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A Class of Mathematical Models for Sorption of Swelling Solvents in Glassy Polymers

G. ASTARITA and G. C. SARTI

*Istituto di Principi di Ingegneria Chimica
Università di Napoli
Naples, Italy*

A class of mathematical models for sorption of swelling solvents in glassy polymers is analyzed. The essential features of these models are the explicit consideration of the kinetics of swelling and of the driving force for swelling. It is shown that, even when all other elementary phenomena are modeled in the simplest possible way, all the experimentally observed features of the processes considered are correctly predicted.

INTRODUCTION

A large amount of experimental evidence on the diffusion of low-molecular-weight solvents in solid polymers has been collected in the last two decades (1-11). The most interesting features of this evidence have been obtained at temperatures below the glass transition temperature; there exists a threshold solvent activity above which the following features have been reported:

(a) A sharp morphological discontinuity can be observed within the polymer, which separates a glassy region where the solvent concentration is negligible from a swollen rubbery region with a high solvent content.

(b) The discontinuity moves through the polymer with a velocity which is initially constant in time.

(c) The amount of solvent sorbed initially increases linearly with time.

(d) The activation energy for the initial front velocity is not of the right order of magnitude for a diffusion process, but is close to that of craze formation.

(e) At intermediate times, the front position vs time curve can be fitted by a power law with an exponent ranging between 0.5 and 1.

(f) Feature (c) ceases to be true earlier than feature (b).

The nomenclature is not standardized, and "case two-transport" or "anomalous diffusion" have been used in the literature to describe some or all of features (a-e). In this work, we use the "case-two-transport" expression to specifically identify features (b) and (c).

Parallel to the experimental work, several attempts to develop a mathematical model have been reported. The models discussed in the literature, from the mathematical viewpoint, focus their attention on the appropriate diffusion equation, with no particular attention to the boundary conditions to be used (physically, this corresponds to ignoring the physics of the phenomena which may be taking place at the swollen glassy interface). With reference to the simple case of a semi-infinite slab, the boundary conditions considered are (A) constant

penetrant concentration at the external interface, and (B) zero flux at infinity. Condition (B) is imposed at the plane of symmetry in the case of a finite thickness slab. The models do not consider explicitly a discontinuous morphological change, the influence of morphology on diffusion being buried in the form of the diffusion equation.

The gradient of internal stresses and chemical potentials have been considered (12, 13); the result can be expressed, in terms of the penetration depth Λ , by:

$$\Lambda = K\sqrt{\mathcal{D}} t^{1/2} + vt$$

which seems at first sight to be able to produce feature (e). Nonetheless, it is evident that, when $t \rightarrow 0$, the square root term predominates, so that feature (b) cannot possibly be described.

Alternate approaches take into account morphological changes by allowing the diffusivity \mathcal{D} to depend on some internal state variables. Crank (14) considered \mathcal{D} to depend on the local stress, while most workers (15-18) focused attention on the dependency of diffusivity \mathcal{D} on concentration c . Indeed, there are forms of the $\mathcal{D}(c)$ function which allow for a very sharp drop of concentration, say, e.g., if \mathcal{D} is constant at $c > c_0$ and zero of $c < c_0$, a moving concentration front is predicted; a similar result with no actual discontinuity is obtained if \mathcal{D} is taken to be an exponential function of c . It is nonetheless important to point out that, no matter what the $\mathcal{D}(c)$ function may be, the weight absorbed is always initially proportional to the square root of time (15), so that no such model can predict feature (c). Duda and Ventras (17), in addition to a concentration-dependent diffusion, have also considered non-negligible convection flux, but this does not eliminate the above-mentioned problem.

Peterlin's model (18) deserves special comment, since it explicitly considers the two-phase nature of the phenomenon of interest. The model *postulates* that the front moves at constant velocity, so that feature (b) is trivially predicted, but of course at all times, contrary to

experimental evidence. The weight sorbed, W , can be calculated from the model as:

$$W = K_1 t + K_2 \sqrt{\mathcal{D}} \operatorname{erf}(bt^{1/2})$$

with b a constant. It is easy to note that dW/dt is infinity at $t = 0$, so that feature (c) cannot be predicted.

The physics of the phenomenon considered suggest that diffusion, no matter how complicated, is not the only relevant phenomenon. Two phases do appear to exist, and the phase transition needs to be considered and modeled appropriately; the kinetics of the phase transition need to be taken into account. Consideration of this physical phenomenon is the contribution which is offered here.

Indeed, in this work we analyze a class of mathematical models for the process considered which share certain basic features. First of all, we make crucial use of the idea that the phenomenon of swelling is a kinetic one, the rate of which depends on how much the local activity of the swelling solvent exceeds some threshold value below which no swelling at all would occur. Attention is therefore focused on two basic parameters: the driving force for swelling, and the type of swelling kinetics. It will be seen in the next section that these two parameters are measured by the values of q and n , to be defined below.

