

# A deformation model for Case II diffusion

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Case II diffusion in glassy polymers is considered in terms of a deformation model. The process is controlled by the mechanical response of the glass just ahead of the sharp front to an osmotic swelling stress. The important factor governing the establishment of the sharp solvent front is taken to be the concentration dependence of the creep response time. These ideas are set in the context of existing models for diffusion in glassy polymers, and experimental evidence is presented to support the deformation mechanism.

## INTRODUCTION

Diffusion of organic penetrants in glassy polymers is characterized by 'anomalous' behaviour, which is not explicable in terms of Fick's laws even with a concentration-dependent diffusion coefficient. Slow relaxation processes occur in the glassy state, and deviations from Fickian behaviour have been associated with the finite times taken for the polymer chain to respond to an osmotic swelling pressure and rearrange themselves to accommodate the diffusing penetrant molecules<sup>1,2</sup>.

The term 'non-Fickian anomalies' has been applied to various complex sorption phenomena e.g. sigmoidal<sup>3</sup>, two-stage<sup>4</sup> and pseudo-Fickian<sup>5</sup> behaviour. The essential feature of these transport processes is their control by coupled diffusion and relaxation mechanisms. In general terms, a sorption process is influenced by polymer segmental motions which occur at about the same rate or slower than the diffusion process, and the condition for 'anomalous' diffusion is that diffusion and relaxation rates are comparable. It is helpful to view the range of anomalous diffusion phenomena in glassy polymers as being bounded by limits of Fickian and relaxation-controlled behaviour.

The concept of relaxation-controlled transport as a second simple limiting case for the sorption behaviour in glassy polymers was first proposed by Alfrey *et al.*<sup>6</sup> who referred to it as *Case II diffusion*. Several characteristics of Case II behaviour can be recognized:

- (i) the mass of absorbed penetrant increases linearly with time;
- (ii) a sharp boundary separates the inner glassy core of unpenetrated polymer from the outer swollen shell, and there is a uniform concentration of penetrant across the swollen layer;
- (iii) the boundary advances with constant velocity.

Case II behaviour has been observed in a variety of glassy polymer-non-solvent systems, e.g. polystyrene in acetone<sup>6</sup> and in n-alkanes<sup>7</sup>, crosslinked epoxies in benzene<sup>8</sup> and PMMA in alcohols<sup>9,10</sup>.

The fact that a sharp Case II front moves into the polymer at a rate independent of its position implies that the diffusion of molecules through the swollen layer up to the front

is not the rate controlling process; otherwise, the rate of front advance would necessarily decrease with increasing penetration depth. The rate controlling process must be occurring at the front, and can be regarded as the movement of polymer segments in response to an osmotic swelling stress.

Case II diffusion is often referred to as 'relaxation-controlled' transport, without any clear indication of the physical nature of the process. In this paper we present new evidence which supports a model of Case II transport, based on the time-dependent deformation of the polymer as the rate controlling mechanism.

## SURVEY OF THE THEORIES OF NON-FICKIAN DIFFUSION IN GLASSY POLYMERS

Before presenting a new approach to Case II transport, it is appropriate to survey the existing models for diffusion in glassy polymers which can be applied where absorption leads to substantial swelling. Most of the models are concerned with the balance between penetrant diffusivity and polymer segmental relaxation processes. Collectively, they describe many of the sorption phenomena observed in glassy polymers. The models will be presented in three sections: firstly, those using a modified form of the classical Fickian diffusion equations; secondly, those incorporating the swelling stress and/or relaxation terms; and, thirdly, those which predict or account for Case II transport.

### *Models based on Fick's equations*

(i) *Prediction of a sharp front.* It has been long recognized that, during swelling, a sharp boundary may exist between the inner glassy core and the outer swollen layer. This visible front often advances with decreasing velocity, and, in some cases, the depth of penetration of the advancing front is proportional to the square root of time. In this latter case, the rate of front penetration depends inversely on its distance from the specimen surface, and penetrant diffusion is the sole rate-controlling factor for front advance. This effect has been predicted theoretically by Crank<sup>12</sup>.

The sharp advancing boundary is regarded as a discontinuity which may be predicted for cases in which the diffusion coefficient,  $D$ , is a discontinuous function of concentration. In particular, one case is considered in which the

