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GENERALIZED ANALYTICAL SOLUTION FOR THE FREEZING OF A SUPERCOOLED AQUEOUS SOLUTION IN A FINITE DOMAIN

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Abstract—A generalized analytical solution to the problem of the unidirectional planar freezing at a constant temperature of a supercooled aqueous solution of finite extent is presented. This solution is valid for both dilute and non-dilute solutions and also at both short and long times. Mathematical approximations are made only to the extent that the mass diffusivity is considered to be independent of concentration. Our theoretical results compare favorably with the experimental results of other investigators and demonstrate that transient non-uniform concentration profiles can exist within the liquid region of systems as freezing progresses and that the volumes of the liquid and solid regions can vary non-linearly with time. The extent of concentration polarization and the velocity of propagation of the liquid–solid interface are found to be functions of the initial degree of supercooling, the mass diffusivity, and the initial size of the system. A comparison is also made between our results for freezing in finite domains and the classical similarity results for freezing in semi-infinite domains.

NOMENCLATURE

A,	area;
c,	molar concentration;
D,	diffusion coefficient;
L,	latent heat of fusion;
l,	length;
n,	index;
T,	temperature;
t,	time;
$\hat{t}$,	non-dimensional time (Fourier modulus);
V,	volume;
v,	velocity;
$\bar{v}$,	apparent molar volume;
s,	length;
y,	position;
$\hat{y}$,	non-dimensional position;
ν,	number of species per molecule.

Superscripts

s,	solute-fixed frame of reference;
V,	volume-fixed frame of reference.

Subscripts

f,	freezing;
i,	initial;
L,	liquid;
S,	solid;
s,	solute or solute-fixed frame of reference;
w,	water;
y,	position;
∞,	final.

INTRODUCTION

IN MANY common engineering situations, heat transfer is accompanied by phase changes and/or compositional changes in the conducting medium because of chemical reactions occurring within the medium or the segregation of material due to changes in phase. Analyses of these phenomena usually involve the simultaneous solution of heat- and mass-transfer equations subject to boundaries whose positions vary with time. Examples of such phenomena are the melting or solidification of common substances such as ice and water, the production of frozen foods, the casting and welding of metals during fabrication, ablation during spacecraft re-entry, the penetration of frost into the earth and the melting of coolant-deficient nuclear-reactor fuel elements. Accordingly, many references to moving boundary multi-phase problems exist and can be found in the literature surveys of Bankoff [1], Muehlbauer and Sunderland [2], Rubinstein [3], Fox [4] and Boley [5].

The essential and common features of these systems is that an interface exists which separates two regions possessing greatly different thermodynamic, chemical, and physical properties and that the position of this interface is neither fixed in space nor is its motion known *a priori*. For example, let us consider the solidification of a finite volume of an aqueous solution which upon freezing forms a pure-ice solid from which the solute is completely rejected. If this solution has an initial uniform composition c_{si} and is at an initial uniform temperature T_i above its initial equilibrium freezing temperature $T_{fi}(c_{si})$, then the systems will remain entirely liquid until the temperature T_{fi} is reached. If we then assume that at this point or at any temperature between T_{fi} and T_{eutectic} (i.e. supercooling), that ice nucleates at the outer surfaces of our system, the freezing process will begin and solute will be rejected by the advancing ice front. Under the conditions of local thermodynamic equilibrium, however, the temperature at the liquid–solid interface will be uniquely related to the composition of the liquid at the interface through the liquidus line of the solution's phase diagram. 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 pure water 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 water to gain access to the pure-ice solid phase. This is especially true for aqueous solutions where the ratio of the thermal diffusivity of 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 only a few exact analytical solutions exist, with the most notable being those of Neumann (see [6]) and Stefan (see [7]) who considered the freezing and melting pure substances initially at the fusion temperature. These exact solutions, however, are characterized by the fact that they deal with semi-infinite domain situations having similarity solutions. For other problems, however, especially those dealing with moving boundaries in finite domains, the velocity of the interface is not related to time through a similarity variable and either numerical (for review, see [8]), or approximate analytical (for review, see [9]) methods have had to be employed. Unfortunately, only Weinbaum and Jiji [9] who analyzed the freezing of pure water in a finite domain have obtained a solution which is valid over the entire domain of time. Most other investigators studying the freezing of substances of finite extent have limited themselves to a discussion of the transients occurring at relatively 'short' times (e.g. [10, 11]) where the long time effects of the finiteness of their systems could be neglected. The factors affecting the long time behavior of finite domain problems, however, are vastly different from the factors affecting the long time behavior of semi-infinite domain problems. Whereas the velocity of the solid–liquid interface will approach zero as time approaches infinity for a semi-infinite domain situation due to the heat-transfer limitation of not being able to remove the sensible and latent heats through a solid phase whose thickness approaches infinity at long times; the interface velocity for a finite domain situation will approach zero as time approaches infinity due to the thermodynamic and mass-transfer limitations that at any temperature above the eutectic temperature a multicomponent solution cannot completely solidify but must remain partially liquid with a uniform equilibrium composition corresponding to that temperature.

