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Diffusion in materials with variable temperature

Part II *Two- and three-dimensional problems*

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The analogy between the differential equations which describe diffusion with constant diffusivity, time-dependent diffusivity, and temperature-dependent diffusivity in non-isothermal conditions is now extended to obtain solutions for two- and three-dimensional problems. The solutions for non-isothermal conditions are derived by substitution of independent variables, and correspond to a change in scale of radial distances on varying the cooling or heating rate. The dependence of the amount transferred across the interface on the rate of change in temperature is also described, and the relative effects can be predicted by selecting suitable combinations of experimental conditions. This conclusion can be extended to diffusion-controlled growth or dissolution of particles.

1. Introduction

The method used to derive solutions for diffusion with variable temperature and temperature dependent diffusivity was outlined in Part I [1] and demonstrated for one-dimensional problems. However, solutions for that particular geometry fail to describe many problems in science and technology, such as materials processing. In fact, assuming nearly spherical or cylindrical symmetry is often closer to real conditions than assuming plane interfaces. Typical examples might be diffusion in small particles, and diffusion-controlled impurity segregation or coalescence of vacancies at grain boundaries in polycrystalline materials. Models for particle growth or dissolution [2–8], and powder reactions [9, 10] are also often based on assuming spherical or cylindrical particles. However, those models were derived for isothermal conditions with constant diffusivity, and this assumption usually fails for variable temperature.

Models for variable temperature are thus needed for interpreting many useful experiments, a typical example of this being models for non-isothermal sintering [11–13], and models for interpreting other results obtained by thermal analysis [14, 15]. This is now extended for other cases when spherical or cylindrical symmetry can be assumed. The method used to obtain solutions for variable temperature is based on transformation of independent variables yielding analogies between the differential equations which describe this case and the differential equations for isothermal processes. This method is used to obtain solutions for the amount, M, of material transferred through a stationary boundary, and to evaluate the role of the rate of change in temperature, α. In addition, the method is extended for cases when boundaries move at a rate which is controlled by diffusion, as expected for the behaviour of particles. A model for interpreting growth or dissolution of spherical particles in non-isothermal conditions confirms this conclusion [16], and the method can be extended for describing the behaviour of cylindrical particles. The kinetics of solid-state reactions in non-isothermal conditions will be addressed separately.

This work also demonstrates the possibility of predicting whether a given process is controlled by diffusion or reaction, even for cases when the exact solutions cannot be computed. This test can be applied on plotting $M\alpha^{1/2}$ (or $a\alpha^{1/2}$) versus temperature, for two or more experiments carried out at different rates of change in temperature, and checking if this yields a single dependence.

2. Two- or three-dimensional diffusion with stationary boundary

The method of finding analogies between diffusion in isothermal and non-isothermal conditions is similar to that outlined in Part I [1] for one-dimensional diffusion. The basic material balance for two- or three-dimensional diffusion with constant diffusivity reduces to [17]

$$\partial C/\partial t \;=\; D\partial^2 C/\partial r^2 + (n/r)D(\partial C/\partial r) \qquad (1)$$

where C is concentration, r is radial distance, D is diffusivity, t is time, and $n = 1$ for the two-dimensional case, or $n = 2$ for the three-dimensional case. Equation 1 can be rewritten

$$\partial C/\partial y \;=\; \partial^2 C/\partial r^2 + (n/r)(\partial C/\partial r) \qquad (2)$$

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TABLE I Solutions for concentration profiles and amount, M, transferred by diffusion internally bounded by a sphere of radius a, with uniform initial concentration C_i, constant surface concentration, C_a, and the following cases: case A, constant diffusivity, D; case B, time-dependent $D(t)$; case C, variable temperature with temperature-dependent $D(T)$

