

A simple way of describing the diffusion phase growth in cylindrical and spherical samples

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It is shown that during diffusional growth of the intermediate phase between substances A and B for cylindrical and spherical samples, the total diffusion flux relative to the center, $-S(r)\tilde{D}\partial c/\partial r$, where S is the area of the interface, varies by a small amount in the radial direction, despite the concentration dependence of the interdiffusion coefficient $\tilde{D}(c)$. In this context we propose a constant-flux method which allows the kinetics of the diffusional phase growth in cylindrical and spherical samples to be described in a rather simple way. Deviations from the parabolic law of phase growth in cylindrical and spherical samples are analyzed.

INTRODUCTION

Describing the growth of intermediate layers during chemical diffusion offers some difficulty. For this reason, many simplifications are made. Major simplifications include putting $\tilde{D}(c) = \text{const}$. This simplification is not altogether correct because there is a considerable concentration dependence of $\tilde{D}(c)$.¹⁻⁴ For example, it has turned out that the mutual-diffusion coefficient in γ brass, Cu_5Zn_8 , increases by more than a factor of 10, while the zinc concentration grows from 0.62 to 0.66.^{2,3} A rigorous $\tilde{D}(c)$ relation is known for only some phases of some binary systems. Therefore, the problem cannot be solved in the general form, for an exact knowledge of the concentration dependence of $\tilde{D}(c)$ is needed for each phase of the system. A solution to the problem is difficult to find in the case of phase growth in cylindrical and spherical samples, since the change in interface area $S(r)$ should be taken into account.

We propose here a universal method for describing the phase growth. This technique necessitates no allowance for the concentration dependence of $\tilde{D}(c)$. The constant-flux method can be applied fairly well to describe intermediate phases and simplifies the description of the kinetics of the phase growth in planar, cylindrical, and spherical samples.

MODEL AND RESULTS

For the sake of simplicity, we consider a binary system, A - B , with a single intermediate phase, $A_{p\pm\delta}B$ [where the atomic concentration of B is $c_L^{\text{at}} = 1/(1+p+\delta)$ and $c_R^{\text{at}} = 1/(1+p-\delta)$], and assuming the mutual solubilities of A and B to be negligibly small (Fig. 1). The results presented below hold for as many phases as desired. It has been shown⁵ that during the diffusion growth of the planar phase layer in the diffusion specimen A - B , the fluxes $-\tilde{D}\partial c/\partial x$ relative to the end of the specimen on the right, J_R , and left, J_L , interface differ slightly:

$$\frac{c_L J_L}{c_R J_R} \approx \frac{c_L}{c_L - \Delta c} \quad (1)$$

Here c_L and c_R are the volume fractions of B on the left-hand and right-hand phase interfaces. For almost every intermediate phase $\Delta c \equiv c_R - c_L > 0$, is not more than 0.1 and frequently less than 0.01. Therefore,

$$\Delta J/J_L (\Delta J/J_R) \sim \Delta c \ll 1, \quad \text{here } \Delta J \equiv |J_L - J_R|.$$

For the case of different molar volumes $\omega_A \neq \omega_B$, one needs to use volume fluxes⁶ rather than atom fluxes and the volume fractions

$$c(x) = \frac{N_B \omega_B}{N_A \omega_A + N_B \omega_B} = \frac{\omega_B}{\omega'} c^{\text{at}}(x)$$

instead of the atomic concentration $c^{\text{at}}(x) = N_B/(N_A + N_B)$. Here N_A and N_B stand for the number of atoms A and B in a small volume in the vicinity of x , and $\omega' = (1 - c^{\text{at}})\omega_A + c^{\text{at}}\omega_B$ is the average atomic volume.

For the planar case, taking the fluxes on the left and right interfaces, $J_L = c_L dx_L/dt$ and $J_R = -(1 - c_R) dx_R/dt$, to be equal to the average flux (Ref. 5)

$$\bar{J} = \frac{1}{X} \int_{x_L}^{x_R} J(x) dx = -\frac{D\Delta c}{X},$$

we obtain the following expression for the phase growth rate

$$v_{\text{pl}} = \frac{dX}{dt} = \frac{1 - \Delta c}{c_L(1 - c_R)} \frac{D\Delta c}{X} \quad (2)$$

Here $X \equiv x_R - x_L$ is the layer width, $D = 1/\Delta c \int_{c_L}^{c_R} \tilde{D}(c) dc$ is an effective interdiffusion coefficient in the phase. The solution (2) is a well-known parabolic law [Fig. 2(a)].

$$X^2 = \frac{2(1 - \Delta c) D\Delta c}{c_L(1 - c_R)} t = K^2 t \quad (3)$$

(K is the growth rate constant).

