Diffusion in Solids under Strain, with Emphasis on Polymer Membranes

A solute diffusing through a solid gives rise to a change in volume. This swelling can be viewed as a strain, and it is possible to obtain the accompanying stress using elasticity theory. The theory provides two ways by which stresses can be generated. The first comes from the condition of impenetrability where the system generates stress to exclude certain configurations during deformation. The second is due to imposed restrictions on the geometry during the swelling process. Larché and Cahn have provided the thermodynamics for such systems, from which the chemical potential can be used to obtain a phenomenological expression for flux and an expression for the solubility. These two are sufficient to obtain the sorption response in most systems. Solutions have been obtained here.

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SCOPE

Diffusion through solids is important particularly because solid containers are used to constrain a solute, or to selectively allow the permeation of a particular species through it. Polymers particularly answer the above purposes; they are used as paints, varnishes, coatings, and other protective linings to prevent contact between the environment and the materials of construction. When the latter are exposed, failures occur through reactions (corrosion) or embrittlement (environmental stress cracking). Failures in such systems occur when sufficient solute diffuses through or when large internal stresses are generated due to the presence of the solute. In contrast, polymer membranes are also used to selectively allow a particular species through. This form of separation holds much future promise. However, the stability of such membranes is often a problem: swelling by solutes can change the characteristics, and material failures can also take place. Further, a number of other processes besides diffusion take place, which makes it difficult to quantitize the permeation through such systems.

In addition to polymer coatings, the commerical success of polymer fibers depends on their response to water vapor and dyes.

Instead of looking only at the detrimental side of internal stresses generated in the presence of a solute, it is interesting to consider the possibilities of modifying diffusion behavior by placing the solid under external stresses or geometric constraints.

This study analyzes the effects of swelling, the main effect of which is to give rise to stresses. The formulation provided here can account for these internal stresses, and externally imposed stresses as well. Consequently a number of the physical processes mentioned above can be investigated. Especially important are the identification of the proper physical parameters and their methods of determination as shown here, as well as the demonstration that the stresses generated can cause failures.

CONCLUSIONS AND SIGNIFICANCE

The formulation of Larché and Cahn (1973) has been used to provide the details of diffusion in a solid where the diffusion is accompanied by swelling. It has been shown to agree with the experiments quantitatively,

and explains some key features of anomalous diffusion in polymers, namely the sigmoidal uptake curves in sorption and the time-dependent solubilities.

Only the first-order effects and linear relations have been used to preserve simplicity. The solutions provide the key parameters in the system and identify correctly the role of diffusivity. The methods for estimating these basic parameters are shown. One effect of swelling is the generation of stresses. The stresses have been shown to be sufficiently high to give rise to material failures. The latter is of great consequence in selecting materials that can withstand a given environment.

Future work in this area should stress the nonlinear effects.

Introduction

Diffusion of a solute in a system is accompanied by a change in volume. In practice, some significance is given to this change in volume by incorporating into the phenomenological expression for the diffusive flux a more realistic (nonideal) solution thermodynamics. That is,

$$j = -\frac{D_o c}{RT}\nabla\mu \tag{1}$$

where μ is the chemical potential and reflects the nonideal solution effects (Sherwood et al., 1975). An additional effect is obtained in such systems under Reynold's transport theorem (Slattery, 1981) in the form of a convective term. Formally, this convective velocity is obtained by solving the equations of motion and continuity; physically, its origin is easy to understand as the solute-rich region will now tend to occupy higher volumes, and if it is restricted from doing so it will then develop higher pressures and give rise to a flow.

This discussion of behavior in fluids is helpful in understanding the behavior in solids where the matrix can deform but does not flow. In contrast to fluids, where this pressure energy is dissipated, an elastic solid will store such energies and affect the chemical potentials. Further, whereas this effect is unimportant in fluids, large stresses can be generated in solids.

The fact that stresses in solids are analogous to pressures in fluids has an important implication. Whereas pressures can only be positive (compressive), stresses can be positive or negative, i.e., compressive or tensile, and hence can increase or decrease the chemical potential. In subsequent sections of this paper the effect of change of volume on diffusion is investigated as well as the magnitudes of the stresses generated, since this can cause material failure for which no analogous cases exist in fluids.

The basic formulation of the effects of swelling has been developed for metallurgical systems by Larché and Cahn (1973, 1978a,b, 1982). The role of swelling in diffusion through solid polymers has been under investigation since the works of Hartley (1946, 1949), Bagley and Long (1955), Long and Richman (1960), and Richman and Long (1960), all of whom obtained results that could not be explained only by Eq. 1. They attributed the anomalous diffusion to the presence of stresses generated either by the swelling effects or imposed externally on such systems. Vrentas and Duda (1979) and Cussler (1976) have reviewed some of these results on polymers. Although quantitative measurements of various parameters involved are few, there have been a large number of experiments made on solid polymer membranes. Without loss in generality, our discussion will involve only polymers.

One popular method for obtaining the diffusion coefficient and the diffusional behaviors is through a sorption experiment. Here a sample (the solid) is equilibrated with a vapor to a concentration c_i and then the concentration on the boundaries is stepped up to c_f. The uptake is measured gravimetrically as a function of time and is used to measure the diffusion coefficients. When c_i and c_f are wide apart the method is called integral sorption. When $c_i = c^* - \Delta c^*/2$ and $c_f = c^* + \Delta c^*/2$, where Δc^* is very small, the response is called differential sorption. The advantage in this case is that if the diffusion coefficient is a function of concentration, then the diffusion coefficient determined with this method provides quite accurately its value at average concentration c^*. Bagley and Long (1955) and Fujita (1961) determined that the differential sorption responses were very different from integral sorption response. A few observations by them are significant:

1. Most differential sorption responses show almost Fickian responses, i.e., those predicted when Eq. 1 is used. When $c^* \approx 0$, the response is completely Fickian. The characteristic of Fickian diffusion is that the response curves are always convex outward.
2. When integral sorption responses were examined they were found to be sigmoidal, i.e., showing changes in the signs of the curvatures. This is an anomalous response, one that cannot be explained with Eq. 1 alone.
3. It was found that the skin concentration or the solubility during the transport process was a function of time.

Two important conclusions can be drawn from the above. In the sorption experiments the concentrations are stepped up by exposing the sample to a solute reservoir at constant chemical potential. Consequently the chemical potential of the solute inside the solid sample immediately adjacent to the reservoir will have a value equal to the constant value of the chemical potential in the reservoir. It would also imply that the solute concentration there—the skin concentration or the solubility—must be a constant. If it is not a constant then inside the solid there must be one other contribution to the chemical potential of the solute that changes with time. Consequently the solute concentrations change with time as a compensating effect such that the chemical potential remains a constant.

Frisch (1964) and Neogi (1983a,b) have proposed that it takes a finite time for the polymer to reach equilibrium at a point because of chain entanglements. This time, called the relaxation time, has an added effect on the chemical potential, one that changes with time. Consequently the solubility there changes with time. As shown by Neigi (1983b) this relaxation mechanism explains a number of diffusional behaviors but it cannot explain the sigmoidal nature of some of the responses observed at times.

