

Specific Heat Capacity Determination by DSC

April 19, 10:00am - 11:00am EDT

Specific heat capacity (c_p) is an important, temperature-dependent material property and is often specified in material data sheets. It is a key property for improving technical processes such as injection molding, spray drying, or crystallization, as well as for the safety analysis of chemical processes and the design of chemical reactors.

Watch this session during the WAS Virtual Conference:



Dr. Jürgen Schawe

[Register Now](#)

On the Dual Mode Gas Transport Model for Glassy Polymers

J. H. PETROPOULOS, *Physical Chemistry Laboratory, Democritos National Research Center, Aghia Paraskevi, Athens, Greece*

Synopsis

The present paper is concerned with a detailed examination of the formalism and the physical basis of the dual mode mobility model used for the theoretical description of gaseous transport in glassy polymers in the light of recent theoretical and experimental work. It is shown that there are no really major differences among the original formulation of the model and later variants. A major modification becomes necessary, however, if the Langmuir sorption mode is assumed to exist in the form of patches or domains extensive enough to constitute a macroscopically recognizable phase rather than in the commonly accepted form of scattered individual adsorption sites. It is shown that the proper treatment of this case reduces to the familiar dual mode mobility formalism only under certain conditions. The interpretation of the experimental results thus far available is considered in some detail, and the usefulness of each of the aforesaid approaches in this respect is discussed.

INTRODUCTION

The sorption of gases by glassy polymers has, so far, been reasonably successfully described in terms of additive Henry law and Langmuir sorption modes (denoted here by subscripts 1 and 2, respectively), which involve, respectively, nonspecific sorption or "dissolution" in the amorphous polymer matrix or "adsorption" in a limited number of Langmuir sites in the form of preexisting microvoids of molecular dimensions dispersed in the polymer matrix.¹⁻³

Gas transport was initially attributed to diffusion of "dissolved" penetrant molecules, "adsorbed" molecules being assumed to be immobilized.^{1,4} It was further assumed^{1,4} that the diffusion coefficient of dissolved molecules (D_1) is constant and that there is local equilibrium between "dissolved" and "adsorbed" penetrant molecules. Subsequently, it was pointed out⁵ that, whereas the postulate of constant D_1 was reasonable in the absence of plasticization effects, the other two assumptions could be subjected to experimental verification. Physically, the postulate of "total immobilization" of adsorbed molecules appeared to be particularly questionable. Accordingly, a more general dual mode mobility model was put forward⁵ in which a diffusion coefficient D_2 was assigned to the adsorbed molecules. The main consequence of practical importance of this theory was that the measured (overall) gas permeability coefficient of the polymer (P_T) should be constant if $D_2 = 0$ but should decrease with rising gas concentration (C_g) or pressure (p) if $D_2 > 0$. It was further predicted,⁵ on the basis of the Eyring transition or activated state diffusion theory,⁶ that the aforesaid concentration dependence of P_T should normally be sufficiently pronounced to be observable and analyzable experi-

mentally. This prediction was soon confirmed in practice.⁷ Since that time, the dual mode mobility analysis has been applied to a considerable number of glassy polymer-gas systems.^{2,3} At the same time, it has become apparent, chiefly as a result of further theoretical work on this subject,^{8,9} that certain aspects of the original theory, particularly as regards the physical significance of D_1 , D_2 , are poorly understood. Although we have indicated previously^{3,5} that D_1 , D_2 are physically interpreted in terms of the Eyring transition state treatment, an actual detailed derivation has not so far been given. We proceed to do this here. Another question raised as a result of recent work⁹ concerns the applicability of the original dual mode mobility model, or of its more recent versions,^{8,9} to the case where the Langmuir sorption mode constitutes a macroscopically recognizable constituent phase of the polymer. The correct way of handling this situation and the possibility of interpreting the observed phenomena thereby are also discussed.

FORMULATION OF SORPTION EQUILIBRIA

Sorption modes 1 and 2 are assumed to be additive. The relevant sorption equilibria are commonly formulated in terms of "apparent" or "practical" equilibrium constants

$$K_1 = C_1/C_g \quad (1a)$$

$$K_2 = C_2/s_2C_g = C_2/(s_{02} - C_2)C_g \quad (1b)$$

where C_1 , C_2 denote the concentrations of the relevant sorbed species per unit volume of polymer; s_{02} , s_2 are the concentrations (in the same units) of Langmuir sites and of unoccupied Langmuir sites, respectively; and C_g denotes the gas phase concentration (often replaced by the gas pressure p) at equilibrium with C_1 , C_2 . A proper thermodynamic formulation, however, requires replacement of the concentrations in eqs. (1a, b) with the respective activities $a_i = \gamma_i C_i$. The definition of a_i is such that $a_i \rightarrow C_i$, hence the activity coefficient $\gamma_i \rightarrow 1$, as $C_i \rightarrow 0$. The Henry law and Langmuir sorption postulates imply that $a_1 = C_1$, $C_2 = a_2$, and $a_{s_2} = s_2$; but the usual experimental C_g range is extensive enough for deviations of a_g from C_g to be increasingly significant for heavier gases. The relevant thermodynamic equilibrium constants are given by

$$K_{01} = C_1/\gamma_g C_g = K_1/\gamma_g \quad (2a)$$

$$K_{02} = C_2/(s_{02} - C_2)\gamma_g C_g = K_2/\gamma_g \quad (2b)$$

Note that K_{01} , K_{02} are not directly comparable, because the respective standard states are not the same.¹⁰

