Horio, M., and C. Y. Wen, "Simulation of Fluidized Bed Combustors," AIChE Annual Meeting, Paper No. 48f, Chicago (1976).

Hougen, O. A., K. M. Watson, and R. A. Ragatz, *Chemical Process Principles*, 2nd Ed., Wiley, NY (1954).

Howard, J. B., G. C. Williams, and D. B. Fine, 14th Symp (Int.) on Combustion, The Combustion Institute, Pittsburgh, 975 (1973).

Inst. of Gas Tech., *Coal Conversion Systems Technical Data Book*, Prepared for the Department of Energy, Chicago, (1978).

Merrick, D., and J. Highley, "Particle Size Reduction and Elutriation in a Fluidized Bed Process," *AIChE Symp. Ser.*, No. 137, **70**, 366 (1974).

Mon, E., and N. R. Amundson, "Diffusion and Reaction in a Stagnant Boundary Layer about a Carbon Particle. 2. An Extension," *Ind. Eng. Chem. Fund.*, **17**, No. 4, 313 (1978).

Mon, E., and N. R. Amundson, "Diffusion and Reaction in a Stagnant Boundary Layer about a Carbon Particle 3. Stability," *Ind. Eng. Chem. Fund.*, **18**, No. 2, 162 (1979).

Overturf, B. W., and G. V. Reklaitis, "Bed: A Generalized Model of a Fluidized Bed Gas-Solid Reactor," Purdue Research Foundation, W. Lafayette, IN (1980).

Overturf, B. W., and G. V. Reklaitis, "A Fluidized Bed Reactor Model with Generalized Particle Balances: Part I: Formulation and Solution," *AIChE J.*, **29** (Sept. 1983).

Overturf, B. W., "Toward a Generalized Description of Gas-Solid Reaction in a Fluidized Bed Reactor," PhD Thesis, Purdue University, W. Lafayette, IN (1980).

Rajan, R., and C. Y. Wen, "Fluidized Bed Coal Combustor Modeling," AIChE Nat. Meeting, Paper No. 57a, Houston (1979).

Sergeant, G. D., and I. W. Smith, "Combustion Rate of Bituminous Coal Char in the Temperature Range 800 to 1700 K," *Fuel*, **52**, 52 (1973).

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Anomalous Diffusion of Vapors through Solid Polymers

Part I: Irreversible Thermodynamics of Diffusion and Solution Processes

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The solubility and diffusivity of vapors in polymers below and in the vicinity of glass transition temperature are known to be explicitly time-dependent. It is assumed here that the polymers are in nonequilibrium states, characterized by an internal order. The latter relaxes with time and moves towards equilibrium. The changes in the internal order bring about changes in the properties of the polymer-solute system.

The time dependence of diffusivity and solubility has been derived for isothermal processes not far from equilibrium. Well-known procedures for analyzing relaxing systems are used to obtain the above results, and the knowledge of how the internal order is related to the molecular properties is not required.

SCOPE

The anomalous effects that are observed in the penetration of a vapor into solid polymers near and below the glass transition temperatures are well known and are caused by the relaxation in the polymer. As a result of these changes, the diffusivity and the solubility change with time. As a first step towards quantifying these effects, it is necessary to obtain the above as functions of time. These have been obtained here using the well-known ideas from irreversible thermodynamics. Using these forms, the mass transfer rates to such systems can be determined; a systematic study of diverse anomalies known from the experiments can be undertaken.

CONCLUSIONS AND SIGNIFICANCE

The time dependence of diffusion and solubility of a vapor penetrating into a solid polymer below or near the glass transition temperature has been obtained. Such media see molecular relaxation in time, and the above time effects are due to this relaxation and proceed at the same rate. The analysis has the advantage that a molecular model for the relaxation is not necessary to arrive at the results. However, it also proves to be a shortcoming since it is not possible to relate the above effects to the glass transition temperature. Use of molecular or phenomenological theories can be incorporated to introduce this feature. The generality of the present analysis allows the incorporation of such theories. However, the results are sufficient to analyze and unify many of the diverse anomalous effects observed in the sorption experiments on such systems and undertaken in Part II.

