Unified Thermodynamic Analysis of Sorption in Rubbery and Glassy Materials

A thermodynamic framework for the analysis of gas sorption in glassy polymers is established in the limit of low sorption levels. The results represent an extension of the Flory-Huggins theory to materials with nonzero internal energy changes due to deformation; the Flory-Huggins theory is recovered in the limit of zero polymer bulk modulus. The sorption isotherm is expressed in terms of the penetrant vapor-phase activity, polymer physical properties, the penetrant partial molar volume, and the heat of mixing. The qualitative form of the isotherm is shown to be unrelated to the presence of excess free volume in the polymer; only quantitative predictions are influenced. The downward curvature of the isotherm is due to the thermodynamics of solid deformation. Explicit relationships between the parameters of this work and the dual-mode model are given for the low-sorption/high-bulk modulus limit.

G. Glenn Lipscomb
Department of Chemical Engineering
University of Cincinnati
Cincinnati, OH 45221

Introduction

Polymeric films and fibers are used in many ways to control gas transport. Through the appropriate material choice, one may separate molecules or form a barrier to transport. Both types of applications are used commercially, such as for nitrogen production from air (Spillman, 1989) and for films, wraps, and bottles for packaging (Ashley, 1985).

Gas transport through these materials is commonly analyzed in terms of equilibrium sorption between a gas phase and the solid polymer followed by bulk diffusion within the solid (Spillman, 1989). The objective of this work is to develop a macroscopic thermodynamic model of the sorption component which would aid in interpreting and predicting experimental data.

Gas sorption in rubbery polymeric materials is characterized by sorption isotherms that are nearly linear, potentially with slight upward curvature, as shown in Figure 1. Such behavior is described by the Flory-Huggins theory (Flory, 1969). The penetrant concentration in the solid is given by

$$\ln\left(\frac{p}{p_s}\right) = \ln(1 - \phi_p) + \phi_p + \chi\phi_p^2 + \frac{\nu_s N_e}{V_0}\left(\phi_p^{1/3} - \frac{\phi_p}{2}\right) \quad (1)$$

where p is the applied gas pressure (Pa), p_s is the penetrant vapor pressure (Pa), ϕ_p is the polymer volume fraction, χ is the Flory-Huggins interaction parameter, ν_s is the penetrant partial molar volume (m^3/kmol), N_e is the effective number of crosslinks (kmol) and V_0 is the initial polymer volume (m^3). For low sorption levels, the relationship between gas concentration and pressure is linear and Henry's law is applicable.

The sorption behavior of a glassy polymeric material differs markedly from that of a rubber in that sorption isotherms possess downward curvature and absolute sorption levels are almost an order of magnitude higher. This difference in sorption behavior is illustrated in Figure 1. Sorption isotherms possess a strong dependence on the thermal, mechanical and prior sorption history of the glassy polymer. As with rubbery materials, Henry's law is obeyed for low sorption levels.

The most widely accepted theoretical model of sorption in glassy polymers is the dual mode model (Vieth et al., 1976; Stannett et al., 1979). This model is based on the concept of two idealized sites for sorption: one in the dense polymer itself (i.e., regions of greater polymer density) and the other in the excess free volume of microvoids (i.e., regions of lower polymer density) present within the material because of the nonequilibrium nature of a polymeric glass.

Sorption into the denser polymer regions is described by Henry's law as with rubbery polymers and low molecular weight liquids. This behavior is expressed by

$$c_D = k_D p \quad (2)$$

where c_D is the concentration of gas in Henry's law type sites

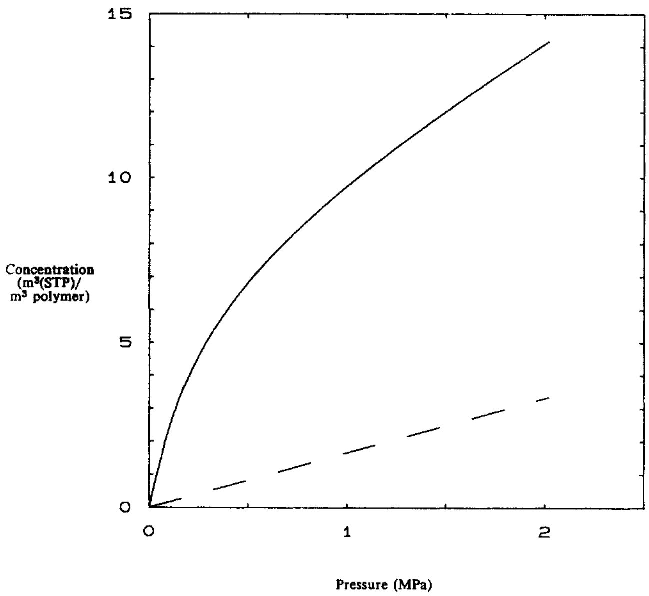

Figure 1. Comparison between sorption in glasses and rubbers.

Curves are from Koros and Paul (1978) for carbon dioxide sorption in poly(ethylene terephthalate) at different temperatures (——— glass, 25°C; — — rubber, 115°C)

[m^3(STP conditions)/m^3 polymer], k_D is the Henry's law coefficient [m^3(STP conditions)/m^3 polymer/Pa], and p is the applied gas pressure (Pa). The Henry's law component of sorption is considered to be a continuation of the rubbery polymer sorption behavior into the glassy regime.

The Langmuir component of sorption is given by,

$$c_H = \frac{c'_H b p}{1 + bp} \tag{3}$$

where c_H is the concentration of gas in Langmuir type sites, b is the Langmuir affinity constant (Pa^{-1}) and c'_H is the Langmuir capacity parameter [m^3(STP conditions)/m^3 polymer]. The presence of a Langmuir sorption component greatly increases the sorption capacity of the glass relative to an equivalent equilibrium rubber.

The total sorbed gas concentration is the sum of the Henry's law and Langmuir components,

$$c = c_D + c_H \tag{4}$$

Equations 2–4 have been used to interpret and correlate pure-gas sorption data over wide ranges of temperature and pressure. Sorption from gas mixtures may be predicted from measurements of the three sorption parameters: k_D, b, and c'_H for pure component sorption (Koros, 1980; Sanders and Koros, 1986).

The sorption parameters also correlate well with gas and polymer material properties. Correlations for the Henry's law coefficient and Langmuir affinity parameter are suggested by the van't Hoff equation in terms of the enthalpy of sorption (Koros and Paul, 1978). The enthalpy of sorption depends strongly on the condensation energy of the gas. This in turn may be related to a Lennard-Jones potential well depth or the gas critical temperature. Koros and Paul also correlate the Langmuir sorption capacity with the unrelaxed volume of the glassy polymer relative to its equilibrium liquid state.

Although the dual-mode model is a useful tool, questions linger about the validity of the underlying assumptions, i.e., two sorption sites. Volume dilation measurements seem consistent with the concept of two sorption sites (Fleming and Koros, 1986). Only the gas entering Henry's law sites contributes to volume dilation and the partial molar volume of the gas at these sites is comparable to that found in low-molecular-weight liquids. However, an alternate explanation of this behavior has been proposed where all gas molecules occupy the same volume in the polymer but the polymer occupied volume decreases (Vrentas and Vrentas, 1989). NMR and scattering measurements of polymer structure have not provided conclusive evidence about the existence of two sorption sites either.

The gas-polymer-matrix model (Raucher and Sefcik, 1983) of gas sorption in glassy polymers is one alternative to the dual-mode model. Contrary to the dual-mode model, a single sorption environment is assumed to exist and an empirical mathematical relationship containing two parameters is proposed to relate sorption to the applied gas pressure. The two models represent experimental data equally well (Barbari et al., 1988). However, the correlations of dual-mode model parameters with material properties seemingly provide more physical insight about the sorption process than the correlations obtained with the gas-polymer-matrix model parameters (Chern et al., 1983; Barbari et al., 1988).

The use of a lattice model of polymer solutions incorporating a single internal state variable, the free volume, is discussed by Astarita et al. (1989). They find that the sorption of carbon dioxide in poly(methyl methacrylate) is well represented by the theory. The authors conclude that the description of other thermodynamic and physical properties may require the use of a different and/or additional internal state variables but did not specify these.

