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THE FREEZING OF FINITE DOMAIN AQUEOUS SOLUTIONS: SOLUTE REDISTRIBUTION

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Abstract—An analysis of the unidirectional freezing of finite domain aqueous solutions during cooling at subzero temperatures is presented. Under conditions where the solute is completely rejected by the advancing ice front, the conventional diffusion equation is invalid and suitable transport expressions can only be obtained by an appropriate variable transformation from the laboratory frame of reference where the volume of the liquid region varies with time to a "solute-fixed" frame of reference where the volume of the liquid region remains constant (Levin *et al.* [34]). Such an analysis results in a nonlinear parabolic partial differential diffusion equation in the laboratory frame with a spatially and time varying effective convective velocity term in addition to the usual time and spatial derivative terms. The analysis is valid at both short and long times and also for both ideal, dilute and non-ideal, non-dilute solutions. Additional approximations are made only to the extent that the liquid–solid interface is assumed to remain planar and that the system is assumed to remain in thermal equilibrium during the freezing process. Generalized results are obtained for initially ideal, dilute aqueous solutions cooled at various rates on one boundary by standard numerical methods. These results indicate that non-uniform concentration profiles can exist within the liquid region of systems during freezing and that the variation with time/temperature of the volumes of the liquid and solid regions is significantly affected by the non-uniform distribution of solutes. Our results also indicate that under certain circumstances (e.g. fast cooling rates) that the solidification process may be limited by mass transfer considerations, that is, by the ability of the solutes to diffuse away from the interface, rather than solely by the heat-transfer considerations of whether or not the sensible and latent heats can be removed.

NOMENCLATURE

A,	area;
B,	cooling/warming rate;
c,	molar concentration;
D,	diffusion coefficient;
E,	apparent activation energy;
k,	thermal conductivity;
L,	latent heat of fusion;
l,	length;
R,	gas constant;
$\mathscr{S}$,	length;
T,	temperature;
t,	time;
V,	volume;
v,	velocity;
$\bar{v}$,	apparent molar volume;
x,	mole fraction;
y,	position.

Greek symbols

γ,	activity coefficient;
η,	viscosity;
ν,	number of species per molecule;
ρ,	density;
ϕ,	volume fraction.

Superscript

s,	solute-fixed frame of reference;
V,	volume-fixed frame of reference;
$\hat{}$,	non-dimensional.

Subscript

EQ,	equilibrium;
EUT,	eutectic;
f,	freezing;
i,	initial;
L,	liquid;
LSI,	liquid–solid interface;
m,	melting;
S,	solid;
s,	solute or solute-fixed frame of reference;
w,	water;
y,	position;
∞,	final.

INTRODUCTION

THE SOLIDIFICATION and melting of common substances such as water and ice, the casting and zone-refining of metals, the production of frozen foods, and the projected use of latent heat-of-fusion energy storage devices are some typical examples of the multitude of engineering situations involving heat and mass transfer in systems experiencing a phase transformation. The essential and common features of these systems is that an interface exists which separates two

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regions possessing greatly different thermodynamic, chemical and physical properties and that the position of the interface is neither fixed in space nor is its motion known *a priori*. Analyses of these phenomena therefore usually involve the simultaneous solution of heat- and mass-transfer equations subject to boundaries whose positions vary with time. Accordingly, many references to moving boundary problems exist in the literature [1–5].

As has recently been pointed out by Sparrow *et al.* [6], the standard model for freezing, and with appropriate changes of wording for thawing, envisions a liquid which is initially at a uniform temperature equal to or greater than its fusion temperature. Then, at a specified instant of time, a cooling process is initiated at the external surface of the system which causes freezing to begin once the surface temperature is below the fusion point. The freezing front then propagates into the liquid with the liquid–solid interface at the fusion temperature. The "sensible heat" of the solid and the "latent heat" released by the freezing process are transported through the frozen layer by conduction and rejected to the environment. If the remaining portion of the liquid is above the fusion temperature, then the "sensible heat" of the liquid will also be transported to the interface by conduction and thence to the solid and the environment. Depending upon the exact circumstances, heat and mass may also be transported by convection within the liquid region.

If the liquid is a multicomponent solution rather than a pure substance, then the above scenario must be modified to include the effects associated with alterations in the fusion temperature and the partitioning of the solutes between the solid and the liquid regions. For systems where the slopes of the solidus and liquidus curves are negative, the presence of solutes lowers the equilibrium freezing point of the solution and the equilibrium distribution coefficient takes a value of from zero, corresponding to the complete rejection of the solutes by the solid phase, to one, corresponding to the complete incorporation of the solutes into the solid phase. If the equilibrium distribution coefficient is less than unity, then some solute will be rejected by the advancing liquid–solid interface causing further lowering of the freezing point. The rejected, unincorporated solute will form a solute rich layer in the liquid region immediately adjacent to the interface due to its relative inability to diffuse into the interior portions of the liquid region. This phenomenon is termed "concentration polarization" and sometimes gives rise to interface instabilities due to the "constitutional supercooling" of the remaining portions of the liquid region of the system (see Appendix).

In multicomponent solutions, continued growth of the solid phase will therefore depend not only upon the ability to remove the latent heat of fusion and the sensible heats of the liquid and solid regions, as is the case for a pure substance when no solutes are present, but also upon the ability of the solutes in the liquid phase to diffuse away from the interface, thereby permitting the solvent to gain access to the solid phase. This is especially true for aqueous solutions where the solutes are usually completely rejected by the ice and where the ratio of the thermal diffusivity of the ice to the thermal diffusivity of the remaining liquid is approximately 10 and the ratio of the thermal diffusivity to the mass diffusivity in the liquid is approximately 100. Hence, under certain circumstances, the solidification process for multicomponent solutions may be rate-limited by mass-transfer considerations, that is, by the ability of the solutes to diffuse away from the interface and for the solvent to diffuse towards the interface, rather than solely by the heat-transfer considerations of whether or not the latent and sensible heats can be removed.

Because of this coupling of heat- and mass-transfer considerations, it is necessary in solving such problems to determine the spatial and time dependence of the temperature and concentration fields and the manner and rate at which the interface will move. It is therefore not surprising to find that most investigators have limited themselves to analyses of the freezing and thawing of pure substances where it is only necessary to solve for the temperature profiles and the interface position and not for the solute concentration profiles. Even so, only a few analytical solutions exist, with the most notable being those of Neumann (see [7]) and Stefan (see [8]) who considered the freezing and melting of pure substances initially as the fusion temperature. For other problems, however, either numerical (for review, see [9]), or approximate analytical (for review, see [10]) methods have had to be employed. Specifically, for the more complicated case of the solidification of multicomponent solutions, a number of different approaches have been taken; (1) well-mixed liquid region approximation [11–19]; (2) constant interface velocity approximation [20–24]; and (3) fully coupled heat and mass-transfer analysis [25–28].

However, despite these numerous studies, the only general finite domain analyses which are valid over the entire domain of time are those for pure substances and well-mixed liquid region multicomponent solutions [10, 14, 17, 30–32]. Investigators* of the fully coupled solidification problem for multicomponent systems have limited themselves to a discussion of the transients occurring at relatively short times where the long time effects of the finiteness of their systems can be neglected [28].