Meares (1958 a,b) investigated the diffusion of gases into polymer membranes below glass transition temperatures T_g, and, from the results, was first to conclude that the diffusion coefficient there was an explicit function of time. Since then Alfrey (1965) found cases where such anomalous effects were strongly pronounced and provided the first concentration of the penetrant vs. temperature map on which regions of anomalous behavior could be depicted. This idea has been explored in great detail by Hopfenberg and Frisch (1969), and by Vrentas, Jarzebski and Duda (1975). Together with anomalous or time-dependent diffusion coefficients, anomalous solubility coefficients have also been identified by Bagley and Long (1955) and Long and Richman (1960). Nor are such anomalous effects confined to below T_g; these are seen to occur at temperatures of 5 to 10°C above T_g as well.

It is necessary to specify what are time-dependent diffusion and solubility coefficients. These time-dependent effects are conventionally referred to as the anomalous, as opposed to the classical, that is, time-dependent. Such references imply explicit dependence of these factors on time, and not indirectly through their dependence on concentration when the latter changes with time. The implicit dependence on time through the dependence on the concentration will not be considered as "time dependence" subsequently.

The anomalous effects below T_g can be explained from the nature of the glassy state. These are noted to be in nonequilibrium states (Rehage and Borchard, 1973; Bueche, 1982); because of their glassy natures they have very slow rates of change towards equilibrium. It is well known that such changes do take place in time and the changes affect their physical properties (Kovacs, 1958). It may also be anticipated that the relaxation rates, that is, the movement towards equilibrium, increase very sharply as the temperatures rise above T_g. Even though the rates of relaxation there are very high, they are finite and one anticipates some anamalous effects close to but above T_g. This has been noted earlier.

Frisch (1964) was the first to attempt to quantify these effects for sorption into polymers. A general theory of relaxing media was known by that time (deGroot and Mazur, 1962; Meixner and Reik, 1959). One must know in principle what changes take place in the polymer molecules with time that bring about these time-dependent effects. These changes could be in orientation, molecular conformation, distribution of the translational energies in the polymer chain segments, internal stress, or phenomenological properties like the "fluidity" of a polymer molecule used in the free-volume theories of polymeric systems (Grest and Cohen, 1981). The specific nature of this parameter will not be a subject of discussion here. The existence of an extensive variable ξ_p, the internal order of the polymer describing the above will be taken for granted. Further, all extensive thermodynamical variables are assumed to be linked by the fundamental equation

$$U = U(S,V,\boldsymbol{n},\xi_p) \tag{1}$$

where $\boldsymbol{n}$ represents vectorially the moles of different species present. The internal order ξ_p changes with time; the rate is written phenomenologically (de Groot and Mazur, 1962; Meixner and Reik, 1959) as

$$\frac{d}{dt}\xi_p = -l_{\xi\xi}\frac{A_p}{T} \tag{2}$$

where

$$\left(\frac{\partial S}{\partial \xi_p}\right)_{U,V,\boldsymbol{n}} = -\frac{A_p}{T} \tag{3}$$

and $l_{\xi\xi}$ is a phenomenological coefficient. Note that the ξ_s of the simple penetrant molecules will always be assumed to be at equilibrium. In future, the assumption of constant temperature will be made. Together with Eqs. 1–3, the phenomenological expression for the fluxes, Frisch (1964) was able to show that the diffusion coefficient and the solubility were explicitly time-dependent. Frisch assumed that $l_{\xi\xi}$ was a function of time. Such an assumption will not be made here. Frisch also assumed certain phenomenological forms which leave the parameters uninterpreted. There is a more attractive alternative method (de Groot and Mazur, 1962; Meixner and Reik, 1959) which allows a derivation in terms of derivatives in variables of Eq. 1. Obviously, in not having an explicit equation, complete results cannot be obtained. Through the derivation given below, one is able to obtain the mathematical structure of the diffusional relaxation and improve on Frisch's results for the solubility relaxation.

The anomalous effects observed in sorption experiments will be discussed in Part II. There are cases where the relaxation times appear to be small but large enough for its effects to be observable. In contrast, there are systems where, in spite of the fact that they are well below T_g, the diffusion appears to be classical. It is concluded that the polymer matrix remains virtually at its initial state during the sorption process due to an extremely slow relaxation (Vrentas and Duda, 1979). Perhaps the more interesting case is where the solute enters the polymer in form of a concentration shock (Alfrey, 1965; Hopfenberg and Stannett, 1973). The imbibition of solute is due virtually alone to the relaxation of the polymer.

