very small flow rates. In such a situation, a large amount of probe is usually injected to improve the signal-to-noise ratio of the detector: then the correction gets larger because $V_{inj}$ is large. The correction is also significant for very small column loadings. As is seen from Figures 1-3 and tables, the slopes for different loadings are very similar due to the fact that $V_r$ and $V_{h/2}$ are more or less proportional to each other. Thus, the correction of $V_r$ is similar for different loadings; for small loadings (small $V_r$) its relative significance increases.

**Acknowledgment.** We are grateful to Hercules, Inc., for financial support of this study through its Grant-in-Aid program.

**Registry No.** Poly(isobutylene), 9003-29-6; hexane, 110-54-3; octane, 111-65-9; nonane, 111-84-2.

## References and Notes

(1) Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1984**, *17*, 803.
(2) Card, T.; Al-Saigh, Z. Y.; Munk, P. *J. Chromatogr.* **1984**, *301*, 261.
(3) Card, T.; Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1985**, *18*, 1030.
(4) Leung, Y.-K.; Eichinger, B. E. *J. Phys. Chem.* **1974**, *78*, 60.
(5) Leung, Y.-K.; Eichinger, B. E. *Macromolecules* **1974**, *7*, 685.
(6) Hammers, W. E.; Deligny, C. L. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 912; *J. Polym. Sci., Part C* **1972**, *39*, 273.
(7) Newman, R. D.; Prausnitz, J. M. *J. Phys. Chem.* **1972**, *76*, 1492.
(8) Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Macromolecules* **1974**, *7*, 565.
(9) Newman, R. D.; Prausnitz, J. M. *AIChE J.* **1973**, *19*, 704.
(10) Braun, J. M.; Guillet, J. E. *Macromolecules* **1975**, *8*, 557.
(11) Fernandez-Berridi, M. J.; Eguiazabal, J. I.; Elorza, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 859.
(12) Munk, P.; Al-Saigh, Z. Y.; Card, T., paper in preparation.

---

# Dual-Mode Transport of Penetrants in Glassy Polymers

**Glenn H. Fredrickson* and Eugene Helfand**

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974.* *Received April 22, 1985*

ABSTRACT: The existing theories of dual-mode penetrant transport in amorphous polymers are critically examined. It is found that terms in the penetrant flux expression that couple the two sorption modes have previously been neglected. The importance of these terms is discussed, and new expressions for the time lag and permeability in permeation experiments are presented. Our theory reduces to previous theories by Paul and Koros and by Petropoulos in particular limits, but the interpretation of certain parameters in these theories is modified.

## I. Introduction

An understanding of penetrant sorption and diffusion in polymers is essential to many industrial applications. Polymer films and membranes are used extensively in food packaging, industrial gas separation processes, drug delivery systems, and reverse osmotic applications. The design of effective coating and casings for the protection of electronic components and transmission cables depends critically on the sorption properties of undesirable penetrants in the protective coatings. A successful theory of sorption and transport can also be applied to the analysis of dye penetration and binding in textiles and to membranes that contain adsorptive fillers for applications demanding controlled penetrant transport.

While the solubility and transport properties of small molecules in rubbery polymers are relatively well understood, much less is known about the microscopic mechanism of sorption and transport in glassy polymers. It is believed that the inability of the sub-$T_g$ matrix to relax to thermodynamic equilibrium can lead to local inhomogeneities in the penetrant environment. Furthermore, gas absorption by polymeric glasses can be accompanied by swelling, crazing, and crack formation. There are several excellent reviews of theory and experiment for penetrant solubility and mobility in glassy systems.[1-3]

Meares[4] was one of the first to suggest that the inhomogeneities present in polymer glasses have a profound effect on penetrant solubility and transport. He proposed a "dual-mode" picture in which penetrant molecules can reside in one of two environments in the glass. The first environment (or "mode") is that of ordinary solution, while in the second mode penetrant molecules reside in "microvoids" or holes that were frozen into the glass at $T_g$. Vieth, Michaels, and Barrie[5,6] demonstrated that various inert gases show highly nonlinear sorption isotherms in glassy polymers. They found that these isotherms could be empirically represented as a sum of a Henry's law contribution and a Langmuir contribution

$$C = C_D + C_H = k_D p + C_H' bp/(1 + bp) \qquad (1)$$

where $C$ is the total concentration of penetrant, $C_D$ is the concentration of "dissolved" molecules, $C_H$ is the concentration of molecules "adsorbed in microvoids," $k_D$ is Henry's law constant, $b$ is the hole affinity constant, $C_H'$ is the concentration in the holes at saturation, and $p$ is the partial pressure of penetrant in the gas phase. The applicability of eq 1 to a wide variety of penetrants and polymers has been demonstrated.[2]

A description of the kinetics of permeation was first given by Vieth and Sladek,[7] who proposed that the molecules in the microvoids are completely immobilized. Petropoulos[8] and Paul and Koros[9] subsequently extended the transport theory to allow partial mobility of the adsorbed penetrant molecules. Tshudy and von Frankenberg[10] also generalized the Vieth-Sladek analysis by relaxing the assumption of local equilibrium. The combination of eq 1 and these transport models is collectively referred to as dual-mode sorption theory. There is increasing evidence[1-11] that the dual-mode description is a realistic picture of sorption and transport for nonswelling penetrants in glassy polymers.

Despite the success of the dual-mode transport theories, there are some unsatisfactory steps and assumptions in the derivation of the working equations. Furthermore, the existing derivations[8,9] leave unanswered questions regarding the physical interpretation of certain transport parameters and the origin of penetrant mobility in the microvoids. The objective of this paper is to clarify some of these issues and to provide a sound physical and mathematical basis for the use of dual-mode theory. Before addressing these objectives in sections II–IV, we will briefly discuss the theories of Paul and Koros[9] and Petropoulos[8] to introduce the subject and to point out the shortcomings of the existing formalism.

