Gas Transport through Polyethylene Membranes

Transport rates were measured by monitoring the pressure decay between two reservoirs connected by a polyethylene membrane. The diffusion equation was integrated to obtain a relation between the pressure difference across the reservoirs and the time, with solubility, expressed by Henry's law constant H, and the diffusivity D as parameters. A procedure was developed whereby both H and D are evaluated from a single set of Δp vs. t measurements. For argon in low-density polyethylene, H and D at 323 K were 35[kg·mol/(m^3 of gas)]/[kg·mol/(m^3 of polymer)] and 2.1×10^{-10} m^2/s, respectively. For the high-density sample these values were 38.7 and 1.11×10^{-10} at 298.1 K.

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SCOPE

A common method of determining the gas diffusivity in polymer membranes involves measuring pressure variation with time in a gas reservoir exposed to the membrane. These data are analyzed by assuming one-dimensional diffusion in the membrane and assuming equilibrium at the gas-polymer interface. No solutions have been proposed for the case where both faces of the membrane are exposed to closed reservoirs containing the diffusing gas (Figure 1). In the general form of this latter problem, time-dependent boundary conditions, the pressure in both reservoirs will change with time. The interpretation of experimental data is simplified if the ratio of reservoir volumes is large. For this special case, the pressure in the large-volume reservoir remains nearly constant. Our first objective in this work was to obtain solutions of the diffusion equation which would be applicable for both forms of the problem.

For large, but finite, times the concentration gradient in the polymer is essentially linear. This asymptotic solution of the diffusion equation gives a relation between the pressure drop, $\Delta p(t)$, between the two reservoirs and the ratio, D/H, of the Henry's law constant and the diffusivity. At shorter times the pressure difference becomes a function of D and H separately. This permits using the solutions to the diffusion equation, along with an appropriate optimization program, to determine both H and D by comparison with measurements of $\Delta p(t)$ over a finite time range. To evaluate this approach, experimental data were obtained for $\Delta p(t)$, in the apparatus shown in Figure 1, for argon diffusion through two different polyethylene membranes.

Barrer (1939), and later Brandt (1959), took advantage of the time dependence of the relationship between D and H by developing an approximate graphical method (time-lag method) to evaluate H and D. The diffusion equation was solved for the special case of both faces of the membrane exposed to diffusing gas at constant pressures, p_1 and p_2. The pressure increase with time was measured on the low pressure (p_1) side. The constant-pressure solution was justified by choosing $p_1 \ll p_2$ so that $\Delta p = p_1 - p_2 \simeq$ constant, independent of time. The solutions presented here do not have these limitations.

CONCLUSIONS AND SIGNIFICANCE

Solutions are given for the transport of gases through a polymer when the membrane is in contact with gas reservoirs in which the pressures are initially different. The solution when both pressures vary with time is difficult, but analytical solutions are possible for small and intermediate time values. If the pressure in one reservoir is constant, the solution is simplified and $\Delta p(t)$ can be expressed in terms of a rapidly converging series.

Pressure-drop data were measured for argon diffusing through polyethylene membranes for the condition of a nearly constant pressure in the high-pressure reservoir. By analyzing the $\Delta p(t)$ data both Henry's constant and the diffusivity can be evaluated from a single run. The results for H were 35 and 38.7 for low and high density polyethylene at 323.1 and 298.1 K, respectively. Diffusivity values were 2.1 and 1.1×10^{-10} m^2/s. The diffusivity values of Durrill and Griskey (1966) are about two orders of magnitude larger (9×10^{-9} m^2/s) for argon-polyethylene. However, their results are at 461 K which is above the polyethylene melting point of 410 K (Wunderlich, 1973). Lundstrom and Bearman (1974) used the time-lag method and found $D = 3.7 \times 10^{-11}$ m^2/s and $H = 19$ for the argon-polyethylene system at 298.1 K. No properties were given for the polymer.

INTRODUCTION

Gas permeability is an important property of polymer films used for packaging. The transport process can be divided into three steps: solution of the gas molecules on one face of the membrane, diffusion through the polymer, and evaporation from the other face (Li and Henley, 1964; Van Amerongen, 1950). Since diffusion is slow compared to solution and evaporation, the assumption of equilibrium has been employed successfully for relating concentrations of the diffusion substances at the gas-membrane interfaces (Durrill and Griskey, 1966; Van Amerogen, 1950). Also, it has been shown that Henry's law is valid for this equilibrium relation for numerous gases over a relatively wide range of temperatures and pressures (Michaels and Bixler, 1961; Myers, et al., 1961; Rogers et al., 1960).

