Theoretical solutions for mixed control of solid state reactions

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The kinetics of solid state reactions has been reexamined to include solutions for mixed control by an interfacial process and diffusion. The Valensi-Carter, Ginstling-Brounshtein, and other quasi steady state models have been extended to include mixed control. Solutions were obtained for planar, cylindrical and spherical particles. Mixed control may occur at either the inner or outer interface for cylindrical or spherical particles, for which significantly different solutions are valid. Mixed control at the outer interface usually gives faster reaction than mixed control at the inner interface. The kinetics of these solid state reactions with mixed control is usually nearly independent of the product to reagent volume ratio.

1. Introduction

Diffusion is usually slow in condensed phases whether their bonding is predominantly ionic or covalent and reactions thus likely to be controlled by diffusion. However, fast ion transport in some solids demonstrates that diffusion is not always slow; also chemical reactions at interfaces are not always rapid, and in this case one expects mixed controlled behaviour. For example, formation of a solid product by reaction of a metal with a gas is not always diffusion controlled. In fact, tarnishing reactions tend to be controlled by diffusion only for cases when the scale is dense, in which case the rate is usually dependent on low ionic or electronic conductivity [1]. Excessive volume change or lattice mismatch often yield a porous scale which grows linearly with time, as expected for control by interfacial reaction. This indicates that mass transport in the gas phase is fast compared to the interfacial reaction. Growth of dense scales might also be reaction- or mixed-controlled when mass transport in the solid is relatively fast, as expected for scales with mixed electronic + oxygen ion conduction, (or electronic + cationic conduction). These conclusions can be extended to other solid state reactions [2]. The oxidation of covalent ceramic materials is also dependent on the transport properties of the reaction product, and might deviate from diffusion controlled behaviour [3, 4].

Diffusion is thus not always the slowest and so controlling step in solid state reactions. It is therefore important to be able to predict what differences in behaviour may be expected if a process is controlled by rate of reaction at the interface or by both diffusion and interfacial reaction. This paper reports quasi steady state solutions for these processes.

Quasi steady state theoretical models have often been used to interpret thermogravimetric data for solid state and solid–liquid reactions. The models most frequently used are those of Jander [5], Valensi [6–8], Ginstling and Brounshtein [9], and Carter [10, 11], see Sharp *et al.* [12] and Beretka [13]. Other theoretical models proposed for diffusion controlled growth or dissolution of particles describe diffusion in the original matrix [14–19], and therefore do not apply to processes which depend on diffusion through a growing product layer.

The accuracy of approximate equations was recently examined for spherical particles [20] and considerable shortcomings were found when the familiar approximations are applied to systems of moderate or high solubility. However, it was confirmed that use of either the Jander or the Ginstling and Brounshtein equation up to about 50% reaction ($\alpha = 0.5$), could be used to determine whether a particular reaction is diffusion controlled, so long as a very narrow size distribution of particles is used. On the other hand these equations cannot be used to deduce values of parameters such as diffusivity and may not give sufficiently accurate predictions of time to reach complete reaction. This theoretical investigation has now been extended to include other simple shapes of particle (cylinder and flat plate). Other complications may of course arise from factors like interaction between adjoining particles. Note that models previously proposed to account for the effect of precipitate volume fraction on diffusion controlled growth or dissolution of particles [21, 22] do not describe processes controlled by diffusion in a growing product layer.

The papers already referred to make it clear that numerical methods must be used to obtain accurate

results for many cases which involve control solely by diffusion. Introducing interface reaction as well as diffusion must make the analysis more complicated and thus implies that numerical analysis will generally be necessary. However, it is always useful to examine what analytical solutions, if any, can be obtained for a particular type of problem. Analytical solutions usually correspond to asymptotic behaviour or limiting regimes, and examination of them often gives useful semi-quantitative insight into a wider range of cases. Analytical solutions also give much better intuition than more complex numerical procedures, and provide a useful tool for validating any numerical procedures developed for a wider range of problems.

This paper examines the behaviour of particles when both reaction at the interface and diffusion in the surrounding layer of product need to be considered and derives the analytical solutions that can be obtained; some typical results are then discussed. The basic assumptions remain the same as usual, that is an isolated particle surrounded by a layer of product is considered and symmetry is retained. It is also assumed that change in size is governed partly by both reaction at one of the interfaces and diffusion in the product phase; any necessary volume relaxation is assumed to occur without constraint; the interfacial chemical reaction is assumed to be first order. Processes with mixed control are sometimes successfully decomposed into separate diffusion and reaction stages; however, to deal with the whole range of phenomena occurring within the transition range between diffusion control and interface reaction control, it is necessary to have methods for dealing with both simultaneously.