If we wish to formulate mode 1 and mode 2 equilibria in a thermodynamically equivalent manner, we may either (1) treat the former mode as Langmuir sorption on a large number of sites⁹ $s_{01} \gg C_1$ or (2) consider the latter mode

as “nonideal dissolution.”¹⁰ Following 1, we may rewrite eq. (2a) as

$$K'_{01} = C_1/(s_{01} - C_1)\gamma_g C_g \cong C_1/s_{01}\gamma_g C_g = K_{01}/s_{01} \quad (3)$$

Following 2, eq. (2b) may be rewritten as

$$K'_{02} = \gamma_2 C_2/\gamma_g C_g = s_{02} K_{02} \quad (4a)$$

$$\gamma_2 = s_{02}/(s_{02} - C_2) \quad (4b)$$

FORMULATION OF DUAL MODE TRANSPORT

Unidimensional dual mode transport, subject to the condition of local equilibrium between sorption modes 1 and 2, was originally described by⁵

$$J_x = -\frac{1}{RT}(D_{T1}C_1 + D_{T2}C_2)\frac{\partial\mu}{\partial x} \quad (5)$$

where J_x is the overall sorbed gas flux density at position x in the polymer; $\mu = \mu_1 = \mu_2$ is the local chemical potential of sorbed gas; R is the gas constant; T is the temperature (in K); and D_{T1} , D_{T2} are the “thermodynamic” diffusion coefficients³ (assumed constant in the absence of plasticization effects) associated with the relevant sorption modes. The formulation of eq. (5) in terms of chemical potential gradient driving forces is consistent (vide infra) with the Eyring transition or activated state theory, which provides the physical basis for this model.^{3,5} Equation (5) may be further developed with the aid of eqs. (2) and (4). If a_g is the gas phase activity which would be in equilibrium with the local concentrations C_1 and C_2 , then $d\mu = d\mu_g = RTd \ln a_g$, and we get

$$\begin{aligned} J_x &= -(D_{T1}C_1/a_g + D_{T2}C_2/a_g)(\partial a_g/\partial x) \\ &= -(D_{T1}K_{01} + D_{T2}K'_{02}/\gamma_2)(\partial a_g/\partial x) \cong P_T(\partial a_g/\partial x) \end{aligned} \quad (6)$$

where P_T is the (overall) “thermodynamic” gas permeability coefficient of the polymer. Integration of eq. (6) yields the “effective” or “integral” permeability coefficient $\bar{P}_T(a_g^0, 0)$, which governs the observed steady state permeation flux density J through a polymer membrane of thickness l , in contact with constant upstream and downstream gas phase activities a_g^0 and zero, respectively. Thus, using eqs. (2b) and (4b) to express γ_2 in terms of a_g , we finally get

$$\bar{P}_T(a_g^0, 0) = Jl/a_g^0 = K_{01}D_{T1} + (s_{02}D_{T2}/a_g^0)\ln(1 + K_{02}a_g^0) \quad (7)$$

Subsequently, a formulation of the dual mode mobility model in terms of concentration gradient driving forces was also given:¹¹

$$J_x = -D_{F1}\frac{\partial C_1}{\partial x} - D_{F2}\frac{\partial C_2}{\partial x} \quad (8)$$

where D_{F1} , D_{F2} are "practical" or "Fick-type" diffusion coefficients, which are considered constant. The relation between thermodynamic and Fick-type diffusion coefficients is such that $D_T \equiv D_F$ for thermodynamically ideal systems. For thermodynamically nonideal concentration-dependent systems, $D_F \rightarrow D_T$ as $C \rightarrow 0$. The integral permeability result derived from eq. (8) in terms of a_g^0 , with the aid of eqs. (2), is³

$$\bar{P}_T(a_g^0, 0) = K_{01}D_{F1} + s_{02}K_{02}D_{F2}/(1 + K_{02}a_g^0) \quad (9)$$

Examination of eqs. (7) and (9) shows that the limiting values $\bar{P}_T(a_g^0 \rightarrow \infty, 0)$ and $\bar{P}_T(a_g^0 \rightarrow 0, 0)$ yield $D_{F1} = D_{T1} = D_1$ and $D_{F2} = D_{T2} = D_2$, respectively; but the predicted functional dependence of \bar{P}_T on a_g^0 is different. It is important to know how significant this difference is likely to be in typical experimental situations.