In order to pursue the implications of the above-mentioned basic features, independently of the additional influence of phenomena previously considered, we make the following two simplifying assumptions:

1. Geometrical complications are excluded from consideration. Attention is therefore focused on a process which is one-dimensional in a Cartesian coordinate system, i.e., sorption of a swelling solvent into a semi-infinite body of polymer from a plane interface located at $x = 0$, where the activity of the solvent is kept constant in time from time 0 onwards.

2. Coupling of the phenomena in the swollen and glassy part of the polymer is excluded from consideration. Implicitly, we assume that either the diffusivity, or the solubility (or both) of the solvent in the glassy polymer is zero. This is bound to be a good approximation at least over some range of values of the operating variables. Furthermore, we neglect convective flux in the swollen polymer.

Let Λ be the thickness of the swollen region, and W the weight of solvent sorbed per unit interface. Of course, both Λ and W are in general functions of time. We refer the Case-II-transport (CTT) conditions to imply that both Λ and W are *linear* functions of time, (i.e., both features (b) and (c) are exhibited) and to pseudo-Fickian transport (PFT) to imply that both Λ and W are proportional to the *square root* of time. We also define four critical times, namely: t'_c = the time below which CTT conditions hold for Λ ; t''_c = the time above which PFT conditions hold for Λ ; t'_{cw} = the time below which CTT conditions hold for W ; and, t''_{cw} = the time above which PFT conditions hold for W .

In these definitions, holding of a given condition is of course understood to within some specified degree of approximation. We seek for the dependency of these

four critical times on the values of the two basic parameters of the models, i.e., n and q .

THE GENERAL MODEL

If the convective flux of solvent is neglected, the diffusion equation in the swollen region takes the following form:

$$\mathcal{D} \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \quad (1)$$

where x is distance from the solvent-polymer interface, \mathcal{D} is the diffusivity in the swollen polymer, t is time and c is the concentration of the solvent in the swollen polymers.

The boundary conditions to be imposed are:

$$x = 0, \quad \forall t, \quad c = c_0 \quad (2)$$

$$x = \Lambda(t), \quad -\mathcal{D} \frac{\partial c}{\partial x} = c \frac{d\Lambda}{dt} \quad (3)$$

where c_0 is the equilibrium solubility of solvent in the swollen polymer, while $\Lambda(t)$ is the time dependent distance of the swollen glassy interface from the solvent-polymer interface. Equation 3 is directly a mass balance across a discontinuity (19) when the hypothesis that no solvent can enter the glassy polymer is considered. Since for the problem considered $\Lambda(0) = 0$, the two boundary conditions in Eqs 2 and 3 are sufficient for the determination of the concentration distribution in the domain \mathcal{R} of interest, say:

$$\mathcal{R} = \{0 \leq x \leq \Lambda(t); 0 \leq t \leq \infty\} \quad (4)$$

provided an equation is written down which determines the $\Lambda(t)$ function. Such an equation is the crucial point of any model of the type discussed in this work, since it would describe the kinetics of swelling as measured by $d\Lambda/dt$.

A very general (but excluding memory-type effects) form of the equation expressing the kinetics of swelling is:

$$\frac{d\Lambda}{dt} = f(c|_{x=\Lambda(t)} - c^*) \quad (5)$$

where $f(\)$ is an unspecified function the values of which have the same sign as the argument, and c^* is the concentration level corresponding to the threshold activity for swelling.

We shall assume, for the time being, that the kinetics are of simple n -order type, though this, as will be discussed later, introduces a dimensional degeneracy which may or may not be relevant. Hence we write:

$$\frac{d\Lambda}{dt} = K|c - c^*|^{n-1} (c - c^*) \quad (6)$$

Since for the problem considered no value of c less than c^* would even be attained in the swollen region, Eq 6 (unless $n = 0$) can be written in the simpler form:

$$\frac{d\Lambda}{dt} = K(c - c^*)^n \quad (7)$$

Equation 7, together with the initial condition $\Lambda(0) = 0$, offers the required determination of the $\Lambda(t)$ curve; the

system 1-3, 7 is clearly a moving boundary problem, in the sense that determination of the boundary $\Lambda(t)$ is coupled with the solution of the differential equation within the domain \mathcal{R} bounded by $\Lambda(t)$.

Nicolais *et al.* (9) have suggested that a phenomenological relationship of the type of Eq 7 is consistent with the observed temperature dependence of the initial (i.e., CTT) penetration kinetics; we here extend this idea by assuming that Eq 7 correctly describes the swollen-glassy interface motion at all times, provided c is taken as the solvent concentration at the interface itself. Nicolais *et al.* (9) did not consider a threshold value for swelling c^* ; it will be seen in the following that the $c^* = 0$ case is in some sense a degenerate one, and a physical justification for that being so will be given.