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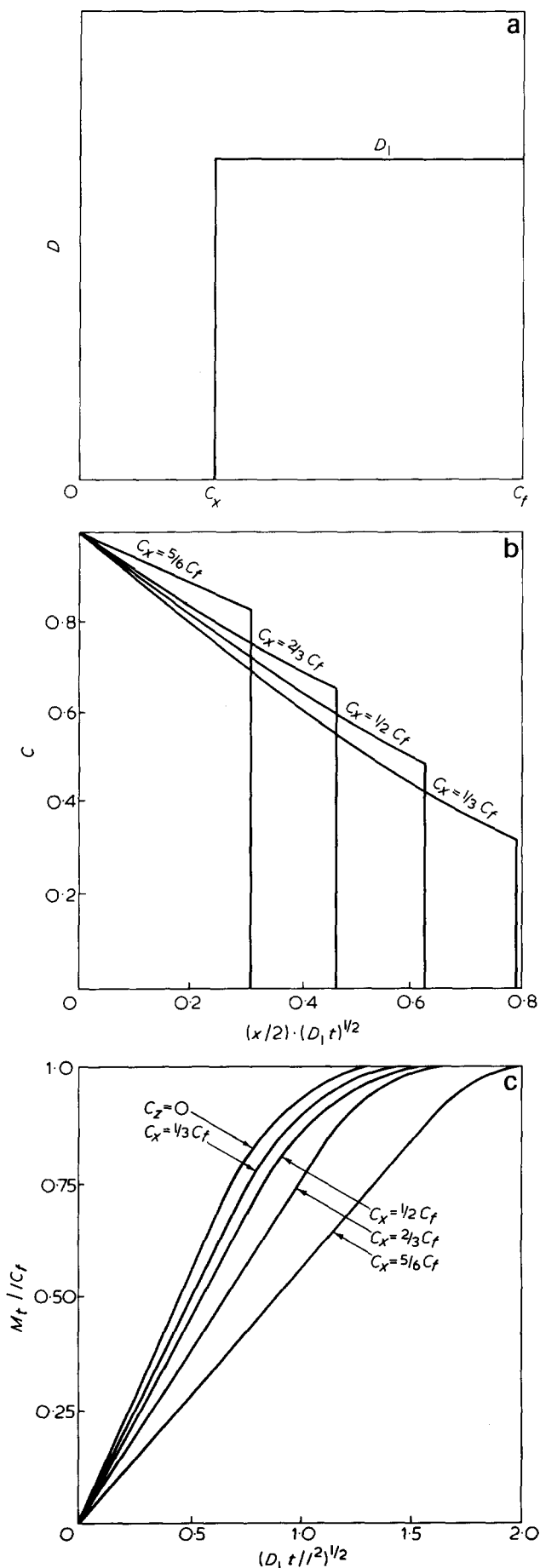


Figure 1 Prediction<sup>12</sup> of a sharp front when the diffusion coefficient,  $D$ , is a discontinuous function of concentration. a, diffusion coefficient plotted against concentration; b, concentration-distance curves; c, absorption versus time<sup>1/2</sup> curves

diffusion coefficient is zero for concentrations less than a certain value ( $C_x$ ) and constant and finite above  $C_x$  (Figure 1a). This situation does indeed have a physical interpretation in terms of the diffusion of liquids in glassy polymers<sup>13</sup>: for, at the point at which the penetrant concentration reaches a value at which the glass becomes a rubber, there should be a discontinuous increase in  $D$  from a value of  $10^{-13} \sim 10^{-16} \text{ m}^2 \text{ s}^{-1}$  typical of a glassy polymer to  $10^{-11}$  typical of a rubber.

According to the calculations of Crank, a discontinuity in concentration gradient occurs at a point  $x(t)$  which moves so that  $x = kt^{1/2}$ , where  $k$  is a constant (Figure 1b). The absorption curve plotted as a function of  $t^{1/2}$  is linear at first and then becomes concave to the time axis (Figure 1c). This deceleration of the advancing front indicates that the model is not relevant to Case II behaviour. Thus, it cannot be explained in terms of a discontinuity in diffusivity with concentration.

(ii) Time-dependent diffusion coefficients. In 1953, Crank proposed a theory based on the 'history-dependent' diffusion coefficient<sup>1</sup>. The model assumes that the surface concentration remains constant during sorption and the diffusion coefficient is a function of time as well as concentration.

Changes in diffusion coefficient with time are assumed to occur in two stages; an instantaneous part followed by a slow drift towards an equilibrium value. This concept is of course analogous to the phenomenological model dealing with instantaneous and retarded elasticity in mechanically deformed polymers, which is not surprising since similar molecular mechanisms must apply in both cases. From solutions of Fick's second law with such a time-dependent diffusion coefficient, it is possible to derive sorption and desorption curves exhibiting many of the features of sigmoidal and pseudo-Fickian behaviour. However, one particular objection may be made to this approach. The predictive value of an equation with five adjustable parameters is limited, and any success in fitting data does not aid elucidation of the underlying molecular mechanism.

(iii) Model due to Long and Richman: (a) description of the model. The above theories (due to Crank) do not provide a satisfactory explanation of sorption processes of the 'two-stage' type. Bagley and Long<sup>4</sup> first observed this type of diffusion behaviour: Long and Richman<sup>14</sup> proposed a model to explain it.

It is assumed that molecular relaxation associated with diffusion can be divided into two stages: an 'initial state' corresponding to molecular rearrangements which can occur almost instantaneously, and a stage of slower response leading up to a final equilibrium. The concentration at the surface ( $C_s$ ) is assumed to vary as follows:

$$C_s(t) = C_0 + (C_\infty - C_0)(1 - e^{-\beta t}) \tag{1}$$

where  $C_0$  is the instantaneous value,  $C_\infty$  is the equilibrium value and  $\beta$  is a rate parameter assumed to be constant.

