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Unidirectional freezing of binary aqueous solutions: an analysis of transient diffusion of heat and mass

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Abstract—A model is presented describing the transient freezing of a binary aqueous solution in a region of finite extent. The model consists of three partial differential equations that are coupled by common non-linear boundary conditions in analogy to similar 'moving boundary' problems. The essential assumptions are as follows: constant cooling rates imposed at the boundaries of the system, transport of heat and mass by diffusion only, macroscopically planar phase boundary, total rejection of solute at the phase boundary and local thermodynamic equilibrium at the phase boundary. Using special numerical techniques this model has been evaluated for a dilute aqueous solution of sodium chloride. Basic results such as kinetics of the phase boundary and space- and time-dependence of temperature and salt concentration, are presented and put up for discussion.

1. INTRODUCTION

THE FIRST order phase transition between the solid and liquid state of such a common substance as water has become the subject of a multitude of engineering situations involving heat and mass transfer in aqueous systems. In this context, production of frozen food, prediction of snow avalanches and desalination of water may serve as theoretical illustrations.

The background of this paper is the cryopreservation of biological cells suspended in aqueous media especially in a so-called 'isotonic', i.e. physiological, solution of sodium chloride in water ($C_0 = 0.1548$ mol l^{-1}). In the case of human blood cells, such a suspension (initially at room temperature) is commonly frozen in flat, plate-shaped containers by exposing the whole arrangement to a liquid nitrogen cooling device [1]. In this way solidification is initiated in the suspending medium [2–4]. Due to the change of composition in the residual liquid during solidification, biological cells can react by an efflux of intracellular substances, whose amount is a decisive quantity for their survival in the whole freezing process [5]. To determine the maximum probability of survival, it is necessary to gain complete knowledge of the freezing behaviour of the suspending medium (i.e. isotonic solution of NaCl in water) under the conditions already outlined. In close connection to the circumstances under which blood cell suspensions are commonly frozen, this paper presents a model for the coupled transient transport of heat and mass in a freezing solution of sodium chloride of finite extent. This model is evaluated by numerical techniques and the first basic results are presented.

Even in 1889, in Stefan's first paper [6], which deals with the melting of polar ice, one important feature of the change of phase under consideration is incorporated: there exists a 'moving boundary' separating the solid from the liquid phase, while its position is an *a priori* unknown function of time during the change of phase. As is generally known, this is the very reason for the difficulties arising in the mathematical treatment of heat and mass transfer problems that include phase transition. So, it does not seem surprising that only a few analytical solutions to these transient problems exist at this time [7, 8] while 'moving boundary' problems have been in permanent discussion since the late nineteenth century. Consequently, the literature concerning these problems is extensive and many reviews and surveys can be found [9–15].

A dilute aqueous solution of sodium chloride exhibits a property that separates it from a multitude of metallic systems. According to the phase diagram [16, 17] there exists a liquidus curve ending in a simple eutectic point ($T_E = 251.95$ K, $C_E = 4.68$ mol l^{-1}), while no solidus line exists in this temperature range. Hence, only water participates in any solidification down to the eutectic, while salt remains completely in the residual liquid. These conditions can either be expressed by a vanishing distribution coefficient ('k' in common nomenclature [18, 19]), or by total salt particle rejection of the moving boundary [20]. This circumstance is taken into account by only a few publications [21, 22]. As can be seen later, these papers are based on assumptions that make a comparison to the results presented here almost impossible.

Today, the solution of coupled transient heat and mass transfer problems, including change of phase, can be obtained by numerous methods, depending on the special set of boundary conditions in the actual problem and also possibly on the computer equipment at one's disposal. In this context the survey of Muehlbauer and Sunderland [23] has to be mentioned, although it requires supplemental information; e.g. Boley's starting solution [24], the analytical work of Portnov [25], Temkin [26], the perturbation method by Weinbaum and Jiji [27], the numerical techniques by Griffin and Smith [28], Gupta and Kumar [29], the

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NOMENCLATURE

B	cooling function [K]
$\dot{B}$	cooling rate [K s^{-1}]
C	salt concentration [mol l^{-1}]
E	plane of symmetry
l	diffusion length [mm]
t	time [s]
T	temperature [K]
x, w, z	spatial coordinates [mm]
y	position of phase boundary [mm]
$\dot{y}$	velocity of phase boundary [mm s^{-1}].

Subscripts

D	diffusion of salt
E	eutectic
l	liquid
Li	liquidus curve
R	room
s	solid
th	thermal
0	zero.

