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Sorption in Glassy Polymers

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ABSTRACT: A model is proposed for analyzing sorption and volumetric behavior of glassy polymer–penetrant systems. It is shown that the proposed theory can predict general trends for sorption and volumetric behavior in the glassy state, and furthermore, it gives good agreement with actual sorption data. The model takes into account the effects of structural arrangements in the polymer matrix on sorption and volumetric behavior.

Introduction

It is well-known that amorphous polymer–penetrant systems generally exhibit very different sorption and volumeric behavior above and below the glass transition temperature of the pure polymer, T_{g2}. The following characteristics have been observed experimentally for sorption in amorphous polymer–penetrant systems:

(1) For low penetrant concentrations in rubbery polymers, the concentration of the sorbed penetrant can be determined by using a Henry's law relationship, and at sufficiently high penetrant concentrations, there can exist deviations from Henry's law behavior.[1–3] The sorption isotherms curve away from the pressure axis as the penetrant pressure is increased, and the sorption behavior can be satisfactorily described by the Flory–Huggins theory[4] of polymer solutions. For glassy polymers, the sorption isotherm is nonlinear. The sorption process is not adequately described by Henry's law even at relatively low penetrant concentrations, and the sorption isotherm curves toward the pressure axis with increasing gas pressure.[1–3,5–9]

(2) For polymer–penetrant systems above T_{g2}, the form of the sorption isotherm is essentially the same for all temperatures.[10] For glassy polymer–penetrant systems, there are significant changes in the shapes of the concentration–pressure curves. The sorption isotherms become more nearly linear as the temperature of the sorption experiment increases.[1,6–9]

(3) For glassy polymers, sorption experiments have shown that it is possible to have a sorption isotherm with a shape characteristic of glassy polymers at low pressures and a shape characteristic of rubbery polymers at sufficiently high pressures.[2] The penetrant concentration at which the transition from glassy to rubbery behavior occurs decreases with increasing temperature. This effect has been attributed to plasticization of the polymer by the sorbed penetrant. Complex isotherms of this type have not been observed for amorphous polymers above T_{g2}.

(4) Solubility measurements reported by Meares[11] show that the dissolution of a gas in a glassy polymer is much more exothermic than the dissolution of the same gas in a rubbery polymer. Meares used the temperature dependence of the solubility of a gas to define a heat of solution for the gas in the polymer. For oxygen sorption in poly(vinyl acetate), the heat of solution was about 5000 cal/mol more negative below T_{g2} than above the glass temperature whereas, for the sorption of argon, the heat of solution for the glassy polymer was about 2000 cal/mol more negative than that for the rubbery polymer.

(5) For glassy polymers, it has been shown[9] that the polymer molecular weight has a strong influence on the shape of the sorption isotherm. At a given temperature, the extent of penetrant sorption at a given pressure increases as the polymer molecular weight increases, and the sorption isotherms become more nearly linear as the polymer molecular weight decreases. For polymers above T_{g2}, it can be shown using the Flory–Huggins equation[4] that polymer molecular weight has a very small effect on the sorption process as long as the polymer molar volume is at least about 50 times larger than the penetrant molar volume.

(6) For glassy polymer–penetrant systems, significant negative departures from volume additivity have been reported. Maeda and Paul[6,7] measured negative excess volumes that were as much as about 5% of the total volume, and Fleming and Koros[3] presented data that showed negative excess volumes which were as much as about 2% of the total volume. On the other hand, volumetric data for three rubbery polymer–penetrant systems[12–14] show a maximum excess volume that is about 0.3% of the total volume.

Two different theories have been proposed in attempts to describe the diverse sorption behavior summarized above: the dual-mode sorption model and the matrix model. For the dual-mode sorption model, it is assumed that there exist two distinct molecular populations of penetrant in the polymer.[8,15,16] One population (the Henry's law mode) dissolves directly into the polymer matrix, and a second population (the Langmuir mode) is sorbed into microvoids or holes in the polymer. An important premise of the dual-mode theory is that the penetrant does not interact with the polymer matrix and hence does not induce significant changes in the polymer structure. The dual-mode model can be used only to correlate sorption data since the expression for the sorption isotherm contains three parameters that cannot be determined independently. The second model that attempts to explain nonlinear sorption behavior of penetrants in glassy polymers is the matrix model.[17,18] For this model, it is assumed that there is only one population of sorbed gas molecules in the polymer and that the structure and properties of the polymer matrix are perturbed by the presence of the sorbed penetrant because of the polymer–penetrant interactions. The matrix model is not a predictive theory since parameters in the expression for the sorption isotherm cannot be determined independently. This theory has two parameters in the sorption isotherm equation that can be determined only by using sorption data.

It is evident from the above discussion that neither the dual-mode model nor the matrix model provides a predictive basis for describing the sorption process in glassy polymers. Furthermore, a major difference in these models is the question of whether the introduction of a penetrant

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induces changes in the polymer matrix. The assumption made in the dual-mode theory that the polymer structure is essentially not modified as penetrant is added appears to us to be somewhat unrealistic. At any temperature T below T_{g2}, the dry polymer exists in a nonequilibrium liquid or glassy state. As penetrant is added to the polymer matrix, the system must eventually reach an equilibrium liquid configuration at the concentration at which $T = T_{gm}$, where T_{gm} is the glass transition temperature of the polymer–penetrant mixture at a particular penetrant mass fraction. It is reasonable to expect that there is a continuous change in the structure of the polymer from the nonequilibrium liquid configuration of the dry polymer to the equilibrium liquid structure at the concentration at which the glass temperature of the mixture has been depressed to the temperature of the system. Indeed, this change of structure is responsible for the type of sorption isotherms described in the third experimental observation described above.

The meaning of structural changes in the polymer matrix can be explained by using the volumetric properties of a polymer cooled below its transition temperature. Below T_{g2}, the glassy polymer is in a nonequilibrium liquid configuration with extra hole free volume which is effectively frozen into the polymer. The polymer specific volume in the glassy state is of course higher than the specific volume of the equilibrium liquid at the same temperature. As penetrant is added to the system, there is an eventual elimination of the extra hole free volume of the system, and there is a change in the molecular structure of the polymer in the sense that both the polymer matrix and the polymer–penetrant mixture are gradually moving toward an equilibrium liquid configuration. When the penetrant concentration is high enough to depress T_{gm} to the temperature of the system, the specific volume of the equilibrium liquid polymer is significantly lower than the specific volume of the glassy polymer since the polymer structure has collapsed to form a thermodynamically stable volumetric state. This change in specific volume is generally of the order of several percent, and the structural change is simply a densification of the polymer matrix.