The requirements of thermodynamic equilibrium between a stressed elastic solid and a contacting fluid are of interest to metallurgists as well. Larche and Cahn (1973, 1978a, b) derive the governing equations from the constraints imposed by the second law of thermodynamics. The solution to these equations gives the equilibrium stress and composition fields. They then determine the influence of stress gradients on the diffusive flux. However, the equilibrium state of the unstressed material, which is of interest here, is left as an experimentally determined parameter.

A significant body of recent work addresses the thermodynamics of coupled mass transport and deformation in polymeric materials; Carbonell and Sarti (1990) give a good overview of much of this effort. The results provide a thermodynamic basis for interpreting the diffusive aspects of transport but, like Larche and Cahn, invariably assume the equilibrium sorption is known *a priori*. Consequently, the present work might be regarded as a constitutive equation for sorption thermodynamics that might be incorporated into the diffusion analyses.

The thermodynamics of sorption are examined here in a manner similar to that used in the derivation of the Flory-Huggins relationship. The free energy is calculated as the sum of a term due to deformation of the solid polymer structure (to permit the inclusion of the penetrant) and a term due to mixing of the penetrant in the deformed polymer matrix. The thermodynamics of deformation are calculated assuming the polymer is an elastic solid, instead of a crosslinked rubber. Mixing is described by the same relationship used in the Flory-Huggins theory. Equating the chemical potential of the penetrant in the solid polymer with that in the gas phase provides the desired sorption isotherm.

The resulting sorption isotherms are concave to the pressure axis. This dual-mode-like behavior is a direct result of the deformation contribution to the penetrant chemical potential in the solid phase. A number of material parameters appear in the isotherm relationship. However, each parameter possesses physical significance and is measurable by independent experiments. Model predictions compare favorably with experimental data for carbon dioxide sorption in polycarbonate where all the parameters may be estimated except for one. Finally, a direct comparison between the material parameters introduced here and those in the dual-mode model suggest that the ratio $(bc'_H)/k_D$ should be identically two for low sorbing gases in high modulus polymers. This relationship is indeed found experimentally for nitrogen sorption in many polymeric materials.

Thermodynamics of Deformation and Mixing

The change in Gibbs free energy accompanying sorption is calculated from the thermodynamic path illustrated in Figure 2. For the analysis presented here, only isothermal conditions are considered. The pure polymer is taken from some reference pressure, p_{Rp}, and arbitrary stress state to the pressure of the sorption experiment. The polymer is then deformed to the shape it will take upon sorption but in the absence of the penetrant. This deformation is accomplished through the application of some fictitious stress. The magnitude of the deformation is related to the quantity of penetrant sorbed through the partial molar volume of the penetrant in the solid polymer. Finally, the penetrant and deformed polymer are mixed as the fictitious stress is removed.

For an ideal elastic solid in the small deformation limit, the change in Gibbs free energy, G, accompanying deformation is given by,

$$\Delta G = V_0 \int_\epsilon (\sigma_{i0} + (C_{ij})_0\epsilon_j + p\delta_i')d\epsilon_i + \int_p V\,dp + O(\epsilon^3) \quad (5)$$

where V is the polymer volume, ϵ_i is the strain, σ_i is the stress, C_{ij} are the isothermal elastic coefficients, p is the pressure and the subscript 0 means evaluated in the undeformed state. The vector constant δ' is defined as,

$$\delta' = [1 \quad 1 \quad 1 \quad 0 \quad 0 \quad 0] \quad (6)$$

The derivation of Eq. 5 is given in the appendix.

The change in Gibbs free energy associated with the first step of the thermodynamic process is obtained from Eq. 5 by integrating from the reference pressure p_{Rp} to the experimental pressure p. This also requires specifying the relationship between σ_i, ϵ_i, and p. The undeformed state will be taken as the solid at the reference pressure and the initial stresses within the solid will be represented by σ_{iR}; this stress must satisfy a force balance, i.e., Eq. A4 in the appendix, but otherwise is arbitrary. A solution to the force balance for homogeneous elastic solids undergoing compression is (Mase, 1970),

$$\sigma_{i0} + (C_{ij})_0\epsilon_j = \sigma_{iR} - p\delta_i' \quad (7)$$

In general the associated strains are a function of the final pressure only. For an isotropic solid they are given by,

$$\begin{aligned} \epsilon_1 = \epsilon_2 = \epsilon_3 &= -\frac{(p - p_{Rp})}{3B_R} \\ \epsilon_4 = \epsilon_5 = \epsilon_6 &= 0 \end{aligned} \quad (8)$$

Therefore, the Gibbs free energy change associated with moving from the reference pressure to the experimental pressure is,

$$\Delta G_1 = V_R\sigma_{iR}\epsilon_{iR} + \int_{p_{Rp}}^{p} V\,dp \quad (9)$$

where the subscript R represents the undeformed state at the reference pressure.

The Gibbs free energy change due to the second step is obtained from Eq. 5 by integrating from the undeformed state to the final deformation state ϵ_i at constant pressure. The undeformed state for this integration is taken to be the final state of the solid after the first step of the thermodynamic path. Integrating Eq. 5 gives,

$$\Delta G_2 = V_0\sigma_{iR}\epsilon_i + \frac{1}{2}V_0(C_{ij})_0\epsilon_i\epsilon_j + O(\epsilon^3) \quad (10)$$

where the subscript 0 now refers to the aforementioned undeformed state. The integration requires a statement of the relationship between the ϵ_i. For the homogeneous deformations considered here, the ratio of any two strains is a constant that is independent of the magnitude of the deformation. This requirement introduces the factor of ½ multiplying the off-diagonal isothermal elastic coefficients just as with the diagonal components. The same result may be obtained by expanding the Gibbs free energy instead of the stress in a Taylor series about the

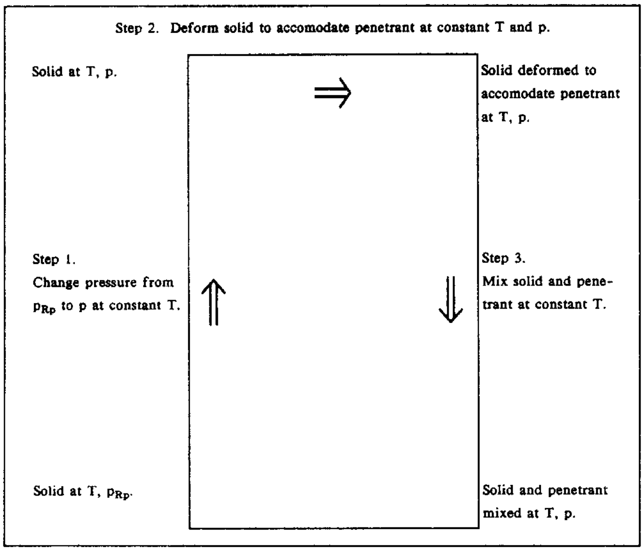

Figure 2. Three steps of the thermodynamic path used to calculate the free energy changes associated with sorption.

undeformed state as Theodorou and Suter (1986) did for the internal energy. The explicit form of the ϵ_i is discussed below.

The total change in Gibbs free energy of the first two steps is the sum of Eqs. 9 and 10,

$$\Delta G_{\mathrm{Deform}} = V_0 \sigma_{iR} \epsilon_i + \frac{1}{2} V_0 (C_{ij})_0 \epsilon_i \epsilon_j + \Delta G_1(p) + O(\epsilon^3) \quad (11)$$

where $\Delta G_1(p)$ is a function of pressure only and is independent of sorption. This expression is general and should apply to all elastic solids, whether rubbery or glass-like, in the small deformation limit if the appropriate material constants are used.

In the derivation, the following assumptions were introduced: 1) small, homogeneous deformations, 2) reversible processes, and 3) isothermal conditions. Nonhomogeneous deformations are described as well if V_0 is replaced by a differential volume and Eq. 5 is integrated over the volume of the system.

Materials that undergo plastic deformation or involve concentration changes that take the material through the glass-rubber transition (i.e., the concentration exceeds the glass transition concentration c_g) will violate the reversibility assumption and consequently will not be adequately described by Eq. 11. For such systems, irreversible heat changes are important and must be accounted for through a memory integral.

