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Combined effects of diffusion and reaction on the growth or dissolution of spherical particles

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An established implicit finite difference method was extended to predict the behaviour of particles when both diffusion and interface reaction effect the kinetics of growth or dissolution. A quasi-steadystate model was also obtained. Mixed behaviour must be expected for a relatively large range of conditions, $0.01 < a_0k/D < 10$, where k is a kinetic constant, a_0 is the initial radius, and D is diffusivity. Evolution from initial mixed control to strictly diffusion controlled growth is possible for moderate a_0k/D, but only when the particle size becomes much larger than the initial size.

1. Introduction

The observed growth or dissolution of particles and drops is often consistent with assuming control by diffusion in the surrounding matrix, with equilibrium at the interface. However, the effect of interfacial energy on the concentration of the solute at the interface of very small particles, predicted by the Gibbs–Thomson law, leads to unreasonable conditions in the matrix because the classic formulation of equilibrium conditions can permit the volume fraction of the solute to exceed unity. This failure can result from one or more of the following constraints:

1. Regular solution behaviour is assumed in deriving equilibrium conditions at the interface, but this must fail at high solute concentration.
2. If rates of transport become very high the process may become controlled by surface reaction kinetics or a mixture of diffusion and interface kinetics.
3. Pressure gradients causing viscous relaxation increase as particles become very small and may require consideration of stress relaxation.

Although it is often reasonable to assume that the slowest of several competing processes will entirely control the behaviour of a system, this is not always true and there may be a significant intermediate regime with mixed control. This paper considers such a case, where the growth or dissolution of a drop or particle may involve interface reaction kinetics as well as diffusion in the matrix.

2. Mathematical formulation

An isolated spherical particle is considered in an extensive uniform body of matrix and spherical symmetry is maintained. In such conditions diffusion in the matrix is described by [1, 2]

$$D\frac{\partial^2 C}{\partial r^2} + \left[\frac{2D}{r} - \varepsilon(a/r)^2\frac{\mathrm{d}a}{\mathrm{d}t}\right]\frac{\partial C}{\partial r} = \frac{\partial C}{\partial t} \qquad (1)$$

where C is the concentration, r is the radial distance, a the radius of the particle, t time, D diffusivity, $\varepsilon = 1 - \nu_A C_s$ in which ν_A is the partial molar volume of the solute in the matrix and C_s is the molar concentration of material in the sphere of pure solute. Diffusivity and partial molar volumes are taken to be constant. Transport through the medium must then correspond to change in the size of particle according to

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

The initial conditions correspond to

$$C(r,0) = C_\infty, \quad r > a \qquad (3)$$

and

$$C(\infty, t) = C_\infty. \qquad (4)$$

The equilibrium concentration at the interface, assuming regular behaviour, will be given by the well known Gibbs–Thomson law

$$C_{eq}(a) = C^*\exp[2\sigma/(aRTC_s)] \qquad (5)$$

where C^* is the equilibrium concentration for a flat interface, σ is the interfacial energy, R is the perfect gas constant and T is the absolute temperature (K).

If reaction at the interface affects the process, the concentration $C(a,t)$ will not be its equilibrium value $C_{eq}(a)$ and, for a first-order reaction, the rate of transfer of material across the interface will be given by

$$C_s(\mathrm{d}a/\mathrm{d}t) = k[C(a,t) - C_{eq}(a)] \qquad (6)$$

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2.1. Dimensionless treatment

For the sake of simplicity in manipulating the equations the following dimensionless variables are used

$$\begin{aligned} x &= r/a & s &= \sigma/(a_o RTC_s) \\ R &= a/a_o & k^* &= ka_o/D \qquad (7) \\ z &= tD/a_o^2 & F(x,z) &= (C - C_\infty)/C_s \end{aligned}$$

Thus Equations 1, 2 and 6 become

$$\frac{\partial^2 F}{\partial x^2} + \left[2/x + R(x - \varepsilon/x^2)\frac{dR}{dz}\right]\frac{\partial F}{\partial x} = R^2 \frac{\partial F}{\partial z} \qquad (8)$$

$$\frac{dR}{dR} = \frac{1}{R\{1 - (1 - \varepsilon)[F(1,z) + \phi + \phi q]\}}\left(\frac{\partial F}{\partial x}\right)_1 \qquad (9)$$

$$dR/dz = k^*[F(1,z) + \phi + \phi q - \phi q \exp(2s/R)] \qquad (10)$$

with

$$\phi = (C_\infty - C^*)/C_s \qquad (11)$$

$$q = C^*/(C_\infty - C^*) \qquad (12)$$

The parameter q is a solubility to oversaturation ratio.