Paul and Koros[9] suggested that to complement the equilibrium relation, eq 1, the nonequilibrium transport of penetrants in polymer glasses could be described by the following expression for the total mass flux of penetrant

$$\mathbf{J} = -D_D \nabla C_D - D_H \nabla C_H \qquad (2)$$

In this expression, $D_D$ and $D_H$ are taken as constants and are interpreted as diffusion coefficients for the molecules in the dissolved and adsorbed modes, respectively. With an assumption of rapid local equilibrium between the two modes, $C_D$ and $C_H$ are related by

$$C = C_D + C_H = C_D + KC_D/(1 + \alpha C_D) \qquad (3)$$

where $K = C_H'b/k_D$ and $\alpha = b/k_D$. Paul and Koros combined eq 2 and 3 to obtain

$$\mathbf{J} = -D_D \left[ \frac{1 + FK/(1 + \alpha C_D)^2}{1 + K/(1 + \alpha C_D)^2} \right] \nabla C \qquad (4)$$

where $F = D_H/D_D$. The combination of eq 4 and the continuity equation

$$\partial C/\partial t = -\nabla \cdot \mathbf{J} \qquad (5)$$

completely specifies the Paul–Koros transport model.

The primary difficulty with the Paul–Koros model is that eq 2 for the penetrant flux contains no terms that couple $C_D$ and $C_H$. Since one expects that the regions of polymer acting as microvoids (sites for adsorption that presumably constitute the discrete phase) are topologically distinct from the rest of the polymer matrix (the continuous phase), the flux expression should contain terms that describe the transport into and out of the microvoids. In section III we derive a flux expression that includes these coupling terms and explore the resulting predictions for the observables in transient permeation experiments in section IV. A further difficulty with eq 2 is that it seems to imply that the hole domains are large enough to sustain diffusion. We will discover that transport behavior similar to that observed in permeation experiments can be obtained even if the hole sites are so small that they can hold only a single penetrant molecule.

Petropoulos[8] presented a theory similar to that of Paul and Koros, but it was based on chemical potential gradients instead of concentration gradients. If for simplicity we restrict consideration to ideal gases, we can replace the activity in Petropoulos' equations with $p$ and write the following flux expression

$$\mathbf{J} = -D_{TD}[(C_D + RC_H)/p] \nabla p \qquad (6)$$

where $R = D_{TH}/D_{TD}$, the ratio of thermodynamically based diffusion coefficients for the hole and dissolved species, respectively. If the local equilibrium approximation is made and eq 6 is combined with eq 1 and 3, the flux can be written

$$\mathbf{J} = -D_{TD} \left[ \frac{1 + RK/(1 + \alpha C_D)}{1 + K/(1 + \alpha C_D)^2} \right] \nabla C \qquad (7)$$

Note that the only difference in the form of eq 4 and 7 is the exponent of $1 + \alpha C_D$ in the terms containing $F$ and $R$. Although both equations were derived by neglecting coupling terms in the flux that account for exchange of molecules between the two modes, we demonstrate in the next section that the Petropoulos expression has the correct functional dependence on $C$ when the intrinsic diffusion coefficient within the hole phase can be neglected and that the Paul–Koros expression has the correct $C$ dependence when the coupling terms can be neglected. In the former situation, the physical interpretation of $R$ is modified, however.

We give a brief summary of our results. Coupling terms in the flux expression that represent exchange of penetrant molecules between hole and dissoved modes must be included. These terms provide "mobility" to molecules that are adsorbed into microvoids, even if the molecules have an intrinsic diffusion coefficient in the hole phase that vanishes. If this intrinsic diffusivity is zero, we find that the Petropoulos expression for the flux is essentially correct, except that $R$ must be reinterpreted as a parameter that quantifies the magntiude of the coupling terms (i.e., an effective exchange rate). For the more general situation where the intrinsic diffusivity in the hole phase is not zero and the coupling terms cannot be neglected, we present new results. Studies of the relative importance of the various flux terms might allow some information about microvoid size and topology to be obtained from permeation experiments.

After the present work was completed, the studies by Chern et al.[21] and Barrer[22] were brought to our attention. Although these papers deal with similar issues, the approach and some of the results are different from ours. In our view, the various studies are complementary and constitute a valuable contribution to the theory of penetrant transport in glassy polymers. The results of the present paper are compared with those of Barrer[22] in section IV.

## II. Phenomenological Transport Equations

There are various levels on which the dynamics of penetrant motion in glassy polymers can be described. At the highest level, one might formulate a statistical mechanical description for the time evolution of all the species in which various effective potentials represent interactions among penetrant molecules and the polymer molecules that constitute the matrix. At a lower level, one can formulate a lattice model governed by stochastic rate equations in which short-ranged repulsive interactions between penetrant molecules are accounted for by excluding configurations with multiple occupancy of cells. In such a model the polymer matrix is not treated explicitly, but the transition rates of penetrant molecules between cells reflect the gross properties of the matrix. Inhomogeneities in the matrix can be incorporated by allowing a distribution of cell energies and transition rates. A third and less rigorous representation of penetrant dynamics is to model transport over large distances and times by macroscopic diffusion equations for the penetrant concentration field. The various transport coefficients reflect the matrix and penetrant properties in some average way.

In the present paper we adopt the third level of description discussed above. Since sorption and permeation experiments are sensitive only to gross macroscopic properties of the polymer–penetrant system, such a description should be adequate. Furthermore, it is likely that the transport features that emerge from such phenomenological equations could be universally applicable to a wide variety of experimental systems. Similar phenomenological descriptions have proved extremely successful in the study of static and dynamic critical phenomena.[12] In the Appendix we demonstrate how the equations of this section can be derived from a lattice model of the type discussed above (second level of description).