This simple formula is valid for any $\tilde{D}(c)$ relation and also for any binary system, owing solely to the constant-flux approximation.

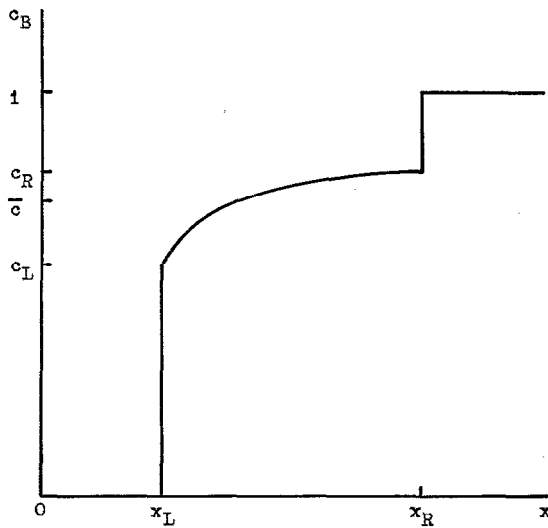


FIG. 1. A concentration profile during diffusion growth of an intermediate phase between substances *A* and *B*. c_L and c_R are the volume fractions of *B* on the left-hand and right-hand interfaces, $\bar{c} \equiv 1/(x_R - x_L) \int_{x_L}^{x_R} c(x) dx$.

In the Appendix we prove that for the phase growth in samples with variable cross sections, the total flux remains almost constant, i.e., $J = -S(x) \bar{D}(c) \partial c / \partial x \approx \text{const.}$ Averaging the flux J of mass $1/S(x)$ yields^{5,7}

$$\bar{J} = -D\Delta c / \left(\int_{x_L}^{x_R} \frac{dx}{S(x)} \right). \quad (4)$$

Applied to cylindrical and spherical samples, Eq. (4) yields⁸

$$\begin{aligned} \bar{J}_{\text{sph}} &= -4\pi r_L r_R D\Delta c / R, \quad R = r_R - r_L, \\ \bar{J}_{\text{cyl}} &= -2\pi D\Delta c / \ln(r_R/r_L). \end{aligned} \quad (5)$$

Here r_L and r_R are the radii of the inner and outer interfaces.

Consider further the influence of surface curvature on phase growth. Setting the fluxes on the inner and outer spherical surfaces, $J_L = 4\pi r_L^2 c_L dr_L/dt$ and $J_R = -4\pi r_R^2 (1 - c_R) dr_R/dt$, equal to the average flux (5) gives an expression for the phase growth rate

$$v_{\text{sph}} = \frac{dR}{dt} = \frac{c_L r_L / r_R + (1 - c_R) r_R / r_L}{c_L (1 - c_R)} \frac{D\Delta c}{R}. \quad (6)$$

A comparison of Eqs. (6) and (2) shows that $v_{\text{sph}} > v_{\text{pl}}$ for the case $R = X$ and $\bar{c} < 0.5$. Therefore, $R(t) > X(t)$ for the same t 's [Fig. 2(b)]. But if $\bar{c} > 0.5$, the spherical phase layer first grows more slowly than the planar layer [Fig. 2(c)], and then, for $R/r_R = 2 - (1 - \Delta c)/c_L$, it starts to grow more rapidly.

Similar equation results for the cylindrical case are obtained

$$v_{\text{cyl}} = \frac{dR}{dt} = \frac{c_L + (1 - c_R) r_R / r_L}{c_L (1 - c_R) r_R} \frac{D\Delta c}{\ln(r_R/r_L)}. \quad (7)$$

Computer calculations using Eq. (7) were done for the case $\Delta c \ll 1$, $c_L \approx c_R \approx \bar{c}$ for $\bar{c} = 0.1, 0.3, 0.75$, and 0.9 (Fig. 2).

The deviation from the parabolic growth law is the more pronounced the greater the difference between \bar{c} and value 0.5 , which, in fact, is obvious from Figs. 2(b) and 2c. For $\bar{c} = 0.75$ and 0.9 the phase grows more slowly, accelerating only towards the sample's center [Fig. 2(c)].

However, for $\bar{c} \approx 0.55 - 0.7$, the phase growth in cylindrical and spherical samples may be described by a parabolic dependence even for $R \gtrsim r_L$, because its deviations are within the experimental error values (~ 1 to 2%).