Superscripts

I	time range I
II	time range II
(k)	number of proposal

List of constants

a_s	thermal diffusivity of ice [1.364 mm^2 s^{-1}]
a_l	thermal diffusivity of liquid [0.115 mm^2 s^{-1}]
D	diffusivity of NaCl in water [7.8 × 10^{-4} mm^2 s^{-1}]
L	half length of considered region [2 mm]
q	latent heat of fusion [0.333 J mm^{-3}]
T_E	eutectic temperature [251.95 K]
T_R	room temperature [293.15 K]
T_0	equilibrium freezing point of pure water [273.15 K]
λ_l	thermal conductivity of liquid 5.36 × 10^{-4} J mm^{-1} s^{-1} K^{-1}]
λ_s	thermal conductivity of ice [2.34 × 10^{-3} J mm^{-1} s^{-1} K^{-1}]
Δt	1 s.

Coefficients of $T_{Li}(c) = b_0 + b_1 c + b_2 c^2 + b_3 c^3 + b_4 c^4$

b_0	273.15 [K]
b_1	-3.362 [K l mol^{-1}]
b_2	-0.0414 [K l^2 mol^{-2}]
b_3	-0.0404 [K l^3 mol^{-3}]
b_4	-6.616×10^{-4} [K l^4 mol^{-4}].

use of Green's theorem by Chuang and Szekely [30], the finite element method by Bonnerot and Jamet [31] and the solution technique by Vichnewetsky [32]. In this paper, the latter method was chosen as it permits one to be able to solve the complete problem on a table computer (HP 9830A).

2. MODEL

As shown in Fig. 1, two parallel plane walls that are at a fixed distance of $2L$ from each other, and that extend into infinity in the z- and w-directions, bound the region under further consideration. This region is filled entirely and homogeneously with an isotonic aqueous solution of sodium chloride ($C_0 = 0.1548$ mol l^{-1}) which is initially held at room temperature (T_R = 293.15 K).

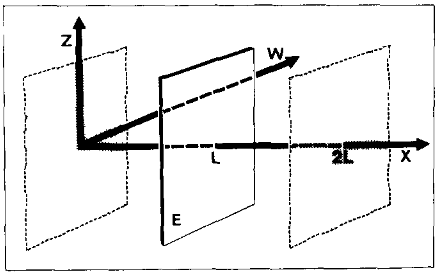

FIG. 1. Definition of geometrical arrangement under consideration.

Beginning at $t_0 = 0$ s, the temperature of the inner surfaces of the boundary walls are described by a spatial independent, monotonously decreasing function $B(t)$ that 'cools down' the salt solution with all the heat being removed by the walls. The whole cooling procedure is divided into two time ranges which are defined as follows:

> time range I ($t_0 \leqslant t \leqslant t^{I}$) is limited by the start of cooling and the first occurrence of the solid phase and it is followed by time range II ($t^{I} \leqslant t \leqslant t^{II}$), until there is total solidification of the salt solution.

In the following, the superscripts I and II refer to this distinction, while the subscripts 's' and 'l' denote the 'solid' and 'liquid' phases.

In time range I, while the whole substance between the walls is in liquid state *per definitionem*, the spatial uniformity of $B(t)$, and the geometrical arrangement under consideration yield the following: first the spatial description reduces to the x-coordinate and secondly, the plane E shown in Fig. 1 represents a plane of symmetry concerning the thermal aspect.

Under these conditions, the system suffices the description

$$a_l \frac{\partial^2 T_l^I}{\partial x^2} = \frac{\partial T_l^I}{\partial t}, \quad 0 \leqslant x \leqslant L \tag{1}$$

making the additional assumption of diffusive transport of heat with constant material properties of the salt solution.

The boundary conditions are:

$$T_l^I(0,t) = B(t) \tag{2}$$

$$\left.\frac{\partial T_l^I}{\partial x}\right|_L = 0 \tag{3}$$

$$T_l^I(x,0) = T_R \tag{4}$$

while the salt concentration satisfies

$$c^I(x,t) = c_0. \tag{5}$$

The description of the system in time range II, while liquid and solid phase are coexistent, is based on the following conception that is supported by experimental data [33]:

At time t^I, the cooling function $B(t)$ reaches the value

$$B(t^I) = T_{Li}(c_0) = 272.65 \text{ K},$$

i.e. the liquidus temperature, where according to the phase diagram of the system, NaCl-H_2O ice formation in isotonic saline can begin [16, 17]. Neglecting any supercooling, solidification shall consequently be initiated at the inner planes of the boundary walls at that time. In the further course of time, solidification shall proceed with macroscopically smooth and planar phase boundaries advancing towards plane E at position L.

