

Again substituting Eq. (24) in Eq. (21) we find

\[
D(e) = D_a X_a \frac{X_c + X_a \ln X_a}{2(X_c + X_a \ln X_a) - \frac{1}{2} X_a (\ln X_a)^2}
\]  

(25)

The precise derivations of Eqs. (24) and (25) are in Appendix II.
And

\[ S = S_a \chi_a \]

Therefore the permeability constant is

\[ P = \frac{\chi}{S} \]

\[
= P_a \chi^2 \frac{X_c + X_a \ln X_a}{2(X_c + X_a \ln X_a) - \frac{1}{2} X_a (\ln X_a)^2}
\]

(26)

In the present work the above equation was tested with the experimental data of permeability, and the fit was compared with that of Lasoski and Cobbs' equation, \( P = P_a \chi^2 \).

B. Permeability Dependence on Density

Various workers have attempted to relate the decrease in polymer gas permeability with increasing density to one or more mathematical or physical models. The first assumption \( (4, 44) \) was that the permeability is a linear function of polymer density.

Second, assuming both solubility and diffusivity are function of the volume fraction of amorphous material,

\[ S = S_a (1 - \Phi) \]

and

\[ D = D_a (1 - \Phi) \]

\( S_a \) and \( D_a \) are the solubility and diffusion coefficient in totally amorphous polymer, respectively, and \( \Phi \) is the volume fraction of crystalline material.
In terms of density,

\[ \Phi = \frac{d - d_a}{d_c - d_a} \]

where \( d \) is the density and subscripts \( a \) and \( c \) refer to amorphous and crystalline phases, respectively. And in the steady state the permeability constant is

\[ P = S_a D_a (1 - \Phi)^2 \]

\[ = P_a (1 - \frac{d - d_a}{d_c - d_a})^2 \]

If we assume \( d_a \) is constant, then the permeability constant is

\[ P = \text{constant} \ (d_c - d)^2 \quad (27) \]

Third, Meyers and et al (45) cited the problem for the flow of current through a medium containing spherical particles of a different dielectric constant as perhaps analogous to gas flow through a semicrystalline polymer membrane. Their treatment leads to the expression for permeability, \( P \), as

\[ P = \text{constant} \ (d_c - d)^2 \quad (28) \]

Fourth, Klute (4, 44), on the basis of another electrical analog, derived the expression for the function:

\[ \frac{P}{P_a} = (1 - \Phi)^2 + (1 - \Phi)(1 - \Xi) \]
or

\[ P = P_a \left( \frac{\tau}{c^2} + \left( \frac{1 - \tau}{c} \right) \right) \]

\[ + \left( \frac{(c \tau - c - 2)}{c^2} \right) d + \left( \frac{d^2}{c^2} \right) \]

(29)

where \( c = (d_c - d_a) \) and \( \tau \) is the slope of a plot \( \frac{P}{P_a} \) versus \( (1 - \Phi) \).

Eqs. (27), (28), and (29) are almost identical, differing only in the physical interpretation of the coefficients which in turn depend on the original model. And so Eqs. (27), (28), and (29) are all special cases of the expression

\[ P = K (d_c - d)^n \]  

(30)

The \( K \) is a constant and \( n \) is not specified. Eq. (30) then express in general terms analogous of semicrystalline membrane permeability. The experimental data were fitted to Eq. (30), and the values of \( K \) and \( n \) for polymers and penetrants were found.

C. Selectivity Ratio of Permeability

The permeability constant can be written, without any detailed knowledge of permeation mechanism, as the product of three factors: the first, \( F \), is a function of polymer properties, such as flexibility of chains, cohesive energy, degree of crystallinity and/or distribution of crystallites, and degree of crosslinking and so on; the second, \( G \), is the nature of penetrant molecule, such as polarity, critical temperature, and the size and shape of gas molecule; and the third, \( \chi_e \), is a function of the interaction of polymer and the penetrants. For many polymers and gases \( \chi_e \) may be considered to be very close to unity.
But in the case of easily condensable vapors, such as organic solvent and water vapor, \( \gamma \), it differs considerably from unity and can be the controlling factor in some extreme cases. For example, in the systems methyl bromide in polyethylene (27), isobutylene-polyethylene (27), and water vapor in nylon, polyvinyl alcohol, and cellophane (28) the gases behave like plasticizers and solvent for the polymer besides being the penetrant molecules.

Thus, the permeability constant of polymer \( i \) for gas or vapor \( k \) may be expressed as the following equation (29).

\[
P_{i,k} = F(\text{polymer } i) \cdot G(\text{gas } k) \cdot \gamma_0(i,k)
\]

(31)

For any given pair of gases or of polymers the selectivity, or ratio of permeability constants is given by the equation

\[
\frac{P_{i,k}}{P_{i,\ell}} = \frac{G(\text{gas } k) \cdot \gamma(i,k)}{G(\text{gas } \ell) \cdot \gamma_0(i,\ell)}
\]

(32)

\[
\frac{P_{i,k}}{P_{j,k}} = \frac{F(\text{polymer } i) \cdot \gamma_0(i,k)}{F(\text{polymer } j) \cdot \gamma_0(j,k)}
\]

(33)

In the case of permanent gases, the interaction forces between gas molecules are small and there is no particular interaction between the gas and polymer molecules. But in the case of condensable vapor, where intermolecular forces between the molecules of vapor are considerably higher, there are two cases: one is that the interaction between polymer and vapor is greater than the cohesive forces of vapor; the other is that cohesive forces of vapor are larger than the interaction forces between polymer and vapor. The former is found
in some organic solvent vapor-polymer systems and water vapor-hydrophilic polymer. The deviation from the ideal is due to the considerable solvent and plasticizing effect. The latter is found in the non-solvent or poor solvent vapor, or condensable inorganic vapor-polymer system and especially water vapor-hydrophobic polymer systems. In this case the solubility of vapor is expected to be very small but the vapor molecules tend to cluster together, depending on the strength of their cohesive forces.

With the above simple relationship one can predict the permeability constants for n-m gas-polymer systems by determining $(n + m)$ values in stead of $n \cdot m$. For any given pair of gases (or polymer) the ratio of permeability constants will give the valuable guide to choose the appropriate gases (or polymers) in the separation processes and the other operations.

One can find out the evidence for the effect of the crystallites in restricting polymer chain probability in the amorphous regions can be obtained through examining of the variation with crystallinity of the selectivity for permeation to gases having different molecular sizes.

Here, Eq. (32) is used to find out the selectivity of permeability of water vapor and carbon dioxide for all samples and water vapor and nitrogen, carbon dioxide and nitrogen for polyethylene.
FIGURE 3 PHOTOGRAPHIC PICTURE OF THE APPARATUS FOR GAS PERMEABILITY
FIGURE 4. SCHEMATIC PICTURE OF APPARATUS FOR GAS PERMEABILITY (38)
LEGEND FOR FIGURE 3 AND FIGURE 4

1. Valve (v-1)
2. Metal Plate Disk Cell
3. Mercury-valve (V-2)
4. Valve (V-3)
5. 3-way Stop Cock (V-4)
6. Mercury Storage
7. Trap
8. Bubbler
9. Mercury Manometer
EXPERIMENTAL PROCEDURE

A. Measurement of Gas Permeability

The permeability apparatus and procedure of operation was essentially the same as that described by Major and Kammermeyer (38). A schematic diagram of the overall apparatus is shown in Figure 4. The filter paper is centered on the glass plate and the film specimen is placed over the filter paper. Next, the O-ring which is slightly bigger than the filter paper is put over the film and the top plate is brought down in film contact with the O-ring by adjusting the toggle action pliers. Carbon dioxide from Cardox Co., with 99.5% purity is then allowed to flow over the film by adjusting the valve V-1 and then to pass through a trap and bubbler with a $\frac{1}{8}$ to $\frac{1}{4}$ inches water level, which permits observation of the gas flow.

The mercury valve V-2 is set to the downward position and valve V-4 is turned toward to vacuum pump and the vacuum pump is then turned on. After equilibrium has been established in the capillary by the evacuation process, the mercury valve is raised to its upward position. Valve V-4 is then turned to cut the vacuum pump and allow atmospheric air to enter the space above the mercury in valve V-2. Permeated gas collects in the capillary volume and causes the mercury level to move downward. Mercury levels in the capillary are read at time intervals.
FIGURE 5. SCHEMATIC PICTURE OF APPARATUS FOR GAS PERMEABILITY UNDER CONSTANT PRESSURE DROP.
LEGEND FOR FIGURE 5

1. Mercury Receiver
2. Valve
3. Vibrator
4. Mercury Plug
5. Cell
6. Pressure Gauge
7. Pressure Regulator
8. Gas Tank
B. Measurement of Gas Permeability under Constant Pressure Drop

The permeability apparatus and procedure of operation under constant pressure drop method was described by Brubaker and Kammermeyer (42). In the cell, a porous disc \( \frac{1}{2} \) inches in diameter was attached on the upper steel plate by epoxy resin. An O-ring which was slightly bigger than the porous material was placed on the lower steel plate and the film specimen was placed over the O-ring. Next, two steel plates were tightened with six bolts and nuts. A schematic picture of the overall apparatus was shown in Figure 5.