The purpose of this study is to present a *generalized* analytical solution to the problem of the unidirectional freezing at a constant temperature of a 'supercooled' aqueous solution of finite extent which is valid at both short and long times. We will therefore consider a simple one-dimensional system of initially uniform composition which is rapidly cooled to a temperature below its initial equilibrium freezing temperature. An analysis is presented to predict the solute concentration profile and the motion of the solid–liquid interface in this system as a function of time under three simplifying assumption.* First, that the sensible and latent heats are capable of being *totally* removed from the system by the environment so that the temperature of system does not 'rebound' back towards its initial equilibrium freezing temperature but remains constant. Secondly, that the solid–liquid interface remains planar in spite of the fact that the solution in front of the advancing ice front is 'constitutionally supercooled' [12]. Finally, that the mass diffusivity is considered to be independent of concentration.

FORMULATION

Let us consider the situation where an aqueous solution having an initial volume V_i and an initial uniform composition c_{si}, corresponding to an equilibrium freezing temperature T_{fi}, is uniformly 'supercooled' to a temperature T_f such that $T_{fi} > T_f > T_{\text{eut}}$ where T_{eut} is the eutectic temperature, before it is allowed to come into chemical and thermodynamic equilibrium with its surroundings by being permitted to freeze uniformly inward from its outer surfaces. Now for the case of a binary solution consisting of a single solvent, w, and a single solute, s, which changes in volume when viewed from the laboratory frame of reference due to the addition or removal of solvent but which remains fixed with respect to the initial volume of solute, Levin *et al.* [13] showed that the conventional diffusion equation is not valid. However, an equation of that form can be arranged by an appropriate coordinate transformation.

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:

$$dy_s = \phi_s dy \tag{1}$$

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:

$$c_w^s = \frac{c_w}{\phi_s}, \qquad c_s^s = \frac{c_s}{\phi_s} = \frac{1}{v_s} = \text{constant} \tag{2}$$

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*A more thorough discussion of the planar freezing of finite domain aqueous solutions in which these assumptions are relaxed is presently being prepared.

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

$$\phi_w = \bar{v}_w c_w, \quad \phi_s = \bar{v}_s c_s \tag{3}$$

where ϕ_w is the water volume fraction in the laboratory frame and

$$\phi_w + \phi_s = 1 \tag{4}$$

it can be shown that

$$\bar{v}_w dc_w + \bar{v}_s dc_s = 0, \tag{5}$$

$$\phi_w^s = 1/\phi_s - 1 \tag{6}$$

and

$$dc_w^s = \frac{1}{\phi_s^2} dc_w. \tag{7}$$

As we have already mentioned, for aqueous solutions the ratio of the thermal diffusivity of pure ice ($1.26 \times 10^{-2}\,\text{cm}^2\,\text{s}^{-1}$) to the thermal diffusivity of the remaining liquid ($1.33 \times 10^{-3}\,\text{cm}^2\,\text{s}^{-1}$) is approximately 10 [14]. Furthermore, the ratio of the thermal diffusivity to the mass diffusivity ($1.18 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ at 0°C) in the liquid is approximately 100. Consequently, if we limit ourselves to systems which are sufficiently small so that the sensible and latent heats are capable of being totally dissipated by the environment then we may assume that the temperature of our system will remain essentially uniform and constant,

$$T = T_f. \tag{8}$$

The continuity equations in the solute-fixed frame for the liquid region of the system therefore take the form [13]

$$\frac{\partial c_s^s}{\partial t} = 0, \tag{9a}$$

and

$$\frac{\partial c_w^s}{\partial t} + \nabla_{ys} \cdot \mathbf{J}_w^s = 0 \tag{9b}$$

where $\mathbf{J}_w^s$ is the molar flux of solvent in the solute-fixed frame. Now Crank [8] has shown that