Consider in addition to the concentration fields $C_D(\mathbf{x},t)$ and $C_H(\mathbf{x},t)$ the saturation fields $C_D'(\mathbf{x})$ and $C_H'(\mathbf{x})$. These fields represent the concentrations of dissolved (adsorbed) penetrant if the dissolved (adsorbed) mode of sorption were fully saturated with penetrant molecules. (For generality we allow the possibility of saturation of the dissolved mode, although this is not experimentally observed. Our results, moreover, do not rely on this generalization. See the simplification following eq 18.) Only homogeneous, isotropic polymers are considered, so $C_D'$ and $C_H'$ will be independent of $\mathbf{x}$. We propose the following pair of master equations to describe the time evolution of $C_D$ and $C_H$:

$$\frac{\partial C_D(\mathbf{x},t)}{\partial t} = \int \mathrm{d}\mathbf{y}\, \{W_{DD}(y)[C_D(\mathbf{x}+\mathbf{y})(C_D' - C_D(\mathbf{x})) - C_D(\mathbf{x})(C_D' - C_D(\mathbf{x}+\mathbf{y}))] + W_{DH}(y)C_H(\mathbf{x}+\mathbf{y})[C_D' - C_D(\mathbf{x})] - W_{HD}(y)C_D(\mathbf{x})[C_H' - C_H(\mathbf{x}+\mathbf{y})]\} \quad (8)$$

$$\frac{\partial C_H(\mathbf{x},t)}{\partial t} = \int \mathrm{d}\mathbf{y}\, \{W_{HD}(y)C_D(\mathbf{x}+\mathbf{y})[C_H' - C_H(\mathbf{x})] - W_{DH}(y)C_H(\mathbf{x})[C_D' - C_D(\mathbf{x}+\mathbf{y})] + W_{HH}(y)[C_H(\mathbf{x}+\mathbf{y})(C_H' - C_H(\mathbf{x})) - C_H(\mathbf{x})(C_H' - C_H(\mathbf{x}+\mathbf{y}))]\} \quad (9)$$

In eq 8 and 9, $W_{KL}(y) = W_{KL}(|\mathbf{y}|)$ are phenomenological coefficients that reflect the rate at which penetrant molecules in mode L are transferred into a region of mode K a distance $y$ away. We assume that the $W_{KL}$'s fall off sufficiently rapidly with distance that all spatial moments exist. These coefficients satisfy the following detailed balance condition at equilibrium:

$$W_{KL}(y)C_L[C_K' - C_K] = W_{LK}(y)C_K[C_L' - C_L] \quad (10)$$

In the Appendix, an approximate derivation of these equations is presented for a simple dynamical model with no spatial correlations among hole sites. Such correlations can be included, but to the same level of approximation they modify only the definition of $W_{KL}$ and not the form of eq 8 and 9.

A standard approach to the solution of master equations like eq 8 and 9 is to introduce a gradient expansion (Kramers–Moyal expansion) for the concentration fields[13,14]

$$C_K(\mathbf{x}+\mathbf{y}) = C_K(\mathbf{x}) + \mathbf{y}\cdot\nabla C_K + (1/2)\mathbf{y}\mathbf{y}:\nabla\nabla C_K + \ldots \quad (11)$$

where K = D or H. When eq 11 is substituted into the integrands of eq 8 and 9, an infinite series of gradient terms results. It is appropriate to drop terms involving gradients of fourth order and higher, except in the unusual case of concentration fields that vary significantly over distances of the order of the range of $W_{KL}$. One obtains

$$\frac{\partial C_D(\mathbf{x},t)}{\partial t} = D_D^0\nabla^2 C_D - A_{HD}C_D\nabla^2[C_H' - C_H] + A_{DH}[C_D' - C_D]\nabla^2 C_H - B_{HD}C_D[C_H' - C_H] + B_{DH}C_H[C_D' - C_D] \quad (12)$$

$$\frac{\partial C_H(\mathbf{x},t)}{\partial t} = D_H^0\nabla^2 C_H + A_{HD}[C_H' - C_H]\nabla^2 C_D - A_{DH}C_H\nabla^2[C_D' - C_D] - B_{DH}C_H[C_D' - C_D] + B_{HD}C_D[C_H' - C_H] \quad (13)$$

where

$$B_{KL} = \int \mathrm{d}\mathbf{y}\; W_{KL}(y) \quad (14)$$

$$A_{KL} = (1/6)\int \mathrm{d}\mathbf{y}\; y^2 W_{KL}(y) \quad (15)$$

$$D_K^0 = A_{KK}C_K' \quad (16)$$

for K, L = D or H. The $D_K^0$ can be interpreted as diffusion coefficients for penetrant within the Kth phase.

Let $a$ be a length that parameterizes the range of $W_{KL}(y)$ and let $L$ be the distance over which the concentration fields change significantly (usually the thickness of the polymer membrane). A simple scaling analysis indicates that the higher order terms neglected in eq 12 and 13 are $O(a^2/L^2)$. We restrict our consideration to systems and conditions for which $a/L \ll 1$, so these terms can be safely neglected. Such systems are those of primary experimental interest.

The detailed balance relation, eq 10, leads to the following equations under conditions of local equilibrium:

$$B_{HD}C_D[C_H' - C_H] = B_{DH}C_H[C_D' - C_D] \quad (17)$$

$$A_{HD}C_D[C_H' - C_H] = A_{DH}C_H[C_D' - C_D] \quad (18)$$

Experimentally, saturation of the "dissolved" mode is not observed. This implies that $C_D' \gg C_D(\mathbf{x})$ in our equations. If we neglect $C_D$ in comparison with $C_D'$ and require eq 3 to be satisfied at equilibrium, eq 17 leads to

$$B_{DH}C_D' = \alpha^{-1}B_{HD} \quad (19)$$

Equation 18 is also satisfied by the choice

$$A_{DH}C_D' = \alpha^{-1}A_{HD} \quad (20)$$

Substitution of eq 19 and 20 into eq 12 and 13, replacement of $C_D' - C_D$ with $C_D'$, and introduction of the notation $B = B_{HD}\alpha^{-1}$, $A = A_{HD}\alpha^{-1}$ lead to

$$\frac{\partial C_D(\mathbf{x},t)}{\partial t} = D_D^0\nabla^2 C_D + A[1 + \alpha C_D]\nabla^2 C_H + BC_H - \alpha BC_D[C_H' - C_H] \quad (21)$$

$$\frac{\partial C_H(\mathbf{x},t)}{\partial t} = D_H^0\nabla^2 C_H + \alpha A[C_H' - C_H]\nabla^2 C_D + \alpha BC_D[C_H' - C_H] - BC_H \quad (22)$$