The time-dependent surface concentration is incorporated into the boundary conditions for diffusion and (with a constant value of  $D$ ) a solution of the classical diffusion equation is obtained. The weight-gain expression consists of two parts: the absorption due to the concentration gradient set up by the initial surface concentration, and that due to penetrant entering as a result of the time-dependence of the surface concentration. When  $\beta$  is small, diffusion due to the initial gradient is complete before there is any significant

change in surface concentration, and this case results in a 'two-stage' sorption process.

The Long and Richman model has successfully described experimental 'non-Fickian' sorption curves in several systems<sup>14,15</sup>. Also, equation (1) has a firm physical basis in that the variation of  $C_s$  with time has been determined experimentally<sup>14</sup>.

One significant result<sup>16</sup> is that the mean retardation times for tensile creep behaviour in the system of atactic PS and benzene at 25°C and 35°C were found to depend on concentration in the same way as the average relaxation times in two-stage sorption in that system. Therefore, there is reason to suppose that the second stage of a two-stage absorption process is governed primarily by a very similar mechanism to that governing creep behaviour under the same conditions<sup>17</sup>. This supports Long and Richman's own interpretation of  $\beta$  (equation (1)) as a measure of the 'stress-relaxation of the polymer structure'. Petropoulos and Roussis<sup>18</sup> have criticized the mathematical formulation of the Long and Richman model in that the concentration gradient of penetrant is assumed to be the driving force for diffusion; whereas, if concentration is directly affected by a relaxation process, it is more correct to take activity as the driving force.

Although there are unresolved difficulties over its interpretation, the Long and Richman approach accounts successfully for diffusion behaviour in a number of systems and indicates an important link between sorption and molecular relaxation processes.

#### Models incorporating swelling stress and/or relaxation terms

(i) *Strain-dependent diffusion model.* Crank has proposed a theory based on transverse differential swelling stresses<sup>1</sup> to estimate the effect of stress on the diffusion coefficient. The swollen layer is assumed to undergo an instantaneous elastic expansion in proportion to the concentration of solvent absorbed, but is held in compression by the glassy core. During the initial stages of absorption, the swollen layer is considered to have a more compact structure than in the absence of the compressive stress and this causes  $D$  to have a decreased value. As diffusion proceeds,  $D$  increases towards its 'unstressed value'.

(ii) *Differential swelling stress model.* This model, proposed by Petropoulos<sup>19</sup>, is an extension of that due to Crank<sup>1</sup> mentioned above. The polymer is treated as a linear viscoelastic medium rather than an elastic solid, and is described in terms of a standard linear solid.

The diffusion coefficient is assumed to depend exponentially on both concentration and stress and an analysis of the mechanical model yields an expression for the rate of change of stress at a given point; this, when solved in conjunction with Fick's second law, predicts absorption and desorption behaviour and an increase in specimen area as a function of time. Curves of sorption *versus* linear time with extensive linear portions are calculated, but these are not necessarily associated with a sharp front as in Case II diffusion.

This model is one of the few to offer direct interpretation of both sorption and transverse swelling kinetics. It combines the sorption process with the mechanical response of the polymer and can predict a wide range of diffusion behaviour, albeit with the help of at least five adjustable parameters. However, it does not predict the existence of the widely observed phenomenon of a sharp diffusion front.

(iii) *Coupled diffusion and relaxation models.* Recently, Berens has described 'anomalous' diffusion behaviour by con-

sidering the individual contributions of the diffusion and relaxation processes<sup>21</sup>. The model assumes linear superposition of first-order relaxation terms with the Fickian diffusion equation, and has been successfully applied to sorption data for vinyl chloride, acetone and methanol in PVC, and n-hexane in PS.

Two-stage sorption behaviour has been explained by Joshi and Asterita<sup>22</sup> in terms of a diffusion-relaxation coupling model. They indicate the importance of considering the 'degree of swelling' as an additional variable to characterize the swollen polymer.

#### Theories which account for Case II transport

(i) *Diffusion-with-convection model.* Frisch *et al.*<sup>23</sup> have proposed a model to account for diffusion in glassy polymers in which the Fickian and Case II components are combined additively. Case II transport is treated as a convection process which is assumed to be caused by internal stresses arising from swelling of the polymer. Solution of the transport equation which includes a convective term gives the relationship<sup>24</sup>:

$$d = at + bt^{1/2} \quad (2)$$

where  $d$  is the depth of penetration (from the original surface position to the front) with a given concentration and  $a$  and  $b$  are constants.

Wang *et al.*<sup>24</sup> have given experimental justification for equation (2) in that it describes the time-dependence of the penetration data of Kwei and Zupko<sup>25</sup> for trichloroethylene and methyl ethyl ketone in an epoxy polymer. It has also been successfully used to analyse experimental results for the diffusion of acetone in PVC<sup>26</sup>.