	$(C - C_i)/(C_a - C_i)$	$(\partial C/\partial r)_a$ *or* $(\partial C/\partial w)_{w_o}$	$M/(C_i - C_a)$
Case A	$(a/r)\operatorname{erfc}\{(r-a)/[2(Dt)^{1/2}]\}$	$(C_i - C_a)[a^{-1} + (\pi Dt)^{-1/2}]$	$Dt/a + 2(Dt/\pi)^{1/2}$
Case B	$(a/r)\operatorname{erfc}\{(r-a)/(2y^{1/2})\}$	$(C_i - C_a)[a^{-1} + (\pi y)^{-1/2}]$	$y/a + 2(y/\pi)^{1/2}$
Case C	$(w_o/w)\operatorname{erfc}[(w-w_o)/(2y^{*1/2})]$	$(C_i - C_a)[w^{-1} + (\pi y^*)^{-1/2}]$	$y^*/(a\alpha) + 2[y^*/(\alpha\pi)]^{1/2}$

where

$$y = \int_0^t D(t')\,\mathrm{d}t' \qquad (3)$$

This is an alternative variable for describing the dependence on time. Equations 2 and 3 also apply both to time dependent diffusivity $D(t)$, and constant diffusivity, in which case the independent variable reduces to $y = Dt$.

Different transformations are needed for non-isothermal conditions. However, when temperature T varies linearly with time one can use transformations identical to those proposed in Part I [1], which correspond to introducing

$$y^* = \left|\int_{T_i}^{T} D(T')\,\mathrm{d}T'\right| \qquad (4)$$

and

$$w = r\alpha^{1/2} \qquad (5)$$

where $\alpha = |\mathrm{d}T/\mathrm{d}t|$ is the absolute value of the rate of change in temperature. Note also that diffusivity is often strongly dependent on temperature, and on using these independent variables w and y^*, Equation 1 should be rewritten

$$\partial C/\partial y^* = \partial^2 C/\partial w^2 + (n/w)(\partial C/\partial w) \qquad (6)$$

Formulae for evaluating the values of y^* were presented in Part I, [1] for the typical case when diffusivity varies at $D(T) = D_o \exp[-E_d/(RT)]$, where E_d is the activation energy, and R is the perfect gas constant. These formulae reduce to

$$y^* = D_o(E_d/R)|I(\Theta) - I(\Theta_i)| \qquad (7)$$

where

$$\Theta = TR/E_d \qquad (8)$$

is a dimensionless temperature. An useful set of discrete pairs Θ_j; $I(\Theta_j)$ was also presented in Table I of Part I [1].

Equations 2 and 6 are identical except for the actual independent variables. Analogy thus corresponds to substitution of y or y^* for Dt, and $r\alpha^{1/2}$ for radial distance r. When the boundary is located at radius a, this must also be replaced by $a\alpha^{1/2}$, to adjust the scale for non-isothermal conditions. This is true even for cases when the process corresponds to a moving boundary, as found for diffusion-controlled growth of particles [16].

2.1. Diffusion in a medium internally bounded by a sphere

The solutions for plane interfaces can also be used for curved surfaces when the radius of curvature is much larger than the boundary-layer thickness. For a nearly flat surface, and in isothermal conditions, with nearly constant diffusivity, the boundary-layer thickness is $\delta = (\pi Dt)^{1/2}$, (see Part I [1]), and models for plane surfaces can be used for radius of curvature obeying the condition $a \gg (\pi Dt)^{1/2}$, or $Dt \ll a^2/\pi$. Similar criteria are readily obtained for other cases, by replacing the independent variables. For time-dependent $D(t)$, the required condition is thus $y(t) \ll a^2/\pi$, and for variable temperature

$$y^*(T) \ll a^2\alpha/\pi \qquad (9)$$

The calculations of y^* are still computed as described by Equation 4, or Equation 7 for the usual dependence $D = D_o \exp[-E_d/(RT)]$.

Equations 1 or 2 and 6 are identical, except for the meaning of the independent variables. One can thus take advantage of solutions originally derived for constant diffusivity [17], by substitution of independent variables. For example, concentration profiles are presented in Table I for the following cases: case A – constant diffusivity; case B – time-dependent diffusivity; case C – variable temperature with temperature-dependent diffusivity. The solution for non-isothermal conditions thus reduces to

$$(C - C_i)/(C_a - C_i) = (w_o/w)\operatorname{erfc}[(w - w_o)/(2y^{*1/2})] \qquad (10)$$