This question has been examined in two quite typical cases with very similar results.^{7,14} The more detailed study concerned the polycarbonate-CO₂ system at 35°C with $p_0 = 1-20$ atm.⁷ However, eq. (9) was used as originally formulated,¹¹ i.e., in terms of practical equilibrium constants and the practical permeability coefficient

$$\bar{P}(C_g^0, 0) = \gamma_g \bar{P}_T(a_g^0, 0) = JI/C_g^0 = \bar{K}_1 D_{F1} + \bar{s}_{02} \bar{K}_2 D_{F2} / (1 + \bar{K}_2 C_g^0) \quad (9')$$

In eq. (9') \bar{K}_1 , \bar{K}_2 , and \bar{s}_{02} were determined by curve-fitting of the C versus C_g (in reality p) isotherm, in the same way as K_{01} , K_{02} , and s_{02} were obtained by curve fitting the C versus a_g isotherm. (Thus, \bar{K}_1 , \bar{K}_2 were not necessarily mean values of the practical equilibrium constants of eqs. (1), as is indicated by the fact that $\bar{s}_{02} \neq s_{02}$.) The resulting degrees of fit were found to be similar.⁷ (Incidentally, the situation was quite different in the case of mixed CO₂-CH₄ sorption isotherms,¹² where use of K_{01} , K_{02} was found to lead to significant improvement in the consistency between theory and experiment.) With the aid of the sets of equilibrium parameters determined as above, no significant nonlinearity could be detected⁷ in experimental plots of $\bar{P}_T(a_g^0, 0)$ versus $\ln(1 + K_{02}a_g^0)/K_{02}a_g^0$ or of $\bar{P}(C_g^0, 0)$ versus $(1 + \bar{K}_2 C_g^0)^{-1}$. Hence, discrimination between eqs. (7) and (9') was not possible within the experimental scatter of the measurements (which is, incidentally, largely attributable to unavoidable subtle changes in the state of "conditioning" of the polymer during experimentation rather than to the experimental technique); even though linearity of one of the above plots should in theory imply appreciable nonlinearity of the other, as illustrated in Figure 1. The values of D_{F1} , D_{F2} obtained differed appreciably (but not markedly) from D_{T1} , D_{T2} , respectively. The question arises whether agreement might be closer, if eq. (9) is used instead of (9'), in line with recent findings based on the transport behavior of CO₂-CH₄ mixtures.¹³

We conclude that, on one hand, the observed concentration dependence of the overall permeability has not, so far, yielded sufficiently precise information about the detailed formulation of the dual mode mobility model. Apart from experimental scatter, the problem may be further compounded by differences in the conditioning of the polymer during sorption and integral

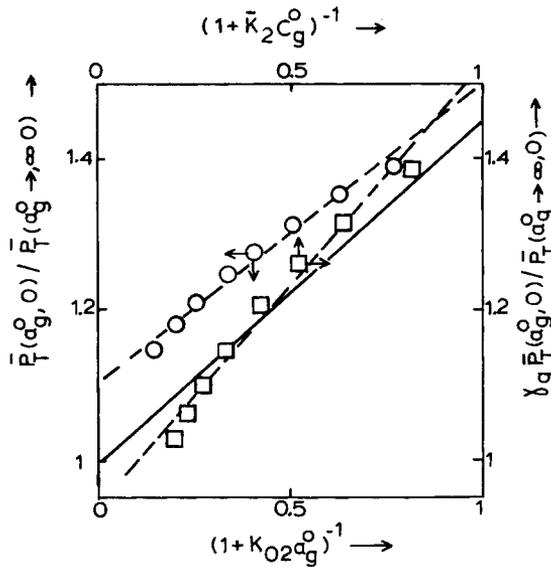


Fig. 1. Simulated experimental plots illustrating the extent of nonlinearity expected if $\bar{P}_T(a_g^0, 0)$ [or the corresponding $\bar{P}(C_g^0, 0) = \gamma_g \bar{P}_T(a_g^0, 0)$] is actually given by eq. (7) (with parameter values as given in Ref. 7) but is plotted in the manner appropriate to eq. (9) (O) or eq. (9') (□). The points cover the experimental p_0 range used in Ref. 7, and the broken lines are straight lines that could reasonably be drawn through these points. The straight line joining the actual limiting values of $\bar{P}_T(a_g^0, 0)$ (at $a_g^0 \rightarrow 0$ or $a_g^0 \rightarrow \infty$) is shown as a solid line.

permeation runs. On the other hand, the aforesaid alternative detailed formulations of the model do not appear to yield materially different results, as far as D_1, D_2 are concerned.

MICROSCOPIC DERIVATION OF EQ. (5)

According to the Eyring transition or activated state theory, most molecules of a sorbed species i are regarded as “immobilized” at appropriate equilibrium sites by potential energy barriers of mean effective height E_i^\ddagger . Only activated molecules, i.e., those possessing sufficient excess energy $\geq E_i^\ddagger$ are mobile, i.e., are able to cross the confining barrier in some direction z . (The fact that E_i^\ddagger may largely reside in the surrounding polymer segments is immaterial for present purposes.) These activated molecules move with the unidimensional Maxwell-Boltzmann mean speed $\bar{u} = (kT/2\pi m)^{1/2}$ (where k = Boltzmann’s constant, m = mass of sorbed species). This is tantamount with a mean effective speed of $\bar{u}C_i^\ddagger/C_i$ for species i molecules, where C_i^\ddagger is the concentration of activated molecules. The latter is evaluated by assuming equilibrium between normal and transition states. The effective velocity in a given direction x is then given by

$$v_{xi} = \kappa \lambda_i (kT/h) K_i^\ddagger = \kappa \lambda_i (kT/h) K_{0i}^\ddagger \gamma_i / \gamma_i^\ddagger = \lambda_i k_{0i} \gamma_i / \gamma_i^\ddagger \tag{10}$$

where h is Planck’s constant; κ is a geometrical factor equal to $\frac{1}{6}$ assuming a homogeneous three-dimensional random walk (i.e., perfectly random orientations of z with respect to x); λ_i is the mean effective diffusion jump length;