When automatic data acquisition methods can determine particle size distributions in powders, suspensions or microstructures, this offers a complementary method for studying the kinetics of some processes. When controlled by surface kinetics one expects the time scale to be proportional to particle radius but when diffusion controls the process time is made dimensionless in terms of radius squared. The change in size distribution with time will often therefore confirm one or the other of these relations and thus indicate the mechanism.

2. Formulation of the problem

Mixed control of reaction of a particle to form a contiguous layer of product may include four possible cases:
Case I: Diffusion from the inner interface with
  Ia: mixed control at the inner interface,
  Ib: mixed control at the outer interface.
Case II: Diffusion from the outer interface with
  IIa: mixed control at the inner interface,
  IIb: mixed control at the outer interface.
Schematic representations of cases IIa and IIb are shown in Fig. 1. Cases Ia and IIa imply that reaction at the outer interface is much faster than at the inner interface; cases Ib and IIb imply the converse. Despite these differences the same general material balance applies to them all, as already shown for reaction of
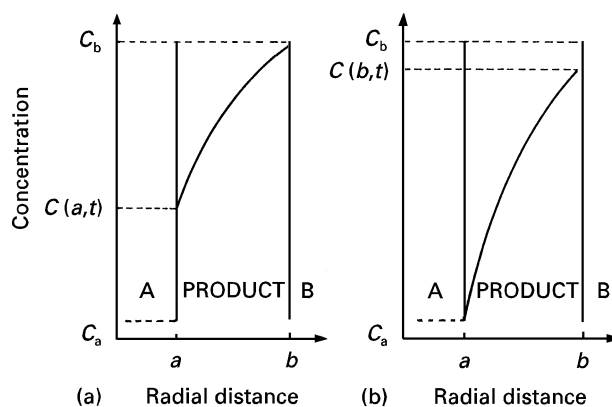
Figure 1 Schematic diagram showing changes in concentration when a solid layer is formed by reaction between reagents A and B. a) Diffusion from the outer interface and mixed control at the inner one; b) diffusion from the inner interface with mixed control at the outer one.

spherical particles [20], and this can be extended to two- and three-dimensional cases. If symmetry is maintained and for a constant diffusivity this may be written

$$r^{-n}\frac{\partial}{\partial r}r^{n}D\frac{\partial C}{\partial r} - \varepsilon(a/r)^{n}\frac{\mathrm{d}a}{\mathrm{d}t}\frac{\partial C}{\partial r} = \frac{\partial C}{\partial t} \qquad (1)$$

where $n = 0, 1, 2$ for the one- two-, or three-dimensional cases, r is radial (or linear) distance, C concentration, t time and D diffusivity. Two other equations describe the motion of both interfaces; these are similar to those previously formulated for control by diffusion alone [20], except for the time dependent interfacial concentrations $C(a,t)$ or $C(b,t)$. For cases Ia and Ib

$$\mathrm{d}a/\mathrm{d}t = \{D/[C_s(1 - v_A C(a,t))]\}(\partial C/\partial r)_a \qquad (2)$$

and

$$\mathrm{d}b/\mathrm{d}t = \varepsilon(a/b)^n(\mathrm{d}a/\mathrm{d}t) - (D/C(b,t))(\partial C/\partial r)_b \quad (3)$$

where a and b are the two interfaces of the product layer, v_A the partial molar volume of solute A in the product and $\varepsilon = 1 - v_A C_s$ if C_s is the concentration of solute in the particle; ε thus measures the volume change caused by transferring solute across the inner interface. Similarly, for cases IIa and IIb

$$\mathrm{d}a/\mathrm{d}t = -\{D/[(1 - \varepsilon)C(a,t)]\}D(\partial C/\partial r)_a \quad (4)$$

and

$$\mathrm{d}b/\mathrm{d}t = \varepsilon(a/b)^n(\mathrm{d}a/\mathrm{d}t)$$
$$+ [v_A D/(1 - v_A C(b,t))](\partial C/\partial r)_b \qquad (5)$$

For cases Ia and IIa the condition on the outer boundary is constant but the inner boundary condition varies with time, $C(a,t)$, according to the interfacial kinetics. As the velocity of the inner boundary is proportional to the rate of transfer this leads to the two conditions

$$C(b,t) = C_b \qquad (6)$$

$$\mathrm{d}a/\mathrm{d}t = -k_a|C(a,t) - C_a| \qquad (7)$$

where k_a is the kinetic constant and C_a is the equilibrium value concentration at the inner interface.