On a macroscopic scale, the phase boundaries may hence be considered as continuous sources of latent heat of fusion (q) being produced at the phase boundaries due to the first order phase transition of water. In connection with the geometrical arrangement under consideration, plane E also represents a plane of thermal symmetry in time range II. Making the same assumptions as for equation (1) this yields:

$$a_s \frac{\partial^2 T_s^{II}}{\partial x^2} = \frac{\partial T_s^{II}}{\partial t}, \quad 0 \leqslant x \leqslant y(t) \tag{6}$$

$$a_l \frac{\partial^2 T_l^{II}}{\partial x^2} = \frac{\partial T_l^{II}}{\partial t}, \quad y(t) \leqslant x \leqslant L \tag{7}$$

where $y(t)$ stands for the position of the phase boundary in the region $0 \leqslant x \leqslant L$.

The following boundary conditions can immediately be stated:

$$T_s^{II}(0,t) = B(t) \tag{8}$$

$$T_s^{II}(x,t_I) = T_{Li}(c_0) \tag{9}$$

$$T_l^{II}(x,t_I) = T_l^I(x,t_I) \tag{10}$$

$$\left.\frac{\partial T_l^{II}}{\partial x}\right|_L = 0. \tag{11}$$

In order to gain a unique solution, these equations have to be completed by two further conditions at the phase boundaries. The first one is the well-known 'moving boundary' condition [8, 34] resulting from a heat balance at the phase boundary:

$$q\dot{y} = \lambda_s \left.\frac{\partial T_s^{II}}{\partial x}\right|_y - \lambda_l \left.\frac{\partial T_l^{II}}{\partial x}\right|_y. \tag{12}$$

The second condition represents the coupling of heat and mass transfer at $y(t)$. As already mentioned, only water participates in the phase transition under consideration [16, 17]. This produces a reduction of the solvent's concentration and hence solute enrichment in front of the phase boundary. The resulting salt concentration in turn influences the temperature of the phase transition. Making the assumption of local thermodynamic equilibrium at the phase boundary, this temperature is uniquely determined by the liquidus curve of the phase diagram:

$$T_s^{II}(y,t) = T_l^{II}(y,t) = T_{Li}[c(y,t)]. \tag{13}$$

On the one hand, the salt concentration in front of the phase boundary is increased by higher velocities of the ice front and on the other hand, this induces a stronger flux of salt particles away from the interface, if transport of salt is assumed to be by diffusion only. Supposing constant diffusivity D, the transport equation

$$D \frac{\partial^2 c^{II}}{\partial x^2} = \frac{\partial c^{II}}{\partial t}, \quad y \leqslant x \leqslant L \tag{14}$$

can hence be complemented by the condition:

$$-D \left.\frac{\partial c^{II}}{\partial x}\right|_y = \dot{y}c^{II}(y,t) \tag{15}$$

representing total rejection of salt particles at the phase boundary [20]. The set of boundary conditions is evidently completed by:

$$c^{II}(x,t_I) = c_0 \tag{16}$$

$$\left.\frac{\partial c^{II}}{\partial x}\right|_L = 0. \tag{17}$$

Due to the assumptions stated above, plane E (Fig. 1) also represents a plane of symmetry for mass transport, as the net flux of salt particles must vanish in this plane. This was already taken into account in the range of validity stated in equation (14).

3. SOLUTION

As is generally known, the principal difficulties in solving a 'moving boundary' problem as shown in Table 1 arise from the *a priori* unknown position of the phase boundary $y(t)$, where a non-linear boundary condition holds. This complication can be circumvented by a numerical variational technique, in connection with a method for the solution of parabolic differential equations as described by Vichnewetsky [32]. Before applying that method to the problem

Table 1. Physical model for unidirectional solidification of a binary aqueous solution of finite extent