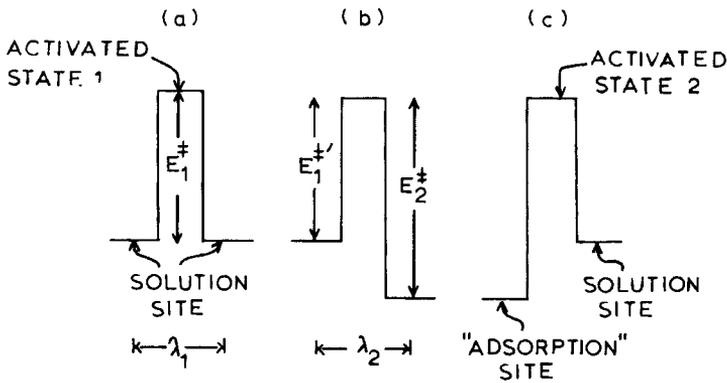


Fig. 2. Types of activation energy barrier (E_i^{\ddagger}) considered in the dual mode mobility model.⁵

K_i^{\ddagger} , K_{0i}^{\ddagger} are the “apparent” and “thermodynamic” equilibrium constants between activated and normal molecules as defined by Glasstone et al. (Ref. 6, pp. 190 and 402); γ_i^{\ddagger} , γ_i are the respective activity coefficients; and k_{0i} is the jump frequency under conditions where the system behaves ideally. In Eyring’s treatment of diffusion in a nonideal solution, $\gamma_i^{\ddagger} = \gamma_i$ in the absence of a concentration gradient, and $\gamma_i^{\ddagger} = \gamma_i + (\lambda_i/2)(\partial\gamma_i/\partial x)$ in the presence of a concentration gradient along x , because of the location of the transition state halfway between donating and receiving equilibrium sites (Ref. 6, p. 534).

In the case under consideration, there are two kinds of transition state, one within the polymer matrix and another at Langmuir sites. In particular, diffusing molecules have to surmount barriers of type a, b, and c (cf., Fig. 2), which are present in concentrations of $s_{01} - s_{02}$, s_{02} , and s_{02} , respectively. (Because of $s_{01} \gg s_{02}$, the juxtaposition of two Langmuir sites is considered to be sufficiently improbable for its effect to be negligible.) Thus, the total macroscopic flux density along $+x$ may be approximately analyzed into components as follows:

$$\vec{J}_x = C_1(1 - s_{02}/s_{01})v_{x1} + C_1(s_{02}/s_{01})v'_{x1} + C_2v_{x2} \quad (11)$$

where [cf. eq. (10)]

$$v_{x1} = \lambda_1 k_{01} \gamma_1 / \gamma_1^{\ddagger} = \kappa (kT/h) \lambda_1 C_1^{\ddagger} / C_1 (1 - s_{02}/s_{01}) \quad (12a)$$

$$v'_{x1} = \lambda_2 k'_{01} \gamma_1 / \gamma_2^{\ddagger} = \kappa (kT/h) \lambda_2 (C_2^{\ddagger} s_{01} / 2C_1 s_{02}) \quad (12b)$$

$$v_{x2} = \lambda_2 k_{02} \gamma_2 / \gamma_2^{\ddagger} = \kappa (kT/h) \lambda_2 (C_2^{\ddagger} / 2C_2) \quad (12c)$$

and C_1^{\ddagger} , C_2^{\ddagger} is the concentration of activated molecules at “solution” and Langmuir sorption sites, respectively. The thermodynamic behavior of the latter activated molecules is similar to that of adsorbed molecules (Ref. 6, p. 349), i.e., $\gamma_2^{\ddagger} = \gamma_2$ at uniform concentration [where γ_2 is given by eq. (4b)]. From eqs. (12b) and (12c) it is obvious that the last two terms in eq. (11) are equal. Thus, in the presence of a macroscopic concentration gradient along x ,

the net diffusion flux density is given by

$$J_x = \vec{J}_x - \bar{J}_x = (1 - s_{02}/s_{01})[v_{x1}C_1 - v_{x1}(C_1 + \lambda_1 \partial C_1/\partial x)] + 2[v_{x2}C_2 - v_{x2}(C_2 + \lambda_2 \partial C_2/\partial x)] \tag{13}$$

which reduces finally (Ref. 6, p. 534) to

$$J_x = -(1 - s_{02}/s_{01})k_{01}\lambda_1^2 C_1 \partial \ln(\gamma_1 C_1)/\partial x - 2k_{02}\lambda_2^2 C_2 \partial \ln(\gamma_2 C_2)/\partial x \tag{14}$$

Equation (14) is equivalent to eq. (5), with $D_{T1} = (1 - s_{02}/s_{01})k_{01}\lambda_1^2 \approx k_{01}\lambda_1^2$ and $D_{T2} = 2k_{02}\lambda_2^2$.