For near-atmospheric pressure, which corresponds to most packaging conditions, concentrations of the diffusing gas are low. Hence, the diffusivity is independent of concentration. Then the following form of Fick's law for one-dimensional transport in an isotropic material is valid:

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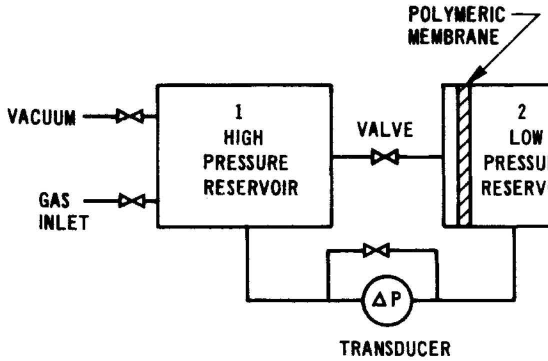

Figure 1. Apparatus.

$$\frac{\partial C_m}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} \tag{1}$$

This expression describes the diffusion step in the overall transport process (Myers, et al., 1961; Van Amerongen, 1946).

Solutions of Eq. 1 are available (Crank, 1956; Barrer, 1939; and Jost, 1960) for a few different sets of boundary conditions, but all for constant gas pressure on exposed faces of the membrane. Durrill and Griskey (1966) initially saturated the membrane at a certain gas pressure and then, at time zero, exposed one face to a higher gas pressure. The other face was held against a metal plate preventing mass transfer. The pressure in the reservoir on the exposed face was measured at time intervals. The constant-pressure solution on one face as given by Crank (1956) or Jost (1960) was used to determine the diffusivity, D (Henry's constant had been established earlier from equilibrium measurements). The authors state that the solution used did not exactly fit the experimental condition since the pressure on the exposed face changed with time. However, the authors estimate that the error in D introduced by this approximation was always less than 10%.

Our experimental procedure was different. Both faces of the membrane were exposed to gas reservoirs (Figure 1). However, the pressure in the low-pressure reservoir varied significantly with time, while the prerssure in the much larger, high-pressure reservoir was essentially constant.

Our objectives were threefold. First, a solution was desired where the pressure in both reservoirs varied with time. This situation exists in an experimental apparatus, such as that shown in Figure 1, unless reservoir volumes differ greatly. Second, we wished to obtain a solution for our experimental condition of a nearly-constant pressure in the high-pressure reservoir. No solutions for Eq. 1 could be found in the literature where the pressures on one or both faces of the membrane varied with time. Finally, we wished to develop a procedure whereby both D and the solubility (Henry's constant H) could be determined from pressure vs. time data. This third development was used with experimental data to evaluate D and H for argon in high and low density polyethylene membranes.

EXPERIMENTAL

Figure 1 presents a schematic of the apparatus. The system is immersed in a constant temperature, silicone-oil bath stable to ±0.01 K. Bath temperature is read using a precision, immersion thermometer. Total uncertainty of the temperature is ±0.1 K. The large reservoir contains a Ruska piston pump, plus connecting lines to the pressure transducer and the membrane. The volume is $0.694 \pm 0.004 \times 10^{-3}$ m^3. The small reservoir has a volume of $4.03 \pm 0.04 \times 10^{-6}$ m^3. Both volumes were determined by gas expansion. Absolute pressure measurements are made using a 0–0.13 MPa Baratron capacitance gauge. Pressure differences are detected using a 0–17 kPa Validyne reluctance transducer. Typically, the random error in Δp measurements had a standard deviation of 2 Pa.

The membrane is contained in a high-pressure, millipore filter holder. The holder contains a porous stainless steel support to prevent membrane rupture. To determine membrane thickness we weighed a rectangular section of membrane. Membrane thickness was computed from the polymer density, membrane weight and rectangle dimensions. Estimated uncertainty in membrane thickness is ±10%. The cross-sectional membrane area for mass transport was assumed to be that of the holder. This overestimates the area since the effective area is slightly reduced by an O-ring seal.

TABLE 1. PRESSURE DIFFERENCE (Δp) VS. TIME DATA FOR DIFFUSION OF ARGON

Low Density Polyethylene (LDPE) $T = 323.1$ K, $L = 2.5 \times 10^{-5}$ m		High-Density Polyethylene (HDPE) $T = 298.1$ K, $L = 1.3 \times 10^{-5}$ m	
Time, s	Δp, kPa	Time, s	Δp, kPa
0.0	11.8790	0.0	24.2689
2.4	11.8765	57.6	24.1219
4.8	11.8727	115.2	24.0177
7.2	11.8686	172.8	23.9136
9.6	11.8647	230.4	23.8095
12.0	11.8609	288.0	23.7115
14.4	11.8566	345.6	23.6135
24.0	11.8407	403.2	23.5094
33.6	11.8263	460.8	23.4053
43.2	11.8110	576.0	23.2093
55.2	11.7941	691.2	23.0133
72.0	11.7723	806.4	22.8173
129.6	11.7096	979.2	22.5417
302.4	11.5545	1094.4	22.3518
590.4	11.3099	1209.6	22.1650
878.4	11.0743	1324.8	21.9751
1166.4	11.8402	1440.0	21.7914
1454.4	10.6239	1555.2	21.6107
1742.4	10.4077	1728.0	21.3381
1800.0	10.3584		