It is shown analytically that for the case of diffusion growth of two phases between *A* and *B*, the curvature of interfaces influences their growth in the following way (Fig. 3). In the case of a slowly growing phase layer, $A_q B(2)$, surrounded by a rapidly growing phase, $A_p B(1)$, phase 2 grows more slowly, both in the spherical and cylindrical cases, than in the planar case [Fig. 3(c)]. If the phase 2 layer surrounds the phase 1 layer, conversely, the phase 2 layer grows faster than in the planar case [Fig. 3(b)]. But a rapidly growing phase 1 can grow either faster (for $\bar{c}_1 < 0.5\bar{c}_2$) or more slowly [for $0.5\bar{c}_2 < \bar{c}_1 < \bar{c}_2$, Fig. 3(b)] than in the planar case.

The above mentioned results were tested and proved experimentally on a Cu-Zn system.⁹ That is why the calculation has been done for case $\bar{c}_1 = 0.68$ and $\bar{c}_2 = 0.84$. Here c is the volume fraction of Zn, phase 1 is the γ brass and phase 2 is the ϵ brass.

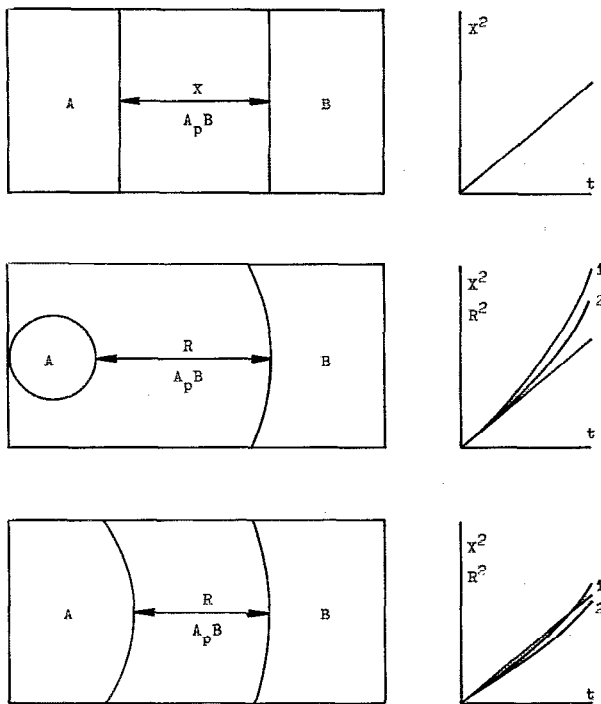


FIG. 2. Influence of geometry on phase growth kinetics: (a) parabolic law of phase growth in planar geometry; (b) phase growth acceleration in case of $\bar{c} < 0.5$ in spherical and cylindrical geometry, $\bar{c} = 0.1$ (1) and $\bar{c} = 0.3$ (2); (c) phase growth slowing in the case of $\bar{c} > 0.5$ in spherical and cylindrical geometry, $\bar{c} = 0.75$ (1) and $\bar{c} = 0.9$ (2), and acceleration towards the sample's center. The calculation has been done for the moment in time, when substance *A* has disappeared.