The problem of how to best express mathematically time-dependent diffusion in a relaxing medium is solved through an analogy with the rheology of viscoelastic materials (Fredrickson, 1974) as

$$j_{s} = -\int_o^t \eta(t-t')\nabla C_s(x,t')dt'$$

It is η as a function of t that will be evaluated subsequently.

THERMODYNAMICS

Let $\boldsymbol{\zeta}$ be the set of extensive thermodynamic variables written in a vector form; for example,

$$\boldsymbol{\zeta} = \begin{pmatrix} n_s \\ n_p \\ V \end{pmatrix}$$

Because the temperature T is a constant, U will be excluded from $\boldsymbol{\zeta}$. ξ_p will be also excluded. One may write now,

$$T\,dS = \boldsymbol{Z}d\boldsymbol{\zeta} - A_p d\xi_p \tag{4}$$

where

$$\boldsymbol{Z} = T\left(\frac{\partial S}{\partial \boldsymbol{\zeta}}\right)\xi_p. \tag{5}$$

$\boldsymbol{Z}$ (in vector form) and A_p are the intensive variables. Following well-established procedure (de Groot and Mazur, 1962; Prigogine, 1967), one assumes that equilibrium is defined for a value ξ_p^o for which the entropy is a maximum. It follows from Eq. 3 that $A_p = 0$ at $\xi_p = \xi_p^o$. To satisfy the condition that S is a maximum, inequalities

$$\left(\frac{\partial^2 S}{\partial \xi_p^2}\right)^0 < 0 \text{ and } \left(\frac{\partial A_p}{\partial \xi_p}\right)^0 > 0$$

are obtained. Further, from the definition, Eq. 3, A_p is always taken to be positive.

Noting that dS is a total differential, a Maxwell-type relation can be obtained as

$$-\left(\frac{\partial A_p}{\partial \boldsymbol{\zeta}}\right)^+_{\xi_p} = \left(\frac{\partial \boldsymbol{Z}}{\partial \xi_p}\right)_{\boldsymbol{\zeta}} \tag{6}$$

In the derivations that follow, it will be assumed that the systems are not far from equilibrium. Thus, for example, $\mu_s(\boldsymbol{\zeta},\xi_p)$ is written as

$$d\mu_s = \left(\frac{\partial \mu_s}{\partial \boldsymbol{\zeta}}\right)_{\xi_p} d\boldsymbol{\zeta} + \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_{\boldsymbol{\zeta}} d\xi_p$$

The differentials are then substituted with Δ denoting deviations from equilibrium, that is $\Delta\mu_s = \mu_s - \mu_s^o$. Thus one has

$$\Delta\mu_s = \left(\frac{\partial\mu_s}{\partial\zeta}\right)_{\xi_p}\Delta\zeta + \left(\frac{\partial\mu_s}{\partial\xi_p}\right)_\zeta\Delta\xi_p, \text{ etc.}$$

Obviously for the above linearized relations to remain valid, only cases close to equilibrium can be analyzed; only then, the partial derivatives of intensive variables with respect to extensive variables can be treated as constants and evaluated at equilibrium.

SOLUBILITY

At equilibrium the chemical potential of the solute in the polymer is equal to the chemical potential of the pure solute in a reservoir with which it is in contact. The properties of the reservoir do not change, hence the chemical potential of the solute in the polymer at equilibrium remains a constant. If, however, under those conditions the concentration of the solute changes in the polymer, it must be at the cost of the changing ξ_p at constant μ_s. Linearizing a relation μ_s (ζ,ξ) about equilibrium, one has

$$\Delta\mu_s = 0 = a\Delta\zeta + \left(\frac{\partial\mu_s}{\partial\xi_p}\right)_\zeta\Delta\xi_p \tag{7}$$

where

$$a = \left(\frac{\partial\mu_s}{\partial\zeta}\right)_{\xi_p}. \tag{8}$$

and Δ denotes departure from equilibrium, e.g., $\Delta\xi_p = \xi_p - \xi_p^o$, etc. Further, one may also linearize $A_p(\zeta,\xi_p)$ about equilibrium. One has

$$A_p = \left(\frac{\partial A_p}{\partial\zeta}\right)_{\xi_p}\Delta\zeta + \left(\frac{\partial A_p}{\partial\xi_p}\right)_\zeta\Delta\xi_p \tag{9}$$