To prepare for a run the total system is filled and evacuated three times and then filled to the desired initial pressure of the small reservoir. Pure grade argon (99.96%) was used. At this point, the transducer is zeroed and the small reservoir, plus membrane, is isolated. The large reservoir is filled to the desired initial pressure in 10 to 20 kPa increments to permit transducer calibration. At each point, we allowed roughly 5 minutes for thermal equilibrium before reading the pressure and adding more gas.

The run is started by opening the valve connecting the membrane to the large reservoir. A minicomputer reads pressure transducer output voltage at equally spaced intervals. For a run time of 30 minutes, the transducer was read every 2.4 s.

Table 1 presents representative, experimental Δp data for two membranes: a high-density (linear) polyethylene and a low-density (branched) polyethylene. Properties of the two membranes are given in Table 2, including the fraction of amorphous polymer. Previous experimental data (for example, the work of Michaels and Bixler, 1961; Michaels and Parker, 1961; Michaels et al., 1963) indicate that solution and diffusion occur only in the amorphous fraction.

THEORY FOR VARIABLE PRESSURE OF BOTH RESERVOIRS

At time zero the membrane (thickness = L) is in equilibrium with the low pressure (2) reservoir. Then the initial and boundary conditions for Eq. 1 are:

$$C_m(x, 0) = C_{2_0}/H \tag{2}$$

$$C_m(0, t) = C_1(t)/H \tag{3}$$

$$C_m(L, t) = C_2(t)/H \tag{4}$$

TABLE 2. PROPERTIES (AT 298 K) OF POLYETHYLENE MEMBRANES

Type	Density kg/m^3	Vol. Fraction Amorphous*	Thickness m	Cross-Sectional Area, m^2 × 10^4
Low-Density (LDPE)	0.939×10^3	0.35	2.5×10^{-5}	13.40
High-Density (HDPE)	0.947×10^3	0.32	1.3×10^{-5}	13.40

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* Estimated from the density, assuming crystalline and amorphous phase volumes of 1.003 and 1.171×10^{-3} m^3/kg, respectively (Wunderlich, 1973).

where x is measured in the direction of diffusion. Writing Eqs. 1–4 in terms of the dimensionless variables $\underline{X} = x/L$, and $\theta_m = [C_m(x, t) - C_m(x, 0)]/C_m(x, 0)$, the resulting equations for $\theta_m(\underline{X}, \tau)$ are:

$$\frac{\partial \theta_m}{\partial \tau} = \frac{\partial^2 \theta_m}{\partial \underline{X}^2} \tag{5}$$

$$\theta_m(\underline{X}, 0) = 0 \tag{6}$$

$$\theta_m(0, \tau) = \theta_1(\tau) = \frac{C_1(t)/H - C_m(0, 0)}{C_m(0, 0)} \tag{7}$$

$$\theta_m(1, \tau) = \theta_2(\tau) = \frac{C_2(t)/H - C_m(L, 0)}{C_m(L, 0)} \tag{8}$$

Equations 5–8 can be solved (Soles, 1980) in the Laplace domain for $\bar{\theta}_m(\underline{X}, s) = \mathcal{L}[\theta_m(\underline{X}, \tau)]$ to yield:

$$\bar{\theta}_m(\underline{X}, s) = \frac{\sinh(1 - \underline{X})s^{1/2}}{\sinh(s^{1/2})}\bar{\theta}_1(s) + \frac{\sinh(\underline{X}s^{1/2})}{\sinh(s^{1/2})}\bar{\theta}_2(s) \tag{9}$$

where $\bar{\theta}_1(s)$ and $\bar{\theta}_2(s)$ are Laplace transforms of the boundary conditions, Eqs. 7 and 8.