Equations 21 and 22 are the working equations of our theory. They will be applied in the next section to the calculation of permeability and time-lag expressions for transient and steady-state experiments. They could also be used to calculate other experimental observables, such as transient sorption isotherms. Before presenting explicit calculations with eq 21 and 22, it is worthwhile to investigate the flux expression implied by these equations. If we add eq 21 and 22, the resulting equation for the total penetrant concentration can be written in the form of eq 5, with

$$\mathbf{J} = -\{[D_D^0 + KA - \alpha AC_H]\nabla C_D + [D_H^0 + A + \alpha AC_D]\nabla C_H\} \quad (23)$$

Compare eq 23 with the Paul–Koros expression, eq 2. Note the presence of the terms containing $\alpha$ in eq 23 that couple the two fields $C_D$ and $C_H$. Furthermore, note that the "bare" diffusion coefficients $D_D^0$ and $D_H^0$ have been renormalized by $KA$ and $A$, respectively. The consequence of this is that even if penetrant molecules in the hole mode have no intrinsic mobility ($D_H^0 = 0$), the exchange of molecules between modes (characterized by the rate parameter $A$) provides mobility to adsorbed molecules. This is in contrast to the Paul–Koros expression. Note, however, that if the exchange process is very slow, $A \ll D_K^0$, either because the holes are very large or because the intrinsic exchange rate is slow, our flux expression reduces to that of Paul and Koros. Because there is experimental evidence to indicate that the equilibration process is extremely rapid, one expects that penetrant transport is dominated by the coupling terms in eq 23.

If $D_H^0$ can be neglected in comparison with $A$ and $\alpha A C_D$ in eq 23 and if it is assumed that equilibration is sufficiently rapid that eq 1 and 3 can be used to relate $C_D$ and $C_H$, then our flux expression can be written

$$\mathbf{J} = -D_D^0\left[\frac{C_D + (2A/D_D^0)C_H}{p}\right]\nabla p \tag{24}$$

If this result is compared with the Petropoulos expression, eq 6, we see that the equations have the same form. The difference arises in the interpretation of $R$. In the Petropoulos theory, $R$ is the ratio of diffusion coefficients for the hole and dissolved modes, respectively. In our expression $R$ is replaced by $2A/D_D^0$, a mobility parameter that arises from exchange between the adsorbed and dissolved modes. For the case of $D_H^0 \neq 0$ our flux expression contains additional terms not present in the Petropoulos theory.

Overall, it is clear that neither the Paul–Koros nor the Petropoulos theory of penetrant transport contains a complete description of coupling between sorption modes and intramode diffusion. Within the context of the dual-mode sorption model, we believe that eq 21 and 22 provide a realistic description of nonswelling penetrant transport.

## III. Application to Steady-State and Transient Permeation Experiments

In this section we present expressions for the steady-state permeability and for the time lag. Both of these quantities can be measured in the laboratory by using a permeation cell.[9,15,16] In a steady-state permeation experiment a gradient in penetrant partial pressure is established at time zero and maintained across a polymer film. After the steady-state concentration profile has fully developed, the constant flux of penetrant, $J^*$, is monitored on the low-pressure side of the permeation cell. The permeability, $\bar{P}$, is then calculated by using the following equation:

$$\bar{P} = J^* l/(p_2 - p_1) \tag{25}$$

where $l$ is the film thickness and $p_2$ ($p_1$) is the partial pressure of penetrant gas applied to the high (low) pressure side of the membrane.

In a typical transient permeation experiment a step increase in penetrant pressure is applied to one side of the membrane. One then monitors as a function of time the amount of penetrant per unit membrane area that enters the low-pressure side, $Q_t$. At sufficiently long times after the application of pressure, the relationship between $Q_t$ and time is linear. The equation describing this linear asymptote serves to define the time lag, $\Theta$

$$Q_t = J^*(t - \Theta) \tag{26}$$

The procedure for calculating $\bar{P}$ and $\Theta$ has been well documented by Paul, Frisch, and co-workers.[9,15,17] We refer the reader to their papers for the details of the calculations.

In the following analysis we assume that the equilibration or "hole-filling" process is extremely rapid compared with diffusive transport of penetrant. Local equilibration is expected to take place on the time scale of molecular motions, while diffusive transport is characterized by the time for concentration gradients to change, $L^2/D$. A consequence of this approximation is that the terms involving $B$ in eq 21 and 22 can be dropped. Tshudy and von Frankenberg[10] have relaxed this local equilibrium approximation for the Vieth–Sladek[7] theory. The corrections they found, however, are not believed to be important for realistic systems and conditions. To see the effect of these terms one would have to perform a high-frequency experiment, perturbing about equilibrium at frequencies of $O(B)$.

A consequence of the local equilibrium assumption is that eq 1 and 3 can be used to relate $C_H$ and $C_D$ in our flux expression, eq 23. With these relations, eq 23 can be rewritten as

$$\mathbf{J} = -D(C_D)\nabla C_D \tag{27}$$

where the effective concentration-dependent diffusion coefficient for the dissolved species is defined by

$$D = D_D^0 + \frac{2KA}{1 + \alpha C_D} + \frac{K D_H^0}{(1 + \alpha C_D)^2} \tag{28}$$

The permeability can now be calculated from

$$\bar{P} = \frac{1}{p_2 - p_1}\int_{k_D p_1}^{k_D p_2} \mathrm{d}C_D\, D(C_D) \tag{29}$$

This integral can be carried out explicitly with the result

$$\bar{P} = D_D^0 k_D\left[1 + \frac{2KS}{(y_2 - y_1)}\ln\left(\frac{1 + y_2}{1 + y_1}\right) + \frac{KF}{(1 + y_1)(1 + y_2)}\right] \tag{30}$$

where $S = A/D_D^0$, $F = D_H^0/D_D^0$, and $y_i = bp_i$ for $i = 1$ or 2.

