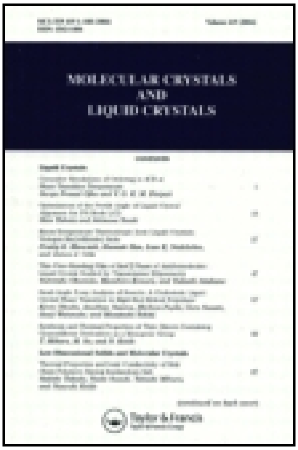

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# Diffusion of Penetrants in Organic Solids Accompanied by other Rate Processes

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**Abstract**—An examination is made of the possibility of studying diffusion occurring concurrently with another rate process of comparable velocity in penetrant-organic solid systems by means of simple experiments. It is shown that a model of diffusion with time-dependent " thermodynamic " permeability and solubility coefficients offers a useful kinetic description of such systems. Attention is drawn to certain advantages of this approach over earlier similar treatments and to the information which can be obtained by comparing uptake and permeation kinetics. These points are illustrated (with the aid of numerical solutions of the relevant equations where necessary) by detailed discussion of two examples of rate processes which can accompany diffusion, namely: (i) penetrant-induced molecular relaxations in glassy organic solids; and (ii) immobilizing irreversible reaction between the penetrant and suitable groups in the solid. The possibility of quantitative characterization of the accompanying rate process under suitable conditions is also illustrated in example (ii). It is, in fact, shown that considerable information can be obtained about the order and magnitude of the rate constant of the reaction, at least in the simplest systems, by methods similar to those of homogeneous reaction kinetics.

## Introduction

Isothermal sorption and diffusion of penetrants in organic solids may, not infrequently, be accompanied by other rate processes. Two examples of such processes will be considered here, namely reversible penetrant-induced change in the microstructure of the solid (at the molecular level) and irreversible chemical reaction. The analysis of kinetic data in such systems is reasonably straightforward, if the accompanying rate process is either very slow or very fast on the diffusion time scale. In the former instance, the two processes may be analyzed separately according to the kinetics appropriate to each. In the latter, the over-all process has all the characteristics of normal (" Fickian ") diffusion[1] (assuming a homogeneous solid). There is considerable difficulty in the intermediate case, however. Here, the observed kinetics differs from that characteristic of either of the concurrent processes alone, and is, furthermore, not subject to relatively simple analysis. This is largely due to the fact that the equations to be solved are generally non-linear. Nevertheless, appreciable progress has been made in the study of systems of this kind.

Our intention here is to indicate what kind of information can be obtained from data as simple as uptake and permeation curves for a given solid. These involve, respectively, measurement of the amount of penetrant (as a function of the time $t$) which has either (i) been taken up by the solid from adjacent reservoirs, or (ii) permeated from one reservoir to another through the solid (acting as a barrier). The usual experimental conditions[2-4] involve constant penetrant activity, $a$, in the reservoirs (which are in equilibrium with the solid surfaces) at all $t > 0$, and uniform initial (i.e. at $t = 0$) penetrant activity in the solid. It is most convenient (from the theoretical, and often also from the practical, viewpoint) to have the solid in the form of a thin slab (thickness $l$), with diffusion occurring along the thickness ($X$ direction).

Experimental data obeying " Fickian " diffusion kinetics can be analyzed by means of appropriate solutions[1,2] of the equation

$$\partial C/\partial t = (\partial/\partial X)[D(\partial C/\partial X)]\,; \quad 0 \leqslant X \leqslant l. \qquad (1)$$

The concentration of penetrant in the solid $C$ is obtained as a function of $a$ through equilibrium uptake measurements. The diffusion coefficient $D$ (which is either constant or a function of $C$ or $a$ only) is deduced from the uptake curve (e.g. the uptake half-time $t'_h$ or the initial constant slope obtained on a $\sqrt{t}$ scale), or from the final linear part of the permeation curve (in particular, the slope or the intercept on the $t$ axis, the latter known as the time lag $L$).[1-4] Incidentally, this type of analysis applies also to other simple geometries of the solid (such as the cylinder or the sphere).[1] It is worth mentioning that method (i) is particularly useful in such cases. It has the added advantage that the requirement of simple geometry can be relaxed to some extent. Thus, solids in powdered form have been used,[5] although marked irregularities in particle shape and/or size render the significance of the values of $D$ so obtained obscure.

As already pointed out, the presence of a concurrent rate process usually leads to deviation from " Fickian " diffusion kinetics. Thus, " non-Fickian " kinetic behavior is frequently, but not always,[4,9] characterized by departure from linearity of the initial portion of the uptake curve (on a $\sqrt{t}$ scale),[2,6–8] and discrepancy between observed and expected (" Fickian ") time lags.[3,4] Study of the nature of such anomalies can yield interesting qualitative and semiquantitative physical information, as is illustrated below.