The mass balance of diffusing component on the high-pressure reservoir of volume V_1 is:

$$\frac{dC_1(t)}{dt} = \frac{AD}{V_1 H}\left(\frac{\partial C_m}{\partial x}\right)_{x=0} \tag{10}$$

with initial condition

$$C_1(0) = C_{1_0} \tag{11}$$

In dimensionless form in the Laplace domain, Eq. 10 with initial condition 11 gives:

$$s\bar{\theta}_1(s) - \theta_1(0) = G\left(\frac{\partial \bar{\theta}_m}{\partial \underline{X}}\right)_{\bar{x}=0} \tag{12}$$

where G is the dimensionless ratio

$$G = \frac{AL}{HV_1} \tag{13}$$

Differentiating Eq. 9 with respect to $\overline{\underline{X}}$ and substitution into Eq. 12 yields:

$$\left[\frac{s^{1/2}\sinh(s^{1/2})}{G} + \cosh(s^{1/2})\right]\bar{\theta}_1(s) - \bar{\theta}_2(s) = \frac{\theta_1(0)\sinh(s^{1/2})}{Gs^{1/2}} \tag{14}$$

This last equation provides one relationship between $\bar{\theta}_1(s)$ and $\bar{\theta}_2(s)$. A mass balance on the low-pressure reservoir of volume V_2, followed by a similar development, gives the following, second relationship:

$$-\bar{\theta}_1(s) + \left[\frac{s^{1/2}\sinh s^{1/2}}{G\beta} + \cosh s^{1/2}\right]\bar{\theta}_2(s) = 0 \tag{15}$$

where

$$\beta = V_1/V_2 \tag{16}$$

Equations 14 and 15 can be solved for $\bar{\theta}_1(s)$ and $\bar{\theta}_2(s)$ and combined to yield:

$$\frac{\bar{\theta}_1(s) - \bar{\theta}_2(s)}{\theta_1(0) - \theta_2(0)} = \frac{Gs^{1/1/2}\left[\dfrac{s^{1/2}\sinh(s^{1/2})}{G\beta} + \cosh(s^{1/2}) - 1\right]}{\left(\dfrac{s}{G^2\beta} + 1\right)\sinh(s^{1/2}) + \dfrac{1}{G}\left(1 + \dfrac{1}{\beta}\right)s^{1/2}\cosh(s^{1/2})} \tag{17}$$

where $\theta_2(0) = 0$ and $\theta,(0) = [C_1(0)/H - C_2(0)/H]/[C_2(0)/H]$, according to the equilibrium between the membrane and the low-pressure reservoir at zero time.

At low pressures the concentration C of diffusing component in the reservoirs is given by p/RT. Therefore, from Eqs. 7 and 8:

$$\frac{\theta_1(\tau) - \theta_2(\tau)}{\theta_1(0) - \theta_2(0)} = \frac{p_1(\tau) - p_2(\tau)}{p_1(0) - p_2(0)} = \frac{\Delta p(\tau)}{\Delta p(0)} \tag{18}$$

or

$$\frac{\Delta p(\tau)}{\Delta p(0)} = \mathcal{L}^{-1}\left[\frac{\bar{\theta}_1(s) - \bar{\theta}_2(s)}{\theta_1(0) - \theta_2(0)}\right] \tag{19}$$

Hence, the inversion of Eq. 17 gives the desired solution for the pressure drop across the membrane as a function of time.

Solution for Intermediate Values of Time

The inversion of Eq. 17 is difficult because of the complex function of s. However, a closed solution valid except for large values of time can be derived in terms of transform functions available in the usual tables: Carslaw and Jaeger (1959), Fodor (1965), Luikor (1968). The procedure is to express the hyperbolic functions in Eq. 17 in terms of negative exponential functions, expand in terms of the binomial theorem, and invert the resulting standard functions, term by term. The results for the first two terms of the series are available (Soles, 1980).

Solution for Small Values of Time

At low time values $s^{1/2}$ is large and $\sinh s^{1/2} = \cosh s^{1/2} = (\exp s^{1/2})/2$. This equality is valid to three significant figures for $\tau < 0.1$. With this simplification inverting Eq. 17 with tables of transforms gives

$$\begin{aligned}\frac{\Delta p(\tau)}{\Delta p(0)} &= \exp(G^2\tau)\, erfc(G\tau^{1/2}) \\ &+ \frac{2\beta}{1-\beta}\{\exp[G\tau^{1/2}(1 + G\tau^{1/2})]erfc(\tau^{-1/2}/2 + G\tau^{1/2})\} \\ &-\exp[G\beta\tau^{1/2}(1 + G\beta\tau^{1/2})]erfc[\tau^{-1/2}/2 + G\beta\tau^{1/2}]\end{aligned} \tag{20}$$

Solution for Large Values of Time

For large run times the concentration profile within the membrane becomes linear. With this simplification:

$$\left(\frac{\partial C_m}{\partial x}\right)_{x=0} = \left(\frac{\partial C_m}{\partial x}\right)_{x=L} = \frac{C_m(0, t) - C_m(L, t)}{L} \tag{21}$$

The boundary conditions become:

$$C_1(t) = HC_m(0, t) = p_1(t)/RT \tag{22}$$

$$C_2(t) = HC_m(L, t) = p_2(t)/RT \tag{23}$$

Now Eqs. 22 and 23, solved for $C_m(0, t)$ and $C_m(L, t)$, can be substituted into Eq. 21 to obtain an expression for $(\partial C_m/\partial x)_{x=0}$ in terms of $p_1(t)$ and $p_2(t)$.