$$\mathbf{J}_w^s = \frac{1}{\phi_s} \mathbf{J}_w \tag{10}$$

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

$$\mathbf{J}_w = -D^v \frac{\partial c_w}{\partial y} \tag{11}$$

and $D^V(c_s, T)$ is the effective diffusivity in the laboratory (volume)-fixed frame. Consequently on the basis of the above relationships [equations (1), (7), (10) and (11)], the continuity equation for the solvent [equation (9b)] can be re-written as

$$\frac{1}{\phi_s^2}\frac{\partial c_w}{\partial t} + \frac{\partial}{\phi_s \partial y}\left(-\frac{D^V}{\phi_s}\frac{\partial c_w}{\partial y}\right) = 0 \tag{12}$$

or, employing equations (3)–(5), as

$$\frac{\partial c_s}{\partial t} = \frac{\partial}{\partial y}\left(D^V \frac{\partial c_s}{\partial y}\right) + v_y \frac{\partial c_s}{\partial y} \tag{13}$$

where

$$v_y = -\frac{D^V}{c_s}\frac{\partial c_s}{\partial y}\bigg|_y \tag{14}$$

is the effective convective velocity in the laboratory frame.

The initial, boundary and final equilibrium conditions corresponding to this situation are

1. $t = 0 \quad c_s = c_{s_i} \qquad$ for all $|y| \le l_i$. (15)
2. $t > 0$

(a) $\dfrac{\partial c_s}{\partial y} = 0 \qquad$ at $y = 0$, (16a)

(b) $c_s = c_{s\infty} = c_s(T_f) \qquad$ at $y = \pm l(t)$. (16b)

3. $t \to \infty\; c_s \to c_{s\infty} \qquad$ for all $|y| \le l_\infty$, (17)

where l_i is the initial 'half-thickness' of the system, l_∞ is the final equilibrium half thickness of the system which because of the constancy of the amount of solute within the liquid region is given by

$$l_\infty = l_i \frac{c_{s_i}}{c_{s\infty}} \tag{18}$$

and $l(t)$ is the size of the system at any time t

$$l(t) = l_i + \int_0^t v_l \,\text{d}t \tag{19}$$

such that v_l is the effective convective velocity at the liquid–solid interface, $y = l(t)$ [see equation (14)], or more appropriately, the thermodynamically-induced solvent-volume flux out of the liquid region and into the solid region. The equilibrium liquidus concentration–temperature relationship for an ideal, dilute aqueous solution can be approximated by the following expression [15]:

$$\nu c_s(T_f) \simeq \frac{L_w(T_{fw} - T_f)}{\bar{v}_w R T_{fw}^2} \tag{20}$$

where ν is the number of species per dissociated solute molecule, L_w is the molar latent heat of fusion of pure water and T_{fw} is the equilibrium freezing temperature of pure water at 1 atm. Using typical values of $L_w \sim 6000\,\text{J mol}^{-1}$, $T_{fw} = 273.15\,\text{K}$, $\bar{v}_w = 18\,\text{cm}^3\,\text{mol}^{-1}$, and $R = 8.314\,\text{J mol}^{-1}\,\text{K}$ [14], this expression can be rewritten as

$$c_s(T_f) = \frac{-(T_f - T_{fw})}{1.86\,\nu}\,\frac{\text{mol l}^{-1}}{\text{K}}. \tag{21}$$

Although the mass-transfer equation together with the initial and boundary conditions given above [equations (13)–(16), (19) and (21)] 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 (16b)], back to the solute-fixed frame of reference where the position of the liquid–solid interface remains stationary [13]. Using equations (3)–(7), it can be shown that the analogous mass-transfer equation in the solute-fixed frame of reference takes the form

$$\frac{\partial c_w^s}{\partial t} = \frac{\partial}{\partial y_s}\left(D^s \frac{\partial c_w^s}{\partial y_s}\right) \tag{22}$$

where

$$0 < y_s < l_s = \phi_{s_i} l_i = \phi_{s,\infty} l_\infty = \text{constant} \tag{23}$$

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

$$D^s = \phi_s^2 D^L. \tag{24}$$

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

1. $t = 0 \quad c_w^s = c_{wi}^s \quad \text{for all } |y_s| \leq l_s.$ (25)

2. $t > 0 \quad \dfrac{\partial c_w^s}{\partial y_s} = 0 \quad \text{at } y_s = 0,$ (26a)

   $c_w^s = c_{w,\infty}^s \quad \text{at } y_s = l_s.$ (26b)

3. $t \to \infty \quad c_w^s \to c_{w,\infty}^s \quad \text{for all } |y_s| \leq l_s.$ (27)

Although transformation of the governing mass transport equation from the laboratory [equation (13)] to the solute-fixed [equation (22)] frame of reference transforms the non-linearity associated with defining a boundary condition at the moving interface $y = l(t)$ to a non-linearity in the governing equation, the solute-fixed expression is inherently easier to solve than the laboratory-fixed expression.