A precise analysis of the changes in the volumetric and thermodynamic properties of a glassy polymer–penetrant system will depend on the temperature and concentration histories of the polymer–penetrant sample. The analysis of changes in these properties involves the solution of a complex problem involving memory effects for the volumetric and thermodynamic properties. The history dependence of the properties of polymer glasses has been amply demonstrated from volumetric and sorption experiments for glassy polymer–penetrant systems.[3,19,20] Consequently, any completely *general* analysis of sorption and volumetric effects in glassy polymers must necessarily include temperature–time and concentration–time effects on the properties of the system. It is, however, instructive to see how a glassy polymer–penetrant mixture behaves when the polymeric samples are prepared in a prescribed manner, which is particularly simple. The formulation of a quantitative model based on a simple sample preparation history permits us to study how changes in polymer structure affect the volumetric and sorption behavior of the system. Furthermore, the simple model may lead to reasonable predictions for the properties of the glassy polymer–penetrant system in some (but, of course, not all) cases when these properties are not overly sensitive to the exact nature of the sample preparation history.

The objective of this article is to propose a model for understanding the volumetric and sorption behavior of a system composed of a glassy polymer and a penetrant. The equations of this model can be used to predict how the behavior of a polymer glass is affected by the addition of a low molecular weight penetrant, and the model predictions can be compared with the general experimental observations listed above. Furthermore, the predictions of the model for the volumetric and sorption behavior of a particular polymer–solvent system can be compared with actual experimental data for that system. The assumptions used to formulate the model are listed in the second section of the paper. The model is an extension of a model formulated previously for the volumetric and free-volume properties of a glassy polymer–solvent system.[21-23] The volumetric and sorption predictions of the model are presented and discussed in the third and fourth sections of the paper, respectively. Comparisons of the theory both with general trends and with actual experimental data are included in these sections.

Assumptions of the Model

The following assumptions are used to formulate a theory for the volumetric and sorption behavior of glassy polymer–penetrant systems:

(1) The pure polymer is characterized by four important thermodynamic variables: α_2, α_{2g}, $\hat{C}_p$, and $\hat{C}_{pg}$. Here, α_2 is the thermal expansion coefficient for the equilibrium liquid polymer, α_{2g} is the thermal expansion coefficient for the glassy polymer, $\hat{C}_p$ is the specific heat capacity at constant pressure for the equilibrium liquid polymer, and $\hat{C}_{pg}$ is the specific heat capacity at constant pressure for the glassy polymer. These thermodynamic variables are approximated by average values in the temperature ranges under consideration, and they are assumed to be effectively independent of polymer molecular weight. Furthermore, in the definition of thermal properties for polymer glasses, some ordering parameter for the polymer structure should be held constant.[24] Here, we assume that structural differences in the polymer glass will not affect α_{2g} and $\hat{C}_{pg}$ significantly. Also, the rapid changes in the thermal expansion coefficient and in the specific heat near T_{g2} will be idealized as step changes from α_{2g} to α_2 and from $\hat{C}_{pg}$ to $\hat{C}_p$ at T_{g2}. Finally, for all expansion coefficients used in the theory and for the temperature intervals of interest, it is assumed that approximations of the form

$$\exp[\alpha_2(T - T_{g2})] = 1 + \alpha_2(T - T_{g2}) \qquad (1)$$

are sufficiently accurate.

(2) At a given penetrant concentration, the polymer–penetrant mixture exists as a nonequilibrium liquid structure at temperatures below T_{gm}. We assume that, once this structure is formed at a given penetrant concentration and temperature, the structure remains effectively invariant during any experiments carried out on the polymer–penetrant mixture until the concentration level is changed. This behavior is analogous to what happens when a pure polymer is cooled below T_{g2}. At some temperature T below T_{g2}, the polymer assumes a glassy volume higher than that of the equilibrium liquid polymer at T, and this volume relaxes only very slowly toward the equilibrium value for the polymeric liquid.

(3) The specific volume, $\hat{V}$, of the equilibrium liquid mixture of polymer and penetrant is given by

$$\hat{V} = \omega_1 \hat{V}_1^{\,0} + \omega_2 \hat{V}_2^{\,0} \qquad (2)$$

at a given concentration for temperatures both above and below the glass transition temperature of the polymer–penetrant mixture, T_{gm}. In this equation, $\hat{V}_1^0$ is the specific volume of the pure penetrant in the liquid state, $\hat{V}_2^0$ is the specific volume of the pure equilibrium liquid polymer, and ω_I is the mass fraction of component I. The subscript 1 refers to the penetrant and the subscript 2 to the polymer. In addition, the specific volume of a glassy polymer–penetrant mixture below T_{gm} is given by the following expression:

$$\hat{V} = \omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_{2g}^0 \tag{3}$$

Here, $\hat{V}_{2g}^0$ is the appropriate specific volume (defined below) of the glassy polymer used to form the nonequilibrium mixture at a given temperature below T_{gm}. Since it is not in general possible to observe the equilibrium liquid structure below T_{gm}, it is the nonequilibrium volume given by eq 3 that is observed in experiments. Both eqs 2 and 3 are formulated by assuming that there is no volume change on mixing. Although volume additivity is assumed in forming the expression for the volume for glassy polymer–penetrant mixtures, it will be evident from the discussion below that $\hat{V}_{2g}^0$ is a function of the penetrant concentration.