We now introduce the following dimensionless quantities:

$$q = \frac{c^*}{c_o - c^*} \quad (0 \leq q \leq \infty) \quad (8)$$

$$\gamma = \frac{c - c^*}{c_o - c^*} \quad (0 \leq \gamma \leq 1) \quad (9)$$

$$\xi = \frac{xK(c_o - c^*)^n}{\mathcal{D}} \quad (10)$$

$$\lambda = \frac{\Lambda K(c_o - c^*)^n}{\mathcal{D}} \quad (11)$$

$$\tau = \frac{tK^2(c_o - c^*)^{2n}}{\mathcal{D}} \quad (12)$$

so that the system 1-3, 7 reduces to:

$$\frac{\partial^2 \gamma}{\partial \xi^2} = \frac{\partial \gamma}{\partial \tau} \quad (13)$$

$$\xi = 0, \quad \forall t, \quad \gamma = 1 \quad (14)$$

$$\xi = \lambda(\tau), \quad -\frac{\partial \gamma}{\partial \xi} = (\gamma + q) \frac{d\lambda}{d\tau} \quad (15)$$

$$\frac{d\lambda}{d\tau} = [\gamma(\lambda, \tau)]^n; \quad \lambda(0) = 0 \quad (16a)$$

The degeneracy related to the power-type kinetics can now be discussed. Had we kept the more general form of Eq 5 instead of Eq 7, and substituted $f(c_o - c^*)$ for $K(c_o - c^*)^n$ in Eqs 10-12, we would still have obtained Eqs 13-15, but Eq 16a would have taken the following form:

$$\frac{d\lambda}{d\tau} = \frac{f[c_o - c^*] \gamma(\lambda, \tau)}{f(c_o - c^*)} \quad (16b)$$

i.e., the $\gamma(\xi, \tau)$ function would have been dependent not only on the parameter q but also on the "driving force" $c_o - c^*$, while the solution to Eqs 13-16a is clearly independent of $c_o - c^*$. This fact is related to a dimensional degeneracy of the power-type form of constitutive equation which has already been discussed in a different context (20).

It is immediately apparent that, once the values of q and n have been assigned, the solution of Eqs 13-16a is unique, i.e., the function $\gamma(\xi, \tau)$ is the same for any value of \mathcal{D} , K , and c_o . The same property is of course shared by the $\lambda(\tau)$ function, as well as by two additional dimensionless functions which may be introduced for conveni-

ence, namely a dimensionless instantaneous rate of sorption ν and a dimensionless total mass sorbed ω :

$$\nu = \frac{N}{K(c_o - c^*)^{n+1}} = - \left. \frac{\partial \gamma}{\partial \xi} \right|_{\xi=0} \quad (17)$$

$$\omega = \frac{K(c_o - c^*)^{n-1} W}{\mathcal{D}} = \int_0^\lambda (\gamma + q) d\xi = \int_0^\tau \nu d\tau \quad (18)$$

where N is the dimensional instantaneous flux of solvent into the polymer.

The fact that λ , ν and ω are functions of τ uniquely determined by the values of q and n implies that the dimensionless critical times are unique functions of n and q , so that one obtains directly from Eq 11:

$$t_c = \tau_c(q, n) \frac{\mathcal{D}}{K^2(c_o - c^*)^{2n}} \quad (19)$$

where t_c stands for any one of the critical times defined in the introduction. Equation 19 shows directly that the class of models considered predicts a strong dependency of the t_c 's on temperature, with an apparent energy of activation twice that of the swelling kinetics. This is, of course, the essence of feature (d). The t_c 's will also be strong functions of the driving force for swelling $c_o - c^*$, unless the order n becomes very small.

As long as n is finite, Eqs 14-16 show that:

$$\left. \frac{d\lambda}{d\tau} \right|_{\tau=0} = 1 \quad (20)$$

and therefore:

$$\lambda = \tau + O(\tau^2) \quad (21)$$

which shows that a CTT region in the neighborhood of $\tau = 0$ always exists, at least as far as λ is concerned (feature (b)). Indeed, the same conclusion is reached by considering Eq 16b instead of 16a, provided $f(\cdot)$ has a finite first derivative at $c_o - c^*$. Furthermore, from Eqs 18 and 21 one obtains:

$$\omega = (1 + q) \tau + O(\tau^2) \quad (22)$$

which shows that a CTT region in the neighborhood of $\tau = 0$ always exists also for ω (feature (c)). Furthermore, from Eq 18 one obtains:

$$\lambda q \leq \omega \leq \lambda(1 + q) \quad (23)$$

which shows that the CTT region for ω may be smaller, but not larger than the CTT region for λ (feature (f)). We find it noteworthy that *the essential features of CTT known from experiments emerge naturally and easily from the class of models considered in this work.*

Equation 23 also shows that, when $q \gg 1$, the value of ω is bound to be quite close to $(1 + q) \lambda$, and that therefore the CTT regions for λ and ω coincide:

$$q \gg 1 \quad \tau'_{c\lambda} = \tau'_{c\omega} \quad (24)$$

If attention is now focused on the $\tau \rightarrow \infty$ behavior of the solution of the system 13-16, the following considerations are in order. The value of λ becomes of course very large, and correspondingly $\gamma(\lambda, \tau)$ becomes very small, i.e., the solvent activity at the swollen glassy interface approaches the threshold value for swelling,

$c(\Lambda, t) \rightarrow c^*$. Therefore, the $\tau \rightarrow \infty$ behavior of the solution will be determined by the kinetics of swelling near $c - c^* = 0$. This implies that, at least presumably, the case $n = 1$ is of particular relevance for the $\tau \rightarrow \infty$ behavior, since it is well known that most kinetics approach first order behavior near equilibrium.