Equation 30 reduces to the Paul–Koros[9] expression for the permeability in the special case that $S = 0$ and $p_1 = 0$. For the special case of $F = 0$, eq 30 reduces to the permeability expression derived by Petropoulos.[8,9] In the latter case, however, $S$ is interpreted as an adsorbed penetrant mobility resulting from coupling to the dissolved mode, while the corresponding parameter $R$ in the Petropoulos expression was introduced as a bare diffusion coefficient within the hole phase. It would be interesting to analyze existing data or to take additional permeability data and study whether both terms in eq 30 can be resolved. If the term involving $F$ is found to contribute, then it is likely that the penetrant molecules have a nonzero intrinsic mobility within the adsorbed phase. This would seem to indicate that the holes are not small, randomly placed regions capable of holding only a single penetrant molecule, but are extended regions capable of sustaining diffusion. Such experiments could lead to a better understanding of the size and nature of the microvoids.

The time lag can be obtained from our flux expression, eq 27, by using the approach discussed by Frisch[17] and Paul.[15] If $C_0$ is the total concentration of penetrant in the polymer membrane before the pressure differential is introduced, the time lag can be obtained from the equation

$$\Theta = \frac{1}{J^* l}\int_0^l \mathrm{d}z \int_z^l \mathrm{d}x\left[C_D(x) + \frac{K C_D(x)}{1 + \alpha C_D(x)}\right] - \frac{C_0 l}{2J^*} \tag{31}$$

We obtain, after considerable but straightforward calculation

$$\frac{6\Theta D_D^0}{l^2} = \frac{6I}{Q^3} - \frac{3C_0\alpha}{Q} \tag{32}$$

where

$$I = I_1 + I_2 + I_3 + I_4 + I_5 + I_6 \tag{33}$$

$$I_1 = -\frac{1}{3}(\upsilon_2{}^3 - \upsilon_1{}^3) + \frac{1}{2}(\upsilon_2 - K + 1)(\upsilon_2{}^2 - \upsilon_1{}^2) + [K + \upsilon_2(K - 1)](\upsilon_2 - \upsilon_1) - K\upsilon_2 \ln \frac{\upsilon_2}{\upsilon_1} \quad (34)$$

$$I_2 = SK\left\{\left[\ln \upsilon_2 - \frac{1}{2}\right](\upsilon_2{}^2 - \upsilon_1{}^2) + 2[\upsilon_2 + (K - 1) \ln \upsilon_2](\upsilon_2 - \upsilon_1) + 2K\upsilon_2\left(\frac{1}{\upsilon_2} - \frac{1}{\upsilon_1}\right) + 2[K - K \ln \upsilon_2 + (K - 1)\upsilon_2] \ln \frac{\upsilon_2}{\upsilon_1} - (\upsilon_2{}^2 \ln \upsilon_2 - \upsilon_1{}^2 \ln \upsilon_1) - 2(K - 1)(\upsilon_2 \ln \upsilon_2 - \upsilon_1 \ln \upsilon_1) + K(\ln^2 \upsilon_2 - \ln^2 \upsilon_1)\right\} \quad (35)$$

$$I_3 = FK\left\{(-1/2\upsilon_2) \times (\upsilon_2{}^2 - \upsilon_1{}^2) - (K - 1)\frac{1}{\upsilon_2}(\upsilon_2 - \upsilon_1) - (K - 1)\upsilon_2\left(\frac{1}{\upsilon_2} - \frac{1}{\upsilon_1}\right) + \frac{1}{2}K\upsilon_2\left(\frac{1}{\upsilon_2{}^2} - \frac{1}{\upsilon_1{}^2}\right) + \left[K\frac{1}{\upsilon_2} + \upsilon_2\right] \ln \frac{\upsilon_2}{\upsilon_1}\right\} \quad (36)$$

$$I_4 = S^2K^2\left\{4[1 + \ln \upsilon_2](\upsilon_2 - \upsilon_1) + 4K[\ln \upsilon_2 - 1] \times \left(\frac{1}{\upsilon_2} - \frac{1}{\upsilon_1}\right) + 4(K - 1) \ln \upsilon_2 \ln \frac{\upsilon_2}{\upsilon_1} - 4(\upsilon_2 \ln \upsilon_2 - \upsilon_1 \times \ln \upsilon_1) - 2(K - 1)(\ln^2 \upsilon_2 - \ln^2 \upsilon_1) - 4K\left(\frac{\ln \upsilon_2}{\upsilon_2} - \frac{\ln \upsilon_1}{\upsilon_1}\right)\right\} \quad (37)$$

$$I_5 = SFK^2\left\{-2\frac{1}{\upsilon_2}(\upsilon_2 - \upsilon_1) - 2\left[K\frac{1}{\upsilon_2} + (K - 1) \ln \upsilon_2\right] \times \left(\frac{1}{\upsilon_2} - \frac{1}{\upsilon_1}\right) + K\left[\frac{1}{2} + \ln \upsilon_2\right]\left(\frac{1}{\upsilon_2{}^2} - \frac{1}{\upsilon_1{}^2}\right) + 2\left[1 - (K - 1)\frac{1}{\upsilon_2} + \ln \upsilon_2\right] \ln \frac{\upsilon_2}{\upsilon_1} - (\ln^2 \upsilon_2 - \ln^2 \upsilon_1) + 2(K - 1)\left(\frac{\ln \upsilon_2}{\upsilon_2} - \frac{\ln \upsilon_1}{\upsilon_1}\right) - K\left(\frac{\ln \upsilon_2}{\upsilon_2{}^2} - \frac{\ln \upsilon_1}{\upsilon_1{}^2}\right)\right\} \quad (38)$$

$$I_6 = F^2K^2\left\{\left[(K - 1)\frac{1}{\upsilon_2} - 1\right]\left(\frac{1}{\upsilon_2} - \frac{1}{\upsilon_1}\right) - \frac{1}{2}\left[(K - 1) + K\frac{1}{\upsilon_2}\right]\left(\frac{1}{\upsilon_2{}^2} - \frac{1}{\upsilon_1{}^2}\right) + \frac{1}{3}K\left(\frac{1}{\upsilon_2{}^3} - \frac{1}{\upsilon_1{}^3}\right) - \frac{1}{\upsilon_2} \ln \frac{\upsilon_2}{\upsilon_1}\right\} \quad (39)$$

$$Q = (\upsilon_2 - \upsilon_1) + 2SK \ln (\upsilon_2/\upsilon_1) - FK(1/\upsilon_2 - 1/\upsilon_1) \quad (40)$$

Here $\upsilon_i = 1 + bp_i$, where $i = 1$ or 2.

