SEGREGATION EFFECTS DURING SOLIDIFICATION IN WEIGHTLESS MELTS

(Interim Report)

August 1974
SEGREGATION EFFECTS DURING SOLIDIFICATION IN WEIGHTLESS MELTS

INTERIM REPORT

(Reporting Period: 5 July 1973 to 4 June 1974)

RE-491

by

Chou Li†

and

Morris Gershinsky‡

Research Department
Grumman Aerospace Corporation
Bethpage, New York 11714

Prepared in partial fulfillment of
Contract NAS 8-29662

for the

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center
Alabama 35812

August 1974

†Research Department, Grumman
Aerospace Corporation

‡Grumman Data Systems Corporation

Approved by: Charles E. Mack, Jr.
Director of Research
This report was prepared by Grumman Aerospace Corporation for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration in partial fulfillment of Contract NAS 8-29662. Our program on Segregation Effects in Weightless Melts has been partially supported by NASA/Marshall under the above contract.
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ACKNOWLEDGMENT

The authors wish to thank Mr. R. C. Ruff of Marshall Space Flight Center for directing and monitoring this contract; they also wish to thank Dr. J. Bredt of NASA Headquarters in Washington, D.C. for helpful discussions.
SUMMARY

This report discusses the work partially supported under NASA Contract NAS 8-29662, "Segregation Effects During Solidification in Weightless Melts." The contract covers the period from July 5, 1973 to July 4, 1974.

During the contract period, the generalized problem of determining the temperature and solute concentration profiles during directional solidification of binary alloys with surface evaporation has been mathematically formulated. Realistic initial and boundary conditions have been defined, and a computer program has been developed and checked out.

The program computes the positions of two moving (evaporation and solidification) boundaries and their velocities of movement, and also the temperature and solute concentration profiles in the semi-infinite material body at selected instants of time.

The program has the following unique features:

- Two moving boundaries are involved, i.e., the evaporative boundary and freezing boundary
- Surface evaporation, and its related effects such as material loss, evaporative segregation, and surface cooling due to the heat of evaporation, have been considered
- Surface temperature is realistically determined by the combined effect of heat radiation, evaporative cooling, and thermal diffusion
• Material parameters such as solid and liquid densities, specific heats, thermal conductivities, mass diffusivities, and latent heat of fusion or evaporation, can all vary with both the temperature and composition.

• Realistic phase diagrams involving curved liquidus and solidus lines are used.

Our computer simulation work on solidification clearly shows that constitutional supercooling readily occurs and within-melt nucleation must then happen, particularly with reduced effective liquid mass transfer under zero-gravity conditions. Such results enabled us to explain and correlate some perplexing space solidification phenomena observed on Skylab, e.g., E. McKannan's weld (M551) and Prof. Adams' braze (M552) results (see Monthly Progress Reports Nos. 10 and 11). Detailed and quantitative application of the results of this computer program, however, still awaits the gathering of pertinent crystal growth data. A final report is expected to be written after these data are gathered and correlated.
INTRODUCTION

Space processing is moving closer to reality. Bigger, better, and more uniform single crystals of important semiconductors and welds or brazes of improved properties have already been made in space, as reported in the Third Space Processing Symposium at Marshall Space Flight Center. Although processing of structural materials may certainly have a profit potential in the long range, it appears that the high cost per pound of single-crystal electronic and optical materials makes these materials the most desirable contenders for immediate profitable returns from space processing. A selected single crystal study is, therefore, highly desirable to help us understand the segregation effects during solidification in weightless melts.

Important tools for understanding these segregation effects are analytic solutions or computer programs that simulate or predict what actually happens during space manufacturing. Such solutions and programs, furthermore, are probably necessary in space processing and other experiments where available time and experimental facilities are limited, the cost per sample or experiment is very high, and yet only a limited total number of tests or test samples can be conducted.

Theoretical predictions often greatly save time while computer simulation saves cost. Specifically, analytic solutions and computer programs allow us to answer many questions during the planning or execution of space experiments on material solidification, such as learning

- What phenomena are most important and what other phenomena are negligible
• Which influences are favorable to our understanding of weightless solidification and which are not
• What conditions lead to optimal combination of the favorable influences or elimination of the unfavorable ones
• What sample and processing conditions should be used
• What is the best way to analyze the resultant samples for understanding a particular phenomenon or influence
• How to save time and money — that is, how to maximize scientific return

We have developed a number of analytic solutions relating to solidification and evaporation (Refs. 1-3). Several important computer programs have also been developed. Some of these solutions and programs were developed under our Contract NAS 8-27891, and they are already proving useful in correlating actual experimental results (Refs. 4 and 5).

These analytic solutions and computer programs are, however, still in their early stages of development. The physical models involved are very simple and require considerable improvements to be used for other applications. It is, therefore, an important objective of this contract to refine and improve these models and the resultant analytic solutions and computer programs.

These refined solutions and programs are more widely useful, have greater predictive value, and provide more accurate results. Such accuracies are absolutely necessary to separate the rather subtle zero-gravity effects on solidification, in the presence of noise due to other unavoidable or unanticipated but ever-present
miscellaneous effects. As a result of this continued work, more efficient space experiments and greater scientific returns appear possible. More meaningful solidification experiments and fuller utilization of the unique space environment may also result.

The predicted results of our refined solutions and programs should, of course, first be checked with selected experiments. Another objective of this contract is, therefore, to design unique experiments to correlate the numerical results to actual solidification processes. This work is yet to be reported.

Review of Previous Contract

Under our NASA Contract NAS 8-27891, "Segregation Effects During Solidification in Weightless Melts" (Ref. 3), two types of melt segregation effects were studied: evaporative segregation, or segregation due to surface evaporation, and freezing segregation, or segregation due to liquid-solid phase transformation.