The other explanation that has been offered is by Bagley and Long (1955), which is that swelling gives rise to a stress that affects the chemical potential in the solid, and is in a way similar to the effect of pressure on a fluid. In the absence of externally applied stresses, the stresses generated in this way will have to vanish at equilibrium when the solid achieves its equilibrium extent of swelling. Thus the stresses are time-dependent and hence the skin concentrations also change with time.

Lastly, we note that observations 1 and 2 above show that the effect of stress, if it is to be used to explain the sigmoidal response and time-dependent solubilities, must show that for $c^* \approx 0$, the effects of swelling must disappear and the response should be classical. That is, the swelling effects are concentration-dependent and second-order.

A number of investigators have attempted to formulate this problem (Thomas and Windle, 1982; Petropoulos and Roussis, 1967, 1978; Petropoulos 1984a,b; Astarita and Sarti, 1978; Astarita and Joshi, 1978; Sarti and Apicella, 1980; Gostoli and Sarti, 1982). Because of the large number of models used, we will not provide a detailed criticism here. The general line of argument is that swelling gives rise to a change in dimensions that is a strain. A constitutive relation between the stress and the strain provides the stress as a function of swelling. If the effect of stress on the chemical potential is known then the diffusional flux, from Eq. 1, and the solubility can be obtained. These are all the information necessary to solve the boundary value problems.

The first point to distinguish clearly is that all changes in dimensions do not lead to stresses. This is well known in thermoelasticity (Boley and Weiner, 1960) and quite well delineated in polymers by Flory (1953). If a solid in absence of external forces is immersed in a solute, then at equilibrium the solute will swell by an equilibrium extent. The chemical potentials of the solute inside and outside the reservoir will be the same and the stresses inside and outside (zero here) will be equal. However if the solid is deformed then displacement

$$\boldsymbol{u} = \boldsymbol{u}^c + \boldsymbol{u}^m \tag{2}$$

where $\boldsymbol{u}^c$ is the displacement of a point due to swelling and $\boldsymbol{u}^m$ is the displacement due to a mechanical force. The strain tensor

$$\boldsymbol{E} = \tfrac{1}{2}[\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T] \tag{3}$$

is thus decomposed as

$$\boldsymbol{E} = \boldsymbol{E}^c + \boldsymbol{E}^m \tag{4}$$

Now, as discussed previously, if $\boldsymbol{E}$ is only $\boldsymbol{E}^c$, i.e., $\boldsymbol{E}^m = \boldsymbol{0}$, then *there are no stresses in* the system. Consequently the constitutive equation is

$$\sigma = f(\boldsymbol{E}^m) \tag{5}$$

Thus the stress σ cannot be determined from $\boldsymbol{E}^c$ alone, a fact overlooked in many models. The second feature comes from Eq. 3, where $\boldsymbol{E}$ must satisfy the compatibility equation

$$\nabla \times \boldsymbol{E} \times \nabla = \boldsymbol{0} \tag{6}$$

Although Eq. 6 has been written in the form of an operator, it is not an operator. The derivatives in the last curl ($\times \nabla$) operate on $\boldsymbol{E}$. Equation 6 is only a compact symbolic representation arranged so that the indices of the components are ordered correctly. Equation 6 excludes certain values of $\boldsymbol{E}$. Physically, we know of at least the simplest case: Consider material points A and B separated by a distance d. The system cannot deform such that A and B superimpose. Any such attempt is opposed by elastic forces. The compatibility equation thus incorporates the condition of impenetrability and is the only source of elastic stresses in externally unstressed systems. None of the previous investigators have used this condition, with the exception of Larché and Cahn (1982) and Kim and Neogi (1984).

Kim and Neogi investigated the sorption response using the above constraints. Their main objective was to determine if the swelling gave rise to discontinuous or nearly discontinuous concentration profiles predicted by the relaxation mechanism (Neogi, 1983a,b). They determined that swelling gives rise to time-dependent solubilities or skin concentrations, but to the approximation used found only that the diffusion was nearly Fickian, in contrast to the experiments.

More detailed investigations have been attempted here for the study of sorption in thin polymer membranes, such that a better understanding along with a quantitative comparison with the experiments can be provided. In keeping with the experimental results of Bagley and Long (1955) and Long and Richman (1960), it is shown here for the first time, with correctly posed mathematical form, that the sorption proceeds in two stages. The first stage is quick equilibriation under diffusion; in the second stage the concentrations change because the solubilities change. This gives rise to the sigmoidal mass uptake response curves. We are able to show that the effects of swelling disappear at very low concentrations, and this is important as the concentrations increase. Ignoring this can provide one with incorrect values for diffusion coefficients under existing methods for analyzing the sorption response. As discussed previously, the stresses generated initially disappear at equilibrium and the changing stresses change the solubilities. The solubilities are compared with the existing data. The levels of stresses generated and the possibilities of material failure are also discussed.

Lastly, sorption in externally stressed systems is investigated with the view of changing the nature of the diffusion process. The changes in diffusion are seen to be not significant, at least under the linear elasticity relation used here. The changes in solubilities are, however, marked.

Sorption

Formulation

The important consideration for us in this case is that the external forces on the thin solid polymeric film are negligible. Consequently the stresses are generated only through the compatibility condition. The membrane has a small thickness L and the faces are large such that the end effects can be neglected. At zero time it is taken to be surrounded by vacuum and solute is then introduced around it and maintained at constant temperature and pressure. Diffusion proceeds into the membrane in the z direction, the direction of the thickness. The faces of the membrane are at $z = \pm L/2$.

The diffusive flux is

$$j_z = -\frac{D_o\phi}{V_1 RT}\left(\frac{\partial\mu}{\partial\phi}\right)\frac{\partial\phi}{\partial z} \tag{7}$$

where ϕ is the volume fraction of the solute. V_1 is the molar volume of the solute. The conservation equation is

$$\frac{1}{V_1}\frac{\partial\phi}{\partial t} = -\frac{\partial}{\partial z}j_z \tag{8}$$

The strain due to swelling $\boldsymbol{E}^c$ is assumed to be isotropic, and from Kim and Neogi (1984)

$$\boldsymbol{E}^c = \eta(\phi - \phi_o)\boldsymbol{I} = \frac{1}{3V_o}\frac{\partial V}{\partial\phi}\bigg|_{\phi=\phi_o}(\phi - \phi_o)\boldsymbol{I} \tag{9}$$

where V_o is the reference volume and ϕ_o a reference concentration. Larché and Cahn (1973) show that in such systems

$$\mu(\sigma, \phi) = \mu(\boldsymbol{0}, \phi) - \eta V_1 tr(\sigma) \tag{10}$$

where tr represents trace and the chemical potential at zero stress is given by the Flory-Huggins-Rehner equation (Flory, 1953)

$$\mu(\boldsymbol{0}, \phi) = \mu_1^o + RT[\ln\phi + (1-\phi) + \chi(1-\phi)^2] + \tfrac{1}{3}EV_1[(1-\phi)^{1/3} - (1-\phi)/2] \tag{11}$$

where χ is the Flory-Huggins coefficient and E is Young's modulus of elasticity.

Following Kim and Neogi, we obtain the solution satisfying the force balance and the compatibility equation

$$tr(\sigma) = \frac{2\eta E}{1-\nu}\left[-\phi + \frac{1}{L}\int_{-L/2}^{L/2}\phi\, dz\right] \tag{12}$$

under the linear Young's law for Eq. 5, and zero net force and net moment on the membrane.