However, this model does not seem to have been generally adopted to explain experimental diffusion data, perhaps because it seems to lack any firm physical basis<sup>18</sup>.

(ii) *Diffusion in a network with discontinuous swelling.* Peterlin has proposed a model based on the linear combination of Fickian and Case II contributions to the transport process<sup>27</sup>. In this model, however, Fickian diffusion is assumed to occur ahead of the Case II sorption discontinuity, so that the predicted concentration distribution<sup>38</sup> consists of a step concentration profile, representing the swollen rubber, with a Fickian precursor extending into the glassy core (Figure 2). This is in contrast to the profiles predicted by Kwei *et al.*<sup>26</sup>, in which the Fickian region is behind as opposed to ahead of the sharp front.

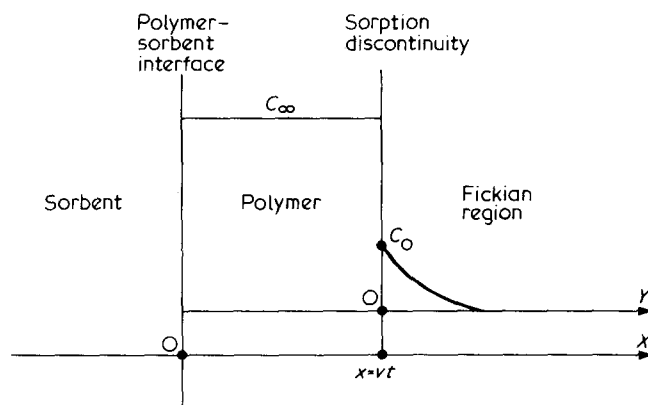


Figure 2 Idealized concentration profile for Case II sorption due to Peterlin<sup>30</sup>

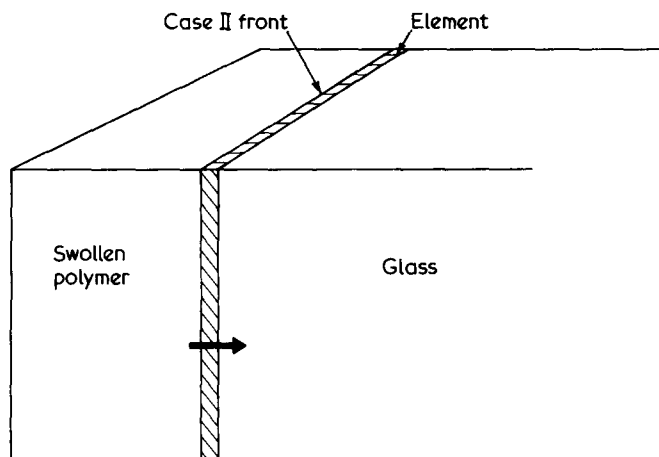


Figure 3 Schematic representation of Case II front preceded by a small element of glassy polymer in which the rate-controlling deformation process is taking place

The predicted uptake of diffusing liquid in Peterlin's model is:

$$W_t = C_0(2/\pi D)^{1/2} t^{1/2} + C_\infty Vt \quad (3)$$

where  $C_0$  is the concentration in the Fickian precursor at the front,  $D$  is the diffusion constant characteristic of the unswollen region,  $C_\infty$  is the constant concentration in the swollen region and  $V$  is the velocity of the Case II front.

Experimental justification for this model has been claimed by Jacques *et al.*<sup>20</sup> because of observations of *super Case II diffusion*. It also seems physically reasonable that there should be a precursor ahead of the Case II front, but the extent of such a precursor will depend on the specific system under consideration, together with the experimental conditions.

The simultaneous occurrence of Fickian and Case II sorption processes, as considered in the models of Frisch and Peterlin, is a useful concept for the qualitative explanation of diffusion behaviour in glassy polymers. However, the quantitative treatment in terms of a linear combination of the two sorption processes is not fully justified and seems to be a considerable oversimplification.

(iii) *Case II diffusion as a particular solution of the conventional diffusion equation.* Peterlin has recently proposed that Case II transport is merely a special case of possible diffusion processes compatible with the conventional diffusion equation, if the diffusion coefficient,  $D$ , and solubility parameter,  $S$ , increase sufficiently fast with penetrant concentration<sup>29</sup>.

The condition for the constant rate of propagation of a concentration profile is taken to be:

$$C(X - Vt) = C(X') \quad (4)$$

The coordinate system is then defined as  $X'$ , where  $X'$  moves at the constant velocity  $V$ , associated with the boundary between swollen and unswollen regions. With this coordinate system, the diffusion equation is solved without any more terms. The chemical potential gradient of the penetrant is taken as the driving force for diffusion.