Then the mass balance in reservoir 1, Eq. 10, can be used to express $(\partial C_m/\partial x)_{x=0}$ in terms of $dC_1(t)/dt$ and Eq. 22 relates $C_1(t)$ to $p_1(t)$. The result gives a differential equation relating $p_1(t)$ and $p_2(t)$:

$$\frac{dp_1(t)}{dt} = -\frac{AD}{V_1 LH}[p_1(t) - p_2(t)] \tag{24}$$

Using the mass balance for reservoir 2, analogous to Eq. 10, and proceeding in the same manner gives:

$$\frac{dp_2(t)}{dt} = \frac{AD}{V_2 LH}[p_1(t) - p_2(t)] \tag{25}$$

Equations 24 and 25 can be integrated with the initial conditions $p_1(0)$ and $p_2(0)$ to yield:

$$\frac{\Delta p(t)}{\Delta p(0)} = \frac{p_1(t) - p_2(t)}{p_1(0) - p_2(0)} = \exp\left[-\left(1 + \frac{V_1}{V_2}\right)\frac{A}{V_1 L}\left(\frac{D}{H}\right)t\right] \tag{26}$$

In Eq. 26 the pressure drop ratio is not a function of D and H separately but depends only on their ratio D/H, which is often called the permeability coefficient.

THEORY FOR CONSTANT PRESSURE IN ONE RESERVOIR

In the experiments reported here the volume of reservoir 1 was 172 times larger than the volume of reservoir 2. Hence, the pressure in 1 remained nearly constant during a run. For this restriction Eqs. 5, 6, and 8 are unchanged but Eq. 7 for the boundary condition in reservoir 1 becomes:

$$\theta_m(0,\tau) = \theta_1 = \text{constant} \tag{27}$$

The mass balance of diffusing component applied to the low-pressure reservoir (2) is:

$$\frac{dC_2(t)}{dt} = -\frac{AD}{V_2}\left(\frac{\partial C_m}{\partial x}\right)_{x=L} \tag{28}$$

with initial condition $C_2(0) = C_{2_0}$. In dimensionaless form Equation (28) becomes:

$$\frac{d\theta_2}{d\tau} = -G\beta\left(\frac{\partial\theta_m}{\partial\underline{X}}\right)_{\underline{X}=1} \tag{29}$$

with initial condition

$$\theta_2(0) = 0 \tag{30}$$

Equations 29 and 8 may be written:

$$\frac{\partial\theta_m}{\partial\tau} + B\frac{\partial\theta_m}{\partial\underline{X}} = 0 \text{ at } \underline{X} = 1 \tag{31}$$

where:

$$B = \frac{AL}{HV_2} \tag{32}$$

Equations 5, 6, 27 and 31 are the same as the dimensionless form of the analogous heat transfer problem solved by Carslaw and Jaeger (1959). Their solution is the series:

$$\frac{\theta_m(\underline{X},\tau)}{\theta_1} = 1 - \sum_{n=1}^{\infty}\frac{2(\alpha_n^2 + B^2)\{\exp(-\alpha_n^2\tau)\}\sin\alpha_n\underline{X}}{\alpha_n(\alpha_n^2 + B^2 + B)} \tag{33}$$

where α_n are the roots of:

$$\alpha_n \tan\alpha_n = \mathrm{B} \tag{34}$$

For constant pressure in reservoir 1, and using the ideal-gas law, Eq. 18 becomes:

$$\frac{\Delta p(\tau)}{\Delta p(0)} = \frac{p_1(0) - p_2(t)}{p_1(0) - p_2(0)} = 1 - \frac{\theta_2(\tau)}{\theta_1} \tag{35}$$

Combining Eqs. 34 and 35 gives the final form of the solution:

$$\frac{\Delta p(\tau)}{\Delta p(0)} = \sum_{n=1}^{\infty}\frac{2(\alpha_n^2 + B^2)[\exp(-\alpha_n^2\tau]\sin\alpha_n}{\alpha_n(\alpha_n^2 + B^2 + B)} \tag{36}$$

The first three roots of Eq. 33 are 0.0316, 3.1419, and 6.2833, while for thin membranes such as employed in this study, B is of the order of 10^{-4}. Hence, the convergence of Eq. 36 is nearly independent of B for realistic cases. Also, as noted later, Eq. 36 gives convergent results for very few terms, even at the lowest time values. Hence, it was an ideal solution for the experimental conditions of this investigation.