The purpose of this study is therefore to present a generalized analysis of the unidirectional freezing of finite domain aqueous solutions under conditions where the solute is completely rejected by the advanc-

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* It should be noted that some investigators of multicomponent solidification phenomena either consciously model their finite systems as being semi-infinite in extent [24, 25] or give the impression that they are modeling closed systems of finite extent by defining a fixed reference volume [26].

ing ice front. The analysis is valid at both short and long times and also for both ideal, dilute and nonideal, non-dilute solutions. Approximations are made only to the extent that the system remains in the thermal equilibrium with its environment during the freezing process; and that the liquid–solid interface remains planar in spite of the fact that the solution in front of the advancing ice front might be "constitutionally supercooled" (see Appendix). Generalized results are obtained by standard numerical methods for initially, dilute aqueous solutions of uniform composition being cooled at various rates on one boundary while the temperature of the other boundary is held constant.

FORMULATION

General thermodynamic considerations

Although most aqueous solutions common to industrial and biological processes are multicomponent and electrolytic, the studies of Levin *et al.* [33–36] have shown that at subzero temperatures, the behavior of multicomponent electrolytic solutions mimic the behavior of pseudobinary solutions consisting of a single solvent, *w* (water), and a single solute, *s*. Consequently, as a typical example, let us consider the case of initially dilute electrolyte (NaCl, KCl, etc.) and non-electrolyte (glycerol, ethylene glycol, etc.) solutions which upon freezing form a pure ice solid from which the solute is completely rejected. Unlike the case for pure water, these types of solutions do not possess a single unique equilibrium freezing (melting) temperature, T_f, but a loci of equilibrium freezing (melting) temperatures which depend upon the instantaneous composition of the solutions. Mathematically, this concentration–temperature relationship is given by the following expression [37]:

$$v c_{sEQ}(T_f) \simeq \frac{L_w(T_{fw} - T_f)}{\bar{v}_w R T_{fw}^2} \tag{1}$$

where c_{sEQ} is the solute concentration, v is the number of species per dissociated solute molecule, L_w is the molar latent heat of fusion for pure water, T_{fw} is the equilibrium freezing (melting) temperature of pure water at 1 atm (273.15 K), and $\bar{v}_w$ is the partial molar volume of water. Using typical values of $L_w \sim 6000$ J/mol, $\bar{v}_w = 18\ \text{cm}^3/\text{mol}$ and $R = 8.314$ J/mol K [38], this expression for the "equilibrium" concentration–temperature relationship can be re-written as:

$$c_{sEQ}(T_f) = \frac{-(T_f - T_{fw})}{1.86\,v}\frac{\text{mol/l}}{\text{K}}. \tag{2}$$

Focusing our attention upon the cooling of a finite volume of solution having an initial uniform composition $c_{s_i}(c_{s_i} < c_{sEUT})$ and at an initial uniform temperature T_i above its equilibrium freezing temperature $T_{f_i}(c_{s_i})$, then the system will remain entirely liquid until the temperature T_{f_i} is reached. If we then assume that ice nucleates, the freezing process will begin and solute will be rejected by the advancing ice front. Now as long as the solid phase consists of pure ice, the number of moles of solute N_s in the liquid region of the system will remain constant for all time. Consequently, under equilibrium conditions and at temperatures $T > T_{EUT}$

$$N_s = c_{s_f} V_L = \text{constant} \tag{3}$$

or, from equation (2),

$$\left.\frac{V_L(T_f)}{V_i}\right|_{EQ} = \frac{c_{s_i}}{c_{sEQ}(T_f)} = \frac{T_{f_i} - T_{f_x}}{T_f - T_{f_w}} \tag{4}$$

where $V_L(T_f)|_{EQ}$ is the "equilibrium" liquid region volume at the liquid–solid interface temperature T_f and V_i is the initial liquid volume of the system. The "equilibrium" volume of the remaining liquid portion of a finite domain system in which the solute is completely rejected by the advancing liquid–solid interface is thus inversely proportional to the equilibrium solution composition and/or the equilibrium liquid–solid interface temperature. Continued lowering of the temperature will result in the progressive growth of the ice phase $\{V_S = (\rho_w/\rho_s)\cdot(V_i - V_L)\}$ until the eutectic temperature is reached at which time the remaining liquid will begin to solidify at a uniform composition, c_{sEUT}.

Transport expressions

The expression given above relating the total liquid volume to the liquid region composition and/or liquid–solid interface temperature (4) is valid only for the equilibrium situation where the liquid region composition is uniform, that is, in the absence of concentration gradients. However, as was also mentioned above, nonuniform concentration profiles are expected to exist within multicomponent systems during solidification. Consequently, for multicomponent solutions which change in volume during solidification due to the removal of solvent but which remain fixed with respect to the initial amount of solute

$$N_s = c_{s_i} V_i = \int_{V(t)} c_s(\mathbf{r}, t)\,d\mathbf{r} = \text{constant} \tag{5}$$

where the solute concentration c_s is now a function of position and time. Mass and heat transport expressions are therefore needed to describe the concentration–temperature–time behavior of such systems. Now Levin *et al.* [34, 35] have shown that the conventional diffusion equation is invalid under these conditions and that suitable transport expressions can only be obtained by an appropriate variable transformation from the laboratory frame of reference where the volume of the liquid region of the system varies with time to the solute-fixed frame of reference where the volume of the liquid region of the system remains constant.

Consequently, let us define a modified scale of length, y_s, such that equal increments of y_s contain equal increments of unit basic volume of solute per unit area:

$$dy_s = \phi_s dy \tag{6}$$

where $\phi_s(y, t)$ is the volume fraction of solute in the laboratory-fixed reference frame. In the solute-fixed reference frame, the water and solute concentrations must be expressed, respectively, as the amount of w and s per unit basic volume of solute:

$$c_w^s = \frac{c_w}{\phi_s},\ c_s^s = \frac{c_s}{\phi_s} = \frac{1}{\bar{v}_s} = \text{constant} \qquad (7)$$

where c_w^s and c_s^s are, respectively, the solvent and solute concentrations in the solute-fixed frame of reference, c_w and c_s are, respectively, the solvent and solute concentrations in the laboratory-fixed frame of reference, and $\bar{v}_w$ and $\bar{v}_s$ are, respectively, the apparent molar volumes of the solvent and the solute (assumed constant). Since by definition

$$\phi_w = \bar{v}_w c_w,\ \phi_s = \bar{v}_s c_s \qquad (8)$$

where ϕ_w is the water fraction in the laboratory frame and

$$\phi_w + \phi_s = 1 \qquad (9)$$

from equations (7)–(9), it can be shown that

$$\bar{v}_w \mathrm{d}c_w + \bar{v}_s \mathrm{d}c_s = 0 \qquad (10)$$

$$\phi_w^s = 1/\phi_s - 1 \qquad (11)$$

and

$$\mathrm{d}c_w^s = \frac{1}{\phi_s^2}\mathrm{d}c_w. \qquad (12)$$

The continuity equations in the solute-fixed frame for the liquid region of the system therefore take the form [34]

$$\frac{\partial c_s^s}{\partial t} = 0 \qquad (13a)$$

and

$$\frac{\partial c_w^s}{\partial t} + \mathbf{\nabla}_{y_s} \cdot \mathbf{J}_w^s = 0 \qquad (13b)$$