## Diffusion Accompanied by Reversible Molecular Relaxations in the Solid

" Non-Fickian " kinetic features of the type mentioned above have been observed in organic solids (usually polymers) near or below the glass transition temperature. Here, penetrant-induced reversible molecular relaxations can occur in the solid at a rate comparable with diffusion. These kinetic features have been interpreted reasonably well by means of Eq. (1), by making $D$ and/or the boundary concentrations simple increasing functions of the time.[2,6–8] The time-dependence of the boundary concentrations has been ascribed to a relaxation process confined to the boundary.[3,10] The assumption of such a localized relaxation process is not considered very realistic, however.[10]

An alternative treatment, not subject to this difficulty, has been developed on the basis of the equation:

$$\partial C/\partial t = \partial(Sa)/\partial t = (\partial/\partial X)[P_T(\partial a/\partial X)]\,; \tag{2}$$

where $P_T = D_T S$, $D_T$, $S = C/a$ are the " thermodynamic " permeability, diffusion, and solubility coefficients respectively.[11] Here, the " non-Fickian " kinetic features in question can be discussed simply in terms of the time-dependence of $P_T$ and $S$. This formulation has other advantages. For example, it emerges that the discrepancy between observed and " Fickian " time lags, $L_T$, reflects the variation with time of $P_T$, whereas uptake kinetics is also influenced by the time-dependence of $S$.[4,11] Hence, complementary information can be obtained from permeation and uptake kinetic measurements.

The treatment based on Eq. (2) has so far been applied to the interpretation of time-lag data. It is, therefore, of obvious interest to apply it to uptake kinetics, particularly with a view of examining more thoroughly the recently suggested possibility of a decrease of $P_T$ with time in certain systems.[11] Accordingly, calculations were performed, in which $C = aS$ and $P_T$ (both these quantities being increasing functions of $a$) were allowed to vary moderately with time by first order kinetics,[6–8,11] at a rate comparable with diffusion. The equations used were exactly analogous to Eq. (1) of Crank,[7] e.g., for $P_T$,

$$\partial P_T(a,t)/\partial t = [\partial P_T(a,0)/\partial a](\partial a/\partial t) + b[P_T(a,\infty) - P_T(a,t)]\ ;$$

where $b$ is the relaxation frequency (for both $P_T$ and $S$). These equations were then solved simultaneously with Eq. (2), by means of a finite difference explicit method, on an IBM 360/40 computer, with the boundary conditions already referred to, namely: $a(0,t) = a(l,t) = a_0$, $a(X,0) = a_1$. In addition,[7,11] $P_T(a_1,\infty) = P_T(a_1,0)$, $C(a_1,\infty) = C(a_1,0)$. For generality, the following dimensionless variables were introduced:

$$\alpha = (a - a_1)/(a_0 - a_1)\,, \qquad \therefore \quad 0 \leqslant \alpha \leqslant 1\ ;$$

$$c = (C - C_1)/(C_0 - C_1)\,, \qquad \therefore \quad 0 \leqslant c \leqslant 1\ ;$$

where $\quad C_1 = C(a_1,\infty)\,, \qquad C_0 = C(a_0,\infty)\ ; \qquad s = c/\alpha\ ;$

$$P = D_T s'/P_0\,, \qquad P_0 = (D_T s')_{\alpha=0}\,, \qquad s' = S(a_0 - a_1)/(C_0 - C_1)\ ;$$

$$T = P_0 t/l^2\ ; \qquad \beta = bl^2/P_0\ ; \qquad x = X/l\,. \tag{3}$$

Examples of computed uptake curves (showing mean fractional concentration of penetrant in the solid as a function of $\sqrt{T}$) are given in Fig. 1. In agreement with the treatment based on Eq. (1),[6–8] there is a marked acceleration effect ($S$ shape), when both $S$ and $P_T$ increase with time (Line 2).‡ A much less marked effect of this kind is found when $S$ alone increases with time (Line 3). This condition is appropriate to the case of " Fickian " diffusion accompanied by an independent immobilizing chemical reaction.[4] The

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‡ Other results (not included in Fig. 1) indicate that this feature persists when $P$, $\beta$ are strongly increasing functions of $\alpha$, as is often the case in practice.