Combining Eqs. 9 and 6

$$A_p = -\left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta^+\Delta\zeta + \left(\frac{\partial A_p}{\partial\xi_p}\right)_\zeta\Delta\xi_p. \tag{10}$$

Eliminating $\Delta\zeta$ from Eq. 10 with Eq. 7 one has

$$A_p = \left[\left(\frac{\zeta A_p}{\partial\xi_p}\right)_\zeta + \left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta^+ a^{-1}\left(\frac{\partial\mu_s}{\partial\xi_p}\right)_\zeta\right]\Delta\xi_p \tag{11}$$

where

$$a^{-1} = \frac{a^+}{|a|^2} \tag{12}$$

From Appendix, Eq. 11 simplifies to

$$A_p = \left[\left(\frac{\partial A_p}{\partial\xi_p}\right)_{\mu_s}\right]\Delta\xi_p. \tag{13}$$

Substituting Eq. 13 into Eq. 2 and assuming an initial value of $\Delta\xi_p^i$, one has on integration

$$\Delta\xi_p = \Delta\xi_p^i \exp\left[-\frac{l_{\xi\xi}}{T}\left(\frac{\partial A_p}{\partial\xi_p}\right)_{\mu_s} t\right] \tag{14}$$

Substituting Eq. 14 into Eq. 7 and assuming an initial value of $\Delta\zeta = \Delta\zeta^i$, one has

$$\Delta\zeta = \Delta\zeta^i \exp\left[-\frac{l_{\xi\xi}}{T}\left(\frac{\partial A_p}{\partial\xi_p}\right)_{\mu_s} t\right]\cdot \tag{15}$$

Thus

$$C_s - C_s^o = (C_s^i - C_s^o)\exp\left[-\frac{l_{\xi\xi}}{T}\left(\frac{\partial A_p}{\partial\xi_p}\right)_{\mu_s} t\right] \tag{16}$$

or on using Eq. 3,

$$C_s - C_s^o = (C_s^i - C_s^o)\exp\left[l_{\xi\xi}\left(\frac{\partial^2 S}{\partial\xi_p^2}\right)_{\mu_s} t\right] \tag{17}$$

where $(\partial^2 S/\partial\xi_p^2)_{\mu_s} < 0$ as discussed earlier.

DIFFUSIVITY

Complex Fourier transform (Bateman, 1954) is taken of Eq. 2 to get

$$i\omega\Delta\bar{\xi}_p = -\frac{l_{\xi\xi}}{T}\bar{A}_p \tag{18}$$

One also transforms Eq. 9 to get

$$\bar{A}_p = \left(\frac{\partial A_p}{\partial\zeta}\right)\Delta\bar{\zeta} + \left(\frac{\partial A_p}{\partial\xi_p}\right)\Delta\bar{\xi}_p \tag{19}$$

assuming that the partial derivatives are not time-dependent. One may also expand Z about the equilibrium and then transform it to get

$$\Delta\bar{Z} = \left(\frac{\partial Z}{\partial\zeta}\right)_{\xi_p}\Delta\bar{\zeta} + \left(\frac{\partial Z}{\partial\xi_p}\right)\Delta\bar{\xi}_p \tag{20}$$

Eliminating $\bar{A}_p$ from Eqs. 18 and 19, one obtains an equation relating $\Delta\bar{\xi}_p$ to $\Delta\bar{\zeta}$. Substituting that in Eq. 20, one has

$$\Delta\bar{Z} = \left[\left(\frac{\partial Z}{\partial\zeta}\right)_{\xi_p} + \left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta\left\{\left(\frac{\partial A_p}{\partial\xi_p}\right)_\zeta + \frac{i\omega T}{l_{\xi\xi}}\right\}^{-1}\left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta^+\right]\cdot\Delta\bar{\zeta} \tag{21}$$