The above analysis clearly shows that

1. D_i in the original dual mode mobility model⁵ (or in a more general multimode mobility model³) is physically defined as a random walk parameter related to the transition or activated state associated with the i th sorption mode. Thus, the said model does not differ in any essential way from the more recent treatments of Refs. 8 and 9, as has been erroneously suggested,⁹ except in its neglect of the effect of contiguous Langmuir sites (which will be further considered below).

2. The aforesaid physical interpretation of D_i applies strictly in the postulated context of a homogeneous random walk. This condition is maintained if $\lambda_1 = \lambda_2$ and the activated states involved are energetically equivalent (i.e., $E_1^{*'} \approx E_1^*$ in Fig. 2);¹⁴ whereupon $C_2^* \approx 2s_{02}C_1^*/(s_{01} - s_{02})$ at high dilution ($\gamma_2 \rightarrow 1$) and hence

$$D_2/D_1 \approx 2k_{02}/k_{01} = 2K'_{01}/K_{02} = 2K_{01}s_{02}/K'_{02}s_{01} \tag{15}$$

Thus, the above treatment cannot be expected to be applicable in a physically meaningful and self-consistent manner, if the relevant value of D_2/D_1 is not in keeping with condition (15) in conjunction with other basic assumptions, notably the relative magnitude of s_{01}, s_{02} ($s_{01} \gg s_{02}$). Thus, the value of D_2/D_1 predicted for CH₄ in oriented polystyrene in Ref. 5 corresponds by eq. (15) to $s_{01}/s_{02} > 10$, which is reasonable. The experimental values of D_2/D_1 , on the other hand, typically correspond to $s_{01}/s_{02} < 10$ with a tendency for s_{01}/s_{02} to be smaller for heavier gases (cf. Table I).¹⁶⁻¹⁹ In the context of the above theory, this implies increasing deviation from eq. (15), i.e., from the condition $E_1^{*'} \approx E_1^*$, in the sense of $E^{*'} < E_1^*$, and hence increasing dis-

TABLE I
Experimental Values of D_2/D_1 (D_{F2}/D_{F1}) and $K'_{02}D_2/K_1D_1$ for a series of gases at 35°C in polycarbonate,¹⁶ polyphenylene oxide,¹⁷ a copolyester,¹⁸ and a polysulphone¹⁹

	$K'_{02}D_2/K_1D_1$				D_2/D_1			
	CO ₂	CH ₄	Ar	N ₂	CO ₂	CH ₄	Ar	N ₂
PPO ¹⁵	0.70	0.61	0.28	0.34	0.097	0.10	0.11	0.14
PC ¹⁴	0.56	0.55	0.23	0.38	0.078	0.115	0.18	0.29
PSF ¹⁷	0.92	1.5	0.53	0.94	0.105	0.35	0.38	0.45
CPE ¹⁶	~ 0.70	~ 0.60	~ 0.28	~ 0.34	~ 0.22	~ 0.38	~ 0.53	~ 0.77

turbance of the homogeneous random walk condition in the neighborhood of Langmuir sites (with z tending to be preferentially oriented towards the Langmuir site), which detracts from the physical significance principally of D_2 . Thus, whereas the experimental D_1 can still be regarded as a quantitative measure of E_1^* , the experimental D_2 values cannot be considered to be more than semiquantitative measures of E_2^* . The concentration dependence of the overall permeability would, presumably, also be affected; but the only way so far proposed to deal more precisely with an analogous situation is to resort to numerical network computations.¹⁵ The preceding remarks are, of course, also applicable to the treatments of Refs. 8 and 9.

3. The assumption of $D_2 = 0$, incorporated in the early transport model of Ref. 4, implies $C_2^* = 0$ in eqs. (12b) and (12c) and is, therefore, unacceptable in principle. This was, in fact, the chief reason for the formulation of the dual mode mobility model (in Ref. 5).

4. There is no justification, as far as one can see, for the suggestion⁸ that D_1 as originally defined includes a contribution from the second term in eq. (11).

5. The belief expressed in Ref. 9 to the effect that D_{T2} was originally⁵ defined as a macroscopic or intraphase diffusion coefficient has no basis in fact. The proper treatment for the case where sorption mode 2 is considered to exist in the form of patches or domains extensive enough to be recognizable as a thermodynamic phase,³ rather than as scattered individual sorption sites, is indicated in the next section.