Time range	Heat – Conduction		Mass – Diffusion
	solid	liquid	
I		$\frac{\partial T_l}{\partial t} = a_l \frac{\partial^2 T_l}{\partial x^2}$ $T_l(x,o) = T_z$ $T_l(o,t) = B(t)$ $\frac{\partial T_l}{\partial x}\Big\vert_L = O$	$c(x,t) = c_0$
II	$\frac{\partial T_s}{\partial t} = a_s \frac{\partial^2 T_s}{\partial x^2}$ $T_s(o,t) = B(t)$ $T_s(x,o) = T_0$	$\frac{\partial T_l}{\partial t} = a_l \frac{\partial^2 T_l}{\partial x^2}$ $T_l(x\,o) = T_l(x,t)$ $\frac{\partial T_l}{\partial x}\Big\vert_L = O$	$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$ $c(x\,o) = c_0$ $\frac{\partial c}{\partial x}\Big\vert_L = O$
	$T_s(y,t) = T_{Li} = T_l(y,t)$		
	$\frac{1}{q}\left(\lambda_s \frac{\partial T_s}{\partial x}\Big\vert_y - \lambda_l \frac{\partial T_l}{\partial x}\Big\vert_y\right) = -D \frac{\partial}{\partial x}(\ln c)\Big\vert_y$		

under consideration, the situation shall be specified as follows:

The cooling function $B(t)$ used below satisfies the equation

$$B(t) = T_R + \dot{B}t, \quad t \geqslant t_0 \tag{18}$$

where

$$-1\ \mathrm{K\,s^{-1}} \leqslant \dot{B} \leqslant -0.05\ \mathrm{K\,s^{-1}}\ \text{('cooling rate')}. \tag{19}$$

This linear dependence is not enforced by the solution technique already mentioned. Rather the reason lies in the theoretical background of this problem, a good approximation of the experimental conditions in that context is represented in equation (18). This argument also holds for the chosen length $L = 2$ mm which is typical of freezing containers used in practice.

As can be seen from equation (13) the liquidus curve of the phase diagram $T_{Li}(c)$ has to be specified. For the system NaCl–H_2O, no uniform mathematical description of this function exists (for detailed discussion see [16]). Based on data from [17], a fourth order polynomial fit was performed to obtain a presentation of $T_{Li}(c)$ with sufficient accuracy ($<0.05\%$). (The coefficients of this fit are listed in the 'Nomenclature' in detail.) This procedure is in accordance to O'Callaghan [35], who used a third order fit, but it differs from other publications [21, 36] where linear approximations of the liquidus curve are preferred.

The values for thermal conductivities, λ_s and λ_l, and thermal diffusivities, a_s and a_l, are determined from data in [17, 37–39] while the diffusivity of sodium chloride, D, is based on experimental data obtained by Körber *et al.* [33], that are in good agreement to [17] and [40].

In time range I, the situation reduces to a pure heat conduction problem having an analytical solution as given by [41]. The solution of the coupled problem in time range II was obtained in the following way.

First the whole set of differential equations and boundary conditions was transformed into a frame of reference (x', t), fixed to the moving boundary [36]. Then, in accordance with the requirements of Vichnewetsky's solution technique [32], time was discretisized in all of the resulting equations

$$t^i = i\Delta t, \quad \Delta t = \text{constant}, \quad i \in \mathbb{N}. \tag{20}$$

After these procedures, determination of the position of the moving boundary, say at time i, was performed in the following way: (here the nature of discretization suggests to proceed successively starting at $i = 1$).

$T_s^{II}(x', i-1)$, $T_l^{II}(x', i-1)$, $c^{II}(x', i-1)$ and $y(i-1)$ are given. By performing a linear extrapolation of $y(t)$ $(t \leqslant i\Delta t)$, a first proposal $y^{(1)}(i)$ is generated. This enables one to solve the mass-transport problem uniquely by Vichnewetsky's technique. Hence the temperature of the phase boundary $y^{(1)}(i)$, $T_{Li}(c^{II}(0, i))$ is given, and a complete solution for $T_s^{II}(x', i)$ and $T_l^{II}(x', i)$ is obtained again by Vichnewetsky's method. Now with this solution, a trial is done to verify the moving boundary condition [equation (12)]. In general, this condition is not satisfied by the first proposal $y^{(1)}(i)$. Hence a second one is generated in the following manner:

$$y^{(k+1)}(i) = y(i-1) \pm \tfrac{1}{2}[y^{(k)}(i) - y(i-1)],$$
$$k = 1, 2, \ldots, \tag{21}$$

where the signs are determined by testing equation (12) with proposal $y^{(1)}(i)$. (If 'r.h.s. of equation (12)' $> q\dot{y}$, then '$-$' and vice versa.)

Proposal $y^{(2)}(i)$ evidently permits one to solve the whole set of differential equations for time i as already cited. Now a new test of equation (12) decides if, in accordance to equation (21), a third proposal has to be generated by repetition of this variational technique. Once equation (12) is satisfied by any proposal $y^{(k)}(i)$, $y(i)$ is determined and time is increased to $i + 1$.