A 100-pound pressure gauge was used for carbon dioxide with polyethylene, polypropylene and cellulose acetate and a 400-pound one was used for carbon dioxide with nylon 6 and nitrogen with polyethylene to measure the pressure drop across the film. The pressure drop for the measurement of carbon dioxide permeability of polyethylene, polypropylene and cellulose acetate was in the ranges of 90 to 95 psig, carbon dioxide of nylon 6 was 160 to 192, and nitrogen of polyethylene was 108 to 150, respectively. A thermometer was used to measure the temperature of the gas leaving the low pressure side of the film. After equilibrium was reached, the rate at which a short column of mercury moved through a section of glass capillary tube about 70 cm length and about 1.5 mm inside diameter was observed to determine the gas rate of flow. The capillary tube was vibrated to ensure a uniform rate of travel of the mercury plug. The volume of capillary was calibrated by displacement of mercury in the capillary at known temperature.
LEGEND FOR FIGURE 6

1. Fan
2. Cup
3. Cabinet for Constant Temperature and Humidity
4. Pump
5. Cooling Tank
6. Refrigerator
7. Dry Bulb and Wet Bulb Temperature Recorder
FIGURE 7. SCHEMATIC PICTURE OF CUP FOR WATER VAPOR PERMEABILITY
C. Measurement of Water Vapor Permeability

Water vapor permeability measurements were carried out by the "cup-method", procedure A, described in ASTM designation: E96-66. The membrane to be tested with rubber packing and an aluminium cover is fastened by three bolts over the mouth of a dish, which contains a desiccant of calcium chloride that is dried at 200°C (392°F) before use. The assembly is placed in an atmosphere of constant temperature and humidity, and the weight gain of the assembly is used to calculate the rate of water vapor movement through the membrane under the following conditions.

Temperature: 23°C (73.4°F)

Relative humidity on the two sides of membrane:
  0% inside dish
  50% outside dish

D. The Measurement of Density

The density apparatus and procedure of measurement was based on ASTM designation D792-66. The apparatus included an analytical balance with a precision of 0.1 mg, a wire, an immersion vessel, and a thermometer. The analytical balance was equipped with a stationary support for the immersion vessel above the balance pan. The wire was instrumental corrosion resistant stainless steel with a diameter of 0.02 inches, obtained from Precision Steel Warehouse. It was attached to the balance and was sufficiently long to reach from the hook above the pan to the support for the immersion vessel. A 250 ml beaker was used for an immersion vessel. The thermometer had a precision ± 1°C.
Five specimens for each sample were cut carefully to avoid the changes in density resulting from compressive stresses. The size was about \(1\frac{1}{2}\) by 2 inches and the edges were made round.

ACS grade isopropanol (\(d = 0.781-0.783\) at 23\(^{\circ}\)C) was used as immersion media for polyethylene, polypropylene and nylon 6, and distilled water (\(d = 0.99626\) at 28\(^{\circ}\)C) was used for cellulose acetate. The specimen was first weighed in air to the nearest 0.1 mg and then attached to the wire on the hook of the balance arm. The immersion vessel was mounted on the support, and the suspended specimen completely immersed in immersion media at a temperature of 28 \(\pm 1^{\circ}\)C. The vessel did not touch the wire and specimen. The bubbles on the wire and specimen surface were removed. Next, the suspended specimen was weighed to the nearest 0.1 mg very rapidly in order to minimize absorption of immersion media by specimen. Then wire in immersion media was weighed with immersion to the same depth as used in the previous step. The procedure was repeated five times for each polymer sample.
RESULTS AND DISCUSSION

The experimental data for the permeability of carbon dioxide and water vapor at different densities and crystallinities in polyethylene, polypropylene, nylon 6, and cellulose acetate and nitrogen in polyethylene and the ratios of permeability are listed in Table 2.

Figs 10, 11, and 12 show the linear relationship between crystallinity and density in polymers, and their experimental and calculated values are listed in Table 3.

Figs. 13, 14, 16, 17, 18, and 19 show the experimental data for permeability of carbon dioxide and water vapor versus amorphous volume percent in polyethylene, polypropylene and nylon 6, and Fig. 15 for nitrogen in polyethylene.

Figs. 20 and 21 show the permeability for water vapor and carbon dioxide calculated by the heterogeneous system model equation, Eq.(26), versus amorphous volume percent.

Figs. 22, 23, 25, 26, 27, and 28 show the experimental data of permeability of carbon dioxide and water vapor versus density in polyethylene, polypropylene and nylon 6, and Fig. 24 for nitrogen in polyethylene. Table 4. contains their experimental and calculated values and Table 5 contains the constants, K and n.

Table 6, 7, and 8 contain the experimental data of permeability to water vapor, carbon dioxide, nitrogen, and the values calculated by
heterogeneous system model equation and Lasoski and Cobb's equation.

Table 10 contains the experimental data of gas permeability by two methods. The experimental data and calculated values of gas permeability in tables and figures are from the method A.

X-ray diffractograms are shown in Figs. 29 (crystallinity = 78.8%), 30 (crystallinity = 58.4%) in polyethylene, 31 (crystallinity = 62.9%), 32 (crystallinity = 46.1%) in polypropylene and 33 (crystallinity = 59.8%), 34 (crystallinity = 48.8%) in nylon 6, and 35 in cellulose acetate.

There is a linear relationship between crystallinity with a 90 to 99% correlation significance in polyethylene, polypropylene, and nylon 6. The results are:

\[
d_{\text{polyethylene}} = 2.02 \times 10^{-3} \text{ (crystallinity %)} + 0.798
\]

\[
d_{\text{polypropylene}} = 3.83 \times 10^{-4} \text{ (crystallinity %)} + 0.878
\]

\[
d_{\text{nylon 6}} = 9.55 \times 10^{-3} \text{ (crystallinity %)} + 1.066
\]

Raff and Allison (24) found a small deviation from the linear relationship between amorphous content versus density in polyethylene at 20°C. Sperati (25) showed a good linear relationship in the range between 35 and 80 percent crystallinity.

A comparison of the heterogeneous system model equation, Eq. (26), with Lasoski and Cobb's equation shows that both equations are in fairly good agreement to the experimental data.

Figs. 20 and 21 show that the shapes of curves are different for different polymers and penetrants, permeation of carbon dioxide
in nylon 6 is very small, and thus the curve in Figure 21 is nearly linear; but for the case of water vapor the curve of nylon 6 is in a higher position than those of polyethylene and polypropylene. This means that the presence of crystallinity is not a sufficient condition for low permeability because in water transmission the permeability also depends on the hydrophilic or hydrophobic properties and crystalline shape and size distribution. Nylon 6 is hydrophilic and polyethylene and polypropylene are hydrophobic polymers.

The K values are different for different polymers and penetrants. It is a reasonable result, because K is a parameter which is a function of \( P_a \) and the densities of the crystalline and amorphous phases. However, the values fall mostly in the range of 1.6 to 2.68, except for 3.88 for carbon dioxide in polyethylene and 0.19 for water vapor in cellulose acetate. From the above results one can see that the solubility and diffusivity dependence on density are not linear functions. Their dependence on density is different for different polymers and penetrants.

An important property of polyolefins, such as polyethylene and polypropylene is low water vapor permeability. On the other hand, they have rather high permeability to gases and organic vapors. As shown in Table 2 the ratio of the permeabilities of water vapor to carbon dioxide for polyethylene and polypropylene is considerably lower than nylon 6 and cellulose acetate. This is due to the chemical nature of polyolefins. They have no polar groups and consequently have extremely low solubility coefficients for water vapor (4); but
they have also low cohesive energies leading to rather high diffusion constants. The tremendous difference of permeability of water vapor and carbon dioxide is mainly due to the high solubility of water vapor in nylon 6 and cellulose acetate.