The above equations simplify to expressions for the time lag given previously by Paul and Koros[9] in the various limits discussed above. In particular, eq 32 reduces to the Paul–Koros result for $p_1 = 0$ and $A = 0$. In the limit $p_1 = 0$ and $D_H{}^0 = 0$, eq 32 reduces to the expression for the time lag derived by Paul and Koros[9] for the Petropoulos model. Furthermore, as discussed previously, the interpretation of $S$ is different from that of $R$, the analogous parameter in the Petropoulos theory.

For situations in which $A$ and $D_H{}^0$ are both nonzero, the above equations are new results. Careful experimental measurements of the pressure dependence of the permeability and time lag would facilitate a study of the relative importance of terms containing $A$ and $D_H{}^0$. Such experiments could give an indication of whether coupling between sorption modes or intrahole diffusion plays a significant role in the transport of penetrants in amorphous polymers.

## IV. Discussion and Conclusions

The principal results of this paper are the following. First, we have found that previous theories of dual-mode transport are incomplete in that they do not properly account for penetrant transfer between the two sorption modes. By starting with nonlocal phenomenological transport equations for the two concentration fields, we were able to derive an expression for the penetrant flux that contains additional terms coupling the two modes. There is no reason to believe that such terms are not important; indeed they may dominate the transport properties of glassy polymers. If this is the case and the coupling terms dominate, then the theory of Petropoulos has the correct form, except that the physical interpretation of the parameter $R$ in his equations (see eq 6) must be changed. For such a situation, $R$ must be replaced by our coupling parameter $2S$. If, instead, the intraphase diffusion terms in the flux expression dominate over the coupling terms, then our theory reduces exactly to that of Paul and Koros. The relative contribution of the two types of flux terms can be probed with permeation experiments and could possibly be used to answer questions regarding the size and topological connectivity of the microvoids. The expressions that we presented for the permeability and time lag should be useful for the interpretation of such experiments.

Experiments other than permeation studies can be carried out to test the theory. One would be a determination of the complete concentration profile within the membrane. Actually, there is no reason in such an experiment to work with a membrane geometry. A bulk sample, which can be sectioned or viewed with a spectroscopic probe, may be much more convenient. Transient sorption and desorption experiments on the time scale of $\Theta$ may be useful, but such macroscopic measurements can provide only limited information about the microstructure and local dynamics within a polymeric system. *Instead*, higher frequency probes are needed, such as NMR experiments, neutron or X-ray scattering studies, or various other spectroscopic techniques. A few NMR experiments have already been performed.[11,18] It may prove useful to introduce temperature gradients, magnetic or electric fields, or competing molecular species in conjunction with such experiments. These types of studies are necessary if we hope to understand fully the anomalous sorption and transport properties exhibited by penetrants in glassy polymers.

After this work was completed, the related studies by Chern et al.[21] and by Barrer[22] were brought to our attention. Chern and co-workers suggested that diffusive jump processes allowing penetrant molecules to be transferred between the two modes of sorption should be included in a proper analysis of transport. Barrer developed this idea mathematically and (using an approach different from ours) derived a flux expression (eq 18 or ref 22) that is identical to our eq 23. He also obtained an expression for the permeability (eq 29 of ref 22) that is a special case of our eq 30 in the limit that $p_1$ approaches zero. Barrer noted the difference between his results and the Paul–

Koros theory but did not investigate the circumstances under which the two theories become equivalent.

Our results complement those of Barrer. We derived an expression for the time lag in transient permeation experiments that retains the coupling between the two sorption modes. In addition, our work illuminates the connection between the present theory and that of Petropoulos and Paul and Koros. We discussed the circumstances under which the Petropoulos and Paul–Koros theories can be applied and the proper physical interpretation of various parameters. Finally, we provided a microscopic derivation of the macroscopic flux equation and discussed the nature of transport in the presence of microvoids.

**Acknowledgment.** We thank Professor Harold Hopfenberg for useful discussions and for bringing ref 21 and 22 to our attention.

## Appendix: Microscopic Derivation of the Phenomenological Transport Equations

Consider the following microscopic model of a polymer–penetrant system. Divide the polymer matrix into a periodic lattice of $N$ cells. The lattice spacing, $a$, should be of the order of the size of a penetrant molecule. Classify each cell as either an adsorbing (hole) region or as a region in which penetrant is "dissolved" in the Henry's law mode. Label the $N$ cells 1, ..., $N$. Associate with the $i$th cell a random variable $\xi_i$ that takes the value 0 if the cell acts as the dissolved mode or takes the value 1 if the cell acts as the adsorbing mode. The microstructure of the polymer matrix is then completely specified within this model by a probability distribution function $F(\xi)$, where $\xi = (\xi_1, ..., \xi_N)$.

We now place $M$ penetrant molecules among the $N$ cells ($M \leq N$). Because $a$ is the same order of magnitude as the penetrant size, configurations in which more than one molecule is placed in any cell are excluded. It is convenient to introduce a second random variable for the $i$th cell, $n_i$, which takes the value 1 if a cell is occupied by a penetrant molecule and 0 otherwise. The equilibrium properties of the polymer–penetrant system can now be described in terms of $F(\xi)$ and a conditional probability distribution function, $P[n|\xi]$, where $n = (n_1, ..., n_N)$. This function represents the probability of penetrant configuration $n$, given that the material has microstructure $\xi$. The form of the distribution function is determined by the microscopic interactions among penetrant molecules and between penetrant molecules and the polymer matrix.

