

Rate of Gas Transport in Glassy Polymers: A Free Volume Based Predictive Model

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Free volume theories of diffusion developed in the literature successfully treat penetrant transport behavior in rubbery polymers. The potential of such a free volume theory to predict the gas transport behavior in glassy polymers is explored here, duly taking into account the excess hole free volume present in the glassy state. The calculations require values for three model parameters appearing in the theory of diffusion which are obtained by fitting experimental gas permeability data in rubbery polymers. The calculations also require an estimate for the hole free volume in the gas-polymer mixture. This is obtained by fitting experimental gas sorption data in rubbery and glassy polymers to a free volume based theory of gas sorption developed here. Thus, the calculation of gas permeability in glassy polymers is strictly predictive in the sense that no use is made of experimental permeation data in the glassy state.

I. Introduction

Free volume concepts have been successfully used for the quantitative description of equilibrium and transport properties of polymeric systems. The equation of state models of Flory (1965, 1970), Prigogine (Prigogine et al., 1953a-c; Prigogine, 1957), Patterson (Patterson, 1969; Patterson and Delmas, 1970), and Sanchez and Lacombe (1976, 1978) are examples of how the free volume concept has been employed in the quantitative treatment of equilibrium behavior. The treatment of viscosity of polymer melts by Williams et al. (1955) (see also Ferry, 1970) and of diffusion by Cohen and Turnbull (1959), Fujita (1961), and Vrentas and Duda (1977a,b, 1979, 1986) are some examples of free volume based treatments of transport behavior. Given the success of free volume models in describing diffusion behavior in rubbery polymers, it is natural to explore whether they can be employed also to describe the permeability behavior of gases in glassy polymers. Specifically, we show in this paper that, from our knowledge of sorption behavior in rubbery and glassy polymers and of diffusion behavior in rubbery polymers, we can reasonably predict the permeability of gases through glassy polymer membranes without using any experimental permeability data in the glassy state.

The free volume theory of diffusion in polymer systems is built on the general premise that the specific volumes of the polymer and the penetrant are composed of three different parts. Figure 1 schematically illustrates these three components of the specific volume for amorphous polymers as a function of the temperature. The illustrative specific volume calculations have been made for poly(ethylene terephthalate) (PET) considered in this study, and the bases of the calculations are discussed in the Appendix. Considering the specific volume components shown in Figure 1, firstly, there is the volume that is directly occupied by the molecules. This is referred to as the specific occupied volume. The remainder of the volume constitutes the free volume. One part of the free volume is assumed to be uniformly distributed among the molecules and is identified as the interstitial free volume. This free volume requires a large energy for redistribution and is, therefore, not affected by random thermal fluctuations. The other part of the free volume is denoted as the hole free volume. The hole free volume is assumed to require negligible energy for its redistribution. Consequently, the hole free

volume is continuously being redistributed due to random thermal fluctuations, thereby causing fluctuations in local density. It is this hole free volume that is considered relevant in determining the transport properties of the polymer systems. According to the free volume theory, the rate of penetrant transport is determined by the amount of hole free volume available and the size of the migrating molecule. The free volume theory has been well developed for rubbery polymer-penetrant systems so that quantitative predictions of diffusivity are possible using only minimal experimental data to estimate some of the molecular parameters appearing in the theory (Vrentas and Duda, 1979, 1986; Duda, 1983).

Amorphous rubbery polymers, when subjected to cooling, undergo a transition to a glassy state. The temperature at which this transition occurs is denoted the glass transition temperature, T_g . In the rubbery state (i.e., above T_g), the amorphous polymer chains are in their equilibrium configurations. In contrast, in the glassy state (i.e., below T_g), the polymer segments do not have adequate mobility required to reach their equilibrium configurations. This results in the trapping of some extra hole free volume in the glassy state. It is necessary to note here that although the segmental motions are not adequate to realize the volume relaxation of the entire polymer to the equilibrium state, such motions do occur leading to hole free volume redistribution and consequent density fluctuations in the glassy state. The glassy state attained is dependent on the mechanical and thermal history of the polymer. The magnitude of the extra hole free volume associated with the glassy state depends on how fast the polymer is cooled through the glass transition temperature. This additional contribution to the specific volume of the polymer arising in the glassy state is also shown in a schematic way in Figure 1. As one would expect, when the temperature of the glassy polymer is increased, the size of the extra hole free volume diminishes and eventually vanishes at T_g .

The excess hole free volume characteristic of the glassy state influences the transport behavior of penetrants in glassy polymers (Barrer et al., 1957a,b, 1958). It is natural to anticipate, in view of the free volume theory, that by properly accounting for this excess hole free volume, one may be able to describe quantitatively the rate of gas transport in glassy polymers. This constitutes the goal of this paper. Specifically, we predict, rather than simply correlate, the permeability of gases in glassy polymers by using the free volume theory of diffusion. The molecular parameters appearing in the diffusion theory are estimated

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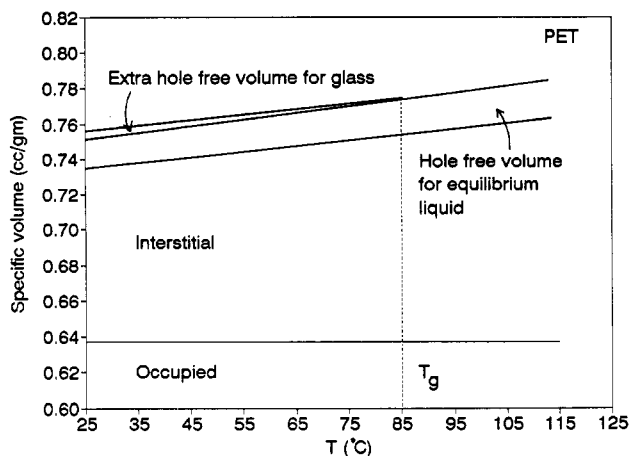


Figure 1. Plot of specific volume vs temperature for PET. The estimation of the occupied volume, the interstitial free volume, and the hole free volume are described in the Appendix. It has been assumed that the specific occupied volume is temperature independent while the interstitial and the hole free volumes display a linear temperature dependence. Also shown are the estimates of the extra hole free volume in the glassy state of the polymer. The contributions shown have been obtained by fitting experimental gas sorption data to glassy polymers as discussed in sections III and IV of this paper.

from experimental gas permeation data for rubbery polymers. The estimate of the available hole free volume required by the diffusion theory is found by fitting experimental gas sorption data in rubbery and glassy polymers to a new free volume model of gas sorption. Therefore, the calculation of the permeability behavior in glassy polymers is strictly predictive in the sense that it does not involve the use of any experimental permeability data in the glassy state.

In the following section, we briefly outline the free volume theory of penetrant diffusion in rubbery polymers. Also, the definition of membrane permeability associated with steady-state experiments is discussed. In section III, a free volume based theory of gas sorption is developed from which one can calculate the specific hole free volume of the polymer-gas mixture as a function of the gas sorption level. In section IV, the parameters of the gas sorption model are estimated using sorption data for rubbery and glassy polymers. In section V, the parameters of the gas diffusion model are estimated using gas permeability data for rubbery polymers. Having estimated all the model parameters, in section VI, the gas permeability behavior in glassy polymers is predicted and compared with experiments. Section VII presents the main conclusions.