(4) The specific Gibbs free energy of a liquid polymer–penetrant mixture, $\hat{G}$, can be expressed as

$$\hat{G} = \omega_1 \hat{G}_1^0 + \omega_2 \hat{G}_2^0 + \Delta \hat{G}_m \tag{4}$$

and $\hat{G}$ for a glassy polymer–penetrant mixture is given by the following expression:

$$\hat{G} = \omega_1 \hat{G}_1^0 + \omega_2 \hat{G}_{2g}^0 + \Delta \hat{G}_m \tag{5}$$

Here, $\hat{G}_1^0$ is the specific Gibbs free energy of the penetrant in the liquid state, $\hat{G}_2^0$ is the specific Gibbs free energy of the equilibrium liquid polymer, and $\hat{G}_{2g}^0$ is the appropriate specific Gibbs free energy (defined below) of the glassy polymer used to form the nonequilibrium liquid mixture below T_{gm}. Clearly, eqs 2 and 4 describe the properties of an equilibrium liquid mixture both above and below T_{gm} whereas eqs 3 and 5 characterize $\hat{V}$ and $\hat{G}$ for the glassy polymer–penetrant mixture below T_{gm}. Furthermore, $\hat{V}_2^0$ and $\hat{G}_2^0$ are functions only of temperature and pressure whereas $\hat{V}_{2g}^0$ and $\hat{G}_{2g}^0$ are functions of temperature, pressure, and the configuration of the polymer matrix. The values of $\hat{V}_{2g}^0$ and $\hat{G}_{2g}^0$ depend on how far removed the structure of the polymer matrix is from the equilibrium liquid configuration. Finally, $\Delta \hat{G}_m$ is the Gibbs free energy of mixing per mass of mixture at some temperature T. For this study, it is convenient due to use the Flory–Huggins expression[4] for $\Delta \hat{G}_m$

$$\Delta \hat{G}_m = RT\left[\frac{\omega_1}{M_1}\ln \phi_1 + \frac{\omega_2}{M_2}\ln \phi_2 + \frac{\chi \omega_1 \phi_2}{M_1}\right] \tag{6}$$

where R is the gas constant, ϕ_I is the volume fraction of component I, M_I is the molecular weight of component I, and χ is the interaction parameter of the Flory–Huggins theory. The parameter χ can be a function of temperature but not of concentration. In the formulation of this mixing term for the Flory–Huggins theory, it is assumed[4] that the same lattice structure can be used at all concentrations. Here, we assume that the lattice at a given temperature is formed by using the equilibrium liquid volume of the polymer, and thus, the volume fractions in eq 6 are defined by the following expressions:

$$\phi_1 = \frac{\omega_1}{\omega_1 + q\omega_2} \tag{7}$$

$$\phi_2 = \frac{q\omega_2}{\omega_1 + q\omega_2} \tag{8}$$

$$q = \frac{\hat{V}_2^0}{\hat{V}_1^0} \tag{9}$$

(5) The values of $\hat{V}_{2g}^0$ and $\hat{G}_{2g}^0$ that are used in eqs 3 and 5 depend on how the polymer–penetrant system is prepared because the structure and properties of glassy polymers are dependent on the sample history. We suppose here that the polymer–penetrant mixture is formed by first mixing the materials at some temperature above T_{gm}, and the system is then cooled to the desired temperature below T_{gm} by using a conventional time scale. The thermal properties α_{2g} and $\hat{C}_{pg}$ of the polymer in the polymer–penetrant mixture are assumed to be the same as those for the pure polymer as it is cooled below T_{g2}. Hence, in this way, it is possible to assign a structure to the polymer in the glassy polymer–penetrant mixture at any temperature T below T_{gm}, and this structure will clearly change as the penetrant mass fraction changes since T_{gm} is of course a function of ω_1. The larger ω_1 is, the closer the polymer matrix is to the equilibrium liquid configurations since T_{gm} approaches T as ω_1 increases. Hence, both $\hat{V}_{2g}^0$ and $\hat{G}_{2g}^0$ effectively depend on ω_1, and this dependence simply reflects the structural changes in the polymer matrix with increasing ω_1. Some justification is given elsewhere[21] that this model provides a valid description of the volumetric properties of a polymer–penetrant mixture, and we suppose here that a reasonable estimate for $\hat{G}_{2g}^0$ at each ω_1 can be obtained in this manner. Consequently, for the glassy polymer matrix at a given mass fraction ω_1 and at a given temperature T below T_{gm}, we can write the following expressions:

$$\hat{V}_{2g}^0(\omega_1,T) = \hat{V}_2^0(T_{gm})[1 + \alpha_{2g}(T - T_{gm})] \tag{10}$$

$$\hat{G}_{2g}^0(\omega_1,T) = \hat{H}_2^0(T_{gm}) + \hat{C}_{pg}(T - T_{gm}) - T\hat{S}_2^0(T_{gm}) - T\hat{C}_{pg}\ln (T/T_{gm}) \tag{11}$$

Here, $\hat{H}_2^0$ and $\hat{S}_2^0$ are the specific enthalpy and specific entropy of the equilibrium liquid polymer. In addition, at a temperature T either above or below T_{gm}, the following expressions are valid for the equilibrium liquid polymer:

$$\hat{V}_2^0(T) = \hat{V}_2^0(T_{gm})[1 + \alpha_2(T - T_{gm})] \tag{12}$$

$$\hat{G}_2^0(T) = \hat{H}_2^0(T_{gm}) + \hat{C}_p(T - T_{gm}) - T\hat{S}_2^0(T_{gm}) - T\hat{C}_p\ln (T/T_{gm}) \tag{13}$$

As noted above, the glassy polymer has a concentration-dependent specific volume and a concentration-dependent specific Gibbs free energy since the configuration of the polymer matrix is dependent on the penetrant concentration level. In the above equations, the pressure dependence of the various quantities is not stated explicitly.

(6) The concentration dependence of T_{gm} can be represented by the following linear approximation at sufficiently low penetrant concentrations:

$$T_{gm} = T_{g2} - A\omega_1 \tag{14}$$

The coefficient A is of course dependent on the nature of

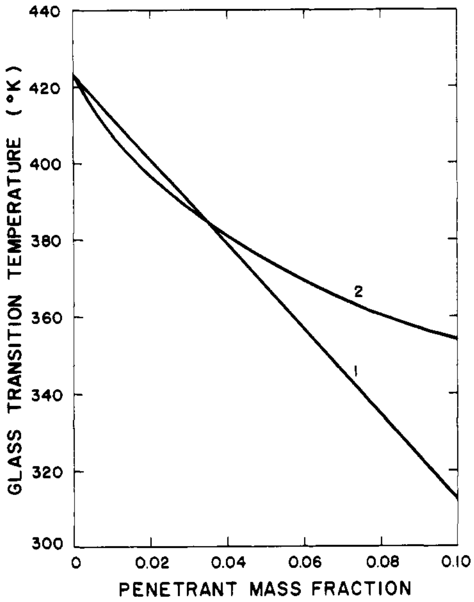

Figure 1. Concentration dependence of T_{gm} for polycarbonate–carbon dioxide system. Curve 1 is based on eq 14, and curve 2 is based on eq 15.