The following initial and boundary conditions apply

$$F(x, 0) = 0, \quad x > 1 \qquad (13)$$

$$F(\infty, z) = 0, \quad z > 0 \qquad (14)$$

2.2. Finite difference technique

Equations 8, 9 and 10 must be solved numerically. Reliable implicit finite difference solutions can be obtained with variable space mesh and time mesh sizes, as shown elsewhere [2, 3]. Those solutions become more complex whenever variable boundary conditions are involved, as happens for multi-component gas bubbles [4, 5], and whenever surface tension or interfacial energy becomes important [6]. Variable boundary conditions also arise when both diffusion and interface kinetics are considered. A finite difference method was also used by Szekely and Fang [7] to deal with non-equilibrium effects. However, the stability of this technique requires very small time intervals; which is efficient for very large ϕ, but might prevent efficient use for all the relevant ranges.

Special algorithms are needed in most situations where variable boundary conditions occur. Otherwise numerical procedures tend to become unstable and fail. Crank and Nicholson [8] showed how to deal with a combination of diffusion and interface kinetics by taking into account that interface kinetics give rise to a linear relation between the interface concentration gradient and the interface concentration. This is strictly true when the equilibrium concentration is a constant, but is not true when interfacial energy influences the equilibrium condition, Equation 5. However, as finite difference solutions are computed by adding small increments in time, these can be controlled to give small relative changes in radius and interface concentration per time step, so that the interface concentration can be transformed into a quasi-linear function of interface concentration as is shown in Appendix A.

Quasi-stationary approximations were used to obtain the initial concentration profile after a short initial time, z_o, when the dimensionless radius becomes $R_o = 1 + \delta R$.

2.3. Reaction control

When k^* becomes sufficiently small the behaviour of the particle becomes controlled by rate of reaction at the interface and, as concentration gradients vanish, $F(1, z) \approx 0$. Then from Equation 10

$$dR/dz = k^*[\phi + \phi q - \phi q \exp(2s/R)] \qquad (15)$$

When the effects of interfacial energy are small enough to be neglected this reduces to a linear dependence of radius on time

$$R = 1 + k^*\phi z \qquad (16)$$

When interfacial effects must be taken into account, but $2s/R \ll 1$, $\exp(2s/R) \approx 1 + 2s/R$ and Equation 15 can be integrated to give

$$R - 1 + 2sq\ln[(R - 2sq)/(1 - 2sq)] = \phi k^* z \qquad (17)$$

However, the condition $2s/R \ll 1$ must fail, at least when a particle approaches complete dissolution. Growth requires $\phi > 0$ and $2s/R < \ln(1 + 1/q)$. Thus if $q \gg 1$ the term $2s/R$ must be small, which validates Equation 17. However, as q tends to zero this approximation fails when the particle size is the order of magnitude of the critical size, $a_c = \sigma/[RTC_s\ln(1 + 1/q)]$, and Equation 15 must be solved numerically. Otherwise, the effect of interfacial energy can be ignored.

2.4. Quasi-steadystate solutions

A quasi-steadystate regime assumes that the time derivative remains negligible, and slow boundary motion [6]. This only occurs for very slow changes in size and corresponds to

$$\frac{\partial^2 F}{\partial x^2} + \frac{2}{x}\frac{\partial F}{\partial x} = 0 \qquad (18)$$

On integration this leads to

$$(\partial F/\partial x)_1 \approx -F(1,z) \qquad (19)$$

and on combining with Equations 9 and 10

$$-F(1,z) = k^* R\{1 - (1 - \varepsilon)[F(1,z) + \phi + \phi q]\} \times [F(1,z) + \phi + \phi q - \phi q \exp(2s/R)] \qquad (20)$$

A quasi-steadystate regime requires very small driving forces, $|F(1,z)| \ll 1$, and this yields an explicit relation between the driving force, $F(1, z)$, and particle size, R

$$F(1,z) \approx \frac{-\phi k^* R[1 - (1 - \varepsilon)(\phi + \phi q)][1 + q - q\exp(2s/R)]}{1 + k^* R[1 - (1 - \varepsilon)(\phi + \phi q)]} \qquad (21)$$