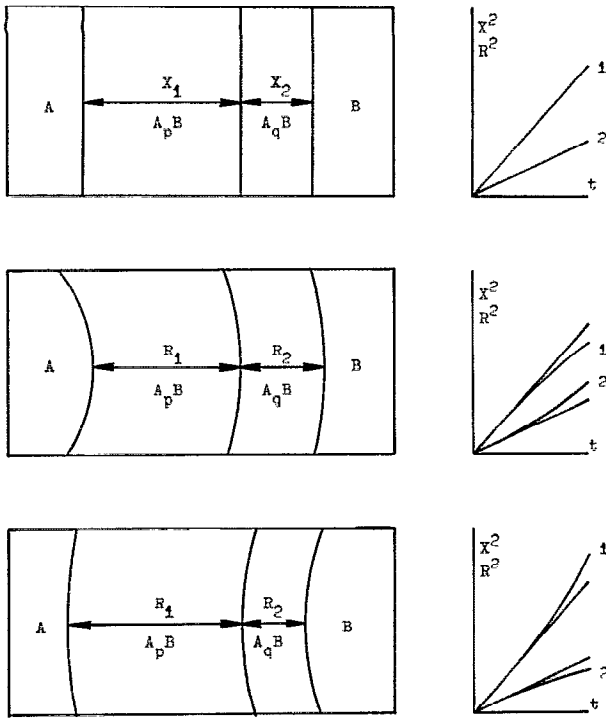


FIG. 3. Influence of geometry on diffusion growth kinetics of two phases, $A_pB(1)$ and $A_qB(2)$, in a binary system. The case of $q < p < 1$. (a) Parabolic law of phases growth in planar geometry; (b) phase 1 growth slowing ($c=0.68$) and phase 2 growth acceleration ($c_2=0.84$) in spherical and cylindrical geometry, a is the volume fraction of B ; (c) phase 1 growth acceleration ($c_1=0.32$) and phase 2 growth slowing ($c_2=0.16$) in spherical and cylindrical geometry, c is the volume fraction of A . The calculation has been done for a time, when substances $A(b)$ and $B(c)$ have not disappeared.

The constant-flux method has allowed us to draw the conclusion that roughness of interfaces should become smooth within diffusion phase growth⁸ (Fig. 4). Such a process is taking place because convexity moves more slowly than the planar interface and concavity moves more rapidly than the planar interface (see arrows in Fig. 4).

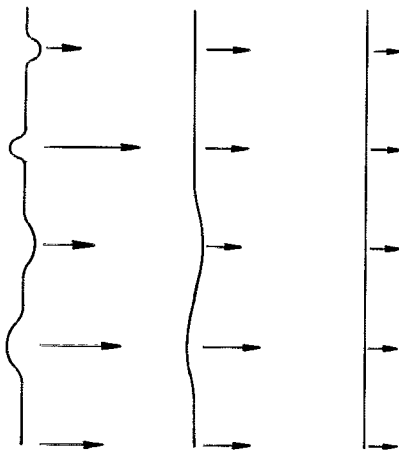


FIG. 4. Roughness smoothing during phase growth. Smoothing rate is the more pronounced, the smaller the roughness radius.

The diffusion flux density decreases at convexity and increases at concavity. The diffusion flux density is likely to have a steady tendency for becoming uniform. Therefore, the roughness of interfaces is apt to be self-smoothing. Attention is drawn to the result, that smoothing rate is the more pronounced, the smaller the roughness radius. The smoothing of interfaces was experimentally observed during the growth of γ -(Cu_5Zn_8) brass at a temperature of 230°C .⁹

CONCLUSIONS

(1) In describing diffusion phase growth in binary systems, it is necessary to use the constant-flux approximation instead of the constant diffusion coefficient approximation. This is because the diffusion coefficient may vary by more than a factor of 10 within the range of phase homogeneity Δc , while the diffusion flux may vary by only a few percent.

(2) The constant-flux approximation permits a fairly simple description of diffusion phase growth in planar, cylindrical, and spherical samples without any distinction for the various binary systems (only c_L , c_R , and radii should be taken into account).

(3) If the average phase concentration of the external substance is less than 0.5, the phase in both cylindrical and spherical cases grows more rapidly than in the planar case. By contrast, if $\bar{c} > 0.5$, the phase in both cylindrical and spherical cases grows more slowly than in the planar case, but the growth accelerates towards the center of the sample.

(4) If $0.55 \lesssim \bar{c} \lesssim 0.7$, the phase growth in cylindrical and spherical samples may be described by a parabolic dependence similar to the planar case.

(5) There are several cases for two-phase binary systems. A slowly growing phase 2 in both cylindrical and spherical cases grows more rapidly than in the planar case; this is so if this phase surrounds a rapidly growing phase 1. Conversely, a slowly growing phase 2 in both cylindrical and spherical cases grows more slowly than in the planar case, if this phase is surrounded by a rapidly growing phase 1. A rapidly growing phase 1 can grow in both cylindrical and spherical cases, either more rapidly or more slowly than in the planar case (see conclusion 3; the value 0.5 is replaced by $0.5\bar{c}_2$).

(6) Attention is also drawn to the result, that the growth rates in convex and concave surfaces, is such that the interface boundary is liable to smoothing during phase growth. The smoothing rate is the more pronounced, the smaller the roughness radius. Therefore, we consider the "ideal" surfaces (plane, cylinder, and sphere) instrumental in describing phase growth.