where

$$\left(\frac{\partial Z}{\partial\zeta}\right)_{\xi_p} + \left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta\left(\frac{\partial A_p}{\partial\xi_p}\right)_\zeta^{-1}\left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta^+ = \left(\frac{\partial Z}{\partial\zeta}\right)_{A_p} \tag{22}$$

from Appendix. The second term on the righthand side within the square brackets in Eq. 21 is a dyadic as well as the second term on the lefthand side in Eq. 22. Taking Z as $-\begin{pmatrix}\mu_s\\ \mu_p\end{pmatrix}$ and $\zeta = \begin{pmatrix}C_s\\ C_p\end{pmatrix}$, and defining

$$F = \mu_s - \mu_p \tag{23}$$

one has from Eqs. 21 and 23,

$$\Delta\bar{F} = \left(\frac{\partial F}{\partial\zeta}\right)_{\xi_p}\Delta\bar{\zeta} + \left(\frac{\partial F}{\partial\xi_p}\right)_\zeta\left\{\left(\frac{\partial A_p}{\partial\xi_p}\right)_\zeta + \frac{i\omega T}{l_{\xi\xi}}\right\}^{-1}\left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta^+\Delta\bar{\zeta} \tag{24}$$

and from Eqs. 22 and 23,

$$\left(\frac{\partial F}{\partial\zeta}\right)_{\xi_p} + \left(\frac{\partial F}{\partial\xi_p}\right)_\zeta\left(\frac{\partial A_p}{\partial\xi_p}\right)_\zeta^{-1}\left(\frac{\partial Z}{\partial\xi_p}\right)_\zeta^+ = \left(\frac{\partial F}{\partial\zeta}\right)_{A_p}\cdot \tag{25}$$

The phenomenological definition of flux of the solute is

$$j_s = -\frac{L_{sp}}{T}\nabla(\mu_s - \mu_p). \tag{26}$$

Substituting Eq. 23 in 26, taking the Fourier transform and using Eq. 24, one has

$$\bar{j}_s = -\frac{L_{sp}}{T}\left[\left(\frac{\partial F}{\partial\zeta}\right)_{\xi_p}\nabla\bar{\zeta} + \left(\frac{\partial F}{\partial\xi_p}\right)_{C_s}\left\{\left(\frac{\partial A_p}{\partial\xi_p}\right)_{C_s} + \frac{i\omega T}{l_{\xi\xi}}\right\}^{-1}\cdot\left(\frac{\partial Z}{\partial\xi_p}\right)^+\nabla\bar{\zeta}\right]$$

On neglecting $\nabla\bar{C}_p$, one has

$$\bar{j}_s = -\frac{L_{sp}}{T}\left[\left(\frac{\partial F}{\partial C_s}\right)_{\xi_p} + \left(\frac{\partial F}{\partial\xi_p}\right)_{C_s}\left\{\left(\frac{\partial A_p}{\partial\xi_p}\right)_{C_s} + \frac{i\omega T}{l_{\xi\xi}}\right\}^{-1}\cdot\left(\frac{\partial\mu_s}{\partial\xi_p}\right)_{C_s}\right]\nabla\bar{C}_s \tag{27}$$

Inversion is accomplished by stipulating that $\nabla C_s = 0$ for $t < 0$, in which case Eq. 27 becomes a Laplace transform with $(i\omega)$ as its variable (Bateman, 1954). Using convolution theorem, the inversion is

$$j_s = -\int_o^t \eta(t - t')\nabla C_s(t')dt' \tag{28}$$

where

$$\eta(t) = \frac{L_{sp}}{T}\left[\left(\frac{\partial F}{\partial C_s}\right)_{\xi_p}\delta(t) + \frac{l_{\xi\xi}}{T}\left(\frac{\partial F}{\partial\xi_p}\right)_{C_s}\cdot e^{-\frac{l_{\xi\xi}}{T}\left(\frac{\partial A_p}{\partial\xi_p}\right)_{C_s} t}\cdot\left(\frac{\partial\mu_s}{\partial\xi_p}\right)_{C_s}\right]\cdot \tag{29}$$

where $\delta(t)$ is Dirac delta function. It is shown in Part II that the diffusion coefficient reached at infinite time is

$$D^o = \int_o^\infty \eta dt \tag{30}$$

or

$$D^o = \frac{L_{sp}}{T}\left[\left(\frac{\partial F}{\partial C_s}\right)_{A_p}\right] \tag{31a}$$

on using Eqs. 29 and 25. Since at infinite time equilibrium is achieved, that is, $A_p = A_p^o = 0$, one has

$$D^o = \frac{L_{sp}}{T}\left(\frac{\partial F}{\partial C_s}\right)^o \tag{31b}$$