the penetrant, which is used to depress the glass transition temperature of a particular polymer. This linear approximately may not be adequate at higher penetrant concentrations, and hence, it is convenient, in such cases, to utilize the approximate theoretical expression derived by Chow[25] for the dependence of T_{gm} on ω_1:

$$\ln\left(\frac{T_{gm}}{T_{g2}}\right) = \beta[(1-\theta)\ln(1-\theta) + \theta\ln\theta] \qquad (15)$$

$$\beta = \frac{zR}{M_p\Delta\hat{C}_p} \qquad (16)$$

$$\theta = \frac{M_p\omega_1}{zM_1(1-\omega_1)} \qquad (17)$$

Here, M_p is the molecular weight of the polymer repeating unit, $\Delta\hat{C}_p$ is the change of the isobaric specific heat capacity of the polymer at T_{g2}, and z is the lattice coordination number. Although the equation derived by Chow has some limitations,[2] it is a useful result because it does not require an estimate for the glass transition temperature of the penetrant. Furthermore, by appropriate choice of the parameter z, it is possible to obtain predictions for T_{gm} that are in reasonably good accord with experimental measurements.[26] The glass transition temperature for the polycarbonate–carbon dioxide system is illustrated in Figure 1 by using both the linear approximation, eq 14, and the theory of Chow, eq 15. The linear approximation is based on the only two T_{gm} data points available for this system.[26] Values of T_{g2} = 150.4 °C, A = 1110 K, z = 2, M_p = 254 g/mol, and $\Delta\hat{C}_p$ = 0.055 cal/(g °C) were used to determine T_{gm} from eqs 14 and 15.[26,27] It is evident from Figure 1 that the two predictions are in reasonably good agreement up to a penetrant mass fraction of about 0.05, but significant deviations occur at higher mass fractions. It is easy to show that these differences in T_{gm} predictions do not necessarily lead to significant differences in volumetric predictions. However, sorption predictions are sensitive to the form chosen for the concentration dependence of T_{gm}.

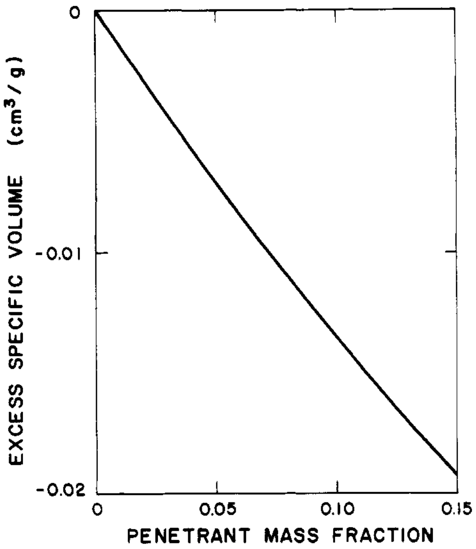

Figure 2. Concentration dependence of $\Delta\hat{V}$ for model polymer–penetrant system at 25 °C.

Table I
Properties of the Model Polymer–Penetrant System

property	value
$T_{g2}(\infty)$	373 K
$T_{g2}(M_2)$	$373 - 2 \times 10^5/M_2$ (K)
$T_{gm}(\omega_1)$	$373 - 500\omega_1$ (K)
A	500 K
$\alpha_2 - \alpha_{2g}$	3×10^{-4} K^{-1}
$\hat{C}_p - \hat{C}_{pg}$	0.06 cal/(g °C)
M_1	100 g/mol
χ	1
q (all temps)	1
$\hat{V}_2{}^0(T_{g2})$	1 cm^3/g

Volumetric Behavior

Since the proposed theory for volumetric behavior for glassy polymers has been discussed previously[21-23] (along with several data–theory comparisons), only a brief outline of the theory and some further data–theory comparisons are included here. An additive or ideal specific volume for a glassy polymer–penetrant mixture can be defined[6] as follows:

$$\hat{V}(\text{ideal}) = \omega_1\hat{V}_1{}^0 + \omega_2\hat{V}_{2g}{}^0(\omega_1{=}0) \qquad (18)$$

Hence, the excess specific volume, $\Delta\hat{V}$, for the glassy polymer–penetrant system at a particular mass fraction can be determined by using the following expression:

$$\Delta\hat{V} = \hat{V}(\text{actual}) - \hat{V}(\text{ideal}) \qquad (19)$$

Consequently, it can be shown[21] by using eqs 3, 10, 12, 14, and 18 in eq 19 that $\Delta\hat{V}$ is given by the following equation:

$$\Delta\hat{V} = -A\omega_1\omega_2\hat{V}_2{}^0(T_{g2})(\alpha_2 - \alpha_{2g}) \qquad (20)$$

The dependence of $\Delta\hat{V}$ on ω_1 for a model polymer–penetrant system at 25 °C is presented in Figure 2. The properties of the model system are listed in Table I. It is evident from Figure 2 that $\Delta\hat{V}$ is as much as about 2% of the total volume of the mixture. Also, the dependence of $\Delta\hat{V}$ on temperature is illustrated in Figure 3. At each temperature, $\Delta\hat{V}$ is evaluated at the concentration at which $T = T_{gm}$ so that this is the maximum value of $\Delta\hat{V}$ for the glassy polymer–penetrant mixture at that particular temperature. It is evident from Figure 3 that the magnitude of $\Delta\hat{V}$ decreases monotonically as T is increased from 25 to 100 °C, the glass transition temperature of the polymer, and the volume change on mixing disappears as the

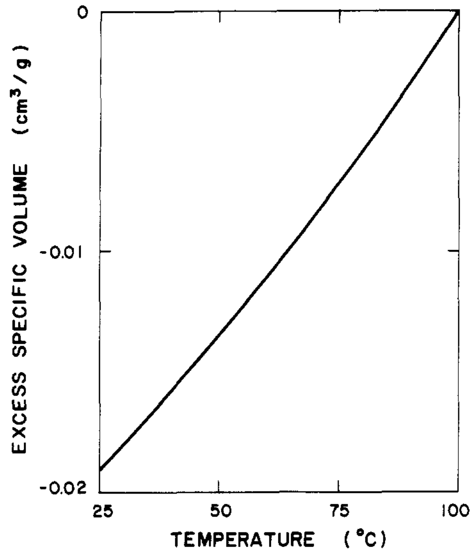

Figure 3. Temperature dependence of maximum $\Delta\hat{V}$ for model polymer–penetrant system.

polymer achieves the rubbery state. The predictions of the theory presented in these two figures are consistent with the sixth experimental observation listed above. Furthermore, it was shown previously[21,23] that the proposed theory gave good predictions for the volumetric behavior of five glassy polymer–diluent systems.