Thus, after specifying s, q, ϕ, ε and k^*, $F(1, z)$ depends only on R. On combining with Equations 9 and 19 when $|F(1, z)| \ll 1$

$$\frac{\mathrm{d}R}{\mathrm{d}z} \approx \frac{\phi k^*[1 + q - q\exp(2s/R)]}{1 + k^*R[1 - (1 - \varepsilon)(\phi + \phi q)]} \qquad (22)$$

which must be solved numerically. However, $2s/R$ is often small, and in this case $\exp(2s/R) \approx 1 + 2s/R$, and Equation 22 can be integrated; this yields

$$\begin{aligned}\phi z = \{&R - 1 + 2sq\ln[(R - 2sq)/(1 - 2sq)]\}/k^* \\ &+ [1 - (1 - \varepsilon)(\phi + \phi q)]\{(R^2 - 1)/2 + 2sq(R - 1) \\ &+ (2sq)^2\ln[(R - 2sq)/(1 - 2sq)]\} \qquad (23)\end{aligned}$$

and the solution for diffusion controlled behaviour reduces to

$$\begin{aligned}z\phi^* \approx\ &(R^2 - 1)/2 + 2sq(R - 1) + (2sq)^2 \\ &\times \ln[(R - 2sq)/(1 - 2sq)] \qquad (24)\end{aligned}$$

where

$$\phi^* = \phi/[1 - (1 - \varepsilon)(\phi + \phi q)] \qquad (25)$$

The parameter q is relevant to the analysis of either strictly diffusion controlled behaviour or mixed control. However, the effects of interfacial energy on the solutions for reaction control (Equation 17) or diffusion control (Equation 24) can be accounted for by a single parameter (sq), rather than separate values for q and s..

For moderate values of $k^* = a_0k/D$, Equation 22 shows that particle growth may evolve from mixed control towards strictly diffusion controlled behaviour as the particle grows. However, this might require increase in size by a factor of 10 or more, (Fig. 1), which is often difficult to achieve experimentally. For example, both solutions for reaction controlled and diffusion controlled particle coarsening [9–11] might fail because experimental size ranges often involve an increase in size by a factor of only about 2. Models for mixed control [12] are then needed.

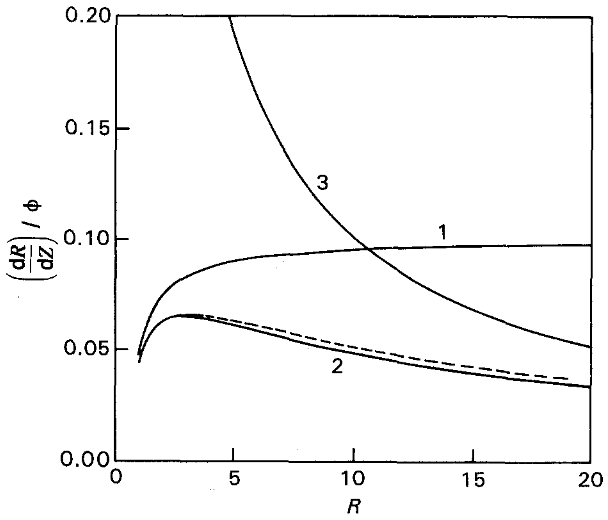

Figure 1 Quasi-steadystate predictions of growth rates for (1) reaction control, (2) mixed control and (3) diffusion controlled behaviour, when $\phi = 0.01$, $q = 5$, $\varepsilon = 0$, $s = 0.05$ and $k^* = 0.1$. The dashed line represents the non-steadystate finite difference solution.

Separate stages might also be assumed for reaction control, mixed control, and diffusion controlled behaviour when $k^* = a_0k/D$ is very small; however, this is even less likely to be observed experimentally than the transition from mixed control to diffusion controlled behaviour.

3. Results

Figs 2 and 3 show the influence of interface reaction rate on growth and dissolution of spherical particles. Fig. 2 shows the predicted times to shrink to one-tenth of the initial radius, that is dissolution of 99.9% of the solute mass. It can be seen that assumption of control entirely by interfacial reaction is nearly true for $k^* < 0.01$, and the differences in behaviour between mixed control and reaction control increase rapidly as k^* increases above 0.1. The behaviour becomes sensitive to the specific value of solubility, ϕ, for $k^* > 0.1$.