6. According to the treatments of Refs. 8 and 9, inclusion of the effect of adjacent Langmuir sites leads to replacement of the second term on the right-hand side of eq. (7) by two terms as follows (in present terminology):

$$\bar{P}_T(a_g^0, 0) = K_{01}D_1 + \frac{s_{02}D_{21}}{a_g^0} \ln(1 + K_{02}a_g^0) + \frac{s_{02}K_{02}D_{22}}{1 + K_{02}a_g^0} \quad (16)$$

where D_{21} is now associated with activated state 2, and D_{22} is related to a third activated state, namely that between juxtaposed Langmuir sites. To determine whether this considerable complication of eq. (7) is worthwhile, we refer back to our original derivation of eqs. (11) and (12), where we now distinguish between isolated Langmuir sites of concentration $s_{02}(1 - s_{02}/s_{01})$ and contiguous Langmuir sites of concentration s_{02}^2/s_{01} . It is not difficult to see that $C_{21}^* = C_2^*(1 - s_{01}/s_{02})$ and hence $D_{21} = D_2(1 - s_{01}/s_{02})$. If the height of the energy barrier separating contiguous Langmuir sites is not appreciably different from that separating a Langmuir site from an adjacent "solution site" (E_2^*), $C_{22}^* \approx C_2^* s_{02}/2s_{01}$, and hence $D_{22} \approx D_2 s_{02}/2s_{01}$, thus indicating that the effect of replacing eq. (7) by eq. (16) is negligible. Assuming the energy barrier between Langmuir sites to be significantly lower (and hence D_{22} significantly higher) than indicated above would, from the theoretical point of view, be inconsistent not only with a homogeneous random walk but also with the postulate of independent Langmuir sites of a single kind made in dual mode sorption theory. Aside from such theoretical arguments, however, and assuming that eq. (16) is applicable with $D_{21} \sim D_{22}$, it still seems unrealistic, from the practical point of view, to expect⁹ that D_{21} , D_{22} might be experimentally distinguishable, in view of the fact that the much more gross discrimina-

tion between eqs. (7) and (9) has not, so far, proved feasible (cf. previous section).

Finally, we note that the physical interpretation of D_{22} [or of D_{F2} in eq. (9)] as an intraphase diffusion coefficient, in the manner suggested in Ref. 9, is subject to severe restrictions and qualifications, as indicated in the following section.

TREATMENT OF THE LANGMUIR SORPTION MODE AS A DISTINCT THERMODYNAMIC PHASE

If sorption mode 2 is assumed to exist in the form of patches or domains extensive enough to constitute a macroscopically recognizable thermodynamic phase,³ then the glassy polymer should presumably be treated as a dilute fine dispersion of this phase (designated in what follows as A) in the dense polymer matrix (designated as phase B). This leaves the treatment of sorption unchanged, each constituent phase contributing additively to the overall concentration of sorbed penetrant in the polymer, namely

$$C = v_A C_A + v_B C_B = C_1 + C_2 \tag{17}$$

where v_A, v_B represent the volume fractions occupied by the relevant phases, and C_A, C_B are defined per unit volume of the respective phases.³

The overall permeability coefficient P_T , however, cannot be expressed by an additive formula analogous to eq. (17), except in the unrealistic situation of phases A and B being arranged in parallel to each other and to the direction of flow.^{3,20} For a dilute dispersion of A in B, a number of formulae are in use, three of the best known of which can be represented by putting $k_a = 0, 1, \text{ or } 2$ in²⁰

$$P_T/P_{TB} = 1 + 3v_A \{ A^{-1} - v_A - k_a v_A (1 - v_A) / (A^{-1} - v_A) + \dots \}^{-1} \tag{18}$$

where

$$A = (\alpha - 1) / (\alpha + 2); \quad \alpha = P_{TA} / P_{TB} \tag{19}$$

In eq. (18), P_{TA}, P_{TB} are the permeability coefficients characteristic of phases A and B, respectively, which may, in turn, be defined in terms of "thermodynamic" or "Fick-type" diffusion coefficients (vide supra). In view of eqs. (1)–(4) and Ref. 3, the final result is

$$P_{TA} = (K'_{02} D_A / v_A) f(a_g) = P_{TA}^0 f(a_g); \quad P_{TB} = K_1 D_B / v_B \tag{20}$$

where $f(a_g) = (1 + K_{02} a_g)^{-n}$ with $n = 1$ or 2 ; and D_A, D_B are the relevant diffusion constants corresponding to D_2, D_1 , respectively. For sufficiently small v_A , eq. (18) simplifies to

$$P_T/P_{TB} = 1 + 3v_A A + 3(1 + k_a) v_A^2 A^2 + \dots \tag{21}$$

As discussed previously, the main features of interest are the limiting values of P_T and its functional dependence on a_g . As can be seen from eqs. (19) and (20), we have $f(a_g) \rightarrow 1, \alpha \rightarrow \alpha_0 = P_{TA}^0 / P_{TB} = K'_{02} D_A v_B / K_1 D_B v_A$ and $A \rightarrow A_0 = (\alpha_0 - 1) / (\alpha_0 + 2)$, when $a_g \rightarrow 0$; and $f(a_g) \rightarrow 0, \alpha \rightarrow 0$ and $A \rightarrow -\frac{1}{2}$,

when $\alpha_g \rightarrow \infty$. Thus, the lower limiting value of P_T is given by

$$P_T(\alpha = 0)/P_{TB} = 1 - \frac{3}{2}v_A + \frac{3}{4}v_A^2(1 + k_a) + \dots \tag{22}$$

and, combining eqs. (21) and (22), we get

$$P_T(\alpha)/P_T(\alpha = 0) = 1 + 3v_A(A + \frac{1}{2}) + 3v_A^2(A + \frac{1}{2})\{(1 + k_a)(A - \frac{1}{2}) + \frac{3}{2}\} + \dots \tag{23}$$