These segregation effects are closely related. In fact, evaporative segregation always precedes freezing segregation to some degree and must often be studied prior to performing meaningful solidification experiments. This is particularly true since evaporation may cause the melt composition, at least at the critical surface regions or layers, to be affected manyfold, often within seconds, so that at the surface region or layer the melting point and other thermophysical properties, nucleation characteristics, base for undercooling, and critical velocity to avoid constitutional supercooling, may be completely unexpected.

To predict the segregation effects of solidification time and temperature and to correlate these predictions with actual experimental data, "normal evaporation equations" were developed (Refs. 1, 4-6). An evaporative congruent temperature (or equi-evaporative
temperature) was then defined and listed for various binary or
ternary alloys. Knowing these congruent temperatures and the
solute and solvent evaporating rates, one can predict the type
(solute depletion or enrichment) and magnitude of compositional
or constitutional changes on the critical melt surface. One app-
plication of this unique temperature is to explain, predict, or
plan "anomalous" evaporative or constitutional melting (on cooling)
or solidification (on heating) experiments. We then computed for
a simple model the reactive jetting forces due to surface evapora-
tion and, in particular, showed that these forces can be very sub-
stantial on a differentially heated sample and may completely
destroy the unique zero-gravity environment in space manufacturing
(Ref. 7). In addition, these jetting forces may initiate surface
deformation and vibration or other fluid disturbances, and may even
produce some convection currents not normally anticipated. These
studies also showed which sample materials are preferable, which
should be avoided, and what impurities are harmful in producing ex-
cessive jetting or effective as stabilizing influences. The rela-
tionship between normal evaporation and normal freezing was then
considered. Finally, applications of evaporation to space manufac-
turing concerning material loss and dimensional control, composi-
tional changes, evaporative purification, surface cooling, mate-
rials standards, and freezing data interpretation were briefly de-
scribed.

In the area of segregation due to solidification, we explained
in some detail the normal freezing process and its successful use
in the semiconductor industry. Various constitutional diagrams
demonstrated the desirability of using nonconstant segregation co-
efficient techniques in metallurgical studies. We then stated the
basic normal freezing differential equation, together with its
solutions for cases where the liquidus and solidus are quadratic, cubic, high-degree polynomial, and exponential functions of the melt temperature. The meaning of constant segregation coefficient was discussed, together with the associated errors due to curvatures of the liquidus and solidus lines and the best value of constant segregation coefficient for a given solidification experiment. Numerical methods for computing the normal freezing behavior were then given. Finally, as an example, the steady state solidification of the Ni-Sn system under conditions of limited liquid diffusion and nonconstant segregation coefficients was described. This system was studied in the M553 experiment on Skylab.
IMPORTANCE OF EVAPORATION

Evaporation is important in space melting and solidification for the following reasons:

- Significant evaporation of alloy components always occurs at high temperatures in space vacuum environments.

- High-temperature evaporation of alloys is generally a neglected area of systematic research. Yet, unless the complete evaporative segregation behavior is understood and analyzed, solidification and its related segregation effects may not be properly studied because of ill-defined initial conditions. Before the liquid alloy can be controllably solidified or even melted, there is invariably some surface evaporation to cause changes in composition, freezing temperature, supercooling characteristics, nucleation and growth morphology conditions, and the like.

- Controlled space evaporation probably most closely meets the requirements of our model of normal evaporation. We may thus be able to obtain material purity or evaporation standards, thermal properties, or even such basic thermodynamic properties as heat of evaporation, activity coefficients, and sticking coefficients that are difficult or impossible to obtain on earth.
• Evaporation is a much simpler process than freezing, since the former does not involve such complicated phenomena as nucleation, phase transformation, and constitutional or nonconstitutional supercooling. Thus, in normal evaporation for specific geometries or alloy systems, we may ideally isolate and investigate such other phenomena as heat conduction or radiation, liquid or solid diffusion, fluid dynamics, and convection currents. Exact knowledge of these phenomena is necessary to understand solidification.

• Evaporation causes surface cooling due to the heat of evaporation. This evaporative cooling effect is particularly important in low-melting materials (Ref. 8).

• Different rates of evaporation at various surface regions give rise to unbalanced forces and momenta that may produce erratic or unwanted accelerations, surface distortions and vibrations, exceedingly large "equivalent gravities," and possibly new types of powerful convection currents in zero-gravity conditions.

• Evaporation may cause the surface composition of certain unwanted or unsuspected impurities to be increased a thousandfold or millionfold within seconds so that the layer's melting point and other thermophysical properties, nucleation characteristics, base for undercooling, and critical velocity to avoid constitutional supercooling may be completely
unexpected. In fact, anomalous "constitutional" or evaporative melting on cooling, or solidification on heating, is possible because of surface evaporation. In addition, very large artificial gravities (e.g., 10 g), strong fluid disturbances, or even new and significant convection currents may be produced from surface evaporation. These phenomena have been observed in the M553 movies, according to Dr. Martin Tobin of Westinghouse Co., Pa.

The much greater evaporative segregation effects, if unaccounted for, would almost certainly conceal any minor or subtle zero-gravity effects, particularly in the presence of other unknown or uncontrolled effects. Definitive space solidification work should probably, therefore, be preceded by an evaporative compatibility study of the sample materials and their possible associated impurities. In fact, evaporation is almost certain to be very important or so overwhelming that the effect of zero-gravity or freezing segregation may be masked or even reversed. A freely suspended molten drop in space may, for example, have its surface solute concentration greatly enriched (as much as a millionfold), by neglected and undetectable trace impurities within seconds of its deployment. We are then dealing at the critical surface layer with a completely new and unanticipated alloy having an entirely different composition, melting point, surface tension, thermophysical properties, latent heat of fusion, undercooling and nucleation characteristics, growth morphology, and the like.