The hydrophobic polyolefin polymers obeys Henry's law over a wide range of relative pressure (31, 4, 32, 33) but nylon 6 and cellulose acetate do not obey Henry's law (35, 36). In polyethylene and polypropylene the diffusion process obeys Fick's law but in cellulose acetate the diffusion process is Fickian at the initial stage and non-Fickian at a later stage. Cellulose acetate has an exceptionally high value of diffusion constant and in nylon 6 the diffusion process depends on the concentration.

Combining these two processes, sorption and diffusion, it is not surprising that nylon 6 and cellulose acetate have a high value of the perm-selectivity to carbon dioxide.

The selectivity ratio of permeability should be independent of crystallinity for any given polymer. However, there is deviation observed as shown in Table 2. Michaels (30) also showed the same result as the above in polyethylenes with different densities. His perm-selectivity ratios were $O_2/N_2$, He/O$_2$, He/N$_2$ and He/CO$_2$. If the effect of the crystallites were only that of an impermeable filler, the ratios of the constants for any gas pair should be the same in all polymer samples. In his work the constancy of selectivity holds for nitrogen and oxygen, where molecular sizes are not very different, but the other pairs have different selectivity with variation of polymer crystallinity. The molecular diameters of oxygen and nitrogen are
2.96 Å and 3.16 Å, respectively. In the present work the diameters of carbon dioxide, water vapor and nitrogen are 4.6 Å, 2.72 Å, and 3.16 Å, respectively. There is a great difference of diameters and the lack of consistency is reasonable by Michael's explanation. This evidently shows that the crystallite is more than an impermeable filler in the polymer matrix.

In the polyethylene and polypropylene data the permeability increases in the high crystalline region. Nylon 6 has no data in that region. For polyethylene, the permeability of water vapor and carbon dioxide at 21.2 percent amorphous content are 4.39 and 6.32 times higher than expected values from calculated by the heterogeneous system model equation, Eq. (26), and for polypropylene, the permeability of water vapor and carbon dioxide at 20 percent amorphous content are 6.7 and 4.33 times higher, respectively than expected values. The deviation from the decreasing trend which it is expected of permeability is great in the data of carbon dioxide in polyethylene. Major and Kammermeyer (38) showed the increment of permeability of carbon dioxide in high density polyethylene from Phillips Petroleum Co. and their results were

\[ P = 0.33 \times 10^{-9} \text{(STD cc)/(cm)}^2 \text{(sec)} \text{(cm Hg)} \quad \text{at } d = 0.929 \text{ g/cc} \]
\[ P = 1.07 \times 10^{-9} \text{(STD cc)/(cm)}^2 \text{(sec)} \text{(cm Hg)} \quad \text{at } d = 0.961 \text{ g/cc} \]

and their permeability constant of high density polyethylene was 3.24 times higher than that of low density. In the present work, the permeability data in polyethylene were
\[ P = 1.32 \times 10^{-9} \text{ (STD cc)}(\text{cm})/(\text{cm})^2(\text{sec})(\text{cm Hg}) \text{ at } d = 0.926 \text{ g/cc} \]

\[ P = 3.22 \times 10^{-9} \text{ (STD cc)}(\text{cm})/(\text{cm})^2(\text{sec})(\text{cm Hg}) \text{ at } d = 0.957 \text{ g/cc} \]

and the low density film was from Du pont Co. and high density film from Phillips Petroleum Co. and the permeability constant of high density is 2.43 times higher than that of low density and it was used the same apparatus which Major and Kammermeyer did. Reduction in permeability is a function of the shape and size-distribution of crystallites, as well as their volume contents. The shape and size-distribution of crystallites are dependent upon thermal history. It has been found \(^{(17)}\), for example, that a linear polyethylene slowly cooled from the melt and subsequently at annealed at a high temperature, even though both membranes have the same crystallinity.

This enhancement phenomenon of permeability (or diffusion constant) can be explained in two ways: the first is that the crystallite size, shape and its distribution in the amorphous matrix is transformed; so that the penetrants pass more easily through polymer matrix. The second explanation is that there is microporosity \(^{(37)}\) in the crystallites which are distributed more or less randomly through the sample.

Wuerth \(^{(26)}\), Frisch \(^{(41)}\) and Michaels and co-workers \(^{(40)}\) suggested the existence of microvoids in the high crystalline region in semi-crystalline polymer. Wuerth and Frisch postulated that the mechanism of gas transport through the small pore is Knudsen type. It is assumed that the value which is greater than the expected one calculated by Eq. \(^{(26)}\) is due to the existence of microvoids in the crystallites. In Figure 8 is shown a system in which the crystalline
Fig. 8.
Schematic Picture of the Existence of a Hole in Crystalline Particle.
region contains holes whose sizes are different and distribution are random. In order to detect the existence of the microvoids or pin holes in the high crystalline polyethylene a selenium sulfide print of the film was made by the following procedure: First, the surface of heavy weight white paper was tinted evenly by selenium sulfide powder. Next the specimen to be tested was put on the amalgamated steel plate and then the tinted yellow paper placed over the specimen, a 5 mil thick polyethylene film put over the paper, and finally the upper steel plate over the top. One week later the yellow tinted paper was examined to see if there were any pin holes or microvoids which would show as black spots on the yellow surface. The result was shown in Figure 9 with comparison of porous Nalfilm from Nalco Chemical Co. with estimated pore size is 60-100 Å and void volume is 61-75%. As shown in Figure 9 no pin holes or microvoids could be detected in high crystalline polyethylene nor in the porous Nalfilm. This means a pore size less than 60 Å cannot be detected with the selenium sulfide print. Permeability of carbon dioxide and nitrogen of Nalfilm were $0.17 \times 10^{-3}$ and $0.25 \times 10^{-3}$ (STD cc)/(cm)/(cm)/(sec)/(cm Hg), respectively and the flow rate was measured by the movement of soap foam in the standard burette under the pressure drop of 1.5 psig. and the temperature was 24.6°C. The permeability ratio of nitrogen and carbon dioxide is 1.5 and it is a little higher than 1.25 which is the ratio of square root of molecular weight of carbon dioxide and nitrogen. The Knudsen type permeability ratio equals to the ratio of inverse of square root of molecular weight at constant pressure and temperature. In the present work it could not
A. POLYETHYLENE (PHILLIPS PT.CO)  
\[ d = 0.957 \]

B. NALFILM (NALCO CHEM.CO.)  
60-100Å POROUS FILM

FIGURE 9. SELENIUM SULFIDE PRINT OF THE FILMS
prove exactly the Knudsen flow for the enhancement of permeability in high crystalline polymers with the permeability data. But from the result of selenium sulfide print pore sizes would be less than 60 Å. And the mean free path of nitrogen, carbon dioxide and water vapor at 20°C from the Handbook of Chemistry and Physics are 471 Å, 376 Å, and 587 Å, respectively. In the case of the mean free path is much greater than pore sizes, the flow is Knudsen type. Here, the mean free path of penetrants are greater than the estimated largest pore size.

Gas permeability data obtained by two methods are compared. There is good agreement except for high density polyethylene and nylon 6. In the case of the high density polyethylene (d = 0.957), the permeability constants of carbon dioxide and nitrogen are $3.22 \times 10^{-9}$ and $0.33 \times 10^{-9}$ by method A, $1.37 \times 10^{-9}$ and $0.097 \times 10^{-9}$ (STD cc)/(cm)$^2$/(sec)(cm Hg) by method B. And the value of method A is 2.36 times higher for carbon dioxide and 3.4 times higher for nitrogen than method B. It can be listed the reasons for the poor agreement of two methods: first, the pressure drop in method A is less than barometric pressure and is changed during the operation while the pressure drop in method B is 90 psig for carbon dioxide and 98 psig for nitrogen and is constant. Even though the operation was under the super atmospheric pressure there was no significant pressure effect on the permeability of carbon dioxide for changing the pressure drop from 42 to 118 psig in method B as shown below,
<table>
<thead>
<tr>
<th>Temperature T(°C)</th>
<th>Barometric Pressure (cm)</th>
<th>Pressure Drop (psig)</th>
<th>Permeability $(\text{STD cc})(\text{cm}) \times 10^9 (\text{cm}^2/\text{sec})(\text{cm Hg})$</th>
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<td>42</td>
<td>1.36</td>
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<tr>
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<td>32</td>
<td>74.54</td>
<td>118</td>
<td>1.35</td>
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</tbody>
</table>

The second possibility is the effect of the flexibility of the film. In general, the high crystalline polymer has the great brittleness and lack of flexibility. In method A one could not make a tight packing with the O-ring for high density polyethylene because of flexibility. With Apiozon Q sealing compound from Associated Electrical Industries Ltd. or plastic rubber cement from The Woodhill Chemical Corp. a better sealing between the film and O-ring could be made. With using sealing compound the permeability constant was reduced from 35-60 to $3.22 \times 10^{-9} (\text{STD cc})(\text{cm})/(\text{cm})^2(\text{sec})(\text{cm Hg})$ in high density polyethylene. Still the permeability of carbon dioxide and nitrogen in method A are higher than in method B is due to the existence of uncontrollable factors such as lack of flexibility of high crystalline polyethylene in the present work.