II. Free Volume Theory of Diffusion and Gas Permeability

The free volume theory of diffusion as developed by Vrentas and Duda (1977a,b, 1979) is used in the present analysis of gas diffusion in glassy polymers. According to the free volume theory, the migration of penetrant molecules or polymer chains is impeded by the presence of neighboring molecules. Under such conditions, a molecule migrates by jumping into a hole which forms because the hole free volume in the system is being continuously redistributed by thermal fluctuations. For small penetrant molecules, the jumping unit is the entire molecule. For a flexible-chain linear polymer, the jumping unit is some small part of the chain which is assumed capable of moving into a hole without affecting the neighboring jumping units of the polymer chain. Before a penetrant or polymer jumping unit can migrate, two requirements must be fulfilled. Firstly, a hole of sufficient size must appear

adjacent to the jumping unit. Secondly, the jumping unit must have enough energy to jump into the hole. Taking into account these two requirements, the self-diffusion coefficient of penetrant D_1 in the penetrant (1)-polymer (2) mixture can be written as

$$D_1 = D_{01} \{ e^{-E/RT} \} \left\{ \exp \left(- \frac{\gamma}{\bar{V}_{FH}} [\bar{w}_1 \hat{V}_{1J} + \zeta \bar{w}_2 \hat{V}_{2J}] \right) \right\} \quad (1)$$

where \bar{V}_{FH} is the average hole free volume per gram of mixture, \hat{V}_{iJ} is the specific critical hole free volume of i required for a jump, ζ is the ratio of the critical molar volume of the penetrant jumping unit to the polymer jumping unit ($\zeta = \hat{V}_{1J}M_{1J}/\hat{V}_{2J}M_{2J}$), and γ is the overlap factor which accounts for the sharing of free volume by the two components. M_{1J} is the molecular weight of the penetrant jumping unit while M_{2J} is that of the polymer jumping unit. \bar{w}_1 and \bar{w}_2 are the weight fractions of the penetrant and the polymer in the mixture, respectively. The first factor within the braces gives the probability that the jumping unit will acquire, from the distribution of thermal energy, sufficient energy E to overcome the attractive forces holding it and make the jump. The second factor within the braces expresses the probability of formation of a hole of size sufficient for a jump. D_{01} is a temperature-independent constant of proportionality.

The mutual-diffusion coefficient D in a penetrant-polymer mixture was shown by Vrentas and Duda (1977a,b) to be the product of the self-diffusion coefficient of the penetrant D_1 and a thermodynamic factor Q , defined as

$$D = D_1 Q, \quad Q = \frac{x_1 x_2}{RT} \frac{\partial \mu_1}{\partial x_1} \quad (2)$$

where μ_1 is the chemical potential of the penetrant and x_1 and x_2 are the mole fractions of the penetrant and the polymer, respectively. Equation 2 was shown to be valid over an extended range of penetrant concentrations, approximately from 0 to 60 wt %, in penetrant-rubbery polymer systems. In such systems, the self-diffusion coefficient D_1 is an increasing function of the penetrant concentration at a given temperature. On the other hand, the thermodynamic factor Q decreases with increasing penetrant concentration. Since the mutual-diffusion coefficient D is a product of these two opposing effects, it exhibits an extremum as a function of the concentration, the extremum being a maximum when the penetrant is a good solvent for the polymer. At low penetrant concentrations the sorption isotherms for rubbery polymers are linear (described by Henry's law) and, consequently, the thermodynamic factor Q approaches unity. Under such conditions, one can equate the self-diffusion coefficient of the penetrant of the mutual-diffusion coefficient, $D = D_1$.

In glassy polymers, the sorption levels of gases are typically low at moderate pressures, the highest value discussed in this paper being about 3 wt % at 20 atm and 25 °C for the system CO_2/PET . However, we cannot approximate the thermodynamic factor Q to unity in penetrant-glassy polymer systems, because the sorption isotherms are not linear but curved even at low sorption levels. Consequently, we have to estimate the thermodynamic factor Q , irrespective of the magnitude of the sorption levels.

The gas permeability in a polymer membrane of thickness l is defined on the basis of steady-state permeation experiments (Barrer et al., 1958). The permeability P at a given upstream pressure p_2 , downstream pressure $p_1 = 0$, and temperature T can be defined as

$$P = \frac{N_s l}{p_2} = \frac{\int_0^{C_0} D(C) dC}{p_2} = \frac{\int_0^{C_0} D_1(C) Q(C) dC}{p_2} \quad (3)$$

where N_s is the steady-state flux, C_0 is the sorption level corresponding to pressure p_2 , and D is the mutual-diffusion coefficient defined in eq 2 which is a function of the penetrant concentration C .

In summary, to predict the gas permeability in a glassy polymer membrane at any given upstream pressure p_2 using eq 3, it is necessary to know the following: (a) The self-diffusion coefficient D_1 of the penetrant as a function of the gas concentration C in the polymer membrane must be known. This is calculated from eq 1 based on the free volume theory of diffusion. In order to use eq 1, we need to know the specific hole free volume \bar{V}_{FH} as a function of the gas sorption level in the membrane. This information can be extracted from the experimental gas sorption data in glassy polymers by employing a free volume based model to describe gas sorption. Other parameters appearing in eq 1 are estimated using experimental gas permeability data for the rubbery state of the polymer. (b) The thermodynamic factor Q as a function of the gas concentration C in the membrane must be known. Q can be calculated by applying eq 2 to the experimental gas sorption data in glassy polymers. (c) The total sorption level C_0 as a function of the pressure p_2 must be known. This is readily obtained from experimental gas sorption data in glassy polymers.

III. Free Volume Model of Gas Sorption

A new thermodynamic model of gas sorption in glassy polymers is developed here, invoking the concepts of pseudoequilibrium, free volume, and lattice visualization. Before discussing the model, it is useful to take note why the above-mentioned concepts are being considered. Firstly, glassy polymers are nonequilibrium systems because they incorporate within them some unrelaxed extra hole free volume. One may expect that the sorption of penetrants will promote the relaxation of the polymer toward its equilibrium state. However, if the sorption levels are small as in the system considered in this study, the gas sorption process may have no effect on the polymer relaxation behavior and the two processes may be considered practically uncoupled. In these circumstances, the time scale of the polymer relaxation process is very slow compared to that of the gas sorption process. Hence, gas sorption may be viewed as a pseudoequilibrium process, despite the nonequilibrium state of the glassy polymer. Secondly, with respect to gas sorption behavior, the distinguishing features of the glassy polymer compared to the rubbery polymer originate from the extra hole free volume trapped in the glassy state. This provides the motivation for developing a sorption model that is explicitly built in terms of hole free volume concepts. Thirdly, the lattice visualization offers a simple and convenient means to calculate the chemical potentials of the different components at a specified system volume. This is the rationale for adopting a lattice formalism. As discussed below, we develop the free volume model for gas sorption in glassy polymers by combining two intuitive and successful concepts already available in the literature. One is the heuristic treatment of equilibrium solutions based on the free volume concept, as proposed by Hildebrand (1947). The other is the dual mode sorption concept of Barrer et al. (1957a,b, 1958) that has proven to be useful for describing the experimental gas sorption behavior in glassy polymers.

We begin by considering the gas sorption behavior in rubbery polymers using a lattice visualization as shown in

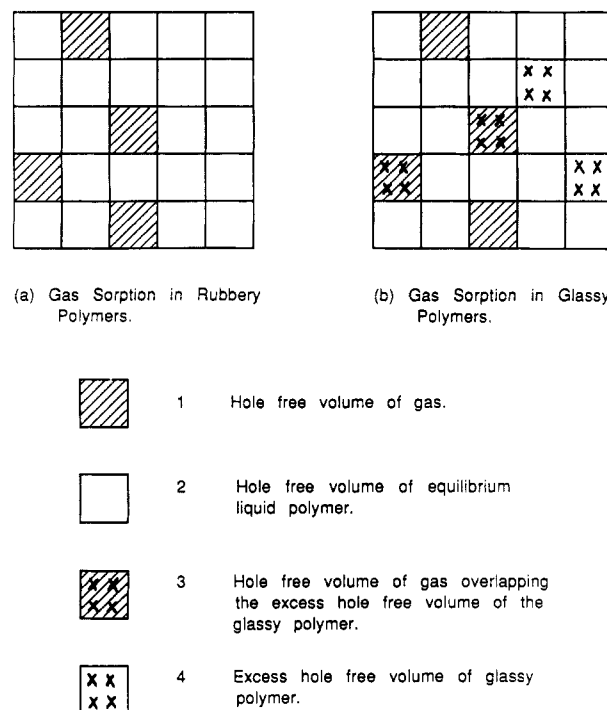


Figure 2. Schematic representation of the free volume based lattice. (a) represents gas sorption in rubbery polymers, and two distinct sites can be identified. (b) represents gas sorption in glassy polymers where four distinct sites can be identified.

