Diffusion in materials with variable temperature

Part I *One-dimensional problems*

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Solutions for diffusion in non-isothermal conditions are derived by analogy with diffusion in isothermal conditions when diffusivity is constant or time dependent. The effects of heating or cooling rates on the concentration profiles, boundary-layer thickness, and amount of material transferred, are described and can be assessed even when the temperature dependence of diffusivity and/or interfacial concentration is unknown. The effects of the rate of change in temperature on the amount of material transferred can be used also to assess whether this is controlled by diffusion or reaction.

1. Introduction

High-temperature processing of materials often involves non-isothermal conditions. The rate of change in temperature is then controlled to achieve the required heat treatment. For example, the glass-ceramic method usually requires heating at a controlled rate from the nucleation stage to an upper temperature for obtaining the required crystallization without deformation of the glass ceramic products. Similarly, non-isothermal heat treatments might be used to optimize phase transformations in metallic or ceramic systems.

Significant diffusion-controlled effects might also occur when materials are spontaneously cooled after processing or heat treated at high temperatures. In fact, quenching is often an efficient method for preventing further changes, except for cases when materials cannot stand thermal shock. Typical diffusion-controlled changes during cooling are probably impurity segregation in many metallic or ceramic systems, and change in concentration of point defects in materials. For example, the concentration of vacancies is likely to drop with decreasing temperature, and this usually requires transport to grain boundaries or other interfaces.

Another method which requires understanding of the expected trends is thermal analysis used for studying powder reactions. Interpretation of this type of result requires solutions for several different mechanisms [1, 2]. In addition, non-isothermal schedules are also often used for improving the sintering of powder compacts [3–6]. Johnson [3] proposed solutions for mechanisms controlled by viscous-flow, lattice diffusion, or grain-boundary diffusion.

If a generic physicochemical process is diffusion controlled, it is often found that diffusivity varies by several orders of magnitude with changes in temperature. The time scale thus decreases on heating and increases on cooling. In addition, the time dependence is also affected, and typical parabolic laws fail. The kinetics of diffusion-controlled processes in non-iso-thermal conditions also changes when a boundary condition such as surface concentration $C(0, t) = C_o(T)$ varies with temperature; this corresponds to changes in driving-force with temperature, and can be transformed to time dependence when temperature varies with time in known ways. Solutions for both time-dependent, diffusivity $D(t)$ and surface concentration $C_o(t)$ can be found in textbooks [7], and have been used by some authors [8] for interpreting properties of materials which might be dependent on diffusion-controlled segregation. The present work is based on expressing the material balances in terms of temperature rather than time, to emphasize the role of the rate of change in temperature, as reported previously for the diffusion-controlled behaviour of particles [9].

Diffusivity is usually extracted by maintaining the surface in contact with a source or sink of solute, for different times, and measuring the concentration profiles attained in this way. Typical experiments are performed in isothermal conditions, and tracer atoms are often used. Alternative methods are feasible only within the detection limits of experimental equipment available for chemical analysis (microprobe, etc.). In addition, experimental techniques can be used only for cases when the spatial resolution of the apparatus is much smaller than the size scale of concentration profiles. Otherwise, diffusivity and interfacial concentrations, and their temperature dependence cannot be evaluated, and assessing whether the behaviour is controlled by diffusion or other mechanism must rely on the time dependence of the amount of material transferred, or related properties.

This paper shows that mathematical modelling can be used to describe the role of cooling or heating rates, as previously reported for diffusion-controlled behaviour of particles [9]. Note that the time dependence cannot be predicted when diffusivity and interfacial concentration vary with temperature in unknown ways. It will be demonstrated that it can still be assessed whether diffusion is the controlling

mechanism by measuring the dependence of the amount transferred (or related properties) on the rate of change in temperature.

Complex analytical solutions or solutions which require time-consuming numerical calculations, are usually avoided by experimentalists. On the contrary, the simplest solutions are most suitable for achieving a comprehensive insight into the mechanisms and meaning of fitting parameters. This is the reason for emphasizing selected theoretical solutions, which are most likely to be useful for interpreting experimental results. However, a poor understanding of the conditions required for deriving simplified mathematical solutions might lead to misinterpretation of results. This risk can be minimized on finding suitable criteria for checking the applicability of the models. Application of these criteria should not require special mathematical skills.

Geometry also matters if attempts are made to establish the kinetics of the process. Standard solutions widely used by experimentalists are often obtained on assuming that the sample can be considered semi-infinite, which is simpler than solutions for finite size. However, finite-layer models are required when one or more of the following conditions are observed: (i) small (or thin) samples, (ii) relatively high diffusivity, (iii) long times. Simple criteria will thus be presented for checking the applicability of semi-infinite models. Solutions for alternative geometries, and also for moving boundaries tend to be more complex than for planar interfaces, and will be dealt with in Part II [10].

Increasing complexity is also found when surface concentration is variable with time or temperature. In this case, one should expect poorer insight into the mechanisms and fitting parameters, and also higher risks of misinterpretation of experimental results. Nevertheless, one might still predict the role of the rate of change in temperature for selected cases.