An asymptotic result applicable for low-time values can be found by simplifying the solution in the Laplace domain for Eqs. 5, 6, 8, and 27. Proceeding in the same way as was used earlier when p_1 and p_2 both changed with time, the following solution can be derived (Soles, 1980).

$$\frac{\Delta p(\tau)}{\Delta p(0)} = 1 - 2\left\{erfc\left(\frac{1}{2\tau^{1/2}}\right) - \exp(B)[\exp(B^2\tau)]erfc\left(B\tau^{1/2} + \frac{1}{2\tau^{1/2}}\right)\right\} \tag{37}$$

For the membranes studied in our work this solution is not applicable. Comparison of results from Eqs. 36 and 37 indicates that the low-time solution is accurate for polymer LDPE only to 2.4 s and to less than that time for HDPE.

EVALUATION OF HENRY'S CONSTANT AND DIFFUSIVITY

Since Eq. 36 converges rapidly for all time values, it was used to obtain final values for H and D. The procedure consisted of these steps:

A. Estimate a starting value for Henry's constant H from available data and correlations.

B. Using Δp vs. t data at the largest time values, determine the ratio D/H from Eq. 26.

C. Use H and D determined in steps A and B in an optimization program with Eq. 36 to establish the final values of H and D.

D. With Eq. 36, and the final values for H and D, calculate Δp vs. t for comparison with the experimental data.

The results for these steps are given in the following paragraphs.

A. Estimates of Henry's constant for argon were made using data and correlations given in four references (Stern, Mullhaupt and Gareis, 1969; Michaels and Bixler, 1961; Maloney and Prausnitz, 1976; Durrill and Griskey, 1966). In all cases H is presented as [kg-mol/(m^3 gas)]/[kg-mol/(m^3 of amorphous plus crystalline polymer)] and is based upon solution and diffusion occurring only in the amorphous fraction (Table 2) of the polymer. For polymer LDPE the four estimated values at 323.1 K were, in order, 33.77, 21.14, 24.80, and 39.96. For polymer HDPE at 298.1 K, the estimated H values, in order, were 33.50, 27.77, 24.61, and 39.64. For starting the optimization computations the Stern et al. values of 33.77 and 33.50 were used.

B. According to Eq. 26, which is applicable for large times, a plot of $ln[\Delta p(t)/\Delta p(0)]$ vs. t should give a straight line. Figure 2 shows that this requirement is met for the data points in the 1,400 to 1,800 s range. Hence, the slopes of the lines in Figure 2, which are proportional to D/H, with the H values already estimated can be used to estimate D. These diffusivities are 1.49×10^{-10} m^2/s for LDPE polymer and 0.83×10^{-10} m^2/s for the HDPE polymer.

C. Using H and D values given in B and C as initial guesses, an optimization program was employed to determine the final values for these two parameters. The function F to be minimized is:

$$F = \sum_{i=1}^{n}(\Delta p_E - \Delta p_c)_i^2 \tag{38}$$

where Δp_E is the measured Δp at a point (time) i and Δp_c is the value calculated from Eq. 36. The direct search method of Hooke and Jeeves (1961) was used for optimization. The method is based upon searching in steps in either direction from the initial point and evaluating F. If F does not show a decrease, the step size is decreased, and the search is continued from the previous point with the smallest F. The method assumes a unimodal function. Therefore, if more than one minimum exists, or the shape of the function is unknown, several sets of initial values (of H and D) should be chosen.

Before using the program it is necessary to know the convergence of Eq. 36 and to test the optimization method. It was found that for τ as low as the order of unity (corresponding to about 2 s for the

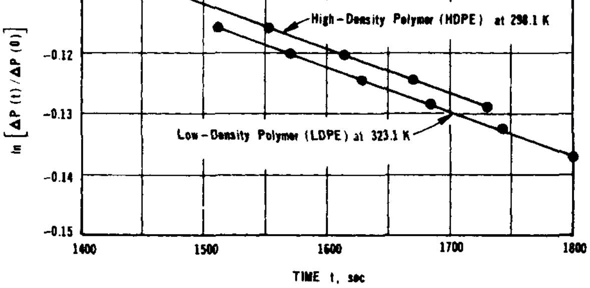

Figure 2. Asymptotic solution plot of $\Delta p(t)$ data for large t.