To construct a model for the penetrant dynamics, we allow single molecule jumps to vacant sites. Similar dynamics were used in the kinetic Ising model constructed by Kawasaki[19] to investigate dynamic critical phenomena. The following master equation describes the dynamics of our penetrant–polymer model system:

$$\frac{\partial}{\partial t}P[n,t|\xi] = -\sum_{\langle ij\rangle} W_{ij}[n|\xi]P[n,t|\xi] + \sum_{\langle ij\rangle} W_{ij}[n^{ij}|\xi]P[n^{ij},t|\xi] \tag{A1}$$

In the above equation, $n^{ij}$ is the configuration obtained from $n$ by exchanging the occupancy of cells $i$ and $j$. The $W_{ij}[n|\xi]$ are transition probabilities that describe the rate at which configuration $n$ is destroyed due to penetrant exchange between cells $i$ and $j$. The sums in eq A1 are over all *distinct* pairs of cells.

At this point we make an explicit choice for $W_{ij}[n|\xi]$. For simplicity, we assume that, except for the excluded volume condition imposed by the lattice, the penetrant molecules are noninteracting. In addition, the $W_{ij}$ are chosen such that $W_{ij}[n|\xi] = W[|i-j|,n_i,n_j|\xi_i,\xi_j]$. A form consistent with these assumptions is

$$W_{ij}[n|\xi] = W_{ij}^{00}[n|\xi] + W_{ij}^{01}[n|\xi] + W_{ij}^{10}[n|\xi] + W_{ij}^{11}[n|\xi] \tag{A2}$$

where

$$W_{ij}^{00}[n|\xi] = \delta[1,n_i + n_j]\delta[0,\xi_i]\delta[0,\xi_j]W_{\mathrm{DD}}(|i-j|) \tag{A3}$$

represents dissolved site-dissolved site transfer

$$W_{ij}^{01}[n|\xi] = \delta[0,\xi_i]\delta[1,\xi_j] \times \{W_{\mathrm{DH}}(|i-j|)\delta[1,n_j]\delta[0,n_i] + W_{\mathrm{HD}}(|i-j|)\delta[1,n_i]\delta[0,n_j]\} \tag{A4}$$

and

$$W_{ij}^{10}[n|\xi] = W_{ji}^{01}[n|\xi] \tag{A5}$$

represent hole-dissolved site transfer or vice versa, and

$$W_{ij}^{11}[n|\xi] = \delta[1,n_i + n_j]\delta[1,\xi_i]\delta[1,\xi_j]W_{\mathrm{HH}}(|i-j|) \tag{A6}$$

represents hole–hole transfer. Here $\delta[i,j]$ is the Kronecker delta.

The local penetrant concentration and saturation fields in the dissolved and adsorbed modes can be defined by

$$C_{\mathrm{D}}(i,t) = \sum_n\sum_\xi P[n,t|\xi]F(\xi)\delta[1,n_i]\delta[0,\xi_i] \tag{A7}$$

$$C_{\mathrm{H}}(i,t) = \sum_n\sum_\xi P[n,t|\xi]F(\xi)\delta[1,n_i]\delta[1,\xi_i] \tag{A8}$$

$$C_{\mathrm{D}}' = \sum_\xi F(\xi)\delta[0,\xi_i] \tag{A9}$$

$$C_{\mathrm{H}}' = \sum_\xi F(\xi)\delta[1,\xi_i] \tag{A10}$$

If, in addition to choosing our penetrant molecules to be noninteracting we choose to distribute the $\xi_i$'s completely at random, then the distribution functions factor at equilibrium

$$P[n|\xi] = \prod_{i=1}^{N} p_1(n_i|\xi_i) \tag{A11}$$

$$F(\xi) = \prod_{i=1}^{N} f_1(\xi_i) \tag{A12}$$

Correlations between sites, which could be important if the holes are extended regions in the material, can be easily included. We do not consider such correlations here. In the above equations, $p_1$ and $f_1$ are the exact one-cell distribution functions. Note that $C_{\mathrm{D}}' = f_1(0)$ and that $C_{\mathrm{H}}' = f_1(1)$.

In order for eq A1 to relax to the proper equilibrium distribution function having the properties described above, the transfer rates $W_{\mathrm{KL}}$ must satisfy the following detailed balance condition:

$$W_{\mathrm{KL}}(|i-j|)C_{\mathrm{L}}(i)[C_{\mathrm{K}}' - C_{\mathrm{K}}(j)] = W_{\mathrm{LK}}(|i-j|)C_{\mathrm{K}}(i)[C_{\mathrm{L}}' - C_{\mathrm{L}}(j)] \tag{A13}$$

It is convenient to define the following nonequilibrium average

$$\langle\langle ... \rangle\rangle = \sum_\xi\sum_n (...)P[n,t|\xi]F(\xi) \tag{A14}$$

We now formulate an equation of motion for $C_{\mathrm{D}}(i)$ and $C_{\mathrm{H}}(i)$ by applying the operators

$$\sum_\xi\sum_n \delta[0,\xi_i]\delta[1,n_i]F(\xi)$$

$$\sum_\xi\sum_n \delta[1,\xi_i]\delta[1,n_i]F(\xi)$$

to both sides of eq A1. The resulting equations can be written

$$\partial C_D(i)/\partial t = \sum_{j(\neq i)} \{\langle \delta[0,n_i]\delta[1,n_j]\delta[0,\xi_i]\delta[0,\xi_j]\rangle W_{DD}(|i-j|) + \langle \delta[0,n_i]\delta[1,n_j]\delta[0,\xi_i]\delta[1,\xi_j]\rangle W_{DH}(|i-j|) - \langle \delta[1,n_i]\delta[0,n_j]\delta[0,\xi_i]\delta[0,\xi_j]\rangle W_{DD}(|i-j|) - \langle \delta[1,n_i]\delta[0,n_j]\delta[0,\xi_i]\delta[1,\xi_j]\rangle W_{HD}(|i-j|)\} \quad \text{(A15)}$$