Hence, the dual mode mobility parameters are given [cf., e.g., eq. (6) with eq. (23)], to first order, by

$$K_{01}D_1 = P_T(\alpha = 0) \simeq K_{01}D_B(1 - \frac{3}{2}v_A)/(1 - v_A) \tag{24a}$$

$$K'_{02}D_2/K_{01}D_1 = P_T(\alpha = \alpha_0)/P_T(\alpha = 0) - 1 \simeq 9v_A\alpha_0/2(\alpha_0 + 2) \tag{24b}$$

Equation (24a) shows that $D_1 \simeq D_B$. Equation (24b) yields

$$D_2/D_1 \simeq 9v_B D_A/4D_B \sim 2D_A/D_B, \quad \text{if } \alpha_0 \ll 2 \ (D_A \ll D_B) \tag{25a}$$

$$D_2/D_1 \simeq 9v_A K_1/2K'_{02}, \quad \text{if } \alpha_0 \ll 2 \ (D_A \geq D_B) \tag{25b}$$

Hence, a close relation between D_A and D_2 , namely $D_2 \simeq 2D_A$ (wherein D_2 could represent D_{T2} , D_{F2} , or D_{22} coupled with $D_{21} = 0$, of the previous section) can be expected only when $D_A \ll D_B$. A more complete and detailed illustration of this point is given by actual numerical examples from eq. (18) (cf., Table II).

Using the case of $f(\alpha_g) = (1 + K_{02}\alpha_g)^{-1}$ as an example for the purpose of examining the concentration dependence of the (overall) permeability, we integrate eq. (23) (to first order) to obtain an expression for the integral permeability analogous to eq. (7). The result is

$$\frac{\bar{P}_T(\alpha_g^0, 0)}{\bar{P}_T(\alpha_g^0 \rightarrow \infty, 0)} \simeq 1 + \frac{9v_A\alpha_0}{4K_{02}\alpha_g^0} \ln\left(1 + \frac{2K_{02}\alpha_g^0}{\alpha_0 + 2}\right) \tag{26}$$

As illustrated in Figure 3, the functional dependence of $\bar{P}_T(\alpha_g^0, 0)$ on α_g^0

TABLE II
Correspondence Between D_2/D_1 and D_A/D_B

$\frac{K'_{02}D_A}{K_{01}D_B}$		$K'_{02}D_2/K_{01}D_1$								
		α_0			$v_A = 0.10$			$v_A = 0.25$		
					Eq. (18)			Eq. (18)		
$v_A = 0.1$	$v_A = 0.25$	$k_a = 0$	$k_a = 1$	$k_a = 2$	Eq. (24b)	$k_a = 0$	$k_a = 1$	$k_a = 2$	Eq. (24b)	
0.01	0.09	0.03	0.021	0.022	0.023	0.019	0.020	0.022	0.026	0.017
0.1	0.9	0.3	0.15	0.16	0.16	0.14	0.18	0.20	0.22	0.16
1	9	3	0.44	0.46	0.49	0.37	1.0	1.1	1.1	0.67
10	90	30	0.54	0.59	0.65	0.44	1.8	2.3	3.4	1.1
100	900	300	0.56	0.61	0.68	0.45	2.0	~ 2.8	~ 5	1.2

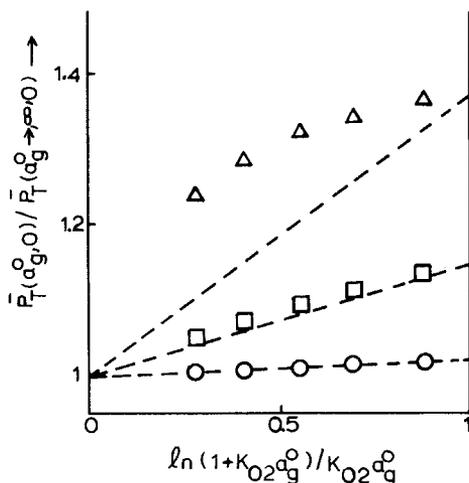


Fig. 3. Functional dependence of $\bar{P}_T(a_g^0, 0)$ on a_g^0 as given by eq. (26) with $v_A = 0.1$ and $\alpha_0 = 0.1$ (\circ), 1 (\square), 10 (Δ). The limiting values of $\bar{P}_T(a_g^0, 0)$ are joined by dashed lines in each case.

predicted by eq. (26) is the same as that given by eq. (7) for small α_0 ($\alpha_0 \ll 2$) but increasingly departs from it at higher α_0 ($\alpha_0 \gtrsim 2$). Analogous results can, of course, be expected in the case of $f(a) = (1 + K_2 a_g)^{-2}$. The experimental detection of deviations from the concentration dependence of \bar{P}_T given by eqs. (7) or (9) will obviously be subject to the limitation noted previously.

