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The Effect of the Moving Boundary on Molecular Diffusion Controlled Dissolution or Growth Kinetics

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Analysis of the kinetics of solute-transport-governed dissolution or exsolution of a slab in the absence of free or forced convection, carried out following the approach of Danckwerts,[3] allows rates to be predicted provided the bulk and saturation concentrations, the partial volume, and the binary diffusion coefficient are known. Motion of the interface between solute and solution characteristic of these processes always contributes to an increase in rate which can be attributed to solute transport at the interface caused by motion of the solution relative to the interface. Modification of the concentration profile due to relative motion of the bulk contributes a secondary effect. The importance of boundary motion is a function only of the fractional volume of the solute (i.e., that fraction of the solution volume attributed to the solute) both in the bulk and at the interface. When these are high, a many-fold increase in rate is obtained over that calculated ignoring boundary motion.

The kinetics of many dissolution and growth processes * are determined by solute transport to the solvent.[1] In some instances, particularly stationary systems of high viscosity and diffusivity when the driving force for free convection (for example, density difference between bulk and saturated solution) is low, there will be relatively long times before the boundary layer attains the thickness required for a steady-state free-convection process. In the interim, a transient process called molecular diffusion governs the rate of dissolution. If the solubility is great, an easily measurable amount of material may be dissolved by molecular diffusion, and in certain practical cases,[2] the time of the initial period may be of the order of hours and the amount of material dissolved during it, several tenths of a millimetre.

Since during the initial period, mass transport is not significantly affected by convection in the liquid, the solution kinetics are simple and hence convenient for experimental examination. For short-term or cyclic corrosion processes in viscous liquids, transient solution kinetics can be of technological importance.

With vanishingly small solubilities and diffusivities in the solute compared to those in the solvent, conservation of solute requires motion of the interface between solute and solvent in the opposite direction to the diffusion flux, making dissolution a special case of a generalized moving boundary treated earlier by Danckwerts.[3]

ANALYSIS

A solute slab A is brought into contact at zero time tith a semi-infinite bath of solvent B. The properties of the pure solute and pure solvent will be designated by subscripts A and B respectively, while the solution properties will not be subscripted. To examine this process, it proves convenient to consider three different reference frames normal to the interface and with positive direction toward the solution: (x_1) fixed with respect to undissolved solute, (x_2) fixed with respect to the

* From here on, the discussion and analysis will relate primarily to dissolution but is applicable to crystal growth.

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solution, and (x_3) fixed with respect to the interface. At time $t = 0$ the origin of all axes is the solute/solution interface and this interface is designated at later times by $x_1 = X_1$, $x_2 = X_2$ and $x_3 = X_3 = 0$.

This relationship between the x_1 and x_2 axes is determined by defining a partial volume $\overset{*}{V}$, the ratio of differential volume increase of the solution compared to the differential volume of pure solute added. As such, it is related to the more common partial molar volume $\overline{V}$ as shown:

$$\overset{*}{V}_A = \left(\frac{\partial V}{\partial V_A}\right)_{V_B,T,P} = \left(\overline{V}_A \frac{\rho_A}{M_A}\right), \tag{1}$$

where M and ρ are molecular weight and mass density.

When $\overset{*}{V}_A$ is constant * in the solution, then from eqn. (1) and recognition that X_1 is the gain of solute thickness and $-X_2$ is the gain of solution thickness,

$$X_1 \overset{*}{V}_A = X_2. \tag{2}$$

The velocity U_3 of the solution relative to interface is the rate of gain of solution thickness, i.e.,

$$U_3 = \frac{dx_3}{dt} = -\frac{dX_2}{dt}. \tag{3}$$

Throughout the solution, the one-dimensional diffusion equation applies with respect to the x_2 frame. Assuming constant diffusion coefficient D,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x_2^2} \quad (x_2 > X_2). \tag{4}$$

The appropriate boundary conditions are:

$$\text{(i) } C(0, x_2) = C_\infty, \quad \text{(ii) } C(t, \infty) = C_\infty, \quad \text{(iii) } C(t, X_2) = C_i,$$

where C_i is the interface or saturation concentration and C_∞ is the bulk or solvent concentration.

The diffusion equation applies however concentration C is measured; but it proves convenient to use volume concentration, i.e., $C = V_A/V$. A solution for the differential equation [8] satisfying the first two boundary conditions is

$$C - C_\infty = (C_0 - C_\infty)\,\mathrm{erfc}\,(x_2/2\sqrt{Dt}), \tag{5}$$

where C_0 is a constant which must be the concentration at the original interface in the x_2 frame, i.e., at $x_2 = 0$. Introducing the third boundary condition gives

$$C - C_\infty = \frac{(C_i - C_\infty)\,\mathrm{erfc}\,(x_2/2\sqrt{Dt})}{\mathrm{erfc}\,(X_2/2\sqrt{Dt})}. \tag{6}$$

* The partial volume of solute as defined in eqn. (1) can be expressed in terms of the pure solute density ρ_A, the solution density ρ, and the mass concentration of solute, $C_m = m_A/V$, by modifying the method suggested by Glasstone [4] for partial molar volume to give

$$\overset{*}{V}_A = \frac{\rho_A}{\rho + (\rho - C_m)(d\rho/dC_m)}.$$

Examination of the solution densities for a number of common salts in aqueous solution [5] and oxides in simple molten silicates [6, 7] reveals a wide range of partial volume (at least from 1·1 to 2·9), depending primarily on the ratio of solute density to solution density. For most cases, the partial volume remains constant within ±10 % for all concentrations, indicating that the assumption of constant partial volume used above may be a good approximation.