Before proceeding any further with the analysis of general properties of the solution of the system 13-16, we analyze in the following section two special cases.

THE $n = 0$ CASE

The zero-order reaction case needs to be analyzed with the subtlety. In view of Eq 6, Eq 16a takes the form:

$$\frac{d\lambda}{d\tau} = \frac{\gamma(\lambda, \tau)}{|\gamma(\lambda, \tau)|} \quad (25)$$

The RHS of Eq 25 has the value 1 whenever $\gamma > 0$, but may have any value between 0 and 1 when $\gamma = 0$ (for the problem considered, negative values, i.e., glassification, need not be considered). In the solution to Eqs 13-15, Eq 25 is expected to show some mild discontinuity, as indeed is usual in diffusion-reaction problems when the order of the reaction is less than unity (21).

Since $\gamma(\lambda, 0) = 1$, the RHS of Eq 25 will be unity in the neighborhood of $\tau = 0$. As τ increases, $\gamma(\lambda, \tau)$ will decrease until it reaches the value zero at some finite time $\tau'_{c\lambda}$, say:

$$\tau < \tau'_{c\lambda}, \quad \gamma(\lambda, \tau) > 0, \quad \lambda = \tau \quad (26)$$

$$\tau > \tau'_{c\lambda}, \quad \gamma(\lambda, \tau) = 0 \quad (27)$$

Notice that, as long as $\tau < \tau'_{c\lambda}$ the CTT equations hold *exactly* for λ , though certainly not for ω .

In view of Eq 26, Eq 15 becomes:

$$\xi = \tau \leq \tau'_{c\lambda}, \quad -\frac{\partial \gamma}{\partial \xi} = \gamma + q \quad (28)$$

which shows that, in the region $0 \leq \tau \leq \tau'_{c\lambda}$, $0 \leq \xi \leq \tau$, the problem considered is not a moving boundary problem, since the $\lambda(\tau)$ curve is obtained independently of the solution of the differential equation.

Now consider the case where $\tau > \tau'_{c\lambda}$. The appropriate boundary condition on the swollen glassy interface now becomes:

$$\xi = \lambda(\tau), \quad \gamma = 0, \quad -\frac{\partial \gamma}{\partial \xi} = q \frac{d\lambda}{d\tau} \quad (29)$$

In order to obtain a closed-form solution, one would first need to solve Eqs 13-14, Eq 28 up to $\tau = \tau'_{c\lambda}$, and then use the calculated $\gamma(\xi, \tau'_{c\lambda})$ as an initial condition for the Eqs 13-14, Eq 29, the solution of which is sought in the region $\tau'_{c\lambda} \leq \tau \leq \infty$, $0 \leq \xi \leq \lambda(\tau)$. However, since Eq 13 is parabolic, the influence of the initial condition fades away in time, so that, as $\tau \rightarrow \infty$, the solution sought will approach the solution of Eqs 13-14, with Eq 29 regarded as appropriate at all times. The latter solution is easily obtained

$$\gamma = 1 - \frac{\text{erf}(\xi/2\sqrt{\tau})}{\text{erf } m} \quad (30)$$

$$\lambda = 2m\sqrt{\tau} \quad (31)$$

where the constant m is the solution of the following equation:

$$\sqrt{\pi} m \text{erf } m e^{m^2} = 1/q \quad (32)$$

Correspondingly, ω is obtained from Eqs 18 and 30:

$$\omega = \frac{\sqrt{4\pi/\pi}}{\text{erf } m} \quad (33)$$

Equations 31 and 33 show that, at sufficiently large τ , a PFT region exists. It is worthwhile noting that ω does not have the value which would be calculated for pure diffusion (i.e., $\sqrt{4\pi/\pi}$) under a driving force $c_0 - c^*$; only when $q \rightarrow 0$ does the proportionality factor $1/\text{erf } m$ approach unity.

Equations 30-32 are interesting in another respect. First, since they are the *exact* solution to the problem considered when Eq 29 holds at all times, they can be used to check the accuracy of any numerical integration scheme. Equation 29 would indeed be the appropriate boundary condition if the rate of swelling could become as large as allowed by diffusion as soon as the activity of the solvent exceeds, even only by a differential amount, the threshold value. This would be the behavior for $n = \infty$, but, as discussed below it is *not* the limiting behavior as $n \rightarrow \infty$.

