MELTING AND DISSOLVING DRIVEN BY
VIGOROUS COMPOSITIONAL CONVECTION

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ABSTRACT

The melting or dissolving that occurs when a binary melt is placed above a solid of a different composition is examined both theoretically and experimentally. In the case considered, the melting or dissolving is driven by vigorous compositional convection that results from a convective instability of the compositional boundary layer in the vicinity of the solid. Scaling analyses are presented that yield theoretical expressions for the interfacial velocities in four distinct physical regimes. These expressions are then confirmed using laboratory experiments in which ice and wax are overlain by hot aqueous solutions. The experiments also demonstrate that, for vigorous convection to occur, the unstable compositional buoyancy needs to be at least twice the stabilizing thermal buoyancy.

INTRODUCTION

Both the melting and the dissolving of solids in fluids are fundamental physical phenomena which are encountered daily. Melting occurs when the temperature of the fluid is significantly greater than the melting temperature of the solid, and is controlled by thermal diffusion. In contrast, dissolving occurs at relatively lower fluid temperatures, and is due to chemical disequilibrium between the solid and fluid. It is controlled by compositional diffusion and will continue for as long as the fluid remains above its freezing temperature.

In the special case where both the thermal and compositional fields in the fluid are gravitationally stable, fluid mechanics does not play a role, and the rate at which either melting or dissolving occurs can be determined analytically. Often however, either or both of the thermal and compositional fields will be unstable and convection will result. Convection invariably enhances the rate of melting or dissolving by assisting the transfer of heat and composition to the solid. In this paper, I summarize some scaling theories and experiments (Kerr 1994a,b) that have quantified this rate in the one-dimensional cases of melting or dissolving driven by vigorous compositional convection.

DISSOLVING

Consider the dissolving of a solid of composition C_s, melting temperature T_m and far-field temperature T_s, overlain by a fluid with a composition C_f and temperature T_f. If the volume of fluid is large, the far-field conditions will not change, and it is expected that the solid dissolves at a constant velocity V. The resulting thermal and compositional profiles are shown in figure 1 and illustrated on a typical phase diagram in figure 2. At the interface between the solid and the fluid, the temperature T_i and composition C_i are constrained thermodynamically to lie on the liquidus curve

$$T_i = T_L(C_i), \qquad (1)$$

which gives the freezing temperature of the fluid as a function of concentration. Within the solid, the temperature is given by

$$T(z) = T_s + (T_i - T_s)e^{-Vz/\kappa_s} , \qquad (2)$$

where κ_s is the thermal diffusivity of the solid.

There are compositional and thermal boundary layers immediately adjacent to the interface. If the respective fluxes to the interface through these layers are F_C and F_T, the effective layer thicknesses can be defined by

$$F_C = \frac{D(C_f - C_i)}{h_C} \text{ and } F_T = \frac{k_f(T_f - T_i)}{h_T},$$
$$(3a,b)$$

where D and k_f are the compositional diffusivity and thermal conductivity of the fluid. If the volume change associated with the phase change is neglected (c.f. Woods 1992), the boundary layer fluxes are also linked to the dissolving rate V by the interfacial conditions

$$F_C = V(C_i - C_s) \text{ and } F_T = V(\rho_s L_s + \rho_s c_s (T_i - T_s)), \tag{4a, b}$$

where ρ_s, L_s and c_s are the density, latent heat and specific heat of the solid.

The aim is to use scaling theory to determine V in the case where dissolving of the solid leads to vigorous compositional convection, a situation which will occur if the density ρ_i of the fluid at the interface is sufficiently less than the density ρ_f of the far-field fluid. I assume that the interface between the solid and the fluid is flat, and that the unstable compositional buoyancy released at the interface dominates the stabilizing thermal buoyancy; i.e. that the ratio $\mathcal{R}$ of these buoyancies satisfies the condition:

$$\mathcal{R} \equiv \frac{\beta(C_f - C_s)}{\alpha[\rho_s L_s + \rho_s c_s (T_i - T_s)]/\rho_f c_f} \gg 1, \tag{5}$$

where α is the coefficient of thermal expansion and β is the equivalent coefficient for the variation of density with composition.