where $\mathbf{J}_w^s$ is the molar flux of solvent in the solute-fixed frame. Now Crank [9] has shown that

$$\mathbf{J}_w^s = \frac{1}{\phi_s}\mathbf{J}_w \qquad (14)$$

where $\mathbf{J}_w$ is the flux of solvent in the laboratory fixed frame

$$\mathbf{J}_w = -D^V \frac{\partial c_w}{\partial y} \qquad (15)$$

and $D^V(c_s, T)$ is the effective diffusivity in the laboratory fixed frame [9, 34]

$$D^V = \left(1 + \frac{\partial \ln \gamma_s}{\partial \ln x_s}\right)\frac{\eta_w}{\eta} D_{sw}(T) \qquad (16)$$

such that the term $(1 + \partial \ln \gamma_s/\partial \ln x_s) \cdot (\eta_w/\eta)$ represents the effects of solution non-ideality and viscosity and the term $D_{sw}(T)$ represents the effect of temperature on the overall diffusivity

$$D_{sw}(T) = D_m^V \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad (17)$$

where T_m is the initial equilibrium freezing (melting) temperature T_{f_i} and D_m^V is the value of the volumetric diffusivity for an ideal, dilute solution at temperature T_m.

Consequently on the basis of the above relationships, equations (6), (12), (14) and (15), the continuity equation for the solvent, equation (13b), can be rewritten as

$$\frac{1}{\phi_s^2}\frac{\partial c_w}{\partial t} + \frac{\partial}{\phi_s \partial y}\left(-\frac{D^V}{\phi_s}\frac{\partial c_w}{\partial y}\right) = 0 \qquad (18)$$

or, employing equations (7)–(9), as

$$\frac{\partial c_s}{\partial t} = \frac{\partial}{\partial y}\left(D^V \frac{\partial c_s}{\partial y}\right) + v_y \frac{\partial c_s}{\partial y} \qquad (19)$$

where

$$v_y = -\frac{D^V}{c_s}\frac{\partial c_s}{\partial y}\bigg|_y \qquad (20)$$

is the effective convective velocity in the laboratory frame and $0 \leqslant y \leqslant l(t)$ such that

$$l(t) = l_i + \int_0^t v_{LSI}\,\mathrm{d}t \qquad (21)$$

is the size of the system at any time t, l_i is the initial size of the system and v_{LSI} is the effective convective velocity at the liquid–solid interface, $y = l(t)$, or more appropriately, the thermodynamically induced solvent volume flux out of the liquid region and into the solid region.

The initial and boundary conditions corresponding to this situation are

(1) At $t = 0$, $c_s = c_{s_i}$ for $0 \leq y \leq l_i$ (22)

(2) For $t > 0$,

(a) $\dfrac{\partial c_s}{\partial y} = 0$ at $y = 0$ (23a)

(b) $c_s = c_{sEQ}(T_{LSI})$ at $y = l(t)$ (23b)

where $c_{sEQ}(T_{LSI})$ is the "equilibrium" solute concentration at the liquid–solid interface temperature, T_{LSI} [see (2) and (27)].

Turning our attention now to the analogous heat transfer problem, for aqueous solutions the ratio of the thermal diffusivity of pure ice (1.26×10^{-2} cm²/s) to the thermal diffusivity of water (1.33×10^{-3} cm²/s) is approximately 10 (HCP, 1978). Furthermore, the ratio of the thermal diffusivity of water to the mass diffusivity of low molecular weight solutes in water ($\sim 1 \times 10^{-5}$ cm²/s at 0°C) is approximately 100. For computational ease we will therefore limit ourselves to situations where our system can be assumed to remain in thermal equilibrium with its environment. Consequently, the temperature profiles within the liquid and solid regions are of the form

$$T_L = T_0 + (T_{LSI} - T_0)(y/l) \qquad \text{for } 0 \le y \le l \quad (24a)$$

$$T_S = T_{LSI} + (T_E - T_{LSI})(y - l)/\mathscr{S}$$

$$\text{for } l \le y \le l + \mathscr{S} \quad (24b)$$

where

$$\mathscr{S}(t) = \frac{\rho_w}{\rho_S}(l_i - l(t)) \qquad (25)$$

is the thickness of the solid region

$$T_0 = T_i = \text{constant} \qquad (26a)$$

is the system temperature at the boundary $y = 0$

$$T_E = T_i + Bt \qquad (26b)$$

is the system temperature at the boundary $y = i + \mathscr{S}$, B is the cooling/warming rate at the boundary $y = l + \mathscr{S}$, and

$$T_{LSI} = \frac{\dfrac{k_S}{\mathscr{S}} T_E + \dfrac{k_L}{l} T_0 - \rho_w L_w v_{LSI}}{\dfrac{k_S}{\mathscr{S}} + \dfrac{k_L}{l}} \qquad (27)$$

is the system temperature at the liquid–solid interface such that k_S and k_L are, respectively, the thermal conductivities of the solid and liquid regions. This last expression for T_{LSI} is based upon the fact that at the liquid–solid interface, the heat flux within the solid is equal to the heat flux within the liquid plus the amount of heat liberated as a result of the phase change occurring at the interface

$$-k_S \left.\frac{\partial T_S}{\partial y}\right|_{LSI} = -k_L \left.\frac{\partial T_L}{\partial y}\right|_{LSI} - \rho_w L_w v_{LSI}. \qquad (28)$$

Although the above relationships, equations (19)–(27), form a complete set of mathematical expressions, solution of this problem is facilitated by transforming these expressions from the laboratory-fixed frame of reference, where a boundary condition at a moving interface must be specified, equation (23b), back to the solute-fixed frame of reference where the position of the liquid–solid interface remains stationary [34, 35]. Using equations (8)–(12), it can be shown that the analogous mass-transfer equation in the solute-fixed frame of reference takes the form

$$\frac{\partial c_w^s}{\partial t} = \frac{\partial}{\partial y_s}\left(D^s \frac{\partial c_w^s}{\partial y_s}\right) \qquad (29)$$

where

$$0 \le y_s \le l_s = \phi_{s_i} l_i = \text{constant} \qquad (30)$$

and D^s is the effective diffusivity in the solute-fixed of reference

$$D^s = \phi_s^2 D^V. \qquad (31)$$

The initial and boundary conditions in the solute-fixed frame of reference are:

$$(1) \qquad t = 0,\ c_w^s = c_{wi}^s \ \text{ for all } |y_s| \le l_s \qquad (32)$$

$$(2) \qquad t > 0,\ \frac{\partial c_w^s}{\partial y_s} = 0 \quad \text{at } y_s = 0 \qquad (33a)$$

$$c_w^s = c_{wEQ}^s(T_{LSI}) \quad \text{at } y = l_s \qquad (33b)$$

where

$$c_{wEQ}^s = \frac{1}{\bar{v}_w}\left(\frac{1.86\nu}{\bar{v}_s(T_{f_w} - T)} \frac{\text{K}}{\text{mol/l}} - 1\right) \qquad (34)$$

Non-dimensionalization

These equations can be non-dimensionalized in following manner. If we define

$$\hat{y}_s = y_s/l_s, \quad \hat{y} = y/l_i \qquad (35)$$

then since $l_s = \phi_{s_i} l_i$,

$$\mathrm{d}\hat{y}_s = \frac{\phi_s}{\phi_{s_i}} \mathrm{d}\hat{y}. \qquad (36)$$