Indeed, as has been discussed previously, the $\tau \rightarrow \infty$ behavior is regulated by the kinetics of swelling near $\gamma(\lambda, \tau) = 0$. Equation 16 shows that, when $1 < n < \infty$

$$\left. \frac{d(d\lambda/d\tau)}{d\gamma(\lambda, \tau)} \right|_{\gamma(\lambda, \tau)=0} = 0 \quad (34)$$

no matter how large n is. In contrast with this, when $n = \infty$, the LHS of Eq 34 becomes infinity. This shows that Eqs 30-32, although they are the exact solution for $n = \infty$, are not the limit of the actual solution for $n \rightarrow \infty$.

Since Eqs 26 and 31 are the lower and upper asymptote for $\lambda(\tau)$, a rough estimate $\tau_{c\lambda}$ for *both* $\tau'_{c\lambda}$ and $\tau''_{c\lambda}$ can be obtained from the value of τ at which the two asymptotic curves cross each other:

$$\tau_{c\lambda} = 4m^2 \quad (35)$$

and of course would expect

$$\tau'_{c\lambda} < \tau_{c\lambda} < \tau''_{c\lambda} \quad (36)$$

From a series expansion of Eq 32 one obtains:

$$q \rightarrow 0, \quad \tau_{c\lambda} = 4 \ln(1/\sqrt{\pi} q) \quad (37)$$

$$q \rightarrow \infty, \quad \tau_{c\lambda} = 1/2q \quad (38)$$

which show, as physically intuitive, that the CTT region becomes very small when the solvent activity barely exceeds the threshold value. As will be seen below, Eq 36 is indeed fulfilled, but $\tau_{c\lambda}$ is often a very poor estimate for both $\tau'_{c\lambda}$ and $\tau''_{c\lambda}$, i.e., the transition from the lower to the upper asymptote is very long and smooth. This implies that, in practice, an experimental $\log \Lambda$ vs $\log t$ plot obtained over a not unreasonably wide range of times may show any slope between the CTT value of 1 and the PFT value of $1/2$ (feature (e)) as indeed has been reported (2).

Finally, it is interesting to observed that, when $q = 0$, Eq 37 ceases to be significant. Mathematically, this im-

plies that, when $q = 0$, no PFT region exists. In practice, if the solvent activity largely exceeds the threshold value, no PFT region would be observed in any experiment with polymer samples of reasonable thickness.

Physically, the $q = 0$ case is in fact unrealistic. If the threshold concentration for swelling were zero, a swollen polymer could never transform to the glassy state, since it would be impossible to desorb the solvent to a zero residual content. The problem can also be looked upon from a different viewpoint: if c^* is the threshold concentration at same temperature T_0 , one could also say that the glass transition temperature is decreased from T_g to T_0 by a c^* concentration of solvent. From this viewpoint $c^* = 0$ would correspond to an infinitely large value of dT_g/dc .

THE $\tau \rightarrow \infty$ ASYMPTOTE

We now focus attention again on the general problem as represented by Eqs 13-16, with $0 < n < \infty$, and seek an asymptotic solution for $\tau \rightarrow \infty$. We assume tentatively that a PFT region exists in a neighborhood of $1/\tau = 0$, at least for λ , and we therefore assume that, when $\tau \rightarrow \infty$, Eq 31 holds, with m a constant to be determined.

It is evident that, should $\gamma(\lambda, \tau)$ become zero Eqs 30-33 are the exact asymptotic solution for $\tau \rightarrow \infty$. This may be the case of $n < 1$ (since reactions of order less than one are known to reach equilibrium in a finite time), but is unlikely if $n \geq 1$. It is nonetheless clear that, as $\tau \rightarrow \infty$, $\gamma(\lambda, \tau)$ becomes vanishingly small, and therefore we assume that the $\gamma(\xi, \tau)$ function approaches the following form:

$$\gamma = 1 - \frac{\text{erf}(\xi/2\sqrt{\tau})}{\text{erf}(m + \epsilon)} \quad (39)$$

where ϵ is much smaller than m , so that one may write:

$$\text{erf}(m + \epsilon) = \text{erf } m + \frac{2}{\sqrt{\pi}} e^{-m^2} \epsilon + O(\epsilon^2) \quad (40)$$

so that:

$$\gamma(\lambda, \tau) = O(\epsilon) \quad (41)$$

$$-\frac{\partial \gamma}{\partial \xi}(\lambda, \tau) = \frac{e^{-m^2}}{\sqrt{\pi} \text{erf } m} [1 + O(\epsilon)] \quad (42)$$

In view of Eq 31, Eqs 15 and 16 become:

$$\xi = 2m\sqrt{\tau}, \quad \gamma = O(\epsilon), \quad -\frac{\partial \gamma}{\partial \xi} = [q + O(\epsilon)] \frac{m}{\sqrt{\tau}} \quad (43)$$

Substitution of Eq 42 into Eq 43 yields:

$$\sqrt{\pi} m \text{erf } m e^{m^2} = \frac{1 + O(\epsilon)}{q} \quad (44)$$

which shows that, to within $O(\epsilon)$, Eqs 30-33 are the $\tau \rightarrow \infty$ asymptotic solution to the problem considered for any value of n . This of course implies that also Eqs 35-38 hold for any value of n , as well as the discussion following them. A PFT region for both λ and ω always exists at sufficiently large times. Of course, this region may not be accessible to measurement in experiments of finite duration on samples of finite thickness.