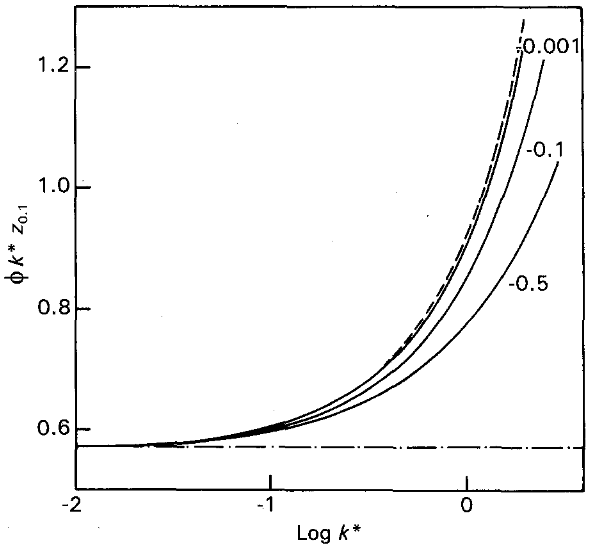

Figure 2 Dimensionless times required to shrink to 10% the initial size ($R = 0.1$) for $s = 0.1$, $\varepsilon = 0$, $q = -1$ and $\phi = -0.001$, -0.1 and -0.5. The quasi-steadystate solutions for: (– – –) negligible $|\phi|$; and (–·–) reaction controlled behaviour.

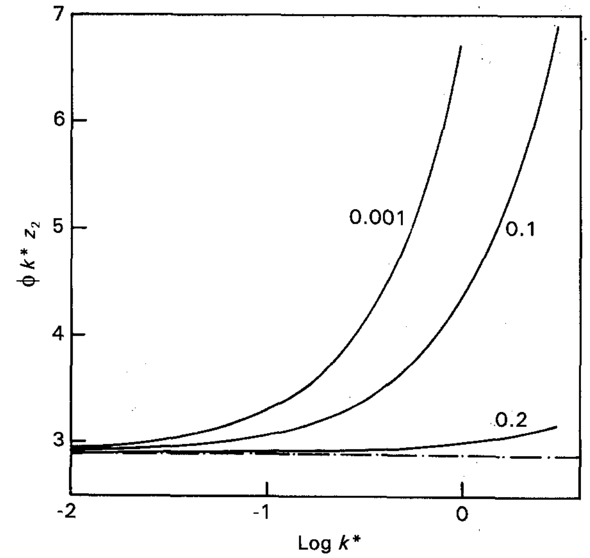

Figure 3 Dimensionless times required to double the size ($R = 2$) for $s = 0.1$, $\varepsilon = 0$, $q = 4$ and $\phi = 0.001$, 0.1 and 0.2.

Fig. 2 includes quasi-steadystate solutions (Equation 22) which should apply for low solubility and the reaction controlled limit. The full numerical solution for $\phi = 0.001$ is sufficiently close to the quasi-steadystate solution to validate the numerical procedures used and indicate that the quasi-steadystate result should only be used for values of $|\phi|$ not exceeding 0.01. Table I also gives the actual dimensionless times for shrinkage to $R = 0.1$, and it may be seen that $k^* > 100$ is needed for the exact value of reaction rate to have only a trivial effect on rate of dissolution; the data in the table show that the transition to diffusion control is slightly dependent on the value of ϕ. To find that the range of values, within which mixed control needs to be considered, extends to at least three orders of magnitude is unexpected.

Fig. 3 shows times to double in size plotted in the same way, and again shows that $k^* < 0.01$ is needed for the role of diffusion to be neglected. Quasi-steadystate solutions are indistinguishable from finite difference predictions for $\phi = 0.001$. Table II shows that the value of k^* above which simple diffusion control can be assumed is definitely dependent on the value of ϕ; for $\phi = 0.001$ one sees that $k^* = 100$ is sufficient, but for $\phi = 0.2$ the limit lies above $k^* = 10^4$.

Fig. 4 illustrates how the actual growth of a sphere would be influenced by interface kinetics in a slightly supersaturated solution. Here the behaviour is indistinguishable from that for pure diffusion controlled growth for $k^* > 10^3$. Smaller values of k^* cause an initial delay in establishing detectable growth, although in all cases the growth eventually achieves the linear relation between size and square root of time characteristic of diffusion control [3]. The asymptotic solution for growth from zero [1] is nearly indistinguishable from the solution for $k^* = 10^3$, for sizes larger than about 10 times the initial size. The apparent induction time can be very prolonged for sufficiently small values of k^*, when reaction controlled behaviour may be assumed at short times.

TABLE I Finite difference (fd) and quasi-steady state (qss) predictions for time $z_{0.1}$ required to shrink to 10% of the initial size ($R = 0.1$), when $\varepsilon = 0$, $s = 0.1$, $q = -1$ and $-\phi = 0.001, 0.1$ and 0.5

k^*	$\lvert\phi\rvert z_{0.1}$					
	$\phi = -0.001$		$\phi = -0.1$		$\phi = -0.5$	
	Fd	Qss	Fd	Qss	Fd	Qss
10^{-3}	571.000	570.000	569.000	571.000	570.0000	571.0000
10^{-2}	57.400	57.400	57.200	57.400	57.2000	57.4000
0.1	6.010	6.060	6.020	6.050	5.9800	6.0400
1	0.912	0.922	0.848	0.903	0.7740	0.8400
10	0.395	0.408	0.292	0.367	0.1760	0.2260
10^2	0.341	0.357	0.227	0.309	0.0848	0.1268
10^3	0.336	0.352	0.220	0.303	0.0696	0.1111
10^4	0.336	0.351	0.220	0.302	0.0676	0.1091

