# Permeation of Gases Through Polyethylene Films at Elevated Pressures

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The passage of gas through a plastic membrane is usually considered to involve three independent physical phenomena (*1, 2, 3*):

1. Solution or sorption of the gas or vapor at one surface of the membrane.
2. Diffusion of the dissolved gas through the membrane.
3. Re-evaporation or desorption.

Since the flow process is generally slow, this permits the use of an equilibrium relationship between the concentrations of sorbed gas at the interfaces and the respective partial pressures. Henry's law can then be assumed to apply:

$$C = kp \tag{1}$$

Polymeric films in general can be regarded as interspersed crystalline and amorphous regions. The gas molecules are assumed to be soluble only in the amorphous region (*4, 5, 6*). They pass through the membrane by a diffusion process following Fick's law:

$$N = -D\frac{dC}{dX} \tag{2}$$

If $D$ the diffusion constant is independent of concentration $C$ and the boundary conditions are

$$X = 0, \quad C = C_1$$

$$X = Z, \quad C = C_2$$

then Fick's law can be integrated to give

$$N = \frac{D}{Z}(C_1 - C_2) \tag{3}$$

From Equations (1) and (3)

$$N = \frac{D\,(k_1 p_1 - k_2 p_2)}{Z} \tag{4}$$

If the Henry's law constant is assumed a function only of temperature and both membrane surfaces are at the same temperature, then

$$k_1 = k_2 = k$$

and

$$N = \frac{Dk}{Z}(p_1 - p_2) \tag{5}$$

The permeability constant $P$ is defined as

$$P = D\,k = \frac{NZ}{p_1 - p_2} \tag{6}$$

or

$$N = \frac{P\,(p_1 - p_2)}{Z} \tag{7}$$

The fundamental postulation by Graham (*3*) that Henry's law applies to the sorption and desorption, and that Fick's law applies to the diffusion process has been well established (*1, 4*) and is generally used as the basis in the study of permeation processes.

In this work gaseous permeation through polyethylene film at pressures up to 11 atm. was investigated by measuring permeation constants at the following conditions:

1. Temperature was varied while both upstream pressure ($p_1$) and downstream pressure ($p_2$) were kept constant.
2. Polar as well as nonpolar gases were used.
3. $p_2$ was varied while the difference between $p_1$ and $p_2$ ($\Delta p$) was kept constant.
4. $\Delta p$ was varied while $p_2$ was kept constant.
5. Polymeric films of different thickness were used.
6. Double layers of films were used.

## MATERIALS, APPARATUS, AND PROCEDURE

### Film

Films of polyethylene were used for 4-mil film runs. The volume fraction of amorphous matrix was calculated from density measurement determined by use of a pycnometer. The average values of $\rho$ the density and $\alpha$, the volume fraction of amorphous phase are

$$\bar{\rho} = 0.922 \text{ g./cc.} \qquad \bar{\alpha} = 0.533$$

Film with a similar density to that of the above film (0.920 g./cc.) was used for the 1- and 2-mil film runs. The characteristics of this latter film are very close to those of the former. Figure 3 shows that the permeation constant of nitrous oxide for both films can be correlated by the same line of ln $P$ vs. $p_2$.

### Apparatus

As shown in Figure 1 the apparatus consisted basically of the following parts.

1. A high pressure and a low pressure reservoir.

These were made of extra heavy iron pipe of 4-in. diameter and 19-in. height. The dimensions of the reservoirs were such that the movement of gas from high to low side would change the pressure by less than 0.1%.

2. A diffusion cell.

The diffusion cell shown in Figure 2 was made of two 2 in. × 5 in. flanges of 304 stainless steel. A polymeric membrane

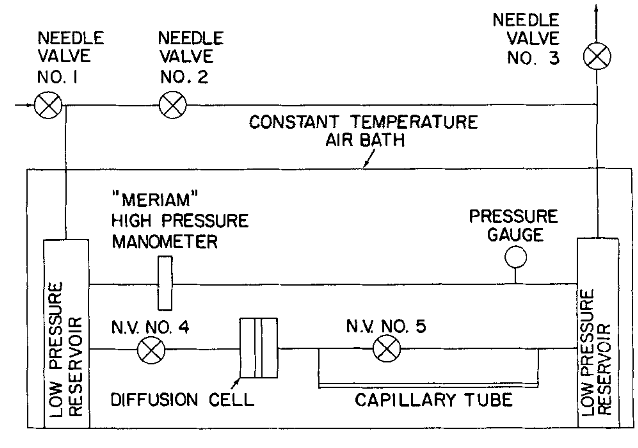

Fig. 1. Schematic diagram of apparatus.