The basic principles of this approach are similar to those proposed by Crank<sup>12</sup> in that  $D$  (and in this case  $S$ ) are assumed to vary discontinuously with activity; these dependences produce a solution of the conventional diffusion equation with

a discontinuity in concentration. However, the predicted step profile must move linearly with time, because the frame of reference is initially set up to move at a constant velocity,  $V$ .

The velocity of the Case II front,  $V$ , is taken as a completely free parameter which determines the steepness of the concentration gradient at the front. Its value is not determined by the diffusion equation, but is thought to be connected with some independent material property. There is clear experimental evidence<sup>7,30</sup> that  $V$  increases greatly with increasing temperature and penetrant activity, as well as with the thermal and mechanical history of the sample. It is concluded that the velocity of the profile must be determined independently from the equation predicting its shape and propagation, i.e. the above model is not a self-contained description of Case II diffusion.

## A NEW MODEL FOR CASE II TRANSPORT

Case II swelling is characterized by a step concentration profile moving at constant velocity<sup>6,9</sup>. Fickian diffusion under conditions in which there is a discontinuity in the relationship between diffusivity and concentration can account for a step profile (see above). However, in this case the sharp front decelerates with increasing penetration, as demonstrated by Crank<sup>12</sup>.

To give a constant front velocity, the rate-controlling process must be independent of front position and will occur at the front itself.

We consider the behaviour of a small element of glassy polymer just ahead of the Case II front (Figure 3). A few penetrant molecules enter this small element; but further swelling is inhibited in part by the constraint of the adjacent glassy polymer. The element can only swell if at the same time it changes shape so as to maintain constant area. The driving force for the shape change is the component of the hydrostatic swelling stress which is not opposed by the reaction of the adjacent glass, i.e. a tensile stress normal to the plane of the element. The rate at which the element changes shape is determined by the combination of the deviatoric component of this tensile stress and the viscoelastic response of the material.

Observations of the macroscopic change in shape of specimens during Case II sorption give a direct indication of the deformation process at the advancing front. For example, when 1 mm sheet specimens of Perspex are swollen in methanol at 24°C, it is found that just before the sharp fronts meet at the centre of the specimen, the sheet thickness has increased by nearly 25% whereas the increase in area is negligible. This considerable shape change on swelling must be a result of the stress state controlling Case II transport<sup>31</sup>.

The mechanical response of the element ahead of the Case II front is time-dependent and the first stages of the shape change of the element can be thought of as creep of the polymer glass which can be characterized by a viscosity, to a first approximation. The first small amount of swelling will create space for more penetrant molecules to enter the element; the plasticizing effect of these molecules causes creep to occur at a greater rate. This autocatalytic response, which is a consequence of a strongly concentration-dependent viscosity, continues until the concentration of penetrant in the element reaches an equilibrium value. Thus, almost all of the swelling response of the element occurs in a time which is much shorter than the time increment required for each subsequent element to reach equilibrium concentration.