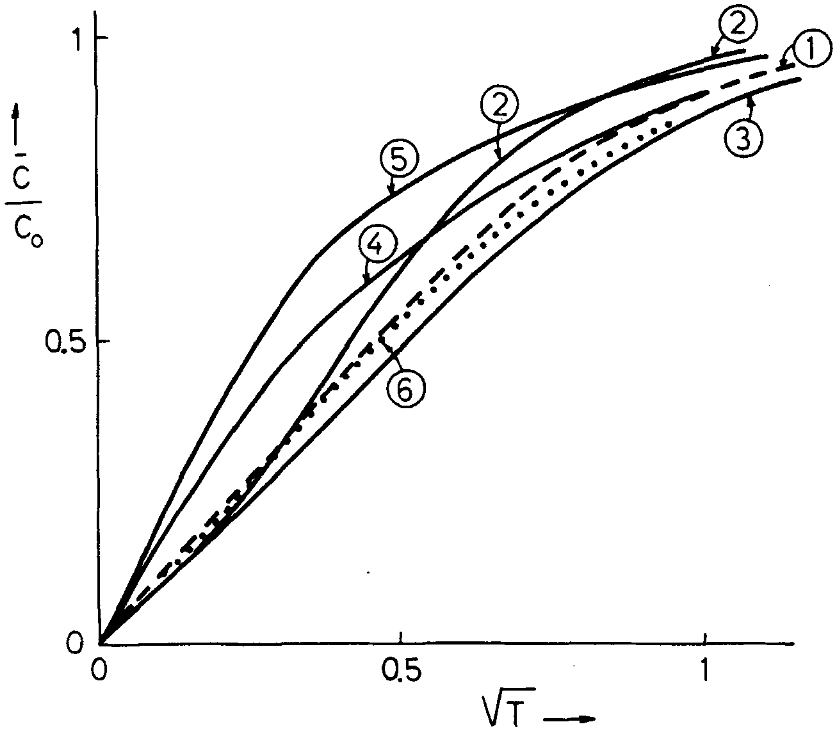

Figure 1. Uptake kinetic curves for: $P(\alpha, \infty) = 1 + 0.5\alpha + 0.5\alpha^2$, $P(\alpha, 0) = 1$ (Line 2); $P(\alpha, \infty) = 1$, $P(\alpha, 0) = 1 + 0.5\alpha + 0.5\alpha^2$ (Lines 4, 5); $P(\alpha, \infty) = 1$, $P(\alpha, 0) = 1 + 0.1\alpha + 0.1\alpha^2$ (Line 6); $P(\alpha, \infty) = P(\alpha, 0) = 1$ (Lines 1, 3); $s(\alpha, \infty) = 0.8 + 0.2\alpha$, $s(\alpha, 0) = 0.55 + 0.05\alpha$ (Lines 2, 3, 4, 6); $s(\alpha, \infty) = s(\alpha, 0) = 0.8 + 0.2\alpha$ (Lines 1, 5); $\beta = 5$.

present result agrees with those of Crank[1] (see, in particular, Fig. 8.7 given by this author). With $P_T$ decreasing with time, the uptake curve tends to assume a shape (Lines 4 and 5) more difficult to distinguish from the " Fickian " form (Line 1). In fact, the opposing tendencies of $S$ and $P_T$ to vary with time may largely " compensate " each other and yield uptake curves of very nearly " Fickian " shape (Line 6).‡ The suggestion[11] that this may be the case in certain polymer-water systems studied by Stannett *et al.*[12]

‡ As a matter of interest, the values of $L_T$ corresponding to the uptake curves of Fig. 1 should be positive for Line 2, zero for Lines 1 and 3, and negative for Lines 4, 5 and 6.

thus receives some further support, although the evidence is not as yet such as to permit more than tentative conclusions.

Nevertheless, the general picture of diffusion accompanied by molecular relaxations which emerges from these conclusions appears to be reasonable. Thus, increase of $S$ with time (at any $a$) is to be expected, since the final (relaxed) molecular configuration of the solid should be thermodynamically more favorable than the initial unrelaxed one.[2,6,7,11] For the corresponding change in $P_T$, however, there appear to be two possibilities: (i) If the solid acts as a " good solvent ", the penetrant will tend to be nearly molecularly dispersed in both initial and final molecular configurations of the substrate. (ii) If, on the other hand, the solid acts as a poor solvent, the tendency of the penetrant towards aggregation should favor a relaxed molecular configuration of the solid permitting higher penetrant clustering than is possible (for steric reasons) in the unrelaxed configuration. If this increase in penetrant clustering is sufficiently pronounced, $P_T$ will tend to be lower in the relaxed than in the unrelaxed state (since clusters are not expected to contribute appreciably to penetrant transport).[11]

More complete characterization of a " non-Fickian " system from a quantitative point of view requires rather elaborate experimentation.[8,9] Study of the accompanying rate process in any given experimental conditions by simple methods is particularly difficult, as pointed out earlier, except in the limiting case where this process is very slow on the diffusion time scale. In principle, this can always be achieved by reducing $l$ sufficiently, but such manipulation of $l$ is often not feasible in practice. Nevertheless, as will be shown below, study of the accompanying rate process is possible, even when its rate is comparable with that of diffusion, provided that it can be followed experimentally independently of the total uptake. This can often be done in the case of a chemical reaction, which is considered below.