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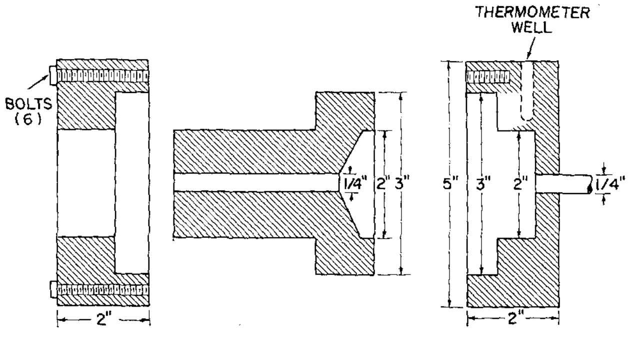

(Not to scale)

Fig. 2. Diffusion cell.

was held between two rubber gaskets and clamped between the flanges by six ⅝-in. bolts and nuts. The membrane was supported by two perforated copper plates with tissue papers inserted in between the polymer film and the copper plate.

3. A device for measuring the rate of diffusion.

This is a pyrex capillary tube with 1-mm. I.D. and 6-mm. O.D. The tube is 25 in. long with both ends flared for metal-glass fittings. The gas rate of flow was determined by observing a small slug of mercury moving inside the tube.

4. Temperature control.

The entire apparatus was enclosed in a wooden thermostated box, 27 in. × 27 in. × 72 in. in size.

5. Tubing, fittings, and valves.

Copper tubing of ¼-in. O.D. was used. All the fittings were of brass, standard compression type. All the valves were ¼-in. stainless steel, corrosion-resistant needle valves.

### Procedure

Permeation constants were determined by following the movement of the mercury slug inside a capillary tube as a function of time. Detailed description of procedures is presented elsewhere (7).

## RESULTS AND DISCUSSION

### Effect of Temperature

The temperature dependence of the permeation constant of carbon dioxide over the range 15° to 40°C. was found to obey the usual Arrhenius type of relationship; that is

$$P = P' \exp\left(-E_p/RT\right) \qquad (8)$$

The values of $P'$ and $E_p$ were calculated to be $5.625 \times 10^{-5}$ and 5.98 respectively.

Data are compared with those of Brubaker and Kammermeyer (8). The agreement is good, especially at 33°C., the temperature used in all the experimental runs except those for studying the effect of temperature, in this work. Values of $P'$ and $E_p$ from different sources are compared in Table 1.

For a gas whose permeability varies as a function of pressure $P'$ and $E_p$ should be function of pressure. For example consider the values of $P'$ and $E_p$ calculated from the permeability data of isobutylene (4). When the vapor activity, which is defined as the ratio of vapor pressure of the gas to its saturation vapor pressure, is increased from 0 to 0.7, $P'$ [cc. standard temperature and pressure (STP), cm./sec./sq.cm. — cm. Hg] is changed from 0.1515 to $0.1208 \times 10^{-4}$ while $E_p$ (Kcal./g., mole) is changed from 10.65 to 8.0. In general the slope of the line of $P$ vs. $1/T$ decreases as the pressure is increased.

Table 1. Permeability and Activation Energy of Carbon Dioxide

| | $E_p$ (Kcal./g. mole) | $P'$ (cc. STP, cm./sec., sq. cm., cm. Hg) |
|---|---|---|
| This work | 5.98 | $5.625 \times 10^{-5}$ |
| Waack et al. (9) | 6.80 | $1.80 \times 10^{-3}$ |
| Brubaker and Kammermeyer (8) | 7.12 | $3.26 \times 10^{-4}$ |
| Michaels and Bixler (6) | 7.20 | — |

### The Effect of Pressure Difference

Study of the effect of $\Delta p$ was made for the gases methane, butane, and nitrous oxide. The downstream pressure $p_2$ was kept constant at 14.7, 27.2, or 36.7 lb./sq.in.abs. The range of $\Delta p$ studied was from 5 to 17 in. Hg.