2. Analogy between solutions for isothermal conditions and for variable temperature

The simplest solutions for diffusion-controlled behaviour usually correspond to assuming a semi-infinite medium with a motionless flat interface, initial uniform concentration, without reactions, and transport controlled by diffusion. For constant diffusivity, the material balance reduces to Fick's second law [7]

$$\partial C/\partial t = D\partial^2 C/\partial x^2 \qquad (1)$$

where x is distance. This can be rearranged to include the case when diffusivity is time dependent

$$\partial C/\partial y = \partial^2 C/\partial x^2 \qquad (2)$$

where time dependence has been transformed by introducing a new independent variable, y, obeying the condition $dy = D(t)\,dt$, or

$$y = \int_0^t D(t')\,dt' \qquad (3)$$

Note that Equation 3 is also valid for constant diffusivity, in which case $y = Dt$.

This method can also be used for variable temperature, when temperature varies with time in known ways. However, the following alternative variables are most suitable for providing some insight concerning the role of the rate of change in temperature

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

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

where, T_i is the initial temperature, and $\alpha = |dT/dt|$ is the absolute value of the rate of change in temperature. The value of y^* is also an absolute value to avoid negative values for cooling. On rearranging Equation 1, one thus obtains

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

Equations 1, 2 and 6 are identical except for the physical meaning (and values) of the independent variables. One can thus use well-known solutions originally derived for isothermal conditions and constant diffusivity to predict the corresponding solutions for temperature-dependent diffusivity. This method is based on the analogy between the differential equations describing those cases, and is readily applied by substitution of y for Dt if diffusivity is time dependent, or y^* for Dt, and $w = x\alpha^{1/2}$ for x in non-isothermal conditions. When the boundaries are located at finite distances (for example $x = L$ for finite samples), boundaries must also be replaced by $L\alpha^{1/2}$, etc., 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 [9]. This method can also be used for cases when a boundary condition is time dependent (such as time dependent, $C(a, t) = C_o(t)$, or temperature dependent, $C_o(T)$).

Obtaining the values of y^* as a function of temperature (or time) usually requires numerical calculations. However, a typical temperature dependence is $D(T) = D_o \exp[-E_d/(RT)]$, where E_d is the activation energy, and R is the perfect gas constant and some solutions were thus obtained by inserting this expression in Equation 4 and using numerical integration. The dimensionless temperature, Θ, is suitable for this purpose

$$\Theta = TR/E_d \qquad (7)$$

and Equation 4 thus becomes

$$y^* = D_o(E_d/R)|I(\Theta) - I(\Theta_i)| \qquad (8)$$

where $\Theta_i = T_i R/E_d$, and $I(\Theta)$ is a function of the dimensionless temperature, Θ

$$I(\Theta) = \int_0^{\Theta} \exp(-1/\Theta')\,d\Theta' \qquad (9)$$

The values of $I(\Theta)$ are shown in Table I, and can be used to calculate the values of y^*, both for heating or cooling, with known values of pre-exponential factor, D_o, activation energy, E_d, and initial and final temperatures.

TABLE I Computed values of $I(\Theta)$ (Equation 9), required to obtain solutions for diffusion-controlled processes with variable temperature

Θ	$I(\Theta)$	Θ	$I(\Theta)$	Θ	$I(\Theta)$
0.01	3.64×10^{-48}	0.042	7.454×10^{-14}	0.4	7.92×10^{-3}
0.011	3.91×10^{-44}	0.045	4.163×10^{-13}	0.45	0.01268
0.012	9.05×10^{-41}	0.05	4.652×10^{-12}	0.5	0.01877
0.013	6.46×10^{-38}	0.055	3.476×10^{-11}	0.55	0.02621
0.014	1.817×10^{-35}	0.06	1.857×10^{-10}	0.6	0.03499
0.015	2.435×10^{-33}	0.065	7.833×10^{-10}	0.65	0.04509
0.016	1.784×10^{-31}	0.07	2.704×10^{-9}	0.7	0.05645
0.017	7.941×10^{-30}	0.08	2.074×10^{-8}	0.8	0.08279
0.018	2.333×10^{-28}	0.09	1.056×10^{-7}	0.9	0.1136
0.019	4.831×10^{-27}	0.1	3.830×10^{-7}	1.0	0.1485
0.02	7.42×10^{-26}	0.11	1.133×10^{-6}	1.2	0.2290
0.021	8.834×10^{-25}	0.12	2.837×10^{-6}	1.4	0.3216
0.022	8.43×10^{-24}	0.13	6.24×10^{-6}	1.6	0.4242
0.023	6.637×10^{-23}	0.14	1.236×10^{-5}	1.8	0.5352
0.024	4.41×10^{-22}	0.15	2.254×10^{-5}	2.0	0.6533
0.025	2.532×10^{-21}	0.16	3.840×10^{-5}	2.2	0.7775
0.026	1.273×10^{-20}	0.17	6.18×10^{-5}	2.4	0.9069
0.027	5.695×10^{-20}	0.18	9.49×10^{-5}	2.6	1.041
0.028	2.295×10^{-19}	0.19	1.399×10^{-4}	2.8	1.179
0.029	8.419×10^{-19}	0.20	1.993×10^{-4}	3	1.321
0.03	2.839×10^{-18}	0.22	3.711×10^{-4}	3.5	1.688
0.032	2.585×10^{-17}	0.24	6.07×10^{-4}	4	2.071
0.034	1.828×10^{-16}	0.26	9.98×10^{-4}	5	2.871
0.036	1.046×10^{-15}	0.28	1.491×10^{-3}	6	3.704
0.038	5.012×10^{-15}	0.3	2.128×10^{-3}	8	5.437
0.04	2.063×10^{-14}	0.35	4.440×10^{-3}	10	7.225