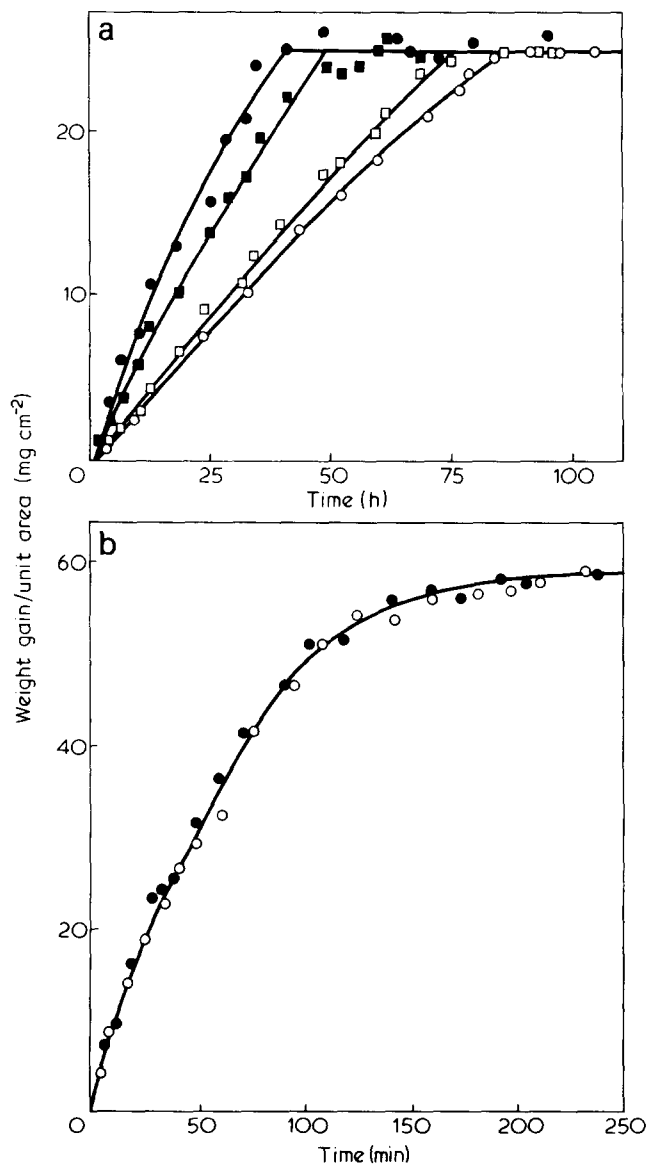


Figure 4 The effect of prior cooling rate on the sorption process in 1 mm (nominal) sheet specimens of PMMA swollen in methanol. a, at 24°C. (Actual average thickness = 0.98 mm); b, at 62°C. (Actual average thickness = 0.98 mm). The cooling rates through  $T_g$  are: ●, 800°C min<sup>-1</sup>; ■, 103°C min<sup>-1</sup>; □, 1.3°C min<sup>-1</sup>; ○, 0.5°C min<sup>-1</sup>

This is the condition for a sharp front. A quantitative treatment of this approach confirming the linear penetration and absorption kinetics is given elsewhere<sup>32</sup>.

#### EVIDENCE TO SUPPORT A DEFORMATION MECHANISM FOR CASE II TRANSPORT

We now present evidence for assuming that Case II transport is best regarded as being controlled by a mechanical deformation process.

##### *The effect of prior heat-treatment on the rate of Case II transport*

In order to test the proposal of a deformation mechanism, we sought to change the creep characteristics of the PMMA in a way which would not similarly affect the diffusivity. It has been demonstrated<sup>33-35</sup> that creep rate is very sensitive to the thermal history of a polymer glass, and in particular to the rate at which it is cooled through  $T_g$ . Hence, we

cooled PMMA specimens at a variety of rates and measured the weight-gain kinetics. Results for Case II penetration by methanol at 24°C are shown in Figure 4a. Under these conditions, the sorption rate is strongly dependent on cooling rate: an increase in cooling rate of three decades causes the sorption rate to increase by nearly a factor of three. Figure 4b shows the sorption rate measurements for specimens which were swollen at 62°C, where the kinetics are largely Fickian (time exponent is 0.65). The absence of cooling rate dependence, under these conditions of essentially diffusion-controlled behaviour, indicated that it is the influence of thermal history on the creep properties (coupled with the dependence of Case II diffusion on creep) which must account for the sensitivity of sorption rate to thermal history observed at 24°C (Figure 4a).

Rapidly-quenched specimens will contain a distribution of internal stress – the planar surfaces in compression and the core in tension – and the possibility that the Case II transport process might be affected cannot be ignored. However, there are two observations which suggest that this is not a major factor. Firstly, a specimen which was bent elastically showed an enhanced front penetration rate on the tensile side<sup>36</sup>. Secondly, the rate of penetration in the quenched specimens showed no significant variation during sorption, despite the fact that most of the internal stress would have been relieved before the front had penetrated to a quarter of the sheet thickness<sup>37</sup>.

Figure 5 shows the rate of sorption at 24°C plotted against the logarithm of the cooling rate. (The rate of sorption is taken as the gradient of the weight-gain graph). Sorption rate is proportional to the rate of front propagation, and so any correlation between cooling rate and sorption rate will necessarily help to define further the process which is controlling the front penetration rate. A linear relationship exists between the logarithm of cooling rate and the sorption rate, and suggests that free volume is an important factor governing Case II transport behaviour.

According to the theory of Fox and Flory<sup>38</sup>, there is a characteristic value of free volume associated with the glass transition. The exact value of the glass transition temperature,  $T_g$ , depends on the rate of cooling, i.e. the greater the cooling rate the more free volume is quenched into the glass and the higher the value of  $T_g$ . Kovacs<sup>39</sup> first attempted to quantify the relationship between cooling rate and the shift in  $T_g$ ; more recently, Hutchinson and Kovacs<sup>40</sup> have shown that the relationship between the logarithm of the cooling rate and the change produced in  $T_g$  is effectively linear.

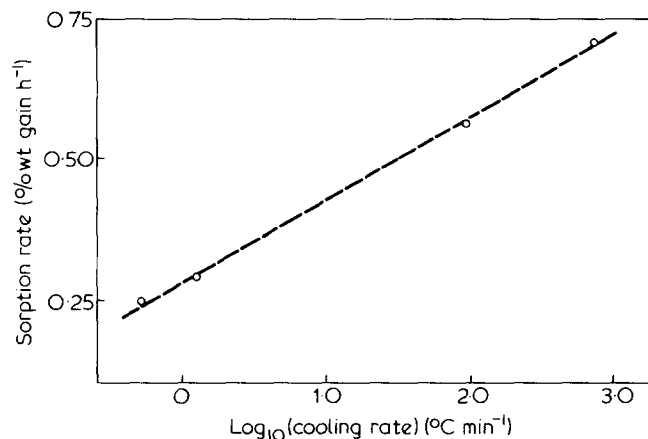


Figure 5 Plot of sorption rate at 24°C against  $\log_{10}$  (cooling rate) of heat-treated specimens