Combining Eqs. 7, 8, 10, 11, and 12, and nondimensionalizing, we have

$$\frac{\partial\phi}{\partial\tau} = \frac{\partial}{\partial\zeta}\left\{\left[(1-\phi) - 2\chi\phi(1-\phi) + S\phi\left(\frac{1}{2} - \frac{1}{3}(1-\phi)^{-2/3}\right) + \frac{6\eta^2 S}{(1-\nu)}\phi\right]\frac{\partial\phi}{\partial\zeta}\right\} \tag{13}$$

where $\tau = 4D_o t/L^2$, $\zeta = z/(L/2)$, and $S = EV_1/3RT$. The apparent diffusion coefficient D is

$$D = D_o\left[(1-\phi) - 2\chi\phi(1-\phi) + S\phi\left(\frac{1}{2} - \frac{1}{3}(1-\phi)^{-2/3}\right) + \frac{6\eta^2 S}{(1-\nu)}\phi\right] \tag{14}$$

where at infinite dilution $D = D_o$.

Combining Eqs. 10, 11, and 12 we have

$$\mu = \mu_1^o + RT[\ln\phi + (1-\phi) + \chi(1-\phi)^2] + \frac{1}{3}EV_1[(1-\phi)^{1/3} - (1-\phi)/2] - \frac{2\eta^2 V_1 E}{(1-\nu)}\left(-\phi + \frac{1}{L}\int_{-L/2}^{L/2}\phi\, dz\right) \tag{15}$$

If at equilibrium ϕ becomes uniformly ϕ_∞, then on simplification, the solubility $\phi|_{z=\pm L/2} = \phi_s$ becomes

$$\begin{aligned}\ln\phi_\infty + (1-\phi_\infty) + \chi(1-\phi_\infty)^2 + S[(1-\phi_\infty)^{1/3} - (1-\phi_\infty)/2] &= \ln\phi_s + (1-\phi_s) + \chi(1-\phi_s)^2 \\ &\quad + S[(1-\phi_s)^{1/3} - (1-\phi_s)/2] \\ &\quad - \frac{6\eta^2 S}{(1-\nu)}\left(-\phi_s + \int_o^1 \phi\, d\zeta\right)\end{aligned} \tag{16}$$

Thus one solves Eq. 13 subject to Eq. 16 and the symmetry condition

$$\frac{\partial\phi}{\partial\zeta}\bigg|_{\zeta=0} = 0 \tag{17}$$

The solubility in Eq. 16 can be seen to be time-dependent since it depends on the concentration distribution.

It is also useful to write the dimensionless stress from Eq. 12 as

$$\sigma^* = -\phi + \int_o^1 \phi\, d\zeta \tag{18}$$

where $\sigma^* = \sigma(1-\nu)/\eta E$. In the convention used here the positive stress is tensile and the negative stress is compressive. For future reference, we note that the sorption response is obtained in the form of fractional mass uptake M_t/M_∞, where M_t is the uptake at time t and M_∞ at $t = \infty$, i.e., at equilibrium; the fractional mass uptake is

$$\frac{M_t}{M_\infty} = \frac{1}{\phi_\infty}\int_o^1 \phi\, d\zeta \tag{19}$$

Results

According to the data compiled by Haward (1973), E varies from 4×10^9 to 2×10^7 Pa (glassy and rubbery polymers). For $V_1 \sim 0.075$ m^3/kmol (for pure saturated benzens), $T \sim 303$ K, and $R = 8.3145 \times 10^3$ J/kmol · K, S works out to range from ~40 for glassy polymers to ~0.2 for rubbery materials. Haward also suggests that $\nu \sim 0.33$, and if it is assumed that volumes are additive, then for $\phi_o = 0$, $\eta = 1/3$.

Equations 13, 16, 17, 18, and 19 have been solved numerically for $\phi_\infty = 0.1$ and initial concentration of zero. Figures 1 and 3 show profiles for $S = 5$ and $S = 50$; in all cases $\eta = 1/3$, $\chi = 0.0$, and $\nu = 0.33$ were used. As seen in the figures, the profiles are very similar to the case of classical (Fickian) diffusion except that the solubility ϕ_s changes with time. As the chemical potential inside the polymer is a function for stress and concentration, the concentration at the surface must change in order to balance the changes in the stresses such that the chemical potential

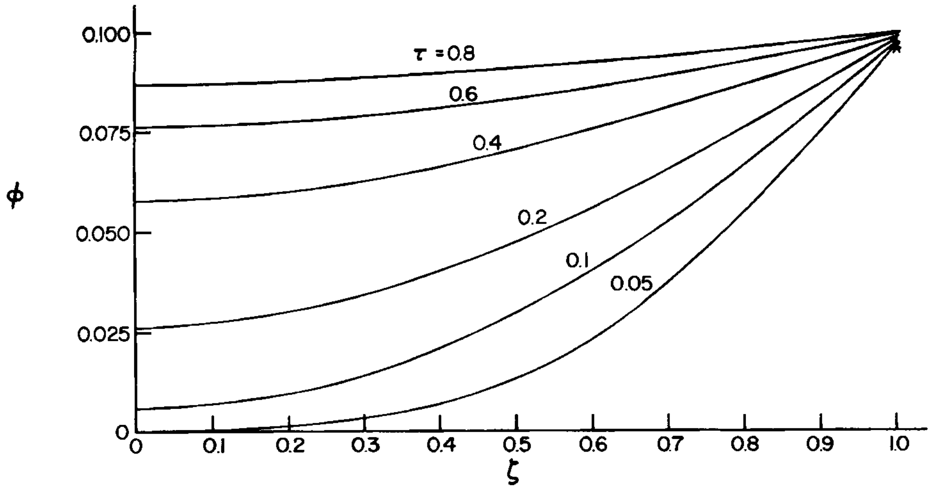

Figure 1. Concentration profiles during sorption.
$S = 5$; $\chi = 0.0$; $\eta = 0.33$; $\nu = 0.33$; $\phi_\infty = 0.1$.

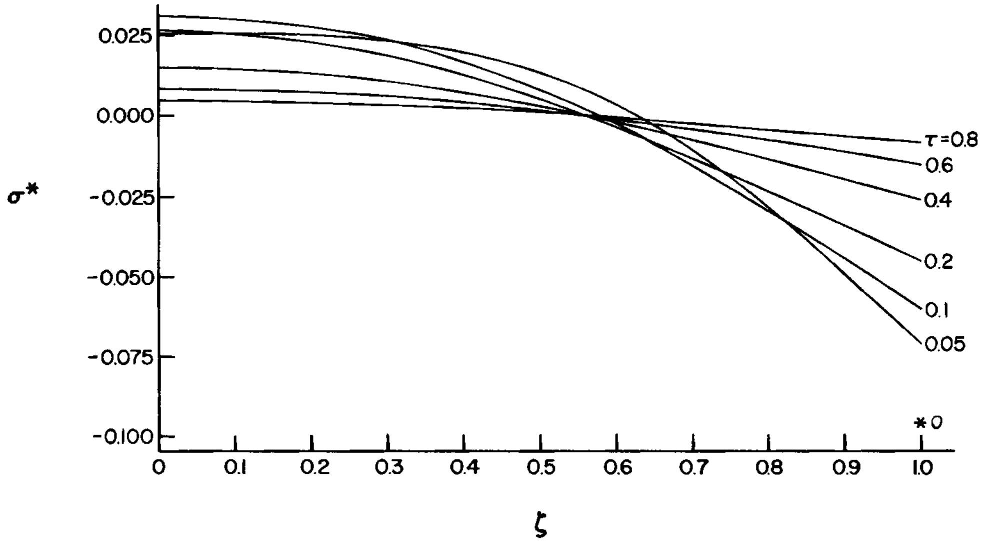

Figure 2. Dimensionless stress profiles for the case shown in Fig. 1.
Positive stresses are tensile.