Cases Ib and IIb have a constant condition at the inner boundary but a time dependent condition at the outer interface which gives

$$C(a, t) = C_a \qquad (8)$$

and either

$$k_b(C(b, t) - C_b) = -(D/C(b, t))(\partial C/\partial r)_b$$
$$\text{[Case Ib]} \qquad (9)$$

or

$$k_b(C(b, t) - C_b) = [\nu D/(1 - \nu C(b, t))](\partial C/\partial r)_b$$
$$\text{[Case IIb]} \qquad (10)$$

Note that the contribution $\varepsilon(a/b)^n(da/dt)$ in Equations 3 and 5 is due to convection.

3. Quasi steady state solutions

Quasi steady state solutions are only accurate for slow changes in concentration, $\partial C/\partial t \approx 0$, and for slow movement of the interfaces, $da/dt \approx 0$ and $db/dt \approx 0$, which permit simplification of the diffusion equation.

3.1. Diffusion from the inner interface
3.1.1. Mixed control at the inner interface (case Ia)

The details of the solutions for this case are given in Appendices A, B and C. These solutions reduce to Equation 11 for flat particles, Equation 12 for cylindrical particles and Equation 13 for spheres.

$$G_1(\alpha, z) = \alpha D/(k_{ra}a_0) + \alpha^2 z/2 = \phi Dt/a_0^2 \qquad (11)$$

$$G_2(\alpha, z) = \{[\alpha + 1/(z - 1)]\ln[1 + (z - 1)\alpha]$$
$$+ (1 - \alpha)\ln(1 - \alpha)\}/4$$
$$+ [1 - (1 - \alpha)^{1/2}]D/(k_{ra}a_0)$$
$$= \phi Dt/a_0^2 \qquad (12)$$

and

$$G_3(\alpha, z) = \{z - [1 + (z - 1)\alpha]^{2/3}$$
$$- (z - 1)(1 - \alpha)^{2/3}\}/[2(z - 1)]$$
$$+ [1 - (1 - \alpha)^{1/3}]D/(k_{ra}a_0)$$
$$= \phi Dt/a_0^2 \qquad (13)$$

In these equations α is the fraction of reacted material, z is the volume of product divided by the volume of the initial particle consumed in forming it and a_0 the initial size of the particle. The other parameters in the equations are

$$k_{ra} = k_a C_s(1 - \nu_A C_a) \qquad (14)$$

$$\phi = (C_a - C_b)/[C_s(1 - \nu_A C_a)] \qquad (15)$$

The terms $[1 - (1 - \alpha)^{1/n}]D/(k_{ra}a_0)$ in Equations 11–13 represent the deviation from the diffusion controlled models derived by Valensi [6–8].

Equation 11 also applies when the volume of product equals the initial volume of solute and no radial flow in the matrix is required. The corresponding equations for cylindrical and spherical particles are, respectively

$$[1 - (1 - \alpha)^{1/2}]D/(k_{ra}a_0) + [\alpha + (1 - \alpha)\ln(1 - \alpha)]/4$$
$$= \phi Dt/a_0^2 \qquad (16)$$

$$[1 - (1 - \alpha)^{1/3}]D/(k_{ra}a_0)$$
$$- \alpha/3 + [1 - (1 - \alpha)^{2/3}]/2 = \phi Dt/a_0^2 \qquad (17)$$

3.1.2. Mixed control at the outer interface (case Ib)

The methods used in Appendices A, B and C are similar to those needed here but the changed boundary conditions produce rather different results for cylinders and spheres. The solutions are, for flat plates, cylinders and spheres, respectively

$$H_1(\alpha, z) = \alpha D/(k_{rb}a_0) + \alpha^2 z/2 = \phi Dt/a_0^2 \qquad (18)$$

$$H_2(\alpha, z) = \{[\alpha + 1/(z - 1)]\ln[1 + (z - 1)\alpha]$$
$$+ (1 - \alpha)\ln(1 - \alpha)\}/4$$
$$+ \{[1 + (z - 1)\alpha]^{1/2} - 1\}$$
$$\times \{D/[k_{rb}a_0(z - 1)]\}$$
$$= \phi Dt/a_0^2 \qquad (19)$$

$$H_3(\alpha, z) = \{z - [1 + (z - 1)\alpha]^{2/3}$$
$$- (z - 1)(1 - \alpha)^{2/3}\}/[2(z - 1)]$$
$$+ \{[1 + (z - 1)\alpha]^{1/3} - 1\}$$
$$\times \{D/[k_{rb}a_0(z - 1)]\}$$
$$= \phi Dt/a_0^2 \qquad (20)$$