Furthermore if we define a non-dimensional time $\hat{t}$ and a nondimensional temperature $\hat{T}$ such that

$$\hat{t} = \frac{D_m^V}{l_i^2}(t - t_m) \qquad (37)$$

and

$$\hat{T} = \frac{T - T_m}{T_i - T_m} \qquad (38)$$

then the governing mass-transfer equation, equation (29), takes the form

$$\frac{\partial \phi_w^s}{\partial \hat{t}} = \frac{\partial}{\partial \hat{y}_s}\left(\frac{\phi_s^2}{\phi_{si}^2} D_T \frac{\partial \phi_w^s}{\partial \hat{y}_s}\right) \qquad (39)$$

for

$$0 \le \hat{y}_s \le 1$$

where from equations (17) and (38), D_T is the temperature dependent portion of the mass diffusivity

$$D_T = \exp\left[\left(\frac{E}{RT_m}\right) \frac{\hat{T}}{\hat{T} + \dfrac{T_m}{T_i - T_m}}\right] \qquad (40)$$

such that $E(T)$ represents the apparent activation energy for the diffusion process and the effects of solution non-ideality and viscosity on the overall diffusion process have been neglected. The initial and boundary conditions take the form

$$(1) \qquad \hat{t} < 0 \ \text{ and } \hat{T} > 0, \qquad (41)$$

$$\phi_w^s = \phi_{wi}^s \quad \text{for } 0 \le \hat{y}_s \le 1$$

$$(2) \qquad \hat{t} \ge 0 \ \text{ and } \hat{T} \le 0, \qquad (42a)$$

(a) at $\hat{y}_s = 0$ (centerline),

$$\left.\frac{\partial \phi_w^s}{\partial \hat{y}_s}\right|_0 = 0$$

(b) at $\hat{y}_s = 1$ (liquid–solid interface),

$$\phi_{w_{LSI}}^s = (1 + \phi_{wi}^s)\left(\frac{\hat{T}_{f_w}}{\hat{T}_{f_w} - \hat{T}_{LSI}}\right) - 1 \qquad (42b)$$

where

$$\hat{T}_{f_w} = \frac{T_{f_w} - T_m}{T_i - T_m} \qquad (43)$$

is the non-dimensional equilibrium freezing–melting temperature of pure water. The temperature of the system is given by

$$\hat{T}_L = \hat{T}_0 + (\hat{T}_{LSI} - \hat{T}_0)\left(\frac{\hat{y}}{\hat{l}}\right) \text{ for } 0 \leq \hat{y} \leq \hat{l} \quad (44a)$$

$$\hat{T}_S = \hat{T}_{LSI} + (\hat{T}_E - \hat{T}_{LSI})\left(\frac{\hat{y} - \hat{l}}{\hat{l} + \mathscr{S}}\right) \text{ for } \hat{l} \leq \hat{y} \leq \hat{l} + \mathscr{S} \quad (44b)$$

where

$$\hat{T}_0 = 1, \quad \hat{T}_E = \hat{B}\hat{t} \quad (45)$$

and

$$\hat{T}_{LSI} = \frac{\frac{k_S}{\mathscr{S}} T_E + \frac{k_L}{\hat{l}} T_0 - \frac{\rho_w L_w}{(T_i - T_m)} D_m^v \hat{v}_{LSI}}{\frac{k_S}{\mathscr{S}} + \frac{k_L}{\hat{l}}} \quad (46)$$

such that

$$\hat{B} = \frac{l_i^2}{D_m^v} \frac{B}{(T_i - T_m)} \quad (47)$$

is the non-dimensional cooling/warming rate and

$$t_m = \frac{-l_i^2/D_m^v}{\hat{B}}. \quad (48)$$

Finally, the time/temperature variation in the volumes of the liquid and solid regions are given by

$$l = \hat{V}_L = V_L/V_i, \quad \mathscr{S} = \hat{V}_S = (\rho_L/\rho_S)\cdot(1 - \hat{V}_L) \quad (49)$$

or

$$\hat{V}_L = 1 + \int_0^{\hat{t}} \hat{v}_{LSI}\, \mathrm{d}\hat{t} \quad (50)$$

where the non-dimensional interface velocity is given by

$$\hat{v}_{LSI} = \frac{v_{LSI} l_i}{D_m^v} = \phi_{s_i} D_T \left(\frac{\phi_S}{\phi_{s_i}}\right)^2 \frac{\partial \phi_w^s}{\partial \hat{y}_s}\bigg|_1. \quad (51)$$

The governing non-dimensional parameter for the present situation is the rate $\hat{B}$ which represents the ratio* of the externally induced volumetric time rate of change in the equilibrium solute concentration $\{(Al_i)B/(T_i - T_m) = -(Al_i)\hat{T}_{f_w}\, \mathrm{d}c_{s_f}/\mathrm{d}t\}$ to the rate of diffusion of the solute within the liquid region $\{A(D_m^v/l_i)c_{s_i}\}$. If $|\hat{B}| \ll 1$, no nonuniform concentration profiles should develop within the liquid region of the system during the freezing process. In this limit there is little, if any, solute polarization because the solute can diffuse away from the advancing ice front almost as fast as the water which is freezing can convectively deposit it at the liquid–solid interface. Consequently, the solidification process will not be rate limited by mass-transfer considerations. On the other hand, if $|\hat{B}| \gg 1$, highly nonuniform concentration profiles should develop within the liquid region of the system during the freezing process. In this limit, a significant amount of solute polarization should occur because the ice front is attempting to propagate faster than the "filtered" solute can diffuse away from the interface and than the water to be frozen can diffuse towards the interface. The solidification process in this instance will be rate-limited by mass-transfer considerations.

METHODS

Model applicability

The model presented is generally applicable to any aqueous solution satisfying the conditions stated. However, in order to solve our set of equations, (39), (41)–(43), some assumptions need to be made regarding the initial composition of the solution, the physical properties of the solute and the solvent, and the temperature range over which the freezing process is occurring. Consequently, as a demonstration of the applicability of the model, we considered the case of an hypothetical ideal aqueous solution having an initial solute concentration of 0.278 mol/*l* cooled to −20°C at various rates. To account for the variation with temperature of the apparent activation energy of the mass diffusivity, equation (40), we have employed the following expression:

$$E = 4.186 \exp\left[\frac{-1.45 \times 10^{-2}\, T}{K} + 5.69\right] \frac{\mathrm{kJ}}{\mathrm{mol\,K}}. \quad (53)$$

This expression results from a "least square fit" analysis over the temperature range of 0 to −40°C of the available data for the self-diffusion of pure water [39]. The apparent activation energy governing the diffusion process therefore increases during the cooling process ($E_{-1\,\mathrm{C}} \sim 24$ kJ/mol K *vis à vis* $E_{-20\,\mathrm{C}} \sim 32$ kJ/mol K). These and other parameters are summarized in Table 1.