## Diffusion with Immobilizing Irreversible Chemical Reaction

This case is of considerable interest in solid state chemistry and will be discussed in some detail. Attention will be directed to simple irreversible chemical reactions and the information which can be obtained about them from reaction curves (i.e. from the extent of reaction as a function of time) determined experimentally. More specifically, we shall consider the general (heterogeneous) reaction in which the penetrant (denoted by $A$) and fixed groups in the solid ($R$) react to form an immobile product ($B$).‡ As in previous studies,[1,13-15] attention will be confined mainly to the simplest system of this kind, namely one in which: (i) the physisorption associated with the diffusion process obeys Henry's law: $S_A = C_A/a_A = \text{constant}$; and (ii) the diffusion and reaction processes do not interact, their respective characteristic rate parameters $D_A$ and $K$ being constant.

It is well known that the reaction $R + A \rightarrow B$, though usually expected to be of second order, can exhibit a variety of mechanisms and hence also of kinetic behavior. To give a few simple examples, this reaction may appear as first order (in $A$ or $R$ respectively), if

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A', \quad R + A' \overset{k_3}{\rightarrow} B, \quad k_1 \ll k_2 \ll k_3, \tag{a}$$

or

$$R \underset{k_2}{\overset{k_1}{\rightleftarrows}} R', \quad R' + A \overset{k_3}{\rightarrow} B, \quad k_1 \ll k_2 \ll k_3, \tag{b}$$

or as third order (second order in $A$ and first order in $R$), if

$$2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A_2, \quad R + A_2 \overset{k_3}{\rightarrow} B, \quad k_3 \ll k_1, k_2, \tag{c}$$

and so on.

An analytical quantitative treatment is generally useful only when the reaction accompanying diffusion is first order (with respect to $A$).[1] For a second order reaction (first order in either reactant), an analytical approach is possible only in limiting cases.[13,14] More recently, Lebedev[15] obtained numerical solutions for the general case of such a heterogeneous second order reaction over a very wide range of conditions. His work has also served to indicate the range of applicability of the more approximate analytical treatments, thus

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‡ The symbols $A$, $R$, $B$ are also used as subscripts to denote quantities referring to the respective species.

facilitating their practical use. Nevertheless, there exists as yet no general method of characterization of a simple heterogeneous reaction of the type considered here (i.e. of determination of its order and reaction constant), comparable to those used in homogeneous reaction kinetics. As will be shown below, however, application of the approach discussed in the previous section offers some new insight into this problem and leads to certain useful results.

Taking the case of the second order reaction as an example, we have

$$\partial C_B/\partial t = -\,\partial C_R/\partial t = KC_AC_R \tag{4}$$

to be solved simultaneously with Eq. (2), in which, under the conditions stated above, $P_T = D_AS_A$.[1,4] We also have: $C = C_A + C_B$, and $C_R^0 = C_R + C_B$, $C_R^0$ being the total concentration (assumed uniform in $X$) of the fixed groups of the solid taking part in the reaction (reacted + unreacted); $C_0 = C_A^0 + C_R^0$, where $C_A^0$ is the concentration of $A$ in the solid at the boundary. Further, in addition to (3), we define $c_A = C_A/C_A^0$, $c_R = C_R/C_R^0$, $a_1 = C_1 = O$ and noting that $c_A = \alpha$, $T = D_AC_A^0t/l^2C_0$, we finally obtain

$$\partial c/\partial T = \partial^2c_A/\partial x^2; \quad -\,\partial c_R/\partial T = (l^2KC_0/D_A)c_Ac_R \tag{5}$$