4. RESULTS AND DISCUSSION

As already mentioned, this paper presents the first basic results of the problem under consideration. For interpretation it may be helpful to remember the 'diffusion length' as defined by [42]:

$$l_{th} = \frac{2a_l}{\dot{y}}$$

for the thermal case, and

$$l_D = \frac{2D}{\dot{y}}$$

for salt diffusion, respectively. It can be seen from Fig. 2 that for the cooling rates considered here, l_{th} has an order of magnitude of 10 mm while $l_D \approx 0.1$ mm. Thus, in comparison to the total length of $2L = 4$ mm, the system under consideration is small with respect to the thermal aspect but large with respect to salt diffusion.

The basic response of the system to the imposed cooling rate [equation (18)] is given by the kinetics of the phase boundary. As can be seen from equations (12) and (15), its propagation is determined by the complex

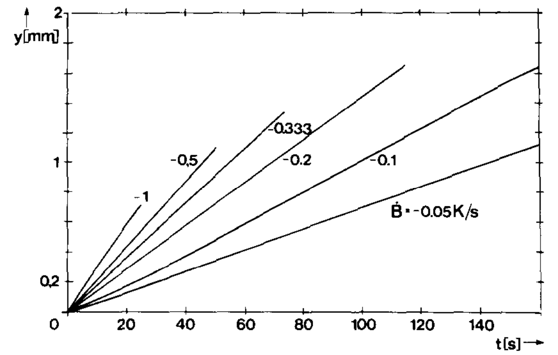

FIG. 2. Position of the phase boundary y vs time t for different cooling rates $\dot{B}$.

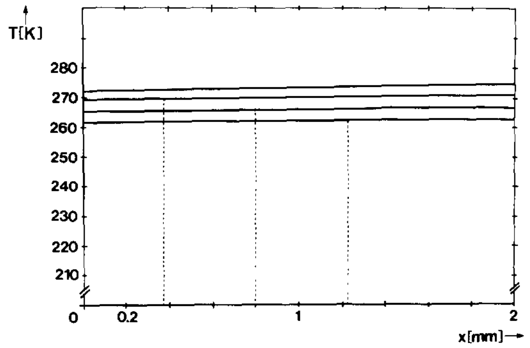

FIG. 4. Temperature distribution within the system vs spatial coordinate x at different times in time range II. Cooling rate $\dot{B} = -0.1$ K s^{-1}, time interval $\Delta t = 20$ s, beginning at $t = 0$ s. Dotted lines represent the position of the phase boundary.

interaction of temperature, salt concentration and their gradients at y. Figure 2 shows the correlation between interface position y and time t for several cooling rates. It can be recognized that these dependencies are non-linear, implying a non-uniform velocity of the phase boundary. This is not unexpected remembering Rubinstein's solution [8], for example, but, due to 'linear cooling' the kinetics presented here do not seem to show any resemblance to a $\sqrt{t}$-dependence. Furthermore, it can be stated that the velocity of the phase boundary does not increase in the same way as the imposed cooling rate. The curves corresponding to the cooling rates greater than -0.1 K s^{-1} have been broken off at the time when the salt concentrations at y had reached the eutectic value of 4.68 mol l^{-1}. At lower cooling rates (-0.1 K s^{-1} and -0.05 K s^{-1}), this did not occur within the first 160 s of freezing. As soon as eutectic conditions appeared at the phase boundary, further calculation were stopped since this situation is not included in the model. Figures 3 and 4 show temperature distributions at different times and different cooling rates. It can be seen that a linear profile in the solid phase may serve as a good approximation which is independent of the cooling rate under calculation. This can be understood in terms of the ratio $a_l/a_s \approx 0.1$ in connection with the comparatively small thickness of the solid phase. Although the imposed cooling conditions are very different here, similar results have also been obtained [8, 42].

The latent heat of fusion shows a negligibly weak influence on T_s^{II} which seems to be independent of time and velocity of the phase boundary. The temperature profiles in the residual liquid may be interpreted as suggested at the beginning of this section, i.e. at low cooling rates (Fig. 4) $T_l^{II}(x')$ is very flat, having temperature gradients that decrease slightly with time. Based on this finding, the necessity of calculation in time range I does not seem to be given. Furthermore, it gives a certain justification for Levin's linearization of the temperature profiles [21]. A different picture is obtained at higher cooling rates (Fig. 3). Although the temperature gradients also decrease with time, the temperature profiles in the liquid zone are evidently non-linear while their shapes can give rise to a second order approximation [22]. However, in all approximative work, it should be kept in mind that the kinetics of the phase boundary are sensitive to improper gradients to a certain extent.