TABLE II Finite difference predictions for time, z_2, required to double the particle size ($R = 0.1$), when $\varepsilon = 0$, $s = 0.1$, $q = 4$ and $\phi = 0.001, 0.01, 0.1$ and 0.2

k^*	ϕz_2			
	$\phi = 0.001$	$\phi = 0.01$	$\phi = 0.1$	$\phi = 0.2$
10^{-3}	2903.00	2903.00	2900.000	2912.00000
10^{-2}	294.00	294.00	292.000	291.00000
0.1	32.90	32.60	30.600	29.10000
1	6.74	6.34	4.340	2.92000
10	4.10	3.66	1.553	0.29800
10^2	3.84	3.38	1.253	0.03390
10^3	3.81	3.36	1.223	0.00707
10^4	3.81	3.35	1.220	0.00432

Fig. 5 shows another example of the effect of varying reaction rate constant, $0.01 < k^* < 1$, in two sets of conditions for both of which $s|q| = 0.1$. These computed results are plotted in the form indicated by

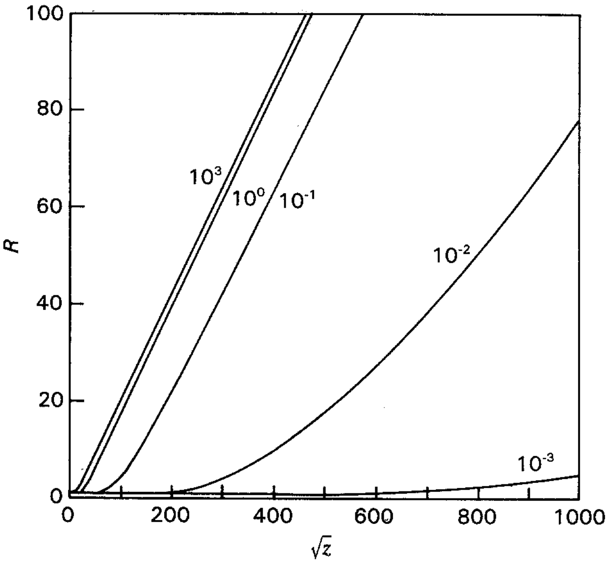

Figure 4 Mixed controlled behaviour for $\phi = 0.01$, $q = 49$, $\varepsilon = 0$, $s = 0.01$ and $k^* = 10^{-3}, 10^{-2}, 0.1, 1$ and 10^3. When $k^* = 10^3$ growth from finite initial size becomes undistinguished from the asymptotic solution describing diffusion controlled growth from zero [1].

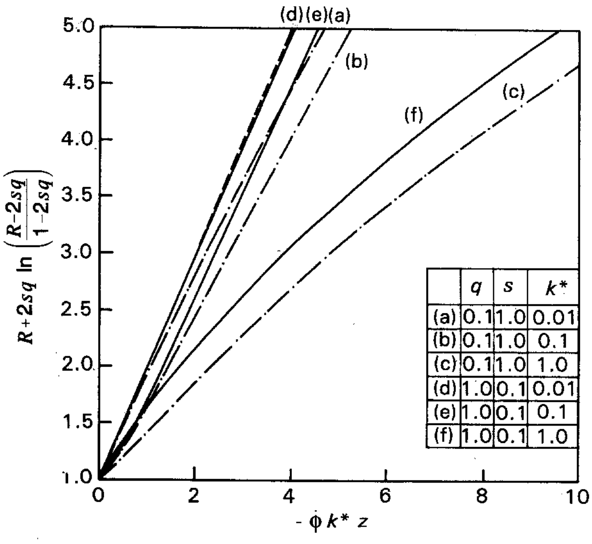

Figure 5 Departure from reaction controlled growth for $\phi = 0.2$, $q = 0.1$ and $\varepsilon = 0.5$. The values of k^* and s are shown in the figure. The dashed line represents reaction control (Equation 17).

Equation 17, which is shown dashed. Although it is a good approximation for $k^* = 0.01$ and $s = 0.1$, it is seriously in error for $s = 1$ even for the lowest value of k^*. This confirms that the condition $s/R \ll 1$ must be met for Equation 17 to be valid, and in that case the solution of the partial differential equations becomes indistinguishable from the reaction controlled behaviour.