Accordingly, it is envisaged both the compositional and thermal boundary layers growing diffusively with time t:

$$h_C \sim \sqrt{Dt}, \quad h_T \sim \sqrt{\kappa_f t}, \tag{6a, b}$$

where c_f and $\kappa_f \equiv k_f/\rho_f c_f$ are the specific heat and thermal diffusivity of the fluid, until a time τ when the buoyant compositional boundary layer undergoes a Rayleigh-Bénard type of instability that drives vigorous compositional convection. Instability can be expected when the Rayleigh number Ra of this boundary layer reaches a critical value Ra_c:

$$Ra_c = \frac{g(\rho_f - \rho_i)h_C^3}{D\mu_f}, \tag{7}$$

where g is the acceleration due to gravity and μ_f is the fluid viscosity. I therefore obtain the estimates:

$$h_C = \left(\frac{Ra_c D \mu_f}{g(\rho_f - \rho_i)}\right)^{1/3}, \quad h_T = h_C \left(\frac{\kappa_f}{D}\right)^{1/2},$$

$$\tau \approx \left(\frac{Ra_c^2 \mu_f^2}{D g^2 (\rho_f - \rho_i)^2}\right)^{1/3}. \tag{8a, b, c}$$

Substitution of (8a) and (3a) into (4a) then yields the prediction that the dissolving velocity

$$V = \left(\frac{g(\rho_f - \rho_i)D^2}{Ra_c \mu_f}\right)^{1/3} \left(\frac{C_f - C_i}{C_i - C_s}\right), \tag{9}$$

while combining (9), (8b), (3b), (4b) and (1) shows that

$$T_f - T_L(C_i) =$$

$$\frac{\rho_s L_s + \rho_s c_s (T_L(C_i) - T_s)}{\rho_f c_f} \left(\frac{D}{\kappa_f}\right)^{1/2} \left(\frac{C_f - C_i}{C_i - C_s}\right). \tag{10}$$

From the above analysis, it is concluded that the dissolving rate is given by (9), once C_i is evaluated from (10). I also note that $Ra_c^{-1/3}$ is equivalent to the constant γ in the semi-empirical expression $Nu = \gamma Ra^{1/3}$ that relates the Nusselt number to the Rayleigh number.

In the above analysis, it has been implicitly assumed that the distance $\sqrt{D\tau}$ over which compositional diffusion occurs is large in comparison with the distance $V\tau$ that the solid has dissolved in the time τ for instability. From (8a), (8c) and (9), it is found that

$$V\tau \approx \frac{h_C}{\mathcal{C}} \tag{11}$$

where

$$\mathcal{C} \equiv \frac{C_i - C_s}{C_f - C_i}. \tag{12}$$

Equations (9) and (10) are therefore asymptotically correct when $\mathcal{C} \gg 1$. If $\mathcal{C}$ is smaller however (i.e. $\mathcal{C} \gtrsim 1$), then (11) suggests that h_C is more accurately estimated by

$$h_C = \left(\frac{Ra_c D \mu_f}{g(\rho_f - \rho_i)}\right)^{1/3} \left(1 + \frac{1}{\mathcal{C}}\right), \tag{13}$$

which results in V and $T_f - T_i$ being given by:

$$V = \left(\frac{g(\rho_f - \rho_i)D^2}{Ra_c \mu_f}\right)^{1/3} \left(\frac{C_f - C_i}{C_f - C_s}\right) \equiv \frac{\mathcal{V}}{Ra_c^{1/3}}, \tag{14}$$

and

$$T_f - T_i(C_i) =$$

$$\frac{\rho_s L_s + \rho_s c_s (T_L(C_i) - T_s)}{\rho_f c_f} \left(\frac{D}{\kappa_f}\right)^{1/2} \left(\frac{C_f - C_i}{C_f - C_s}\right). \tag{15}$$

However, when $\mathcal{C} \ll 1$, the compositional profile becomes very nonlinear, equation (3a) is no longer accurate, and a new scaling analysis is required.