Here the parameters are

$$k_{rb} = k_b C_a \qquad (21)$$

$$\phi = (C_a - C_b)/[C_s(1 - \nu_A C_a)] \qquad (22)$$

The latter is the same as Equation 15.

Equation 11 is again valid for the case of flat plates with $z = 1$ and the corresponding results for cylinders and spheres are respectively

$$[D/(k_{rb}a_0)]\alpha/2 + [\alpha + (1 - \alpha)\ln(1 - \alpha)]/4$$
$$= \phi Dt/a_0^2 \qquad (23)$$

$$[D/(k_{rb}a_0)]\alpha/3 - \alpha/3 + [1 - (1 - \alpha)^{2/3}]/2$$
$$= \phi Dt/a_0^2 \qquad (24)$$

Note that the solutions for control purely by interface kinetics at a stationary outer interface, that is for $z = 1$, reduce to linear relations between the fraction reacted and time

$$\alpha = m\phi k_{rb}t/a_0 \qquad (25)$$

where m is 1 for a plane surface, 2 for a cylinder and 3 for a sphere.

3.2. Diffusion from the outer interface
3.2.1. Mixed control at the inner interface (case IIa)

The procedure used for Case Ia is easily adapted to derive the solutions for this and again leads to Equations 11, 12, 13, 16 and 17. However the relevant parameters now become

$$k_{ra} = k_a C_a (1 - \varepsilon) \tag{26}$$

$$\phi = (C_b - C_a)/[C_a(1 - \varepsilon)] \tag{27}$$

3.2.2. Mixed control at the outer interface (case IIb)

Equations 18, 19, 20, 23, and 24 are also true for case IIb, except for the definition of the dimensionless parameters. The definition of ϕ is the same for both cases Ib and IIb (Equation 27), and the kinetic constant is

$$k_{rb} = k_b(1/\nu_A - C_a) \tag{28}$$

4. Results and discussion

The first point to note is that, although all the solutions contain the characteristic parameter $D/(k_{ra}a_0)$ or $D/(k_{rb}a_0)$, it is defined in different ways in the four cases whilst two different definitions of the effective solubility ϕ are required. Any attempt to deduce the fundamental parameters from fitting the theoretical relations to experimental data can therefore only be done when the nature of the system has already been identified.

The departure from diffusion control occurs for $k_{ra}a_0/D < 100$, $(k_{rb}a_0/D < 100)$, as demonstrated in Fig. 2 for spherical particles. Typical differences in the time scale are about 30% for $k_{ra}a_0/D = 10$ or $k_{rb}a_0/D = 10$. These conclusions are nearly true also
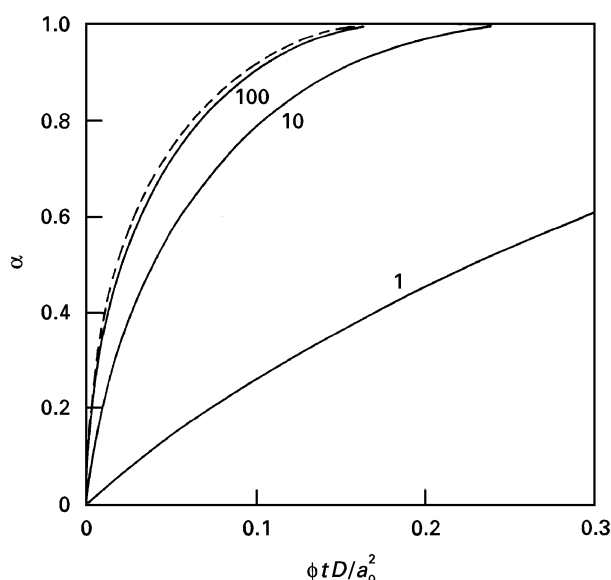