Using the Gibbs-Duhem equation at equilibrium, $C_s^o d\mu_s^o + C_p^o d\mu_p^o = 0$, one has

$$\left(\frac{\partial F}{\partial C_s}\right)^o = \frac{1}{1 - x_s^o}\left(\frac{\partial \mu_s}{\partial C_s}\right)^o \cdot$$

Substituting into Eq. 31b, one has

$$D^o = \frac{L_{sp}}{T(1 - x_s^o)}\left(\frac{\partial \mu_s}{\partial C_s}\right)^o \tag{32}$$

Equation 34 is the well-known phenomenological definition for classical diffusion coefficient. Thus, when diffusional relaxation time is small, it will be $\ll$ times of experiments, the diffusion coefficient will be time-independent and given by Eq. 32.

If the magnitude of the second term within the square brackets in Eq. 28 is much less than the first term, one has

$$\eta \approx \frac{L_{sp}}{T}\left(\frac{\partial F}{\partial C_s}\right)_{\xi_p} \delta(t).$$

Substituting into Eq. 29, one has

$$j_s = -D^i \nabla C_s \tag{33}$$

where

$$D^i = \frac{L_{sp}}{T}\left(\frac{\partial F}{\partial C_s}\right)_{\xi_p} \cdot \tag{34}$$

On comparing Eq. 34 to Eq. 31, one notes that D^i is an appropriate initial diffusion coefficient.

Equation 26 thus has the structure of

$$\eta = D^i\delta(t) + \frac{(D^o - D^i)}{t^*} e^{-t/t^*} \tag{35}$$

where t^* is a constant. Although η is not the instantaneous diffusion coefficient, its integral with respect to time is related to the above. In that Eq. 35 provides a simple interpretation that starting from an initial value D^i, the diffusion coefficient reaches a final value of D^o at infinite time.

DISCUSSION

It can be noted from Eqs. 17 and 29 that time dependence of solubilities and diffusivity persists for the small amount of time, being characterized by the same time constant $[l_{\xi\xi}(-\partial^2 S/\partial \xi_p^2)]^{-1}$. However, this is not sufficient to say that both processes are equally important in the sorption experiments. From Eqs. 14 and 17 it becomes apparent that the extent of solubility relaxation $(C_s^i - C_s^o)/C_s^o$ is dependent on the ranges of ξ_p alone. In the case of diffusion relaxation, Eq. 29 shows that the extent $(D^i - D^o)/D^o$ is strongly dependent on the effect of ξ_p on the chemical potentials μ_s and μ_p. It will be shown in Part II that the anomalous effects observed in sorption can be attributed either mainly to time-dependent diffusion or to time-dependent solubility, and in all the cases studied, never equally to both.

The fact that both diffusivities and solubilities have the same constant

$$\left[l_{\xi\xi}\left(-\frac{\partial^2 S}{\partial \xi_p^2}\right)\right]^{-1}$$

is somewhat significant. Expanding Eq. 2 for small deviations from equilibrium, one has for a closed system

$$\frac{d}{dt}\Delta\xi_p = -\frac{l_{\xi\xi}}{T}\left(\frac{\partial A_p}{\partial \xi_p}\right)\Delta\xi_p.$$

On integration, one has

$$\Delta\xi_p = \Delta\xi_p^i \exp\left[-\frac{l_{\xi\xi}}{T} \cdot \left(\frac{\partial A_p}{\partial \xi_p}\right)\right] = \Delta\xi_p^i \exp\left[l_{\xi\xi}\left(\frac{\partial^2 S}{\partial \xi_p^2}\right) t\right] \cdot$$

Thus the change in ξ_p is given by the same time constant. This is not surprising in light of the fact that ξ_p changes with time that leads to time-dependent nature of the diffusivity and the solubility. The latter two should persist for the same time as the former.