TABLE II Solutions for concentration profiles, concentration gradients, boundary-layer thickness $\delta = (C_i - C_o)/(\partial C/\partial x)_0$, and amount, M, transferred by diffusion (per unit area) in a semi-infinite medium with a flat surface, and for uniform initial concentration C_i, constant surface concentration, C_o, and case A – constant diffusivity (see Crank [7]), case B – time dependent $D(t)$; case C – variable temperature with temperature dependent $D(T)$. Equation 3 is used to compute y and Equation 4 (or 8) is used to compute y^* with data shown in Table I

	Case A	Case B	Case C
Independent variables	x and Dt	x and y	$w = x\alpha^{1/2}$ and y^*
$(C - C_o)/(C_i - C_o)$	$\mathrm{erf}\{x/[2(Dt)^{1/2}]\}$	$\mathrm{erf}[x/(2y^{1/2})]$	$\mathrm{erf}[w/(2y^{*1/2})]$
$(\partial C/\partial x)_0$ or $(\partial C/\partial w)_0$	$(C_i - C_o)/(\pi Dt)^{1/2}$ —	$(C_i - C_o)/(\pi y)^{1/2}$ —	— $(C_i - C_o)/(\pi y^*)^{1/2}$
δ	$(\pi Dt)^{1/2}$	$(\pi y)^{1/2}$	$(\pi y^*/\alpha)^{1/2}$
$M/(C_i - C_o)$	$2(Dt/\pi)^{1/2}$	$2(y/\pi)^{1/2}$	$2[y^*/(\alpha\pi)]^{1/2}$

3. Semi-infinite medium with flat surface and constant surface concentration

Solutions for constant diffusivity are well known and can be found in textbooks [7]. Analogy between the relevant differential equation was then used to obtain the corresponding solutions for cases when diffusivity varies with time or temperature, as shown in Table II, with uniform initial concentration, C_i, and constant surface concentration C_o. This was based on changing the independent variables as shown above. For the case when diffusivity is temperature dependent, surface concentration is nearly constant, and temperature varies linearly with time this yields the following solutions for the concentration profile, and boundary layer thickness $\delta = |(C_i - C_o)/(\partial C/\partial x)_0|$

$$(C - C_o)/(C_i - C_o) = \mathrm{erf}\{x\alpha^{1/2}/[2y^{*1/2}(T)]\} \quad (10)$$

$$\delta = (\pi y^*(T)/\alpha)^{1/2} \quad (11)$$

Equations 10 and 11 provide some insight into the role of cooling or heating rates, even when the temperature dependence of diffusivity is unknown, and $y^*(T)$ cannot be calculated. In fact, the scale of the independent variable $w = x\alpha^{1/2}$ is the same for different values of rate of change in temperature, α, when the initial and final temperatures are identical for every experiment, and one can thus conclude that the actual scale of x varies as $\alpha^{-1/2}$. This is also true for the boundary layer thickness $\delta = (\pi y^*/\alpha)^{1/2}$.

The effect of cooling or heating rates on the amount transferred by diffusion in non-isothermal conditions, is a two-fold effect both because the boundary layer thickness decreases as $\alpha^{-1/2}$ for identical initial and final temperatures, and also because the actual time scale decreases with increasing rate of change in temperature. Combination of both effects is described in Appendix A and yields the following expression for

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the amount transferred per unit area

$$M = 2\alpha^{-1/2}(C_i - C_o)(y^*(T)/\pi)^{1/2} \quad (12)$$

When transfer is controlled by an interfacial process the amount of material transferred should vary as α^{-1} (see also Appendix A).

4. Semi-infinite media with flat surface and variable surface concentration

The simplest solution for variable surface concentration corresponds to nearly constant diffusivity, and was obtained by analogy with heat conduction in solids [11]

$$C - C_i = \frac{x}{2\pi^{1/2}}$$

$$\times \int_0^t \frac{[C_o(t') - C_i]\exp\{-x^2/[4D(t-t')]\}}{[D(t-t')]^{3/2}} D\,dt'$$

(13)

with uniform initial concentration, C_i.