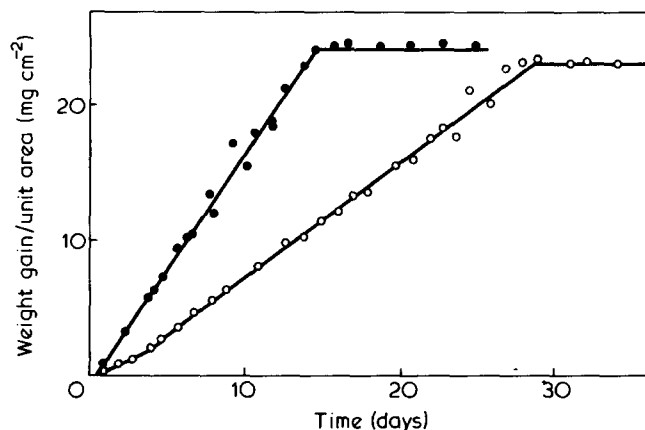


Figure 6 Weight-gain data as a function of time for 1 mm PMMA sheet swollen in methanol. ●, 15°C; ○, 10°C. (Average thicknesses = 1.00 and 0.94 mm respectively)

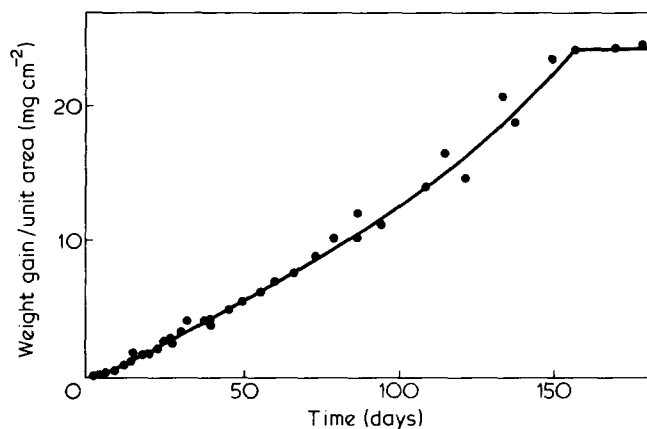


Figure 7 Weight-gain data as a function of time for 1 mm PMMA sheet swollen in methanol at 0°C. (Average sheet thickness = 0.98 mm)

Furthermore, if it is assumed that an increase in  $T_g$  is associated with a corresponding increase in free volume, then free volume will vary with the logarithm of the cooling rate. Since Figure 5 indicates that there is a linear relationship between the rate of Case II sorption and the logarithm of the cooling rate, we suggest that the rate controlling process for front propagation may depend linearly on the free volume in the polymer.

Other investigations of the effect of sample history on Case II swelling in glassy polymers include work by Ensore *et al.*<sup>41</sup>. They found that annealing of submicron diameter polystyrene spheres prior to swelling in n-hexane caused a reduction in sorption rate relative to that measured in the 'as-received' sample. These effects, which are in accord with our observations, were stated to be due to densification on annealing, i.e. a reduction in free volume in the glass, causing a decrease in the rate of Case II sorption.

#### Case II behaviour at low temperatures

Sorption of methanol in PMMA was measured at sub-ambient temperatures to investigate whether Case II behaviour occurs for a system in which the fully swollen polymer is still below its  $T_g$ .

The experiments were carried out at 15°C, 10°C and 0°C using sheet specimens (40 × 20 × 1 mm) of PMMA (Perspex) which had been annealed for 1 h at 130°C and oven-cooled. The weight-gain data at the three temperatures are plotted

in Figures 6 and 7. There is a linear relationship between weight-gain and time, indicating Case II behaviour; this is confirmed by the step-like concentration profiles (Figure 8) obtained at all three temperatures, using a sectioning technique described elsewhere<sup>9</sup>. In addition, there is an increased incubation period at the lower temperatures. For Case II diffusion at 24°C, the equilibrium swollen polymer behind the front (21 wt% methanol) appears to be in the region of its glassy transition. For example, when the fronts penetrating from opposite faces meet, the swollen material relaxes to its original shape over a period of 10 h. For samples swollen at 15°C, only about 10% shape reversion occurred over a period of 45 days after the fronts had met. This is shown in Figure 9. No shape reversion was observed for the samples swollen at 10°C and 0°C.

These experiments demonstrate that sorption behaviour completely typical of Case II occurs when both swollen and unswollen material is in the glassy state. Thus we argue that the existence of a sharp front does not depend on a discontinuity in the relationship between diffusivity and concentration which has played a part in some theories previously advanced<sup>30</sup>.