$$\partial C_H(i)/\partial t = \sum_{j(\neq i)} \{\langle \delta[0,n_i]\delta[1,n_j]\delta[1,\xi_i]\delta[1,\xi_j]\rangle W_{HH}(|i-j|) + \langle \delta[0,n_i]\delta[1,n_j]\delta[1,\xi_i]\delta[0,\xi_j]\rangle W_{HD}(|i-j|) - \langle \delta[1,n_i]\delta[0,n_j]\delta[1,\xi_i]\delta[1,\xi_j]\rangle W_{HH}(|i-j|) - \langle \delta[1,n_i]\delta[0,n_j]\delta[1,\xi_i]\delta[0,\xi_j]\rangle W_{DH}(|i-j|)\} \quad \text{(A16)}$$

Equations A15 and A16 couple the time dependence of $C_D(i)$ and $C_H(i)$ to the evolution to two-cell correlation functions like $\langle n_i n_j \rangle$. The corresponding equations of motion for these higher order correlation functions, however, are coupled to even higher order cell functions. Thus, to obtain a closed set of equations one must truncate the hierarchy at some level. The simplest approximation one could adopt is to approximate the two-cell correlation functions by the product of two one-cell correlation functions. For two arbitrary functions $g$ and $h$, this approximation takes the form

$$\langle g(\xi_i,n_i)h(\xi_j,n_j)\rangle \approx \langle g(\xi_i,n_i)\rangle \langle h(\xi_j,n_j)\rangle \quad \text{(A17)}$$

This approximation is the familiar dynamical mean field approximation that has been used to treat kinetic Ising models.[20] It is a reasonably accurate description of spin dynamics away from the critical point. Because we are interested in penetrant dynamics away from any thermodynamic or kinetic singularity, such as a percolation threshold, this approximation should be accurate for the present problem as well.

When eq A17 is used to simplify the two-cell correlation functions appearing on the right-hand side of eq A15 and A16, the following equations result:

$$\partial C_D(i)/\partial t = \sum_{j(\neq i)} \{W_{DD}(|i-j|)[C_D(j) \times (C_D' - C_D(i)) - C_D(i)(C_D' - C_D(j))] - W_{HD}(|i-j|)C_D(i)(C_H' - C_H(j)) + W_{DH}(|i-j|)C_H(j)(C_D' - C_D(i))\} \quad \text{(A18)}$$

$$\partial C_H(i)/\partial t = \sum_{j(\neq i)} \{W_{HH}(|i-j|)[C_H(j) \times (C_H' - C_H(i)) - C_H(i)(C_H' - C_H(j))] - W_{DH}(|i-j|)C_H(i)(C_D' - C_D(j)) + W_{HD}(|i-j|)C_D(j)(C_H' - C_H(i))\} \quad \text{(A19)}$$

These equations are easily recognized as the discrete analogue of the master eq 8 and 9. We emphasize that it is probable that microscopic models other than the one presented here can lead to the same set of equations. For example, if spatial correlations are included among the hole cells, the above mean field approximation leads to equations similar to eq A18 and A19, except that the $W_{KL}$'s are replaced by new effective rates in the correlated medium.

## References and Notes

(1) Hopfenberg, H. B.; Stannett, V. "The Physics of Glassy Polymers"; Haward, R. N., Ed; Wiley: New York, 1973.
(2) Vieth, W. R.; Howell, J. M.; Hsieh, J. H. *J. Membr. Sci.* **1976**, *1*, 177.
(3) Frisch, H. L. *Polym. Eng. Sci.* **1980**, *20*, 2.
(4) Meares, P. *J. Am. Chem. Soc.* **1954**, *76*, 3415.
(5) Michaels, A. S.; Vieth, W. R.; Barrie, J. A. *J. Appl. Phys.* **1963**, *34*, 1.
(6) Michaels, A. S.; Vieth, W. R.; Barrie, J. A. *J. Appl. Phys.* **1963**, *34*, 13.
(7) Vieth, W. R.; Sladek, K. J. *J. Colloid Sci.* **1965**, *20*, 1014.
(8) Petropoulos, J. H. *J. Polym. Sci., Part A-2*, **1970**, *8*, 1797.
(9) Paul, D. R.; Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 675.
(10) Tshudy, J. A.; von Frankenberg, C. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 2027.
(11) Assink, R. A. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1665.
(12) Ma, S. "Introduction to Critical Phenomena"; Benjamin/Cummings; Reading, MA, 1976.
(13) Kramers, H. A. *Physica* **1940**, *7*, 284. Moyal, J. E.; *J. R. Stat. Soc. (London)* **1949**, *B11*, 150.
(14) Van Kampen, N. G.; *Can. J. Phys.* **1961**, *39*, 551.
(15) Paul, D. R.; *J. Polym. Sci., Part A-2*, **1969**, *7*, 1811.
(16) Koros, W. J.; Paul, D. R.; Rocha, A. A. *J. Polym. Sci., Polym. Phys. Ed.*, **1976**, *14*, 687.
(17) Frisch, H. L.; *J. Phys. Chem.* **1957**, *61*, 93.
(18) Sefcik, M. D.; Schaefer, May, F. L.; Raucher, D.; Dub, S. M. *J. Polym. Sci., Polym. Phys. Ed.*, **1983**, *21*, 1041. Sefcik, M. D.; Schaefer, J. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1055.
(19) Kawasaki, K. *Phys. Rev.* **1966**, *145*, 224.
(20) Stanley, H. E. "Introduction to Phase Transitions and Critical Phenomena"; Oxford University Press: New York, 1971.
(21) Chern, R. T.; Koros, W. J.; Sanders, E. S.; Chen, S. H.; Hopfenberg, H. B. *ACS Symp. Ser.* **1983**, *No. 223*, 47.
(22) Barrer, R. M. *J. Membr. Sci.* **1984**, *18*, 25.