In the case of nylon 6 the permeability of carbon dioxide by method A is 2 to 3 times higher than those values by method B. The reasons for poor agreement might be the accuracy of the apparatus of method A and using the super atmospheric pressure drop, 160 psig, in method B.
CONCLUSIONS

There is a linear relationship between crystallinity and density with 90% correlation significance in polypropylene and a 99% correlation significance in polyethylene and nylon 6. If we know the density in the polymers, we can get crystallinity from the linear relationship.

Analysis of permeability in semi-crystalline polymers by heterogeneous system and the heterogeneous model equation, Eq. (26), are good agreement over a 30% amorphous region.

Permeability enhancement of high crystalline region in polyethylene and polypropylene may be due to microvoids with flow of the Knudsen flow type. This cannot be detected by the selenium sulfide print.

The permeability ratio of water vapor and carbon dioxide in cellulose acetate and nylon 6 is 30-100 times greater than the polyolefins. The permeability ratio of carbon dioxide and water vapor to nitrogen, and water vapor to carbon dioxide are 5.2-10.6, 79-143, and 7.4-22.4, respectively in polyethylene. The lack of consistency of permeability ratio in the same polymer sample with variation of crystallinity could be due to the great difference in molecular diameters in water vapor, carbon dioxide and nitrogen.

In permeability dependence on density the constant, K, varies
with different polymer and penetrant. The values of \( n \) fall mostly in the range of 1.6 to 2.68.

Density and crystallinity are not enough to characterize polymer structure, and the transport of penetrant does not depend only on the crystalline content of the polymer. It depends also on the crystallites shapes and sizes and their distributions, and the chemical properties of polymer and properties of penetrants.

In the present work it is hard to conclude which is the dominant factor in determining permeability. The degree of crystallinity, shape and size and distribution of crystallites, chemical properties of the polymer, and the property of penetrant, all affect the permeability. Generally speaking, polymer characterization by the other analytical method used has on the whole proven difficult, nevertheless, it has proved valuable supporting evidence for the morphological picture evolving from permeation studies.

In the comparison of the gas permeability by two methods, there is a good agreement except the high density polyethylene and nylon 6.
### Table 1: List of Films Used

<table>
<thead>
<tr>
<th>Film Sample No.</th>
<th>Trade Name</th>
<th>Composition</th>
<th>Thickness (mil)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td></td>
<td>Polypropylene (d&lt;0.900)</td>
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<td>Phillips Petroleum Co.</td>
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</tbody>
</table>

*Note: The composition and thickness values are approximate and may vary slightly.*
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<thead>
<tr>
<th>Film Sample No.</th>
<th>Trade Name</th>
<th>Composition</th>
<th>Thickness (mil)</th>
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<th>S.D.</th>
<th>P_N2</th>
<th>S.D.</th>
<th>P_H2O</th>
<th>S.D.</th>
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- **d**: Density, g/cc
- **P**: Permeability, \((\text{STD cc})(\text{cm})/(\text{cm})(\text{sec})(\text{cm Hg}) \times 10^9\)
- **S.D.**: Standard Deviation
- **X_0**: Crystallinity
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<th>(P_{H_2O}) S.D.</th>
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TABLE 5

K AND n IN THE EQUATION \( P = K (d_c - d)^n \)

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### Table 6
Experimental Data and Calculated Values of Permeability of Water Vapor

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### Table 7

**Experimental Data and Calculated Values of Permeability of Carbon Dioxide**

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<th>Lasoski and Cobbs' Equation</th>
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TABLE 10

COMPARISON OF GAS PERMEABILITY WITH TWO METHODS

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<td>25.8</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>PC-3</td>
<td>1.307</td>
<td>1.26</td>
<td>26.2</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>PC-4</td>
<td>1.313</td>
<td>2.75</td>
<td>26.2</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>PC-5</td>
<td>1.301</td>
<td>1.48</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PC-6</td>
<td>1.356</td>
<td>1.34</td>
<td>26.1</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>PN-1</td>
<td>1.124</td>
<td>0.057</td>
<td>25.5</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>PN-2</td>
<td>1.123</td>
<td>0.045</td>
<td>27.4</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>PN-3</td>
<td>1.112</td>
<td>0.075</td>
<td>25.3</td>
<td>0.036</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 10. CRYSTALLINITY VS DENSITY OF POLYETHYLENE

DATA OF SPERATI et al (25)
DATA OF MATTHEWS et al (24)
EXPERIMENTAL
CALCULATED

% CRYSTALLINITY

DENSITY, (GM/CC)

0.93  0.94  0.95  0.96

90  80  70  60  50
Figure 11. Crystallinity vs Density of Polypropylene
FIGURE 12. CRYSTALLINITY vs DENSITY OF NYLON 6
Figure 13: Permeability of Water Vapor vs Amorphous Volume Percent of Polyethylene
FIGURE 14. PERMEABILITY OF CARBON DIOXIDE vs AMORPHOUS VOLUME PERCENT OF POLYETHYLENE
Figure 15. Permeability of Nitrogen vs Amorphous Volume Percent of Polyethylene
FIGURE 17. PERMEABILITY OF CARBON DIOXIDE vs AMORPHOUS VOLUME PERCENT OF POLYPROPYLENE
Figure 18. Permeability of water vapor vs amorphous volume percent of nylon 6.
FIGURE 19. PERMEABILITY OF CARBON DIOXIDE vs AMORPHOUS VOLUME PERCENT OF NYLON 6
Figure 20. Permeability of water vapor vs amorphous volume percent calculated by model equation.
Figure 21. Permeability of Carbon Dioxide vs Amorphous Volume Percent Calculated by Model Equation
FIGURE 22. PERMEABILITY OF WATER VAPOR vs DENSITY OF POLYETHYLENE
FIGURE 23. PERMEABILITY OF CARBON DIOXIDE VS DENSITY OF POLYETHYLENE

\[
\frac{\text{PERMEABILITY}}{(\text{CM}^2)(\text{SEC})(\text{CM HG})}{(\text{STG CC})(\text{CM} \times 10^9)}
\]
Figure 24. Permeability of nitrogen vs density of polyethylene.
FIGURE 25. PERMEABILITY OF WATER VAPOR VS DENSITY OF POLYPROPYLENE
FIGURE 26. PERMEABILITY OF CARBON DIOXIDE VS DENSITY OF POLYPROPYLENE
FIGURE 27. PERMEABILITY OF WATER VAPOR VS DENSITY OF NYLON 6

\[
\text{PERMEABILITY, } \frac{(\text{cm}^2)(\text{sec})(\text{cm} \text{ Hg})}{(\text{std cm})(\text{cm} \times 10^{-9})}
\]

CALCULATED
EXPERIMENTAL
Figure 28. Permeability of carbon dioxide vs density of nylon 6.
FIG. 29. X-RAY DIFFRACTOGRAM OF POLYETHYLENE PE-3
FIGURE 30. X-RAY DIFFRACTOGRAM OF POLYETHYLENE PE-6
FIG. 31. x-RAY DIFFRACTOGRAM OF POLYPROPYLENE PP-1
FIGURE 32. X-RAY DIFFRACTOGRAM OF POLYPROPYLENE PP-4
FIG. 33. X-RAY DIFFRACTOGRAM OF NYLON 6 PN-2
FIGURE 34. X-RAY DIFFRACTOGRAM OF NYLON 6 PN-3

INTENSITY
FIGURE 35. X-RAY DIFFRACTOGRAM OF CELLULOSE ACETATE PC-2

Intensity
BIBLIOGRAPHY

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11. Rayleigh, Lord, Phil. Mag., 34, 481 (1892)
29. Rogers, C. E., V. Stannett, and M. Szwarc, Tappi, 39, 741 (1956)
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APPENDIX I

Calculation of Water Vapor Permeability in Polyethylene, PE-1

Permeability = permeance x thickness

\[ \text{Permeance} = \frac{\text{dw}}{\text{dt}} \cdot \frac{1}{\Delta P \cdot A} = \frac{\text{dw}}{\text{dt}} \cdot \frac{1}{S(R_1 - R_2)} \]

\[ \frac{\text{dw}}{\text{dt}} = \text{rate of water vapor transmission, in g/hr x } 10^4, \]

equals the slope of straight line from the plot of weight gain vs time as shown in Figure 29