where $w = r\alpha^{1/2}$, $w_o = a\alpha^{1/2}$,C_i is the initial spatially uniform concentration, and $C(a,t) = C_a$ is a constant interfacial concentration. The concentration gradient for every case is easily obtained by differentiating $C(r,t), C(r,y)$ or $C(w,y^*)$ with respect to distance r or w (see Table I), and these solutions can be used to derive solutions for the amount transferred across the surface, using the method outlined in Appendix A. For non-isothermal conditions this yields

$$M = (C_i - C_a)\{y^*/(a\alpha) + 2[y^{*1/2}/(\alpha\pi)]^{1/2}\} \qquad (11)$$

Equation 11 still retains the effect of actual size. However, the effects of varying simultaneously the rate of change in temperature, α, and radius, a, cancel by maintaining $a\alpha^{1/2}$ constant, and for identical initial and final temperatures. One can thus assess whether processes are diffusion-controlled or reaction-controlled by plotting $M\alpha^{1/2}$ versus temperature for different rates of change in temperature, with identical initial

TABLE II Solutions for concentration profiles and amount, M, transferred by diffusion in a sphere, with uniform initial concentration, C_i, constant surface concentration, C_a, and the following: case A, constant diffusivity, D; case B, time-dependent $D(t)$; case C, variable temperature with temperature-dependent $D(T)$

$(C - C_i)/(C_a - C_i)$	Case A	$1 + 2a/r \sum_1^\infty (-1)^n (\pi n)^{-1} \sin(n\pi r/a) \exp[-Dt(\pi n/a)^2]$
	Case B	$1 + 2a/r \sum_1^\infty (-1)^n (\pi n)^{-1} \sin(n\pi r/a) \exp[-y(\pi n/a)^2]$
	Case C	$1 + 2a/r \sum_1^\infty (-1)^n (\pi n)^{-1} \sin(n\pi r/a) \exp[-y^*(T)(\pi n)^2/(a^2\alpha)]$
M/M_∞	Case A	$1 - 6 \sum_1^\infty (\pi n)^{-2} \exp[-(\pi n/a)^2 Dt]$
	Case B	$1 - 6 \sum_1^\infty (\pi n)^{-2} \exp[-(\pi n/a)^2 y]$
	Case C	$1 - 6 \sum_1^\infty (\pi n)^{-2} \exp[-y^*[(\pi n)^2/(a^2\alpha)]\}$

temperature and identical values of $a\alpha^{1/2}$. Several experiments should thus give a single dependence. This test can be used also for a temperature-dependent interfacial concentration, $C_a(T)$, and for cases when obtaining the solutions for concentration gradients is cumbersome, or not feasible due to unknown temperature dependence of the relevant parameters such as $D(T)$ or $C_a(T)$. Note that maintaining a constant value of $a\alpha^{1/2}$, and identical initial temperature for every experiment, are essential for this test.

2.2. Diffusion in a sphere

Useful solutions for diffusion in a sphere with constant diffusivity can be found in textbooks [17], and the analogy between Equations 1, 2 and 6 can again be taken advantage of to obtain solutions for time-dependent diffusivity, and also for variable temperature with $D(T)$, as shown in Table II. For uniform initial concentration, constant surface concentration, temperature-dependent diffusivity, and temperature varying with time at a rate α, the relevant solutions become

$$\frac{(C - C_i)}{(C_a - C_i)} = 1 + (2a/r) \sum_1^\infty (-1)^n (\pi n)^{-1} \sin(n\pi r/a) \times \exp[-y^*(T)(\pi n)^2/(a^2\alpha)] \qquad (12)$$

$$M/M_\infty = 1 - (6/\pi^2) \sum_1^\infty n^{-2} \times \exp[-y^*(T)(\pi n)^2/(a^2\alpha)] \qquad (13)$$

where M_∞ is the maximum amount of material for $y^* = \infty$. These solutions also demonstrate that the role of curvature can be accounted for by $a\alpha^{1/2}$ when temperature varies linearly with time. Note that the rate of mass transfer drops rapidly for $y^*(T) > 1$.