Solution technique

Although the set of mass and heat-transfer expressions presented above to describe the redistribution of solute within an aqueous solution of finite extent during freezing can be written in the solute-fixed reference frame to avoid the complications imposed by analyzing a boundary condition at the moving liquid–solid interface, equation (23b), the strong concentration and temperature dependence of

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* From equations (46), (26b), (4) and (43),

$$\hat{B} = \frac{(Al_i)\frac{B}{(T_i - T_m)}}{A(D_m^v/l_i)} = \frac{(Al_i)\frac{\mathrm{d}T/\mathrm{d}t}{(T_i - T_m)} c_{s_i}}{(D_m^v/l_i)\, c_{s_i}} = \frac{-(Al_i)\, T_{f_w}\, \mathrm{d}c_{s_f}/\mathrm{d}t}{A(D_m^v/l_i)\, c_{s_i}}. \quad (52)$$

Furthermore, since for most aqueous solutions the diffusion coefficient is of the order of 1×10^{-5} cm²/s at $T_i = 20$°C, on the basis of equations (17) and (53) $D_m^v \sim 0.5 \times 10^{-5}$ cm²/s at $T_m = -1$°C. Hence,

$$\hat{B} = l_i^2 B(1 \times 10^4)/\mathrm{cm}^2\ {}^\circ\mathrm{C/s}.$$

Consequently, if $\hat{B} = -1$, then $B = -10^{-4}$ °C/s for $l_i = 1$ cm.

Table 1. Physical parameters

Initial concentration	c_{s_i}	0.278 mol/l
Solute apparent molar volume	$\bar{v}_s$	36.0 cm^3/mol
Chemical species per solute molecule	v	2.0
Initial volume fraction	ϕ_{s_i}	0.01
	$\phi^s_{w_i}$	99.0
Water apparent molar volume	$\bar{v}_w$	18.0 cm^3/mol
Ice/water density ratio	ρ_S/ρ_w	0.917
Liquid region thermal conductivity	k_L	5.6 mW/cm K
Solid/liquid thermal conductivity ratio	k_S/k_L	4.0
Latent heat of fusion	L_w	6.0 kJ/mol
Initial temperature	T_i	293.15 K (20°C)
Equilibrium freezing/ melting temperature of pure water	T_{fw}	273.15 K (0°C)
Equilibrium freezing/ melting temperature	T_m	272.11 K (−1°C)
Mass diffusivity at T_m	D^c_m	0.5×10^{-5} cm^2/s
Mass diffusivity activation energy	E	$4.186 \exp\left(-\frac{1.45 \times 10^{-2}\, T}{K} + 5.69\right)$ kJ/mol K

the mass diffusivity in the solute-fixed frame, equations (31) and (40) necessitates that the transport expressions, equations (39), (41)–(42), (44)–(46), be solved numerically. Consequently, an implicit method of differences using the Thomas tridiagonalization method [40] was employed to solve the governing non-linear parabolic partial differential transport equation. Typically, 21 nodal points of unequal spacing ($8 \times 0.1 + 8 \times 0.02 + 4 \times 0.01$) with the finest mesh located closest to the liquid–solid interface and the coarsest mesh located near the centerline together with a time step which was small enough to yield values for the stability parameter $\Delta\hat{t}/(\Delta\hat{y}_{\min})^2$ of between 1 and 10 was used. Doubling of the number of mesh points and/or a decrease in the size of the time step by an order of magnitude yielded results which were not statistically different from those obtained under normal conditions. The principle usually adopted for non-linear parabolic equations of using a single time step predictor–corrector iterative scheme to evaluate unknown parameters was also employed in the present study. The error tolerance was typically 1×10^{-4}. Finally, on the basis of equation (5) which describes the conservation of solutes within the liquid region of the system, we estimate the "error" of the numerical solution to be less than ±0.1%.

RESULTS AND DISCUSSION

For the case $\hat{B} = -5$, the spatial variation at various times during the freezing process of the temperature in the liquid and the solid regions and of the solute volume fraction in the liquid region are shown in Fig. 1. The variation with time of the temperature at the boundary $\hat{y} = \hat{l} + \mathscr{S}$ $(\hat{T}_E)$, at the liquid–solid interface $\hat{y} = \hat{l}\,(\hat{T}_{LSI})$, and at the boundary $\hat{y} = 0$ $(\hat{T}_0)$, and of the solute volume fraction at the liquid-solid interface $\hat{y} = \hat{l}(\phi_{s_{LSI}})$ and at the boundary $\hat{y} = 0$ (ϕ_{s_0}) are shown in Fig. 2. As can be seen, the solute volume fraction at the boundary $\hat{y} = 0$, ϕ_{s_0}, lags behind the solute volume fraction at the liquid–solute interface, $\phi_{s_{LSI}}$, due to the polarization phenomenon. Initially, the solute volume fraction at the liquid–solid interface will increase with time (see Fig. 2) as a result of the fact that the interface temperature initially decreases with time and of the assumption of local thermochemical equilibrium at the interface. The solute volume fraction at the boundary $\hat{y} = 0$, however, initially does not change as ice first forms at $\hat{y} = \hat{l}$ because all of the water initially being frozen is coming from the region of the system near the liquid-solid interface. Only after a finite period of time (for the case $\hat{B} = -5$, $\hat{t} \gtrsim 0.02$ and $\hat{T}_E \lesssim -0.2$) will the effects of the solidification process begin to manifest themselves at the inner regions of the system due to the diffusion of solute (water) away from (towards) the liquid–solid interface. At long times though, the solute volume fraction in the interior portions of the liquid region will approach the solute volume fraction of the liquid–solid interface due to the fact that at temperatures between T_{f_i} (or T_m) and T_{EUT}, the "equilibrium" state of an aqueous solution of finite

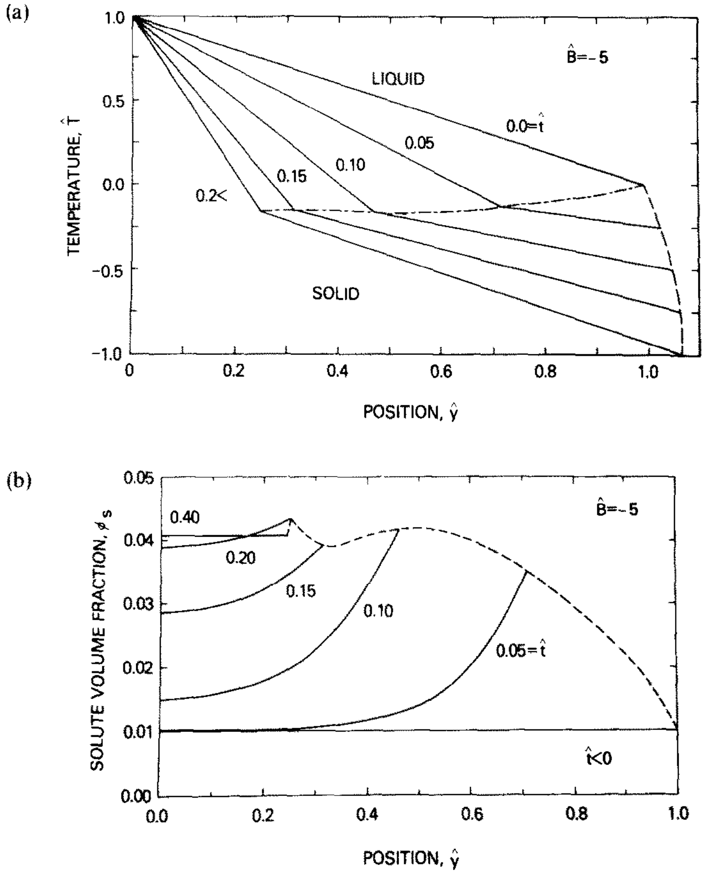

FIG. 1. The spatial variation of the temperature (a) and the solute volume fraction (b) for a cooling rate of $\hat{B} = -5$ at various times.

extent is a partially frozen system with the remaining liquid having a uniform equilibrium concentration corresponding to the interface temperature (see Fig. 2). One additional point should be noted about the spatial and time dependence of the temperature and solute volume fraction profiles of the system. Namely, that at any given spatial position, the temperature and solute volume fraction might undershoot [see Fig. 2(a)] or overshoot [see Fig. 2(b)] their final equilibrium values. This is a direct result of the fact that non-uniform concentration profiles exist within the liquid region of the system for cooling rates $|\hat{B}| > 1$ and that the spatial and time dependence of the temperature of the system is directly related to the magnitude of the latent heat released by the solidification process at the liquid–solid interface which in turn is a function of the solute concentration and the solute concentration gradient at the interface.