The final step of the thermodynamic path illustrated in Figure 2 involves the Gibbs free energy change associated with mixing the deformed polymer and penetrant. A commonly used expression for the free energy change upon mixing for polymeric solutions is given by Flory (1969)

$$\Delta G_{\mathrm{Mix}} = kT[n_s \ln(\phi_s) + n_p \ln(\phi_p) + \chi n_s \phi_p] \quad (12)$$

where n_s and n_p are the number of sorbed penetrant and polymer molecules, respectively; ϕ_s and ϕ_p are the volume fraction of sorbed penetrant and polymer, respectively; χ is the interaction parameter for the given penetrant-polymer system. The first two terms of Eq. 12 represent the entropy of mixing while the last term accounts for enthalpic effects.

Although Eq. 12 does not provide a perfect description of real polymer solutions, it does appear to contain the essential components of the free energy change due to mixing (Prausnitz, 1969). For certain systems, the interaction parameter is found to vary with polymer volume fraction (Barton, 1990). In the small deformation limit, however, this should not be a problem since concentration changes are small.

The total change of Gibbs free energy accompanying the thermodynamic path of Figure 2 is given by the sum of Eq. 11 and 12,

$$\Delta G = V_0 \sigma_{iR} \epsilon_i + \frac{1}{2} V_0 (C_{ij})_0 \epsilon_i \epsilon_j + kT \cdot [n_s \ln(\phi_s) + n_p \ln(\phi_p) + \chi n_s \phi_p] + \Delta G_1(p) + O(\epsilon^3) \quad (13)$$

Finally, to obtain a sorption isotherm, the chemical potential of the penetrant must be calculated from,

$$\mu_s = \frac{\partial(G)}{\partial n_s} \quad (14)$$

Evaluation of the partial derivatives requires knowledge of the relationships between n_s, ϵ_i, ϕ_s, and ϕ_p; n_p will be taken as a constant since the polymer volatility is negligible at the temperatures of interest here.

To obtain these relationships, an expression for the total volume of polymer and penetrant is needed. The total volume is related to n_s and V_0 through,

$$V = V_0 + V_s = V_0 + \frac{n_s \nu_s}{N_{AV}} \quad (15)$$

where V_s is the volume occupied by the penetrant, ν_s is the partial molar volume of the penetrant in the polymer, and N_{AV} is Avogadro's number. Note that all molecules are assumed to produce the same volume change upon sorption; this change is given directly by ν_s. The volume fraction of penetrant and polymer may be expressed as follows,

$$\begin{aligned} \phi_s &= \frac{V_s}{V} = \frac{n_s \nu_s}{V_0 N_{AV} + n_s \nu_s} \\ \phi_p &= 1 - \phi_s = \frac{V_0 N_{AV}}{V_0 N_{AV} + n_s \nu_s} \end{aligned} \quad (16)$$

Evaluation of ϵ_i as a function of n_s requires specification of the deformation field accompanying sorption. For an unconstrained isotropic homogeneous polymer sample, a solution to the force balance is a state of uniform hydrostatic tension characterized by the following strains,

$$\begin{aligned} \epsilon_1 &= \epsilon_2 = \epsilon_3 = \frac{\epsilon}{3} \\ \epsilon_4 &= \epsilon_5 = \epsilon_6 = 0 \end{aligned} \quad (17)$$

For this deformation field, the volume of the sample is related to ϵ through,

$$V = V_0[1 + tr(\underline{\underline{\epsilon}})] = V_0(1 + \epsilon) \quad (18)$$

Substituting the above expressions for ϵ_i, ϕ_s, and ϕ_p, the chemical potential of the penetrant in the polymer becomes,

$$\begin{aligned} \mu_s - \mu_{Rs} = \Bigg\{ & \left(\frac{tr(\underline{\underline{\sigma}}_R)}{3}\right)\left(\frac{\nu_s}{N_{AV}}\right) + B_0 \left(\frac{\nu_s}{N_{AV}}\right)^2 \left(\frac{n_s}{V_0}\right) \\ & + kT\left[\ln\left(\frac{n_s \nu_s}{V_0 N_{AV} + n_s \nu_s}\right) + \left(\frac{V_0 N_{AV}}{V_0 N_{AV} + n_s \nu_s}\right) \right. \\ & \left. \cdot \left(1 - \left(\frac{n_p \nu_s}{V_0 N_{AV}}\right)\right)\right] + \chi \left(\frac{V_0 N_{AV}}{V_0 N_{AV} + n_s \nu_s}\right)^2 \Bigg\} \end{aligned} \quad (19)$$

where μ_{Rs} is an appropriate reference chemical potential. Equation 19 does not contain an explicit dependence on the experimental pressure; the dependence on pressure is contained implicitly by the dependence of penetrant concentration on pressure.

The chemical potential of the penetrant in the vapor phase is related to its activity by,

$$\mu_s - \mu_{Rs} = kT \ln(a_s) = kT \ln\left(\frac{\gamma p}{p_{Rs}}\right) \quad (20)$$

where the activity, a_s, is replaced by an activity coefficient, γ, and a reference pressure, p_{Rs}, at which the penetrant activity is unity, i.e., the vapor pressure at the experimental temperature. Note that the reference chemical potential for the solid (polymer) phase is taken to be the same as that for the gas phase. If the experimental temperature is greater than the critical temperature of the penetrant, the vapor pressure, and hence Eq. 20, is undefined. One may overcome this limitation for small departures above the critical temperature by simply extrapolating the vapor pressure data (Prausnitz, 1969). For temperatures much greater than the critical temperature, one may utilize a hypothetical liquid for the reference state, but p_{Rs}/γ may not be specified *a priori* because this quantity must be determined experimentally.

Equating the chemical potential of the penetrant in the gas to that in the polymer one obtains,

$$p = \left(\frac{p_{Rs}}{\gamma}\right) \exp\left[\frac{tr(\underline{\underline{\sigma}}_R)\nu_s}{3RT}\right] \cdot \left(\frac{c\nu_s}{1 + c\nu_s}\right) \exp\left[\left(\frac{1 - c_p\nu_s}{1 + c\nu_s}\right) + \chi\left(\frac{1}{1 + c\nu_s}\right)^2 + \left(\frac{B_0\nu_s}{RT}\right)c\nu_s\right] \quad (21)$$

where c and c_p are the molar concentrations, per unit volume polymer, of penetrant and polymer, respectively

$$c = \frac{n_s}{V_0 N_{AV}} \qquad c_p = \frac{n_p}{V_0 N_{AV}} \quad (22)$$

The definition of c_p is equivalent to the polymer molar density.

In the literature, penetrant concentration is most commonly expressed in units of $m^3(STP)/m^3$ polymer. The polymer volume is that measured at the experimental temperature and atmospheric pressure in the absence of sorption. To convert the concentration in Eq. 37 to these units, one must multiply by $22.4(V_0/V_{\text{atm}})$. The ratio V_0/V_{atm} converts the polymer volume from the experimental pressure to atmospheric pressure while the factor of 22.4 converts moles penetrant to m^3(STP). After substituting $(p - p_{\text{atm}})$ for $(p - p_{Rp})$ in Eq. 8 to calculate the strains due to the accompanying compression or expansion, the ratio V_0/V_{atm} is given by Eq. 34,

$$\frac{V_0}{V_{\text{atm}}} = 1 - \frac{(p - p_{\text{atm}})}{B_0} \quad (23)$$

For pressures up to 1% of the bulk modulus, this ratio is unity to within less than one percent error. Glassy polymers have bulk moduli on the order of 10^9 Pa; 1% of this figure corresponds to approximately 100 atm.

Equation 21 is the final result for the sorption isotherm relating penetrant vapor pressure to concentration in the polymer. It differs from the Flory-Huggins theory of penetrant-induced swelling in rubbers only in the stress related terms, i.e., the preexponential factor involving the stress and the bulk modulus term in the exponential. The magnitude of these terms reflects the importance of the Gibbs free energy change of deformation relative to the Gibbs free energy change of mixing. The origin of these terms and the differences between the Flory-Huggins approach and the thermodynamics presented here become more apparent if one explicitly considers the internal energy and entropic contributions to the free energy.

Deformation of the rubbery state is primarily entropic in nature since the internal energy change of an ideal rubber is identically zero. The magnitude of the associated free energy change is small, relative to that for mixing, except for highly crosslinked materials (Flory, 1969). For glassy materials, however, Theodorou and Suter (1986) show that the internal energy contribution is much larger than the entropic contribution to the free energy change of deformation. These changes in thermodynamics are due to physical changes associated with the rubber-glass transition and appear in the sorption isotherm given by Eq. 21 as a dramatic increase in the bulk modulus (from a value of zero corresponding to the Flory-Huggins theory to some finite value). The quantitative effect of bulk modulus is discussed further in the next section. Consequently, one might view the current work as an extension of the Flory-Huggins theory to materials with nonzero internal energy changes of deformation.