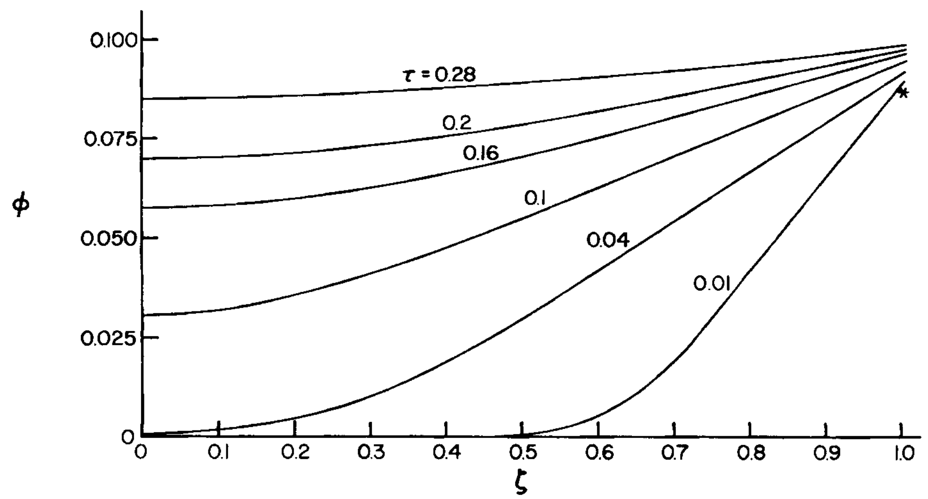

Figure 3. Concentration profiles during sorption.
$S = 50$; $\chi = 0.0$; $\eta = 0.33$; $\nu = 0.33$; $\phi_\infty = 0.1$.

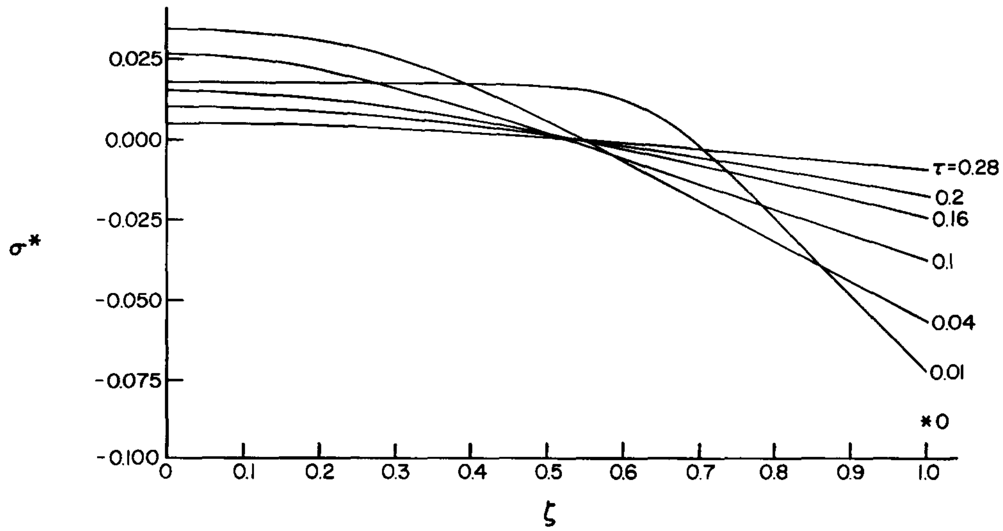

Figure 4. Dimensionless stress profiles for the case shown in Fig. 3.
Positive stresses are tensile.

remains a constant at the surface and is equal to the chemical potential of the reservoir. It is also to be noted that Figures 1 and 3 show two stages. At short times the profiles are sharp or have significant concentration gradients. At larger times, $\tau \sim 0.4$ in Figure 1 and ~0.16 in Figure 3, the profiles are flatter but they rise due to increased solubilities. This has been observed directly or inferred indirectly from the experiments by Bagley and Long (1955), Long and Richman (1960), and by Smith and Fisher (1984). In the first stage quick diffusion gives rise to a pseudo-equilibrium, and in the second stage the membrane as a whole tends to equilibriate with the reservoir. The elastic effects in Figure 3 are larger than in Figure 1 ($S = 50$ compared to 5 in Figure 1), and one finds that the gradients disappear at shorter times. Indeed Kim and Neogi (1984) suggest that when the elastic effects are very large the concentration profiles are flat and increase with time. It has also been shown that if the initial concentrations are zero, as in the cases here, then the solubilities do not change with time in the limit of high elasticity. As shown in Figures 1, 3, and 5 the solubility changes are completed more rapidly with increasing S. In Figure 5, the solubility changes have been plotted as ln $[\phi_\infty - \phi_s/\phi_\infty - \phi_s(0)]$ against τ. As suggested by the experiments of Bagley and Long, such plots are almost linear. (The experimental points and the dashed curve in Figure 5 will be discussed later.)

The stresses σ^* corresponding to Figure 1 and 3 have been plotted in Figures 2 and 4, respectively. Small tensile stresses (positive values) are observed near the center of the membranes, and large compressive stresses (negative values) are observed near the surface. The nature of these stresses can be explained by considering the fact that near the surface the polymer has more solute and consequently attempts to swell more, however it is prevented from doing that as the solute content is less in the interior, which can swell less. This restraint placed on the polymer near the surface gives rise to compression there, and the higher swelling tendency near the surface gives rise to tension in the interior. Petropoulos and Roussis (1978) and Petropoulos 1984a,b) had this feature in mind when they used as a boundary condition the constraint that the net deformation over the cross section is zero. Such a constraint is too restrictive but nevertheless expresses a physical feature of the problem.

The highest compressive stresses, which occur at the membrane faces at zero time, have been plotted as a function of S in Figure 6, for $\chi = 0.0$ and $\chi = 0.5$. It is seen that stresses are higher for the vapor with good solvating power, $\chi = 0.0$, than when the solvating power is poor, $\chi = 0.5$. This is understandable from the point of view that the vapor with $\chi = 0.0$ gives rise to higher swelling. When the dimensional value of $\sigma_{xx} = \sigma_{yy}$ is obtained corresponding to $-\sigma^*_{max} \sim 0.1$ in Figure 6, one has a compressive stress of 2×10^8 Pa for glassy materials ($S \sim 40$), which yield (Haward, 1973) at $\sim 10^7$ Pa. It becomes quite conceivable that failure may occur in such systems in the form of postyield flow. Since this failure is due to a concentration shock that occurs at the membrane surface due to the stepped-up concentrations during sorption, it can probably be avoided by decreasing the extent of step change. Indeed the calculations show that if the stepped-up concentration $[\phi_\infty - \phi(0)]$, here $= 0.1$, is lowered to 0.01, the stresses are also lowered by an order of magnitude (approximately). That this kind of failure does happen in practice has been noted by Tamura et al. (1963).