It has also been shown[22] that the proposed theory predicts that V_m, the total volume of a glassy polymer–penetrant mixture, can be determined by using the equation

$$\frac{V_m}{V_0} = \frac{\frac{\omega_1}{1-\omega_1}\hat{V}_1^0 + \hat{V}_{2g}^0(\omega_1)}{\hat{V}_{2g}^0(\omega_1=0)} \tag{21}$$

where V_0 is the volume of the pure polymer and where $\hat{V}_{2g}^0$ can be calculated from eq 10. The predictions of this equation were compared previously[22] with experimental data for the polycarbonate–carbon dioxide system,[3] and it was found that the theoretical predictions and the experimental data were in reasonably good agreement. This data–theory comparison was based on using eq 14 for T_{gm}. However, comparable deviations between theory and experiment are obtained when eq 15 is used to calculate T_{gm}. There are no adjustable parameters in the theory for volumetric behavior.

Sorption Behavior

At sorption equilibrium at constant and uniform temperature and pressure, the following equation must be satisfied[28] by the penetrant:

$$\hat{G}_1 = \hat{G}_1^g \tag{22}$$

Here, $\hat{G}_1$ is the partial specific Gibbs free energy of the penetrant in the polymer–penetrant mixture and $\hat{G}_1^g$ is the specific Gibbs free energy of the essentially pure gas phase of the penetrant at temperature T and pressure p_1. If the gas phase is ideal, $\hat{G}_1^g$ is given by the usual expression[28]

$$\hat{G}_1^g = \hat{G}_1^{g0} + \frac{RT}{M_1}\ln\left(\frac{p_1}{p_{10}}\right) \tag{23}$$

where $\hat{G}_1^{g0}$ is the specific Gibbs free energy of the gas at temperature T and reference pressure p_{10}. Furthermore, $\hat{G}_1$ can be defined by using the following equation set:

$$\left(\frac{\partial\hat{G}}{\partial\omega_1}\right)_{T,p} = \hat{G}_1 - \hat{G}_2 \tag{24}$$

$$\hat{G} = \omega_1\hat{G}_1 + \omega_2\hat{G}_2 \tag{25}$$

Here, $\hat{G}_2$ is the partial specific Gibbs free energy of the polymer in the mixture. These two equations yield the following result for $\hat{G}_1$

$$\hat{G}_1 = \hat{G} + \omega_2\left(\frac{\partial\hat{G}}{\partial\omega_1}\right)_{T,p} \tag{26}$$

so that $\hat{G}_1$ can be evaluated if the concentration dependence of $\hat{G}$, the specific Gibbs free energy of the mixture, is known. For a liquid polymer–penetrant mixture (the actual state of the binary system above T_{gm}), $\hat{G}$ is given by eqs 4 and 6 where $\hat{G}_2^0$ is not a function of concentration. Consequently, it is easy to show by using eqs 4, 6, and 26 that $\hat{G}_1$ for the penetrant for $T \geq T_{gm}$ is given by the expression

$$\hat{G}_1 = \hat{G}_1^0(T,p_1) + \frac{RT}{M_1}[\ln\phi_1 + \phi_2 + \chi\phi_2^2] \tag{27}$$

when the polymer molecular weight is sufficiently high. Equation 27 is the usual Flory–Huggins result[4] for rubbery polymer–penetrant systems, and $\hat{G}_1^0$, the specific Gibbs free energy of the pure liquid penetrant, is evaluated at T and p_1.

For a glassy polymer–penetrant mixture (the actual state of the binary system below T_{gm}), $\hat{G}$ is given by eqs 5 and 6 where $\hat{G}_{2g}^0$ is a function of the penetrant concentration. Consequently, it follows from eqs 5, 6, and 26 that $\hat{G}_1$ for the penetrant for $T < T_{gm}$ is given by the following expression for sufficiently high polymer molecular weights:

$$\hat{G}_1 = \hat{G}_1^0 + \omega_2^2\left(\frac{\partial\hat{G}_{2g}^0}{\partial\omega_1}\right)_{T,p_1} + \frac{RT}{M_1}[\ln\phi_1 + \phi_2 + \chi\phi_2^2] \tag{28}$$

Clearly, the expression for $\hat{G}_1$ in the glassy state differs from the expression for $\hat{G}_1$ in the rubbery state by the addition of a term reflecting the structural or concentration dependence of $\hat{G}_{2g}^0$. From eqs 11 and 13, it is easy to derive the expression

$$\hat{G}_{2g}^0(\omega_1,T) = \hat{G}_2^0(T) + (\hat{C}_{pg} - \hat{C}_p)\left[(T - T_{gm}) - T\ln\left(\frac{T}{T_{gm}}\right)\right] \tag{29}$$

so that

$$\left(\frac{\partial\hat{G}_{2g}^0}{\partial\omega_1}\right)_{T,p_1} = (\hat{C}_{pg} - \hat{C}_p)\frac{dT_{gm}}{d\omega_1}\left(\frac{T}{T_{gm}} - 1\right) \tag{30}$$

Consequently, $\hat{G}_1$ for the penetrant in the glassy polymer–penetrant mixture takes the following form

$$\hat{G}_1 = \hat{G}_1^0(T,p_1) + \omega_2^2(\hat{C}_{pg} - \hat{C}_p)\frac{dT_{gm}}{d\omega_1}\left(\frac{T}{T_{gm}} - 1\right) + \frac{RT}{M_1}[\ln\phi_1 + \phi_2 + \chi\phi_2^2] \tag{31}$$

where again $\hat{G}_1^0$ is evaluated at T and p_1.