Seven material parameters appear in the sorption isotherm: γ, p_{Rs}, ν_s, c_p, χ, B_0, and $tr(\underline{\underline{\sigma}}_R)$. Fortunately, four may be readily obtained from the literature or measured *a priori*. The polymer bulk modulus and molar density are tabulated for many common polymers in the Polymer Handbook (Brandup and Immergut, 1975). These properties may be determined independently if they are not available in the literature or one suspects a strong dependence on processing conditions, e.g., quenching and annealing. If the experimental temperature is not much greater than the penetrant's critical temperature, expressions for the vapor pressure and activity coefficient of numerous gases are available in standard reference texts (Reid et al., 1977). Otherwise, the ratio p_{Rs}/γ must be determined from experimental sorption data.

It is more difficult to evaluate the remaining three parameters. It is possible, however, to measure the partial molar volume of the penetrant in the polymer (Fleming and Koros, 1986). Since the data reduction requires knowledge of the sorption isotherm, use of these measurements would not permit *a priori* sorption predictions but the volumetric data should provide a check on the consistency of the thermodynamic analysis. Finally, an upper limit on the magnitude of the partial molar volume may be obtained from measurements in low-molecular-weight liquids as discussed by Fleming and Koros.

Values of the interaction parameter for many polymer-penetrant pairs are tabulated by Barton (1990). If the desired information is unavailable, one could determine the interaction parameter from calorimetric measurements of the heat of sorption. Such data are present in the literature for some systems based on measurements using small molecule analogues. The small energy changes resulting from solid deformation (Chrysochoos and Martin, 1989) adsorption on solid surfaces (Woodbury and Noll, 1987) and heats of immersion (Aukett, 1988) are also directly observable using a microcalorimeter, but these techniques have not been applied to penetrant sorption in glassy polymers.

Finally, the stress state at the reference pressure, i.e., residual stresses in the glassy polymer, could be minimized through annealing and thereby neglected in the sorption isotherm. Direct experimental measurement of residual stresses is also possible (Hornberger and DeVries, 1987). The effect of annealing on experimental measurements is well known (Chan and Paul, 1979; Moe et al., 1988), and most sorption isotherms are determined using well annealed or conditioned samples to promote reproducibility.

Experimental Comparison

As a test of the proposed sorption isotherm, the predictions of Eq. 37 are compared with the recently published experimental data of Fleming and Koros (1986). In this particular work, complimentary sorption and volume dilation data are provided for carbon dioxide sorption in polycarbonate. From the experiment data, the authors calculate ν_s for the carbon dioxide penetrant.

For this system, one may also obtain all but one of the required material parameters from the literature and three physically realistic approximations. The low vapor pressures and concomitant low sorption levels, which are required for validity of the thermodynamics, suggest that one may take the carbon dioxide vapor-phase activity coefficient to be unity. However, the vapor pressure of carbon dioxide at the experimental temperature of 35°C is undefined, since the temperature is slightly above the critical temperature of 31.2°C. Following Fleming and Koros, the vapor pressure data are extrapolated beyond the critical temperature to obtain a reasonable estimate of p_{R_s} for determination of the vapor-phase activity. This extrapolation gives a value of 7.8 MPa.

The initial stress state, $tr(\underline{\underline{\sigma}}_R)$, is assumed to be that of near zero stress. Such an approximation should be good for well annealed samples as discussed previously. Indications of high residual stress might be indicated by curling of the unsupported film. For residual stresses to be significant, the stresses would have to be of order $B_0 c \nu_s$ which for low sorption levels is of order 1.0 MPa. Hornberger and DeVries (1987) found that compressive residual stresses in rapidly quenched glassy polycarbonate could reach 14–18 MPa which is much larger than the 1.0 MPa threshold. Obviously, residual stresses can be important but their effect is neglected here.

At infinite dilution, Fleming and Koros give the value of ν_s as 0.018 m^3/kmol. This number increases nearly linearly with sorption pressure over a range of 50 atm; however, we are concerned with only the low sorption pressure range. Interestingly, ν_s in the glassy polycarbonate is almost three times smaller than that observed in low-molecular-weight liquids. One might expect the penetrant partial molar volume in a glass to be smaller than that in a liquid, because the nonequilibrium nature of the glass introduces excess free volume which a penetrant molecule can partially occupy. Consequently, the volume of solid that a penetrant molecule must displace, i.e., its partial molar volume, is reduced; and as the excess free volume is filled, ν_s should increase. Although the concept of excess free volume helps provide a physical understanding of the temperature and composition dependence of ν_s, one does not explicitly take into account excess free volume once the partial molar volume is known.

The polymer molar density, c_p, is readily calculated from the polymer density and molecular weight. While the polycarbonate density is given by Fleming and Koros, the molecular weight is not. However, for any physically realistic molecular weight, $c_p \nu_s$ should be much less than unity and may be neglected.

Finally, the *Polymer Handbook* (Brandup and Immergut, 1975) gives a value of 2.4 GPa for the bulk modulus of a generic polycarbonate. The bulk modulus will be taken to be independent of pressure so that B_0 is a constant and equal to B_R. As previously discussed, one could independently perform mechanical tests on the as-processed membrane to determine the bulk modulus if literature values are questionable.

Combining the literature information and above approximations provides values for all the material parameters except the interaction parameter, χ. The interaction parameter may be estimated by fitting the functional form of Eq. 21 to the experimental sorption data. For the purposes of this estimation, the data are represented by the dual-mode model equations (Eqs. 2–4). Values for the material parameters are given by Fleming and Koros and are listed in Table 1. Virtually all of the data used to obtain these parameters are outside of the pressure range of interest here. However, the dual-mode model should still provide a reasonable estimate of sorption at lower pressures.

The parameter space $-5 < \chi < 5$ was systematically searched to find the minimum of the following objective function,

$$\int_{p=0}^{p=1\,\text{atm}} \left[\frac{c_T - c_{DM}}{c_{DM}(1\text{ atm})}\right]^2 dp \tag{24}$$

where c_T and c_{DM} are the penetrant concentrations predicted by the present work, Eq. 21 and the dual-mode model, Eqs. 2–4, respectively. Note that the concentration appearing in Eq. 21 must be multiplied by $22.4(V_0/V_{\text{atm}})$ to get c_T. The upper limit on p corresponds to almost 0.5% vol. change; and one would not expect volume changes greater than this to be adequately described by the thermodynamic analysis.

A plot of Eq. 24 as a function of χ is given in Figure 3 clearly indicating a single local minimum exists in the parameter space scanned. The minimum occurs at a χ value of 0.16. In contrast to this work, Muruganandam et al. (1987) estimated χ as 0.22 for carbon dioxide sorption in polycarbonate from experimental sorption data. A comparison of the pressure–concentration relationships obtained from Henry's law (in this figure and all subsequent figures, the Henry's law slope is taken as the initial slope of the sorption isotherm, i.e., $k_D + bc'_H$), the dual-mode model and the present work is shown in Figure 4. The agreement between dual-mode predictions and the thermodynamic results is quite good. The complete set of material parameters used to obtain Figure 4 are summarized in Table 2.