Other cases of failures have also been reported. Smith and Fisher (1984) observe that there is no failure on sorption but that failure occurs in the case of desorption in the form of

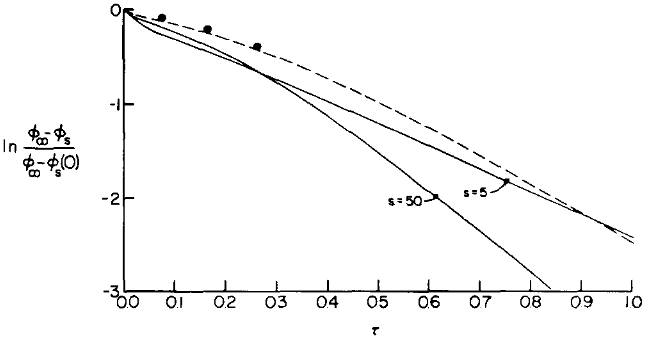

Figure 5. Changes in solubility, or skin concentration, during sorption with time.
$S = 5$ and 50; other parameters constant at $\chi = 0.0$; $\eta = 0.33$; $\nu = 0.33$; $\phi_\infty = 0.1$. ---- theoretically predicted plot for experimental points, O.

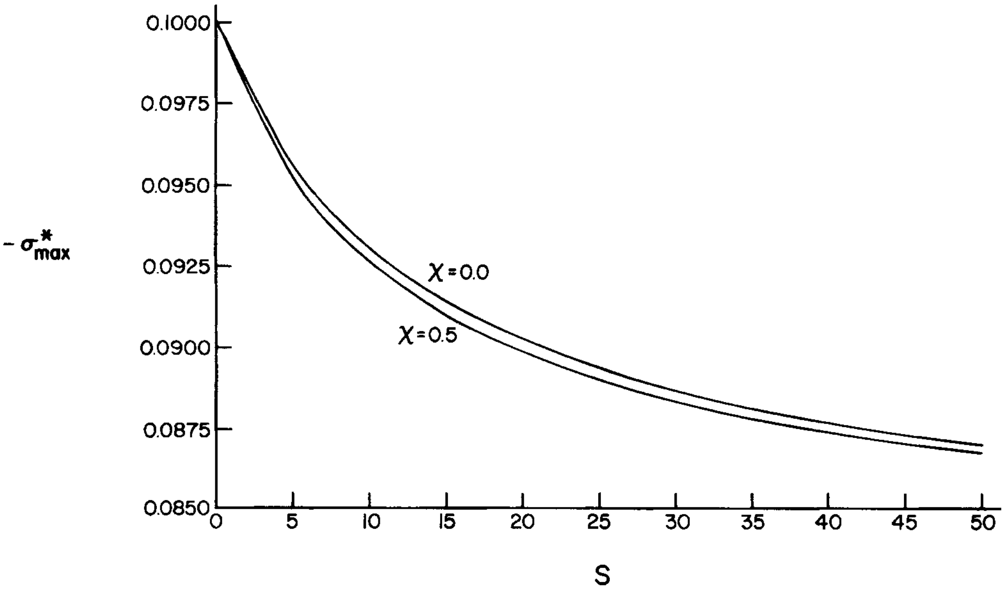

Figure 6. Maximum stresses during sorption.
σ^* at $\zeta = 1$ and $\tau = 0$ shown as a function of S for $\chi = 0.0$ and 0.5. Other parameters constant at $\eta = 0.33$; $\nu = 0.33$; $\phi_\infty = 0.1$.

cracks. It is to be noted that in the case of desorption, the highest stress is tensile in nature and the materials under tension fail more readily, in the form of cracking and crazing.

In Figure 7 the fractional mass uptake has been plotted against $\tau^{1/2}$ for $S = 0$ (no swelling effect), 5, and 50. The effect of swelling gives rise to sigmoidal curves, whereas the case with no swelling shows only a convex upward shape. The dashed line and the experimental points there are discussed next.

Comparison with experiments

The physical parameters necessary to compare theory with experiments are rarely reported. Long and Richman (1960) are close, where with some additional assumptions a successful comparison can be made. They report the solubility data and the fractional mass uptake data against time for the sorption of methyl iodide in cellulose acetate. The properties of cellulose acetate vary with the percent acetate and the degree of hydrogen bonding. However, Moore (1971) reports that χ for halogenated lower hydrocarbons ≈ 0.33 at low concentrations of the solute in cellulosic materials. Haward (1973) suggests that $\nu \approx 0.33$. Long and Richman (1960) provide values of final solubility and the initial solubility, which for specific gravity ~1.3 for cellulose acetate and 2.28 (Merck, 1983) for methyl iodide, provide $\phi_\infty = 0.0836$ and $\phi_s(0) = 0.0196$. The two are connected by Eq. 16, which at zero time becomes

$$\begin{aligned}\ln \phi_\infty + (1 - \phi_\infty) + \chi(1 - \phi_\infty)^2 \\ + S[(1 - \phi_\infty)^{1/3} - (1 - \phi_\infty)/2) \\ = \ln \phi_s(0) + [1 - \phi_s(0)] + \chi[1 - \phi_s(0)]^2 \\ + S\{[1 - \phi_s(0)]^{1/3} - [1 - \phi_s(0)]/2\} + \frac{6\eta^2 S}{(1 - \nu)} \phi_s(0) \quad (20)\end{aligned}$$

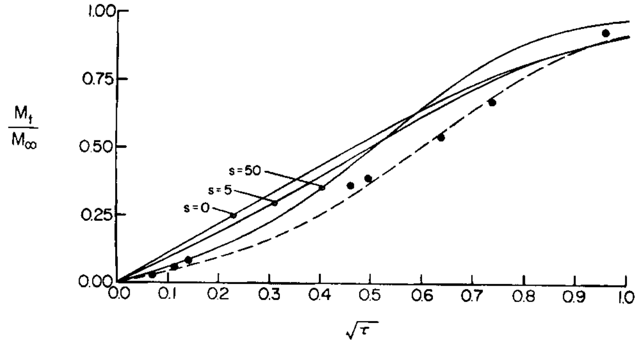

Figure 7. Fractional mass uptake during sorption with τ.
$S = 0$, 5, and 50; other parameters constant at $\chi = 0.0$; $\eta = 0.33$; $\nu = 0.33$; $\phi_\infty = 0.1$. ---- theoretically predicted plot for the experimental points, O.

A value for η is required to obtain S. Jefferies (1957) shows experimentally that the density of cellulose acetate-acetone mixture varies linearly with the weight fraction of acetone and hence suggests that for polar solutes in cellulose acetate, the volumes are additive. This conclusion is probably reasonable when the densities of the two are not too far apart, as in the cellulose acetate-acetone system. However, methyl iodide has a very high density. If the volumes are additive then $\eta = 1/3$, and if it is assumed that the density varies linearly with the weight fraction of the solute, then $\eta = 0.62$. The first value provides an unrealistic value for S but the second provides $S = 23.25$, an entirely reasonable value. The value of E calculated from this value is 2.8×10^9 Pa. This value is an appropriate estimate (Haward, 1973).