Equations (5) show that, on the diffusion time scale ($T$) defined here (which, it is worth noting, differs from that used by other workers),[1,13–15] the rate of reaction is governed by an " effective rate constant " $K_E = l^2KC_0/D_A$. The value of $K_E$ may serve as a measure of the extent to which the observed rate is controlled by either of the concurrent processes. For example, as $K_E$ decreases, the observed rate becomes increasingly reaction-controlled, until, in the limit, conditions of homogeneous reaction kinetics are established. Under these conditions, as is well known, characterization of the reaction is quite simple, e.g. by examination of the half-time, $t_h$, of the reaction curve. This parameter has a known fixed value when measured on a dimensionless reaction time scale $\tau$. For example, under the present boundary conditions ($C_A^0$ = constant during the course of the reaction), Eq. (4) yields $\tau_h = KC_A^0t_h = \ln 2$. The expression for $\tau_h$ naturally depends on the order of the reaction, which is obtained experimentally by suitable variation of the initial concentrations of the reactants. Thus, for the second order reaction under examination, $t_hC_A^0$ should be found to be constant, when $C_A^0$, $C_R^0$ are varied. The form of Eq. (5) led us to suppose that similar behavior might be observed under conditions of heterogeneous reaction kinetics, if care was taken to vary $C_A^0$, $C_R^0$ in a way not affecting the relative rates of the concurrent processes, i.e. the value of $K_E$.

Equations (5) were solved simultaneously for a wide range of values of $K_E$ by the methods previously described, and with boundary conditions:

$$c_A(0,t) = c_A(l,t) = 1;\quad c_A(X,0) = 0;\quad c_R(X,\ 0) = 1;\quad c_B(X,0) = 0\,.$$

The close approach to complete reaction and diffusion control respectively at each end of the $K_E$ range used is indicated by the tendency of the dimensionless reaction ($\tau_h$) and uptake ($T_h'$) half-times to the correct limiting values (that of $T_h'$ depending on $C_A^0/C_R^0$[1]), as shown in Fig. 2. This figure also shows that our original hypothesis is borne out to a remarkable extent, $\tau_h$ being very insensitive to a change in $C_A^0/C_R^0$, at constant $C_0$, by a factor of as much as $10^4$ (although its value departs from that for homogeneous reaction kinetics), until the reaction becomes quite strongly diffusion controlled.

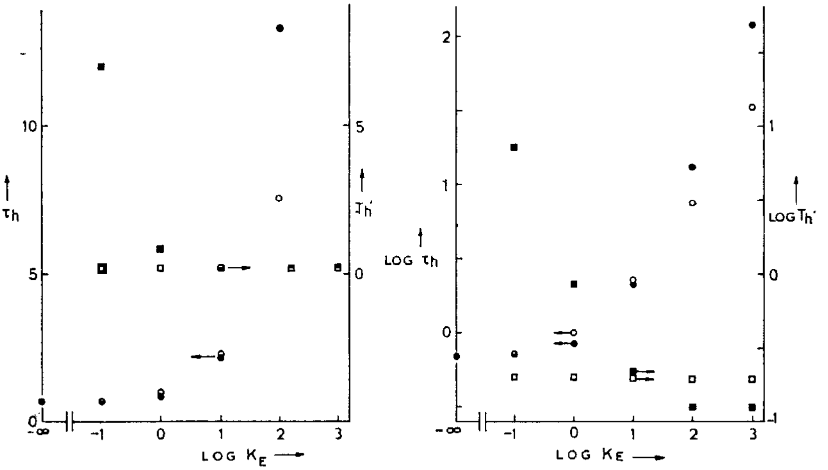

Figure 2. Dimensionless reaction (○, ●) and uptake (□, ■) half-times for second order reaction. $\tau_h = KC_A^0t_h$; $T_h' = D_A C_A^0 t_h'/l^2C_0$; $K_E = l^2KC_0/D_A$ $C_A^0/C_R^0 = 10^{-2}$ (●, ■) to $10^2$ (○, □).