Figure 2a. Here, the lattice sites denote the hole free volumes associated with the gas and the equilibrium liquid polymer, respectively. Such a representation is based on Hildebrand's suggestion (1947) that the mixing of components in a solution can be treated as being equivalent to the mixing of the free volumes of the components. The free energy change on the sorption of gas by the equilibrium liquid polymer is then given by

$$\Delta F_m/kT = n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + \chi_{12} n_1 \Phi_2 \quad (4)$$

where

$$\Phi_i = \frac{n_i v_i^{H_i}}{\sum (n_i v_i^{H_i})} \quad (5)$$

and $v_i^{H_i}$ is the hole free volume of component i . Specifically, $v_1^{H_1}$ is the hole free volume associated with a gas molecule when it is sorbed in the polymer while $v_2^{H_2}$ is the hole free volume associated with a polymer molecule in its equilibrium liquid state. Here, one may observe that the size of a lattice site is implicitly set equal to the hole free volume associated with a gas molecule. The free volume fractions appearing in eq 4 can be related to the experimentally measurable weight fractions (w_i) of the polymer and the sorbed gas.

$$\Phi_i = \frac{w_i \hat{V}_i}{\sum (w_i \hat{V}_i)} \quad (6)$$

where $\hat{V}_i (=v_i^{H_i}/M_i)$ is the specific hole free volume of component i whose molecular weight is M_i . The first two terms of eq 4 represent the entropy of mixing while the third term involving the χ_{12} parameter accounts for the contact free energy dissimilarity as in the Flory-Huggins equation for polymer solutions (Flory, 1962; Patterson, 1969). The contact free energy dissimilarity between components i and j can be related to the pairwise interaction energies ω_{ij} through the relation $kT\chi_{ij} = (\omega_{ii} + \omega_{jj} - 2\omega_{ij})$. Thus, the Hildebrand picture yields a description

of equilibrium polymer solutions that is formally similar to the Flory-Huggins lattice model. The molar volume fractions appearing in the Flory-Huggins model are simply replaced here by the hole free volume fractions. Denoting by Φ_i^* the molar volume fractions and by χ_{12}^* the interaction parameter appearing in the Flory-Huggins model, one can express the free volume fraction in terms of the molar volume fraction by the relation

$$\Phi_i = \frac{\Phi_i^*(v_i^H/v_i)}{\sum (\Phi_i^*(v_i^H/v_i))} \quad (7)$$

By comparing the Hildebrand and Flory-Huggins equations, we can also relate the Hildebrand parameter χ_{12} to the Flory-Huggins parameter χ_{12}^* via the expression

$$\chi_{12} = \frac{v_2}{v_2^H} \sum \Phi_i^* \left(\frac{v_i^H}{v_i} \right) \left[\chi_{12}^* + \frac{1}{\Phi_2^*} \ln \left(\frac{v_1}{v_1^H} \sum \Phi_i^* \frac{v_i^H}{v_i} \right) + \frac{v_1}{v_2} \frac{1}{\Phi_1^*} \ln \left(\frac{v_2}{v_2^H} \sum \Phi_i^* \frac{v_i^H}{v_i} \right) \right] \quad (8)$$

Equations 7 and 8 show that if the free volume to the molar volume ratio is the same for both components present in solution, then $\Phi_i = \Phi_i^*$, $\chi_{12} = \chi_{12}^*$, and Hildebrand's model based on free volume fractions becomes identical to the Flory-Huggins model involving molar volume fractions. On the other hand, if the free volume to the molar volume ratio is different for the components, then χ_{12} appearing in the Hildebrand equation may be positive or negative depending upon the free volume to the molar volume ratio of the different components, given a positive Flory-Huggins parameter χ_{12}^* . It is known that gas sorption in rubbery polymers can be well described at low sorption levels by Henry's law (linearized version of the Flory-Huggins equation) and at high sorption levels by the Flory-Huggins equation. Consequently, eq 4, which has the same functional form as the Flory-Huggins equation, can be expected to describe well the gas sorption data in rubbery polymers at both low and high gas sorption levels. This has been verified by our calculations not discussed here.

Now we consider gas sorption in glassy polymers using the lattice visualization shown in Figure 2b. The lattice includes the extra hole free volume of the glassy polymer as well. Further, we incorporate the dual mode sorption concept (Barrer et al., 1957a,b, 1958), which postulates two gas populations that can be distinguished by their different sorbing modes. One population consists of gas molecules which sorb in a manner identical to their sorption in rubbery polymers. Therefore, the representation of this population on the lattice (Figure 2b) is exactly equivalent to that of gas sorbed on rubbery polymers (Figure 2a). The second population consists of gas molecules which sorb by utilizing the excess hole free volume present in the glassy polymer. This latter population is shown on the lattice by the overlapping of the hole free volume of the gas on the extra hole free volume characteristic of the glassy state. One can thus distinguish four kinds of sites on the lattice representing the gas-glassy polymer system as indicated in Figure 2b. We have already defined (in discussing the lattice shown on Figure 2a) component 1 to be the hole free volume associated with the population of gas sorbing as in rubbery polymers and component 2 to be the hole free volume associated with the equilibrium liquid polymer. The hole free volume associated with the second population of gas molecules that use (by overlapping) the extra hole free volume of the glassy state is defined to be component 3. The extra hole free volume of the glassy state

not yet utilized for gas sorption is defined as component 4.

In this quaternary mixture, we denote the number count of component i by n_i and the free volume fraction of component i by Φ_i . Equation 5 defines the free volume fractions while eq 6 relates them to experimentally measurable weight fractions. One should not that the weight fraction w_4 is zero since component 4 denotes the extra hole free volume unoccupied by gas molecules and hence \bar{V}_4 is infinitely large. Consequently, the free volume fraction of component 4, Φ_4 is not obtained from eq 6 but from the conservation statement that the sum of all free volume fractions must add up to unity, $\sum \Phi_i = 1$. The free energy change on mixing the four components in the pseudoequilibrium mixture can be written in the framework of the Hildebrand model as

$$\Delta F_m/kT = n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + n_3 \ln \Phi_3 + n_4 \ln \Phi_4 + \chi_{12} n_1 \Phi_2 + \chi_{32} n_3 \Phi_2 \quad (9)$$

As specified earlier, the size of a lattice site is assumed equal to the hole free volume associated with a gas molecule. Consequently, v_1^H , v_2^H , and v_4^H are all equal to one another and have a magnitude equal to the hole free volume associated with a gas molecule when it is in the polymer. v_2^H is the hole free volume associated with a polymer molecule in its equilibrium liquid state. Equation 9 includes four entropy terms involving all four components, but only two of the six possible interactional terms. Concerning the latter, one may note that χ_{12} and χ_{32} , which refer to gas-polymer interactions, are different from one another (even though both 1 and 3 refer to the gas molecules and ω_{11} and ω_{33} are equal) because components 1 and 3 are in different microenvironments with respect to the polymer (implying that ω_{12} and ω_{32} should be different from one another). The term involving χ_{13} does not appear because χ_{13} is equal to zero (since $\omega_{11} = \omega_{33} = \omega_{13}$). The term involving χ_{14} , χ_{24} , and χ_{34} have been excluded in the above free energy expression. This is equivalent to postulating that component 4 (extra hole free volume sites not occupied by gas molecules) contributes to the system entropy but not to interactions. It will be shown that the resulting formulation accurately correlates the gas sorption data and the relaxation of this approximation results in a model that contains more parameters than can be uniquely determined by such a correlation.