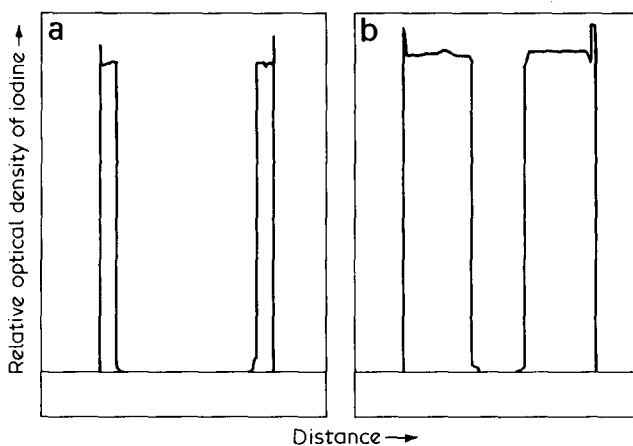


Figure 8 Microdensitometer traces from sections of 1 mm of PMMA specimens swollen in methanol/iodine solution at 10°C. a, at 6 days; b, at 23 days

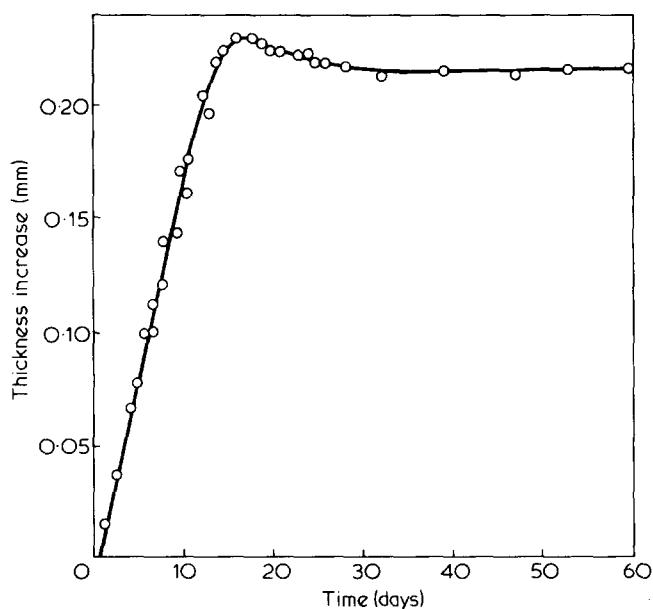


Figure 9 Thickness increase of 1 mm specimens swollen at 15°C. (Initial average thickness = 1.00 mm)

Table 1 Front velocity and equilibrium weight-gain as a function of temperature

Temperature (°C)	Velocity of Case II front (mm hr <sup>-1</sup> )	% Equilibrium weight-gain (g g <sup>-1</sup> )
24	$6.7 \pm 0.4 \times 10^{-3}$	$21.2 \pm 0.3$
15	$1.4 \pm 0.1 \times 10^{-3}$	$20.8 \pm 0.3$
10	$7.6 \pm 0.4 \times 10^{-4}$	$21.4 \pm 0.3$
0	$1.4 \pm 0.1 \times 10^{-4}$	$20.9 \pm 0.3$

### Measurement of activation energies

Several authors have drawn attention to the fact that the apparent activation energy for Case II diffusion is considerably higher than the range of values normally associated with Fickian diffusion<sup>42,43</sup>. However, activation energy measurements are often complicated by the fact that the concentration at the advancing front may decrease with penetration and the equilibrium weight-gain may vary with temperature. In the system PMMA—methanol at subambient temperatures, the equilibrium absorption is independent of temperature (Table 1) and provides an opportunity to obtain a reliable activation energy. An Arrhenius plot of the penetration rate data in Table 1 gives an activation energy of  $27.0 \pm 0.5$  kcal mol<sup>-1</sup>, which lies in the range of values reported<sup>44,45</sup> for creep of glassy PMMA, i.e. 17–30 kcal mol<sup>-1</sup>.

### CONCLUSIONS

The purpose of this paper has been to demonstrate that a description of Case II diffusion in terms of the creep response of an element of polymer at the advancing front to the thermodynamic swelling stress can account satisfactorily for the important aspects of the process. We have set up this initial argument for the model, not in terms of its ability to predict correct numbers in a particular system, but on a basis of the general characteristics of the Case II diffusion process. Discrimination between this model and previous ones is best achieved by focussing on selected aspects of Case II behaviour. We have used the system PMMA—methanol to demonstrate these aspects. The marked dependence of the process on the thermal history of the polymer, a dependence not shown by Fickian diffusion but similar to that shown by creep rate, is the basis of the first argument. The second depends on results obtained at subambient temperatures, which show ideal Case II behaviour under conditions where the equilibrium swollen polymer remains a glass. The observations demonstrate the inadequacy of theories which depend on a discontinuity in the relationship between diffusivity and the concentration of penetrant. The third point is also made on the basis of the low temperature data which happens to be particularly suitable for determining a reliable activation energy. The measured activation energy of 27 kcal mol<sup>-1</sup> is far in excess of values appropriate to Fickian diffusion in glassy polymers, and lies in the range of values variously reported for the activation energy for creep in glassy PMMA.

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