From this we can also see that any analytical, numerical, or experimental study on solidification may yield completely unexpected or irrelevant results if the important and ever-present evaporation phenomena is not adequately taken care of. This is
particularly true in the study of nucleation, undercooling, and space manufacturing. Another important aspect of the present contractual work is to incorporate this generally neglected evaporation phenomena to define the exact initial and boundary conditions before and during the alloy solidification process.
Solidification, even in one-g, is a complicated process involving a multitude of interrelated phenomena such as mass and heat transfer, phase change, and fluid motion. Comprehensive reviews on solidification have been given, for example, by Chalmers (Ref. 9), Tiller (Ref. 10), Christian (Ref. 11), and Li (Ref. 12).

Solidification in zero-g is still very complicated. Here, gravitational force is negligibly small, but other effects as a result become important. For example, surface tension often plays a dominant role in determining the sample shape, processing technique and the resulting contamination level of the processed samples. Evaporation is another ever-present, complicating or dominating factor, but one that may be used to advantage when understood. Neglected, or improperly controlled evaporation may drastically change sample surface composition, fluid motion, equivalent gravities, nucleation, and undercooling characteristics as previously described. The previous program, under Contract NAS 8-27891, however, does not deal with evaporation.

Mathematical Definition of Solidification Problem

To understand thoroughly solute segregation either from combined evaporation and solidification, or in single-crystal growth, one requires a complete characterization of the (mass) diffusion and temperature fields in the solid crystal and remaining melt. The zero-gravity effect on the solidification may be overshadowed by other effects invariably present (such as evaporation) in any such growth process — a condition necessitating that such characterization be accurately defined. Unfortunately, the coupled partial differential equations for the diffusion and temperature
fields are generally not solvable. Although special case solutions have been given for some types of usually physically nonsatisfying, two-phase Stefan problems, for the general case solution we must resort to numerical computations. Existing numerical methods are always subject to such unrealistic assumptions as constancy of interfacial velocity, temperature or temperature gradients, segregation coefficients, diffusion constants, and other material thermophysical properties.

Under NAS 8-27891, a number of computer programs were developed to study the unidirectional solidification of a binary alloy. These programs employ analytical and numerical methods. The analytic program is based on some closed-form solutions of a simple model and gives results for our numerical program to compare. The model for the analytic program deals with a binary alloy at a constant temperature and concentration throughout the initial liquid melt, with the surface temperature instantaneously dropped below the liquidus temperature. The liquid-solid interface temperature is assumed constant, and the concentrations of the alloy at the interface are given by the phase diagram having curved liquidus and solidus lines. In addition, the interface boundary plane moves according to a square root law relative to the solidification time. The program also allows the interface temperature and interface boundary to vary from these fixed rules, but in practice the variation is negligible and not above the computer error level (Ref. 3).

Although covered in detail in the final report on NAS 8-27891, the mathematical formulation of the model is presented below for the sake of completeness.

We deal in unidirectional solidification with a liquid binary alloy to be directionally solidified into two phases, liquid and
solid. We consider the liquid alloy to be semi-infinite with original (at \( t = 0 \)) temperature \( T_0 \) and concentration \( C_0 \). Solidification occurs when the temperature at \( x = 0 \) is changed from \( T_0 \) to a lower value \( T_1 \), either instantaneously or gradually, so that \( T_1 \) is below the temperature \( T_2 \) at which the liquid mixture at concentration \( C_0 \) can be in equilibrium with a solid phase. As solidification occurs, the solid phase grows and its boundary is located at \( x = y(t) \), and the interface temperature at this point is \( T_1(t) \). The partial differential equations describing the solidification process are the following:

\[
\begin{align*}
\frac{a_s^2}{\alpha_s} \frac{\partial^2 T_s}{\partial x^2} &= \frac{\partial T_s}{\partial t}, & \frac{D_s}{\alpha_s} \frac{\partial^2 C_s}{\partial x^2} &= \frac{\partial C_s}{\partial t} & \text{for } 0 < x < y(t) \\
\frac{a_l^2}{\alpha_l} \frac{\partial^2 T_l}{\partial x^2} &= \frac{\partial T_l}{\partial t}, & \frac{D_l}{\alpha_l} \frac{\partial^2 C_l}{\partial x^2} &= \frac{\partial C_l}{\partial t} & \text{for } y(t) < x < \infty
\end{align*}
\]

where the variables \( T, C \) represent the temperature and concentration (of solute in solvent) and the subscripts \( l, s \) denote the liquid and solid phases, respectively. The thermal and mass diffusion coefficients \( a_s, a_l, D_s, D_l \) are assumed constant. The following conditions are usually assumed throughout:

(a) \( T_l(x,0) = T_0 \) and \( C_l(x,0) = C_0 \)

(b) \( T_l(\infty,t) = T_0 \) and \( C_l(\infty,t) = C_0 \)

(c) \( T_s(y(t),t) = T_l(y(t),t) = T_1(t) \)

(d) \( C_s(y(t),t) = f_s(T_1(t)) \)
(e) \( C_s(y(t),t) = f_s(T_i(t)) \)

(f) \( \rho \gamma \dot{y}(t) = k_s \frac{dT_s}{dx} - k_l \frac{dT_l}{dx} \) for \( x = y(t) \)

(g) \[ f_s(T_i(t)) - f_l(T_i(t)) \] \( \dot{y}(t) = D_s \frac{\partial C_l}{\partial x} - D_s \frac{\partial C_s}{\partial x} \)

for \( x = y(t) \)

In many cases, it is also assumed

(h) \( y(t) = \alpha \sqrt{t} \).