The extra hole free volume associated with the glassy polymer at temperature T (before exposure to penetrant gas) is a fixed quantity influenced only by the polymer processing history. Therefore, $n_3 + n_4 = n_0 = \text{constant}$. We denote the ratio between the extra hole free volume of the glassy polymer prior to exposure to the gas and the hole free volume of the equilibrium liquid polymer by η .

$$\eta = \frac{n_0 v_1^H}{n_2 v_2^H} = \frac{\Phi_3 + \Phi_4}{\Phi_2} \quad (10)$$

From eq 9, the chemical potentials of the gas populations sorbing by the two different modes (components 1 and 3) can be obtained. The standard states for both components 1 and 3 are the same, and it is taken to be that associated with the hypothetical liquid state of the penetrant gas at the given temperature and pressure. The activity of component 1 (associated with the first gas population that sorbs as in rubbery polymers) is given by

$$\ln a_1 = \frac{\partial}{\partial n_1} \left(\frac{\Delta F_m}{kT} \right)_{n_0, n_2, n_3, T, P = \text{const}} = \ln \Phi_1 + \Phi_2 [1 + \chi_{12}(1 - \Phi_1) - \chi_{32}\Phi_3] \quad (11)$$

One may note that because of the large molecular weight of the polymer, the factor $(1 - v^H_1/v^H_2)$ appearing in the expression for chemical potential has been approximated to unity. Similarly, the activity of component 3 (associated with the second gas population that sorbs by utilizing the extra hole free volume of the glassy state) can be written as

$$\ln a_3 = \frac{\partial}{\partial n_3} \left(\frac{\Delta F_m}{kT} \right)_{n_0, n_1, n_2, T, p = \text{const}} = \ln \frac{\Phi_3}{\Phi_4} + \chi_{32} \Phi_2 \quad (12)$$

The activity of the gas in the contacting gas phase is given by

$$a = f/f_0 = p/p_0 \quad (13)$$

where f is the fugacity and p is the partial pressure of the gas, while f_0 and p_0 are the standard-state fugacity and the vapor pressure, respectively, of the hypothetical liquid at that temperature. In writing the above equation, we have assumed the contacting gas phase to be ideal. However, the gas phase may be nonideal at low temperatures and high pressures and one can expect the fugacity coefficient to deviate from unity. The most severe gas-phase nonideality and, hence, the smallest fugacity coefficient over the range of experimental conditions considered here should occur at 25 °C and 20-atm pressure. At this condition, the fugacity coefficient calculated using the Peng-Robinson equation of state for the sorbent gas is 0.89. At lower pressures and higher temperatures where most of the experimental data relevant to this study are available, the fugacity coefficient is closer to unity. Although the fugacity coefficient of the gas phase could have been readily incorporated, we deliberately leave out this correction in the present calculations. This is because, in calculating the ratio f/f_0 , there is intrinsic uncertainty in defining and calculating the standard-state fugacity for the penetrant gas in its hypothetical liquid state. The standard-state fugacity is taken here to be the vapor pressure obtained by extrapolating the Antoine equation to the hypothetical liquid range. Given the uncertainty in the estimation of f_0 , the minor fugacity coefficient correction is not of any practical importance and, hence, $f = p$.

The standard state of the penetrant gas phase is identical to that of components 1 and 3. Hence, the activities $a_1 = a_3 = a$, at equilibrium. Therefore, we get the following sorption isotherms:

$$\ln \frac{p}{p_0} = \ln \Phi_1 + \Phi_2 [1 + \chi_{12}(1 - \Phi_1) - \chi_{32}\Phi_3] \quad (14)$$

and

$$\ln \frac{p}{p_0} = \ln \frac{\Phi_3}{\Phi_4} + \chi_{32}\Phi_2 \quad (15)$$

Using eq 10, we can rewrite eq 15 in the form

$$\frac{\Phi_3}{\Phi_2} = \eta \frac{(e^{-\chi_{32}\Phi_2}/p_0)p}{1 + (e^{-\chi_{32}\Phi_2}/p_0)p} \quad (16)$$

One may note that eq 14 resembles Henry's law at low sorption levels and the Flory-Huggins equation at higher sorption levels. Equation 16 resembles the Langmuir adsorption isotherm equation. Henry's law and the Langmuir adsorption isotherm equation have been used very effectively to describe the two modes of gas sorption in the dual mode gas sorption model (Stannett et al., 1979).

The free volume based gas sorption model (eqs 14 and 16) has three parameters, namely, η , χ_{12} , and χ_{32} . If these

parameters are determined by fitting the experimental gas sorption data in glassy polymers to the sorption isotherms (eqs 14 and 16), then the specific hole free volume of the polymer-gas mixture can be readily calculated at any sorption level. From Figure 2b we note that the total hole free volume is the sum of the hole free volume of the equilibrium liquid polymer, the extra hole free volume of the glassy state prior to exposing the polymer to the gas, and the hole free volume of the first population of gas molecules that sorb as in rubbery polymers. The hole free volume of the second population of gas molecules simply overlaps the extra hole free volume of the glassy state. Therefore, the total hole free volume per gram of the polymer-gas mixture can be written as

$$\hat{V}_{FH} = w_1 \hat{V}_1 + w_2 \hat{V}_2 (1 + \eta) \quad (17)$$

Here, $\hat{V}_1 (=v^H_1/M_1)$ and $\hat{V}_2 (=v^H_{seg}/M_{seg})$ are the specific hole free volumes of the gas and the equilibrium liquid polymer, respectively. v^H_1 and v^H_{seg} denote the hole free volumes while M_1 (=44 for CO₂) and M_{seg} (=192.2 for PET) denote the molecular weights of the gas molecule and the monomer repeat unit of the polymer, respectively. w_1 is the weight fraction of that population of gas which sorbs as in rubbery polymers while w_2 is the weight fraction of the polymer. The weight fraction of the gas that sorbs by utilizing the extra hole free volume of the glass is w_3 , and the sum of all weight fractions must be unity.

$$w_1 + w_2 + w_3 = 1 \quad (18)$$

The weight fractions are related to the hole free volume fractions through eq 6. They are computed using the hole free volume ratios via the following relations:

$$w_1 = \frac{\Phi_1/\Phi_2}{\Phi_1/\Phi_2 + \Phi_3/\Phi_2 + \hat{V}_1/\hat{V}_2} \quad (19)$$

$$w_2 = \frac{\hat{V}_1/\hat{V}_2}{\Phi_1/\Phi_2 + \Phi_3/\Phi_2 + \hat{V}_1/\hat{V}_2} \quad (20)$$

$$w_3 = \frac{\Phi_3/\Phi_2}{\Phi_1/\Phi_2 + \Phi_3/\Phi_2 + \hat{V}_1/\hat{V}_2} \quad (21)$$

The estimate for the specific hole free volume of the mixture \hat{V}_{FH} needed by eq 1 can be readily found using eq 17 if we know the values for the three parameters of the sorption model.