TABLE 3. TEST OF OPTIMIZATION PROGRAM (POLYMER HDPE)

	H [kg-mol/(m^3 gas)]/ [kg-mol/m^3 polymer]	D (m^2/s) × 10^{10}
Starting Values	30.00	0.910
Optimal Results	33.38	0.838
Correct Values	33.50	0.830

TABLE 4. OPTIMAL VALUES OF HENRY'S CONSTANT AND DIFFUSIVITY

	Argon-Low Density Polyethylene (LDPE) at 323.1 K	Argon-High Density Polyethylene HDPE at 298.1 K
Henry's constant, H [kg-mol/(m^3 gas)]/ [kg-mol/(m^3 polymer)]	35.0	38.7
Diffusivity $D \times 10^{10}$, m^2/s	2.10	1.11

experimental conditions), the second term was but 10^{-4} as large as the first term; therefore, only one term need be used to fit the data. This is because of the large difference between the first two values of α. The series is remarkably convergent. The optimization program was tested in the following way. Taking $H = 33.50$ and $D = 0.83 \times 10^{-10}$ m^2/s, and the properties for polymer HDPE, Eq. 36 was used to generate ficticious $\Delta p(t)$ data. These ficticious data points then were used with the optimization program starting with values about 10% different from those used to generate the data. The results of the test gave H within 0.35%, and D within 0.96% of the correct values, as shown in Table 3. Returning to the actual pressure drop data, the values of H and D determined from the optimization program are given in Table 4.

D. The optimal values of H and D given in Table 4 were used in Eq. 36 to predict $\Delta p(t)$. These predicted results are compared with the measured pressure drop data in Figures 3 and 4 for the two polymer membranes. The agreement is excellent for polymer HDPE and reasonably good for LDPE.

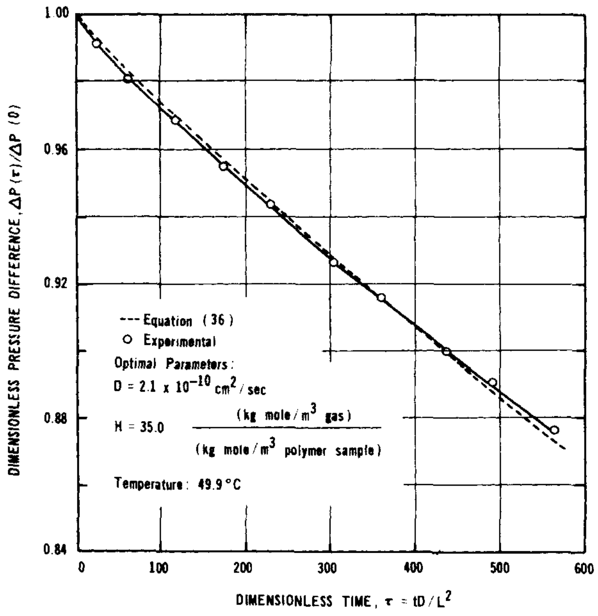

Figure 3. Dimensionless pressure difference vs. dimensionless time: argon-low density polyethylene (LDPE) system.

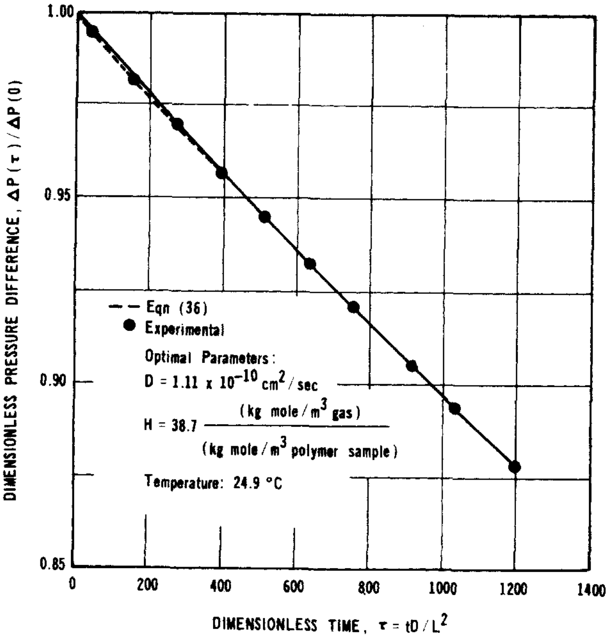

Figure 4. Dimensionless pressure difference vs. dimensionless time: argon-high density polyethylene (HDPE) system.

SENSITIVITY OF THE METHOD TO H AND D

In order to determine the accuracy of the method for evaluating H and D, the pressure drop was calculated by varying each of the parameters individually over a range of 40%. The results are shown for HDPE in Figures 5 and 6. The sensitivity to H decreases somewhat as H increases. However, since Δp can be measured to less than 0.0666 kPa (0.5 torr), it should be possible to determine H with an accuracy of better than 5% in the range of conditions covered in this study. Similarly, Figure 6 shows that an accuracy of the same level should be possible for the diffusivity.