As shown by Figs. 3–5, very similar results are obtained with first

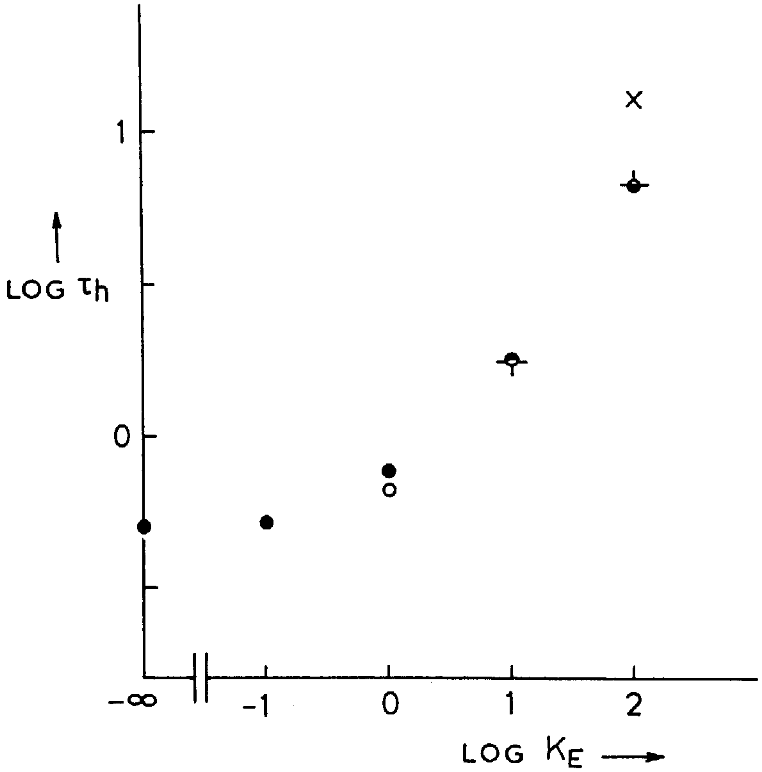

Figure 3. Dimensionless reaction half-times for first order (with respect to $A$) reaction. $\tau_h = KC_A^0 t_h/C_R^0$; $K_E = l^2 KC_0/D_A C_R^0$. $l^2 KC_0/D_A = 0.1$ (●), 1 (○), 10 (+), 100 (×).

and third order reactions, i.e. cases (a) to (c),‡ provided, of course, that the appropriate expressions for $\tau_h$ and $K_E$ are used, with the exception of the results for (b) (Fig. 4). This discrepancy can be explained readily, however, because, in this case, the diffusion process interferes with the kinetics of the reaction. In fact, on moving away from the homogeneous kinetics region, the reaction ceases to be simple first order for any reasonable values of $k_1$, $k_2$, $k_3$ (at the same time the accuracy of the computed $\tau_h$ decreases, while the computing time increases very markedly, so that it was not considered worthwhile to pursue the computations further).

‡ The condition $y \gg z$ in the theoretical schemes was rendered by $y = 100z$ in the computations.

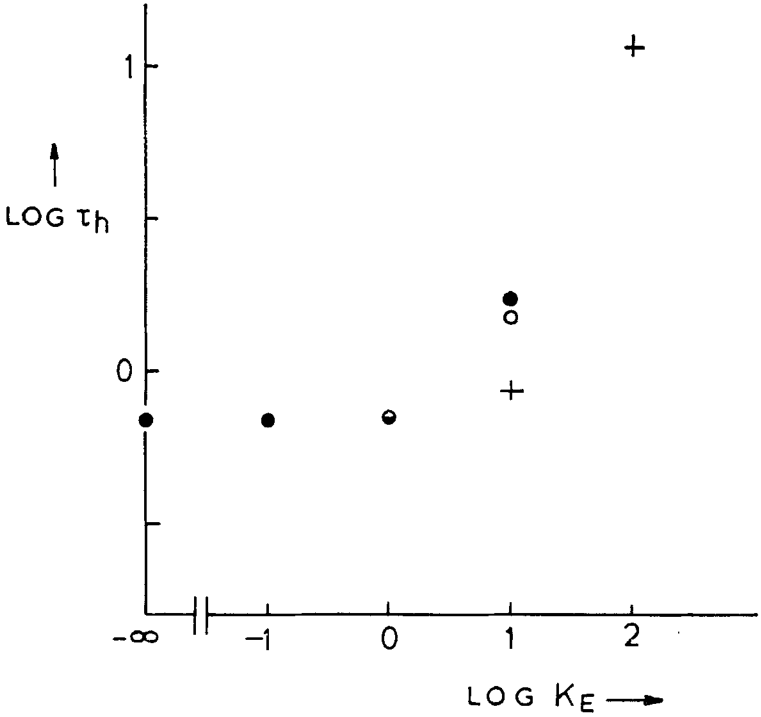

Figure 4. Dimensionless reaction half-times for " first order " (with respect to $R$) reaction. $\tau_h = Kt_h$; $K_E = l^2KC_0/D_AC_A^0$. $l^2KC_0/D_A = 0.1$ (●), 1 (○), 10 (+).

From the above results, it follows that, outside the region of strong diffusion control, there is, in general, a possibility of obtaining information about the order of a simple heterogeneous reaction and the approximate value of $K$ by measuring $t_h$ with suitable variation of $C_A^0$, $C_R^0$. For example, if one keeps $C_A^0 \ll C_R^0$, reactions which are first or second order in $A$ can be distinguished by the fact that, as $C_A^0$ increases, $t_hC_A^0$ will tend respectively to be nearly constant or to decrease. Examination of the variation of $t_hC_A^0$ with $C_0$ (e.g. by varying $C_A^0$, when $C_A^0 \gtrsim C_R^0$) should then permit an approximate estimate of $K$ (and also of $P_T$) to be made by comparison with the results of the present calculations, if the reaction is first order in $R$. If not, the order with respect to $R$ must, of course, be determined before $K$ can be estimated. This can be done conveniently in systems where it is possible to vary $C_R^0$ easily without materially affecting the