Although the results obtained here are very simple and general, they have a shortcoming in that their relation to glassy state or T_g are not known. Frisch (1964) assumed that $\xi_p = \xi_p^o$ for $T > T_g$ to introduce this effect. Here it has been assumed that ξ_p above T_g is not necessarily at its equilibrium value, but is characterized by a very large rate of relaxation towards equilibrium. When this rate is large, the relaxation times are small, as seen in the analysis of anomalous sorption results above T_g (Part II). When this rate is infinite, as should be the case for $T \gg T_g$, the system is relaxed; i.e., $\xi_p = \xi_p^o$ and the sorption is classical. Thus, ξ_p changes from nonequilibrium values to ξ_p^o quickly in the vicinity of T_g, but not necessarily suddenly. It is also obvious that to incorporate the effects of T_g, one needs to have the complete Eq. 1.

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NOTATION

A = Affinity, Eq. 3
a = Eq. 8
C = concentration
D = diffusion coefficient
F = Eq. 23
i = $\sqrt{-1}$
j = diffusional flux
$l_{\xi\xi}$ = phenomenological relaxation coefficient, Eq. 2
L = phenomenological diffusion coefficient, Eq. 26
n = moles of different species expressed as a vector
S = entropy
T = temperature
t = time
t^* = time constant
U = internal energy
V = volume
x = mole fraction
Z = intensive variables corresponding to ζ, a row vector

Greek Letters

ξ = internal order
ζ = extensive variables corresponding to Z, a column vector
μ = chemical potential
ν = diffusional relaxation function, Eq. 28
Δ = deviation from equilibrium value
∇ = gradient operator
δ = Dirac delta function

Subscripts

g = glass
p = polymer
s = solute

Superscripts

o = equilibrium
$+$ = transpose
i = initial

APPENDIX

One may write

$$dA_p = \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta d\xi_p + \left(\frac{\partial A_p}{\partial \zeta}\right)_{\xi_p} d\zeta \tag{A1}$$

then,

$$\left(\frac{\partial A_p}{\partial \xi_p}\right)_{\mu_s} = \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta + \left(\frac{\partial A_p}{\partial \zeta}\right)_{\xi_p} \left(\frac{\partial \zeta}{\partial \xi_p}\right)_{\mu_s} \tag{A2}$$

One also has

$$d\mu_s = \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_\zeta d\xi_p + \left(\frac{\partial \mu_s}{\partial \zeta}\right)_{\xi_p} d\zeta \tag{A3}$$

and at constant μ_s,

$$\left(\frac{\partial \zeta}{\partial \xi_p}\right)_{\mu_s} = -a^{-1} \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_\zeta \tag{A4}$$

where a is given by Eq. 8. Substituting Eq. A4 into Eq. A2 and using the Maxwell relation, Eq. 6, one has

$$\left(\frac{\partial A_p}{\partial \xi_p}\right)_{\mu_s} = \left(\frac{\partial A_p}{\partial \xi_p}\right)_\zeta + \left(\frac{\partial Z}{\partial \xi_p}\right)^+_\zeta a^{-1} \left(\frac{\partial \mu_s}{\partial \xi_p}\right)_\zeta \tag{A5}$$

Similarly

$$dZ = \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta d\xi_p + \left(\frac{\partial Z}{\partial \zeta}\right)_{\xi_p} d\zeta \tag{A6}$$

which yields

$$\left(\frac{\partial Z}{\partial \zeta}\right)_{A_p} = \left(\frac{\partial Z}{\partial \zeta}\right)_{\xi_p} + \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta \left(\frac{\partial \xi_p}{\partial \zeta}\right)_{A_p} \tag{A7}$$

From Eq. A1

$$\left(\frac{\partial \xi_p}{\partial \zeta}\right)_{A_p} = -\left(\frac{\partial A_p}{\partial \xi_p}\right)^{-1}_\zeta \left(\frac{\partial A_p}{\partial \zeta}\right)_{\xi_p} \tag{A8}$$

Using Eq. 6, Eq. A6 in Eq. A5 one has

$$\left(\frac{\partial Z}{\partial \zeta}\right)_{A_p} = \left(\frac{\partial Z}{\partial \xi_p}\right)_{\xi_p} + \left(\frac{\partial Z}{\partial \xi_p}\right)_\zeta \left(\frac{\partial A_p}{\partial \xi_p}\right)^{-1}_\zeta \left(\frac{\partial Z}{\partial \xi_p}\right)^+_\zeta \tag{A9}$$

LITERATURE CITED

Alfrey, T., "Glassy Polymer Diffusion," *Chem. Eng. News*, **43**, No. 41, 64 (1965).