Now a better indicator of the magnitude of the solute polarization that occurs within systems of finite extent during freezing is the ratio of the solute concentration at the liquid–solid interface, $c_{s_{LSI}}$, to the solute concentration at the boundary $\hat{y} = 0$, c_{s_0}. This ratio is plotted as a function of time, $-\hat{B}\hat{t}$, for several different non-dimensional cooling rates $\hat{B}$ in Fig. 3. As can be seen, in general, the ratio $c_{s_{LSI}}/c_{s_0}$ first increases with time from its initial value of unity before decreasing back towards unity. The initial increase in the ratio $c_{s_{LSI}}/c_{s_0}$ is due to the fact the the liquid–solid interface solute concentration $c_{s_{LSI}}$ increases with decreasing temperature because of the assumption of local thermodynamic equilibrium and constant cooling rate while the solute concentration c_{s_0} at $\hat{y} = 0$ initially is not affected by the freezing process and remains essentially equal to its initial value c_{s_i}. As time progresses, however, and the rejected solute is able to diffuse away from the liquid–solid interface and into the interior portions of the liquid region, the $\hat{y} = 0$ solute concentration c_{s_0} begins to rise, causing the ratio $c_{s_{LSI}}/c_{s_0}$ to decrease with time. Finally, as equilibrium is achieved as $\hat{t} \to \infty$, the ratio $c_{s_{LSI}}/c_{s_0}$ approaches an equilibrium value of unity. In addition to varying with time/temperature during freezing, the magnitude of the ratio $c_{s_{LSI}}/c_{s_0}$ is also a strong function of the cooling rate B. For example, when $\hat{B} = -0.1$, the maximum value of the ratio $c_{s_{LSI}}/c_{s_0}$ is only 1.1 (at $\hat{B}\hat{t} = -0.03$) while when $\hat{B} = -10.0$, the maximum value of the ratio $c_{s_{LSI}}/c_{s_0}$ is 5.6 (at $\hat{B}\hat{t} = -0.52$). The reason for this strong dependence of the magnitude of the ratio $c_{s_{LSI}}/c_{s_0}$ on the cooling rate is that when $|\hat{B}| \ll 1$ almost no solute polarization occurs because the rejected solute can diffuse away from the advancing ice front almost as fast as the water which is freezing can convectively deposit it at the liquid–solid interface. However, when $|\hat{B}| \gg 1$, a significant amount of solute polarization occurs because the "filtered" solute can-

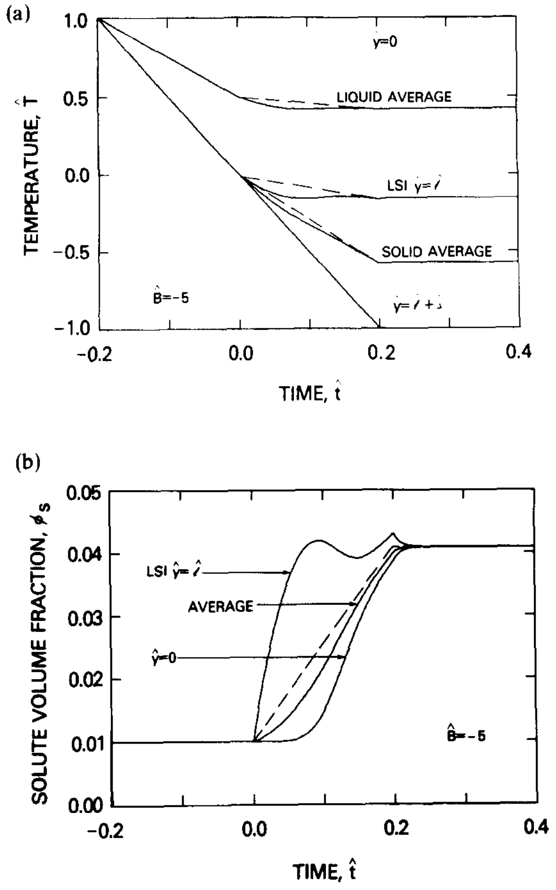

FIG. 2. The variation with time of the temperature (a) and the solute volume fraction (b) for a cooling rate of $\hat{B} = -5$ at various spatial positions. The dashed curves represent the conditions in the presence of a uniform solute concentration profile.

not initially diffuse away from the interface as fast as the ice front is attempting to propagate.

The effect that the solute polarization phenomenon has on the overall freezing process can be seen more easily in Fig. 4 where the relative volume of the liquid region of the system $\hat{V}_L$ at a given time, $-\hat{B}\hat{t}$, is plotted for several different non-dimensional cooling rates $\hat{B}$. Since essentially no nonuniform concentration profiles develop for $|\hat{B}| \ll 1$, the liquid region volumes for systems of finite extent will essentially be equal to (actually, slightly greater than) the "equilibrium" liquid volume of the system at any temperature T_{LSI}. On the other hand, for $|\hat{B}| \gg 1$ highly non-uniform concentration profiles develop within the liquid region of a system [see Fig. 1(b)] such that the solute concentration at the liquid–solid interface greatly exceeds the solute concentration within the interior portions of the system (see Fig. 3). More unfrozen water as compared to the equilibrium case will therefore be present at any temperature below the initial freezing point for fast cooling rates. Furthermore, since the extent of solute polarization increases with faster cooling rates, the amount of unfrozen water (ice) present at any temperature will increase (decrease) as the cooling rate is increased. However, as the freezing process continues and the solute rejected by the advancing ice front has time to diffuse into the interior portions of the liquid region which is continually diminishing in volume, the volume of the liquid region will approach its final equilibrium value as $\hat{t} \to \infty$ for any fixed final temperature $\hat{T}_{LSI}$ between 0 and $\hat{T}_{EUT}$.