Truncation can be used to obtain simpler solutions for relatively long times. For example, changes in concentration at the centre of the sphere reduce to

$$(C - C_a)/(C_i - C_a) \approx (2/\pi)(a/r)\sin(\pi r/a) \times \exp[-\alpha^{-1}(\pi/a)^2 y^*(T)] \qquad (14)$$

A simple solution can also be used for describing the material gained by the sphere for long times, as found for the case when diffusivity is constant [17]. The equivalent solution for non-isothermal conditions with temperature-dependent $D(T)$ becomes

$$M/M_\infty \approx 1 - (6/\pi^2)\exp[-(\pi/a)^2\alpha^{-1}y^*(T)] \qquad (15)$$

Equations 14 and 15 are nearly true for $y^*/(\alpha a^2) > 0.5$, in non-isothermal conditions, or the original condition $Dt/a^2 > 0.5$, for isothermal conditions and constant D.

The solution for a time-dependent interfacial concentration and constant diffusivity is also available in the literature [17], for the case when the initial concentration is zero. That solution can be extended for non-zero C_i by making $C - C_i$ the dependent variable and introducing $C_a(t) - C_i$, rather than $C_a(t)$. Changing the independent variables (y^* for Dt, $w = r\alpha^{1/2}$ for r, and $w_o = a\alpha^{1/2}$ for a), was then the basis for obtaining the corresponding solution for non-isothermal conditions, when both diffusivity and interfacial concentration are likely to change

$$C - C_i = -2(\alpha a r)^{-1} \sum_1^\infty (-1)^n \pi n \sin(n\pi r/a) \times \int_0^{y^*} \exp[(\pi n)^2(y^{*\prime} - y^*)/(a^2\alpha)] \times ([C_a(y^{*\prime}) - C_i)]\, dy^{*\prime} \qquad (16)$$

Equation 16 is a confirmation that the role of curvature can be accounted for by $w_o = a\alpha^{1/2}$, (and $r\alpha^{1/2}$), as found for constant boundary conditions, and the other relevant variable is y^*, or temperature. Note that $y^*(T)$ is a function of temperature only, and the temperature dependent interfacial concentration is accounted for by $C_a[y^*(T)]$.

Equation 16 was solved numerically, using a method outlined in Appendix B, and some predictions are shown in Fig. 1, for the case when surface concentration is initially C_i and then drops with decreasing temperature as $C_a(T) = C_i \exp[(E_c/R)(T_i^{-1} - T^{-1})]$. Note that the trends for diffusion in a sphere are similar to those for a plane sheet (see

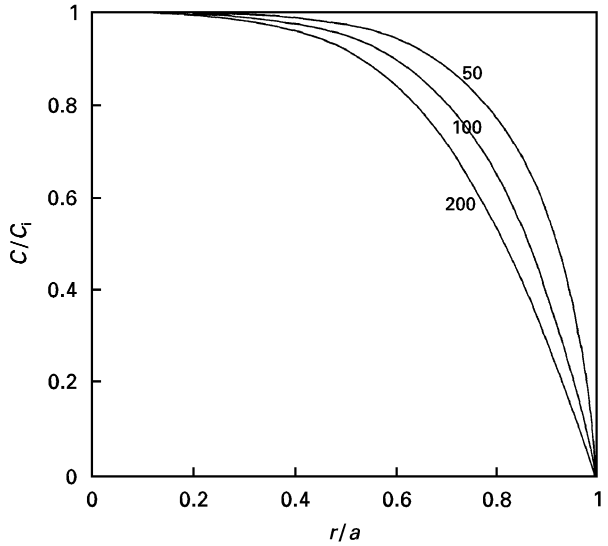

Figure 1 Concentration profiles developed on cooling from initial temperature $T_i = 1273$ K to room temperature (298 K), in a sphere with uniform initial concentration, C_i, and temperature-dependent surface concentration $C_a = C_i \exp[(E_c/R)(T_i^{-1} - T^{-1})]$, with $E_c = 50, 100, 200\ \mathrm{kJ\,mol^{-1}}$ (shown in the figure). Diffusivity varies as $D(T) = D_o \exp[-E_d/(RT)]$, with $E_d = 100\ \mathrm{kJ\,mol^{-1}}$. The remaining parameters obey the condition $D_i T_i (a^2 \alpha) = 2$, with $D_i = D(T_i)$.