THE TRANSITION REGION

In order to obtain an estimate of the τ_c 's, it is necessary to evaluate the values of τ at which deviations from the asymptotic behavior become significant. While we were unable to perform a perturbation analysis around the $\tau \rightarrow \infty$ asymptote, the perturbation around the $\tau \rightarrow 0$ asymptote is comparatively easy.

We define the quantity δ as follows:

$$\gamma(\lambda, \tau) = 1 - \delta(\tau) \quad (45)$$

and we tentatively assume that $\delta(\tau)$ can be Taylor series expanded around $\tau = 0$. Since quite obviously $\delta(0) = 0$, one may write:

$$\frac{\delta}{\lambda} = A + O(\tau) \quad (46)$$

Now consider the following distribution of γ :

$$\gamma = 1 - \frac{\delta}{\lambda} \xi \quad (47)$$

which satisfies the boundary condition at $\xi = 0$, and degenerates properly into Eq 45 when $\xi = \lambda$. In view of Eq 46, one obtains from Eq 47:

$$\frac{\partial \gamma}{\partial \tau} = -\xi O(1) = O(\tau) \quad (48)$$

which shows that Eq 47 also satisfies, to within $O(\tau)$, the differential equation (in other words, the curvature $\partial^2 \gamma / \partial \xi^2$ is of $O(\tau)$, and therefore a linear distribution such as in Eq 47 is appropriate).

By imposing the boundary condition at $\xi = \lambda$, and the equation for $d\lambda/d\tau$, one obtains by straight forward algebra:

$$\lambda = \tau [1 - \frac{n(1+q)}{2} \tau + O(\tau^2)] \quad (49)$$

$$\omega = (1+q) \tau [1 - \frac{1+n(1+q)}{2} \tau + O(\tau^2)] \quad (50)$$

$$\delta = (1+q) \tau [1 - \{1 + \frac{3n}{2}(1+q)\} \tau + O(\tau^2)] \quad (51)$$

From Eqs 49 and 50 we may draw the following conclusions:

- Both $\tau'_{c\lambda}$ and $\tau'_{c\omega}$ increase with increasing n and with increasing q .

- $\tau'_{c\omega}$ is always less than $\tau'_{c\lambda}$, but approaches it when either n or q , or both, grow sufficiently large.

Of course, the straight forward (but not very illuminating) way of obtaining all the information desired is by numerical integration. Numerical solutions to Eqs 13-16 are comparatively easy to obtain, although the classical numerical techniques, which require the time interval to be proportional to the square of the space interval for Eq 13, cause the numerical procedure to be rather slow at low values of τ , say in the CTT region. Numerical solutions reported below have been obtained on an HP 9825 desk-top computer.

Figure 1 is a log-log λ vs $\sqrt{\tau}$ plot for $q = 1$ and several values of n . The two straight lines correspond to Eqs 21 and 31, respectively. The prediction that both the lower and the upper asymptote are independent of n is borne

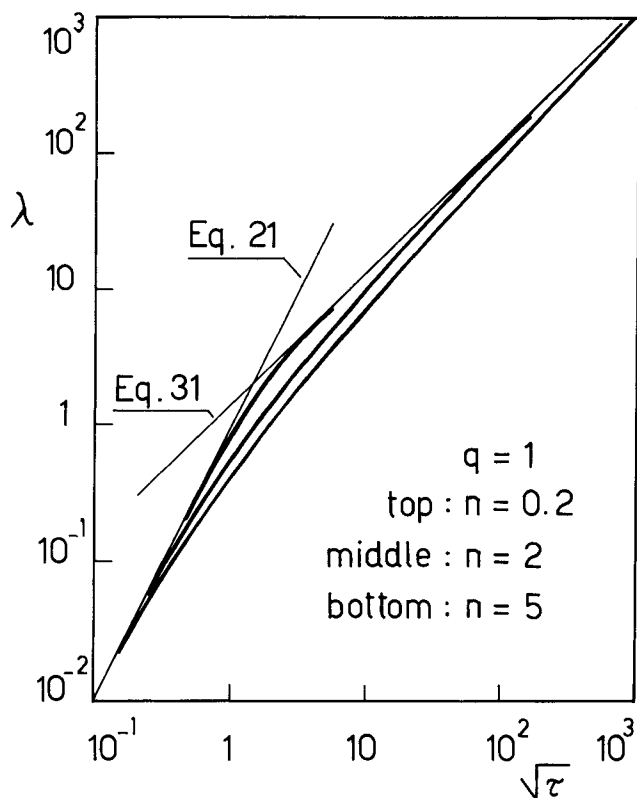


Fig. 1. Depth of penetration vs square root of time; influence of the order of the reaction.

out by the numerical results. The transition from the lower to the upper asymptote is rather sharp when $n \leq 1$, so that the value of $\tau_{c\lambda}$ given by Eq 35 is a rather good estimate of both $\tau'_{c\lambda}$ and $\tau''_{c\lambda}$.