Figures 5 and 6 represent the salt concentration profiles at different times and different cooling rates. As

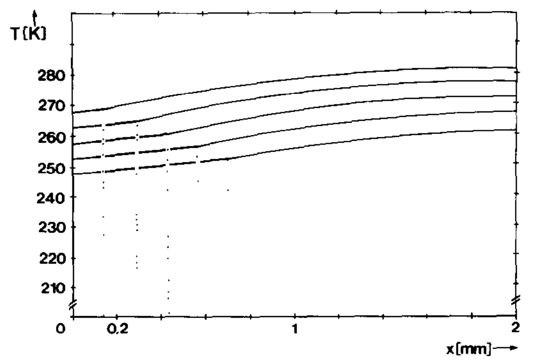

FIG. 3. Temperature distribution within the system vs spatial coordinate x at different times in time range II. Cooling rate $\dot{B} = -1$ K s^{-1}, time interval $\Delta t = 5$ s, beginning at $t = 5$ s. Dotted lines represent the position of the phase boundary.

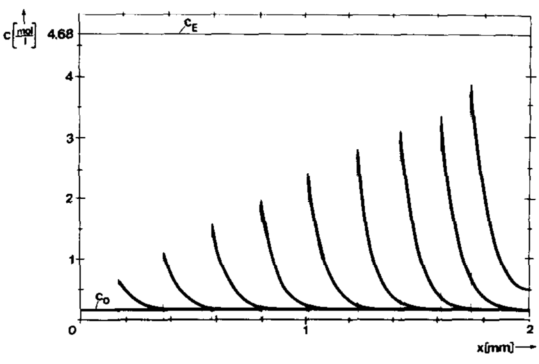

FIG. 5. Concentration profiles at different times in time range II. Time interval $\Delta t = 20$ s beginning at $t = 20$ s, cooling rate $\dot{B} = -0.1$ K s^{-1}. Dotted lines represent the position of the phase boundary.

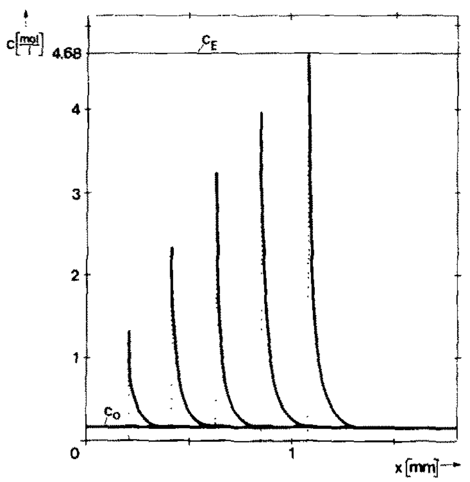

FIG. 6. Concentration profiles at different times in time range II. Time interval $\Delta t = 10$ s beginning at $t = 10$ s, cooling rate $\dot{B} = -0.5$ K s^{-1}. Dotted lines represent the position of the phase boundary.

expected under the assumptions stated above, stationary profiles do not develop. Especially at higher cooling rates, the total rejection of salt particles produces a sharp increase of salt and hence very steep concentration gradients in front of the moving phase boundary. Eutectical conditions therefore occur at the phase boundary after a comparatively short time of freezing, depending on the imposed cooling rate. Considering that salt concentration and its gradient affect the kinetics of the phase boundary on their part, it seems quite remarkable that these circumstances develop.

At lower cooling rates, this situation turns out to be less extreme (Fig. 5). In these cases it was possible to carry out calculations until the phase boundary was sufficiently close to position $x = L$. The concentration of salt at this position causes a further increase of concentration at the phase boundary. Consequently the velocity of the phase boundary is slightly decreased by this effect.