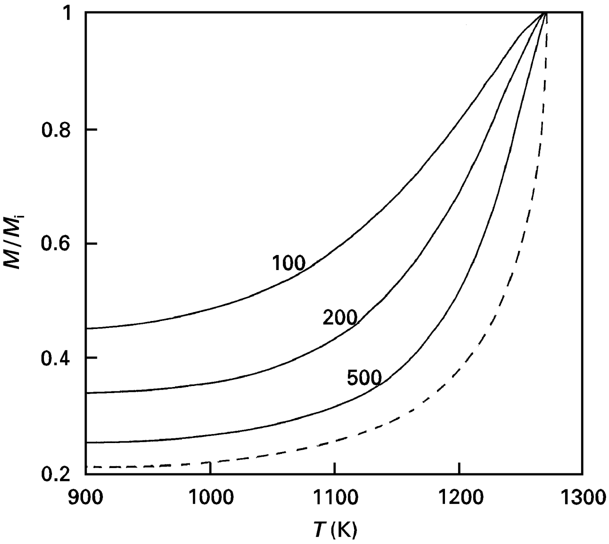

Figure 2 Changes of solute content in a sphere on cooling from initial temperature $T_i = 1273$ K, with uniform initial concentration, C_i, temperature-dependent surface concentration, $C_a = C_i \exp[(E_c/R)(T_i^{-1} - T^{-1})]$, with $E_c = 100, 200, 500\ \mathrm{kJ\,mol^{-1}}$ (shown in the figure), and diffusivity $D(T) = D_o \exp[-E_d/(RT)]$, with $E_d = 100\ \mathrm{kJ\,mol^{-1}}$. The remaining parameters obey the condition $D_i T_i/(a^2 \alpha) = 5$, with $D_i = D(T_i)$.

Part I [1]). Other examples were used to compute changes in total solute content in the sphere (Fig. 2).

2.3. Diffusion in a cylinder

The main conclusions drawn for the role of curvature and rate of change in temperature on diffusion in a sphere also apply to diffusion in a cylinder. For example, the solutions for spatially uniform initial concentration, C_i, and constant surface concentration, C_a, were obtained by analogy with solutions reported for isothermal conditions with constant diffusivity [17], on changing the dependence $C(r, t)$ to $C(w, y^*)$. Solutions for concentration profiles and amount of material gained by the cylinder are presented in Table III, including the following solutions for variable temperature

$$(C - C_i)/(C_a - C_i) = 1 - 2 \sum_1^{\infty} \exp[-b_n^2 y^*(T)] \\ J_o(b_n r \alpha^{1/2})[b_n a \alpha^{1/2} J_1(b_n a \alpha^{1/2})]^{-1} \quad (17)$$

$$M/M_\infty = 1 - 4 \sum_1^{\infty} (b_n a \alpha^{1/2})^{-2} \exp[-(b_n^2) y^*(T)] \quad (18)$$

where $J_o(x)$ is the Bessel function of order zero, $J_1(x)$ is the Bessel function of first order, and the value b_n is obtained on solving $J_o(b_n a \alpha^{1/2}) = 0$.

The parameters b_n have dimensions identical to $(a\alpha^{1/2})^{-1}$, and one can thus rewrite Equations 17 and 18 in terms of the alternative roots $c_n = b_n a \alpha^{1/2}$ of the Bessel function of zero order ($c_1 = 2.40$, $c_2 = 5.52$, $c_3 = 8.65, \ldots$). Therefore, a truncated first-order approximation for the amount of material transferred at relatively long times reduces to

$$M/M_\infty = 1 - 0.692 \exp[-5.78 y^*(T)/(a^2 \alpha)] \quad (19)$$

This should hold for $Dt/a^2 > 0.5$, or $y^*/(a\alpha^{1/2}) > 0.5$, as previously found for diffusion in a plane sheet or in spheres.