When $n > 1$, the transition becomes very smooth; so that $\tau'_{c\lambda}$ increases and $\tau''_{c\lambda}$ decreases with increasing n . Since experimentally measured values of n tend to be rather high (5), it is not surprising that equations of the form:

$$\lambda \propto \tau^m \quad (52)$$

with $\frac{1}{2} \leq m \leq 1$ have been reported as good correlations of experimental data.

Figure 2 is a log-log plot of λ vs $\sqrt{\tau}$ for $n = 1$ and several values of q , including $q = 0$. First of all, it is interesting to observe that the curve for $q = 0$ does not have a PFT asymptote, as implied by Eq 37. Also, one may note that, when q is small, the transition from the lower to the upper asymptote becomes very smooth: again, since small values of q are typical for experimental conditions, correlations of the form of Eq 52 are predictable.

Since the transition is often very smooth, the distinction between τ'_c , τ_c and τ''_c is not irrelevant. Of course, τ'_c and τ''_c are somewhat arbitrarily defined; Table 1 reports values calculated from the requirement that the appropriate asymptotic value be approached to within 20 percent. It is interesting to observe that in all cases $\tau'_{c\omega} < \tau'_{c\lambda}$ (particularly so when $q \rightarrow 0$), while in general $\tau''_{c\omega} < \tau''_{c\lambda}$, i.e., the PFT behavior is approached first by the weight sorbed. Also, for large values of n and/or small values of q , τ'_c and τ''_c are different enough for feature (e) to be

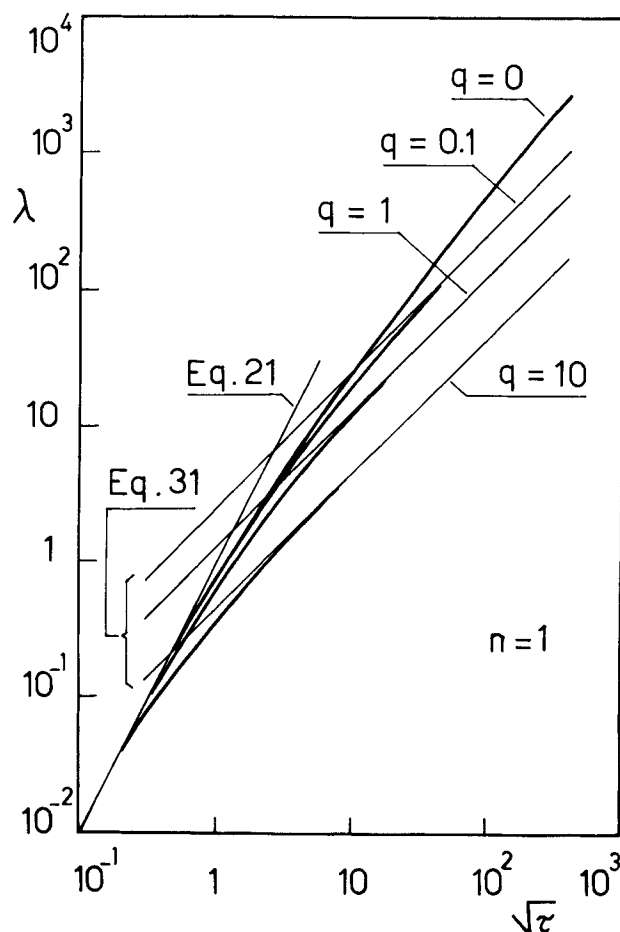


Fig. 2. Depth of penetration vs square root of time; influence of q . The case $q = 0$ corresponds to an absolutely irreversible swelling reaction.

exhibited over a large range of experimental conditions.