IV. Free Volume Model of Sorption: Parameter Estimation

Experimental gas sorption data are available in the form of total amount of gas sorbed C as a function of the gas phase pressure p , where C is expressed usually in units of cm³ of gas (STP) per cm³ of glassy polymer. The total sorption level C defined in this manner can be related to the variables appearing in the free volume model of gas sorption via the equation

$$\left[\frac{\Phi_1 + \Phi_3}{\Phi_2} \right] \frac{v^H_{seg}}{v_{seg}} \frac{v_1}{v^H_1} \frac{1}{[1 + \eta v^H_{seg}/v_{seg}]} \frac{22415}{v_1} = C \quad (22)$$

Here, v^H_1 and v_1 are the hole free volume and the molar volume, respectively, of the gas in its hypothetical liquid state at a given temperature while v^H_{seg} and v_{seg} are the hole free volume and the molar volume of the monomer repeat unit of the equilibrium liquid polymer. v^H_1 , v_1 , v^H_{seg} , and v_{seg} are all molecular properties whose values are estimated as described in the Appendix. All the volumes in eq 22 are expressed in units of cm³/mol.

Table I. Temperature Dependence of the Sorption Model Parameters for the System Carbon Dioxide/Poly(ethylene terephthalate) [Experimental Sorption Data from Koros and Paul (1978a)]

$T, ^\circ\text{C}$	η	χ_{12}	χ_{32}
25	0.250	-0.016	-3.471
35	0.185	-0.281	-3.433
45	0.152	-0.338	-3.500
55	0.115	-0.487	-3.480
65	0.088	-0.598	-3.296
75	0.061	-0.793	-3.163
85	0.032	-0.926	-3.230
95		-1.110	
105		-1.216	
115		-1.262	

The vapor pressure p_0 appearing in the sorption isotherm equations (14) and (16) is determined by extrapolating the Antoine equation (which correlates the vapor pressure with temperature) to the hypothetical liquid region. By correlating the vapor pressure data of CO_2 (Perry and Chilton, 1973), we find the Antoine equation to be

$$\ln \frac{73}{p_0} = 2023.81 \left(\frac{1}{T} - \frac{1}{304.1} \right) \quad (23)$$

where p_0 is in atmospheres and T is in kelvin.

Given the sorption levels C as a function of the pressure p , we need to find the three model parameters η , χ_{12} , and χ_{32} simultaneously solving the two sorption isotherm equations (14) and (16), the concentration conversion equation (22), and the Antoine equation (23). The numerical procedure involved in determining the three model parameters is as follows. We start with trial values for the model parameters η , χ_{12} , and χ_{32} . In eq 14, the hole free volume fraction Φ_3 is substituted for by using eq 16 and the hole free volume fraction Φ_1 is substituted for by using the relation

$$\Phi_1 = 1 - \Phi_2 - \Phi_3 - \Phi_4 = 1 - \Phi_2(1 + \eta) \quad (24)$$

Equation 14 now contains only one unknown, namely, Φ_2 , which can be calculated at any value of the pressure p . Equation 14, which is implicit in the variable Φ_2 , is solved using a standard IMSL (International Mathematical and Statistical Library) routine ZSP0W (this routine provides solutions to nonlinear algebraic equations). Once Φ_2 is known, Φ_3 is calculated from eq 16 and Φ_1 from eq 24. Since the sum of the hole free volume fractions is unity, Φ_4 is also determined. Knowing the four free volume fractions, one can calculate Φ_1/Φ_2 and Φ_3/Φ_2 . The sum of these two ratios is directly related to the total gas sorption level, as shown by eq 22. The values of parameters η , χ_{12} , and χ_{32} that minimize the sum of squares of the difference between the experimental sorption level C and the calculated sorption level (the left-hand side of eq 22) over the experimental range of pressure are found using a standard IMSL minimization subroutine ZXMIN. For every set of η , χ_{12} , and χ_{32} which the subroutine ZXMIN computes during the process of minimization, $(\Phi_1 + \Phi_3)/\Phi_2$ is computed for all experimental pressures as outlined in the previous paragraph. The left-hand side of eq 22 is then evaluated. ZXMIN performs the parameter search until it finds a solution set for the three parameters which minimizes the residual sum of squares.

The parameters of the free volume model of gas sorption listed in Table I have been obtained by fitting the experimental sorption data of Koros and Paul (1978a) for the system CO_2/PET . Figure 3 provides a comparison of the experimental sorption data and the sorption levels calculated from the free volume model using the listed model parameters. The free volume model of sorption

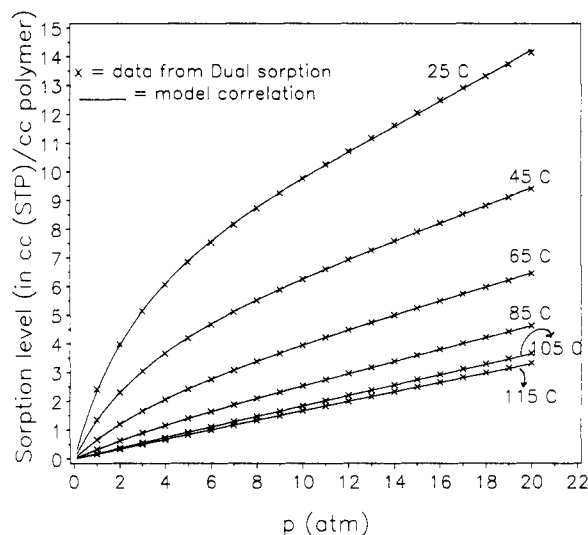


Figure 3. Sorption isotherms for the system CO_2/PET . X's represent the sorption levels calculated using the dual mode sorption model by Koros and Paul (1978a) which correspond very well with measured sorption levels. The solid lines are the correlations of the free volume based sorption model developed in this work.

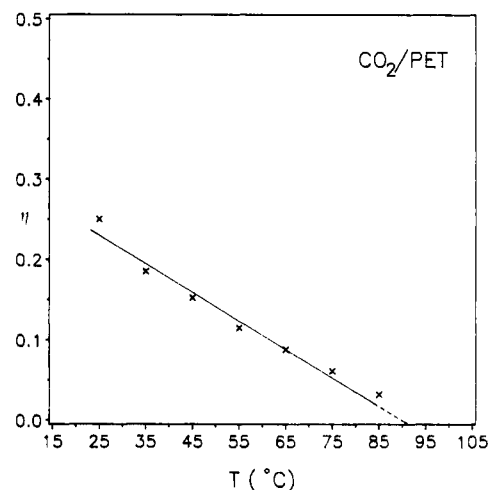


Figure 4. Plot of free volume based sorption model parameter η as a function of T for the system CO_2/PET . The X's correspond to the values of η shown in Table I. The solid line is simply a smooth line connecting η values at various temperatures. The extrapolation of the line to $\eta = 0$ provides T_g .

provides excellent correlation of the experimental sorption data. One may note that what is referred to as experimental data in the figure is not the raw experimental data. Instead, it is the correlation based on the dual mode sorption model provided by Koros and Paul (1978a). They have shown that the experimental sorption data are correlated excellently by the dual mode sorption model.

The parameter η has to approach 0 as T approaches T_g , since it represents the size of the excess hole free volume characteristic of the glassy state. For the system in Table I (CO_2/PET), extrapolation of η to 0 (Figure 4) yields a glass transition temperature of 90 °C. For comparison, the T_g reported for PET by Koros and Paul (1978a) is about 85 °C.