As discussed in detail in the next section permeability is found to be a function of pressure at constant $\Delta p$; consequently it is expected that there should also be a variation in permeability when $\Delta p$ is varied. However for all practical purposes permeability can be considered independent of $\Delta p$. This finding has an important bearing on the data of permeability at various pressures because although integrated permeability was obtained at certain $\Delta p$, it is actually equal to the more significant differential permeability. Mathematically this is illustrated below:

$$\bar{P} = \frac{1}{\Delta p}\int_{p-1/2\,\Delta p}^{p+1/2\,\Delta p} P_o e^{Ap}\, dp \qquad (9)$$

Integrating Equation (9) one obtains

$$\bar{P} = P\,\frac{\sinh\left(\dfrac{A\Delta p}{2}\right)}{\dfrac{A\Delta p}{2}} \qquad (10)$$

In order for the integrated permeability to be equal to the differential permeability the condition requires that

$$A\Delta p < 1.0 \qquad (11)$$

Since the values of $A\Delta p$ for methane, butane, and nitrous oxide are 0.1642, 0.0910, and 0.1190, it is obvious that the above condition is met by all the three gases.

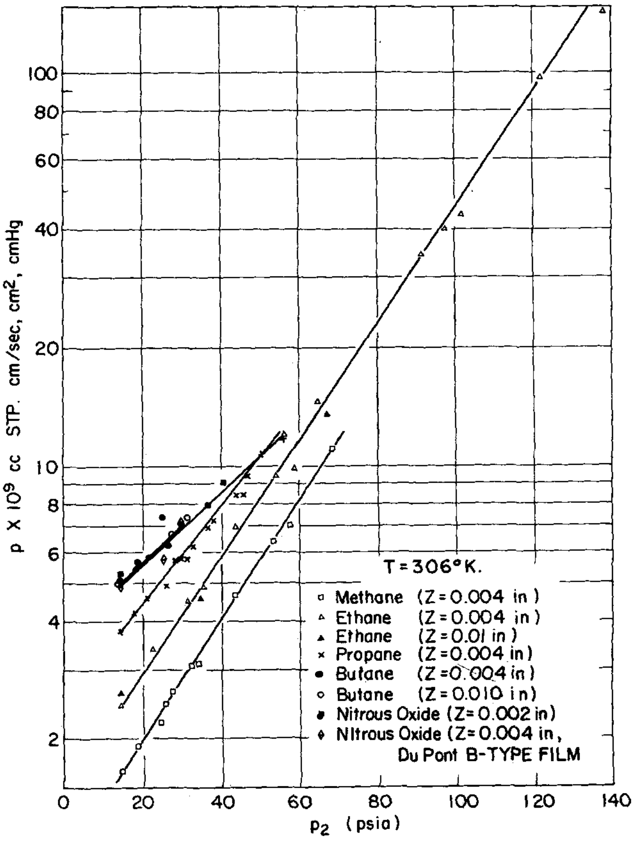

Fig. 3. Permeation constants of methane, ethane, propane, butane, and nitrous oxide.

### Effect of $p_1$ and $p_2$ at Constant $\Delta p$ and Temperature

The experimental results for the gases methane, ethane, propane, butane, ethylene, Freon-12, carbon dioxide, and nitrous oxide at $t = 33°C.$ and $\Delta p = 17$ in. Hg are plotted in Figure 3 and 4. These figures show that the permeability can be represented as an exponential function of $p_2$ for constant $\Delta p$ and temperature:

$$\overline{P} = \overline{P}_{op}\, e^{Ap_2} \tag{12}$$

or

$$\overline{P} = \overline{P}_o\, e^{Ap} \tag{13}$$

As discussed in the last section the permeability evaluated from the volume measurement is an average value over $\Delta p$. Since the change of $P$ with respect to $\Delta p$ is in general so small that it can not be observed, $\overline{P}$ can be considered as the point value $P$. In other words for all practical purposes the integrated permeability is equal to the differential permeability:

$$\overline{P} = P \tag{14}$$

Then

$$P = P_o e^{Ap} \tag{15}$$

The value of $A$ is usually small; therefore Equation (15) can be approximated by a linear equation:

$$P = P_o \left(1 + Ap + \frac{1}{2} A^2 p^2\right) \tag{16}$$

Fick's law [Equation (1)] can then be written as

$$N = P_o \frac{\Delta p}{Z} + P_1 \frac{\Delta p}{Z} \tag{17}$$

It should be noted that $P_o$, the permeability at $p_2 = 0$, is independent of the pressure, and

$$P_1 = \frac{P_o}{2} A\,(p_1 + p_2) \tag{18}$$

In summary at high pressures gaseous permeation is considered to follow a modified Fick's first law in which the variation of permeability with pressure has been taken into account. This modified Fick's law can be written in the following forms:

$$N = (P_o e^{Ap})\,(\Delta p/Z) \tag{19}$$

$$N = (P_o + P_1)\,(\Delta p/Z) \tag{20}$$

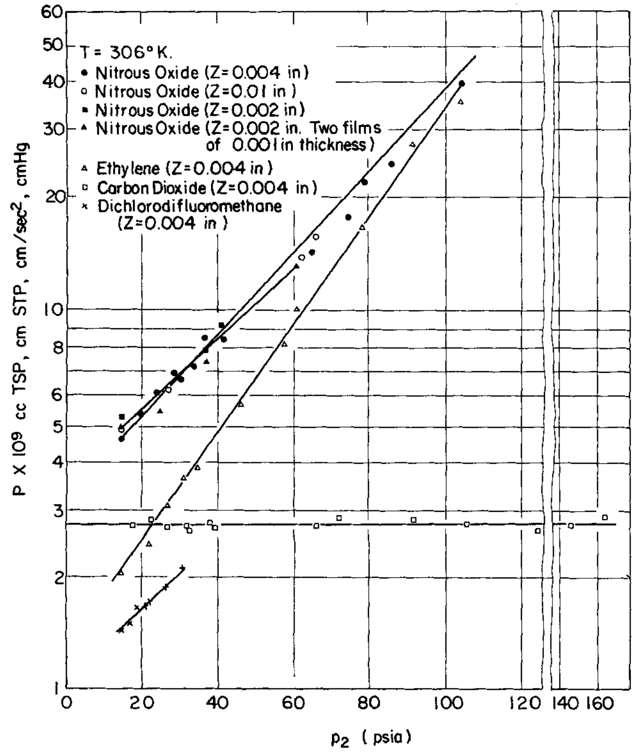

Fig. 4. Permeation constants of ethylene, nitrous oxide, carbon dioxide, and dichlorodifluoromethane.

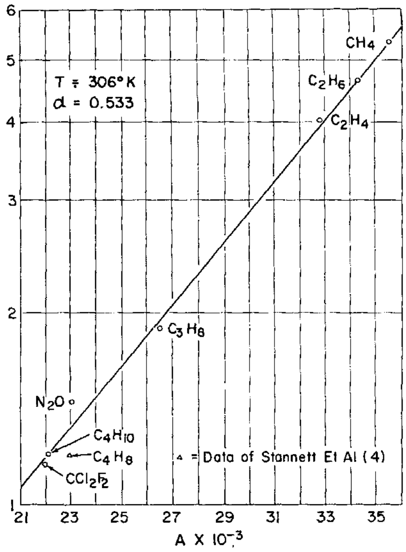

Fig. 5. Correlation of A for organic gases.

In the second form $P_1$ may be called a *second permeation constant.* It is essentially a correction term for pressure. For organic gases which are very pressure dependent, that is with high values of $A$, Equation (16) may be expanded to contain terms of order higher than 2 to give better accuracy in estimating permeability. For simple inorganic gases such as nitrogen, oxygen, carbon dioxide, etc. A will be zero and one will have the original Fick's first law.