Fig. 6 shows some predictions for dissolution plotted in the same way as in the previous figure. For $k^* \leqslant 0.1$ the solutions are almost the same as for the reaction controlled case given by Equation 17, because of the condition $s = 0.01$. However, for $s = 0.1$, see Fig. 7, deviations are significant even for very small k^*; although the curve for $k^* = 0.001$ represents the limit for reaction control. Note that decrease in size enhances s/R, and this causes failure of the condition $2s/R \ll 1$.

Fig. 8 shows the role of interface kinetics during dissolution, even for $k^* > 10$. One of the major weakness of the classic diffusion controlled formulation is that increase in concentration at the interface is unbounded, which can make the volume fraction of solute in the solution exceed unity. As this is impossible, that model must fail at some particular size. This occurs at about $R = 0.05$ in this example. Physically, interface reaction kinetics is one mechanism which could prevent this happening; alternatively, flow under stress relaxation might become the limiting process which would prevent this.

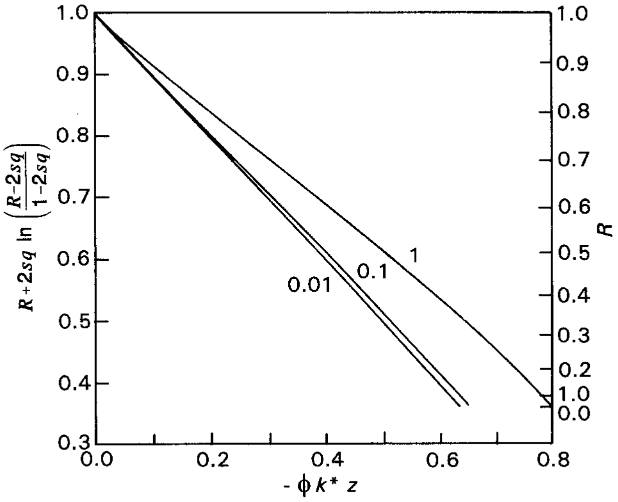

Figure 6 Departure from reaction controlled dissolution for $\phi = -0.1$, $q = -10$, $\varepsilon = 0.5$, $s = 0.01$ and $k^* = 0.01$, 0.1 and 1.

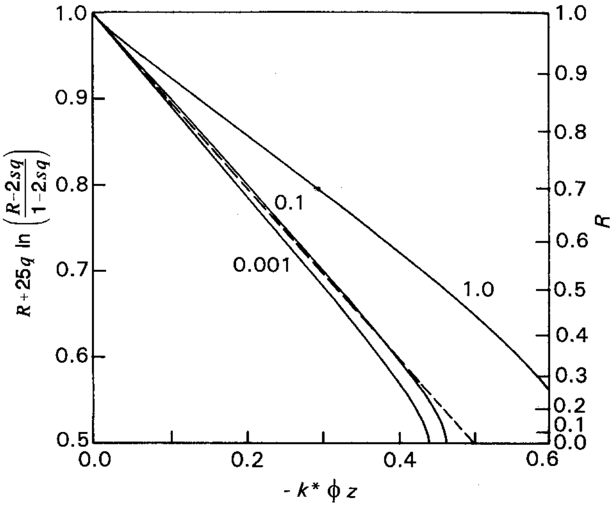

Figure 7 Departure from reaction controlled dissolution for $\phi = -0.1$, $q = -2$, $\varepsilon = 0.5$, $s = 0.1$ and $k^* = 0.001$, 0.1 and 1. The dashed line represents reaction control (Equation 17).

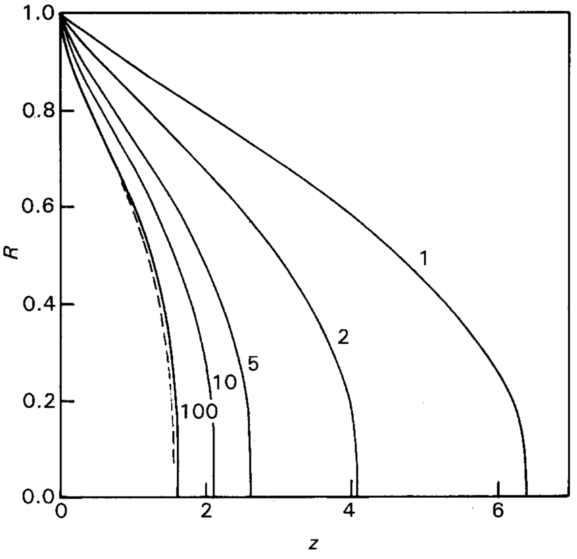

Figure 8 Departure from diffusion controlled dissolution for $\phi = -0.1$, $q = -2$, $\varepsilon = 0.5$, $s = 0.1$ and $k^* = 1$, 2, 5, 10 and 100. Diffusion controlled behaviour is shown dashed.