Equation (a) describes the condition that the original mixture is all liquid at temperature \( T_0 \) and concentration \( C_0 \). Equation (b) is a consequence of the semi-infinite nature of the mixture so that at any time \( t \), the portion near infinity is unchanged. Equation (c) assumes that at the solid-liquid interface plane there is an interface temperature \( T_i(t) \) and that both the solid and liquid phases at \( x = y(t) \) have this temperature. There is no discontinuity in temperature. Equations (d) and (e) state that the concentrations of solid and liquid at the interface are given by the solidus and liquidus curves, respectively, of the constitutional diagram for the alloy. Equation (f) connects the derivative of the moving boundary with the redistribution of temperature and Eq. (g) connects the same boundary with that of concentration. Equation (h) relates the position of the interface boundary to the solidification time \( t \).

The conditions on \( T_s(0,t) \) and \( C_s(0,t) \) are not fixed in our discussion, and a number of alternatives are considered:
1. $T_s(0,t) = T_1(t)$ with $T_1(t)$ equal to a constant for all $t$;

2. linear, $T_1(t) = T_o + t(T_1 - T_o)/s$ for $t < s$ and $T_1(t) = T_1$ for $t \geq s$;

3. exponential, $T_1(t) = T_1 + (T_o - T_1) e^{-t/s}$ so $T_1(0) = T_o$ and $T_1(\infty) = T_1$.

For $C_s(0,t)$ the conditions considered are $C_s(0,t) = C_i$ usually taken $C_s(T_2)$ or at times a condition conserving mass between 0 and $\infty$.

The two approaches we have pursued may be designated as analytic and numerical. The numerical approach can be applied to all three conditions on temperature whereas the analytic approach holds only the case of constant temperature instantaneously applied. A variant of this analytic method to apply to linear varying temperature has been investigated.

An analytic solution to the coupled partial differential equations (1) and (2) subject to the initial and boundary conditions (a) through (g) has been given (Ref. 13). A numerical program has been designed for the analytic solution.

These numerical programs developed under NAS 8-27891 are based upon finite difference approximations of the partial and ordinary derivatives and involve a variable spacing (for improved computing efficiency). The programs have given acceptable results and compared well with the reference analytic solution, where comparable. The basic physical properties such as densities, diffusivities, specific heats, thermal conductivities, and heat of fusion have been held to be constant, and independent of temperatures and concentrations.
Under the present contract, we have extended the programs to allow for reasonable variation of these physical properties. The approach that has first been taken is to base the values of these physical properties upon extrapolated values of temperature and concentration, and then to determine the values of temperature and concentration. The process is then repeated by re-evaluations of the physical properties. Other modifications of our original program are: 1) to store the physical properties for each of the mesh points and to employ the appropriate quantities at each step, and 2) to recheck the mass and heat diffusion equations to make certain that the constancy of these properties is not assumed.

An additional major program modification has been the inclusion of evaporation effects. This includes evaporation before solidification that is mathematically identical to the problem of simple solidification in binary alloys. After solidification starts, significant evaporation may still exist. We then have to deal with two moving (solid-gas and solid-liquid) boundaries located at $y(t)$ for evaporation and at $z(t)$ for solidification, as will be described.

Modification of the initial and boundary conditions a-h has also been made to make the problem more physically meaningful. One such modification is to include a surface heat radiative loss term involving $T^4$. This term affects the convergence of the problem and creates the need for different algorithms. As reported previously, (Ref. 14), the surface cooling due to evaporation is negligible for many metallic systems such as nickel and iron alloys, or other higher melting materials, and has not been studied in detail under this contract.
To obtain solutions for realistic boundary conditions and to include the various mass transfer effects, numerical solutions of the partial differential equations of heat and mass transfer are required. We have again used the finite difference method to obtain the numerical solution.

The boundary conditions for surface temperature include radiation cooling as given by the Stefan-Boltzmann equation and also include evaporative cooling for both components of the alloy. Raoult's law has been assumed in determining the evaporation rates. At the interface it is assumed that the temperature and concentration relationships for each phase are given by the constitutional diagram for the alloy. The temperature dependence of the thermal and mass diffusion coefficients are allowed for each phase.
Evaporative Solidification of a Binary Alloy

Given a semi-infinite binary alloy melt, initially at concentration $C_0$ and temperature $T_0$, we consider the solidification of the alloy due to surface heat loss by evaporation and radiation (Fig. 1). There are two separate regimes to be considered. The first is concerned with temperature and concentration variations before solidification begins; the evaporation causes the original liquid-vapor boundary to change. Thus, we have a moving boundary problem. The second regime begins with the solidification which introduces a boundary between the freezing solid and remaining liquid phases whose compositions, we assume, follow the phase diagram, i.e., solidus and liquidus curve relations hold. Consequently, after solidification begins, there are two moving boundaries: one is the evaporative boundary and the other is the freezing or solidification boundary.

Fig. 1 Evaporation-Solidification of 0.01 Sb-Ge
Initially at 970°C at 0.01 Second
Equations at the Evaporative Boundary

We denote the evaporative boundary as \( x = y(t) \) where \( y(0) = 0 \). The evaporation rates in mol/m\(^2\)/sec for pure solute and solvent are, respectively (Ref. 15),

\[
U = K_e \frac{A_u B_u}{T} \left( \frac{M_s}{T_s} \right)^{-\frac{1}{2}}
\]

\[
V = K_e \frac{A_v B_v}{T} \left( \frac{M_s}{T_s} \right)^{-\frac{1}{2}}
\]

where \( K_e = 5.83 \times 10^{-5} \), \( M_u, M_v \) are molecular weights for solute and solvent atoms, \( T_s \) is the evaporating surface temperature in degree K, and \( A_u, B_u, A_v, B_v \) are the evaporating constants for solute and solvent, respectively. If \( \rho_u \) and \( \rho_v \) are the solute and solvent densities, then

\[
\frac{dy}{dt} = \frac{UM_u C}{\rho_u} + \frac{VM_v (1 - C)}{\rho_v}
\]

where \( C \) is the concentration at the moving boundary.