The dependence of χ_{12} on inverse temperature is shown in Figure 5. The parameter values are fitted by the empirical relation $\chi_{12} = -5.474 + 1625.9/T$, where T is in kelvin. Such a temperature dependence is analogous to that of the classical Flory-Huggins χ_{12}^* parameter. On the other hand, χ_{32} does not show any recognizable dependence on temperature. For all practical purposes it

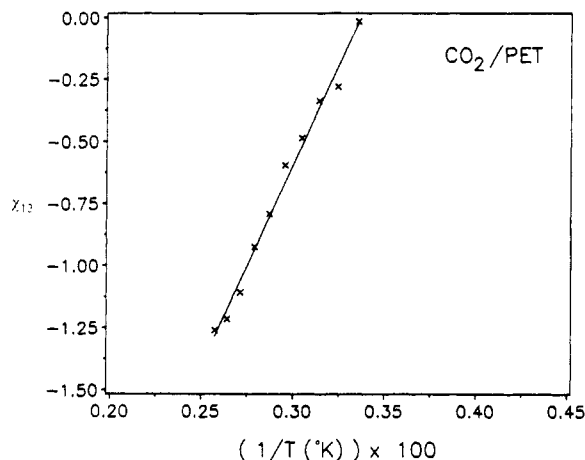


Figure 5. Dependence of free volume based sorption model parameter χ_{12} on inverse temperature for the system CO_2/PET . The 'x's correspond to the values of χ_{12} shown in Table I. The solid line represents the least squares fit of χ_{12} to inverse temperature.

appears to be a constant, $\chi_{32} = -3.33 \pm 0.17$.

V. Free Volume Model of Diffusion: Parameter Estimation

The effective gas diffusivity as a function of gas sorption level is calculated using eq 1. In this equation, the variables \bar{w}_1 , \bar{w}_2 , and \bar{V}_{FH} are obtained from the gas sorption data. Specifically, the total mass fraction of the gas sorbed \bar{w}_1 is calculated as $\bar{w}_1 = w_1 + w_3$, where w_1 and w_3 are obtained from eqs 19 and 21. The mass fraction \bar{w}_2 of the polymer is equal to w_2 and is obtained from the mass balance $\bar{w}_2 = 1 - \bar{w}_1$. The specific hole free volume of the polymer-gas mixture \bar{V}_{FH} is calculated from eq 17.

The specific critical hole free volume of i required for a jump \bar{V}_{ij} is approximated by the specific volume at 0 K. For the gas, the jumping unit is taken as the gas molecule itself. For the polymer, the jumping unit need not be the monomer repeating unit. Usually, the size of the jumping unit can be obtained only by correlating experimental diffusivity data with the free volume model. An estimate for the PET jumping unit on such a basis is presently not available, and hence, in this paper, we take the polymer jumping unit to be the monomer repeat unit itself. Some justification for such a choice is found in an empirical correlation between the glass transition temperature and the molar volume of the polymer jumping unit recently obtained by Zielinski (1991). The molar volumes of the polymer jumping units employed to generate the correlation had been obtained by fitting experimental diffusion data for seven rubbery polymers. It was found that

$$V_{2J}(\text{cm}^3/\text{mol}) = 0.6224T_g(\text{K}) - 86.95 \quad (25)$$

The polymer PET considered in the present paper has a glass transition temperature of 85 °C (Koros and Paul, 1978a). Correspondingly, the molar volume of the polymer jumping unit based on the above correlation is 135.9 cm^3/mol . For comparison, the molecular volume of a segment of PET at 0 K is 122.43 cm^3/mol (see Appendix). Thus, in the absence of a more direct estimate for the polymer jumping unit, we consider the monomer repeat unit to be the jumping unit. The molar volume of the gas jumping unit at 0 K is 25.92 cm^3/mol , and hence, $\bar{V}_{1J} = 25.92/M_{1J} = 0.589 \text{ cm}^3/\text{g}$. Similarly, the molar volume of the polymer jumping unit at 0 K is 122.43 cm^3/mol , and therefore, $\bar{V}_{2J} = 122.43/M_{2J} = 0.637 \text{ cm}^3/\text{g}$. The ratio ξ of the polymer volume of penetrant jumping unit to the polymer jumping unit, both at 0 K, is $\xi = 25.92/122.43 =$

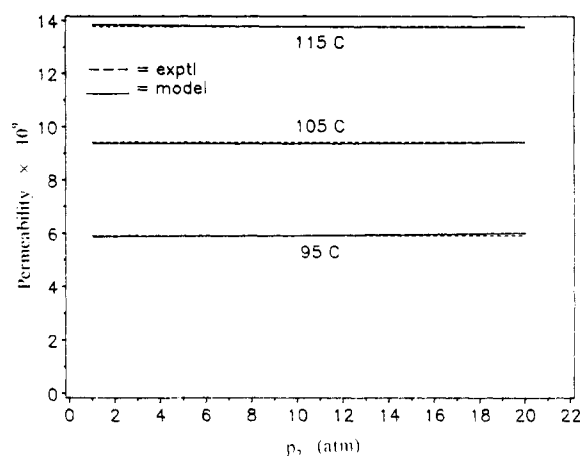


Figure 6. Permeability of CO_2 in rubbery PET as a function of temperature and upstream pressure. The dashed lines are the correlations based on the dual mode sorption and transport model obtained by Koros and Paul (1978b) which agree very well with the actual measurements. The solid lines represent the correlations of the free volume theory.

0.212. Details of the volume estimations are discussed in the Appendix.

The only parameters that remain to be determined are D_{01} , E , and γ . These three parameters are estimated by fitting the experimental permeability vs pressure data of Koros and Paul (1978b) obtained at temperatures in the rubbery region of PET (namely 95, 105, and 115 °C) to the diffusivity equation (1) and permeability equation (3). For these temperatures, the sorption isotherms are linear and the thermodynamic factor Q is thus unity. The IMSL subroutine ZXMIN is used for the data fitting. The three parameters are found to be $D_{01} = 6.72 \text{ cm}^2/\text{s}$, $E/R = 6728 \text{ K}$, and $\gamma = 0.137$. Figure 6 compares the experimental permeability data in the rubbery region with the permeabilities calculated by the free volume model (using fitted model parameters), thus indicating the quality of fit with the model.

VI. Prediction of Gas Permeability in Glassy Polymer Membrane

All model parameters necessary for the calculation of gas permeability in the glassy polymer membrane have now been determined. Thus at any given gas-phase pressure p , we can use the free volume based sorption model and the free volume diffusion model to calculate the permeability defined by eq 3.

First, we need to estimate the thermodynamic factor Q appearing in eq 2 for the mutual diffusion coefficient. As mentioned earlier, Q deviates from unity for glassy polymers even at low sorption levels, because of the pronounced curvature of the sorption isotherms. Combining the definition for Q in eq 2 with eq 13 for the gas-phase activity, we get

$$Q = \frac{x_1 x_2}{RT} \frac{\partial \mu_1}{\partial x_1} = \frac{x_1 x_2}{p} \frac{\partial p}{\partial x_1} \quad (26)$$

Q can be calculated as a function of the sorption level or pressure using the experimental sorption data available as $C \text{ cm}^3$ of gas (STP) per cm^3 of glassy polymer. Representing the molar volume of the glassy polymer by $v_G \text{ cm}^3$, the mole fractions x_1 and x_2 are given by the expressions

$$x_1 = \frac{C/22415}{C/22415 + 1/v_G}, \quad x_2 = \frac{1/v_G}{C/22415 + 1/v_G} \quad (27)$$

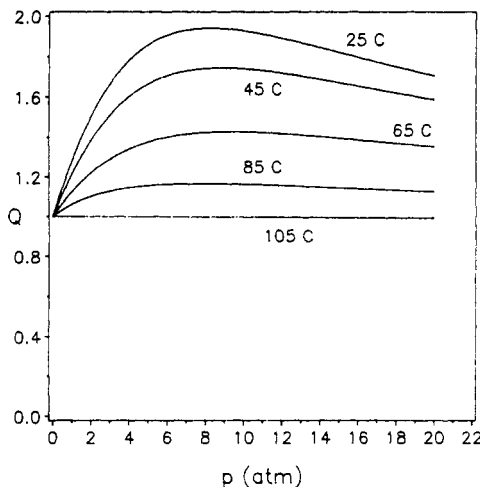


Figure 7. Thermodynamic factor Q (defined in eq 2) as a function of penetrant gas pressure at various temperatures below the glass transition temperature of PET. The factor Q has been calculated from the experimental gas sorption data on the basis of eq 29.