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Substituting into the diffusion equation reveals that eqn. (6) and hence eqn. (5) are solutions only if $X_2/2\sqrt{Dt}$ is constant. This assumption is made, and the constant is labelled

$$X_2/2\sqrt{Dt} = \alpha;$$

conservation of solute at the interface is used to determine X_2 and confirm the assumption. The diffusion flux density j_D at the interface is

$$(j_D)_{x_2=X_2} = -D\left(\frac{dC}{dX_2}\right)_{x_2=X_2} = \left(\frac{D}{\pi t}\right)^{\frac{1}{2}}(C_i - C_\infty)\frac{\exp -(\alpha)^2}{\operatorname{erfc}(\alpha)}. \tag{7}$$

Transport of solute relative to the interface occurs also by motion of the solution relative to the interface for which the flux density j_c at the interface is obtained using eqn. (3),

$$(j_c)_{(x_2=X_2)} = U_3 C_i = -C_i(dX_2/dt). \tag{8}$$

With concentration defined as volume concentration, the flux densities are the volume of pure solute crossing the interface per unit area per unit time. Conservation of solute requires that the rate of change of solute volume per unit area equal the net solute flux density at the interface. Thus,

$$\frac{dX_1}{dt} - C_i\left(\frac{dX_2}{dt}\right) + \left(\frac{D}{\pi t}\right)^{\frac{1}{2}}\frac{(C_i - C_\infty)}{\operatorname{erfc}(\alpha)}\exp(-\alpha)^2 = 0. \tag{9}$$

Substituting the relation between X_1 and X_2, eqn. (1) gives

$$\frac{dX_2}{dt} - \overset{*}{V}_A C_i\left(\frac{dX_2}{dt}\right) + \left(\frac{D}{\pi t}\right)^{\frac{1}{2}}\overset{*}{V}_A\frac{(C_i - C_\infty)}{\operatorname{erfc}(\alpha)}\exp(-\alpha)^2 = 0. \tag{10}$$

It is seen that the original assumption was valid because integrating eqn. (10) confirms that $X_2/2\sqrt{Dt}$ is constant and simplifications give

$$f(\alpha) \equiv \pi^{\frac{1}{2}}\alpha\operatorname{erfc}\alpha\exp\alpha^2 = -\frac{\overset{*}{V}_A(C_i - C_\infty)}{(1 - \overset{*}{V}_A C_i)}. \tag{11}$$

which allows α to be determined from curves of $f(\alpha)$ [9] or tabulation of error and exponential functions [10] when the saturation and bulk concentrations and the partial volume are known. It is clear that α depends on both $\overset{*}{V}_A C_i$ and $\overset{*}{V}_A C_\infty$. Substitution of the definitions for partial volume and concentration reveals that their product, $\overset{*}{V}_A C$, which we call $\overset{*}{C}_A$, is another type of volume concentration, the fractional volume of the solution attributed to the solute, i.e.,

$$C\overset{*}{V}_A \equiv \overset{*}{C} \equiv \ddot{V}_A/V,$$

where $\ddot{V}_A$ is the volume of the solution attributed to the solute.* As such, $\overset{*}{C}$ has approximate † limits of unity and zero, and rewriting eqn. (11) gives

$$\pi^{\frac{1}{2}}\alpha\operatorname{erfc}\alpha\exp\alpha^2 = -\frac{(\overset{*}{C}_i - \overset{*}{C}_\infty)}{(1 - \overset{*}{C}_i)}. \tag{12}$$

* Note $\overset{*}{C}$ can be obtained by multiplying any concentration expressed as quantity per unit volume by the appropriate partial volume, i.e., molar concentration and partial molar volume; mass concentration and partial specific volume; volume concentration and partial volume.

† Since $\overset{*}{V}$ can have slightly negative values at low concentration [11] it can also have values slightly above unity at high concentration.

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Once α is determined from eqn. (12) the rate of solution in terms of rate of change of solute thickness is fixed, since from eqn. (2) and the definition of α,

$$j_{(x_1=X_1)} = -\frac{dX_1}{dt} = -\left(\frac{1}{\overset{*}{V}_A}\frac{dX_2}{dt}\right) = -\left(\frac{\alpha}{\overset{*}{V}_A}\right)\left(\frac{D}{t}\right)^{\frac{1}{2}}. \tag{13}$$

Measurements of dissolution rates [2] of sapphire single crystals in molten calcium aluminium silicate have been found to be consistent with rates predicted by eqn. (13).