The generally observed increase of $P$ with pressure implies a relationship between the extent of polymer-penetrant interaction and the value of the slope $A$. A useful measure of polymer-penetrant interaction is the difference between the Hildebrand solubility parameters of the polymer and the penetrant.

This solubility parameter ($\delta$) is defined as

$$\delta = (\Delta H_v / V^1)^{1/2} \tag{21}$$

In Figure 5 the logarithm of the absolute value of the difference between the Hildebrand solubility parameters of the polymer and penetrant ($\Delta\delta$) was plotted against $A$. For a small difference the interaction energy is small, and therefore the chemical compatibility and solubility of the system will be great. It is apparent from Figure 5 that there is a good correlation between $\Delta\delta$ ($\Delta\delta = |\delta_g - \delta_p|$) and $A$ in the sense that for large values of $\Delta\delta$ the slope of the ln $P$ vs. $p_2$ curve is large. In other words permeability increases more rapidly with pressure for a slowly permeating gas than for a rapidly permeating gas.

It is interesting to compare the permeability values of carbon dioxide, the only gas for which no correlation is obtained, and nitrous oxide. Both of these gases have the same molecular weight and similar molecular forms. However the nitrous oxide permeability varies with pressure, while carbon dioxide shows a constant permeability throughout the pressure range investigated (17.7 to 162.5 lb./sq.in.abs.). Moreover nitrous oxide shows a much higher permeability than carbon dioxide at the same pressure. This in a way coincides with the observation of Hildebrand and Scott (10), compared with carbon dioxide "nitrous oxide is more soluble in the non-polar solvent."

TABLE 2. PERMEATION, DIFFUSION, AND SOLUBILITY CONSTANTS OF METHANE, ETHANE, AND CARBON DIOXIDE

$T = 306°\text{K.}$ $\qquad$ $p_2 = 14.7$ lb./sq. in. abs.

| | $k \times 10^3 \left(\dfrac{\text{cc. STP}}{\text{cc. polymer, cm. Hg}}\right)$ | $D \times 10^7 \left(\dfrac{\text{sq. cm.}}{\text{sec.}}\right)$ | $P \times 10^9 \left(\dfrac{\text{cc. STP, cm.}}{\text{sec., sq. cm., cm. Hg}}\right)$ |
|---|---|---|---|
| $CH_4$ | 0.533 | 31.0 | 1.65 |
| $C_2H_6$ | 7.58 | 3.27 | 2.48 |
| $CO_2$ | 2.95 | 9.24 | 2.72 |

In this work polyethylene can be regarded as a nonpolar solvent. Another tentative explanation can be offered based on Buckley's recent adsorption model (*11*). In accordance with this model gas molecules pass through the polymer by adsorption on successive molecular chains of the polymer. Polymer chains therefore appear to play an active role in the transport process rather than the passive one required by the hole theory of diffusion. Since nitrous oxide is polar, with a dipole moment of 0.17 Debye, while carbon dioxide is nonpolar, it may be easier for nitrous oxide to be adsorbed on the polymer molecules owing to its stronger Van der Waal's force. Adsorption depends on pressure; therefore the permeability of nitrous oxide is pressure dependent and greater than that of carbon dioxide.

The constant value of the permeability of carbon dioxide throughout the pressure range of 11 atm. may also be related to the molecular diameter. Carbon dioxide has a molecular diameter of 3.9 Å (*10*) which is very close to that of oxygen (3.5 Å) and nitrogen (3.7 Å), while nitrous oxide has a much larger molecular diameter, 4.6 Å which is between that of methane (4.1 Å) and ethane (5.2 Å). Therefore carbon dioxide behaves like a permanent gas, such as nitrogen and oxygen which as mentioned before have permeabilities independent of pressure.

Recent measurement of the solubility constant of carbon dioxide for pressures up to 40 lb./sq.in.abs. by Eastburn (*12*) shows that solubility coefficient is also a constant. This finding is in agreement with the permeability data as far as pressure is concerned.