Changes in surface concentration are mostly likely to be related to variable temperature, $C_o(T)$, as usually found for interphase equilibria, and in addition, diffusivity is also likely to vary with temperature. However, one can also take advantage of the analogy between Equations 1 and 6, to obtain the solution for the non-isothermal problem by replacing $y^*(T)$ for Dt, $w = x\alpha^{1/2}$ for x, and $C_o(T)$ or $C_o[y^*(T)]$ for $C_o(t)$

$$C - C_i = \frac{x\alpha^{1/2}}{2\pi^{1/2}} \int_0^{y^*(T)}$$

$$\times \frac{[C_o(y^*') - C_i]\exp\{x^2\alpha/[4(y^*' - y^*)]\}}{(y^* - y^*')^{3/2}} \, dy^*'$$

(14)

Equation 14 still requires numerical integration for a generic temperature dependence of surface concentration. Nevertheless, the concentration profiles $C = f[w, y^*(T)]$ described by Equation 14 remain unchanged for several experiments with different rates of change in temperature, provided that the initial and final temperatures are the same for every experiment. For identical scales of variable $w = x\alpha^{1/2}$, one expects the scale of original distance x to vary as $\alpha^{-1/2}$, as previously found for constant surface concentration. This trend describes the effect of the rate of change in temperature on the boundary-layer thickness. Therefore, by cooling from a given initial temperature to room temperature, at different rates, one should expect

$$\delta_2/\delta_1 = (\alpha_1/\alpha_2)^{1/2} \quad (15)$$

The unique concentration dependence $C = f[w, y^*(T)]$, with a temperature-dependent boundary condition $C(0,t) = C_o(T)$ or $C[y^*(T)]$, also shows that the concentration gradient $(\partial C/\partial w)_0$ depends on temperature only. This condition is sufficient to ensure that the amount of material transferred varies as $\alpha^{-1/2}$ (see Appendix A), or

$$M = \alpha^{-1/2}M^*(T) \quad (16)$$

For example, for two experiments performed on cooling from a given temperature to room temperature, at different rates, the amount transferred should vary as $M_2/M_1 = (\alpha_1/\alpha_2)^{1/2}$. Alternatively, several data for different rates of change in temperature can be plotted as $M\alpha^{1/2}$ versus T, and should fit a single dependence if the process is controlled by diffusion.

5. Plane sheet with constant surface concentration

Real systems are finite and one must thus check the validity of the assumptions upon which this semi-infinite model was derived, namely: (i) behaviour identical to that expected for semi-infinite media, and (ii) nearly flat interface. The semi-infinite condition is nearly true when the boundary layer thickness is sufficiently smaller than the dimensions of the sample. Actually, the boundary layer thickness varies with time and with the order of magnitude of diffusivity, and this dependence is very simple for constant diffusivity, in which case $\delta = (\pi Dt)^{1/2}$. For example, δ can be lower than 1 μm for $D \approx 10^{-16}$ m² s⁻¹ and $t \leqslant 1$ h, in which case semi-infinite models can be used for describing processes such as diffusion-controlled impurity segregation at grain boundaries in polycrystalline materials with average grains sizes as small as 10 μm. The boundary layer thickness must also be much smaller than the radius of curvature to validate the assumption that the interface is nearly flat.

Typically, the boundary-layer thickness should be smaller than half sample size for cases when diffusion is asymmetrical and transfer occurs at a single side of the plane sheet, or smaller than $L/2$ for nearly symmetrical diffusion at both surfaces, where $2L$ is the thickness of the sheet. In this case one might write $(\pi Dt)^{1/2} < L/2$ for constant diffusivity, $(\pi y)^{1/2} < L/2$ for time-dependent diffusivity $D(t)$, or $(\pi y^*/\alpha)^{1/2} < L/2$ for variable temperature. The semi-infinite criterion might be rewritten $Dt/L^2 < 0.08$, or $y/L^2 < 0.08$ for isothermal processes, and

$$y^*/(L^2\alpha) < 0.08 \quad (17)$$

for variable temperature.

A plane sheet may be a suitable geometrical model for platelet-like particles, with a small thickness to length ratio, and this should be described by solutions for diffusion in plane sheets. Analogy between Equations 1, 2 and 6 can be used to obtain the solution for time-dependent $D(t)$, or temperature dependent $D(T)$ with variable temperature, for uniform initial concentration C_i, and constant surface concentration at both surfaces (Table III). The solutions for constant D are available in textbooks [7], and solutions for variable temperature (case C) become:

$$\frac{(C - C_o)}{(C_i - C_o)} = (4/\pi)\sum_0^\infty (-1)^n (2n+1)^{-1}$$

$$\times \cos[(2n+1)\pi x/(2L)]$$

$$\times \exp[-\pi^2(2n+1)^2 y^*(T)/(4L^2\alpha)] \quad (18)$$

TABLE III Solutions for concentration profiles and amount of material gained by a plane sheet of thickness $2L$ for cases when case A, diffusivity is constant (Crank [7]; case D, diffusivity is time dependent; case C, variable temperature with temperature dependent $D(T)$