Combining the above two equations, we get a relation for Q that is directly linked to the experimental C - p data:

$$Q = \frac{C}{p} \frac{\partial p}{\partial C} \quad (28)$$

A convenient way to estimate Q will be to fit the experimental C - p data to an analytical expression and thus obtain an analytical expression for the derivative appearing in eq 28. The task is made simpler by the availability of the excellent correlation based on the dual mode sorption model (Koros and Paul, 1978a). Using this correlation, we obtain for Q the relation

$$Q = \frac{C}{p} \left[k_D + \frac{C'_H b}{(1 + bp)^2} \right]^{-1} \quad (29)$$

where k_D , C'_H , and b are parameters of the dual mode sorption model which have been estimated by Koros and Paul (1978a). The calculated thermodynamic factor Q as a function of pressure is plotted in Figure 7 at various temperatures of interest. Indeed Q deviates significantly from unity at low temperatures and becomes closer to unity near the glass transition temperature where the sorption curves tend to be linear.

The gas permeabilities can be calculated using eq (3) since $D_1(C)$ is obtained from eq 1 and $Q(C)$ is obtained from eq 29. The calculated gas permeabilities as a function of the temperature T and the upstream pressure are shown as solid lines in Figure 8. Also shown for comparison are the experimental permeability data. Again, the experimental data shown are not the raw data but their excellent correlation based on the dual mode sorption and transport models (Koros and Paul, 1978b). The predicted gas permeabilities in the glassy region show a markedly stronger dependence on the upstream pressure when compared to the experimental data. At 25 °C, the lowest temperature investigated, the deviations ((predicted/experimental) - 1) of the gas permeability data range from 20% at 1 atm to -25% at 20 atm. At 85 °C, near the glass transition temperature, the deviations in permeabilities range from 24% at 1 atm to 1% at 20 atm. One may note that a 25% deviation in the permeability can arise from only a 8% deviation in the specific hole free volume \bar{V}_{FH} of the polymer-gas mixture. Therefore, given the sensitivity of the present model to the estimates of free volume, the reasonable comparison between the a priori predictions

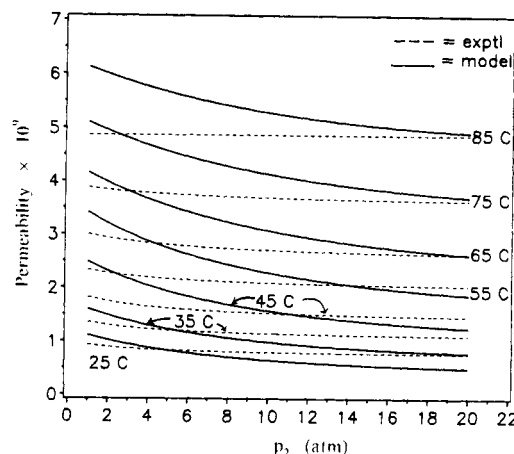


Figure 8. Permeability of CO_2 in glassy PET as a function of temperature and upstream pressure. The dashed lines are the correlations based on the dual mode sorption and transport model obtained by Koros and Paul (1978b) which represent very well the actual measurements. The solid lines are the a priori predictions provided by the free volume theory developed in this paper.

of the model and the measured gas permeabilities is very encouraging.

The hole free volume parameters v^{H_1} and $v^{H_{\text{seg}}}$ play a vital part in determining the specific hole free volume of the mixture since they influence the sorption correlations and thereby dictate the relative magnitude of \bar{V}_{FH} . Of these, v^{H_1} corresponds to the hypothetical liquid state of the penetrant. By definition, this is not an experimentally accessible quantity. Therefore, we have simply assumed a linear dependence of the molar volume on the temperature (see Appendix) for estimating the hole free volume. The molecular parameter $v^{H_{\text{seg}}}$ corresponds to the equilibrium liquid polymer. Reliable estimates of this hole free volume can be obtained from experimental rheological data in the framework of the Williams-Landel-Ferry model (Ferry, 1970). Because of the unavailability of such data at present, $v^{H_{\text{seg}}}$ has been estimated here using the approximate universality of the fractional hole free volumes at T_g and assuming a linear dependence on temperature for the molar volume (see Appendix). In future, these estimates could be improved by carrying out viscosity vs temperature measurements on PET, thereby obtaining the free volume data directly. Further, we have assumed that the polymer jumping unit is its monomer repeat unit for estimating the parameter ξ . This estimate could be improved by obtaining diffusivity data in rubbery PET which can be correlated with the free volume model to provide a good value for ξ . It is obvious from eq 1 for the self-diffusion coefficient of penetrant D_1 and eq 17 for the total hole free volume that the pressure dependence of \bar{V}_{FH} and D_1 will be altered if we modify the estimates for v^{H_1} , $v^{H_{\text{seg}}}$, and ξ . Consequently, it is possible to reduce, if not eliminate, the pressure dependence of gas permeability observed in the present model calculations by reconsidering the simplifying assumptions made for the estimation of the hole free volumes, in the absence of other direct information. We conclude that the free volume theory is promising because it is not simply a correlative model but is able to predict gas permeability, though with up to a 25% deviation from the measurements.

VII. Conclusions

The free volume theory of penetrant diffusion in rubbery polymers has been utilized in this study to predict the permeabilities of gases in glassy polymers. Three of the model parameters appearing in the theory of diffusion are

estimated from experimental gas permeability data for the rubbery polymer. The specific hole free volume of the gas-polymer mixture appearing in the theory of diffusion is estimated by correlating the experimental gas sorption data in rubbery and glassy polymers to a free volume model of gas sorption developed in this paper. The permeability of CO₂ in the glassy state of the polymer PET has been calculated in the temperature range of 25–85 °C and for membrane upstream pressures in the range of 1–20 atm. The predicted permeabilities are in reasonable agreement with experimental gas permeability data with the largest deviation between predicted and measured permeabilities being about 25%. Such a large deviation in permeability can stem from a deviation of only 8% in the estimate for the mixture hole free volume. More importantly, the calculated permeabilities show a marked dependence on pressure which is not observed in the experiments. We expect, on the basis of the functional form of the diffusion equation, that the use of better estimates for the hole free volume of the penetrant gas and the equilibrium polymer liquid in the calculations will modify the pressure dependence of the permeability as well as improve the quantitative agreement between calculated and measured gas permeabilities.