Since permeability is defined as the product of the solubility constant and diffusivity, increase of permeability with increase of pressure generally means that both solubility constant and diffusivity are functions of pressure. Solubility constants of methane and ethane were recently measured at various pressures by Eastburn (*12*), Lundberg, Wilk, and Huyett (*13*), and Kittelberger (*14*) respectively. Their results show that the solubility constants for both of these gases are pressure dependent and can be correlated by an exponential equation similar to Equation (13). If permeation and solubility constants are known, diffusivity can be easily calculated from Equation (6). Table 2 shows the experimental values of permeation and solubility constants and the calculated values of diffusivity of methane, ethane, and carbon dioxide at 1 atm.

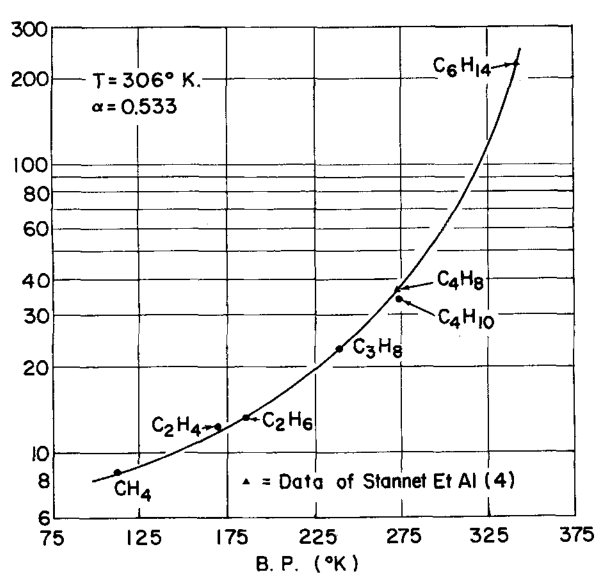

Fig. 6. Correlation of $P_0$.

The increase of diffusivity with increasing sorbed gas concentration has been demonstrated by the work of Stannett et al. (*4*). In their work organic vapors of methyl bromide, isobutylene, benzene, and *n*-hexane were used. Data were satisfactorily correlated by plotting integrated diffusivity vs. vapor activity and also by an exponential equation similar to Equation (13).

The dependence of diffusivity on pressure is considered due largely to the plasticizing effect. The recent hypothesis of Buckley discussed before may serve as an initial step in the complete understanding of this effect. Since Buckley suggested that the mechanism of transport process through polymer may be expressed by the model of successive adsorption of the penetrant molecules on successive polymer chains rather than by the model of Eyring's hole theory, there can be more than one penetrant molecule adsorbed on the same site of the polymer chain, thus creating a plasticizing effect.

Although measured at subatmospheric pressure, permeation data of isobutylene obtained by Stannett et al. (*4*) are pressure dependent. The data were therefore scaled up to fit the experimental conditions of this work, namely temperature of 33°C. and a polymer with amorphous phase content of 53.3 vol. %. In addition the data were changed from integrated form to differential form by

$$P = (Ap + 1)\,\overline{P} \qquad (22)$$

When the above mentioned data were recalculated to give differential permeabilities at various pressures under the experimental conditions of this work, slope A was evaluated and then plotted against the logarithm of the absolute value of $\delta_p - \delta_g$ in Figure 5. It can be seen that the proposed correlation of permeability and pressure works well on the data of isobutylene.

In evaluating the solubility parameter of a pure gas above its critical temperature hypothetical internal energies of vaporization and liquid volume cannot be obtained accurately by extrapolation procedures. Hildebrand (*10*) suggests calculating the solubility parameter of such a gas from its solubility data. In this work the solubility parameters of methane, ethane, and ethylene are calculated in this way.

An attempt was made to correlate $P_o$, which is defined by Equation (15) as a constant independent of pressure, with some physical property of the organic compounds. Figure 6 shows that when $P_o$ of the gas is plotted against its boiling point, a good correlation is obtained. The $P_o$ values used in the correlation are those of methane, ethane, ethylene, propane, and butane, the gases studied in this work. Additional data of isobutylene and *n*-hexane (*4*) measured directly at subatmospheric pressures are also shown in Figure 6. It should be noted that similar correlation were proposed by Othmer (*15*) and by Kammermeyer (*16*) for flow in micropores barriers.