	$(C - C_o)/(C_i - C_o)$	$M/[L(C_o - C_i)]$
Case A	$(4/\pi)\sum_0^\infty (-1)^n (2n+1)^{-1} \cos[(2n+1)\pi x/(2L)]$ $\times \exp\{-[\pi(2n+1)/(2L)]^2 Dt\}$	$1 - 8\sum_0^\infty [\pi(2n+1)]^{-2} \exp\{-[\pi(2n+1)/(2L)]^2 Dt\}$
Case B	$(4/\pi)\sum_0^\infty (-1)^n (2n+1)^{-1} \cos[(2n+1)\pi x/(2L)]$ $\times \exp\{-[\pi(2n+1)/(2L)]^2 y\}$	$1 - 8\sum_0^\infty [\pi(2n+1)]^{-2} \exp\{-[\pi(2n+1)/(2L)]^2 y\}$
Case C	$(4/\pi)\sum_0^\infty (-1)^n (2n+1)^{-1} \cos[(2n+1)\pi x/(2L)]$ $\times \exp\{-[\pi(2n+1)]^2 y^*(T)/(4L^2\alpha)\}$	$1 - 8\sum_0^\infty [\pi(2n+1)]^{-2} \exp\{-[\pi(2n+1)]^2$ $\times y^*(T)/(4L^2\alpha)\}$

and

$$\frac{M}{L(C_o - C_i)} = 1 - 8\sum_0^\infty [\pi(2n+1)]^{-2}$$
$$\times \exp[-\pi^2(2n+1)^2 y^*(T)/(4L^2\alpha)] \tag{19}$$

In these equations, L is half thickness of the plane sheet, with $0 < x < L$, and M is the amount of material gained by the plane sheet (per unit area). Equation 4 (or Equation 8) can be used to calculate the values of y^*.

For $Dt/(4L^2)$ or $y^*/(4\alpha L^2)$ larger than about 0.5 one may neglect the second term and terms of higher order. For example, the truncated solution for changes of concentration reduces

$$(C - C_o)/(C_i - C_o) \approx (4/\pi)\cos[\pi x/(2L)]$$
$$\times \exp[-\pi^2 y^*(T)/(4\alpha L^2)] \tag{20}$$

and the truncated solution for the amount transferred becomes

$$M/[L(C_o - C_i)] \approx 1 - (8/\pi^2)$$
$$\times \exp\{-[\pi/(2L)]^2 \alpha^{-1} y^*(T)\} \tag{21}$$

The quantity $M_\infty = L(C_o - C_i)$ is the amount transferred for $y^* = \infty$, which corresponds to a state when the final concentration becomes uniform, and equal to C_o throughout the sample. Actually, M_∞ may not be reached during cooling because y^* cannot exceed a maximum value, as found by using Equations 7–9, with data shown in Table I. Note that $I(\Theta)$ decreases rapidly with decreasing Θ, especially for Θ lower than about 0.5, which is the case even for relatively low activation energies. For example, an activation energy as low as $10\,kJ\,mol^{-1}$ gives $\Theta_i = RT_i/E_d \approx 1$ at $1000\,°C$, and $\Theta \approx 0.25$ room temperatures, and in this case $I(\Theta_i) - I(\Theta) \approx I(\Theta_i)$. One may thus conclude that the maximum value of y^* reached on cooling is

$$y^*_{max} \approx D_o(E_d/R)I(\Theta_i) \tag{22}$$

where $\Theta_i = T_i R/E_d$. Substitution of y^*_{max} in Equation 19 can be used to evaluate the maximum gain (or loss) on cooling. Fig. 1 shows that the rate of mass transfer vanishes at a temperature at which $y^*(T)$
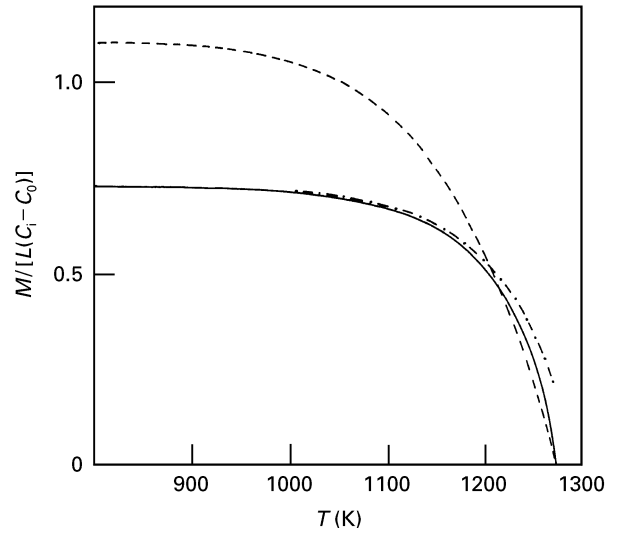

Figure 1 Weight loss of a plane sheet per unit area, on cooling, for constant surface concentration, C_o, and (——) uniform initial concentration, C_i; (—·—) the first order aproximation (Equation 21), (———) the dependence of $y^*(T)$, (Equation 4). The initial temperature is $T_i = 1273\,K$, the diffusion coefficient varies as $D(T) = D_o\exp[-E_d/(RT)]$, with activation energy $E_d = 100\,kJ$ mol^{-1}. The remaining parameters correspond to the condition $D_iT_i/(4L^2\alpha) = 50$, with $D_i = D(T_i)$.

becomes nearly independent of further decrease in temperature. Note also that the truncated solution (Equation 21) is nearly true for $y^*/(4L^2\alpha)$ greater than about 0.5.