RESULTS AND DISCUSSION

If we neglect the probable concentration dependence of the diffusion coefficient D^s in the solute-fixed frame of reference,* then the solute-fixed mass-transfer relationships can be solved analytically [6], yielding the following expression for the time and spatial variation of the water concentration c_w^s in the solute-fixed frame and the solute concentration c_s in the laboratory-fixed frame:

$$\frac{c_w^s - c_{w,\infty}^s}{c_{wi}^s - c_{w,\infty}^s} = \frac{1/c_s - 1/c_{s,\infty}}{1/c_{si} - 1/c_{s,\infty}} = \frac{2}{\pi}\sum_{n=1}^{\infty}\left\{\frac{(-1)^{n-1}}{(n-1/2)}\cdot\cos\left[\left(n-\frac{1}{2}\right)\pi y_s/l_s\right] \cdot\exp\left[-\left(n-\frac{1}{2}\right)^2\pi^2 D^s t/l_s^2\right]\right\}. \tag{28}$$

Since at temperatures above the eutectic, the amount of solute within the liquid region remains constant, the volume of the liquid region at any time t, $V_L(t)$, and hence, of the solid region, $V_S(t)$, can easily be obtained from the above expression for c_w^s by first noting that at $t = 0$, $\phi_{s_0} V_i = V_s$ where V_i is the initial volume of the system, and as $t \to \infty$, $\phi_{s,\infty} V_{L,\infty} \to V_s$ where $V_{L,\infty}$ is the final equilibrium volume of the liquid region, and secondly, that

$$V_L = \frac{1}{\bar{\phi}_s} V_s = \int_0^{l_s} (\bar{v}_w c_w^s + 1) A \, dy_s \tag{29}$$

where $\bar{\phi}_s$ is the spatially averaged solute volume fraction at any time t and A is the area of the system normal to the direction of ice propagation. Performing the above integration we obtain

$$\frac{V_L(t) - V_{L,\infty}}{V_i - V_{L,\infty}} = \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp\left[-\left(n-\frac{1}{2}\right)^2\pi^2 D^s t/l_s^2\right]}{\left(n-\frac{1}{2}\right)^2} \tag{30a}$$

and

$$V_s(t) = V_i - V_L(t). \tag{30b}$$

Finally, by differentiating with respect to time the above expression for the time variation of the liquid region volume [equation (30a)], we can obtain the following expression for the velocity of the liquid–solid interface at any time t:

$$v_l = \frac{-2(V_i - V_{L,\infty})}{A}\frac{D^s}{l_s^2} \times \sum_{n=1}^{\infty}\exp\left[-\left(n-\frac{1}{2}\right)^2\pi^2 D^s t/l_s^2\right]. \tag{31}$$

The concentration profile within the liquid region, the overall liquid and solid region volumes, and the velocity of the liquid–solid interface at any time are presented graphically in Figs. 1–3, respectively. Specifically, in Fig. 1(a) the dimensionless water concentration ratio $[c_w^s - c_{w,\infty}^s]/[c_{wi}^s - c_{w,\infty}^s]$ is plotted as a function of the dimensionless time modulus $\hat{t} = D^s t/l_s^2$ with the non-dimensional position $\hat{y}_s = y_s/l_s$ as a parameter; while in Fig. 1(b), the dimensionless water concentration in the solute fixed frame is plotted in three dimensional form as a function of both $\hat{t}$ and $\hat{y}_s$. In Fig. 2, the dimensionless overall liquid $[V_L - V_{L,\infty}]/[V_i - V_{L,\infty}]$ and solid region $V_S/[V_i - V_{L,\infty}]$ volumes are shown as a function of the dimensionless time modulus $\hat{t}$; and in Fig. 3, the negative

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*It should be noted that inclusion in the analysis of the non-linearity associated with the ϕ_s^2 concentration dependence of the diffusion coefficient D^s [equation (24)] precludes an analytical solution. The effect of this non-linearity on the results is currently being investigated by numerical methods for the more general freezing problem of the uniform cooling at finite rates of aqueous solutions and will be reported shortly [16].