4. Conclusions

Quasi-steadystate models and a finite difference technique were developed for particle growth or dissolution when the behaviour is mix controlled by interface reaction and solute diffusion in the surrounding matrix.

Interface reaction cannot be ignored for a significant range of conditions when $0.01 < a_0k/D < 10$. This effect can become very important after shrinkage to very small sizes, especially if the solute volume fraction is large. On the contrary, the role of interface reaction decreases with increase in size. However, the transition from mixed control to diffusion controlled behaviour only occurs when the particle becomes much larger than the initial size.

References

1. L. E. SCRIVEN, *Chem. Eng. Sci.* **10** (1959) 1.
2. J. R. FRADE, PhD Thesis, University of Sheffield, (1983).
3. M. CABLE and J. R. FRADE, *J. Mater. Sci.* **22** (1987) 149.
4. *Idem., ibid.* **22** (1987) 919.
5. M. WEINBERG and R. S. SUBRAMANIAN, *J. Amer. Ceram. Soc.* **63** (1980) 527.
6. M. CABLE and J. R. FRADE, *Proc. Roy. Soc. Lond.* **A420** (1988) 247.
7. J. SZEKELY and S. D. FANG, *Chem. Eng. Sci.* **28** (1973) 2127.
8. J. CRANK and P. NICHOLSON, *Proc. Camb. Phil. Soc.* **43** (1947) 50.
9. C. WAGNER, *Z. Electrochem.* **65** (1961) 581.
10. I. M. LIFSHITZ and V. S. SLYOZOV, *J. Phys. Chem. Solids* **19** (1961) 35.
11. A. J. ARDELL, *Acta Metall.* **20** (1972) 61.
12. R. J. WHITE, *Mater. Sci. Eng.* **40** (1979) 15.

13. J. CRANK, "The Mathematics of Diffusion", 2nd Edn, (Clarendon Press, Oxford, 1975) p. 102.
14. P. S. EPSTEIN and M. S. PLESSET, *J. Chem. Phys.* **18** (1959) 1505.

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Appendix 1. Finite difference solutions

The basis for the finite difference solutions is a matrix of discrete values of concentrations $F_{j,k}$, corresponding to radial positions $x_1 = 1, x_2, x_3, \ldots, x_{j-1}, x_j, x_{j+1}, \ldots, x_n$ and times $t_1 = 0, t_2, t_3, \ldots, t_{k-1}, t_k, t_{k+1}, \ldots$; this reduces to an implicit scheme which assumes the form of linear equations (Equations A1, A2 and A3) in which $F_{j-1,k+1}$, $F_{j,k+1}$ and $F_{j+1,k+1}$ become the dependent variables. Details are given elsewhere (Frade [2], Cable and Frade [3]).

$$\alpha_{2,1}F_{1,k+1} + \alpha_{3,1}F_{2,k+1} = \alpha_{4,1} \tag{A1}$$

$$\alpha_{1,j-1}F_{j-1,k+1} + \alpha_{2,j-1}F_{j,k+1} + \alpha_{3,j-1}F_{j+1,k+1} = \alpha_{4,j-1}, \quad j = 2,3,\ldots,n-1 \tag{A2}$$

$$\alpha_{1,n-1}F_{n-2,k+1} + \alpha_{2,1}F_{n-1,k+1} = \alpha_{4,n-2} \tag{A3}$$

Quasi-stationary approximations are assumed to obtain the required initial conditions.

Equations A1 and A3 are easily obtained for cases when the boundary concentrations remain constant. On the contrary, special algorithms are usually needed for time dependent boundary conditions in order to avoid instabilities of the numerical method.

A1.1. Boundary conditions

On adding an additional fictive point at $x_o = 1 - \delta x$, with $\delta x = (x_2 - x_1)$ and concentration $F_{0,k+1}$, the radial derivatives become

$$(\partial F/\partial x)_{1,k+1} = (F_{2,k+1} - F_{0,k+1})/(2\delta x) \tag{A4}$$

$$(\partial^2 F/\partial x^2)_{1,k+1} = (F_{2,k+1} - 2F_{1,k+1} + F_{0,k+1})/(\delta x)^2 \tag{A5}$$

and, on assuming a linear relation between the first derivative and concentration