A = exposed area of specimen, in cm²

\[ = (3.5)^2 \frac{\pi}{4} = 9.62112 \text{ cm}^2 \]

S = saturation vapor pressure, in cm Hg

\[ = 2.1068 \text{ cm Hg at } 23°C \]

\[ \Delta P = \text{vapor pressure difference, in cm Hg} \]

\[ \Delta P = S(R_1 - R_2) = (2.1068)(0.50) = 1.0534 \text{ cm Hg} \]

R_1 = relative humidity inside of dish

R_2 = relative humidity outside of dish

Convert weight to STD cc/sec

\[ \frac{\text{w}}{18} \times \frac{22400}{3600} = 0.34568 \frac{\text{STD cc}}{\text{sec}} \]
\[ P = \frac{\frac{\text{d}W}{\text{d}t}(10^{-4})(0.34568)(2.54 \times 10^{-3} \times L)}{9.62112 \times 1.0524} \]

\[ = (2.3045)(1)(8.6673) \times 10^{-9} \]

\[ = 19.97 \times 10^{-9} \frac{(\text{STD cc})(cm)}{(cm)^2(\text{sec})(cm \text{ Hg})} \]

**Calculation of Gas Permeability in Polyethylene, PE-1**

By the permeability equation (38)

\[ P = \frac{V_s \cdot L}{t \cdot A \cdot \Delta P} \]

The volume of gas permeated is computed in STD cc from the relation:

\[ V_s = \frac{(P_2V_2 - P_1V_1)T_o}{P_o^2} \]

Then \( P \) is

\[ P = \frac{(P_2V_2 - P_1V_1)T_o}{P_o^2} \cdot \frac{L}{t \cdot A \cdot \Delta P} \]

\( P \) = permeability constant, \( \frac{(\text{STD cc})(cm)}{(cm)^2(\text{sec})(cm \text{ Hg} \ \Delta P)} \)

\( V_s \) = volume of gas permeated, standard cc

\( L \) = specimen thickness, cm

\( t \) = duration of test, second

\( A \) = area of specimen under test, cm

\( \Delta P \) = pressure drop across film, cm Hg
\( P_1 \) = initial pressure of gas on low pressure side of film, cm Hg abs.

\( P_2 \) = final pressure of gas on low pressure side of film, cm Hg abs.

\( V \) = total system volume at any given manometer reading (includes capillary and void volume), cc

\( V_1 \) = initial total volume of gas on low pressure side of film, cc

\( V_2 \) = final total volume of gas on low pressure side of film, cc

\( T \) = temperature of gas on low pressure side of film, \( ^\circ \text{K} \)

\( T_c = \text{standard temperature, } 273.16^\circ \text{K} \)

\( P_0 \) = standard pressure 76 cm Hg abs.

Data

Temperature 23.3\(^\circ\)C

Barometric pressure 74.8 cm Hg

Specimen area \( \frac{1.97 \times 2.54}{2} \times 3.14 = 19.6657 \text{ cm}^2 \)

Thickness 1 mil
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Manometer Reading (cm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.05</td>
</tr>
<tr>
<td>30</td>
<td>69.5</td>
</tr>
<tr>
<td>60</td>
<td>67.9</td>
</tr>
<tr>
<td>90</td>
<td>66.5</td>
</tr>
<tr>
<td>120</td>
<td>65.1</td>
</tr>
<tr>
<td>150</td>
<td>63.7</td>
</tr>
<tr>
<td>180</td>
<td>62.6</td>
</tr>
<tr>
<td>210</td>
<td>61.55</td>
</tr>
<tr>
<td>240</td>
<td>60.6</td>
</tr>
<tr>
<td>270</td>
<td>59.6</td>
</tr>
<tr>
<td>300</td>
<td>58.7</td>
</tr>
</tbody>
</table>

The volume between the membrane and the top of the capillary is the void volume of the filter paper. This void volume was determined to be $0.326 \text{ cm}^3/19.6657 \text{ cm}^2$ of the filter paper by ASTM method. The calibration of the capillary volume was carried by the displacement of mercury in the capillary. The relation between the capillary volume and its height was found by the Least Square Method. And then the total volume is given by:

$$V = 2.6955 - 0.0316 H + \text{void volume}$$

$$= 3.0215 - 0.0316 H$$

The permeability between 66.5 cm Hg and 65.1 cm Hg in manometer reading can be calculated by the following:

$$V_1 = 3.0215 - (0.0316)(66.5) = 0.9201 \text{ cm}^3$$
\[ V_2 = 3.0215 - (0.0316)(65.1) = 0.9643 \text{ cm}^3 \]

and the product of PV are

\[ P_1V_1 = (74.8 - 66.5)(0.9201) = 7.6368 \text{ cm}^3 - \text{ cm Hg} \]

\[ P_2V_2 = (74.8 - 65.1)(0.9643) = 9.3537 \text{ cm}^3 - \text{ cm Hg} \]

\[ P = \frac{(9.3537 - 7.6368)(273)(1)(2.54 \times 10^{-3})}{(76)(296)(30)(19.6657)(74.8 - (74.8 - 66.5) + (74.8 - 65.1)} \]

\[ = 1.368 \times 10^{-9} \text{ (STD cc)(cm)/(cm)}^2(\text{sec})(\text{cm Hg}) \]

Likewise, Permeability between 71.05 cm Hg and 58.7 cm Hg are listed below.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Manometer Reading (cm Hg)</th>
<th>Permeability ( x \times 10^9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.05</td>
<td>1.091</td>
</tr>
<tr>
<td>30</td>
<td>69.5</td>
<td>1.091</td>
</tr>
<tr>
<td>60</td>
<td>67.9</td>
<td>1.273</td>
</tr>
<tr>
<td>90</td>
<td>66.5</td>
<td>1.242</td>
</tr>
<tr>
<td>120</td>
<td>65.1</td>
<td>1.368</td>
</tr>
<tr>
<td>150</td>
<td>63.7</td>
<td>1.498</td>
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<tr>
<td>180</td>
<td>62.6</td>
<td>1.272</td>
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<tr>
<td>210</td>
<td>61.55</td>
<td>1.296</td>
</tr>
<tr>
<td>240</td>
<td>60.6</td>
<td>1.243</td>
</tr>
<tr>
<td>270</td>
<td>59.6</td>
<td>1.384</td>
</tr>
<tr>
<td>300</td>
<td>58.7</td>
<td>1.313</td>
</tr>
</tbody>
</table>

\( P_{\text{average}} = 1.3211 \), \( \text{Standard Deviation} = 0.08291 \times 10^{-9} \)
Permeability constant under constant pressure drop across film is calculated as

\[ P = \frac{Q \cdot \ell_o}{A \cdot t \cdot \Delta p} \]

where
- \( Q \) = quantity of gas permeated, cc
- \( \ell_o \) = thickness of membrane, mil
- \( A \) = area of membrane, \( \text{cm}^2 \)
- \( t \) = time, seconds
- \( \Delta p \) = pressure drop across the membrane, \( \text{cm Hg} \)

Data

Temperature 26°C

Barometric pressure 74.67 cm Hg

Pressure drop across the membrane 90 psig

Time 3.58 min

Quantity of gas permeated 1.272 cc

Area of the membrane \( \frac{2.25 \times 2.54 \times 10^{-2}}{2} \times 3.14 = 25.632 \text{ cm}^2 \)

Permeability constant at standard condition is calculated as

\[
P = \frac{(1.272)(1)(2.54 \times 10^{-3})(74.67)(273.3 + 26)}{(76)(273)(25.632)(3.58 \times 60)(90/14.696 \times 76)}
= 1.357 \times 10^{-9} \text{ (STD cc)(cm)/(cm)}^2 \text{ (sec)(cm Hg)}
\]

Likewise the average permeability is

\[
P_{\text{average}} = \frac{1.357 + 1.365 + 1.34}{3} = 1.36, \text{ S.D.} = 0.02
\]
Calculation of Density in Polyethylene, PE-1

\[ d = \left( \frac{g}{g + h - b} \right) d_p \]

- \( d_p \) = density of isopropanol, g/cc
- \( g \) = weight of specimen without wire in air, in grams
- \( b \) = weight of specimen completely immersed and of the wire partially immersed in liquid, in grams
- \( h \) = weight of partially immersed wire, in grams

Temperature = 28°C

<table>
<thead>
<tr>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>0.0573</td>
<td>0.0556</td>
<td>0.0548</td>
<td>0.0563</td>
<td>0.0551</td>
</tr>
<tr>
<td>b</td>
<td>0.2480</td>
<td>0.2474</td>
<td>0.2472</td>
<td>0.2482</td>
<td>0.2474</td>
</tr>
<tr>
<td>h</td>
<td>0.2389</td>
<td>0.2390</td>
<td>0.2389</td>
<td>0.2390</td>
<td>0.2390</td>
</tr>
<tr>
<td>d</td>
<td>0.92964</td>
<td>0.92117</td>
<td>0.92158</td>
<td>0.93475</td>
<td>0.92262</td>
</tr>
</tbody>
</table>

\[ d_{\text{average}} = 0.92596 \text{ (g/cc)} \]

Standard deviation = 0.0042

Density = 0.926 ± 4.58 %
Calculation of Crystallinity in Polypropylene, PP-1

For the calculation of crystallinity from X-ray diffractogram the most important and essential thing is to separate the background (amorphous curve) from the crystalline interferences. However, unavoidably, it always involves certain uncontrollable assumptions.