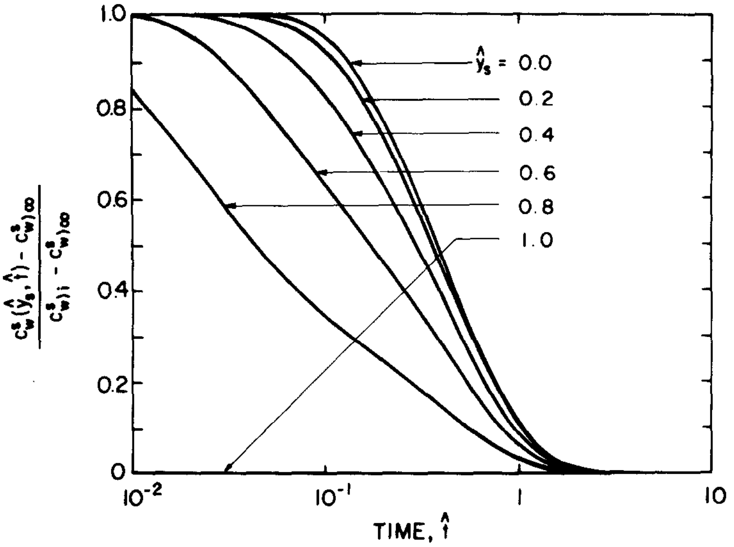

FIG. 1(a). The time variation ($\hat{t} = D^s t/l_s^2$) of the solute-fixed water concentration $[(c_w^s - c_{w\infty}^s)/(c_{wi}^s - c_{w\infty}^s)]$ or solute concentration $[(1/c_s) - 1/c_{s\infty})/(1/c_{si} - 1/c_{s\infty})]$ at various positions ($\hat{y}_s = y_s/l_s$) within an infinite aqueous solution layer of thickness $2l_s$ at an initial concentration c_{si} which is freezing at a uniform constant temperature corresponding to an equilibrium concentration $c_{s\infty}$.

of the dimensionless interface velocity $(v_l A/[V_i - V_{L\infty}])(l_s^2/D^s)$ is shown as a function of the dimensionless time modulus $\hat{t}$.

From these figures, it is obvious that non-uniform concentration profiles exist within the liquid region of the system as freezing progresses and that the volumes of the liquid and solid regions together with the velocity of the liquid–solid interface vary non-linearly with time. As expected, due to the removal of water from the liquid region by the advancing ice front and the relative inability of the 'filtered' solute to diffuse away from the advancing interface, the water (solute) concentration is lowest (highest) at the liquid–solid interface and increases (decreases) towards the center of the system. This so-called concentration polarization effect is most pronounced at short times ($\hat{t} \lesssim 2$). For example, by $\hat{t} \sim 0.1$, the dimensionless water-concentration ratio at the interface has decreased to ~35% of its initial value while the dimensionless water-concentration ratio at the center has decreased to only ~95% of its initial value even though the dimensionless volume of the liquid (solid) region has

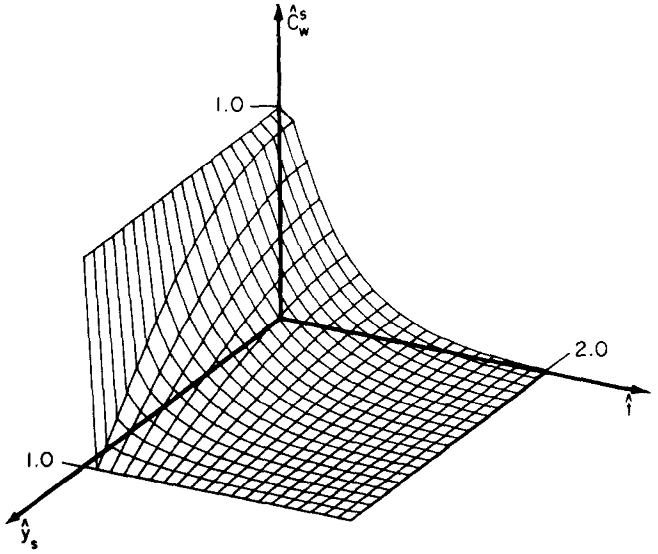

FIG. 1(b). Three dimensional representation of the spatial ($\hat{y}_s = y_s/l_s$) and time ($\hat{t} = D^s t/l_s^2$) variation in the solute-fixed water concentration $[\hat{c}_w^s = (c_w^s - c_{w\infty}^s)/(c_{wi}^s - c_{w\infty}^s)]$ of a supercooled aqueous solution during freezing.