Figure 3 Deviations from reaction control with increasing reaction rate constant when the particles are spherical and for mixed control at the inner interface. The product to reagent volume ratio is unity ($z = 1$), and the values of $k_{ra}a_0/D$ are shown in the figure.
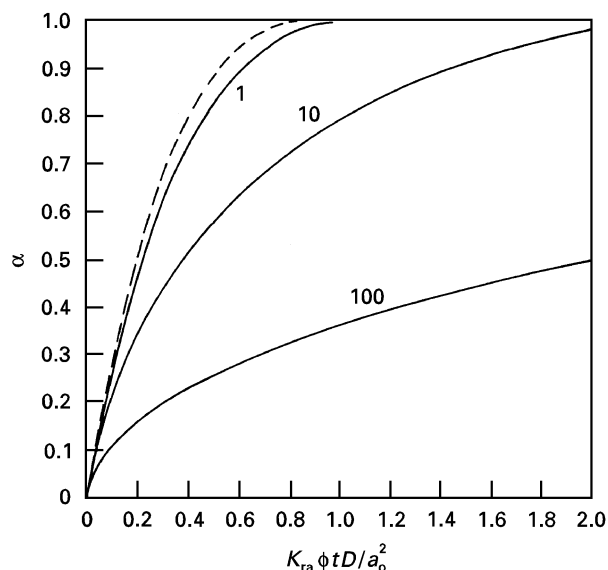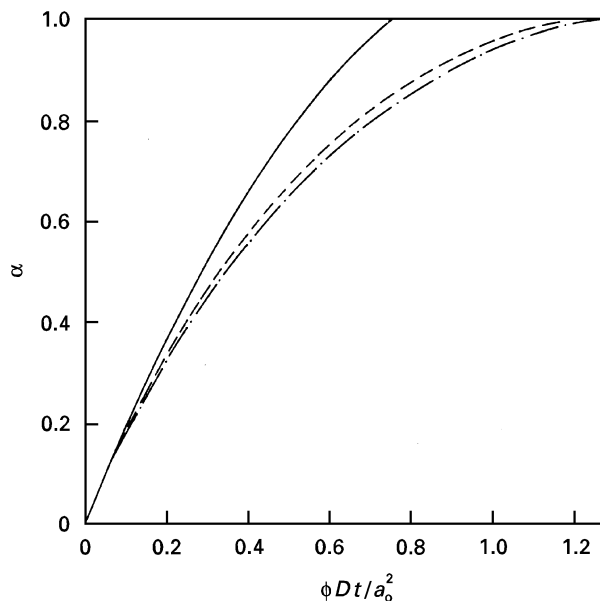

Figure 4 Solutions for reactions of cylinders with mixed control at the outer interface (solid line) or inner interface (dashed and dashed-dotted lines) when $D/(k_{ra}a_0) = 1$ or $D/(k_{rb}a_0) = 1$. The dashed line is for unit product to reagent volume ratio ($z = 1$) and other cases are for $z = 1.5$.

for planar or cylindrical particles, both with ($z \neq 1$) or without change in volume ($z \approx 1$). Fig. 3 also demonstrates the departure from reaction control with increasing kinetic constant. The differences in time scale are still in the range 10–20% for $k_{ra}a_0/D = 1$ or $k_{rb}a_0/D = 1$. Wide ranges of conditions thus require solutions for mixed control, especially for $1 \leqslant (k_{ra}a_0/D) \leqslant 10$ or $1 \leqslant (k_{rb}a_0/D) \leqslant 10$.

Fig. 4 shows the predictions for cylindrical particles with mixed control at either the inner or outer interface for $D/(k_{ra}a_0) = 1$ (or $D/(k_{rb}a_0) = 1$) and demonstrates the differences between them. Mixed control at the outer interface (solid line) usually gives faster
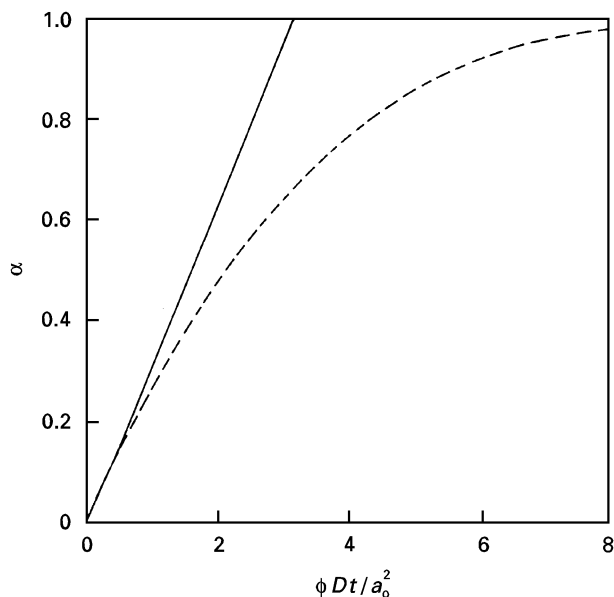