Equations 18 and 19 describe how the rate of change in temperature and thickness of the slab determine the concentration profiles and amount transferred across the surface. This type of effect is easily anticipated by taking into account that the relevant scale for non-isothermal conditions is $x\alpha^{1/2}$ rather than x (and $L\alpha^{1/2}$ rather than L). For example, two experiments might be designed by adjusting the thickness of the samples and the rate of change in temperature to ensure identical values of $L^2\alpha$, or

$$\alpha_2/\alpha_1 = (L_1/L_2)^2 \tag{23}$$

with identical initial and final temperatures. In this case, the relative amount of material transferred $M/[L(C_o - C_i)]$ should still be the same for every experiment.

6. Plane sheet with temperature dependent surface concentration and diffusivity

Some solutions for time-dependent surface concentration and constant diffusivity have been derived by analogy with equivalent heat-conduction processes [11]. However, temperature is the factor most likely to cause changes in surface concentration, $C_o(T)$, and diffusivity $D(T)$, and one should thus recover the temperature dependence proposed for non-isothermal conditions. In this case, the analogy between Equations 1 and 6 is again suitable to obtain the relevant solutions after the required changes in independent variables. For example, for uniform initial concentration, C_i, and when surface concentration is $C_o(T)$ at both interfaces (symmetry) one obtains

$$C - C_i =$$

$$\sum_{0}^{\infty} (-1)^n 4\pi(2n + 1) \cos[(2n + 1)\pi x/(2L)]$$

$$\times \int_{T_i}^{T} [C_o(y^{*\prime}) - C_i](4L^2\alpha)^{-1}$$

$$\times \exp\{[\pi(2n + 1)]^2(y^{*\prime} - y^*)/(4L^2\alpha)\} \qquad (24)$$

for $0 \leqslant x \leqslant L$. The amount of material gained by the sample (per unit area) can be calculated on integrating $[C(x) - C_i]\,dx$.

Obtaining numerical solutions of Equation 24 is time consuming because the decay of high order terms in Equation 24 is very slow. In addition, adding a very large number of terms leads to significant rounding-off of errors. These were the reasons for using an alternative method to compute concentration profiles (Appendix B).

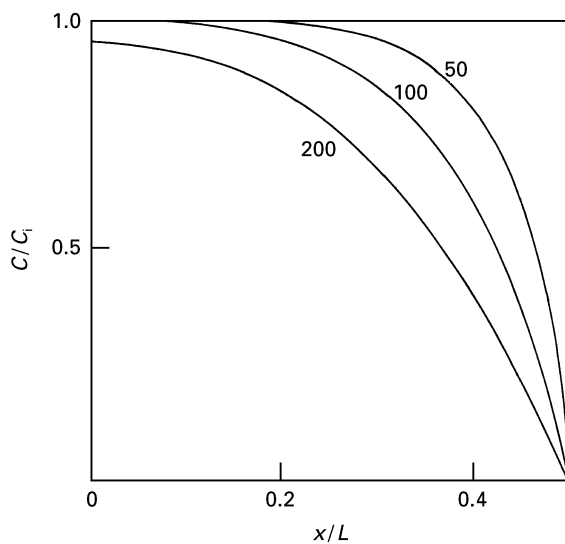Selected cases might be useful to provide some insight into conditions when simpler models can be used. For example, Figs 2 and 3 show concentration profiles and Fig. 4 shows the mass transferred, computed for cases when surface concentration is described by $C_o(T) = C_i\exp[(E_c/R)(T_i^{-1} - T^{-1})]$. In this case, the rate of change of $C_o(T)$ with variable T increases with the activation energy E_c, and for very high E_c the surface concentration drops to zero within a short time interval, and for a small drop in temperature. This change is nearly step-like for very high E_c, and solutions thus tend towards Equations 18 and 19, with negligible surface concentration $C_o \approx 0$ (shown dashed). However, this only occurs if the relative rate of change in surface concentration is much higher
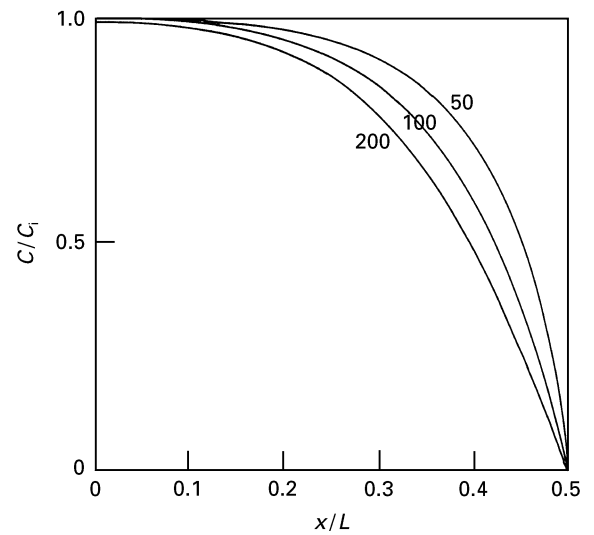
Figure 3 Concentration profiles developed in a plane sheet, on cooling from initial temperature $T_i = 1273$ K to room temperature (298 K), for diffusivity $D(T) = D_o\exp[-E_d/(RT)]$, with $E_d = 100\,\text{kJ}\,\text{mol}^{-1}$, and surface concentration $C_o(T) = C_i\exp[(E_c/R)(T_i^{-1} - T^{-1})]$, with $E_c = 50$, 100 and $200\,\text{kJ}\,\text{mol}^{-1}$ (shown in the figure). Other parameters correspond to the condition $D_iT_i/(4L^2\alpha) = 1$.