3. Solutions for diffusion-controlled growth or dissolution of particles

Analogy also applies to the basic differential equations which describe diffusion-controlled behaviour of particles for constant diffusivity, time-dependent $D(t)$, or temperature-dependent $D(T)$ with variable temperature. The basic equations for isothermal conditions can be written

$$\frac{\partial C}{\partial y} = \frac{\partial^2 C}{\partial r^2} + [(n/r) - \varepsilon (a/r)^n (\mathrm{d}a/\mathrm{d}t)] \frac{\partial C}{\partial r} \quad (20)$$

where ε is a measure of the relative change in volume. Equation 20 describes the cases when diffusivity is nearly constant [2, 8], by making $y = Dt$, or time-dependent $D(t)$, in which case y is described by Equation 3. In addition, the rate of change in particle size can be described by

$$\mathrm{d}a/\mathrm{d}y = -[C_s(1 - v_A C_a)]^{-1} (\partial C/\partial r)_a \quad (21)$$

where $v_A C_a$ is the solute volume fraction at the interface. The corresponding differential equations for variable temperature have also been reported for spherical particles [16], by suitable changes of the independent variables. Extending this method for cylindrical

$$\frac{\partial C}{\partial y^*} = \frac{\partial^2 C}{\partial w^2} + [(n/w) - \varepsilon (w_o/w)^n (\mathrm{d}w_o/\mathrm{d}y^*)] \frac{\partial C}{\partial w} \quad (22)$$

$$\mathrm{d}w_o/\mathrm{d}y^* = -[C_s(1 - v_A C_a)]^{-1} (\partial C/\partial w)_{w_o} \quad (23)$$

TABLE III Solutions for concentration profiles and amount of material gained by a cylinder with uniform initial concentration, C_i, constant surface concentration, C_a, and: case A, isothermal conditions with constant D; case B, isothermal conditions and time-dependent $D(t)$; case C, variable temperature with $D(T)$. The values of b_n correspond to solutions of $J_o(b_n a) = 0$ for isothermal conditions, or $J_o(b_n a\alpha^{1/2}) = 0$ for non-isothermal conditions

$(C - C_i)/(C_a - C_i)$	Case A	$1 - 2\sum_1^{\infty} \exp[-b_n^2 Dt] J_o(b_n r)/[b_n a J_1(b_n a)]$
	Case B	$1 - 2\sum_1^{\infty} \exp[-b_n^2 y] J_o(b_n r)/[b_n a J_1(b_n a)]$
	Case C	$1 - 2\sum_1^{\infty} \exp[-b_n^2 y^*(T)] J_o(b_n r\alpha^{1/2})/[b_n a\alpha^{1/2} J_1(b_n a\alpha^{1/2})]$
M/M_∞	Case A	$1 - 4\sum_1^{\infty} (b_n a)^{-2} \exp[-(b_n^2)Dt]$
	Case B	$1 - 4\sum_1^{\infty} (b_n a)^{-2} \exp[-(b_n^2)y]$
	Case C	$1 - 4\sum_1^{\infty} (b_n a\alpha^{1/2})^{-2} \exp[-(b_n^2)y^*(T)]$

TABLE IV Solutions for diffusion-controlled growth or dissolution of spheres, for the following cases: case A, diffusivity is constant; case B, diffusivity is time-dependent; case C, diffusivity is temperature-dependent and T varies at a rate $|dT/dt| = \alpha$

	Case A/References	Case B	Case C
Growth of sphere or cylinder from zero	$a = 2\beta(Dt)^{1/2}$ [2, 6]	$a = 2\beta y^{1/2}$	$a\alpha^{1/2} = 2\beta y^{*1/2}$
Growth of sphere or cylinder from finite size	$a^2 \approx a_o^2 + 4\beta^2(Dt)$ [6, 8]	$a^2 \approx a_o^2 + 4\beta^2 y$	$a^2\alpha \approx a_o^2\alpha + 4\beta^2 y^*$
Quasi steady-state behaviour of a sphere	$a^2 = a_o^2 + 2\phi Dt$ [18]	$a^2 = a_o^2 + 2\phi y$	$a^2\alpha = a_o^2\alpha + 2\phi y^*$
Quasi stationary behaviour of a sphere	$da/dt = \phi D[a^{-1} + (\pi Dt)^{-1/2}]$ [19]	$da/dy = \phi[a^{-1} + (\pi y)^{-1/2}]$	$d(a\alpha^{1/2})/dy^* = \phi(a\alpha^{1/2})^{-1} + (\pi y^*)^{-1/2}]$
Generic behaviour of a sphere or a cylinder	a/a_o versus Dt/a_o^2 [6, 7]	a/a_o versus y/a_o^2	a/a_o versus $y^*/(a_o^2\alpha)$