The heat loss rate equation at the boundary due to radiation and evaporation is given by

\[
\frac{\partial T}{\partial t} = - \epsilon T^4 - U_{\gamma_u} C - V_{\gamma_v} (1 - C)
\]

where \( \epsilon \) is emissivity coefficient, \( \sigma \) the Stefan-Boltzmann constant, and \( \gamma_u \) and \( \gamma_v \) are specific heats for solute and solvent, respectively.

The equation for the rate of concentration change is

\[
\frac{\partial C}{\partial t} = - (U - V) C
\]
Since the evaporative boundary is a moving one, and since both the evaporation temperature $T$ and solute concentration $C$ are functions of distance $x = y(t)$ and time $t$, i.e., $T = T(x, t)$ and $C = C(x, t)$, the total derivatives $\frac{dT}{dt}$ and $\frac{dC}{dt}$ may be obtained from the partials, i.e.,

$$\frac{dT}{dt} = \frac{\partial T}{\partial t} + \left(\frac{\partial T}{\partial x}\right)_{x=y} \left(\frac{dy}{dt}\right)$$

$$\frac{dC}{dt} = \frac{\partial C}{\partial t} + \left(\frac{\partial C}{\partial x}\right)_{x=y} \left(\frac{dy}{dt}\right)$$

where $\frac{\partial T}{\partial x}$ and $\frac{\partial C}{\partial x}$ are evaluated at the moving boundaries.

Given $\frac{dy}{dt}$, $\frac{dT}{dt}$, and $\frac{dC}{dt}$, we can integrate for $y$, $T$, and $C$ for the moving boundary using a modified Euler method.

$$v^{(i)}(t) = v_t + \Delta t \left(\frac{dv}{dt}\right)_t$$

$$v^{(i+1)}(t+\Delta t) = v_t + \frac{\Delta t}{2} \left[ \left(\frac{dv}{dt}\right)_t + \left(\frac{dv}{dt}\right)_{t+\Delta t}\right]$$

where $\frac{dv}{dt}^{(i)}$ is the value of the derivative at time $t + \Delta t$ using the value $v^{(i)}$ for $v$.

To determine $\frac{\partial T}{\partial x}$ at time $t$ and $t + \Delta t$ requires knowledge of the distribution of temperatures at both times. Those at time $t + \Delta t$ are initially approximated by an extrapolation and are corrected using an approximated value of the temperature of the evaporating boundary with the heat diffusion difference equations. Since the change in temperature at the boundary is greatest due to the heat of evaporation, more iterations are applied to determine
it than to the determination of temperature distribution by means of diffusion equations. Similar considerations hold for the determination of $\frac{\partial C}{\partial x}$ and $\frac{dC}{dt}$.

The computations of the position of the evaporation boundary $[y = y(t)]$, temperature $(T)$, and solute concentration $(C)$ at this boundary constitute an initial value problem in ordinary differential equations. Thus, given $y_0 = 0$, $T = T_0$, $C = C_0$, at time $t = 0$, and given also the equations for velocity of movement of this boundary $dy/dt$, and rate of change of temperature and solute concentration $dT/dt$, and $dC/dt$, we can determine for selected times the values of $y$, $T$, and $C$. The method used is an iterated Euler scheme:

$$y_{n+1} = y_n + \frac{\Delta t}{2} (y'_n + y'_{n+1})$$

where the initial value $y'_{n+1}$ is taken as $y'_n$. This scheme must be connected to the problem of determining the temperature and solute concentration distribution within the semi-infinite body because the derivatives $dy/dt$, $dT/dt$, and $dC/dt$ depend upon these quantities. The first step is to determine a first approximation of the temperature and solute concentration by extrapolation and then correct these values from the newly approximated values of the boundary position and the temperature and concentration thereat.

**Start of Solidification**

To determine the time when solidification has begun, the boundary temperature is compared with the temperature obtained by the inverse function for the liquidus curve evaluated at the boundary concentration. If the former is greater, then solidification has not yet begun. If it is smaller, then solidification has begun. In order to avoid an exact iterative procedure to determine the instant of solidification and to follow it up by a starting procedure for the first time interval thereafter, a simplified
approach has been taken that introduces a small error in the evaporative boundary and freezing boundary. By allowing the temperature to be below the solidification temperature by a small amount and by assuming that the temperatures at both boundaries are the same, a starting value of \( x = z(t) \) of the freezing boundary is determined so that the loss in concentration due to solidification is compensated by the gain in concentration at the liquidus. Given the new temperature \( T_1 \) below the temperature at which solidification begins, we compute \( CSS = FS(T_1) \) and \( CLL = FL(T_1) \), the corresponding solid and liquid concentrations given by the phase diagram. To determine \( DEL_2 = Z_1 - Y_2 \), the distance between the evaporative boundary and solid-liquid interface, we assume that the solid is entirely at concentration \( CSS \), and the liquid varies linearly from \( CLL \) to \( CC(II) \), the concentration at the first mesh point \( x(II) \) after the evaporative boundary. The total concentration is to equal the concentration in the whole regime had no solidification taken place. We assume it to be \( CL_2 \) computed at \( Y_2 \) and to vary linearly to \( CC(II) \) at \( x(II) \). This yields the equation

\[
CSS \cdot DELZ + \frac{(CLL + CC(II))}{2} \cdot (x(II) - Y_2 - DELZ) = \frac{(CL_2 + CC(II))}{2} \cdot (x(II) - Y_2)
\]