Figure 2 Deviations from diffusion control with decreasing reaction rate constant when the particles are spherical and for mixed control at the inner interface. The product to reagent volume ratio is unity ($z = 1$), and the values of $k_{ra}a_0/D$ are shown in the figure.

Figure 5 Solutions for reactions of spheres with mixed control at the outer interface (solid line) or inner interface (dashed line) when $D/(k_{ra}a_0) = 1$ or $D/(k_{rb}a_0) = 1$ and $z = 1.5$ for both cases.
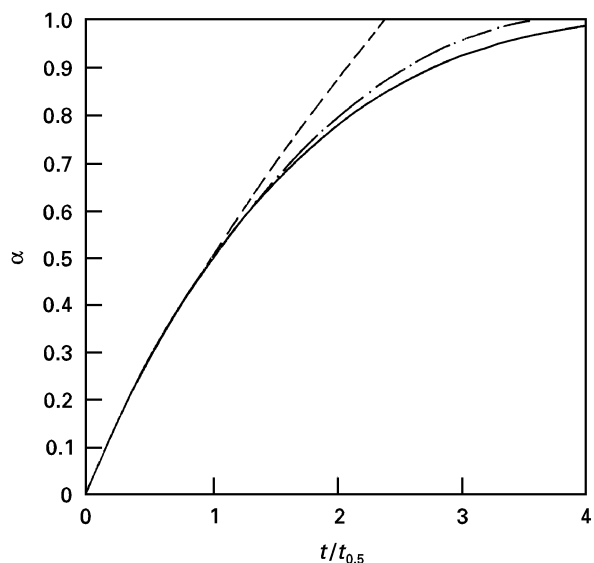

Figure 6 Fraction reacted plotted against reduced time, where $t_{0.5}$ is the time to reach 50% reacted, for different particle shapes, with unit product to reagent ratio, ($z = 1$), and mixed control at the inner interface, ($D/(k_{ra}a_0) = 1$). The solid line is for spheres, the dashed-dotted line for cylinders and the dashed line for planar particles.

reaction than control at the inner interface (dashed-dotted line); as the surface area of the outer interface is greater this is reasonable. Varying the volume change parameter z between 1 (dashed line) and 1.5 (dashed-dotted line) has little effect. Similar results for cylinders with other values of $D/(k_{ra}a_0)$ or $D/(k_{rb}a_0)$. Fig. 5 shows that differences between mixed control at the inner interface (dashed line) and mixed control at the outer interface (solid line) are slightly larger for spherical particles.

Experimental data are often made dimensionless with respect to the time to reach $\alpha = 0.5$. Fig. 6 shows some results for $D/(k_{ra}a_0) = 1$ for flat, cylindrical and spherical particles plotted in this way. Although the curves diverge for $\alpha \geqslant 0.5$, they are almost identical
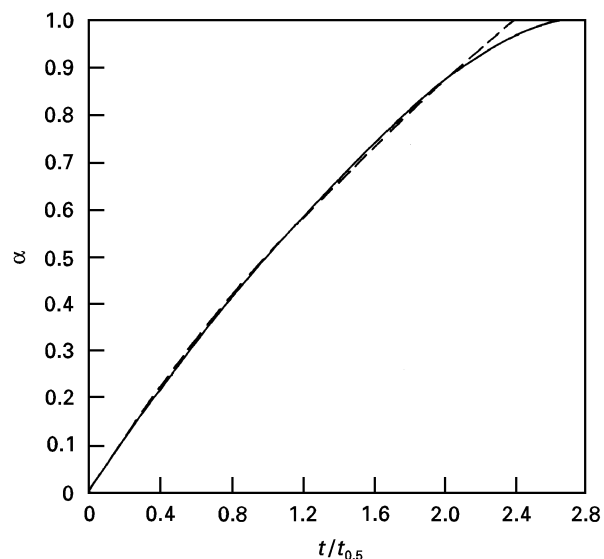