An extension of the results to higher pressures is shown in Figure 5; the material constants are the same as those in Figure 4. A much better fit is possible by taking any two of the material constants as adjustable parameters, but this would just be an exercise in curve fitting. The volumetric data of Fleming and Koros does suggest, however, that a larger value of ν_s should be used because the penetrant partial molar volume increases with pressure. Increasing ν_s to 0.0255 m^3/kmol while holding the remaining parameters constant gives Figure 6. (This figure is approximately the average value over the pressure range shown.) The qualitative features are certainly reproduced while the quantitative agreement is remarkably good. One could further

Table 1. Dual-Mode Model Parameters for CO_2 Sorption in Polycarbonate

Parameter	Value
k_D	$0.685\ 10^{-5}$ m^3 (STP)/(m^3 Polymer)/Pa
b	$0.262\ 10^{-5}$ Pa^{-1}
c'_H	18.8 m^3 (STP)/(m^3 Polymer)

From Fleming and Koros (1986)

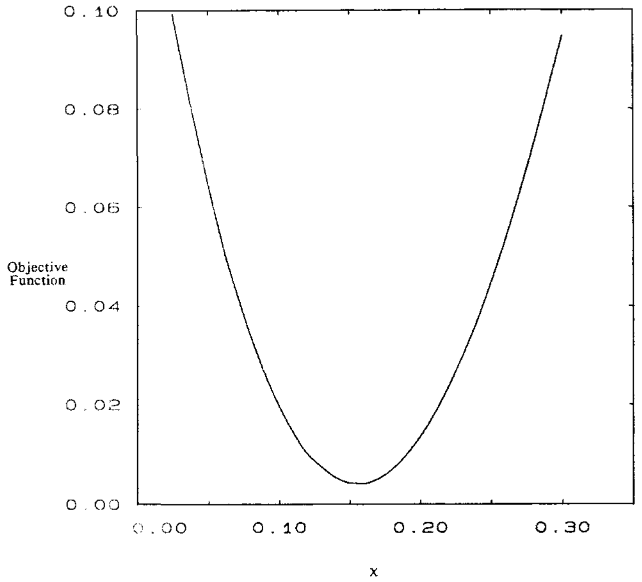

Figure 3. Objective function of Eq. 24 as a function of the interaction parameter, χ.

improve the quantitative predictions by explicitly accounting for the dependence of ν_s on concentration instead of using an average value. The proper procedure for doing this is being developed.

The effect of changing the bulk modulus is illustrated in Figure 7 to demonstrate that both glassy and rubbery sorption isotherms are predicted by the thermodynamic analysis. Increasing the bulk modulus from the literature value increases the downward concavity while decreasing the bulk modulus decreases it. In the limit of a zero reference stress state and bulk modulus, the sorption isotherm (Eq. 21) reduces to the Flory-Huggins theory of penetrant-induced swelling in rubbery materials as previously discussed. This limit should correspond to the glass-rubber transition since the rubber bulk modulus is two or three orders of magnitude smaller than the bulk modulus of the equivalent glass (Cowie, 1973).

Table 2. Material Parameters and Constants Used to Obtain the Sorption Isotherms of Figure 4

Parameter	Value
R	8314 (Pa · m^3)/(kmol · K)
T	308 K
p_{Rs}	7.8 MPa
γ	1
$tr(\underline{\underline{\sigma}}_R)$	0 Pa
ν_s	0.018 m^3/kmol
c_p	0 kmol/m^3
χ	0.16
B_0	2,400 MPa

Figure 7 also shows the sorption predictions for an equivalent rubbery material with a bulk modulus of 1 MPa and using the value of ν_s found for low-molecular liquids, 0.046 m^3/kmol. The qualitative form of the curve is indeed that of a rubber and the magnitude of the sorption is approximately three times smaller than that of the glass at low pressures. Such a prediction might be tested by measuring sorption of carbon dioxide in a liquid of polycarbonate monomer, i.e., a small molecule analogue of the polycarbonate polymer.

Relationship to the Dual-Mode Model

The results of the previous section indicate that the thermodynamic analysis of penetrant uptake in elastic solids, i.e., gas sorption in glassy polymers, can provide a quantitative description of sorption isotherms at low pressures and a qualitative picture of sorption behavior over a much wider pressure range. In particular, the concave downward nature of a sorption

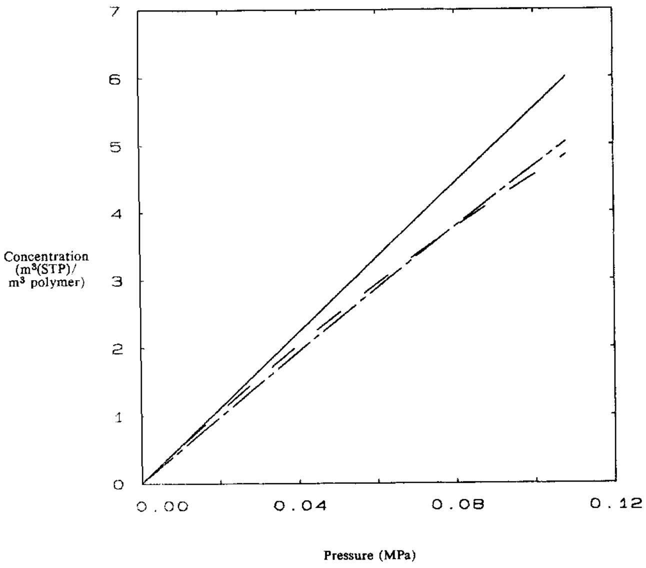

Figure 4. Low-pressure sorption isotherms for carbon dioxide in polycarbonate.

Predicted by Henry's law (———); dual-mode theory (— —); and the current work (—·—)

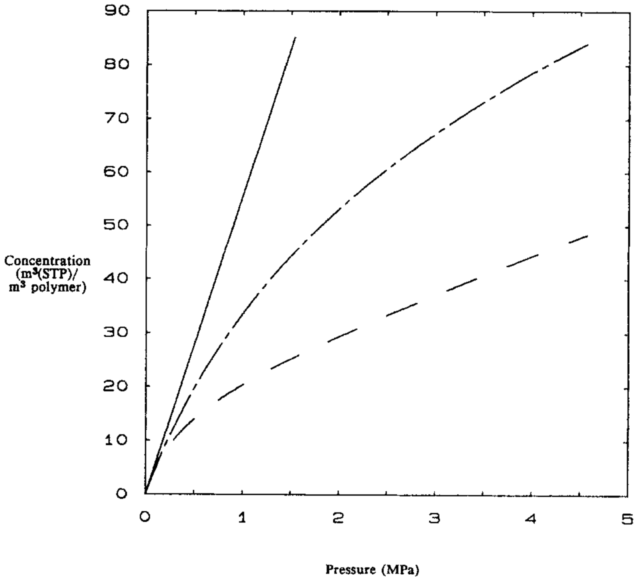

Figure 5. Extension of the results in Figure 4 to higher sorption pressures.

(———) Henry's law; (— —) dual-mode theory; (—·—) current work

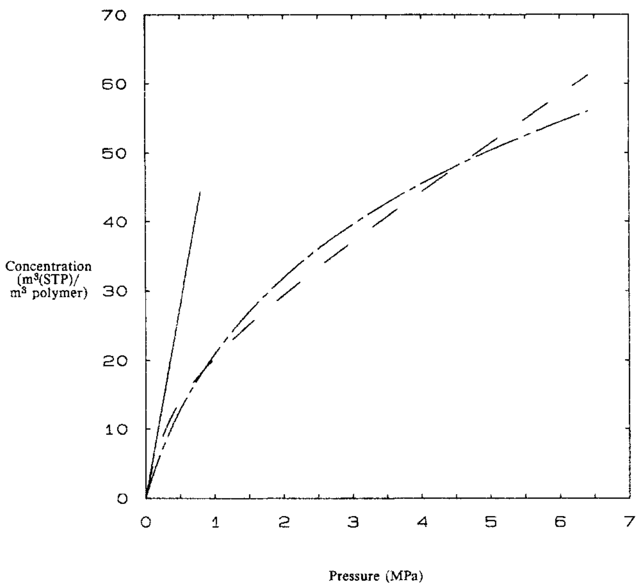

Figure 6. Effect of changing the carbon dioxide partial molar volume to a more realistic value on the high-pressure sorption isotherm.

(———) Henry's law; (— —) dual-mode theory; (—·—) current work

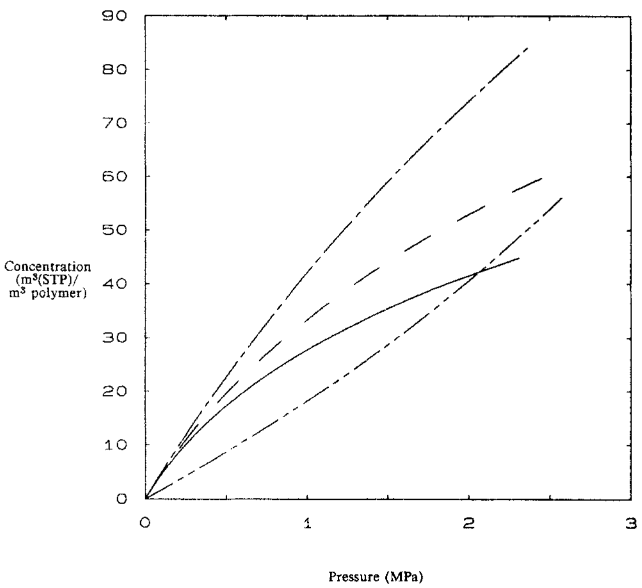

Figure 7. Effect of varying the polycarbonate bulk modulus on carbon dioxide sorption.