Figure 2 Concentration profiles developed in a plane sheet, on cooling from initial temperature $T_i = 1273$ K to room temperature (298 K), for $D(T) = D_o\exp[-E_d/(RT)]$, with values $E_d = 50$, 100, 200 shown in the figure, and surface concentration $C_o(T) = C_i\exp[(E_c/R)(T_i^{-1} - T^{-1})]$, with $E_c = 100\,\text{kJ}\,\text{mol}^{-1}$. Other parameters correspond to the condition $D_iT_i/(4L^2\alpha) = 1$.
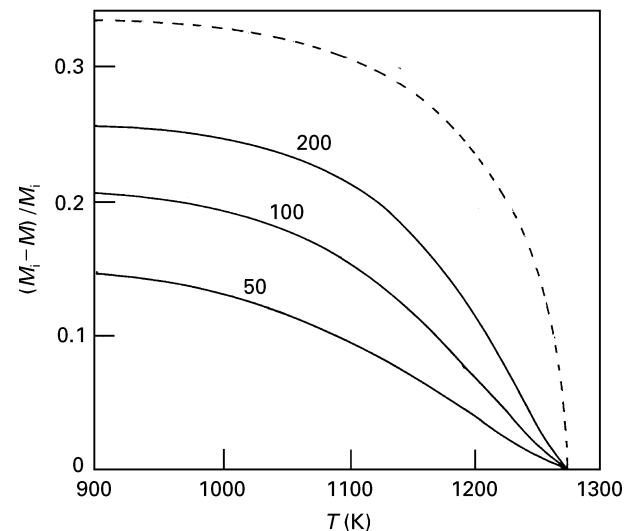
Figure 4 Relative weight changes on cooling from initial temperature $T_i = 1273$ K, with diffusivity $D(T) = D_o\exp[-E_d/(RT)]$, and surface concentration $C_o(T) = C_i\exp[(E_c/R)(T_i^{-1} - T^{-1})]$. M_i is the initial solute content of the plane sheet. The values of activation energies are $E_d = 100\,\text{kJ}\,\text{mol}^{-1}$, and $E_c = 50$, 100 and $200\,\text{kJ}\,\text{mol}^{-1}$ (shown in the figure). Other parameters correspond to the condition $D_iT_i/(4L^2\alpha) = 1$.

than the rate of changes in diffusivity, which is true for $E_c \gg E_d$.

7. Conclusions

A number of solutions for diffusion with constant diffusivity were extended to describe diffusion in non-isothermal conditions with temperature-dependent $D(T)$ and temperature-dependent $C_o(T)$. Some interesting solutions describe the effects of the rate of change in temperature, α. The simplest analysis is for a nearly flat interface, when the spatial changes in concentration can be adjusted by a factor $\alpha^{1/2}$, and the boundary-layer thickness is proportional to $1/\alpha^{1/2}$. The theoretical predictions can be checked by plotting several concentration profiles measured for different rates of change in temperature. In addition, experiments may be interpreted even when the actual dependence for $D(T)$ and $C_o(T)$ is unknown.

The effects of the rate of change in temperature on the amount transferred are also useful to assess whether the process is controlled by diffusion or by an interfacial process, even when the actual temperature dependence of some relevant physicochemical parameters is unknown.

Diffusion in a plane sheet is dependent on its thickness. However, several sets of experimental data for different cooling or heating rates are still expected to reduce to a unique temperature-dependent concentration profile when the thickness, L, and the rate of change in temperature, α, are both adjusted to maintain a constant value of $L\alpha^{1/2}$.