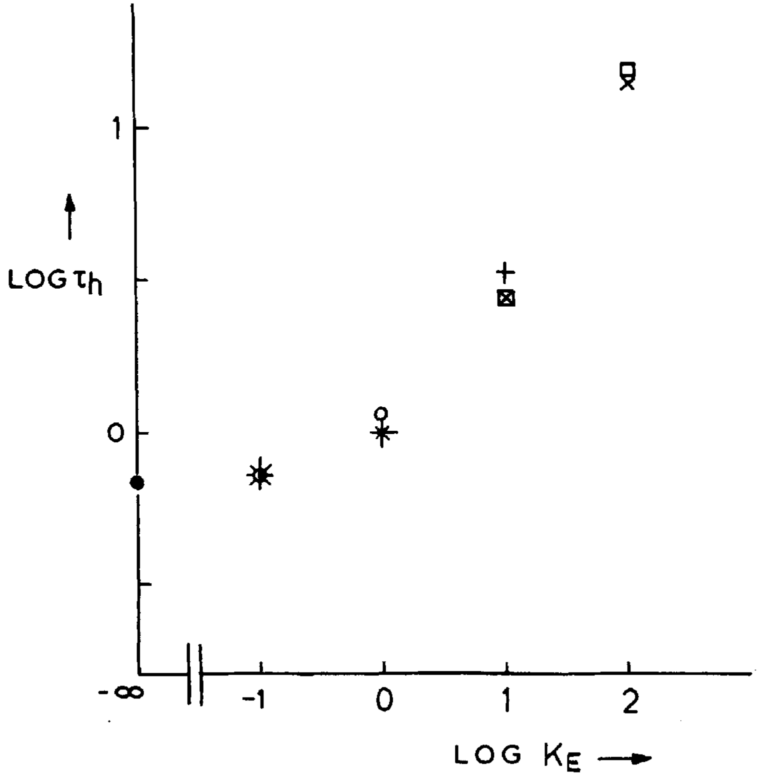

Figure 5. Dimensionless reaction half-times for third order (second order in $A$, first order in $R$) reaction. $\tau_h = KC_A^{0\,2}t_h$; $K_E = l^2KC_A^0C_0/D_A$. $l^2KC_0/D_A = 0.1$ (●), 1 (○), 10 (+), 100 (×), 1000 (□).

structure of the solid, and hence the values of $D_A$, $S_A$ and $K$.[16] In addition, Fig. 2 suggests that the behavior of $t_h'$ might also provide useful information.

The model investigated above is probably not unrealistic for many simple experimental systems. Furthermore, simple models have often proved sufficient to interpret various aspects of the behavior of experimental systems known to be quite complex.[10,11,17] Hence, there appears to be little point in elaborating the present treatment extensively, except in the light of the behavior of particular experimental systems to which it is to be applied. Nevertheless, it is well to bear in mind that $D_A$ and $K$, and possibly also $S_A$, can be very structure sensitive particularly in crystals, where the presence of crystal lattice defects tends to enhance both diffusion and reaction rates.[18] Since formation of the reaction product usually implies introduction of further defects into the parent crystal lattice, autocatalytic phenomena can be expected in many such systems. Account of such effects can be taken in the simple model by making $D_A$ and/or $K$ increasing functions of $C_B$, although these phenomena can be much more complex than is implied by this simple approach.‡