The results obtained above clearly indicate that use of the dual mode mobility model with D_2 interpreted as an intraphase diffusion coefficient (and with the qualification that $D_2 \sim 2D_A$ not $D_2 \sim D_A$) is theoretically justifiable only under conditions of $D_A \ll D_B$. As D_A/D_B increases, the relation between D_2 and D_A becomes increasingly tenuous, and the functional dependence of P_T on a_g changes. As illustrated in Table II, these effects are more marked at low v_A , where D_2/D_1 soon attains a limiting value as $D_A/D_B \rightarrow \infty$. (Reference to the exact formulae given in Ref. 20 shows that D_2/D_1 is bounded as $D_A/D_B \rightarrow \infty$ for all $v_A < 1$ in the case of $k_a = 0$ and $k_a = 1$ and for $v_A < 0.3$ in the case of $k_a = 2$.) Comparison of Table I with the middle rows of Table II shows that interpretation of the observed D_2/D_1 values, without gross departure from the observed concentration dependence of \bar{P}_T , is possible in principle, if it is assumed that $v_A \sim 0.25$. Under these conditions, correspondence between D_A/D_B and D_2/D_1 is quite close (notably $D_A/D_B \sim D_2/D_1$ for the heavier gases and $D_A/D_B \sim D_2/2D_1$ for the lighter gases). However, the physical implications of the result $D_A/D_B < 1$ are difficult to sustain, because phase A is supposed to have lower density than B.

CONCLUSION

In the present paper we have given the detailed Eyring-type microscopic derivation of the dual mode mobility model as originally formulated and have attempted to clarify certain fundamental points concerning the proper formulation, physical significance, and limitations of this type of approach. We have shown, in particular, that the said original model does not differ in essence from recent more elaborate treatments.^{8,9} The latter, in our opinion, intro-

duce more diffusion parameters than can reasonably be expected to be measurable on the basis of past experience^{7,14} and, at the same time, pay little attention to the limitations imposed by the conditions of the mathematical derivation on the physical meaning of the parameters in question. The nature of the aforementioned limitations has been indicated here, and it has been shown that experimental values of D_2 cannot, in fact, be assigned more than semiquantitative significance. This is perhaps not surprising, in view of the highly idealized nature of both dual mode sorption and dual mode mobility theories.

The proper treatment of the case considered in Ref. 9, where the Langmuir sorption mode is regarded as a (low density) macroscopically recognizable phase dispersed in the polymer matrix, has also been indicated here. It has been shown that such a treatment can be reduced to the dual mode sorption model formalism (with $D_1 = D_B$, $D_2 = 2D_A$) only if $D_B \gg D_A$. A semiquantitative interpretation of existing data on this basis would be feasible, except for the fact that the conditions imposed are not easy to sustain physically.

Extensive fruitful discussions with Prof. W. J. Koros are gratefully acknowledged.

References

1. W. R. Vieth, J. M. Howell, and J. H. Hsieh, *J. Membr. Sci.*, **1**, 177 (1976).
2. V. T. Stannett, W. J. Koros, D. R. Paul, H. K. Lonsdale, and R. W. Baker, *Adv. Polym. Sci.*, **32**, 69 (1979).
3. J. H. Petropoulos, *Adv. Polym. Sci.*, **64**, 93 (1985).
4. W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).
5. J. H. Petropoulos, *J. Polym. Sci.*, **A2**, **8**, 1797 (1970).
6. S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes*, McGraw-Hill, New York, 1941.
7. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 687 (1976).
8. R. M. Barrer, *J. Membr. Sci.*, **18**, 25 (1984).
9. G. H. Fredrickson and E. Helfand, *Macromolecules*, **18**, 2201 (1985).
10. W. A. Steele, *The Interaction of Gases with Solid Surfaces*, Pergamon Press, Oxford, 1974, Chap. 3.
11. D. R. Paul and W. J. Koros, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 675 (1976).
12. E. S. Sanders, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, *J. Membr. Sci.*, **18**, 53 (1984).
13. R. T. Chern, W. J. Koros, B. Yui, H. B. Hopfenberg, and V. T. Stannett, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 1061 (1984).
14. E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, and S. T. Wang, *Ind. Eng. Chem. Res.*, **26**, 433 (1987).
15. F. Jagodic, B. Borštnik, and A. Ažman, *Makromol. Chem.*, **173**, 221 (1973).
16. W. J. Koros, A. H. Chan, and D. R. Paul, *J. Membr. Sci.*, **2**, 165 (1977).
17. K. Toi, G. Morel, and D. R. Paul, *J. Appl. Polym. Sci.*, **27**, 2997 (1982).
18. P. Masi, D. R. Paul, and J. W. Barlow, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 15 (1982).
19. A. J. Erb and D. R. Paul, *J. Membr. Sci.*, **8**, 11 (1981).
20. J. H. Petropoulos, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 1309 (1985).

Received June 15, 1987

Accepted October 17, 1987