Finally, the variation with time, $-\hat{B}\hat{t}$, of the rate of growth of ice can be seen in Fig. 5 where the non-dimensional interface velocity $\hat{v}_{LSI}$ is plotted for several different non-dimensional cooling rates $\hat{B}$. Several

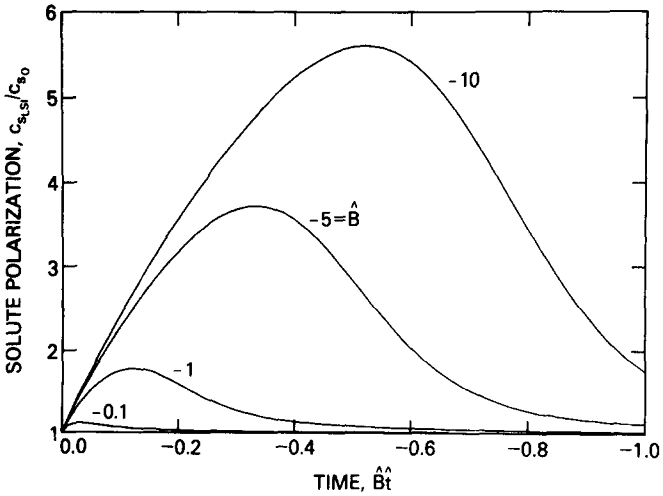

FIG. 3. The variation with time of the ratio of the solute concentration at the liquid–solid interface, $\hat{y} = \hat{l}$, to the solute concentration at $\hat{y} = 0$ for various cooling rates.

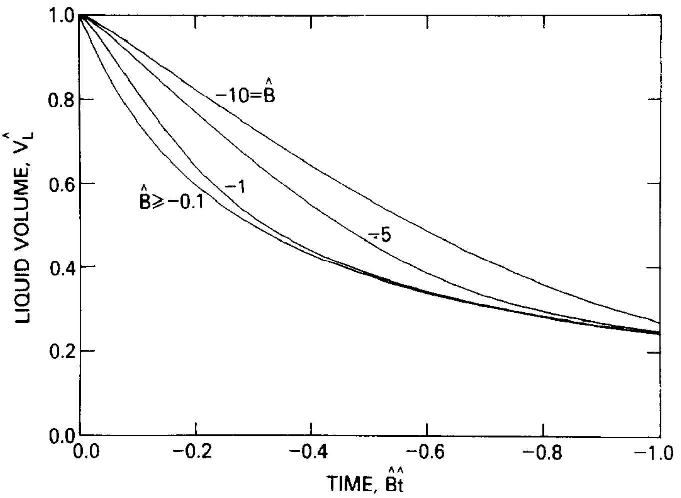

FIG. 4. The variation with time of the relative liquid region volumes for various cooling rates.

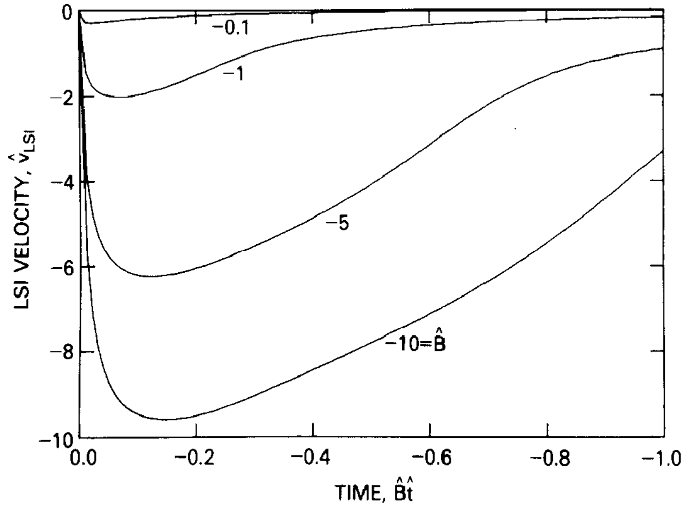

FIG. 5. The variation with time of the liquid–solid interface velocity for various cooling rates.

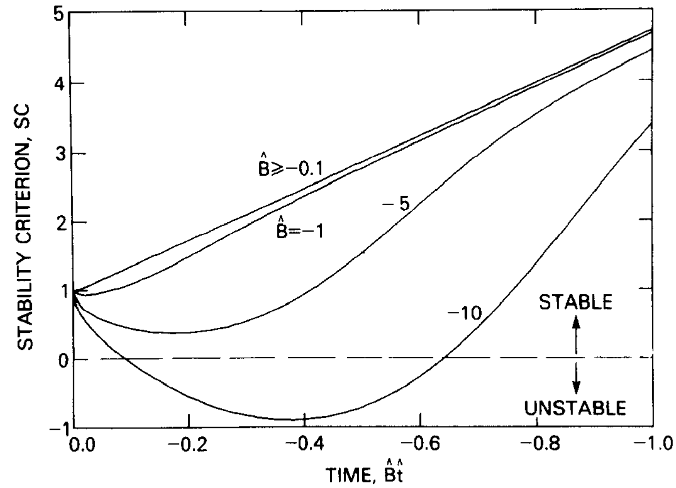

FIG. 6. The variation with time of the stability criterion for various cooling rates.

facts should be noted about the time dependence of the liquid–solid interface velocity. First, in general, the faster the cooling rate, the larger will be the interface speed at any given time. This should be expected since less time is available between any two temperatures at the faster cooling rates for finite domain systems to attempt to re-establish thermochemical equilibrium. Secondly, because the system is beginning to freeze at its initial equilibrium freezing temperature T_f (or T_m) rather than supercooling, the initial ice growth rate at $\hat{t}=0$ is zero rather than infinite. Likewise, as time progresses the interface accelerates, causing the ice growth rate to increase, rather than decelerate as it would for the case of a sudden change in surface temperature. The continuing buildup of rejected solute in the liquid region of the system adjacent to the interface and the relative inability of "fresh" water to diffuse towards the interface and freeze, however, eventually causes the ice front to decelerate resulting in some maximum value for the speed of the liquid–solid interface. Eventually, the speed of the liquid–solid interface will asymptotically approach zero as equilibrium is achieved within the finite domain system as $t \to \infty$.

SUMMARY AND CONCLUSION

A non-ideal, non-dilute pseudo-binary solution model has been presented to describe the concentration polarization of solutes during the planar unidirectional freezing of finite domain aqueous solutions at both short and long times. Our results indicate that the diffusion of solutes within the liquid region of systems of finite extent where the solid phase consists of pure ice is not governed by the "ordinary" diffusion equation. This is a direct result of the facts that the sizes of the solid and the liquid regions vary with time–temperature and that the total volume of solute within the remaining liquid remains constant. Generalized results are obtained by standard numerical techniques for initially ideal, dilute aqueous solutions cooled at various rates on one boundary. These results indicate that non-uniform concentration profiles can exist within the liquid region of systems during freezing and that the volumes of the liquid and solid regions at any time/temperature are significantly affected by the extent of solute polarization. More specifically, our results indicate that for "fast" cooling rates, the solidification process may be rate-limited by mass-transfer considerations, that is, by the ability of the solutes to diffuse away from the interface, rather than solely by the heat-transfer considerations of whether or not the latent and sensible heats can be removed.

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APPENDIX

Throughout our current discussion of the solidification of aqueous solutions, one of our major assumptions has been that the moving liquid–solid interface remains planar during the entire freezing process. Unfortunately, stability of a moving planar ice front cannot always be guaranteed [41]. It is therefore appropriate for us to briefly discuss the region of validity of our current analysis of aqueous solution freezing.