Bagley, E., and F. A. Long, "Two-Stage Sorption and Desorption of Organic Vapors in Cellulose Acetate," *J. Amer. Chem. Soc.*, **77**, 2172 (1955).

Bateman, H., "Tables of Integral Transforms," **1**, McGraw-Hill, New York (1954).

Bueche, F., "Physical Properties of Polymers," Interscience Pub., 85 (1962).

de Groot, S. R., and P. Mazur, "Non-Equilibrium Thermodynamics," Interscience, New York, 221 (1962).

Fredrickson, A. G., "Principles of Rheloogy," Prentice-Hall, Inc. (1974).

Frisch, H. L., "Isothermal Diffusion in Systems with Glasslike Transitions," *J. Chem. Phys.*, **41**, 3679 (1964).

Grest, G. S., and M. H. Cohen, "Liquids, Glasses, and the Glass Transition: A Free Volume Approach," *Advances in Chemical Physics*," **48**, 455 (1981).

Hopfenberg, H. B., and H. L. Frisch, "Transport of Organic Micromolecules in Amorphous Polymers," *J. Polym. Sci.*, **137**, 405 (1969).

Hopfenberg, H. B., and V. Stannett, in *The Physics of Glassy Polymers*, R. N. Howard, Ed., John Wiley, New York, 504 (1973).

Kovacs, A. J., "La Contraction Isotherm du Volume des Polymeres Amorphes," *J. Polym. Sci.*, **30**, 131 (1958).

Long, F. A., and D. Richmann, "Concentration Gradients for Diffusion of Vapors in Glassy Polymers and Their Relation to Time Dependent Diffusion Phenomena," *J. Amer. Chem. Soc.*, **82**, 513 (1960).

Meares, P., "Diffusion of Allyl Chloride in Polyvinyl Acetate. Part I. The Steady State Permeation," *J. Polym. Sci.*, **27**, 391 (1958a).

Meares, P., "Diffusion of Allyl Chloride in Polyvinyl Acetate. Part II. The Transient State Permeation," *J. Polym. Sci.*, **27**, 405 (1958b).

Meixner, J., and H. G. Reik, "Thermodynamics of Irreversible Processes," *Handbook of Physics*," **III-2**, 413 (1959).

Neogi, P., "Anomalous Diffusion of Vapors through Solid Polymers. II: Anomalous Sorption" (Sept. 1983).

Prigogine, I., "Introduction to Thermodynamics of Irreversible Processes," 3rd Ed., Interscience Pub. (1967).

Rehage, G., and W. Borchard, *The Physics of Glassy Polymers*, R. N. Howard, Ed., John Wiley, New York, 54 (1973).

Vrentas, J. C., C. M. Jarzebski, and J. L. Duda, "A Deborah Number for Diffusion in Polymer-Solvent Systems," *AIChE J.*, **21**, 894 (1975).

Vrentas, J. C., and J. L. Duda, "Molecular Diffusion in Polymer Solutions," *AIChE J.*, **25**, 1 (1979).

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Part II: Anomalous Sorption

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Sorption of vapors in polymer membranes in the vicinity of and below the glass transition temperatures do not follow the Fickian (classical) diffusion. The reasons have been attributed to the molecular relaxation which affects both diffusivities and solubilities.

A time- and memory-dependent diffusion coefficient has been evaluated in Part I, in a form which is analogous to the treatment in the rheology of such materials. Together with a time-dependent solubility, the conservation equation for the sorption process has been solved. Two special cases are considered, where the relaxation times are short and where they are long. The results explain the anomalous behavior observed in the experiments. Comparison with the experiments has been made.

SCOPE

Mass transfer of small molecules in polymers is important in all stages. The kinetics of polymerization and polymer processing conditions are affected by it. Special features like dyeing and sorption of water vapor from the atmosphere are of great importance in the properties and the durability of polymeric fibers. Of importance in future is the use of polymer membranes