For separation of background from the crystalline interference the Hermans and Weidinger method (46) is used for polypropylene, the Tobolsky and Krimm method (47) for polyethylene and the Rybnikar method (42) for nylon 6.

Here is explained the method for polypropylene as an example.

The basic point in the Hermans and Weidinger procedure is that the height of the maximum of the background is assumed to correspond that of the minimum between the two crystalline peaks, which occur at $2\theta = 14^\circ$ and $17.0^\circ$, respectively as shown in Fig. 31 (62.87 % crystallinity). Further, the maximum of the background is at $2\theta = 16.3^\circ$.

For construction of background the following steps are taken:

1. A straight line is drawn to connect the points of the diffraction curve corresponding $2\theta = 9^\circ$ and $31^\circ$.

2. Vertical distance $a$ from the background maximum to this straight line is determined at $2\theta = 16.3^\circ$.

3. Another point of the background at $2\theta = 15^\circ$ is then found at the vertical distance $0.9a$ above the straight line.

4. Background curve is finally finished as a smooth curve passing through two constructed points and tangent to the diffractogram at the diffraction angles of about $12^\circ$, $20^\circ$, $23^\circ$, respectively.
The areas of the upper (crystalline region) and (lower amorphous region) part of background in diffractogram were measured by planometer, and the crystallinity is

$$\epsilon = \frac{A_c}{A_c + A_a} \times 100$$

$\epsilon$ = Crystallinity, percent

$A_t$, $A_c$ and $A_a$ are total, amorphous and crystalline areas, respectively.

<table>
<thead>
<tr>
<th>Run</th>
<th>$A_t$ (in$^2$)</th>
<th>$A_a$ (in$^2$)</th>
<th>$A_c$ (in$^2$)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.45</td>
<td>2.70</td>
<td>4.75</td>
<td>63.76</td>
</tr>
<tr>
<td>2</td>
<td>7.20</td>
<td>2.75</td>
<td>4.45</td>
<td>61.81</td>
</tr>
<tr>
<td>3</td>
<td>7.37</td>
<td>2.73</td>
<td>4.46</td>
<td>62.96</td>
</tr>
<tr>
<td>4</td>
<td>7.32</td>
<td>2.72</td>
<td>4.60</td>
<td>62.84</td>
</tr>
<tr>
<td>5</td>
<td>7.43</td>
<td>2.75</td>
<td>4.68</td>
<td>62.99</td>
</tr>
</tbody>
</table>

$\epsilon_{\text{average}} = 62.87\%$

Standard deviation = 0.63

Crystallinity = 62.9 ± 1 %
APPENDIX II

Derivation of the Equations (20) and (21)

The gradient of a scalar, \( \nabla f \) and the Laplacian of scalar, \( \nabla^2 f \), in terms of spherical coordinates are

\[
\nabla f = \hat{e}_s \frac{\partial f}{\partial s} + \hat{e}_\theta \frac{1}{s} \frac{\partial f}{\partial \theta} + \hat{e}_\phi \frac{1}{s \sin \theta} \frac{\partial f}{\partial \phi}
\]

\[
\nabla^2 f = \frac{1}{s^2} \frac{\partial}{\partial s} \left( s^2 \frac{\partial f}{\partial s} \right) + \frac{1}{s^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{s^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2}
\]

Using the above spherical coordinates let us derive the Equations (20) and (21). In the vector notation, the Equation (18) will be

\[
\nabla \cdot (H(s) \nabla k(s, \theta)) = \nabla H(s) \cdot \nabla k(s, \theta) + H(s) \nabla^2 k(s, \theta) = 0 \quad \text{(36)}
\]

\[
\nabla H(s) = \hat{e}_s \frac{dH}{ds}
\]

\[
\nabla k(s, \theta) = \hat{e}_s \frac{\partial k}{\partial s} + \hat{e}_\theta \frac{1}{s} \frac{\partial k}{\partial \theta} + \hat{e}_\phi \frac{1}{s \sin \theta} \frac{\partial k}{\partial \phi}
\]

\[
(\nabla H(s)) \cdot (\nabla k(s, \theta)) = \frac{dH}{ds} \frac{\partial k}{\partial s}
\]
\[ \nabla^2 k(s, \theta) = \frac{1}{s^2} \frac{\partial}{\partial s} \left( s^2 \frac{\partial k}{\partial s} \right) + \frac{1}{s^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial k}{\partial \theta} \right) \]

\[ + \frac{1}{s^2 \sin \theta} \frac{\partial^2 k}{\partial \theta^2} \]

then

\[ \nabla \cdot (H(s) \nabla k(s, \theta)) \text{ will be} \]

\[ \frac{dH}{ds} \frac{\partial k}{\partial s} + H \left[ \frac{1}{s^2} \frac{\partial}{\partial s} \left( s^2 \frac{\partial k}{\partial s} \right) + \frac{1}{s^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial k}{\partial \theta} \right) \right] = 0 \]

(37)

Dividing Equation (37) by \( H \), if \( H(s) \neq 0 \)

\[ \frac{1}{s^2} \frac{\partial}{\partial s} \left( s^2 \frac{\partial k}{\partial s} \right) + \frac{1}{H} \frac{dH}{ds} \frac{\partial k}{\partial s} + \frac{1}{s^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial k}{\partial \theta} \right) = 0 \]

(38)

And from Equation (19), \( k(s, \theta) \) is

\[ k(s, \theta) = A q(s) s \cos \theta + k(\theta, \theta, \theta) \]

where

\[ A = \frac{\langle D(\mathbf{r}) \mathbf{C}, \mathbf{k} (\mathbf{r}) \rangle}{\langle D(\mathbf{r}) \rangle} \]

Differentiate Equation (19) with respect to \( s \) and \( \theta \), the results are

\[ \frac{\partial k}{\partial s} = A s \cos \theta \frac{dA}{ds} + A q(s) \cos \theta \]

(39)

\[ \frac{1}{s^2} \frac{\partial}{\partial s} \left( s^2 \frac{\partial k}{\partial s} \right) = \frac{2}{s} \frac{\partial k}{\partial s} + \frac{\partial^2 k}{\partial s^2} \]

(40)
\[ \frac{d^2 k}{ds^2} = 2A \cos \Theta \frac{dq(s)}{ds} + As \cos \Theta \frac{d^2 q(s)}{ds^2} \]  

\[ \sin \Theta \frac{\partial k}{\partial \Theta} = \sin \Theta Aq(s) s (-\sin \Theta) \]

\[ = -Aq(s) s \sin^2 \Theta \]  

\[ \frac{1}{s^2 \sin \Theta} \frac{\partial}{\partial \Theta} (\sin \Theta \frac{\partial k}{\partial \Theta}) = \frac{1}{s^2 \sin \Theta} (-Aq(s) s(2 \sin \Theta \cos \Theta)) \]

\[ = \frac{-2Aq(s)}{s} \cos \Theta \]  

Substitute the Equations (39), (40), (41), (42), and (43) in Equation (38), and it will be

\[ 2A \cos \Theta \frac{dq(s)}{ds} + As \cos \Theta \frac{d^2 q(s)}{ds^2} + \left( \frac{2}{s} + \frac{1}{H} \frac{dH}{ds} \right) (As \cos \Theta \frac{dq(s)}{ds} \]

\[ + Aq(s) \cos \Theta ) - \frac{2q(s)A}{s} \cos \Theta = 0 \]  

\[ (44) \]