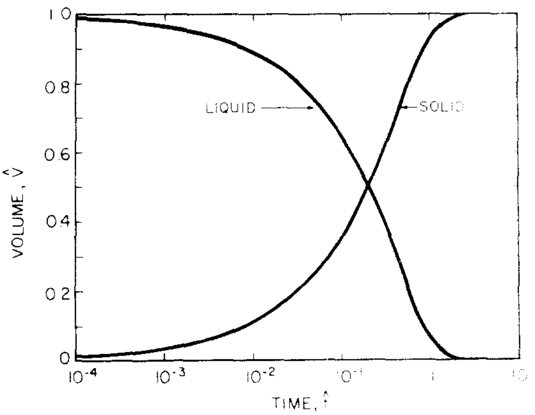

FIG. 2. The time variation ($\hat{t} = D^s t/l_s^2$) of the liquid [$(V_L - V_{L\infty})/(V_i - V_{L\infty})$] and solid [$V_S/(V_i - V_{L\infty})$] region volumes of a supercooled aqueous solution during freezing.

decreased (increased) by ~35%. However, by $\hat{t} \sim 1$, the difference between the dimensionless water concentration ratio at the interface (~3% of initial value) and at the center (~12% of initial value) has narrowed while the dimensionless volume of the liquid (solid) region has decreased (increased) by ~93% from its initial value. Finally, during the time course of the freezing process, the velocity of the liquid–solid interface has also varied in the expected manner—decreasing monotonically from an initial negatively infinite value,* which is due to the step change in the interface solute concentration, and hence, infinite interface solute concentration gradient at zero time, to a final equilibrium value of zero as time approaches infinity.

Lastly, this type of behavior has been noted by several experimental investigators (Terwilliger and Dizio [17], Grange *et al.* [10], Körber and Schiewe [18]) in their studies of the freezing characteristics of salt-water solutions. Unfortunately, in the analysis of their data they have for the most part followed the lead of the majority of theoretical investigators who have modeled finite systems as being semi-finite and have either assumed that the position of the interface varies linearly with time [19, 20] or varies with the square root of time (see Newmann's similarity development in Carslaw and Jaeger [6], Tiller [21], Terwilliger and Dizio [17]). On the basis of the present thermodynamic treatment of the freezing of aqueous solutions in finite domains, the assumption of a constant interface velocity is obviously a grossly incorrect mathematical approximation. However, comparison of our finite-domain theoretical results with the semi-infinite domain theoretical results of Terwilliger and Dizio [17] lends some credence to the use of the semi-infinite domain similarity treatment for the reduction of experimental data. In Figs. 4 and 5, the logarithm of the non-dimensional interface position measured with respect to the initial freezing point $\hat{s}(t) = 1 - l(t)/l_i$ and the negative of the non-dimensional interface velocity $\hat{v}_{LSI}$, respectively, are plotted versus the logarithm of the non-dimensional time $\hat{t}$. A casual inspection of these curves would lead one to believe that at short times ($\hat{t} \lesssim 0.5$), when less than ~75% of the original solution has solidified, the interface position is proportional to $t^{1/2}$ as the classical semi-infinite domain similarity solutions would predict. Closer inspection of these curves, however, would show that while this approximation would probably be valid within the usual limits of experimental error, the supposedly

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*For more general freezing problems, the initial ice front propagation velocity will be finite [16].