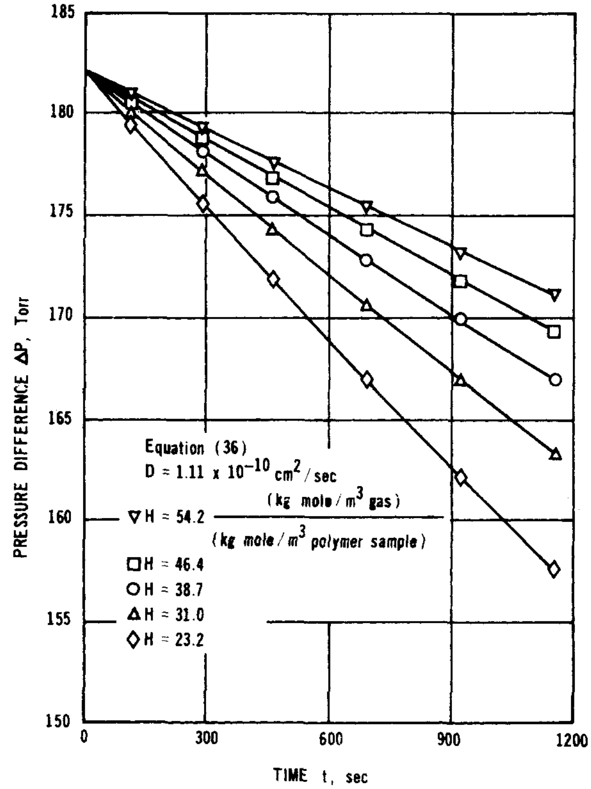

Figure 5. Pressure difference vs. time. Sensitivity to Henry's constant: HDPE system at 298 K.

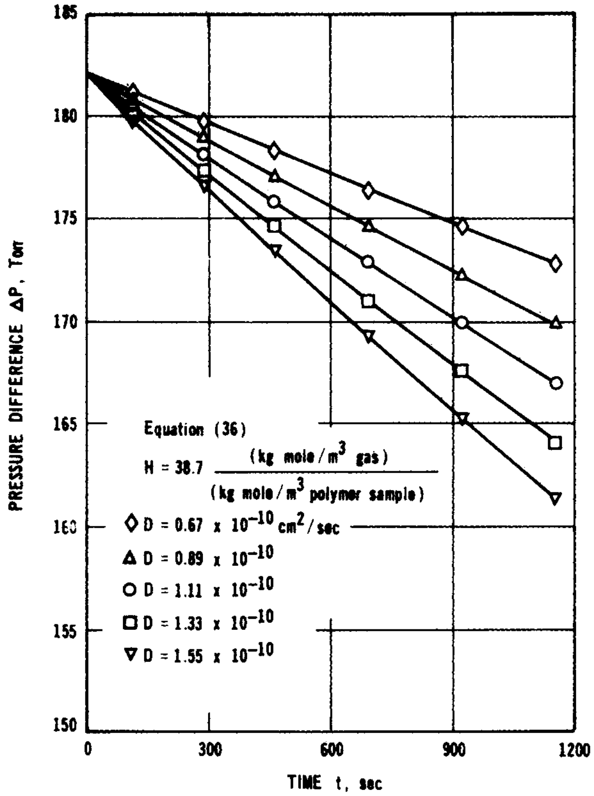

Figure 6. Pressure difference vs. time. Sensitivity to the effective diffusivity: HDPE system at 298 K.

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NOTATION

A = area of membrane perpendicular to the direction of diffusion, m^2
B = AL/HV_2
C_m = concentration of dissolved argon in the polymer membrane, kg·mol/m^3
C_1, C_2 = concentration of argon gas in the high and low pressure reservoirs, respectively, kg·mol/m^3; C_{1_0} and C_{2_0} are initial concentrations
D = effective diffusivity of argon in the membrane, m^2/s
F = objective function defined by Eq. 38, $(torr)^2$
G = AL/HV_1
H = Henry's constant, [kg·mol of argon/(m^3 of gas)]/[kg·mol/(m^3 of total polymer sample)]
L = thickness of polymer membrane, m
p = pressure, torr; p_1 and p_2 represent pressures in reservoirs 1 and 2; Δp represents the pressure difference $p_1 - p_2$
R = gas constant
s = Laplace transform variable for dimensionless time, τ
t = time, s
T = absolute temperature, K
V_1, V_2 = volumes of reservoirs 1 and 2, m^3
x = distance in direction of diffusion, m
$\underline{X}$ = dimensionless distance, x/L

Greek Letters

β = V_1/V_2
α_n = roots of Eq. 34
θ_m = dimensionless concentration in the membrane, $[C_m(x,t) - C_m(x,0)]/C_m(x,0)$
θ_1, θ_2 = dimensionless concentrations in reservoirs 1 and 2, defined by Eqs. 7 and 8
τ = dimensionless time, tD/L^2

Superscripts and Subscripts

— = variable in the Laplace domain
1,2 = high- and low-pressure reservoirs, respectively

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