From the usual thermodynamic relationships,[28] we can write

$$\hat{G}_1^0(T,p_1) = \hat{G}_1^0(T,p_1^0) + \hat{V}_1^0(p_1 - p_1^0) \tag{32}$$

where p_1^0 is the vapor pressure of the pure liquid penetrant at T and where

$$\hat{G}_1^{\,0}(T,p_1^{\,0}) = \hat{G}_1^{\,g0} + \frac{RT}{M_1}\ln\left(\frac{p_1^{\,0}}{p_{10}}\right) \tag{33}$$

Consequently, since the second term in eq 32 is often negligible, combination of eqs 22, 23, and 31–33 produces the following equation for the sorption isotherm for the glassy polymer–penetrant system for $T < T_{gm}$ at the mass fraction ω_1 of interest:

$$\frac{p_1}{p_1^{\,0}} = \phi_1 \exp[\phi_2 + \chi\phi_2^{\,2}]e^F \tag{34}$$

$$F = \frac{M_1\omega_2^{\,2}(\hat{C}_{pg} - \hat{C}_p)\dfrac{\mathrm{d}T_{gm}}{\mathrm{d}\omega_1}}{RT}\left(\frac{T}{T_{gm}} - 1\right) \tag{35}$$

When T_{gm} is given by eq 14, we have the following special form for F:

$$F = \frac{M_1\omega_2^{\,2}(\hat{C}_p - \hat{C}_{pg})A}{RT}\left(\frac{T}{T_{gm}} - 1\right) \tag{36}$$

Clearly, $F = 0$ at $T = T_{gm}$ and $F < 0$ for $T < T_{gm}$. Simnilarly, if we have a rubbery polymer, eq 27 replaces eq 31, and we recover the usual Flory–Huggins equation[4] for the sorption isotherm, valid for $T \geq T_{gm}$ at the mass fraction ω_1 of interest:

$$\frac{p_1}{p_1^{\,0}} = \phi_1 \exp[\phi_2 + \chi\phi_2^{\,2}] \tag{37}$$

It is evident from eqs 34 and 35 that the sorption equation for the glassy polymer contains well-defined properties of the polymer ($\hat{C}_p$, $\hat{C}_{pg}$, $\hat{V}_2^{\,0}$), of the penetrant (M_1, $p_1^{\,0}$, $\hat{V}_1^{\,0}$), of the polymer–penetrant mixture (the T_{gm}–ω_1 relationship), and the additional parameter χ. Of course, the parameter χ also occurs in the sorption equation for the rubbery polymer. Since χ can be estimated from solubility parameter considerations,[29] it should not be regarded simply as an adjustable constant since a value of χ close to the estimated value should be used.

For some cases, the gas phase over the polymer sample is not ideal, and furthermore, the second term in eq 32 cannot be neglected. In such cases, we can replace eq 34 by the more general sorption isotherm equation:

$$\frac{p_1}{p_1^{\,0}} = \frac{\xi^0}{\xi}e^{-y}\phi_1 \exp[\phi_2 + \chi\phi_2^{\,2}]e^F \tag{38}$$

Here,

$$\xi = \frac{f_1}{p_1} \tag{39}$$

$$\xi^0 = \frac{f_1^{\,0}}{p_1^{\,0}} \tag{40}$$

$$y = \frac{M_1\hat{V}_1^{\,0}}{RT}(p_1^{\,0} - p_1) \tag{41}$$

and f_1 and $f_1^{\,0}$ are the fugacities of the gas at T and at p_1 and $p_1^{\,0}$, respectively. All of the above results have been formulated for a polymer of infinite molecular weight. The major effect of polymer molecular weight on the sorption equation is its influence on T_{g2}. The following equation can be used to estimate the dependence of T_{g2} on the polymer molecular weight M_2:

$$T_{g2}(M_2) = T_{g2}(\infty) - B/M_2 \tag{42}$$

Here, B is an appropriate constant for a particular polymer.

A solubility coefficient s can be defined as follows

$$s = \left(\frac{C}{p_1}\right)_{\omega_1=0} \tag{43}$$

where C is the concentration of the sorbed gas in cm^3 (STP)/cm^3 polymer. Utilization of eqs 34 and 43 gives the result

$$\ln s = -(\ln p_1^{\,0}) - \ln\left(\frac{M_1\hat{V}_1^{\,0}}{22\,400}\right) - (1 + \chi) - \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{R}\left(\frac{1}{T_{g2}} - \frac{1}{T}\right) \tag{44}$$

when eq 14 is used for the concentration dependence of T_{gm}. A molar heat of solution can be defined as follows

$$\Delta\tilde{H} = RT^2\frac{\mathrm{d}\ln s}{\mathrm{d}T} \tag{45}$$

and combination of eqs 44 and 45 produces the following result for heat of sorption effects in a glassy polymer:

$$\Delta\tilde{H} = -\frac{RT^2}{p_1^{\,0}}\frac{\partial p_1^{\,0}}{\partial T} - RT^2\frac{\partial\chi}{\partial T} - M_1(\hat{C}_p - \hat{C}_{pg})A \tag{46}$$

The first and third terms in this equation are negative, and, since $\partial\chi/\partial T < 0$, the second term is positive. For a rubbery polymer, the heat of solution is given by the first two terms of eq 46.

The predictions of the above theory are now compared with experimental observations. First, predictions of the sorption behavior for the model polymer–penetrant system described in Table I are compared with the general experimental observations listed in the first section of this paper. Second, sorption data for the polycarbonate–carbon dioxide system[3] are compared with the predictions of the proposed theory. Sorption isotherms for the model polymer–penetrant system at 25 and 100 °C are presented in Figure 4. The polymer is in the rubbery state at 100

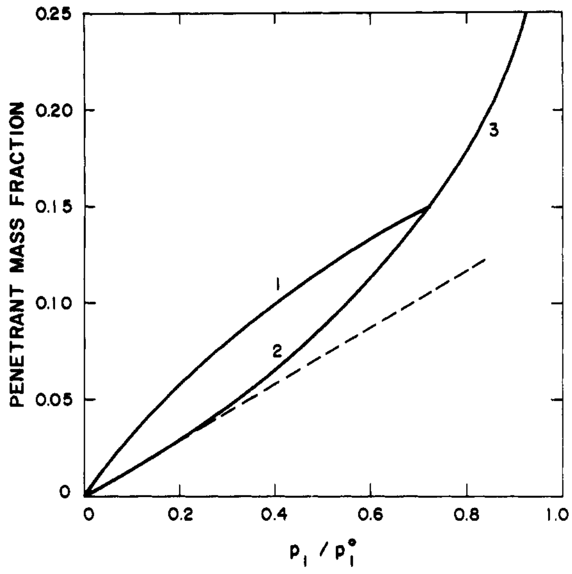

Figure 4. Sorption isotherms for model polymer–penetrant system at 25 and 100 °C. Curves 1 and 3 are for 25 °C, and curves 2 and 3 are for 100 °C. The dashed line is the linear Henry's law region for 100 °C at low pressures. Curve 3 represents the rubbery state of the system at both temperatures.