Now the stability of our planar liquid–solid interface can easily be determined by applying the Chalmers stability criterion [22], which for our purposes reduces to the following expression

$$SC = \left.\frac{\partial T_L}{\partial y}\right|_{LSI} - \left.\frac{\partial c_s}{\partial y}\frac{\partial T_f}{\partial c_s}\right|_{LSI} \underset{\text{unstable}}{\overset{\text{stable}}{\gtrless}} 0. \qquad (54)$$

This expression states that if the magnitude of the temperature gradient within the liquid region at the liquid–solid interface is greater than the magnitude of the gradient in the "equilibrium freezing" temperature at the interface, then a propagating planar ice front will be stable. If this condition is violated, then higher order dendritic configurations are more stable than a simple planar surface. Application of this criterion to our current analysis of the freezing of finite domain aqueous solutions (see Fig. 6) yields the results that the assumed planar interface will be stable if $|\hat{B}| < 6.5$ but might be unstable at some times $-\hat{B}\hat{t} > 0$ if $|\hat{B}| > 6.5$. Our present analysis should therefore be valid for non-dimensional cooling rates, $|\hat{B}|$, less than approximately five.

LE GEL DES SOLUTIONS AQUEUSES EN VOLUME FINI: REDISTRIBUTION DU SOLUTE

Résumé—On présente l'analyse du gel unidirectionel des solutions aqueuses de volume fini pendant le refroidissement à des températures basses. Dans ces conditions, alors que le soluté est complètement rejeté par le front de glace qui avance, l'equation classique de la diffusion n'est pas valable et des expressions convenables du transport peuvent être obtenues seulement par une transformation de variable appropriée entre le système de référence où le volume de liquide varie en fonction du temps et le système de référence à 'soluté fixe' où le volume de liquide reste constant (Levin *et al.*, *J. Heat Transfer* **99**, 322, 1977). Cette analyse conduit à une équation de diffusion aux dérivées partielles parabolique et non linéaire avec un terme de vitesse de convection variant dans l'espace et dans le temps, en plus des termes usuels de dérivation par rapport au temps et à l'espace. L'analyse est valable à la fois pour les temps courts et longs et aussi bien pour les solutions idéales, diluées et non idéales ou concentrées. Les résultats montrent que des profils de concentration non uniforme peuvent exister dans la phase liquide pendant le gel et que la variation en fonction du temps et de la température du volume des régions liquide et solide est sensiblement affectée par la distribution non uniforme du soluté. Les résultats indiquent aussi que dans certaines circonstances (comme les grandes vitesses de refroidissement), le mécanisme de solidification peut être limité par le transfert massique, c'est-à-dire par la possibilité pour le soluté de diffuser loin de l'interface, plutôt que par le transfert de chaleur associé au déplacement de chaleur sensible ou latente.

DAS GEFRIEREN VON WÄSSRIGEN LÖSUNGEN IN BEGRENZTEN BEREICHEN: UMVERTEILUNG DES GELÖSTEN STOFFES

Zusammenfassung—Es wurde eine Untersuchung des eindimensionalen Gefriervorgangs von wäßrigen Lösungen in begrenzten Bereichen mit Wärmeentzug bei Temperaturen unterhalb des Gefrierpunkts durchgeführt. Unter Bedingungen, bei denen der gelöste Stoff von der vordringenden Eisfront vollständig verdrängt wird, ist die herkömmliche Diffusionsgleichung ungültig. Passende Transportbeziehungen können nur durch eine Variablentransformation vom Laborbezugssystem, bei dem sich das Volumen des Flüssigkeitsgebiets mit der Zeit verändert, auf ein in Bezug auf den gelösten Stoff fixiertes Bezugssystem, bei dem das Volumen des flüssigen Gebiets konstant bleibt, erhalten werden. Dieses Vorgehen führt auf eine nichtlineare parabolische partielle Diffusionsdifferentialgleichung für das Laborsystem mit einem räumlich und zeitlich veränderlichen effektiven Konvektionsgeschwindigkeitsglied zusätzlich zu den üblichen Ableitungen nach den Orts- und Zeitkoordinaten. Die Beziehungen sind für ideale, verdünnte und nichtideale nichtverdünnte Lösungen für kurze und lange Zeiten gültig. Zusätzliche Vereinfachungen werden nur insofern eingeführt, als die Fest/Flüssig-Grenzfläche als eben und die Temperatur des gesamten Systems während des Gefriervorgangs als örtlich gleichförmig betrachtet wird. Allgemeingültige Ergebnisse wurden für anfänglich ideal verdünnte wäßrige Lösungen bei verschiedenen Abkühlungsgeschwindigkeiten mit numerischen Standardmethoden berechnet. Diese Ergebnisse zeigen, daß ungleichförmige Konzentrationsverläufe im Flüssigkeitsgebiet von Systemen während des Erstarrens auftreten können und daß die Veränderung der Volumina des flüssigen und des festen Bereichs signifikant mit Temperatur und Zeit von der ungleichförmigen Verteilung des gelösten Stoffes beeinflußt wird.

Unsere Ergebnisse weisen ebenfalls darauf hin, daß unter bestimmten Umständen (insbesondere bei hohen Abkühlungsgeschwindigkeiten) der Erstarrungsvorgang durch den Stofftransport begrenzt werden kann, d.h. mehr durch die Möglichkeit des gelösten Stoffes, von der Grenzfläche wegzudiffundieren, als allein durch die Möglichkeiten des Wärmetransports, d.h. ob die fühlbare und latente Wärme abgeführt werden kann oder nicht.

ЗАМЕРЗАНИЕ ВОДНЫХ РАСТВОРОВ КОНЕЧНОГО ОБЪЕМА. ПЕРЕРАСПРЕДЕЛЕНИЕ РАСТВОРЕННОГО ВЕЩЕСТВА

Аннотация — Представлен анализ процесса замерзания водных растворов конечного объема при охлаждении раствора до температуры ниже нуля. При полном отторжении растворенного вещества продвигающимся фронтом льда нельзя использовать обычно применяемое уравнение диффузии. Соответствующие уравнения переноса можно вывести только путем преобразования переменных из лабораторной системы отсчета, в которой происходит изменение во времени объема жидкой фазы, к системе отсчета, фиксированной в растворенном веществе, в которой объем с жидкой фазой остается величиной постоянной (см. Левин и др., журнал «Теплопередача» т. 99, стр. 322, 1977 г.). Такое преобразование позволяет получить нелинейное параболическое уравнение диффузии в частных производных в лабораторной системе отсчета, куда, помимо обычных пространственно-временных производных, входит член с эффективной конвективной скоростью, изменяющейся в пространстве и времени. Анализ справедлив как для малых, так и больших времен, а также для идеальных, разбавленных, и неидеальных, неразбавленных, растворов. Дополнительные упрощения связаны с предположениями, что граница раздела жидкость-твердое тело остается плоской, а температура всей системы — однородной в пространстве на протяжении всего процесса замерзания. Обычными численными методами получены результаты для первоначально идеальных, разбавленных водных растворов, охлаждаемых с различной скоростью. Эти результаты показывают, что при замерзании в объеме жидкой фазы могут иметь место неоднородные профили концентрации и что неоднородное распределение растворенного вещества оказывает большое влияние на зависимость температуры от времени для объемов жидкости и твердого вещества. Кроме того показано, что при определенных условиях (т. е. высокой скорости замерзания) процесс затвердевания может затормаживаться массопереносом, то есть диффузией растворенного вещества от границы раздела более, чем чисто теплообменными процессами такими, как изменение теплосодержания или выделение скрытой теплоты.