(———) $B_0 = 4{,}000$ MPa; (— —) $B_0 = 2{,}400$ MPa; (—·—) $B_0 = 1{,}000$ MPa; and (—----—) predicted sorption isotherm of the equivalent rubber

isotherm is predicted. It also predicts the experimental observation that gas solubilities in the glass are significantly higher than in the equivalent rubber. The ratio of gas solubilities at zero pressure is given by,

$$\frac{\left(\dfrac{\partial c}{\partial p}\right)_{c=0,\,\text{Glass}}}{\left(\dfrac{\partial c}{\partial p}\right)_{c=0,\,\text{Rubber}}} = \frac{\nu_{s,\,\text{Rubber}}}{\nu_{s,\,\text{Glass}}} \exp\left(-\frac{tr(\underline{\underline{\sigma}}_R)\nu_{s,\,\text{Glass}}}{3RT}\right) \tag{25}$$

where the rubber solubility is given by Eq. 21 when the bulk modulus is zero, as discussed in the previous section. Experimental data indicate that the ratio of penetrant partial molar volumes can be a factor of three (Fleming and Koros, 1986). One would expect this ratio to be greater than or equal to one for all materials which possess excess free volume due to the nonequilibrium nature of the glass-rubber transition as discussed in the previous section. Additionally, one would expect the apparent penetrant partial molar volume in unannealed samples to be smaller than in well annealed samples based on the decrease in sorption capacity and volume which accompanies annealing (Moe et al., 1988).

Although neglected for well annealed samples, the reference stress state could conceivably contribute another factor of three to Eq. 41 in unannealed samples if it is the same order of magnitude as RT, 2.5 MPa at 300 K. As noted in the previous section, residual stresses of such magnitude can appear in rapidly quenched materials.

The relationship between the material parameters of the thermodynamic analysis and the dual-mode model is of interest. Although a straightforward identification is not possible, one may expand both expressions in Taylor series expansions and compare terms of equal order. This is most conveniently done by expanding the pressure in terms of the penetrant concentration about the point of zero concentration.

Such an expansion permits only one clear identification from the $O(c)$ term and that is,

$$k_D + bc'_H = \left(\frac{22.4\gamma}{p_{Rs}\nu_s}\right) \exp\left[-\frac{tr(\underline{\underline{\sigma}}_R)\nu_s}{3RT} - 1 - \chi\right] \tag{26}$$

where the ratio V_0/V_{atm} is taken to be unity. The quantity $k_D + bc'_H$ is the low-pressure slope of the sorption isotherm. Since c'_H is zero above the glass transition temperature and nonzero below, the temperature dependence of this quantity changes discontinuously at the glass transition temperature. An equivalent change occurs in the righthand side of Eq. 42 because of the temperature dependence of the penetrant partial molar volume, i.e., the effect of excess free volume arising from the glass–rubber transition on ν_s discussed previously.

When $(B_0\nu_s/RT)$ is much larger than unity, equality of the first three terms in the Taylor series expansions require the relationships given in Table 3. Note that k_D and bc'_H are

Table 3. Thermodynamic vs. Dual-Mode Model Material Parameters for Low-Sorption Gases in High-Modulus Polymers

Parameter	Relationship
k_D	$\left(\frac{22.4\gamma}{3p_{Rs}\nu_s}\right)\exp\left[-\frac{tr(\underline{\underline{\sigma}}_R)\nu_s}{3RT} - 1 - \chi\right]$
b	$\left(\frac{(9/2)}{22.4}\right)\left(\frac{B_0\nu_s^2}{RT}\right)k_D$
c'_H	$\left(\frac{22.4}{(9/4)}\right)\left(\frac{RT}{B_0\nu_s^2}\right)$

Table 4. Dual-Mode Parameters for Nitrogen Sorption in Polymers Based on Bis-Phenol *A*

Polymer	k_D 10^5 m^3(STP)/ (m^3 Polymer)/Pa	b 10^5 Pa^{-1}	c'_H m^3(STP)/ (m^3 Polymer)	bc'_H/k_D
Polycarbonate	0.091	0.056	2.11	1.3
Polysulfone	0.075	0.016	9.98	2.1
Polyetherimide	0.063	0.045	4.15	3.0
Polyarylate	0.081	0.074	1.22	1.1
Tetramethyl Polycarbonate	0.102	0.032	8.43	2.6
Tetrachloro Polycarbonate	0.145	0.046	6.22	2.0
Tetrabromo Polycarbonate	0.148	0.061	4.63	1.9

From Muruganadam et al. (1987); Barbari et al. (1988)

independent of the bulk modulus and that the ratio (bc'_H/k_D) is identically two. This prediction is readily tested using literature data, but is strictly valid only for gas-polymer pairs in which: 1. $(B_0 \nu_s/RT)$ is much larger than unity; 2. the partial molar volume of the gas is a constant; and 3. deformations are small and reversible. Although the above relationships are limited in applicability, they can provide physical insight into the sorption process.

A significant amount of experimental sorption data for a number of different gases and polymers based on Bis-phenol *A* is available from Koros' research group (Muruganandam et al., 1987; Barbari et al., 1988). Simple calculations clearly show that k_D/bc'_H is generally greater than two and varies from 1.1 to 12 for the data taken at 35°C. One would expect the lowest sorbing gas with the highest modulus polymer to obey the relationships most closely in Table 3. Of the gases considered, nitrogen sorption is the lowest. Table 4 summarizes the dual-mode model parameters obtained for nitrogen sorption into seven polymers based on Bis-phenol *A*. As indicated in Table 4, the ratio of k_D/bc'_H is indeed very close to two. In fact, Barbari et al. (1988) take this ratio as 1.5 to obtain a value of k_D in polyhydroxyether when their nonlinear least squares regression failed to provide physically realistic parameters.

When the penetrant partial molar volume ν_s is relatively constant for a series of polymers, the relationships of Table 3 suggest that c'_H should decrease and b should increase with increasing bulk modulus at constant temperature. Such a trend is observed for the tetramethyl-, tetrachloro- and tetrabromo-polycarbonates, if one approximates the bulk moduli with the shear moduli reported by Yee and Smith (1981). For these polymers, one might not expect ν_s to be constant due to differences in the size of the substituents and polymer packing. The densities reported by Muruganandam et al. (1987) suggest that the number density of polymer repeat units is the same for all three. Furthermore, estimates of the Lennard-Jones collision diameter for the substituents are within a factor of 1.1 if the collision diameters of atomic bromine and chlorine may be approximated by those of argon and krypton, respectively (Hirschfelder et al., 1954). This suggests that the repeat unit occupied volume is also virtually identical for the three polymers. These observations support the initial assumption that the penetrant partial molar volume is roughly a constant for this series of polymers.

Like the gas-polymer-matrix model, this work also postulates a single type of sorption site. The thermodynamic analysis, however, introduces physically meaningful material parameters that potentially can offer insight into the sorption process. This is the principal drawback of the gas-polymer-matrix model which has been discussed extensively in the literature.

In contrast with the lattice theories of sorption and the dual-mode model, the thermodynamic analysis does not postulate two sorption sites nor explicitly require the concept of excess free volume to produce dual-mode-like sorption behavior. Excess free volume can and does enter into the value of the material parameters; and most notably, ν_s is much smaller for sorption into a glassy material than a rubbery one. However, as long as ν_s and B_0 are greater than zero in the limit of zero excess free volume, Eq. 37 yields sorption isotherms which are concave downward to the pressure axis. As discussed previously, one expects ν_s to increase with decreasing excess free volume, as well as B_0, and only exacerbate the concavity. This is due to the large positive Gibbs free energy change associated with polymer deformation discussed previously.