APPENDIX

Here it is shown that in the cylindrical and spherical cases, when S is a function of radius, the total diffusion flux relative to the center will be almost constant along the radial direction. We have the following problem

$$S(r) \frac{\partial c}{\partial t} = \frac{\partial}{\partial r} \left(S(r) \tilde{D} \frac{\partial c}{\partial r} \right) = -\frac{\partial J}{\partial r},$$

$$c[t, r_L(t)] \equiv c_L; c[t, r_R(t)] \equiv c_R; c_R - c_L = \Delta c,$$

$$S(r_L) c_L \frac{dr_L}{dt} = J_L = -S(r_L) \tilde{D} \frac{\partial c}{\partial r} \Big|_{r_L}, \quad (\text{A1})$$

$$-S(r_R) (1 - c_R) \frac{dr_R}{dt} = J_R = -S(r_R) \tilde{D} \frac{\partial c}{\partial r} \Big|_{r_R},$$

$$r_L(0) = r_R(0) = r_A;$$

$$S[r_L(0)] = S[r_R(0)];$$

$$c(t=0, r) = \begin{cases} 0, & r < r_A, \\ 1, & r > r_A. \end{cases}$$

Here r_L and r_R are the radii of inner and outer phase interfaces, $S(r_L)$ and $S(r_R)$, respectively, their areas, c_L and c_R are the equilibrium concentrations on phase interfaces. In this case, the Boltzman solution $x/t^{1/2} \rightarrow r/t^{1/2}$ is invalid since S is a function of radius only. It is assumed that $c(r, t)$ is a monotonous function of r . This assumption is confirmed experimentally. It allows us to go from the function $c(t, r)$ to the function $r(t, c) \equiv r_c(t)$, which describes the motion of the constant-concentration surfaces. Then the first equation of the system Eq. (A1) becomes

$$S[r(t, c)] \frac{\partial r}{\partial t} = -\frac{\partial}{\partial c} \left(S[r(t, c)] \tilde{D} \right) = \frac{\partial J}{\partial c}. \quad (\text{A2})$$

Taking the partial derivative of Eq. (A2) with respect to c yields

$$\frac{\partial}{\partial c} \left(S \frac{\partial r}{\partial t} \right) = \frac{\partial}{\partial t} \left(S \frac{\partial r}{\partial c} \right) = -\frac{\partial^2}{\partial c^2} \left(S \tilde{D} \right) = \frac{\partial^2 J}{\partial c^2}. \quad (\text{A3})$$

Integration of Eq. (A3) from c_L to c ($c < c_R$) yields

$$\frac{d}{dt} \int_{c_L}^{c_R} S \frac{\partial r}{\partial c} dc = \frac{dV(c_L, c)}{dt} = \frac{\partial J}{\partial c} - \frac{\partial J}{\partial c} \Big|_{c_L}. \quad (\text{A4})$$

Here $V(c_L, c)$ is a part of the volume with the concentration varying from c_L to c . On the phase boundaries c_L and c_R the derivative of J with respect to c transforms to a finite difference

$$\frac{\partial J}{\partial c} \Big|_{c_L} = \frac{J_L - 0}{c_L - 0} = \frac{J_L}{c_L}, \quad \frac{\partial J}{\partial c} \Big|_{c_R} = \frac{0 - J_R}{1 - c_R} = -\frac{J_R}{1 - c_R}. \quad (\text{A5})$$

For $c = c_R$ Eqs. (A4) and (A5) give

$$\frac{dV(c_L, c_R)}{dt} = \frac{-J_R}{1 - c_R} \frac{J_L}{c_L}. \quad (\text{A6})$$

Integrating Eq. (A4) between c_L and c_R and allowing for Eq. (A6), we obtain

$$\Delta J \equiv |J_R - J_L| = \left| \frac{\partial J}{\partial c} \Big|_{c_L} \Delta c - \int_{c_L}^{c_R} \frac{dV(c_L, c)}{dt} dc \right|$$

$$\leq \left(\frac{|J_L|}{c_L} + \frac{|J_L|}{c_L} + \frac{|J_R|}{1 - c_R} \right) \Delta c. \quad (\text{A7})$$

Equation (A7) gives

$$\frac{c_L}{c_R + \Delta c} \frac{1 - c_R - \Delta c}{1 - c_R} \leq \frac{J_L}{J_R} \leq \frac{c_L}{c_L - 2\Delta c} \frac{1 - c_L}{1 - c_R}. \quad (\text{A8})$$

According to Eq. (A8), the region of possible values of J_L/J_R is somewhat wider than that for planar case (1), but it remains rather small: $\Delta J/J_L (\Delta J/J_R) \sim \Delta c \ll 1$.

Thus, the approximation of constant total flux is much more acceptable than that of constant interdiffusion coefficient (see, for example, Ref. 10). The latter can vary by a factor of 10 to 50 over the region of homogeneity Δc (Refs. 1-4).

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