The magnitude of salt concentration gradients in connection with the small temperature gradients at the interface brings up the question of the stability of the moving boundary that was assumed to remain planar during freezing. As is generally known, the first basic work on the this topic by Rutter and Chalmers [42, 43] introduced the concept of constitutional supercooling. Here, with regard to the liquidus curve as the curve of thermodynamic equilibrium, stability of planar phase boundaries is related to a comparison of thermal gradients. Figures 7 and 8 show the development of constitutionally supercooled regions in front of the advancing icefronts at two different cooling rates. It can be seen that these regions develop in a very different manner depending on the cooling rate. At very low cooling for a long period of time, they approach the assumptions stated in Langer's stability analysis [44, 45], i.e. a homogeneously supercooled liquid region in front of the phase boundary. Furthermore, all analysis based on the stationary state at the ice front cannot be applied to the results produced here [46, 47]. In the sense of Rutter's and Chalmers' stability criterion, all solutions obtained here yield unstable phase boundaries, but Delves [48] has pointed out that this 'constitutional supercooling criterion' is not the complete answer to stability.

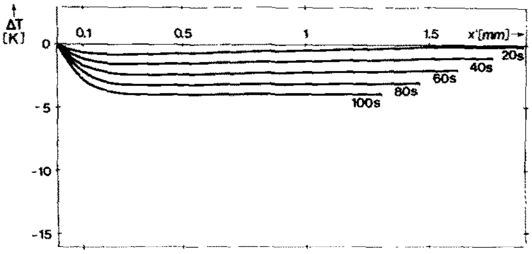

FIG. 7. Constitutional supercooling of the residual liquid during time range II. Cooling rate $\dot{B} = -0.05$ K s^{-1}, $\Delta T = T(x', t) - T_{Li}[c(x', t)]$.

5. TEST OF RESULTS

Because of the special set of boundary conditions, the possibility of comparing the results with those of other publications is very restricted *in toto* [21, 22]. However, there are three different possibilities for checking the accuracy of the calculation.

From the total rejection of salt at the phase boundary, it follows immediately that conservation of the salt content must always hold in the residual liquid. For that reason, numeric integration of $c^{II}(x', t)$ was installed into the programme as an additional check and any further calculation would have been interrupted if conservation of the salt content would not have been guaranteed. It should be mentioned, however, that this integral testing procedure is a rather weak criterion concerning the validity of calculated results.

As the whole programme is structured in a subroutine technique, the subroutine for evaluation of

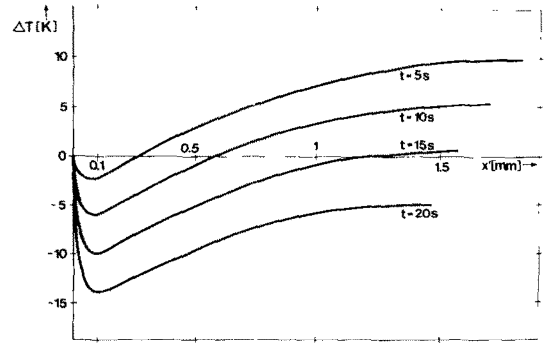

FIG. 8. Constitutional supercooling of the residual liquid during time range II. Cooling rate $\dot{B} = -1$ K s^{-1}, $\Delta T = T(x', t) - T_{Li}[c(x', t)]$.

salt concentration can be handled separately if kinetics of the moving boundary is assumed. For constant phase boundary velocities, the calculated concentration profiles must be identical with the analytical solution given in [16] and [33] as long as the concentration of salt does not increase markedly at position $x = L$. This comparison provides a precise test of Vichnewetsky's method in this application. In order to gain the possibility of comparison within a fairly long time range, calculations were performed for the velocity $\dot{y} = 5\ \mu\mathrm{m\ s}^{-1}$. This testing procedure yielded a maximum error of 0.9%. Moreover it was found that there was no systematic increase of deviation as time progressed. This may be interpreted as positive evidence for the validity of the pure mass diffusion subroutine.

It is possible that a reduction of accuracy in calculation occurs from numerical testing of the equality in equation (12). The influence of the resulting numerical error was investigated as follows: if one erases the subroutine for salt diffusion, the programme can also be run for the solidification process in pure water. Resulting from this calculation, the kinetics of the phase boundary allows a comparison with the numerical results obtained by Breitmar [49] who treated this problem by applying the technique of Smith [50] and Goodrich [51]. In this case, a maximum difference of 0.8% was observed. Breitmar again could verify Maegerlin's fourth order approximation [34] by a modification of his programme up to 0.8%, too. This suggests that the heat diffusion subroutine runs with sufficient accuracy. As both subroutines, pure heat and pure mass diffusion, could be verified separately, it may be expected that their combination used to treat the coupled problem leads to correct results.