Conclusions

A thermodynamic description of penetrant sorption into elastic solids is presented here which treats sorption as two distinct processes: 1) solid deformation, followed by 2) mixing with the penetrant. The results are expressed as a sorption isotherm relating penetrant pressure to concentration in the solid and represent an extension of the Flory-Huggins theory to the swelling of solids, for which deformation-induced internal energy changes are significant. The analysis is valid for all elastic solids provided: 1) deformations are small and homogeneous; 2) deformations are reversible; and 3) sorption is isothermal.

The predicted sorption isotherms are concave downward to the pressure axis for physically realistic material parameter values. Such predictions are consistent with the qualitative nature of gas sorption in glassy polymers. Quantitative analysis is also possible as demonstrated by a detailed comparison for carbon dioxide sorption in polycarbonate. The experimental observation that the ratio k_D/bc'_H is approximately two for nitrogen sorption is shown to be a consequence of the thermodynamics. The variation of other dual-mode parameters with polymer material properties is discussed.

The concept of two sorption sites and/or excess free volume is not a necessary condition for dual-mode behavior. Excess free volume can affect the sorption isotherm quantitatively, but the concave downward nature is qualitatively due to the large internal energy contribution to the free energy that arises from deformation of the glass. By letting the bulk modulus go to zero, the sorption isotherm for a rubber is recovered. This is consistent with the experimental observation that the bulk modulus of a rubber is two or three orders of magnitude less than that of the glass.

Acknowledgment

The author wishes to acknowledge the many helpful comments of the reviewers.

Notation

a_s = penetrant (solvent) vapor-phase activity
b = Langmuir affinity constant
B = bulk modulus

c = penetrant concentration
c_D = penetrant concentration in Henry's-law-type sites
c_{DM} = penetrant concentration predicted from dual-mode theory
c_g = glass transition concentration
c_H = penetrant concentration in Langmuir-type sites
c'_H = Langmuir capacity parameter
c_p = polymer concentration
c_T = penetrant concentration predicted from thermodynamic analysis
$\underline{\underline{C}}$ = isothermal elastic coefficients
$\underline{d}$ = displacement vector
$\bar{G}$ = Gibbs free energy
G_1 = Gibbs free energy of the first step in the thermodynamic path
G_2 = Gibbs free energy of the second step in the thermodynamic path
G_{Deform} = sum of G_1 and G_2
G_{Mix} = Gibbs free energy of the third step in the thermodynamic path
$\underline{\underline{I}}$ = identity tensor
$\bar{k}$ = Boltzmann's constant
k_D = Henry's law coefficient
n = number of molecules
N_{AV} = Avogadro's number
N_e = effective number of crosslinks
p = pressure
p_{atm} = atmospheric pressure
p_s = penetrant vapor pressure
$\underline{r}$ = material position vector after deformation
$\underline{R}$ = material position vector prior to deformation
$\bar{R}$ = gas constant
S = entropy
T = temperature
T_g = glass transition temperature
$\bar{U}$ = internal energy
V = volume
V_{atm} = volume at atmospheric pressure

Greek letters

χ = Flory-Huggins interaction parameter
δ' = identity vector defined by Eq. 6
ϵ = material strain
γ = penetrant (solvent) vapor phase activity coefficient
λ = Lame constant
μ = Lame constant
μ_s = chemical potential of penetrant (solvent)
∇ = gradient operator
ν = partial molar volume
ϕ = volume fraction
σ = material stress

Subscripts and superscripts

g = glass
l = equilibrium liquid
p = polymer (solid)
s = solvent (penetrant)
R = evaluated at reference conditions
0 = evaluated in the undeformed state

Literature Cited

Ashley, R. J., "Permeability and Plastics Packaging," *Polymer Permeability*, J. Komyn, ed., Elsevier, London (1985).

Astarita, G., M. E. Paulaitis, and R. G. Wissinger, "Thermodynamics of the Glass Transition," *J. Polym. Sci. B Polym. Phys.*, **27**, 2105 (1989).

Aukett, P. N., "New Membrane Cell for the Determination of Heats of Immersion using the Setaram C-80 Microcalorimeter," *J. Therm. Anal.*, **33**, 323 (1988).

Barbari, T. A., W. J. Koros, and D. R. Paul, "Gas Sorption in Polymers Based on Bisphenol-A," *J. Polym. Sci. B Polym. Phys.*, **26**, 729 (1988).

Barton, A. F. M., *CRC Handbook of Polymer–Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Boca Raton, **29**, 1194 (1990).

Brandup, J., and E. H. Immergut, eds., *Polymer Handbook*, Wiley-Interscience, New York (1975).

Carbonell, R. G., and G. C. Sarti, "Coupled Deformation and Mass Transport Processes in Solid Polymers," *Ind. Eng. Chem. Res.* (1990).

Chan, A. H., and D. R. Paul, "Influence of History on the Gas Sorption, Thermal, and Mechanical Properties of Glassy Polycarbonate," *J. Appl. Polym. Sci.*, **24**, 1539 (1979).

Chern, R. T., W. J. Koros, E. S. Sanders, S. H. Chen, and H. B. Hopfenberg, "Implications of the Dual Mode Sorption and Transport Models for Mixed Gas Permeation," *ACS Symp. Ser.*, **223**, 47 (1983).

Chrysochoos, A., and G. Martin, "Tensile Test Microcalorimetry for Thermomechanical Behavior Law Analysis," *Mat. Sci. Eng. A Struc. Mat.*, **A108**, 25 (1989).

Cowie, J. M. G., *Polymers: Chemistry and Physics of Modern Materials*, International Textbook Co., Aylesbury, Bucks (1973).

Fleming, G. K., and W. J. Koros, "Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures: 1. Silicone Rubber and Unconditioned Polycarbonate," *Macromol.*, **19**, 2285 (1986).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY (1969).

Fung, Y. C., *Foundations of Solid Mechanics*, Prentice-Hall, Englewood Cliffs, NJ (1965).

Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954).

Hornberger, L. E., and K. L. DeVries, "The Effects of Residual Stress on the Mechanical Properties of Glassy Polymers," *Polym. Eng. Sci.*, **27**, 1473 (1987).

Koros, W. J., "Model for Sorption of Mixed Gases in Glassy Polymers," *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 981 (1980).

Koros, W. J., and D. R. Paul, "CO_2 Sorption in Poly(ethylene Terephthalate) above and below the Glass Transition," *J. Polym. Sci. Polym. Phys. Ed.*, **16**, 1947 (1978).

Larche, F., and J. W. Cahn, "A Linear Theory of Thermochemical Equilibrium of Solids under Stress," *Acta Metal.*, **21**, 1051 (1973).

———, "A Nonlinear Theory of Thermochemical Equilibrium of Solids under Stress," *Acta Metal.*, **26**, 53 (1978).

———, "Thermochemical Equilibrium of Multiphase Solids under Stress," *Acta Metal.*, **26**, 1579 (1978).

Mase, G. E., *Continuum Mechanics*, McGraw-Hill, New York (1970).

Moe, M. B., W. J. Koros, and D. R. Paul, "Effects of Molecular Structure and Thermal Annealing on Gas Transport in Two Tetramethyl Bisphenol-A Polymers," *J. Polym. Sci. B Polym. Phys.*, **26**, 1931 (1988).

Muruganandam, N., W. J. Koros, and D. R. Paul, "Gas Sorption and Transport in Substituted Polycarbonates," *J. Polym. Sci. B Polym. Phys.*, **25**, 1999 (1987).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1969).

Raucher, D., and M. D. Sefcik, "Sorption and Transport in Glassy Polymers: Gas-Polymer-Matrix Model," *ACS Symp. Ser.*, **223**, 111 (1983).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York (1977).

Sanders, E. S., and W. J. Koros, "Sorption of CO_2, C_2H_4, N_2O and their Binary Mixtures in Poly(methyl methacrylate)," *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 175 (1986).

Spillman, R. W., "Economics of Gas Separation Membranes," *Chem. Eng. Prog.*, **85**, 41 (1989).

Stannett, V. T., W. J. Koros, D. R. Paul, H. K. Lonsdale, and R. W. Baker, "Recent Advances in Membrane Science and Technology," *Adv. Polym. Sci.*, **32**, 69 (1979).

Theodorou, D. N., and U. W. Suter, "Atomistic Modeling of Mechanical Properties of Polymeric Glasses," *Macromol.*, **19**, 139 (1986).