MELTING

During the melting of a solid (figure 3), compositional diffusion can be neglected in comparison to thermal diffusion, so that there is a sharp step in the compositional profile (figure 4). In the case where melting of the solid leads to vigorous compositional convection, a thin boundary layer of buoyant melt is envisaged that continually grows and periodically detaches to drive this convection. The timescale τ and wavelength λ for exponential growth of the fastest growing linear Rayleigh-Taylor instabilities to this buoyant layer are given by

$$\tau = P\left(\frac{\mu_f}{\mu_m}\right) \frac{\mu_m}{g h_m (\rho_f - \rho_m)} \text{ and } \lambda = Q\left(\frac{\mu_f}{\mu_m}\right) \pi h_m, \tag{16}$$

where h_m is the thickness of this layer, μ_m and ρ_m are the viscosity and density of the melt, and P and Q are known functions of $\frac{\mu_f}{\mu_m}$ (Kerr 1994a).

The typical thickness of the melt layer can be predicted from the argument that the time to grow the melt layer, h_m/V, must be comparable to the timescale, τ, of the gravitational instabilities that drain the layer and drive the overlying compositional convection. This argument leads to the estimates

$$\tau \sim \left(\frac{P\mu_m}{gV(\rho_f - \rho_m)}\right)^{1/2} \qquad (17)$$

and

$$h_m \sim \left(\frac{PV\mu_m}{g(\rho_f - \rho_m)}\right)^{1/2}. \qquad (18)$$

In the typical time given by (17), heat is conducted to the interface from a fluid layer of thickness

$$h_T \sim \sqrt{\kappa_f \tau} \sim \left(\frac{P\mu_m \kappa_f^2}{gV(\rho_f - \rho_m)}\right)^{1/4}. \qquad (19)$$

For the moment I shall assume that

$$h_T \gg h_m \frac{k_f}{k_m}, \qquad (20)$$

where k_m is the thermal conductivity of the melt, so that an accurate estimate of the heat flux from the fluid to the interface is

$$F \approx \frac{k_f(T_f - T_m)}{h_T}. \qquad (21)$$

The heat flux F is linked to the melting rate V by the interfacial condition

$$F = V(\rho_s L_s + \rho_s c_s(T_m - T_s)). \qquad (22)$$

Substitution of (19) and (21) into (22) yields the prediction that the melting velocity

$$V \sim \left(\frac{g(\rho_f - \rho_m)\kappa_f^2}{P\mu_m \mathcal{S}^4}\right)^{1/3}, \qquad (23)$$

where the Stefan number $\mathcal{S}$ is defined by

$$\mathcal{S} = \frac{\rho_s L_s + \rho_s c_s(T_m - T_s)}{\rho_f c_f(T_f - T_m)}. \qquad (24)$$

Using (23), τ and h_m can be estimated from (17) and (18) as

$$\tau \sim \left(\frac{P^2 \mu_m^2 \mathcal{S}^2}{g^2(\rho_f - \rho_m)^2 \kappa_f}\right)^{1/3} \qquad (25)$$

and

$$h_m \sim \left(\frac{P\mu_m \kappa_f}{g(\rho_f - \rho_m)\mathcal{S}^2}\right)^{1/3}. \qquad (26)$$

It can then be shown that our assumption that compositional diffusion can be neglected in the compositional boundary layer, which requires that $\tau \ll h_m^2/D$, is satisfied if

$$\mathcal{S} \ll \left(\frac{\kappa_f}{D}\right)^{1/2}. \qquad (27)$$

In dimensional terms, (27) is equivalent to

$$T_f - T_m \gg \frac{\rho_s L_s + \rho_s c_s(T_m - T_s)}{\rho_f c_f}\left(\frac{D}{\kappa_f}\right)^{1/2}, \qquad (28)$$

a quantitative result that shows that a sufficiently large superheat is required for melting to occur rather than dissolving.