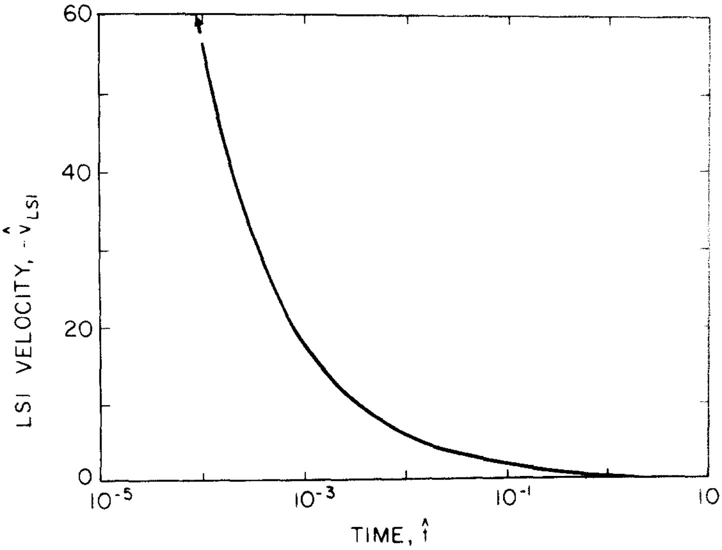

FIG. 3. The time variation ($\hat{t} = D^s t/l_s^2$) of the liquid–solid interface velocity $\hat{v}_{LSI} = d[V_L - V_{L\infty})/(V_i - V_{L\infty})]/d\hat{t}$ for a supercooled aqueous solution during freezing.

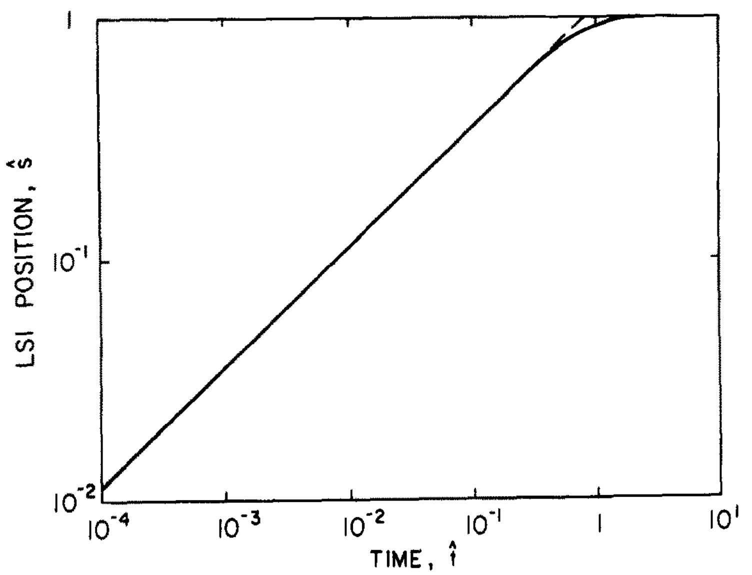

FIG. 4. The time variation ($\hat{t} = D^s t/l_s^2$) of the liquid–solid interface position ($\hat{s} = 1 - l/l_i$) for a supercooled aqueous solution during freezing.

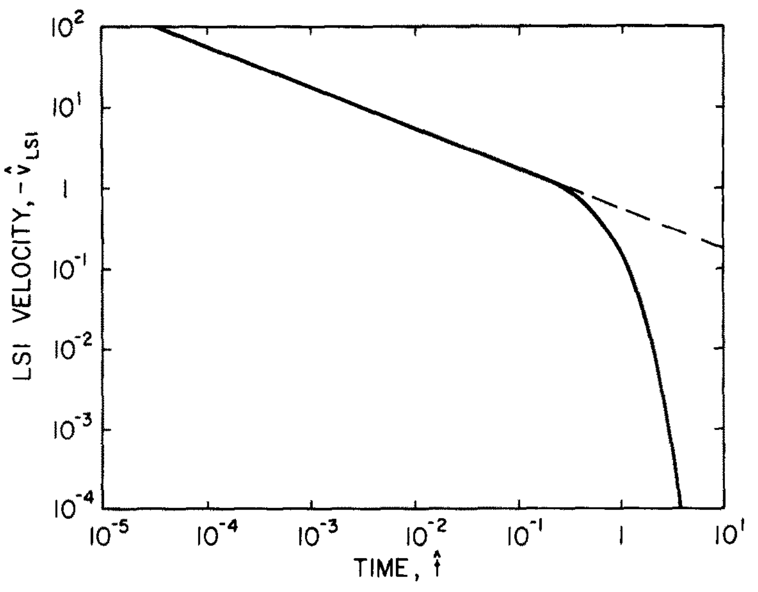

FIG. 5. The time variation ($\hat{t} = D^s t/l_s^2$) of the liquid–solid interface velocity ($\hat{v}_{LSI} = -d[V_S/(V_i - V_{L\infty})]d\hat{t}$ for a supercooled aqueous solution.

constant similarity parameter actually varies by over 100% within the time interval $10^{-4} < \hat{t} < 10^{-1}$. Consequently, experimentalists should be cautious in their use of the semi-infinite domain similarity approximation in the reduction of their experimental data. This is especially true at long times ($\hat{t} > 0.5$) when thermodynamics dictates that for systems of finite extent the velocity of the moving interface, and hence, the rate of loss of liquid and growth of solid must approach zero not necessarily because of heat and mass transfer considerations but because of equilibrium chemical thermodynamic considerations.