The analogy between Equations 20 and 22, and Equations 21 and 23 shows that solutions reported for isothermal conditions can still be useful to obtain the corresponding solutions for variable temperature, by suitable substitutions of independent variables ($w = r\alpha^{1/2}$ for r, $w_o = a\alpha^{1/2}$ for a, and y^* for Dt). The values of y^* are readily computed for the usual exponential law $D = D_o \exp[-E_d/(RT)]$ by using Equation 7 and data shown in Table I of Part I [1].

Several solutions for diffusion-controlled growth or dissolution of spherical or cylindrical particles are shown in Table IV, including the original solutions for constant diffusivity. For example, the solution for growth from zero in isothermal conditions, with constant diffusivity and constant interfacial concentration reduces to $a = 2\beta(Dt)^{1/2}$ [2]. Formulae required for computing the growth constant β, and solutions for wide ranges of conditions have been reported elsewhere, both for spheres [2, 6] and cylinders [8]. Substitution of $a\alpha^{1/2}$ for radius a, and y^* for Dt yields the solution for growth from zero, with variable temperature.

$$a\alpha^{1/2} = 2\beta y^{*1/2} \quad (24)$$

Note also that Frade and Cable [16] have shown that the growth constant, β, is the same as for isothermal processes, as expected, and an identical conclusion holds for cylinders.

Growth from finite size or dissolution require solutions for transient regimes, which have been computed for isothermal conditions with constant diffusivity [3–8]. The corresponding solutions for variable temperature are then easily obtained by replacing a *by* $a\alpha^{1/2}$, and Dt by y^*. For example, $a^2 - a_o^2 = 4\beta^2 Dt$ nearly describes growth of spheres [6] or cylinders [8] from finite size when diffusivity is constant, and substitution of y^* for Dt and $a\alpha^{1/2}$ for size a yields the corresponding solution for variable temperature

$$a^2\alpha - a_o^2\alpha = 4\beta^2 y^* \quad (25)$$

Other solutions usually correspond to discrete data, or graphs of a/a_o versus Dt/a_o^2, and analogy shows that these data can also be read as $[a\alpha^{1/2}/(a_o\alpha^{1/2})] = (a/a_o)$ versus $y^*/(a_o^2\alpha)$ for the case when temperature is variable.

Some approximate solutions also apply to growth or dissolution of spheres when the driving force is relatively low. For example, quasi steady-state solutions [18] reduce to $a^2 - a_o^2 = 2\phi Dt$, for constant diffusivity, ϕ being the driving force, and the following solution is easily obtained for variable temperature on replacing a^2 by $a^2\alpha$, a_o^2 by $a_o^2\alpha$, and Dt

by $y^*(T)$

$$a^2\alpha - a_o^2\alpha \;=\; 2\phi y^* \qquad (26)$$

A quasi stationary model has also been proposed, and reduces to $\mathrm{d}a/\mathrm{d}t = D\phi[a^{-1} + (\pi Dt)^{-1/2}]$, for constant diffusivity [19]. However, this equation does not represent a significant improvement relative to quasi steady-state solutions. In fact, the quasi stationary model still requires numerical integration, and it also fails for moderate or large ϕ.

The method of replacing $a\alpha^{1/2}$ for radius a, and $y^*(T)$ for Dt might be useful also to have some insight about the effect of the rate of change in temperature, when the interfacial concentration varies with temperature, $C_a(T)$. For example, the quasi steady-state solutions derived by Frade and Cable [16] reduce to

$$\alpha(a^2 - a_o^2) \;=\; \int_{T_i}^{T} D(T)(C_\infty - C_a(T)) \times [C_s - (1-\varepsilon)C_a(T)]^{-1}\,\mathrm{d}T \qquad (27)$$

where C_∞ is the initial bulk concentration, C_s is the concentration in the sphere, and ε measures the relative volume change. Note that the right-hand side of Equation 27 still depends on temperature only.