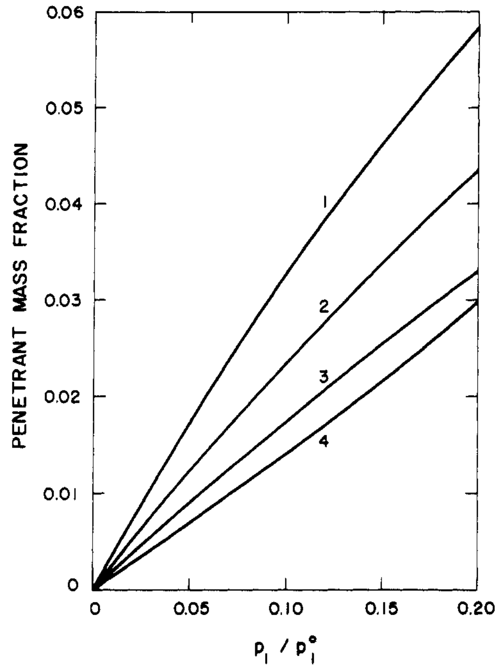

Figure 5. Temperature dependence of sorption isotherms for model polymer–penetrant system. Curves 1, 2, 3, and 4 represent 25, 50, 75, and 100 °C, respectively.

°C, and the isotherm at this temperature has a linear Henry's law region at low penetrant concentrations. In addition, the isotherm curves away from the pressure axis at higher penetrant pressures. The isotherm at 25 °C for the glassy polymer is nonlinear and has no significant Henry's law region even at the lowest penetrant mass fractions. Furthermore, the sorption isotherm curves toward the pressure axis with increasing gas pressure. These predictions of the theory are consistent with the first experimental observation listed above. Sorption isotherms at 25, 50, 75, and 100 °C are presented in Figure 5. It is clear that the sorption isotherms become more nearly linear as the temperature increases, and this prediction is consistent with the second experimental observation presented above.

The sorption isotherms for 25, 50, and 75 °C are presented in Figure 6 along with a curve that represents the behavior of the rubbery polymer at all temperatures. Each of the isotherms exhibits a shape characteristic of sorption in glassy polymers at low pressures and then achieves the shape for the rubbery polymer at higher pressures. The transition from glassy to rubbery behavior occurs at mass fractions of 0.15, 0.1, and 0.05 for the temperatures 25, 50, and 75 °C, respectively. Clearly, the transition mass fraction decreases with increasing temperature. All of these predictions are consistent with the third experimental observation presented above. The effect of polymer molecular weight on the sorption isotherm at 25 °C is depicted in Figure 7. It is evident from this figure that the extent of penetrant sorption at a given pressure increases as the polymer molecular weight increases. In addition, the sorption isotherms become more nearly linear as the polymer molecular weight decreases. These predictions are consistent with the fifth experimental observation presented above. Finally, eq 46 gives the molar heat of solution for sorption in glassy polymers whereas the heat of solution for rubbery polymers is given by eq 46 without the third term. Consequently, the presence of the negative third term for the glassy sorption process leads to the prediction that the dissolution process in a glassy polymer will be more exothermic than the dissolution process for the same gas into the rubbery form of the polymer. Furthermore, for our model polymer–penetrant system, the magnitude of the difference in sorption heats above and below T_{g2} should be of the order of 3000 cal/mol (the third term in eq 46). All of these predictions are consistent with the fourth experimental observation presented above.

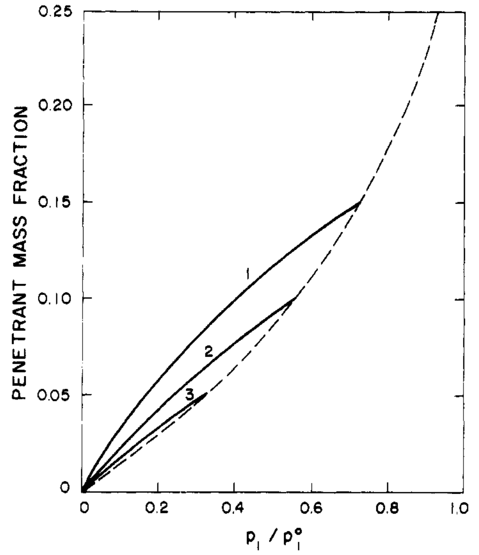

Figure 6. Sorption isotherms for model polymer–penetrant system. Curves 1, 2, and 3 represent 25, 50, and 75 °C, respectively, and the dashed line represents the rubbery state of the system at all temperatures.

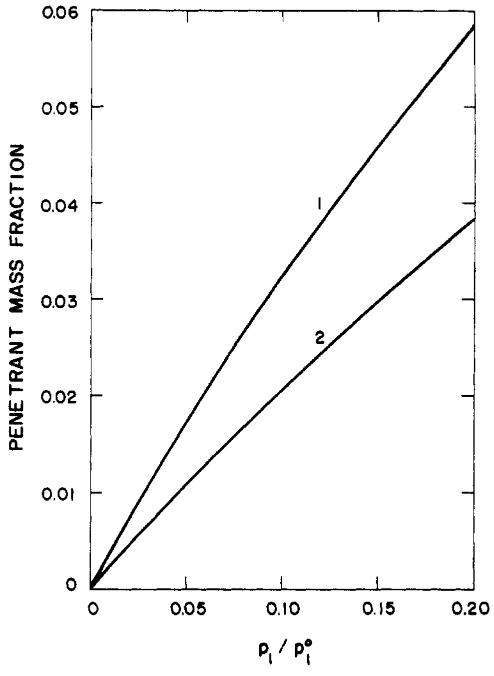

Figure 7. Effect of polymer molecular weight on sorption isotherm for model polymer–penetrant system at 25 °C. Curve 1 is for $M_2 = \infty$, and curve 2 is for $M_2 = 5000$.