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SOLUTION ANALYTIQUE GENERALISEE POUR LE GEL D'UNE SOLUTION AQUEUSE DANS UN DOMAINE FINI

Résumé—On présente une solution générale analytique du problème du gel unidirectionnel à température constante d'une solution aqueuse. Cette solution est valable pour des solutions diluées ou non et aussi pour des temps cours ou longs. Des approximations mathématiques sont faites uniquement dans l'idée que la diffusivité massique est indépendente de la concentration. Les résultats théoriques se comparent favorablement aux résultats expérimentaux d'autres auteurs et ils montrent que les profils de concentration peuvent exister dans le liquide quand le gel progresse et que les volumes des régions liquide et solide peuvent varier non linéairement en fonction du temps. Le degré de polarisation de concentration et la vitesse de propagation de l'interface liquide–solide sont des fonctions du sous-refroidissement initial, de la diffusivité massique et de la taille initiale du système. On compare les résultats du gel dans des domaines finis aux résultats classiques dans des domaines semi-infinis.

ALGEMEINE ANALYTISCHE LÖSUNG BEIM GEFRIERVORGANG EINER UNTERKÜHLTEN WÄSSRIGEN LÖSUNG FÜR EIN ENDLICHES GEBIET

Zusammenfassung—Eine allgemeine analytische Lösung des Problems des eindimensionalen ebenen Gefriervorgangs einer unterkühlten wäßrigen Lösung bei konstanter Temperatur mit endlicher Ausdehnung wird angegeben. Diese Lösung ist gültig sowohl für verdünnte als auch für unverdünnte Lösungen für kurze und lange Zeiten. Mathematische Näherungen wurden unter der Annahme gemacht, daß das Diffusionsvermögen von der Konzentration unabhängig ist. Unsere theoretischen Ergebnisse stimmen sehr gut mit den experimentellen Resultaten anderer Forscher überein und zeigen, daß instationäre ungleichförmige Konzentrationsverläufe innerhalb des Flüssigkeitsgebiets während des Gefrierens existieren können und daß die Volumina der Flüssigkeits- und Feststoffgebiete zeitlich nichtlinear variieren können. Der Grad der Konzentrationspolarisation und die Fortpflanzungsgeschwindigkeit der Phasengrenzfläche ergeben sich als Funktionen des anfänglichen Unterkühlungsgrades, des Diffusionskoeffizienten und der Anfangsgröße des Systems. Ein Vergleich zwischen unseren Ergebnissen für das Gefrieren in begrenzten Gebieten und der klassischen Ähnlichkeitslösungen für den Gefriervorgang in halbunendlichen Gebieten wurde ebenfalls angestellt.

ОБОБЩЕННОЕ АНАЛИТИЧЕСКОЕ РЕШЕНИЕ ЗАДАЧИ ЗАМЕРЗАНИЯ ПЕРЕОХЛАЖДЕННОГО ВОДНОГО РАСТВОРА В КОНЕЧНОЙ ОБЛАСТИ

Аннотация — Представлено обобщенное аналитическое решение задачи направленного плоского замерзания при постоянной температуре переохлажденного водного раствора в конечной области. Решение является справедливым как для разбавленного, так и для неразбавленного растворов, а также для малых и больших интервалов времени. Математические допущения заключаются в том, что коэффициент диффузии рассматривается не зависящим от концентрации. Результаты теоретических расчетов хорошо согласуются с экспериментальными данными других работ и свидетельствуют о том, что в жидкой фазе в процессе замерзания могут иметь место нестационарные неоднородные профили концентрации и что объемы жидкой и твердой фаз могут нелинейно изменяться со временем. Найдено, что перепад концентрации и скорость распространения границы раздела фаз зависят от начальной степени переохлаждения раствора, коэффициента диффузии и начальных размеров системы. Проведено также сравнение полученных в работе результатов для объема конечных размеров с классическими автомодельными решениями для полубесконечных областей.