Dividing Equation (44) by As \cos \Theta

\[ \frac{2}{s} \frac{dq(s)}{ds} + \frac{2}{s} \frac{d^2 q(s)}{ds^2} + \left( \frac{2}{s} + \frac{1}{H} \frac{dH}{ds} \right) \frac{dq(s)}{ds} + \frac{q(s)}{s} - \frac{2}{s^2} q(s) = 0 \]

or

\[ \frac{d^2 q(s)}{ds^2} + \frac{2}{s} \frac{dq(s)}{ds} + \frac{2}{s} \frac{dq(s)}{ds} + \frac{2}{s} q(s) + \frac{1}{H} \frac{dH}{ds} - \frac{dq(s)}{ds} \]

\[ + \frac{1}{sH} \frac{dH}{ds} q(s) - \frac{2}{s} q(s) = 0 \]

\[ \frac{d^2 q(s)}{ds^2} + \frac{4}{s} \frac{dq(s)}{ds} + \frac{1}{H} \frac{dH}{ds} \frac{dq(s)}{ds} + \frac{1}{sH} \frac{dH}{ds} q(s) = 0 \]
Since $\frac{1}{H} \frac{dH}{ds} = \frac{d \ln H}{ds}$

$$\frac{d^2q(s)}{ds^2} + \left( \frac{k}{s} + \frac{d \ln H}{ds} \right) \frac{dq(s)}{ds} + \frac{1}{s} \frac{d \ln H}{ds} \cdot q = 0 \quad (20)$$

For derivation of Equation (21), from the Equation (17) with boundary conditions the Equation (17) can be written as the following,

$$k_{r_1}(s) \rightarrow \frac{\langle D(r) \rangle \langle C_{r_1}(r + s) \rangle}{\langle D(r) \rangle}$$

$$+ \frac{\langle D(r + s) \rangle \langle C_{r_1}(r + s) \rangle}{\langle D(r + s) \rangle} - \langle C_{r_1}(r + s) \rangle$$

$$= \langle C_{r_1}(r + s) \rangle$$

$$\text{or} \quad = \langle C_{r_1}(r) \rangle$$

From Equation (19) $k_{r_1}(s)$ can be written as the following, $\lambda$ is direction cosine and equals $\cos \theta$.

$$k_{r_1}(s) = (s \lambda \frac{dq(s)}{ds} + \lambda q(s)) \frac{\langle D(r) \rangle C_{r_1}(r) \langle \rangle}{\langle D(r) \rangle}$$

$$\text{or} \quad k_{r_1}(s) = (s \cos \theta \frac{dq(s)}{ds} + \cos \theta q(s)) \frac{\langle D(r) \rangle C_{r_1}(r) \langle \rangle}{\langle D(r) \rangle} \quad (45)$$

$$\lim_{s \to \infty} k_{r_1}(s) = \langle C_{r_1}(r) \rangle \lim_{s \to \infty} (s \cos \theta \frac{dq(s)}{ds} + \cos \theta q(s))$$

$$= \langle C_{r_1}(r) \rangle$$
Hence, we obtain the following boundary conditions as \( s \) approaches infinite,

\[
\lim_{s \to \infty} \frac{dq(s)}{ds} = 0
\]

\[
\lim_{s \to \infty} q(s) = 1
\]

and \( q(o) \): finite

Then, the flux vector in the \( \ell \)-direction, \( J_\ell(\mathbf{r}) \), can be written from the Equation (7) and take average.

\[
J_\ell(\mathbf{r}) = -D(\mathbf{r})C_\ell(\mathbf{r})
\]

\[
\langle J_\ell(\mathbf{r}) \rangle = -\langle D(\mathbf{r})C_\ell(\mathbf{r}) \rangle
\]

From the Equation (17)

\[
\langle J_\ell(\mathbf{r}) \rangle = -\langle D(\mathbf{r}) \rangle \left[ (k,\ell)(s)\bigg|_{s=0} + \langle C_\ell(\mathbf{r}) \rangle \right]
\]

and since, from Equation (45)

\[
k_\ell(s)\bigg|_{s=0} = q(o) \frac{\langle D(\mathbf{r})C_\ell(\mathbf{r}) \rangle}{\langle D(\mathbf{r}) \rangle}
\]

Note: If we take it in the \( i \)-direction, "cos\( \theta \)" must be included before \( q(o) \). And we are interested only in \( \ell \)-direction in which the overall transfer occurs, so we should take

\[
\langle J_\ell(\mathbf{r}) \rangle = -\langle D(\mathbf{r}) \rangle \cdot \frac{1}{2} \left[ q(o) \frac{\langle D(\mathbf{r})C_\ell(\mathbf{r}) \rangle}{\langle D(\mathbf{r}) \rangle} + \langle C_\ell(\mathbf{r}) \rangle \right]
\]

\[
= -\frac{1}{2} q(o) \langle D(\mathbf{r})C_\ell(\mathbf{r}) \rangle - \frac{\langle D(\mathbf{r}) \rangle \langle C_\ell(\mathbf{r}) \rangle}{2}
\]

(46)
Comparing Equation (46) and Equation (7) we get

$$2 \langle D(r)C_{ij} (r) \rangle = q(o) \langle D(r)C_{ij} (r) \rangle + \langle D(r) \rangle \langle C_{ij} (r) \rangle$$

or

$$\langle D(r)C_{ij} (r) \rangle = \frac{\langle D(r) \rangle \langle C_{ij} (r) \rangle}{2 - q(o)} = \langle J_{ij} (r) \rangle$$

Then, finally we get the Equation (21)

$$p(e) = \frac{\langle D(r) \rangle}{2 - q(o)}$$

(21)

Derivation of Equations (24) and (25)

From Equations (20), (22), and (23),

$$\frac{d^2 q}{ds^2} + \left( \frac{d}{ds} \ln H \right) + \frac{4}{s} \frac{dq}{ds} + \frac{1}{s} \left( \frac{d}{ds} \ln H \right) q = 0$$

(20)

$$H(s) = D_a^2 \left[ X_a - \frac{1}{2} P_{12}(s) \right]$$

(22)

$$P_{12}(s) = \left\{ \begin{array}{ll}
2 X_a \left( 1 - e^{-bs} \right) & s < \frac{\ln X_a}{b} \\
2 X_a X_c & s > \frac{\ln X_a}{b} 
\end{array} \right.$$

(23)

Let us consider the Equation (20) in the domain $s < \frac{\ln X_a}{b}$.

Then, Equation (22) will be

$$H(s) = D_a^2 \left( X_a - X_c X_c \right)$$

$$\frac{d}{ds} \ln H(s) = 0$$
Equation (20) reduces to

\[
\frac{d^2 q^+}{ds^2} + \frac{4}{s} \frac{dq^+}{ds} = 0
\]  

(47)

Where \( q^+ \) is the solution of Equation (20) in the domain \( s > -(n X_a)/b \).

Equation (47) is the form of Cauchy-Euler equation. Let us assume the solution of Equation (47) is

\[ q^+ = \lambda s^n \]  

(48)

Differentiate Equation (48) with respect to \( s \), then we get the following ones:

\[ \frac{dq^+}{ds} = n \lambda s^{n-1} \]

\[ \frac{d^2 q^+}{ds^2} = n (n - 1) \lambda s^{n-2} \]  

(49)

Substitute Equation (49) in Equation (47)

\[ n (n - 1) + 4 n = 0 \]

\[ n (n + 3) = 0 \]

\[ n = 0, \quad n = -3 \]

When \( n = 0 \), the first solution, \( q^+_1 = \lambda_1 \)

\[ n = -3, \] the second solution, \( q^+_- = \lambda_2 s^{-3} \)

Then the total solution is

\[ q^+ = q^+_1 + q^+_2 = \lambda_1 + \lambda_2 s^{-3} \]

Since \( q^+(\infty) = 1, \quad \lambda_1 = 1 \)
therefore, the solution is
\[ q^+ = L_1 + L_2 s^{-3} \]
\[ = 1 + \frac{L_2}{s^3} \]

Next, let us consider Equation (20) in the domain \( s < -\frac{(\ln X_a)}{b} \).
Then,

\[ H(s) = D_a^2 \left[ X_a - \frac{1}{2} (X_a) (1 - e^{-bs}) \right] \]
\[ = D_a^2 \left[ X_a e^{-bs} \right] \]

\[ \ln H(s) = -bs + \ln (D_a^2 X_a) \]
\[ \frac{d \ln H(s)}{ds} = -b \] (50)

Substitute Equation (50) in Equation (20), and then Equation (20) reduces to

\[ \frac{d^2 q^-}{ds^2} + \left( \frac{4}{s} - b \right) \frac{d q^-}{ds} - \frac{b}{s} q^- = 0 \] (51)