Using (26), it can also be shown that the assumption expressed by (20) is equivalent to $\mathcal{S} \gg \frac{k_f}{k_m}$, which is not surprising since the latent heat to form a melt layer of thickness h_m is derived from the overlying fluid layer of thickness h_T. For somewhat smaller $\mathcal{S}$ ($\gtrsim \frac{k_f}{k_m}$), h_m cannot be neglected in comparison with h_T in estimating F, and F and V are more accurately given by:

$$F \approx \frac{(T_f - T_m)}{\frac{h_T}{k_f} + \frac{h_m}{k_m}} = \frac{k_f(T_f - T_m)}{h_T}\left(1 + \frac{k_f}{k_m \mathcal{S}}\right)^{-1} \qquad (29)$$

and

$$V \propto \mathcal{V} \equiv \left(\frac{g(\rho_f - \rho_m)\kappa_f^2}{P\mu_m \mathcal{S}^4}\right)^{1/3}\left(1 + \frac{k_f}{k_m \mathcal{S}}\right)^{-1}. \qquad (30)$$

Finally, if $\mathcal{S} \ll \frac{k_f}{k_m}$, then the temperature profile is very nonlinear, equation (29) is no longer accurate, and a new scaling analysis is required.

EXPERIMENTS

In order to test the above scaling analyses, several series of laboratory experiments were performed in which either ice or a water-soluble polyethylene glycol wax (PEG 600) was melted or dissolved by overlying dense aqueous solutions. Figure 3 shows a photograph of one of the melting experiments, in which plumes of buoyant melted wax stream away from a flat interface and drive vigorous compositional convection in the overlying hot fluid. Observations taken from videos confirmed that vigorous convection resulted in an interfacial velocity that was constant for both melting and dissolving. Using experiments in which ice was melted, the critical value of the buoyancy ratio $\mathcal{R}$ required for vigorous compositional convection was found to be about 2.0.

In figures 5 and 6, the measured interfacial velocities for melting and dissolving an ice floor are compared with the respective theoretical expressions (30) and (14). In both figures, the collapse of the data onto a straight line provides strong support for the scaling laws.

REFERENCES

KERR, R.C. 1994a Melting driven by vigorous compositional convection. *J. Fluid Mech.* **280**, 255–285.

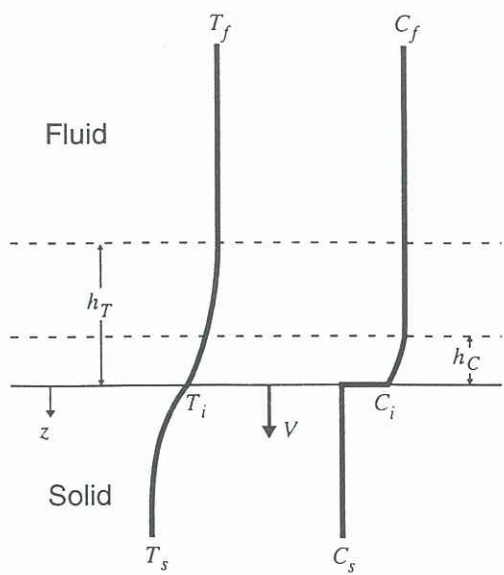KERR, R.C. 1994b Dissolving driven by vigorous compositional convection. *J. Fluid Mech.* **280**, 287–302.