Figure 7 Fraction reacted plotted against reduced time, where $t_{0.5}$ is the time to reach 50% reacted, for spheres (solid line) or planar particles (dashed line), with unit product to reagent ratio, ($z = 1$), and mixed control at the outer interface, ($D/(k_{rb}a_0) = 1$).

below this. Note that there is very little difference between results for mixed control by diffusion and reaction at the outer interface (Fig. 7), and a greater difference when there is mixed control by diffusion and reaction at the inner interface. When it is remembered that other effects, such as interactions between adjacent particles or a distribution of particle sizes, are likely to influence the kinetics for $\alpha > 0.5$, it can be seen that the shape of the curve is not a very reliable indicator of the details of the process being studied.

Appendix A
Solutions for planar particles
Quasi steady state solutions of Equation 1 are easily obtained for slow changes in concentration ($\partial C/\partial t \approx 0$) and slow movement of the interfaces ($\mathrm{d}a/\mathrm{d}t \approx 0$, and $\mathrm{d}b/\mathrm{d}t \approx 0$). For a flat layer Equation 1 can be solved to give

$$\frac{\mathrm{d}C}{\mathrm{d}r} = \frac{(C_b - C(a,t))}{b - a} \tag{A1}$$

This equation can be combined with Equations 2 and 7 to give

$$C(a,t) = [C_a k_{ra}(b - a)/D + C_b]/[1 + k_{ra}(b - a)/D] \tag{A2}$$

$$k_{ra} = k_a C_s(1 - v_A C_a) \tag{A3}$$

The volume fraction of solute is assumed to be nearly constant, that is $v_A C(a,t) \approx v_A C_a$, because quasi steady state solutions are only accurate for small concentration differences. Substitution of $C(a,t)$ into Equation A1 and combination with Equations 2, 3 and 6 gives

$$\frac{\mathrm{d}(b - a)}{\mathrm{d}t}$$

$$= \frac{D(C_a - C_b)[(1 - \varepsilon) + C_s/C_b - vC_s(C_a/C_b)]}{C_s(1 - vC_a)[(b - a) + D/k_{ra}]} \tag{A4}$$

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In addition, for small concentration differences, $C_a/C_b \approx 1$ and $1 - \varepsilon$ is defined as νC_s so that the term $(1 - \varepsilon) + C_s/C_b - \nu C_s(C_a/C_b) \approx C_s/C_b \approx z$ and represents the volume of product formed per unit volume reacted. Integration of Equation A4 gives

$$(b - a)^2/(2z) + (D/k_{ra})(b - a)/z \;=\; \phi Dt \quad \text{(A5)}$$

with

$$\phi \;=\; (C_a - C_b)/[C_s(1 - \nu_A C_a)] \qquad \text{(A6)}$$

The volume ratio z may also be defined as

$$z \;=\; (b - a)/(a_0 - a) \qquad \text{(A7)}$$

so that Equation A5 can be expressed in terms of the fraction of solute reacted, $\alpha = (a_0 - a)/a_0$, giving

$$(z/2)\alpha^2 + \alpha D/(x_0 k_{ra}) \;=\; \phi Dt/a_0^2 \qquad \text{(A8)}$$

Appendix B
Solutions for cylindrical particles
The method is similar to that used for planar particles. The quasi steady state solution of Equation 1 becomes

$$\frac{dC}{dx} \;=\; \frac{C_b - C(a,t)}{r \ln(b/a)} \qquad \text{(A9)}$$

Combination of Equations A9, 2 and 7 thus yields

$$C(a,t) \;=\; [C_a(k_{ra}a/D)\ln(b/a) + C_b]/$$
$$[1 + (k_{ra}a/D)\ln(b/a)] \qquad \text{(A10)}$$

which can be inserted into Equation A9, together with Equations 2, 3, and 6,

$$\frac{d(a^2)}{dt} \;=\; \frac{2D(C_b - C_a)}{C_s(1 - \nu C_a)[D/(k_{ra}a) + \ln(b/a)]} \quad \text{(A11)}$$

$$\frac{d(b^2)}{dt} \;=\; \frac{2D(C_a - C_b)(z - 1)}{C_s(1 - \nu C_a)[D/(k_{ra}a) + \ln(b/a)]} \quad \text{(A12)}$$