Where \( q^- \) is the solution in the domain;

\[ 0 < s < -\frac{(\ln X_a)}{b} \]

Let us assume Equation (51) has the solution of a kind of the following series

\[ q^- = \sum_{\lambda} a_{\lambda} s^k + \lambda \] (52)

As it is done before, differentiate Equation (52) with respect to \( s \) and put them into Equation (51), then we get
\[ \sum a_\lambda (k + \lambda)(k + \lambda - 1) s^k + \lambda - 2 \]
\[ \sum 4 a_\lambda (k + \lambda) s^k + \lambda - 2 \]
\[ - \sum b a_\lambda (k + \lambda) s^k + \lambda - 1 = 0 \]
or
\[ a_\lambda(k + \lambda)(k + \lambda - 1) + 4 a_\lambda(k + \lambda) - b a_\lambda - 1 \]
\[ - b a_\lambda - 1 = 0 \]
or
\[ a_\lambda(k + \lambda)(k + \lambda + 3) = b a_\lambda - 1(k + \lambda) \]

if \( k + \lambda \neq 0 \)

\[ a_\lambda = \frac{b}{k + \lambda + 3} a_\lambda - 1 \] (53)

Then, the solution will be

\[ q^- = a_o(1 + \frac{b}{4} s + \frac{b^2}{5 \cdot 4} s^2 + \frac{b^3}{6 \cdot 5 \cdot 4} s^3 + \ldots) \]
\[ + a_o(s^{-3} + bs^{-2} + \frac{b^2}{2} s) + a_3(1 + \frac{b}{4} s + \frac{b^2}{5 \cdot 4} s^2 + \ldots) \]
\[ = a_o(s^{-3} + bs^{-2} + \frac{b^2}{2} s) + (a_o + a_3)(1 + \frac{b}{4} s + \frac{b^2}{5 \cdot 4} s^2 + \ldots) \]

Since \( q(o) \) is finite, \( a_o \) must vanish.

Therefore,

\[ q^- = (a_o + a_3)(1 + \frac{b}{4} s + \frac{b^2}{5 \cdot 4} s^2 + \ldots) \] (54)
And consider the Taylor series of $e^{bs}$

$$e^{bs} = 1 + bs + \frac{(bs)^2}{2} + \frac{(bs)^3}{3!} + \ldots$$  \hspace{1cm} (55)

To make Equation (54) in the form of Equation (55), multiply the Equation (54) by $\frac{3!}{s^3b^3}$, then

$$q = \frac{3!}{s^3b^3} \left[ (1 + bs + \frac{(bs)^2}{2} + \frac{(bs)^3}{3!} + \frac{(bs)^4}{4!} + \ldots) - 1 - bs - \frac{(bs)^2}{2} \right]$$

$$= \frac{B}{s^3} \left[ e^{bs} - 1 - bs - \frac{(bs)^2}{2} \right]$$ \hspace{1cm} (56)

Where

$$B = \frac{(a_0 + a_2) 3!}{b^3}$$

therefore, the solutions are

$$q^+ = 1 + \frac{2}{s^3} \quad \text{for} \quad s > \frac{-\ln X_a}{b}$$ \hspace{1cm} (57)

$$q^- = \frac{B}{s^3} \left[ e^{bs} - 1 - bs - \frac{(bs)^2}{2} \right] \quad \text{for} \quad s < \frac{-\ln X_a}{b}$$ \hspace{1cm} (58)

Matching the above solutions at $s = \frac{-\ln X_a}{b}$ for the functions and their derivatives to find $B$ and $\mathcal{L}_2$. 
\[ q^+ = 1 + \frac{2}{(-\ln x_a)^3} = 1 - \frac{b^3 L_2}{(\ln x_a)^3} \]  
(59)

\[ q^- = -\frac{B b^3}{(\ln x_a)^3} \left( \frac{1}{x_a} - 1 + \ln x_a - \frac{(\ln x_a)^2}{2} \right) \]  
(60)

therefore \( L_2 \) is

\[ L_2 = \frac{(\ln x_a)^3}{b^3} \left\{ 1 + \frac{B b^3}{(\ln x_a)^3} \right\} \]

\[ \left[ \frac{1}{x_a} - 1 + \ln x_a - \frac{(\ln x_a)^2}{2} \right] \]

\[ = \frac{(\ln x_a)^3}{b^3} + B \left( \frac{1}{x_a} - 1 + \ln x_a - \frac{(\ln x_a)^2}{2} \right) \]  
(61)

\[ \frac{dq^+}{ds} = -\frac{3 L_2}{s^4} \]

\[ \frac{dq^-}{ds} = -\frac{3 B}{s^4} \left( e^{b s} - 1 - b s - \frac{b^2 s^2}{2} \right) - \frac{b}{s^3} \left( b s^{b s} - b - b^2 s \right) \]

\[ -\frac{3 b^4 L_2}{(\ln x_a)^4} = -\frac{3 b^4 B}{(\ln x_a)^4} \left[ \frac{1}{x_a} - 1 + \ln x_a - \frac{(\ln x_a)^2}{2} \right] \]

\[ -\frac{b^3 B}{(\ln x_a)^3} \cdot \left( b \frac{1}{x_a} - b + b \ln x_a \right) \]
\[ L_2 = B \left\{ \left[ \frac{1}{X_a} - 1 + \ln X_a - \frac{\ln X_a^2}{2} \right] \right. \]
\[ + \frac{\ln X_a}{3b} \left[ b \frac{1}{X_a} - b + b \ln X_a \right] \right\} \]

From Equations (61) and (62)

\[ B \left\{ \left[ \frac{1}{X_a} - 1 + \ln X_a - \frac{\ln X_a^2}{2} \right] \right. \]
\[ + \frac{\ln X_a}{3b} \left[ b \frac{1}{X_a} - b + b \ln X_a \right] \right\} = \frac{(\ln X_a)^3}{b^3} + B \left\{ \frac{1}{X_a} - 1 + \ln X_a - \frac{\ln X_a^2}{2} \right. \]
\[ B \left\{ \frac{\ln X_a}{3b} \left[ b \frac{1}{X_a} - b + b \ln X_a \right] \right\} = \frac{(\ln X_a)^3}{b^3} \]

\[ B = \frac{(\ln X_a)^3}{b^3} \cdot \frac{\ln X_a}{3b} \left( b \frac{1}{X_a} - b + b \ln X_a \right) \]
\[ = - \frac{3(\ln X_a)^2}{b^3} \cdot \frac{1}{\frac{1}{X_a} + 1 - \ln X_a} \]
From Equations (54), (56), and (55), we get

\[ q(\theta) = \frac{B}{31} b^3 \]

\[ = \left( -\frac{3(\ln x_a)^2}{b^3} \cdot \frac{x_a}{x_a - 1 - x_a \ln x_a} \right) \]

\[ = -\frac{(\ln x_a)^2}{2} \cdot \frac{x_a}{x_a - 1 - x_a \ln x_a} \]

Substitute Equation (24) into Equation (21)

\[ D(e) = \frac{\left< D \right>}{2 - q(\theta)} \]

or

\[ D(e) = \frac{\left< D \right>}{2 - \frac{(\ln x_a)^2}{2} \cdot \frac{x_a}{x_c + x_a \ln x_a}} \]

\[ = \frac{\left< D \right> (x_c + x_a \ln x_a)}{2 (x_c + x_a \ln x_a) - \frac{x_a (\ln x_a)^2}{2}} \]

\[ D(e) = D_a x_a \frac{x_c + x_a \ln x_a}{2(x_c + x_a \ln x_a) - \frac{x_a}{2} (\ln x_a)^2} \]
VITA

Kook-Wha Koh was born July 11, 1936 in a remote place in the mountains near Kapsan, North Korea, the only daughter of Chang-Hyun and Juk-Jul Kim. In 1945 after World War II, her family moved from North Korea to South Korea.

The candidate was educated in elementary schools in Manchuria and in Seoul, Korea. She was graduated from Sook-Myung Girls' Middle and High School in 1955. She went to the Seoul National University, graduating with the B. S. degree in Chemical Engineering in 1960, and the M. S. degree in Chemical Engineering in 1964.

Except for the six months experience at Dong-Yang Cosmetics Manufacturing Co., the first professional experience was as a research engineer in Dai-Han Paint and Printing Ink Manufacturing Co., from March 1960 to August 1961.

She came to the University of Iowa in 1965 to continue her education.

She is an associate member of Sigma Xi and American Institute of Chemical Engineers.

She was married in 1963 and has three children.