6. SUMMARY AND CONCLUSION

A physical model has been presented to describe the solidification of a dilute binary aqueous solution in a finite domain. In this connection, the boundary conditions have been chosen to be analogous to the circumstances that are commonly found in cryopreservation processes for human blood cell suspensions. In the case of a dilute aqueous solution of sodium chloride, the model has been evaluated by special numerical methods yielding the following results.

Based on the assumptions stated, the system under consideration is small with respect to the thermal aspect, but large with respect to mass diffusion. Being determined by the complex interaction of temperature, salt concentration and their gradients at the phase boundary, the kinetics of solidification does not appear to be stationary. Due to the total rejection of salt particles at the phase boundary, the system allows for very steep concentration profiles being built up in front of the solid–liquid interface. This leads to eutectic salt concentrations after a certain time of freezing depending on the imposed cooling conditions. The finite extent of the system under consideration influences solidification kinetics by a further increase of salt concentration at the phase boundary, and hence by slowing down the velocity of the liquid–solid interface.

The results obtained give rise to the question on the stability of the phase boundary that has been assumed to remain planar during the whole solidification process. This should be one topic of future work on the problem under consideration as the applicability of existing stability criteria is very restricted.

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SOLIDIFICATION UNIDIRECTIONNELLE DE SOLUTIONS AQUEUSES BINAIRES: UNE ANALYSE DE LA DIFFUSION VARIABLE DE CHALEUR ET DE MASSE

Résumé—On décrit un modèle de la solidification variable d'une solution binaire aqueuse dans une région d'étendue finie. Le modèle contient trois équations aux dérivées partielles qui sont couplées par des conditions aux limites communes et non linéaires, en analogie avec les problèmes à frontière mobile. Les hypothèses principales sont les suivantes : flux constants de refroidissement imposés aux frontières du système, transfert de chaleur et de masse uniquement par diffusion, frontière en phases macroscopiquement plane, réjection totale du soluté à l'interface et équilibre thermodynamique local à l'interface. En utilisant des techniques numériques spéciales, ce modèle a été évalué pour une solution diluée aqueuse de chlorure de sodium. Des résultats sur la cinétique de l'interface et sur la dépendance espace–temps de la température et de la concentration en sel sont présentés et discutés.

DIE GERICHTETE ERSTARRUNG BINÄRER WÄSSRIGER LÖSUNGEN: EINE UNTERSUCHUNG DES INSTATIONÄREN DIFFUSIVEN WÄRME- UND STOFFTRANSPORTS

Zusammenfassung—Es wird ein Modell vorgestellt, das das instationäre Gefrierverhalten einer binären wässrigen Lösung endlicher Ausdehnung beinhaltet. Dieses Modell wird im wesentlichen durch drei partielle Differentialgleichungen dargestellt, die, wie von ähnlichen 'moving-boundary'-Problemen bekannt ist, durch nichtlineare Randbedingungen gekoppelt sind. Als wesentliche Voraussetzungen wurden getroffen: Abkühlung durch aufgeprägte konstante Kühlraten, rein diffusiver Wärme- und Stofftransport, makroskopisch planare Phasengrenze, kein Einbau gelöster Substanzen in die feste Phase und lokales thermodynamisches Gleichgewicht an der Phasengrenze. Unter Verwendung spezieller numerischer Methoden wurde dieses Modell für den Fall einer verdünnten Kochsalzlösung berechnet. Grundlegende Ergebnisse wie die Kinetik der Phasengrenze und Raum- und Zeitabhängigkeit von Temperatur und Salzkonzentration, werden präsentiert und zur Diskussion gestellt.

НАПРАВЛЕННОЕ ВЫМОРАЖИВАНИЕ БИНАРНЫХ РАСТВОРОВ: АНАЛИЗ НЕСТАЦИОНАРНОГО ПРОЦЕССА ДИФФУЗИИ ТЕПЛА И МАССЫ

Аннотация—Представлена модель, описывающая нестационарный процесс вымораживания бинарного водного раствора в ограниченной области. Модель состоит из трех дифференциальных уравнений в частных производных, которые связаны нелинейными граничными условиями, по аналогии с подобными задачами 'движущейся границы'. Сделаны следующие основные предположения: постоянство скорости охлаждения на границах системы; тепло-и массоперенос осуществляется только диффузией; фазовая граница является макроскопически плоской; полное отделение раствора и локальное термодинамическое равновесие на фазовой границе. При использовании специальных численных методов эта модель была реализована для разбавленного водного раствора поваренной соли. Обсуждаются основные результаты: кинетика фазовых границ и пространственно-временные зависимости температуры и концентрации.