Hence

\[
DELZ \cdot [CSS - \frac{(CLL + CC(II))}{2}] = (x(II) - Y_2) \cdot (CL_2 - CLL)/2
\]

where

\[
DELZ = \frac{(CLL - CL_2)}{2} \cdot \frac{(x(II) - Y_2)}{(CLL + CC(II))/2 - CSS}
\]

Then

\[
ZI_2 = Y_2 + DELZ \quad \text{and} \quad \frac{d}{dt} = \frac{DELZ}{DELTs}
\]
This enables us to begin the next time step with initial values for \( y(t_s), z(t_s), \) \( \frac{dy}{dt}, \frac{dz}{dt}, T(y(t_s)) = T(z(t_s)) = T_{12}, \) and \( C(y(t_s)) = CSS, C_s(z(t_s)) = CSS, C_{s}(z(t_s)) = CLL. \)

The Two-Boundary Problem-Derivative Estimation

The equations at the freezing boundary are those given in the Grumman Final Report RE-458 to Contract NAS 8-27891 (Ref. 3), with the exception that the freezing boundary is now called \( x = z(t) \) and not \( x = y(t) \) as in Eq. 49 c-g. At every time step we must compute (in addition to the temperature and concentration at the evaporation boundary) the temperature at the freezing boundary. The concentrations are determined by the phase diagram. The method we employ is that which determines \( T \) (the solidification temperature) and \( \frac{dz}{dt} \) by means of Eq. (49) f,g. Having obtained \( \frac{dz}{dt} \) we obtain \( z(t) \) by means of a modified Euler method. Since the Eq. (49) f,g required approximation for \( \left( \frac{\partial T_{12}}{\partial x} \right)_{z,t} \) and \( \left( \frac{\partial C_{12}}{\partial x} \right)_{z,t} \), we must develop techniques for these approximations appropriate to various situations for mesh points. In addition, for the computation of \( \frac{dy}{dt}, \frac{dT}{dt}, \) and \( \frac{dc}{dt} \) at the evaporative boundary, we also need \( \left( \frac{\partial T}{\partial x} \right)_{y,t} \) and \( \left( \frac{\partial C}{\partial x} \right)_{y,t} \). When there are two mesh points between \( y \) and \( z \), then the techniques alluded to above are available. This involves determining \( \frac{\partial^2 T}{\partial x^2} \) at both \( y \) and \( z \) and the same for \( \frac{\partial^2 C}{\partial x^2} \). When there is only one mesh point between \( y \) and \( z \), then \( \frac{\partial^2 T}{\partial x^2} \) at both points are the same. When there are no mesh points between \( y \) and \( z \), then we can assume either that \( \frac{\partial^2 T}{\partial x^2} \) is zero and hence \( \left( \frac{\partial T}{\partial x} \right)_{y} = \left( \frac{\partial T}{\partial x} \right)_{z} = \frac{T(z) - T(y)}{z - y} \) or that
\[ \frac{\partial^2 T}{\partial x^2} = k \frac{\partial T}{\partial x} \] and hence \[ (\frac{\partial T}{\partial x})_y = \left(1 - \frac{z - y}{2} k\right) \frac{\partial T}{\partial x} \] and \[ (\frac{\partial T}{\partial x})_z = \left(1 + \frac{z - y}{2} k\right) \frac{\partial T}{\partial x} \]. The choice of \( k \) must be small so that \[ \frac{\partial^2 T}{\partial x^2} = k \frac{\partial^2 T}{\partial x^2} = k^2 \frac{\partial T}{\partial x} \] is negligible. Thus, since \( z - y \) is also very small this option is indistinguishable from \( \frac{\partial^2 T}{\partial x^2} = 0 \). We have three cases: 1) no mesh points between two boundaries and we assume \( \frac{\partial^2 T}{\partial x^2} = 0 \), \( (\frac{\partial T}{\partial x})_y = (\frac{\partial T}{\partial x})_z \), 2) one mesh point between \( y \) and \( z \) when \( \frac{\partial^2 T}{\partial x^2} \) is obtained from the three points and \[ (\frac{\partial T}{\partial x})_y = \frac{T(z) - T(y)}{z - y} - \frac{(z - y)}{2} \frac{\partial^2 T}{\partial x^2} \] and \[ (\frac{\partial T}{\partial x})_z = \frac{T(z) - T(y)}{z - y} + \frac{(z - y)}{2} \frac{\partial^2 T}{\partial x^2} \], and 3) when two or more mesh points, say \( x_i \) and \( x_{i+1} \), are between \( y \) and \( z \) so that we can compute \( (\frac{\partial T}{\partial x})_y \) and \( (\frac{\partial T}{\partial x})_z \) separately and distinct. Then \[ (\frac{\partial T}{\partial x})_y = \frac{T(x_i) - T(y)}{x_i - y} - \frac{(x_i - y)}{2} \left(\frac{\partial^2 T}{\partial x^2}\right)_y \] and \[ (\frac{\partial T}{\partial x})_z = \frac{T(z) - T(x_{i+1})}{z - x_{i+1}} + \frac{(z - x_{i+1})}{2} \left(\frac{\partial^2 T}{\partial x^2}\right)_z \].