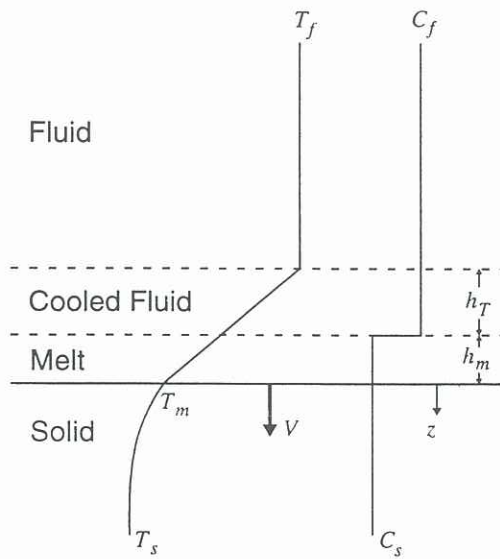Figure 1: The thermal and compositional profiles when a solid dissolves into a fluid at velocity V.
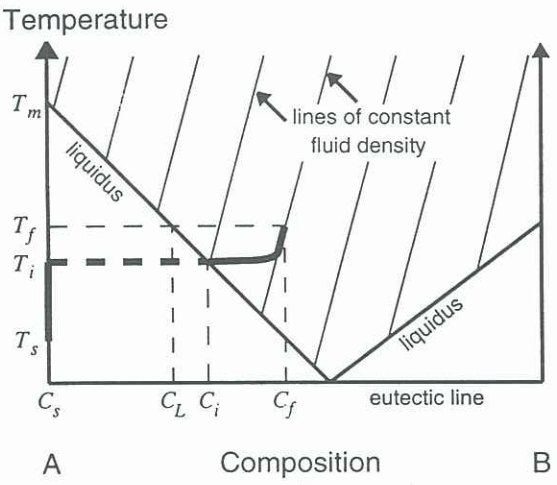

Figure 2: The path on a simple phase diagram of the thermal and compositional profiles shown in figure 1. The dotted portion of the path represents the jump in composition at the dissolving interface.
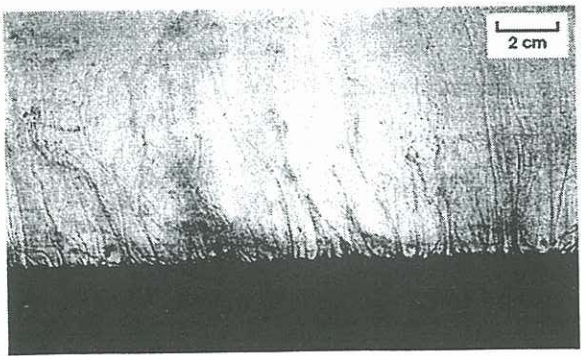

Figure 3: Photograph of a wax floor that is melting underneath a hot, dense aqueous solution of $NaNO_3$.
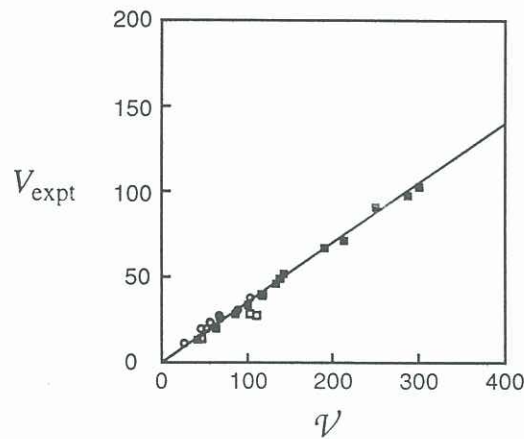

Figure 4: Schematic diagram of the envisaged intermediate layers of melted solid and cooled fluid during the melting at velocity V, driven by vigorous compositional convection, of a solid that is in contact with a hot fluid.

Figure 5: The melting velocities V_{expt} (in $\mu m\ s^{-1}$) in comparison with the velocity scale $\mathcal{V}$ defined in (30).
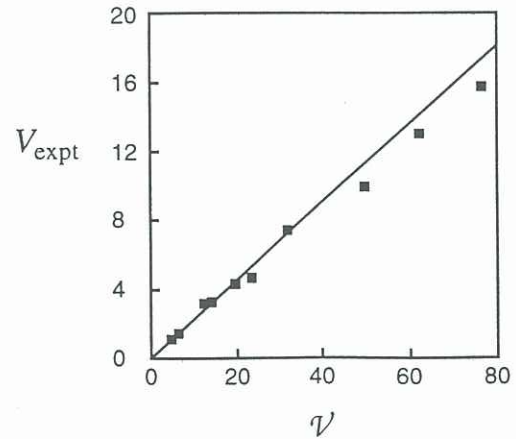

Figure 6: The dissolving velocities V_{expt} (in $\mu m\ s^{-1}$) in comparison with the velocity scale $\mathcal{V}$ defined in (14).