4. Conclusion

Suitable transformation of variables can be used to demonstrate the analogy between the differential equations which describe diffusion-controlled processes in isothermal conditions and for variable temperature. This has been extended for conditions nearly described by spherical or cylindrical symmetry.

Diffusion in spheres or cylinders is dependent on their size, which effects both the concentration profiles and amount M gained or lost. However, the effect of changing the radius a can be compensated by adjusting the rate of change in temperature, α, and maintaining a constant value of $a\alpha^{1/2}$. For example, the dependence of $M\alpha^{1/2}$ should be unique for experiments carried out by cooling from a given initial temperature to room temperature at different rates, if the radius is also adjusted to fulfil the conditions $a\alpha^{1/2} = \text{constant}$. Identical conclusions can be drawn for diffusion in a very large medium internally bounded by a sphere.

The initial size, a_o, also affects the diffusion-controlled behaviour of particles, and is accounted for by $a_o\alpha^{1/2}$, for the case of solutions for non-isothermal conditions.

Appendix A. Solutions for the amount transferred in non-isothermal conditions

The basis for obtaining these solutions is similar to the method outlined for one-dimensional diffusion (see Appendix A, Part I [1]). Therefore, the rate of transfer $\mathrm{d}M/\mathrm{d}t = D(\partial C/\partial r)_a$ is rearranged as a function of temperature ($\mathrm{d}t = \mathrm{d}T/\alpha$)

$$\mathrm{d}M \;=\; \alpha^{-1/2}(\partial C/\partial w)_{w_o} D(T)\,\mathrm{d}T \qquad (\text{A1})$$

where $(\partial C/\partial w)_{w_o}$ varies with $y^*(T)$ and also $w_o = a\alpha^{1/2}$, which corresponds to the effect of curvature. Integration of Equation A1 thus yields

$$M \;=\; \alpha^{-1/2} M^*[T, (a\alpha^{1/2})] \qquad (\text{A2})$$

where

$$M^*[T, (a\alpha^{1/2})] \;=\; \int_{T_i}^{T} (\partial C/\partial w)_{w_o} D(T')\,\mathrm{d}T' \qquad (\text{A3})$$

varies with temperature and $w_o = a\alpha^{1/2}$. For example, the solution for constant surface concentration is easily obtained by taking into account the concentration gradient shown in Table I, and reduces to

$$M \;=\; (C_i - C_o)\{y^*/(a\alpha) + 2[y^*/(\alpha\pi)]^{1/2}\} \qquad (\text{A4})$$

Appendix B

A large number of terms is also needed to solve Equation 16 because these terms decay slowly with increasing n; this might be responsible for excessive computing time and also significant rounding-off errors, as pointed out for plane sheet (see Part I). A transformation of Equation 16 must thus be performed to avoid these limitations, which yields

$$C - C_i \;=\; 2\sum_{1}^{\infty}(-1)^n[a/(r\pi n)]\sin(n\pi r/a) \times [F(\infty,\xi) - F(n,\xi)] - F(\infty,\xi)S_2(\infty) \qquad (\text{A5})$$

where

$$\xi \;=\; y^*\pi^2/(a^2\alpha) \qquad (\text{A6})$$

and

$$F(n,\xi) \;=\; \int_{0}^{n^2\xi} \exp(\xi' - n^2\xi)[C_o(\xi') - C_i]\,\mathrm{d}\xi' \qquad (\text{A7})$$

$$S_2(N) \;=\; 2\sum_{1}^{N}\{(-1)^n[a/(\pi n r)]^{-1}\sin(n\pi r/a) \qquad (\text{A8})$$

This transformation yields terms $F(n,\xi)$ which converge rapidly to $F(\infty,\xi)$, and the differences $F(n,\xi) - F(\infty,\xi)$ thus vanish rapidly, avoiding the complications related to computing a very large number of terms. In addition $S_2(\infty) = 1$.

Additional details concerning the calculations of $T_j; y_j^*$ pairs, and other features of the numerical method, are identical to those reported for plane sheet (Part I [1]).

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