A comparison of experimental sorption data[3] for the polycarbonate–carbon dioxide system at 35 °C with the predictions of the proposed model is presented in Figure 8. Values of the parameters used to compute the predictions of the theory are presented in Table II. With the exception of the parameter χ, the property values included in this table have been taken from previous publications.[3,22,26,27] The concentration dependence of T_{gm} was computed by using the theory of Chow.[25] As noted above, there is some uncertainty as to the shape of the T_{gm} versus

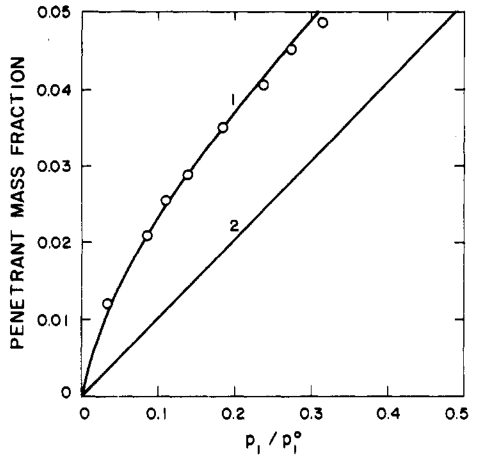

Figure 8. Comparison of theory and experiment for the sorption isotherm at 35 °C for the polycarbonate–carbon dioxide system. Curve 1 is the prediction for the glassy polymer–penetrant system, and curve 2 represents the prediction if the system were in the rubbery state. The open circles are the data of Fleming and Koros.[3]

Table II
Properties of the Polycarbonate–Carbon Dioxide System at 35 °C

property	value
T_{g2}	150.4 °C
$T_{gm}(\omega_1)$	use eq 15
M_p	254 g/mol
$\hat{C}_p - \hat{C}_{pg}$	0.055 cal/(g °C)
M_1	44 g/mol
z	2
$\hat{V}_1^0$	0.85 cm^3/g
$\hat{V}_2^0$	0.8135 cm^3/g
p_1^0	78 atm
χ	1.75

ω_1 curve for $\omega_1 > 0.05$, and consequently, the data–theory comparison was carried out only up to $\omega_1 = 0.05$. Since carbon dioxide is not an ideal gas at the pressures used in the experiments,[3] eq 38 was used to compute the theoretical isotherm. The fugacity coefficients, ξ and ξ^0, were calculated by using corresponding states correlations.[28] The parameter χ was estimated by using a solubility parameter approach[29] for nonpolar systems:

$$\chi = 0.35 + \frac{M_1 \hat{V}_1^0}{RT}(\delta_1 - \delta_2)^2 \qquad (47)$$

Here, δ_1 and δ_2 are the solubility parameters for the solvent and polymer, respectively. For polycarbonate, the following estimate[30] was used:

$$\delta_2 = 9.6\ (\text{cal/cm}^3)^{1/2} \qquad (48)$$

The solubility parameter for carbon dioxide was estimated by using the regular solution theory presented by Prausnitz[31] and data[32] for the carbon dioxide–carbon tetrachloride system at 20 °C. From this analysis, we obtain

$$\delta_1 = 5.0\ (\text{cal/cm}^3)^{1/2} \qquad (49)$$

and this gives $\chi = 1.64$. A value of $\chi = 1.75$ was used in the theory prediction.

It is evident from Figure 8 that there is good agreement between the theory and the experimental data. There are effectively no adjustable parameters in the theory although only an estimate can generally be obtained for χ. In this paper, it has been shown that the proposed theory can predict general trends and can give reasonably good agreement with actual data for volumetric and sorption behavior. It is thus fair to conclude that volumetric and sorption behavior in the glassy state can be explained by using a model that takes into account structural rearrangements of the polymer matrix. The present theory should be useful in understanding the general nature of volumetric and sorption effects in glassy polymers, and in some cases, useful predictions for the behavior of a particular system can be obtained. However, because of the history dependence of glassy-state properties, it is obvious that the proposed model will not provide good estimates in all cases. Indeed, the simple model proposed here can of course not explain the differences that have been observed in sample volumes and in sorption uptake when different sample preparation histories are utilized. However, it is reasonable to expect that the different volumetric and sorption behavior observed for different histories can be explained if appropriate account is taken of the different structural rearrangements that occur when glassy polymer samples are prepared in different ways.

In the above theory of sorption in glassy polymers, it is assumed that there is only one gas population, and a relaxation mechanism based on a simple sample preparation history is proposed for the polymer matrix. The principles of thermodynamics are then used to develop a predictive theory. The theory has no adjustable parameters since χ can be estimated from solubility parameter considerations. All of the other parameters of the theory are generally available with the possible exception of $\hat{V}_1^0$ and p_1^0 for gaseous penetrants significantly above their critical temperatures. However, methods have been developed[31] for providing reasonable estimates for these quantities. The problem of estimating the properties of a gaseous penetrant in the liquid state is also encountered when the Flory–Huggins equation is used to predict sorption isotherms for rubbery polymers. Furthermore, the term in eqs 34 and 35 that distinguishes glassy and rubbery polymers does not depend on $\hat{V}_1^0$ or p_1^0.

In the original versions of the dual-mode theory, it is assumed that there are two different molecular populations of penetrant in the polymer, and as implied above, no *explicit* mechanism for any polymer–penetrant interaction is considered. Modified versions of the dual-mode theory have been proposed[33-35] to account for significant plasticization of the polymer by the penetrant. In these modified versions, a concentration dependence is used for some of the dual-mode parameters. For example, an empirical concentration dependence is used for the Langmuir capacity constant. The modification is empirical because it is based on observed sorption behavior rather than theoretical principles. The modified theory of Chiou and Paul[33] has three, temperature-dependent adjustable parameters, and the theory of Kamiya et al.[34,35] has five adjustable parameters. It can be argued that the Henry's law part of the dual-mode sorption equation can be estimated by using method applicable to rubbery polymers. However, even if this were done, this still leaves at least two adjustable, temperature-dependent parameters for the dual-mode theory that must be determined by using sorption data at each temperature. Consequently, the dual-mode framework can be used only in a *correlative* rather than a predictive sense, whereas the theory proposed here is a *predictive* theory. Consequently, even though the modified dual-mode theory includes an empirical modification for the plasticization effect, there is little similarity between the two methods of describing sorption in glassy polymers.

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