The relation between the volume ratio $z = C_s/C_b$ in Equation A12 and original variables was discussed in Appendix A. In addition the volume ratio may be defined as

$$z \;=\; (b^2 - a^2)/(a_0^2 - a^2) \qquad \text{(A13)}$$

which on differentiating gives,

$$d(b^2 - a^2) \;=\; [z/(z - 1)]d(b^2) \;=\; -z\,d(a^2) \qquad \text{(A14)}$$

Therefore, subtracting Equation A11 from Equation A12 and integrating gives

$$(b/a_0)^2 \ln[(b/a_0)^2]/[4(z - 1)] + (a/a_0)^2 \ln[(a/a_0)^2]/4$$
$$+ (1 - a/a_0)D/(a_0 k_{ra}) \;=\; \phi Dt/a_0^2 \qquad \text{(A15)}$$

or in terms of the fraction reacted $\alpha = (a_0^2 - a^2)/a_0^2$

$$G_2(\alpha, z) \;=\; \{[\alpha + 1/(z - 1)]\ln[1 + (z - 1)\alpha]$$
$$+ (1 - \alpha)\ln(1 - \alpha)\}/4$$
$$+ [1 - (1 - \alpha)^{1/2}]D/(k_{ra}a_0)$$
$$=\; \phi Dt/a_0^2 \qquad \text{(A16)}$$

The solution for negligible change in volume ($z \approx 1$) can be obtained by integrating Equation A11 for $b = a_0$; which gives

$$[1 - (1 - \alpha)^{1/2}]D/(k_{ra}a_0) + [\alpha + (1 - \alpha)\ln(1 - \alpha)]/4$$
$$=\; \phi Dt/a_0^2 \qquad \text{(A17)}$$

Appendix C
Solutions for spherical particles
The quasi steady state solution of Equation 1 now becomes

$$\frac{dC}{dr} \;=\; \frac{a(C_b - C(a,t))}{r^2(1 - a/b)} \qquad \text{(A18)}$$

and combining with Equations 2 and 7 gives

$$C(a,t) \;=\; [C_a(k_{ra}a/D)(1 - a/b) + C_b]/$$
$$[1 + (k_{ra}a/D)(1 - a/b)] \qquad \text{(A19)}$$

which can be combined with Equations 18, 2, 3, and 6 to give

$$\frac{d(a^3)}{dt} \;=\; \frac{3D(C_b - C_a)}{C_s(1 - \nu C_a)[D/(k_{ra}a^2) + 1/a - 1/b]} \qquad \text{(A20)}$$

and

$$\frac{d(b^3)}{dt} \;=\; \frac{3D(C_a - C_b)(z - 1)}{C_s(1 - \nu C_a)[D/(k_{ra}a^2) + 1/a - 1/b]} \qquad \text{(A21)}$$

The volume change parameter may now be defined as

$$z \;=\; (b^3 - a^3)/(a_0^3 - a^3) \qquad \text{(A22)}$$

which leads to

$$d(b^3 - a^3) \;=\; -z\,d(a^3) \;=\; [z/(z - 1)]d(b^3) \qquad \text{(A23)}$$

and subtracting Equation A20 from A21 then integrating yields

$$(1 - a/a_0)D/(a_0 k_{ra}) + (b/a_0)^2/[2(1 - z)]$$
$$+ (a/a_0)^2/2 - z/[2(z - 1)] \;=\; \phi Dt/a_0^2 \qquad \text{(A24)}$$

or in terms of the fraction reacted, which is $\alpha = (a_0^3 - a^3)/a_0^3$

$$G_3(\alpha, z) \;=\; \{z - [1 + (z - 1)\alpha]^{2/3}$$
$$- (z - 1)(1 - \alpha)^{2/3}\}/[2(z - 1)]$$
$$+ [1 - (1 - \alpha)^{1/3}]D/(k_{ra}a_0)$$
$$=\; \phi Dt/a_0^2 \qquad \text{(A25)}$$

The solution for a negligible volume change is again obtained by integrating Equation A20 for $b = a_0$ which gives

$$[1 - (1 - \alpha)^{1/3}]D/(k_{ra}a_0) - \alpha/3 + [1 - (1 - \alpha)^{2/3}]/2$$
$$=\; \phi Dt/a_0^2 \qquad \text{(A26)}$$

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