With these values Eqs. 13, 16, 17, and 19 are solved, and the solution fitted to the experimental data to obtain D_o, which is found to be 2.08×10^{-11} cm²/s. From Eq. 14, the ratio between the diffusion coefficient at $\phi_\infty = 0.0836$ and that at infinite dilution (D_o) is found as

$$\frac{D(\phi = 0.0836)}{D_o} = 7.875$$

The results as well as the nondimensionalized experimental values using parameters determined here are shown in Figures 5 and 7. The predicted curves are shown by dashed lines and the experimental values by circles; the fit is good. The parameters, their values, and the method or assumptions under which they have been determined are given in Table 1. In addition, we note that where the diffusivities are constant, plots of M_t/M_∞ vs. $t^{1/2}$ are sufficient for obtaining the diffusivities either from the half times $t_{1/2}$ where $M_t/M_\infty = 1/2$, or from the slopes at $t = 0$ (Crank and Park, 1968). Figure 7 makes it clear that both are in error in the present case. Thus Long and Richman (1960), when they determine the diffusion coefficient from the slope at $t = 0$, obtain a value that should be approximately D_o (since $t = 0$, $\phi = 0$), as 3.33×10^{-10} cm^2/s, a value substantially different from the one obtained here.

Smith and Fisher (1984) also provide data, but in the form of fractional uptake. To estimate the parameters from such data would be extremely difficult as it would be necessary to obtain the coefficients in a stiff partial differential equation. It has not been attempted.

Diffusion in Prestressed Systems

Formulation

Obviously the question to ask now is: since the diffusion of a solute into a solid gives rise to stresses that affect the rate of diffusion, could the stresses be exerted from the outside such that the diffusion process is modified? Equation 10 says that such tailoring may be achieved. Of the great many boundary value problems that can be formulated, we pick the one for which some experimental observations exist, namely that by Hartley (1946, 1949). Hartley studied diffusion rates under tension and found that these decreased substantially with increased tension. The direction of flux was the direction of tension in those cases. The results obtained here under small deformation theory cannot be checked quantitatively with Hartley's experiments since those were performed at 240% elongations. In those cases irreversible changes and anisotropy set in, which cannot be handled under the present formulation.

Table 1. Basic Data for Figures 5 and 7

Parameter	Value	Method
ν	0.33	Assumed from list of Haward (1973)
χ	0.33	Assumed from the data on cellulose acetate at low solute concentrations (Moore, 1971)
η	0.62	On assumption that the densities are linearly dependent on the weight fraction of the solute (Jefferies, 1957)
S	23.25	From Eq. 20 using above parameters and experimentally determined values of ϕ_∞ and $\phi_s(0)$ of Long and Richman (1960). Volume fractions obtained using specific gravity of 1.3 for cellulose acetate and 2.28 for methyl iodide (Merck, 1983).
E	2.8×10^9 N/m^2	Calculated from S using experimental value of T and pure methyl iodide density for V_1. Value obtained checks out well with estimates available (Haward, 1973).
D_o	2.08×10^{-11} cm^2/s	Calculated by curve-fitting to the data. Note that one parameter is used to fit to two curves. Value of $L = 5 \times 10^{-3}$ cm given by Long and Richman (1960).

Some general observations can be made. Whereas diffusion in fluids can be studied under pressure, it cannot be studied under tension. The novelty that diffusion can however be studied under tension in solids is worth keeping in mind. One interesting feature is observed when solids under stress, and hence elongation, are compared to solids externally unstressed but swollen by a solute by an equilibrium extent. Consider a solid of length L_o stretched to $L_o + \ell$; consider also a solid of length L_o swollen to $L_o + \eta\Delta\phi L_o$. There is a stress in the former but none in the latter. Now, we combine the two, that is, stretch L_o to $L_o + \ell$ mechanically and then allow a solute to penetrate it. The mechanical deformation now is only $\ell - \eta\Delta\phi L_o$ and the stress is dependent only on this quantity. Obviously the equilibrium concentration in such a system will be ϕ_∞ only if $\ell - \eta\Delta\phi L_o = 0$; here ϕ_∞ is the equilibrium concentration reached in an externally unstressed system. Thus in general we expect that in an externally stressed system the equilibrium concentration will not be ϕ_∞ except as a special case. If Eq. 10 is examined it is seen that $\mu(\phi, \mathbf{0})$ increases with ϕ and if the stresses are tensile then $tr(\sigma) > 0$, which lowers the total potential $\mu(\phi, \sigma)$. Consequently, if the system is in tension then the skin concentration $\phi_s > \phi_\infty$ to compensate for the lowering of the chemical potential due to the tensile nature of the stress.

The geometry under consideration is shown in Figure 8. A membrane of length L is stretched along the length (z direction) by an amount ℓ and is pinned down at the two ends. Under small-deformation theory, z extends only from 0 to L and the deformations $u_z(z)$ are such that $u_z(0) = 0$ and $u_z(L) = \ell$ at all times. The membrane is now of thickness $2a$ and clamped into position by two impermeable glass plates from the top and the bottom. The solute is introduced from the left end of the membrane and the righthand side is made impermeable. The assembly is infinite in the y direction.

As there are no end effects in the y direction $\partial u/\partial y = \mathbf{0}$, and in particular $u_y = 0$ because of the infinite extent in y. Also $u_x = 0$ at $x = \pm a$ and at $x = 0$ from symmetry, making it feasible to assume that $u_x = 0$. Similarly $\partial\phi/\partial x = 0$ at $x = \pm a$ and at $x = 0$ from symmetry, thus $\partial\phi/\partial x = 0$. This last statement implies that the deformation due to swelling is uniform in the x direction, and so must be the total deformation, that is, $\partial u_z/\partial x = 0$.

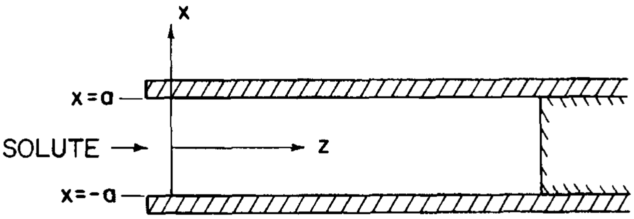

Figure 8. Arrangement used in solving the problem under external constraints.

Thus of the nine components of the derivatives ∇u, only $\partial u_z/\partial z$ is not zero.