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Nomenclature

a = activity of the penetrant gas in the gas phase
 a_1 = activity of gas that is sorbed in a manner identical to sorption in rubbery polymers
 a_3 = activity of gas that is sorbed by utilizing the extra hole free volume associated with the glassy state of the polymer
 C = total volume of gas sorbed cm³(STP) per cm³ of glassy polymer, where STP refers to standard conditions of temperature and pressure
 C_0 = gas concentration corresponding to the upstream pressure p_2
 k = Boltzmann constant
 M_1 = molecular weight of gas (=44 for CO₂)
 M_{1J} = molecular weight of gas jumping unit (= M_1)
 M_{seg} = molecular weight of monomer repeat unit (=192.2 for PET)
 M_{2J} = molecular weight of polymer jumping unit (= M_{seg})
 n_1 = number of gas molecules that sorb in a manner identical to sorption in rubbery polymers
 n_2 = number of polymer molecules
 n_3 = number of gas molecules that sorb by utilization of the extra hole free volume associated with the glassy state
 n_4 = number of extra hole free volume sites in the glassy polymer not utilized by sorbing gas
 p = equilibrium gas pressure
 p_1 = downstream gas pressure (=0)
 p_2 = upstream gas pressure
 p_0 = vapor pressure of penetrant treated as a hypothetical liquid calculated from eq 23
 P = gas permeability at a given T and upstream pressure
 R = universal gas constant
 T = temperature
 T_g = glass transition temperature
 v_1 = molar volume of the penetrant at hypothetical liquid state (= $v_1^H + v_1^O + v_1^I$)
 v_1^H = hole free volume associated with the penetrant
 v_1^O = occupied volume of the penetrant (=molar volume at 0 K = 25.92 cm³/mol for CO₂)
 v_1^I = interstitial free volume of the penetrant
 \hat{V}_1 = specific free volume of the penetrant (v_1^H/M_1)

\hat{V}_{1J} = specific volume of penetrant jumping unit (= v_1^O/M_1 = 0.589 cm³/g)
 v_2 = molar volume of equilibrium liquid polymer
 v_2^H = hole free volume associated with a polymer molecule in its equilibrium liquid state
 \hat{V}_2 = specific hole free volume of the equilibrium liquid polymer per segment (= v_2^H/M_{seg})
 \hat{V}_{2J} = specific volume of polymer jumping unit (= v_2^O/M_{seg} = 0.637 cm³/g)
 v_{seg} = volume of a monomer repeat unit in equilibrium liquid polymer (= $v_{seg}^H + v_{seg}^O + v_{seg}^I$)
 v_{seg}^H = hole free volume associated with a monomer repeat unit in equilibrium liquid polymer
 v_{seg}^O = occupied volume of monomer repeat unit (=molar volume at 0 K = 122.43 cm³/mol for PET)
 v_{seg}^I = interstitial free volume of monomer repeat unit
 w_1 = weight fraction of gas that sorbs in a manner identical to sorption in rubbery polymers
 w_2 = weight fraction of equilibrium liquid polymer
 w_3 = weight fraction of gas that utilizes the extra hole free volume associated with the glassy state of the polymer
 x_1 = mole fraction of sorbed gas in the penetrant-polymer mixture
 x_2 = mole fraction of glassy polymer in the penetrant-polymer mixture
 α_1^H = thermal expansion coefficient of hole free volume of 1
 α_1^I = thermal expansion coefficient of interstitial free volume of 1
 α_{seg}^H = thermal expansion coefficient of hole free volume of segment
 α_{seg}^I = thermal expansion coefficient of interstitial free volume of segment
 γ = overlap factor
 η = ratio of the extra hole free volume in the glassy polymer before exposure to gas to the hole free volume of the equilibrium liquid polymer
 ξ = ratio of the molar volume of a gas jumping unit to the molar volume of the polymer jumping unit (= v_1^O/v_{seg}^O = 0.212)
 Φ_1 = hole free volume fraction of the gas that sorbs in a manner identical to sorption in rubbery polymers
 Φ_2 = hole free volume fraction of the equilibrium polymer liquid
 Φ_3 = hole free volume fraction of gas that utilizes the extra hole free volume associated with the glassy state of the polymer
 Φ_4 = hole free volume fraction of sites in the glass which are available for utilization by the gas at any given gas pressure
 Φ_1^* = molar volume fraction of solvent in the Flory-Huggins solution model
 Φ_2^* = molar volume fraction of polymer in the Flory-Huggins solution model
 χ_{12} = dissimilarity parameter between the polymer and the gas species 1
 χ_{12}^* = dissimilarity parameter between the polymer and the solvent 1 in the Flory-Huggins solution model
 χ_{32} = dissimilarity parameter between the polymer and the gas species 3
 ω_{ij} = pair interaction energy between components i and j

Appendix. Estimation of Hole Free Volume of Equilibrium Liquids

In order to estimate the hole free volume of the penetrant gas in the hypothetical liquid state and of the equilibrium polymer liquid, the following assumptions are made.

1. The fractional hole free volume at the glass transition temperature is treated as a universal constant which is obtained from the Williams-Landel-Ferry treatment (1955)

$$(f)_{T_g} = \left(\frac{v_1^H}{v_1} \right)_{T_g} = \left(\frac{v_{seg}^H}{v_{seg}} \right)_{T_g} = 0.025 \quad (A-1)$$

where $v_1 = v_1^H + v_1^O + v_1^I$, $v_{seg} = v_{seg}^H + v_{seg}^O + v_{seg}^I$. Here, the superscripts H, O, and I refer to the hole free volume, occupied volume and the interstitial free volume, respectively.

2. The occupied volumes v_1^O and v_{seg}^O are considered temperature independent and taken equal to the respective molar volumes at 0 K.

3. The interstitial and hole free volumes, and hence, the molar volumes v_1 and v_{seg} are all assumed to have a linear dependence on the temperature.

$$v_1^H = \alpha_1^H T, \quad v_1^I = \alpha_1^I T, \quad v_{seg}^H = \alpha_{seg}^H T, \quad v_{seg}^I = \alpha_{seg}^I T \quad (A-2)$$

where α 's refer to the thermal expansion coefficients of the different volume components.

Penetrant Gas in Hypothetical Liquid State. An estimate of v_1^O is obtained by dividing the van der Waals volume by a dimensionless packing density at 0 K. The dimensionless packing density for CO₂ is 0.76 (Bondi, 1968). In this way, v_1^O is estimated to be 25.92 cm³/mol. At the triple point temperature of 216.6 K, the solid density and the liquid density are known. The solid state is assumed to contain negligible hole free volume. Therefore, from the solid density of 0.0344 mol/cm³ at the triple point, we obtain the sum of the occupied volume and the interstitial free volume, $v_1^O + v_1^I = 1/0.0344 = 29.07$ cm³/mol. Consequently, the thermal expansion coefficient of interstitial free volume is $\alpha_1^I = 0.01454$ cm³/(mol K). At the triple point, the molar volume of the liquid is 37.42 cm³/mol. Since the occupied and interstitial volumes are already known, we estimate the thermal expansion coefficient of hole free volume to be $\alpha_1^H = 0.03855$ cm³/(mol K). Finally, by dividing v_1^O by the molecular weight of the gas (which equals 44) $\bar{V}_{1,l}$ is obtained to be 0.589 cm³/g.

Monomer Repeat Unit of the Equilibrium Liquid Polymer. The van der Waals volume of the polymer segment can be estimated using a group contribution method described in Van Krevelan (1972), or it can be directly obtained from Van Krevelan (1972) if available. v_{seg}^O is estimated by multiplying the van der Waals volume per segment by a geometrical packing factor of 1.3 (Bondi, 1968; Van Krevelan, 1972). For a PET segment, v_{seg}^O is estimated to be 122.43 cm³/mol. Taking the density of equilibrium liquid polymer at 25 °C to be 1.331 g/cm³, we estimate that $v_{seg} = 144.4$ cm³/mol. Therefore, the sum of the thermal expansion coefficients of interstitial and hole free volumes is calculated to be $\alpha_{seg}^H + \alpha_{seg}^I = 0.073685$ cm³/mol. Given the experimental value of $T_g = 85$ °C = 358.16 K, and the universal fractional hole free volume $(f)_{T_g} = 0.025$, the thermal expansion coefficient of the hole free volume is found from eq A-1 to be $\alpha_{seg}^H = 0.010388$ cm³/(mol K). Therefore, $\alpha_{seg}^I = 0.063297$ cm³/(mol K). Specific volumes are obtained by dividing the above volume estimates by the segmental molecular weight of 192.2 g/mol. These different specific volumes are schematically shown in Figure 1. Finally, the parameter ξ is estimated by dividing v_1^O by v_{seg}^O and is determined to be 0.212.

Registry No. PET, 25038-59-9; CO₂, 124-38-9.

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