It is worthwhile noting that, since the models considered in this work neglect any amount of solvent which may actually be absorbed in the glassy region, the results obtained, which refer to a semi-infinite slab, also hold for slabs of finite thickness as long as Δ is less than the half-thickness of the slab, Δ . In particular, since at $\tau < \tau'_{c\omega}$ CTT conditions prevail, a slab of finite thickness is predicted to exhibit CTT behavior throughout the duration of the experiment provided Δ satisfies the following condition:

$$\Delta < \tau'_{c\omega} \frac{\mathcal{D}}{K(c_0 - c^*)^n} \quad (53)$$

and the whole sorption process would require a time given by:

$$t = \frac{\Delta}{K(c_0 - c^*)^n} \quad (54)$$

Table 1. Calculated Values from Equations

n	q	$\tau'_{c\omega}$	$\tau'_{c\lambda}$	$\tau''_{c\lambda}$	$\tau''_{c\omega}$
1	0	0.25	1	∞	∞
1	0.1	0.3	1	200	30
1	1	0.2	0.25	20	10
1	10	0.1	0.1	2.0	1.0
0.2	1	0.5	1.2	2.0	1.5
5	1	0.05	0.08	2×10^4	10^4

When $\tau'_{c\omega}$ is appreciably less than $\tau'_{c\lambda}$, slab half-thicknesses may fall in the following range:

$$\tau'_{c\omega} \frac{\mathcal{D}}{K(c_0 - c^*)^n} < \Delta < \tau'_{c\lambda} \frac{\mathcal{D}}{K(c_0 - c^*)^n} \quad (55)$$

In such a case, the model would predict that the two swollen glassy interfaces move at constant speed until they meet at the plane of symmetry at the time given by Eq 54, but sorption of solvent would still proceed after that time. This behavior has indeed been observed experimentally.

Concentration profiles calculated numerically are, at $\tau < \tau'_{c\omega}$, essentially constant ($\gamma = 1$) up to $\xi = \lambda$ and of course drop to zero afterwards. In the transition region, concentration profiles are very close to linear in the $0 \leq \xi \leq \lambda$ region; i.e., Eq 47 is a very good approximation. A few calculated concentration profiles in the transition region are reported in Figs. 3 and 4. Finally, in the PFT region, the concentration profiles are given by Eq 39.

CONCLUSION

Any mathematical model which incorporates as a basic feature the description of the kinetics of swelling and takes into account the driving force for swelling predicts, at least qualitatively, all the essential features (say features (a-f) described in the Introduction) of the processes of sorption of swelling solvents in glassy poly-

mers, even with the simplest possible description of all other elementary processes.

This does not, of course, imply that such effects as concentration-dependent diffusion, stress distribution and so on need not be considered at all; refinements of the class of mathematical models considered in this work are of course possible, but they are, indeed, refinements. The essential phenomenological features are adequately described by simple models which incorporate the swelling kinetics. Also the latter, of course, may be molded with more sophistication, say, e.g., memory-type effects could conceivably be included. This would not alter the predictions for the *first* cycle of sorption, but would be able to explain differences between a first and a second cycle of sorption which have been reported in the literature. Also, explicit consideration of diffusion in the glassy region could yield an extremely low times pseudo-Fickian asymptote, which has indeed been observed with experiments on sorption into very fine powders (22). The main conclusion of the present work is not claimed to be the contribution of the ultimate mathematical model, but only the identification of some basic features which such an ultimate model should necessarily incorporate.

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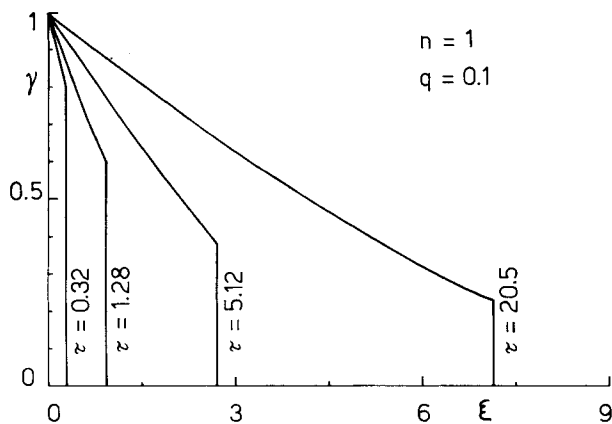


Fig. 3. Concentration profiles in transition region; $n = 1$, $q = 0.1$.

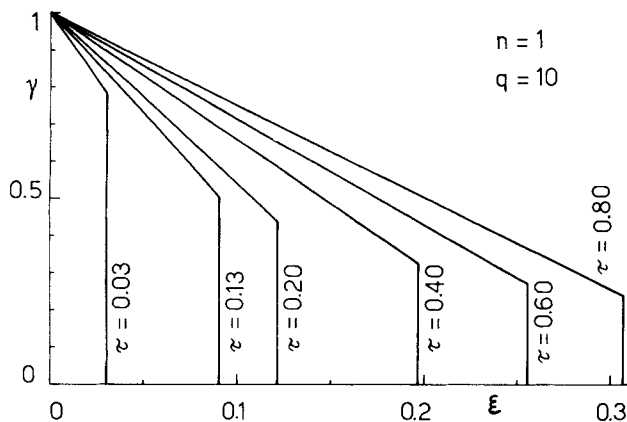


Fig. 4. Concentration profiles in transition region; $n = 1$, $q = 10$.

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