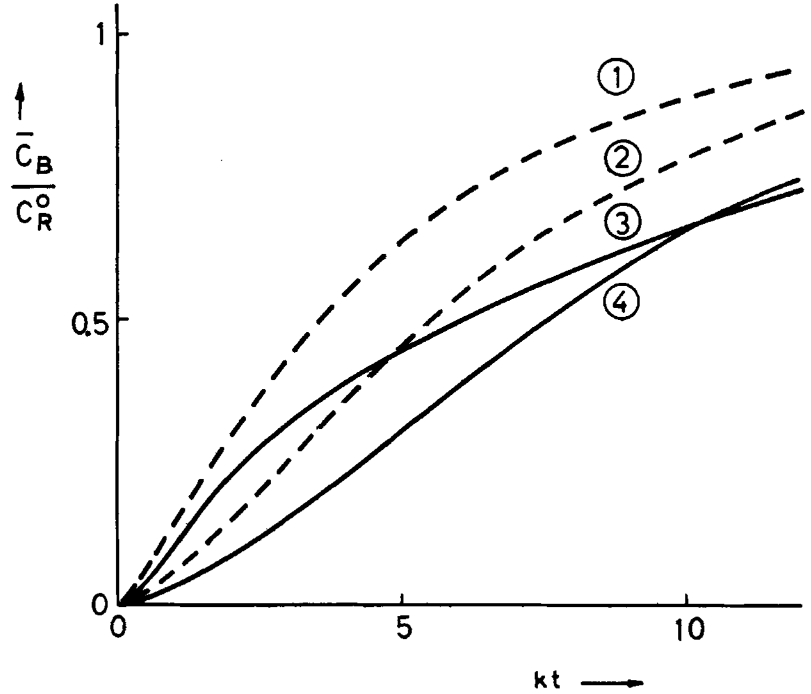

Figure 6. Reaction curves for second order reaction with: $C_A^0 = 0.05, C_R^0 = 1$; ——— $D_A/l^2 = 1$, ---- $D_A/l^2 = 1 + 10C_B$; $K = 5$ (Line 1), 60 (Line 2), $10 + 100C_B$ (Line 3); $1 + 10C_B$ (Line 4); $k = 1$ (Lines 1, 4), 10 (Line 2), 5 (Line 3).

Some calculations for a second order reaction with $K$ increasing linearly with $C_B$ show that the reaction curve tends to be $S$ shaped,

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‡ Reaction-induced structural changes in crystals may range from minor changes in dimensions of the parent lattice to formation of a completely new phase. The possibility that the overall effect may be one of autoretardation rather than autocatalysis also exists, of course.

but becomes progressively less markedly so on moving away from the region of reaction control to that of diffusion control (Fig. 6). This $S$ shape should not be used indiscriminately as a criterion for autocatalysis, because our calculations show that an $S$-shaped curve is obtained in the absence of autocatalysis, if $C_A^0/C_R^0$ is sufficiently high (Fig. 7). Excluding this case, $S$-shaped reaction curves are also

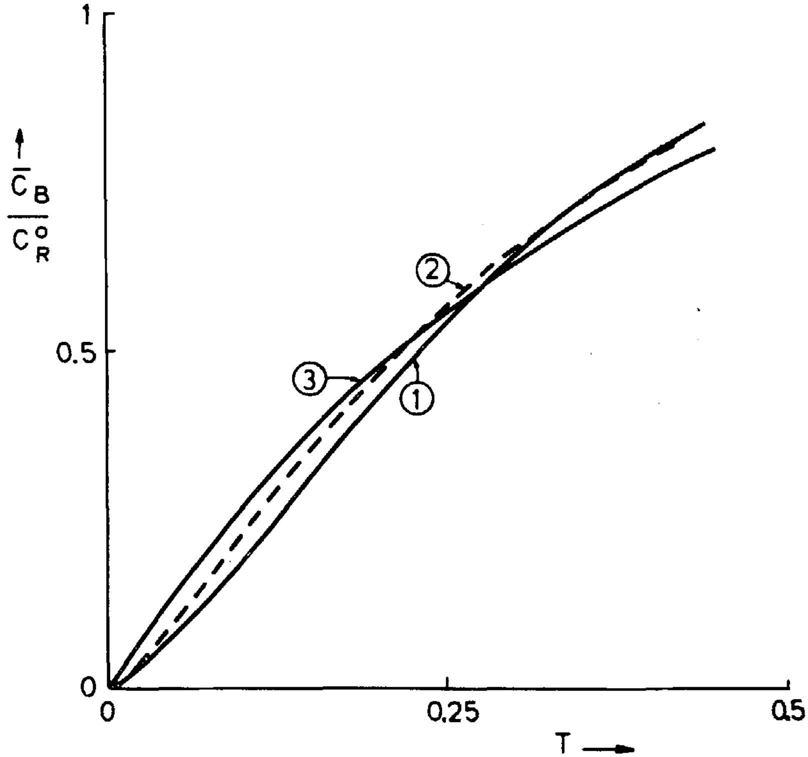

Figure 7. Reaction curves for second order reaction with $l^2KC_0/D_A = 10$; $C_A^0/C_0 = 0.95$ (Line 1), 0.5 (Line 2), 0.05 (Line 3).

obtained when $D_A$ increases with $C_B$ under conditions where neither of the concurrent processes is strongly rate-controlling (Fig. 6). Increase of $D_A$ (or $S_A$) with $C_B$ is also indicated, incidentally by $L_T > 0$, in contradistinction with the previous case of $K = K(C_B)$ for which one expects $L_T = 0$. Thus, here again, comparison of two types of kinetic measurements can yield useful information. In fact, in experimental systems for which the present model has some validity, the results presented here offer the possibility of assessing roughly the extent to which acceleration of each of the concurrent processes contributes to observed autocatalytic phenomena.

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