DISCUSSION

To illustrate the effect of the moving boundary, the rate of dissolution is calculated where movement of the solution relative to the interface is ignored, and it is assumed that only the diffusion flux contributes to dissolution. The diffusion flux density j_D is obtained for a stationary interface by substituting $X_2 = 0$, the position of the stationary boundary, into eqn. (7):

$$(j_D)_{X_2=0} = \pi^{-\frac{1}{2}}(C_i - C_\infty)(D/t)^{\frac{1}{2}}. \tag{14}$$

The quotient of eqn. (13) and (14) called λ, and given below, is a multiplying factor correcting the result obtained by ignoring the boundary motion, and thus is a measure of the importance of boundary motion to dissolution rates:

$$\lambda = -\alpha\pi^{\frac{1}{2}}/(\overset{*}{C}_i - \overset{*}{C}_\infty) \tag{15}$$

Since α is a function only of the fractional volume at saturation $\overset{*}{C}_i$, and in the bulk $\overset{*}{C}_\infty$, λ is also dependent only on these two properties. Fig. 1 shows values of λ against the interface fractional volume $\overset{*}{C}_i$. Two sets of curves are shown; the darker has bulk fractional volume $\overset{*}{C}_\infty$ as a parameter; the lighter has fractional volume difference, $\Delta\overset{*}{C} = (\overset{*}{C}_i - \overset{*}{C}_\infty)$, as the parameter. Broken lines represent regions of precipitation, and solid lines, dissolution. The curves on fig. 1 are consistent with the premise that the motion of solution relative to the interface causes two distinct effects, one related to motion at the interface and the other to motion in the bulk.

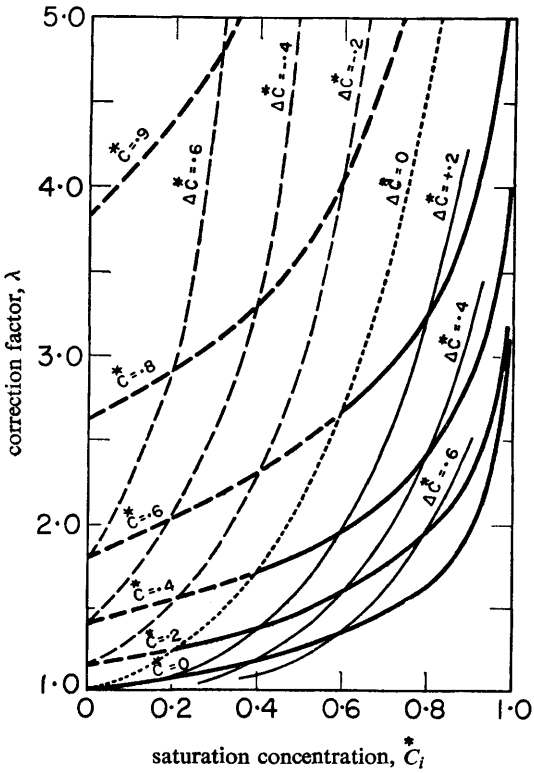

FIG. 1.—Effect of moving boundary on dissolution or growth rate of slab controlled by molecular diffusion.

At the interface the motion always transports the solute or precipitant in the same direction as the diffusion flux. Thus, it always tends to increase the rate of dissolution (or growth). For a given solution velocity relative to the interface, the amount

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of solute transported by this motion is proportional to the interface volume concentration C_i. Also, for a given rate of change of solute thickness, the solution velocity is proportional to $\overset{*}{V}_A$. Thus, with other factors fixed, i.e., $\overset{*}{C}_\infty$ or $\Delta\overset{*}{C}$, the greater the product $\overset{*}{V}_A C_i = \overset{*}{C}_i$, the greater is the effect of the motion.

Motion of the bulk solution likewise is in the same direction as the diffusion flux. Since the concentration of the interface is fixed, motion of the bulk solution always tends to increase the concentration gradient. An increase in concentration gradient decreases the diffusion flux *away* from the interface or increases the diffusion flux *towards* the interface. Thus, for dissolution, the motion of the bulk in part counteracts the effect of the added transport at the interface. The influence of the bulk motion diminishes as the negative concentration gradient, $(-\mathrm{d}C/\mathrm{d}x_2)$, or concentration differential ΔC, decreases until when $\Delta C = 0 = \Delta\overset{*}{C}$, the motion in the bulk has no effect and the curve $\Delta\overset{*}{C} = 0$ shows the correction from relative motion at the interface only. For precipitation, the change in gradient caused by motion of the bulk increases the diffusion flux toward the interface, reinforcing the correction caused by the relative motion at the interface. The amount of correction is proportional to the gradient itself; thus it continues to increase as ΔC decreases. As noted previously, the velocity of relative motion is proportional to $\overset{*}{V}$, thus the net effect from bulk motion is a function of $(\overset{*}{V}\Delta C) = \Delta\overset{*}{C}$ rather than ΔC alone.

It is clear that the influence of the moving boundary can be marked. The rate of dissolution for high saturation concentrations and the rate of exsolution or crystal growth for a wide range of conditions can be many times that estimated by ignoring relative motion and using instead the simple heat transfer case, eqn. (14). Only for materials of low solubilities (measured in terms of fractional volume) does the correction prove unimportant.

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