It is seen that the only nonzero component of the strain is $E_{zz} = \partial u_z/\partial z$. The compatibility equations are satisfied if E_{zz} is independent of x; we already know that it is independent of y. Thus the mechanical strains become

$$E^m_{zz} = \frac{\partial u_z}{\partial z} - \eta\Delta\phi \qquad (21a)$$

$$E^m_{yy} = E^m_{xx} = -\eta\Delta\phi \qquad (21b)$$

The last two strains show that the mechanical strains can also be built up solely because the material is being prevented from swelling by rigid boundaries. The stresses are obtained from linear Young's law and the force balance equations lead to

$$\frac{\partial^2 u_z}{\partial z^2} = \frac{(1+\nu)}{(1-\nu)}\eta\frac{\partial\phi}{\partial z} \qquad (22)$$

Equation 22 is integrated subject to the conditions that $u_z(0) = 0$ and $u_z(L) = \ell$, to give

$$u_z = \frac{(1+\nu)}{(1-\nu)}\eta\left[\int_o^z \phi\, dz - \frac{z}{L}\int_o^L \phi dz\right] + z\frac{\ell}{L} \qquad (23)$$

the elasticity relations and Eq. 10 give

$$\mu = \mu_1^o + RT[\ln\phi + (1-\phi) + \chi(1-\phi)^2] + \frac{1}{3}EV_1[(1-\phi)^{1/3} - (1-\phi)/2] - \frac{\eta V_1 E}{(1-2\nu)}\left[\frac{(1+\nu)}{(1-\nu)}\eta\left\{\phi - \frac{1}{L}\int_o^L \phi\, dz\right\} + \frac{\ell}{L} - 3\eta\Delta\phi\right] \qquad (24)$$

Using Eqs. 7, 8, and 24 and nondimensionalizing, we get

$$\frac{\partial\phi}{\partial\tau} = \frac{\partial}{\partial\zeta}\left\{1 - \phi - 2\chi\phi(1-\phi) + S\phi\left[\frac{1}{2} - \frac{1}{3}(1-\phi)^{-2/3}\right] + \frac{6\eta^2 S}{(1-\nu)}\phi\right\}\frac{\partial\phi}{\partial\zeta} \qquad (25)$$

and using the definition of ϕ_∞ as the equilibrium solubility in a stressless system, we get

$$\ln\phi_\infty + (1-\phi_\infty) + \chi(1-\phi_\infty)^2 + S[(1-\phi_\infty)^{1/3} - (1-\phi_\infty)/2] = \ln\phi_s + (1-\phi_s) + \chi(1-\phi_s)^2 + S[(1-\phi_s)^{1/3} - (1-\phi_s)/2] - \frac{3\eta S}{(1-2\nu)}\left[\frac{(1+\nu)}{(1-\nu)}\eta\left(\phi_s - \int_o^1 \phi\, d\zeta\right) + \epsilon - 3\eta(\phi_s - \phi_o)\right] \qquad (26)$$

where $\epsilon = \ell/L$. Equation 25 is to be solved subject to Eq. 26 and the condition

$$\left.\frac{\partial\phi}{\partial\zeta}\right|_{\zeta=1} = 0 \qquad (27)$$

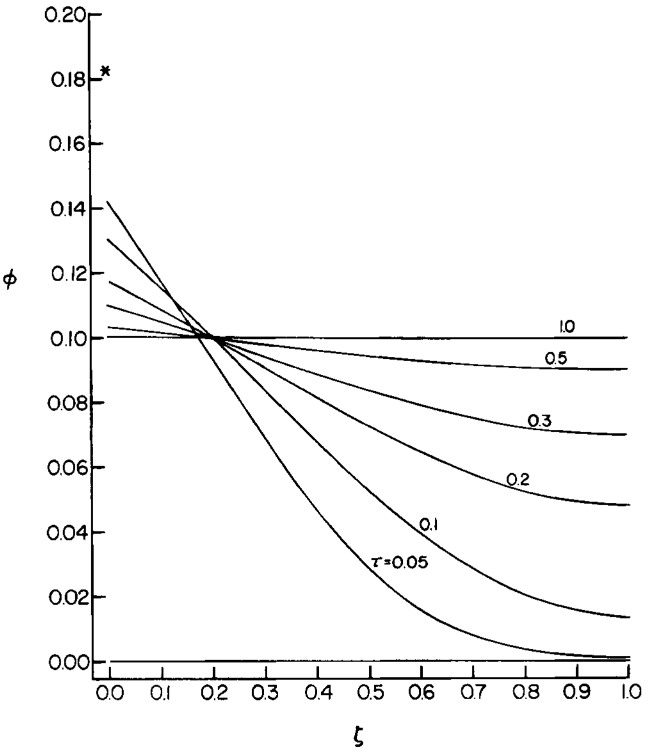

Figure 9. Concentration profiles during sorption in an externally confined membrane shown in Fig. 8.
$\chi = 0.0$; $\eta = 0.33$; $\nu = 0.33$; $\phi_\infty = 0.1$; $\phi_o = 0.0$; $S = 5$.

Here, $\phi_s = \phi_{\zeta=0}$, $\zeta = z/L$, $\tau = D_o t/L^2$, $\epsilon = \ell/L$, $S = EV_1/3RT$, and ϕ_o is the reference concentration at which η is determined.

According to Eq. 25 the effective diffusion coefficient is the same as that in Eq. 14. That is, the effect of deformation, in the form of extension ℓ/L does not modify the diffusivity in the linear theories of small deformations, and the differences we expect to find are mainly the effects of the boundary condition, Eq. 26.

Results

Solutions have been obtained below for $\phi_o = 0$, $\epsilon = 0.1$, $\chi = 0$, $\nu = 0.33$, and $\eta = 0.33$. Figures 9 and 10 have been drawn for $\phi_\infty = 0.1$ and $S = 5$, and 50, respectively. For these values the residual stresses are zero and the solubility ϕ_s reaches ϕ_∞ at infinite time. These figures show ϕ as functions of ζ at different times τ. We have also investigated cases with the above values but with $\phi_\infty = 0.05$ and 0.2. The results are not very different, except that ϕ_s at infinite time does not approach ϕ_∞. When $\phi_\infty = 0.05$, the residual stress is tensile in nature and ϕ_s at $\tau = \infty$ is higher than ϕ_∞. However when $\phi_\infty = 0.2$, the swelling is higher and the residual stress is compressive in nature, thus $\phi_s(\tau = \infty)$ is lower than ϕ_∞. The solubilities ϕ_s/ϕ_∞ have been plotted against τ in Figure 11. The diffusion process is otherwise undistinguished, the rates are seen to increase with increasing S, as found in the case where the membranes were externally unstressed. That is, the diffusion is independent of ℓ/L.

Some general observations can be made regarding the diffusion in prestressed isotropic media under arbitrary forms of prestressing and directions of diffusion under the present formulation. Because of the linear nature of the elasticity relation the

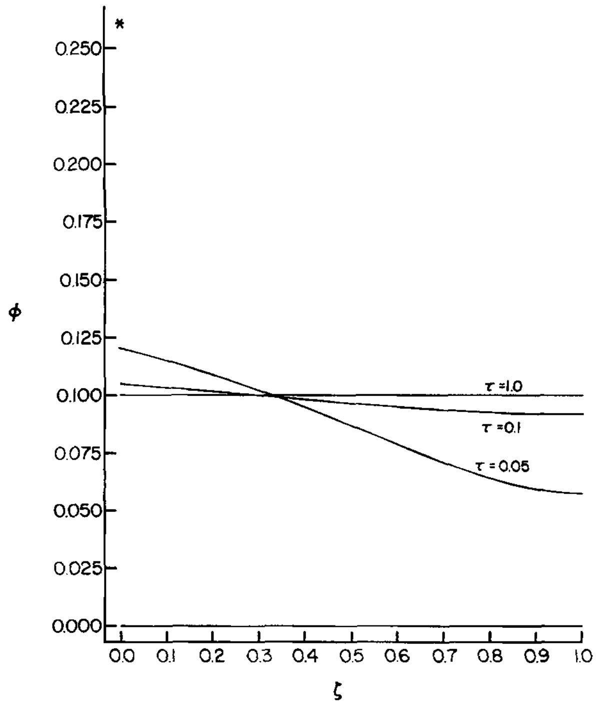

Figure 10. Concentration profiles during sorption in an externally confined membrane shown in Fig. 8.
$\chi = 0.0; \eta = 0.33; \nu = 0.33; \phi_\infty = 0.1; \phi_o = 0.0; S = 50.$