Appendix A. Effects of rate of change in temperature on the amount transferred

The amount transferred is related to concentration gradients when the process is controlled by diffusion, and the amount lost per unit area across a plane surface varies as

$$dM = D(\partial C/\partial x)_0 \, dt \qquad (A1)$$

One can thus use the concentration gradients shown in Table II to obtain the solutions for describing M versus t. A similar method can be used to obtain solutions for cases when diffusivity is time-dependent, with constant surface concentration, by substitution of $D \, dt$ by dy. The concentration gradient can be read from Table II and substitution in Equation A1 yields $dM = (C_i - C_o)(\pi y)^{-1/2} \, dy$, which is easily integrated to give the solution shown in Table II

$$M = 2(C_i - C_o)(y/\pi)^{1/2} \qquad (A2)$$

The solution for temperature-dependent diffusivity is affected by the dependence of concentration gradients on the rate of change in temperature. Taking into account the inverse transformation of variables $x = w/\alpha^{1/2}$ one obtains $(\partial C/\partial x)_0 = \alpha^{1/2}(\partial C/\partial w)_0$, and substitution of this result, and also $dt = dT/\alpha$ in Equation A1 yields

$$dM = \alpha^{-1/2}(\partial C/\partial w)_0 D \, dT \qquad (A3)$$

The dependence on time has thus been transformed to yield an alternative temperature dependence. Note that $(\partial C/\partial w)_0$ is also a function of temperature (or y^*) only, as demonstrated for the case when surface concentration is constant (Table II). Therefore, Equation A4 still describes a unique dependence of the amount transferred on temperature

$$M = \alpha^{-1/2} M^*(T) \qquad (A4)$$

where

$$M^*(T) = \int_{T_i}^{T} (\partial C/\partial w)_0 D(T) \, dT \qquad (A5)$$

This generic dependence described by Equation A4 is true even for the case when surface concentration varies with temperature, $C(0, t) = C_o(T)$, which can be rewritten $C_o(y^*)$.

The simplest solution is for constant surface concentration, in which case $(\partial C/\partial w)_0 = (C_i - C_o)/(\pi y^*)^{1/2}$ (Table II). On recovering the transformation of variable $D(T) \, dT = dy^*$, and solving Equation A5 one thus obtains

$$M = 2(C_i - C_o)[y^*/(\pi\alpha)]^{1/2} \qquad (A6)$$

The rate of change in temperature also effects the amount transferred for cases when mass transfer is controlled by a slow interfacial process. In these cases the rate of transfer is dependent on the difference between equilibrium and actual concentration $(C_{eq} - C)$, and on assuming first-order kinetics

$$dM/dt = K(T)(C_{eq} - C) \qquad (A7)$$

where $K(T)$ is a temperature-dependent kinetic constant. In addition, one might assume that the driving force $(C_{eq} - C)$ is either constant or temperature dependent, and substitution of $dt = dT/\alpha$ in Equation A7 thus yields

$$M = \alpha^{-1} \int_{T_i}^{T} K(T')(C_{eq} - C) \, dT' \qquad (A8)$$

Appendix B

Obtaining solutions for Equation 24 requires numerical integrations for sufficiently large values of n. Unfortunately, the high-order terms decay slowly, and a large number of terms must be computed for this purpose. In addition to requiring long computing time, adding a very large number of terms also increases rounding-off errors. These complications can be minimized by transforming Equation 24 as follows

$$C - C_i = 4 \sum_{0}^{\infty} (-1)^n [\pi(2n + 1)]^{-1}$$

$$\times \cos[(2n + 1)\pi x/(2L)]$$

$$\times [F(n, \xi) - F(\infty, \xi)] + F(\infty, \xi) S_1(\infty) \quad (A9)$$

where

$$\xi = y^* \pi^2/(4L^2\alpha) \qquad (A10)$$

and

$$F(n, \xi) = \int_0^{(2n+1)^2 \xi} \exp[\xi' - (2n+1)^2 \xi]$$

$$\times (C_o(\xi') - C_i) \, d\xi' \qquad (A11)$$

$$S_1(N) = 4 \sum_0^N (-1)^n [\pi(2n+1)]^{-1} \cos[(2n+1)\pi x/(2L)]$$

$$(A12)$$

This transformation yields terms $F(n, \xi)$ which converge rapidly to $F(\infty, \xi)$. Typically $F(n, \xi) \approx F(\infty, \xi)$ for $n \geqslant 10$, and the differences $F(n, \xi) - F(\infty, \xi)$ thus vanish rapidly, avoiding the complications related to having to compute a very large number of terms. In addition, $S_1(\infty) = 1$.

The numerical method is then started by using a multistep integration formula to solve Equation 4 as follows

$$T_{j+1} = T_j + 4\delta \qquad (A13)$$

$$y_{j+1}^* = y_j^* + \delta(14D(T_j) + 64D(T_j + \delta)$$

$$+ 24D(T_j + 2\delta) + 64D(T_j + 3\delta)$$

$$+ 14D(T_j + 4\delta))/180 \qquad (A14)$$

where δ corresponds to the increments of temperature. The increment δ was sequentially adjusted to yield relative changes of diffusivity smaller than 0.1% per step, and was also kept smaller than ± 1 K. This algorithm yields a set of discrete pairs of values T_j; y_j^*, and the corresponding values of ξ_j were computed by multiplying by $\pi^2/(4L^2\alpha)$.

The values of $F(n, \xi)$, (Equation A11), were calculated by decomposition in small intervals, and $C_o(\xi') - C_i$ thus varies almost linearly with ξ', which yields analytical solution for every interval.

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