In general, it is necessary to compute \( \frac{\partial^2 T}{\partial x^2} \) and \( \frac{\partial^2 C}{\partial x^2} \) in three ways, two ways indicated above for the solid regime and a third for the liquid side of the freezing boundary. It is similarly necessary to compute \( \frac{\partial T}{\partial x} \) and \( \frac{\partial C}{\partial x} \) in three ways.

**Boundary and Mesh Points**

When boundary points come close to mesh points, the computation of derivatives may be vitiated by closeness to mesh point.
Therefore, tests are made to determine when such closeness occurs as usually expressed in terms of a decimal fraction of the interval. In that case, the reference point is moved to the next mesh point and the values of $T$ and $C$ at the skipped mesh point are obtained by linear interpolation. This interpolation depends on which side of the solid-liquid interface the mesh point lies. For the evaporative boundary similar considerations hold.

Solution for Remaining Points

The solution for the remaining points is obtained as in the Final Report previously mentioned, pages 3-14 and 3-15 (Ref. 3). One change is, however, necessary because the first mesh point (or more) are no longer under consideration if the evaporative boundary has passed them. The subroutine TRIST is used to solve for the remaining points. In this subroutine we compute the values of temperature and concentration at intermediate mesh points when given the values at the two extreme mesh points. We replace the values at the mesh point to the left of the evaporative boundary by those at the evaporative boundary point, before solving for the intermediate points. This can be done without destroying any useful information since that mesh point is no longer used in the computations. The subroutine TRIST does not depend upon equal spacing or any regular spacing and therefore can accommodate this usage.

Convergence

The convergence problem is the crux of the program. Oscillation tends to cause the needed quantities to overflow. Thus, tests must be made on all the quantities to contain them within reasonable bounds. The subroutine MOTON is used to check the monotonicity of these consecutive points. In addition, the temperature at the evaporative boundary is necessarily less than the temperature at
the freezing boundary. This condition is always imposed in the program.

In addition, the solution for the solidification temperature and freezing boundary derivative (especially the latter) involves very rapidly changing quantities. More iterations should, therefore, be expended in this part of the program. Fewer iterations are needed for determining the evaporative boundary, and the temperature and concentration at that boundary. The program allows five iterations in the former for each of the latter. The number of iterations of the latter is used in a manner analogous to that described in Final Report RE-458 (Ref. 3).

An input quantity NIT (usually a multiple of 4) gives the maximum number of iterations. When NIT/2 iterations occur and convergence is not reached, the time step size is halved. This process is continued until either convergence is attained or the minimum step allowed by the program has been iterated NIT + 1 times. In this case the program may stop or continue on using the nonconverged quantities. Very often these quantities are sufficiently smooth so that convergence will occur on the next interval and the program gives satisfactory results.

However, if the program proceeds with the minimum step and the maximum number of iterations, the results may be spurious. In case of overflow, there is no doubt of it. Otherwise the user must look at results to decide whether he finds them reasonable.
IMPROVED COMPUTER PROGRAM

The complete computer program for the generalized solidification problem is listed herein (see appendix), together with a glossary explaining the special names used in the program. This computer program has the following unique features:

- Surface evaporation, and its related effects such as material loss, evaporative segregation, and surface cooling due to the heat of evaporation, have been considered.

- Material parameters such as solid and liquid densities, specific heats, thermal conductivities, mass diffusivities, and latent heat of fusion or evaporation, are allowed to vary with the temperature and composition.

- Realistic phase diagrams involving curved liquids and solidus lines are used.

- Two moving boundaries are involved, i.e., the evaporative boundary and freezing boundary.

- Surface temperature is determined by the combined effect of heat radiation, evaporative cooling, and thermal diffusion.

Use of Computer Program

The computer program works well if the following three input program parameters are properly chosen: 1) time step size (DELT), 2) grid spacing (DELX), and 3) maximum iteration count (NIT).
The solidification boundary is sensitive to the grid spacing. This is because in passing through a mesh point, discontinuity in the computation occurs for the following reasons. We compute the derivatives in terms of the temperatures and concentrations at the discrete mesh points. When one mesh point is dropped because solidification occurs near it, the derivative based on a substituting new mesh point is discontinuous with that based on the previous mesh point. Though this discontinuity can be reduced by using a smaller time step size, it would be a self-defeating strategy. An alternative is to accept the discontinuous results as they occur, advantages being taken of the fact that the program corrects itself. Although the derivative $\frac{dz}{dt}$ is large when the solid-liquid interface passes through a mesh point, it becomes smaller thereafter thereby correcting the solidification boundary position.

The frequency of this self-correction depends on the grid spacing. Too small a grid spacing would cause too frequent self-corrections. Too large a grid spacing, on the other hand, would obscure the rapid temperature variations around the solidification boundary. This indicates that a proper choice of the grid spacing is required to achieve an optimal tradeoff between accuracy and computing time. There is another tradeoff between the time step size and maximum iteration count for optimal computing results.

Since each evaporation-solidification problem represents a different and unique physical situation, each case must be dealt with separately. However, based on our experience, the following guidelines would be helpful:

The first consideration for the choice of the grid spacing is the behavior of the evaporation boundary after solidification begins. If the evaporation boundary is virtually stationary as
compared to the solidification boundary, the grid spacing should be chosen so that the evaporation boundary is within the first mesh interval (between the first and second mesh points). If, on the other hand, the evaporation boundary is moving at velocities comparable to those of the solidification boundary, then the grid spacing can be selected more freely. The major consideration in this case is the relationship between the grid spacing and the time step size. For a fixed time step size, the grid spacing should be chosen so that at least four time intervals (of step sizes) occur before the solidification boundary passes through a mesh point.