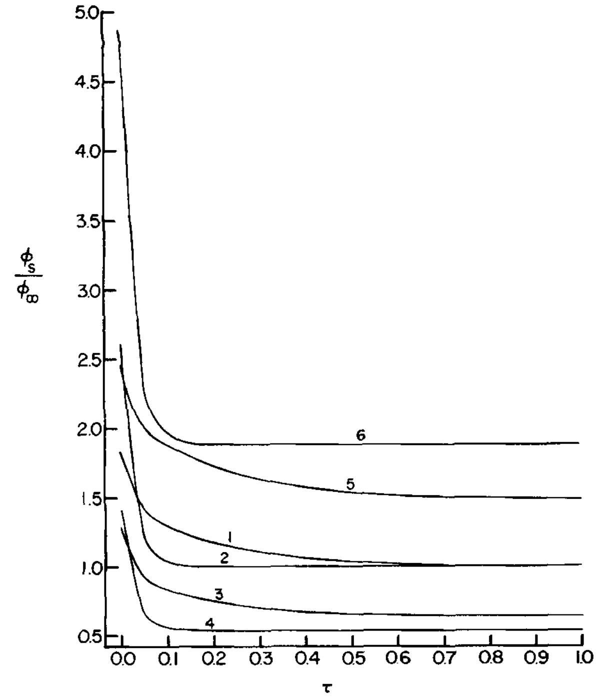

Figure 11. Solubilities as functions of time.
$\chi = 0.0; \eta = 0.33; \nu = 0.33; \phi_o = 0.0.$
(1) $S = 5; \phi_\infty = 0.1$
(2) $S = 50; \phi_\infty = 0.1$
(3) $S = 5, \phi_\infty = 0.2$
(4) $S = 50, \phi_\infty = 0.2$
(5) $S = 5, \phi_\infty = 0.05$
(6) $S = 50, \phi_\infty = 0.05$

effect of the deformation ℓ/L will be a linear addition to the chemical potential and the proportionality factor will be a constant independent of ϕ. As this expression is differentiated with respect to ϕ the term in ℓ/L will drop out and the diffusion will be independent of ℓ/L. However this term will not drop out if the higher order effects—namely, nonlinear swelling, that is, a variable η, and the plasticizing effect, that is, a concentration-dependent Young's modulus—are taken into account, or alternatively, nonlinear elasticity theories are used.

Discussion

In general, the system of equations presented here applies to all solids, not only to polymers. As a matter of fact the equations were first derived for applications in metallurgical systems. The differences among various systems arise in the term $\mu(0, \phi)$, that is, the chemical potential of a stressless system, which for polymers is given by the Flory-Huggins-Rehner equation. In spite of this generality, there are some confining assumptions made; these are:

1. Use of the constitutive equation in the form of the linear Young's law, which is not valid under large deformations.
2. Use of constant values for η and E. Most often when the swelling is large the swelling will be a nonlinear function of ϕ in a marked way. Similarly, E will also depend on ϕ. However incorporation of these effects complicates matters considerably, and only simple forms have been retained such that the basic physical effects are exposed. It is also quite likely that such a simplistic treatment is sufficient in many situations.
3. Use of a constant mobility D_o/RT. In solids the presence of solute alters the mobilities. This effect has not been incorporated for it can obscure the effect of swelling in the calculations, as some of the calculations of Petropoulos (1984a,b) can be used to demonstrate. By choosing to maintain D_o/RT a constant the basic features of swelling can be demonstrated more clearly, and as the comparison with experiments shows, the solutions are none the worse for it, at least in one case. We have however checked our calculations against a model for concentration-dependent mobility using data obtained by Kulkarni and Stern (1983), who used refined methods of parameter estimation. No significant differences were observed although these differences were present.

It has been shown here that some types of anomalous diffusion in polymers can be explained with swelling effects. Other cases can be explained through relaxation, where the basic nature of solute-polymer interactions are assumed to change with time. These are two different mechanisms, and it is quite probable that in many real systems both apply. This introduces additional difficulties, as in that case η, E, and D_o/RT will also be functions of time, the forms of which are not known. It is important to note that relaxation is measured through a relaxation time τ_R. When τ_R is very small, the relaxation is instantaneous and its effects are not observed. When τ_R is very large, the diffusion process is finished long before any significant relaxation can take place. Table 2 describes the regions where the solutions are known.

Lastly, the solutions to the equations can also be used to obtain the stresses in the system. These stresses can be quite large and can cause failures. Such failures have been reported in the experiments. The criteria for failures have not been developed, but it is worth pointing out that some quantitative features have been provided for the first time using theory to show that

Table 2. Swelling and Relaxation Effects

Relaxation Time	Extent of Swelling: Very Small	Moderate	Large
Very small	Both effects may be neglected; diffusion is classical.	Relaxation can be neglected; solution provided here holds.	No solutions known in this region, the chief reason being that deformations are large and models for these are yet to be developed.
Moderate	Swelling can be neglected; solutions given by Neogi (1983 a,b) hold.	Both effects and their interactions are important; solutions are not known.	
Large	Both effects may be neglected; diffusion is classical; special case of solution by Neogi (1983 a,b).	Relaxation can be neglected; solution provided here holds.	

these failures—popularly known as environmental stress cracking—can take place under diffusion.

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Notation

c = concentration of a solute
D_o = diffusion coefficient at infinite dilution
D = effective diffusivity
E = Young's modulus
E, E_{ij} = strain tensor and its components
I = identity tensor
j, j_z = flux vector and its component in the z direction
ℓ = deformation length
L = length or width of the diffusion path in a membrane
M = mass uptake, increase in mass of the solute in the membrane
n = number of moles
R = universal gas constant
$S = EV_1/3RT$ (or entropy)
t = time
tr = trace
T = absolute temperature
u, u_i = deformation vector and its component
U = internal energy
V = volume
V_1 = partial molar volume of the solute in the membrane
x, y = coordinates perpendicular to the direction of flux, see also Fig. 8.
z = coordinate in the direction of flux

Greek Letters

μ = chemical potential
σ, σ_{ij} = stress tensor and its components
σ^* = dimensionless stress $\sigma(1 - \nu)/\eta E$
ϕ = volume fraction of the solute
ϕ_s = solubility in terms of volume fraction
η = coefficient of expansion, Eq. 9
ν = Poisson's ratio
χ = Flory-Huggins parameter
τ = dimensionless time
ζ = dimensionless distance
Δ = difference from a reference value
∇ = vector differential, del operator

Superscripts

c = contribution from swelling
m = contribution from mechanical force
T = transpose

Subscripts

i = initial
f = final
∞ = equilibrium
o = reference value

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