### Effect of Film Thickness

All the runs made with single films of 1, 2, 4, and 10 mil thickness indicate that the permeability of gases is independent of thickness, so that the flow is inversely proportional to thickness. The results are plotted in Figure 3 and 4.

In the double film runs for nitrous oxide the permeability value for the single film was found to be the same as that of a double film of the same total thickness (see Figure 4).

## CONCLUSIONS

1. Henry's law and Fick's law are obeyed for carbon dioxide permeation through polyethylene at pressures up to 11 atm.

2. For the condition where the upstream pressure and downstream pressure were kept at 1.57 and 1.0 atm., respectively, the temperature dependence of the permeation constant of carbon dioxide was found to obey an Arrhenius type relationship $P = P' \exp(-Ep/RT)$ which was proposed originally for a condition of zero downstream pressure and an upstream pressure smaller than 1 atm. (*2, 4*). The temperature range investigated was from 14° to 40°C.

3. From the first conclusion and the existing data it may be safe to say that the Arrhenius equation is applicable to carbon dioxide at pressures at least up to 11 atm. and that for a gas whose permeation constant is pressure dependent the activation energy $E_p$ is a function of pressure.

4. Thickness of polyethylene film has no influence on the permeation constant either at low or high pressure over the thickness range investigated. Film thicknesses tested were 1, 2, 4, and 10 mil.

5. The permeabilities of methane, ethylene, ethane, propane, butane, nitrous oxide, and dichlorodifluoromethane were found to be pressure dependent. The upward trend of permeability with pressure in polyethylene, that is permeability increases with increasing pressure, gives qualitative support to the argument of the strong plasticizing effect exerted by organic and inorganic polar vapors and gases.

6. The effect of pressure on permeability may be accounted for by the exponential equation $P = P_o e^{Ap}$ or the modified Fick's first law $P = P_o \dfrac{\Delta p}{Z} + P_o \dfrac{A}{Z} (p_1 + p_2) \dfrac{p}{Z}$. A second permeation constant $P_1$ can be defined as $P_o \dfrac{A}{Z} (p_1 + p_2)$ which is essentially a correction term for pressure.

7. Boiling point was used in giving a satisfactory correlation of $P_o$ for nonpolar, organic gases. An organic gas here is defined as an organic compound which has a normal boiling point below 33°C., the temperature used for all the experiments except those for studying the effect of temperature in this work. The data used in the correlation are those of methane, ethylene, ethane, propane, butane, butene (*4*) and hexane (*4*).

8. Since boiling point can be related to the condensability of the gas, it can be stated that despite other possible factors the ease of condensation is an important condition in having a high permeation constant $P_o$.

9. The constant $A$ is successfully correlated by $\Delta\delta$ the absolute value of the difference between the Hildebrand's solubility parameters of the gas and the polymer. The data used in the correlation are those of methane, ethylene, ethane, propane, butane, nitrous oxide, methyl bromide and butene (*4*). This correlation is quite general in the sense that it applies to polar, nonpolar, unsaturated, and saturated organic gases.

10. The value of $\Delta\delta$ represents the degree of compatibility of the polymer and the permeating gas. Therefore gases with small values of $\Delta\delta$ will have high permeability and a small degree of pressure dependency.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = parameter characterizing the dependence of $\overline{P}$ on $p$
$C$ = concentration in molar units
$D$ = diffusivity
$E_p$ = activation energy for permeation
$\Delta H_v$ = heat of vaporization at temperature $t$, (°C.)
$k$ = solubility constant
$N$ = mass transfer rate defined in moles/time-area
$P$ = differential permeation constant
$\overline{P}$ = integrated permeation constant
$P'$ = permeation constant at infinite temperature
$P_{op}$ = permeation constant at zero downstream pressure ($p_2$)
$P_o$ = permeation constant at zero pressure
$p$ = gas pressure
$R$ = gas constant
$T$ = absolute temperature
$V^1$ = molal volume of liquid
$X$ = distance of permeation in polymer film
$Z$ = film thickness
$\alpha$ = volume fraction of amorphous polymer
$\delta$ = solubility parameter
$\rho$ = density

### Subscripts

1 = high-pressure side
2 = low-pressure side
$g$ = gas
$p$ = polymer

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