$$(\partial F/\partial x)_{1,k+1} = g_{k+1} + h_{k+1}F_{1,k+1} \tag{A6}$$

Equations A11 and A12 are used to compute the relevant coefficients g_{k+1} and h_{k+1}. On combining Equations A4 and A6, $F_{0,k+1}$ can be expressed as a linear function of both $F_{1,k+1}$ and $F_{2,k+1}$. A similar solution can be assumed for time step z_k, and taking the space derivative as the average for time steps z_k and z_{k+1}. Equation A1 takes the discrete form

$$\begin{aligned} &F_{2,k+1} - [1 + h_{k+1}\delta x(1 - \lambda\delta x) - \xi]F_{1,k+1} \\ &= (g_k + g_{k+1})\delta x(1 - \lambda\delta x) + (1 - \xi)F_{1,k} - F_{2,k} \end{aligned} \tag{A7}$$

where

$$\lambda = 1 + (R_{k+1} + R_k)(1 - \varepsilon)(\mathrm{d}R/\mathrm{d}z)/4 \tag{A8}$$

$$\begin{aligned} \xi = {} & (2/3)[R_k^2 + R_k R_{k+1} + (R_{k+1})^2](\delta x)^2/ \\ & \times (z_{k+1} - z_k) \end{aligned} \tag{A9}$$

On combining Equations 9 and 10 one also obtains

$$\begin{aligned} (\partial F/\delta x)_{1,k+1} = {} & k^* R_{k+1}[1 - (1 - \varepsilon)(F_{1,k+1} + \phi + \phi q)] \\ & [F_{1,k+1} + \phi + \phi q - \phi q\exp(2s/R_{k+1})] \end{aligned} \tag{A10}$$

and by controlling time increments the change in concentration can be kept small, that is $|(F_{1,k+1} - F_{1,k})/F_{1,k}| < 0.01$. Therefore, $(F_{1,k+1})^2 \approx 2F_{1,k+1}F_{1,k} - (F_{1,k})^2$, and Equation A10 can be replaced by Equation A6 where

$$\begin{aligned} g_{k+1} = {} & k^* R_{k+1}\{\phi[1 + q - q\exp(2s/R_{k+1})] \\ & \times [1 - (1 - \varepsilon)(\phi + \phi q)] + (1 - \varepsilon)(F_{1,k})^2\} \end{aligned} \tag{A11}$$

$$\begin{aligned} h_{k+1} = {} & k^* R_{k+1}[1 - 2(1 - \varepsilon)(F_{1,k} + \phi + \phi q - q) \\ & + (1 - \varepsilon)\phi q\exp(2s/R_{k+1})] \end{aligned} \tag{A12}$$

The space derivative is readily computed from a known profile at time step z_{k+1}. This may be done by Equation A10, which gives a value $(\partial F/\partial x)_A$; however the effect of interface kinetics vanishes for very large k^* and the following value may be computed for the concentration gradient

$$(\partial F/\partial x)_B \approx (F_{2,k+1} - F_{1,k+1})/(x_2 - x_1) \tag{A13}$$

For the general case a compromise is achieved by equating

$$(\partial F/\partial x)_{1,k+1} = [(\partial F/\partial x)_A + k^*(\partial F/\partial x)_B]/(k^* + 1) \tag{A14}$$

A1.2. Initial conditions

The initial concentration profile was based on the quasi-stationary approximation [13]

$$F(x, z_o) = F(1, z_o)x^{-1}\mathit{erfc}[(x - 1)/(2z_o^{1/2})] \tag{A15}$$

where z_o corresponds to very small change in radius, that is $|R - 1| < 0.005$. A quasi-stationary solution is also used for the rate of change in size, as proposed by Epstein and Plesset [14]

$$\mathrm{d}R/\mathrm{d}z = -F(1, z_o)[1/R + 1/(\pi z)^{1/2}] \tag{A16}$$

For small change in radius $|\delta R| \ll 1$, and assuming that $F(1, z)$ remains almost unchanged, Equation A16 yields

$$R_o - 1 = -2F(1, z_o)[z_o/(1 + R_o) + (z_o/\pi)^{1/2}] \tag{A17}$$

In addition, if $F(1, z) \approx F(1, z_o)$ and $R_o \approx 1$, Equation 10 gives

$$\begin{aligned} \mathrm{d}R/\mathrm{d}z & \approx (R_o - 1)/z_o \\ & \approx k^*\{F(1, z_o) + \phi + \phi q - \phi q \\ & \quad \times \exp[4s/(1 + R_o)]\} \end{aligned} \tag{A18}$$

Equations A17 and A18 were thus used to obtain the starting values of z_o and $F(1, z_o)$ for $\delta R = 0.01$.