Truesdell, C., and R. A. Toupin, "The Classical Field Theories," *Encyclopedia of Physics*, S. Flugge, ed., **3/1**, Springer-Verlag, Berlin (1965).

Vieth, W. R., J. M. Howell, and J. H. Hsieh, "Dual Sorption Theory," *J. Membr. Sci.*, **1**, 177 (1976).

Vrentas, J. S., and C. M. Vrentas, "Volumetric Behavior of Glass Polymer-Penetrant Systems," *Macromol.*, **22**, 2264 (1989).

Woodbury, G. W., and L. A. Noll, "Heats of Adsorption from Flow Calorimetry: Relationships Between Heats Measured by Different Methods," *Colloids and Surfaces*, **28**, 233 (1987).

Yee, A. F., and S. A. Smith, "Molecular Structure Effects on the Dynamic Mechanical Spectra of Polycarbonates," *Macromol.*, **14**, 54 (1981).

Appendix: Gibbs Free Energy of an Ideal Elastic Solid

The thermodynamics of deformation are well established and thus will just be reviewed here (Theodorou and Suter, 1986). Before doing this, though, a measure of deformation must be introduced. Consider an undeformed body. Each material point of this body may be represented by a position vector $\underline{R} = (R_1, R_2, R_3)$ with respect to some fixed coordinate system. After deformation, let $\underline{r} = (r_1, r_2, r_3)$ be the new position vector of each material point with respect to the same coordinate system. The displacement is defined by,

$$\underline{d} = \underline{r} - \underline{R} \tag{A1}$$

and the material strain tensor $\underline{\underline{\epsilon}}$ is defined as follows,

$$\underline{\underline{\epsilon}} = \frac{1}{2}[\nabla_R \underline{d} + (\nabla_R d)^+] + \frac{1}{2}((\nabla_R \underline{d})^+ \nabla_R \underline{d}) = \frac{1}{2}[(\nabla_R \underline{r})^+ \nabla_R \underline{r} - \underline{\underline{I}}] \tag{A2}$$

The following development is limited to small deformations so that the terms of second order in the spatial derivative of displacement are neglected. With this approximation, material and spatial strain become identical. The strain components ϵ_{ij} are not independent and are related to each other through the compatibility equations (Mase, 1970).

Volumetric changes are related to ϵ_{ij} in the small deformation limit by,

$$dV = tr(d\underline{\underline{\epsilon}})V_0 = (d\epsilon_{ii})V_0 \tag{A3}$$

where *tr* represents the trace of a tensor, V_0 is the undeformed volume, and a summation is implied over repeated indices. This expression is accurate to second order in deformation.

Furthermore, let $\underline{\underline{\sigma}}$ represent the total material and, in light of the above approximation, spatial stress. The stress must satisfy the requirements of mechanical equilibrium, i.e., the force balance,

$$\nabla \cdot \underline{\underline{\sigma}} = 0 \tag{A4}$$

where body forces are neglected. For small deformations, this constraint follows from the second law of thermodynamics as shown by Larche and Cahn (1973). Boundary conditions consist of specified surface stresses and/or deformations.

Because of the symmetry of $\underline{\underline{\epsilon}}$ and $\underline{\underline{\sigma}}$, these tensors are often represented as six component vectors (Mase, 1970),

$$\underline{\epsilon} = [\epsilon_{11}, \epsilon_{22}, \epsilon_{33}, 2\epsilon_{23}, 2\epsilon_{13}, 2\epsilon_{12}] \tag{A5}$$

$$\underline{\sigma} = [\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{13}, \sigma_{12}] \tag{A6}$$

One may write a general expression for the change in Gibbs free energy associated with taking the polymer from its reference state to the deformed state at the sorption pressure by considering the total differential of G,

$$dG = dU - d(TS) + d(pV) \tag{A7}$$

where U is the internal energy, T is the temperature, S is the entropy, p is the pressure, and V is the volume. The total differential of the internal energy for an elastic solid undergoing small, reversible, homogeneous deformations due to an imposed stress is (Theodorou and Suter, 1986),

$$dU = TdS + \sigma_{ij}d\epsilon_{ij}V_0 \tag{A8}$$

where V_0 is the undeformed polymer volume.

Combining Eqs. A5–A8 and applying the isothermal assumption leads to the following expression for dG,

$$dG = (\sigma_i + p\delta_i')d\epsilon_i V_0 + Vdp \tag{A10}$$

where

$$\delta' = [1 \quad 1 \quad 1 \quad 0 \quad 0 \quad 0] \tag{A11}$$

and deformation is substituted for volumetric changes through Eq. A3. The isothermal restriction is representative of the experiments, from which most sorption data are obtained. Removing this simplification requires specification of the entropy of the system as a function of pressure and deformation.

Equation A1 may be integrated to obtain the change in Gibbs free energy associated with the first two steps of the thermodynamic path illustrated in Figure 2. If the stress is independent of deformation, this integration is trivial; however, for any real material, the stress is strongly dependent on strain. One may account for this dependence by proposing a constitutive relationship between stress and strain. Alternatively, one could use a Taylor series expansion of the stress in terms of the imposed strain about some reference strain state; the accuracy of the expansion would depend on the number of terms retained.

For small deformations, the latter approach is especially attractive because one would expect an accurate representation from the first few terms of the series and these terms are defined in terms of physically meaningful quantities. Expanding the material stress in terms of strain about the undeformed state at constant temperature gives,

$$\sigma_i = \sigma_{i0} + \left(\frac{\partial \sigma_i}{\partial \epsilon_j}\right)_{T,\epsilon_{k \neq j},0} \epsilon_j + O(\epsilon^2) \tag{A12}$$

where the subscript 0 again denotes the undeformed state. Note that the undeformed stress state may be nonzero which allows some freedom in defining what this undeformed state is. By definition, the derivative of stress with respect to strain at constant temperature is the isothermal elastic coefficients,

$$C_{ij} = \left(\frac{\partial \sigma_i}{\partial \epsilon_j}\right)_{T,\epsilon_{k \neq j}} \tag{A13}$$

Stress symmetry and the further assumption of isotropic materials require the C_{ij} to be symmetric. The only nonzero components are given by,

$$\begin{aligned} C_{11} &= C_{22} = C_{33} = \lambda + 2\mu \\ C_{44} &= C_{55} = C_{66} = \mu \\ C_{12} &= C_{13} = C_{23} = \lambda \\ C_{ij} &= C_{ji} \end{aligned} \tag{A14}$$

The parameters λ and μ are the Lame constants relating stress to bulk volume changes and colinear strain, respectively. From these material parameters, one may readily calculate the commonly measured mechanical properties (i.e., the bulk modulus, B, is given by $\lambda + 2\mu/3$).

Substituting Eq. A12 into Eq. A10 gives the following integral equation for the change in Gibbs free energy of a deformable elastic solid,

$$\Delta G = V_0 \int_\epsilon [\sigma_{i0} + (C_{ij})_0 \epsilon_j + p\delta_i'] \, d\epsilon_i + \int_p V \, dp + O(\epsilon^3) \tag{A15}$$

which is accurate to $O(\epsilon^3)$ as indicated.

As shown by Truesdell and Toupin (1960), one may define a Gibbs function or thermodynamic potential (Fung, 1965) for an ideal elastic solid at constant temperature by

$$\Delta G = V_0 \int_\sigma \epsilon_i \, d\sigma_i \tag{A16}$$

in contrast to Eq. A15. Such an expression is obtained by replacing the definition of G given above, Eq. A7, with

$$dG = dU - d(TS) + d(\epsilon_i \sigma_i) \tag{A17}$$

where dU is still given by Eq. A8. Truesdell and Toupin introduce this definition because of the simplified development of further thermodynamic relationships and the ambiguity of a thermodynamic pressure for many systems. However, they also note that Gibbs' original definition is useful when the temperature is held constant and a uniform hydrostatic pressure is maintained.

The choice of definition to be used is influenced primarily by the necessity to apply the same definition to both the solid and gas. Use of Eq. A17 for the gas results in a chemical potential quite different from the conventional result obtained from Eq. A7. In fact, the use of a stress-strain relationship to calculate the Gibbs function in a gas phase is inappropriate. For this reason, the definition of the Gibbs function proposed by Truesdell and Toupin is not adopted here.

Manuscript received Mar. 23, 1990, and revision received Aug. 7, 1990.