In cases where the evaporation boundary is virtually stationary, one must experiment to determine an optimum time step size in terms of accuracy and computing time. The conditions of the experiment are as follows. Set both the minimum time step size (DELTM) and the time printing interval (DELP) to zero. Setting the time printing interval to zero will cause the computer to print out every computer time step. Setting the minimum time step size to zero will not cause the program to cut back indefinitely but will use, as the minimum, the time step size divided by 1024. By examining the computed results, one can see at what time step sizes the program is running. By examining the actual iteration count (IT), one can see if the program is converging or not. If not converging repeatedly, a smaller time step size is indicated. If the program is converging most of the time, then the minimum time step size can be set at the level of the most frequent time step size and the actual iteration count re-examined to see if the program still converges most of the time. For long runs, the time printing interval must not be zero or small, but must be chosen in consideration with the amount of the required output.
To improve the computing time on long runs, one should consider enlarging the grid spacing as suggested above as one of the tradeoffs. In addition, one may change the maximum iteration count upwards or downwards to also improve the computing time.

Our computer program has the capability for assuming equal or unequal (doubling) mesh point spacings. Our experience, as indicated in Tables 1-4, shows that the unequal spacing scheme gives practically the same accuracy with far less computations as compared with the equal spacing scheme. This may be due to the rapidity at which the temperature declines at the evaporation boundary. Other physical situations may give different results and may indicate that the equal spacing scheme should be used.

The program input parameters consist of a set of integers IX, IAM, NIT, IM, N, and NCN; and a set of real numbers DELX, DELT, DELTM, DELP, TF, and S. IX is the maximum number of mesh points to be used in the program. Present, IX = 28. IAM is the spacing option indicator. If IAM equals 0, the points of mesh are equally spaced with grid spacing DELX. If IAM = 1, an unequal spacing is indicated. The first two intervals are equal and set to DELX. Thereafter, each interval is double the previous interval in spacing. NIT is the maximum number of iterations as interpreted in the context of halving the time step size. If the step is begun at the minimum time step, the NIT is the maximum number of iterations allowed. IM is the number of mesh points in actual use. The input value of IM introduces the minimum number of mesh points to be used. Thereafter additional mesh points are added as required by a substantial change in temperature at next to last mesh point, that is, 1 degree below the initial temperature. IM is increased until IM is equal to IX.
TABLE 1 VARIATION OF TEMPERATURE (°C) AT EVAPORATIVE BOUNDARY FOR VARIOUS COMPUTATION SCHEMES

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* Hand interpolations
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### TABLE 3 VARIATION OF POSITION (\(\mu\text{m}\)) OF SOLID-LIQUID INTERFACE

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<td>0.350</td>
<td>0.350*</td>
</tr>
<tr>
<td></td>
<td>0.36875</td>
<td>0.283</td>
<td>0.283</td>
<td>0.866</td>
<td>0.860*</td>
</tr>
<tr>
<td></td>
<td>0.52875</td>
<td>0.429</td>
<td>0.429</td>
<td>2.291</td>
<td>N.C.</td>
</tr>
</tbody>
</table>

### TABLE 4 VARIATION OF TEMPERATURE (\(^\circ\text{C}\)) AT SOLID-LIQUID INTERFACE

<table>
<thead>
<tr>
<th>Scheme</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td>0.01</td>
<td>0.01</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0001 cm</td>
</tr>
<tr>
<td>Spacing</td>
<td>equal</td>
<td>unequal</td>
<td>equal</td>
<td>unequal</td>
<td>unequal</td>
</tr>
<tr>
<td>time, ms</td>
<td>0.21</td>
<td>933.8</td>
<td>933.8</td>
<td>933.8</td>
<td>933.9</td>
</tr>
<tr>
<td></td>
<td>0.24875</td>
<td>927.7</td>
<td>927.7</td>
<td>927.7*</td>
<td>927.9*</td>
</tr>
<tr>
<td></td>
<td>0.28875</td>
<td>924.5</td>
<td>921.4</td>
<td>921.5*</td>
<td>921.6*</td>
</tr>
<tr>
<td></td>
<td>0.36875</td>
<td>909.3</td>
<td>909.3</td>
<td>909.3*</td>
<td>909.4*</td>
</tr>
<tr>
<td></td>
<td>0.52875</td>
<td>885.8</td>
<td>885.8</td>
<td>885.8</td>
<td></td>
</tr>
</tbody>
</table>

*Hand interpolations
N.C. not computed
NONCN is a nonconvergence option. Failure to converge occasionally is not necessarily an indication of unacceptable results. Therefore, it is desirable to continue computations and examine the results to see if they are acceptable. This is done by setting NONCN to 1. If NONCN is set at 0, the nonconvergent results are not printed unless called for by the print interval. If NONCN is -1, the program stops on nonconvergent results.

The quantity DELX is the grid spacing. Equal spacing and unequal double spacing both make use of this quantity as indicated in the discussion of IAM. The quantity DELT is the maximum time interval (step size) for computation. The quantity DELTM is the input minimum time interval. The program uses as its actual minimum the larger of the quantities DELT/1024 and DELTM. Thus, even if DELTM is set at 0, the number of halving on cutting back the time interval is at most 10 \(2^{10} = 1024\). The program in its presolidification phase starts with its actual time step DELTS set to DELT/8 and allows it to build up to DELT by quick convergence.

On the other hand, near the beginning of solidification, DELTS is allowed to cut back to as small as DELT/256 in order to find an acceptable start of solidification. After solidification has begun, then the restriction of DELTS is between DELTK and DELT. If halving reduces DELTS below DELTK, it is set to DELTK. The quantity DELP is the present interval. If DELP = 0, then every time step is printed. TPR is the time for outputing results. TPR is set originally to DELP and after printout is reset to TPR + DELP. The program prints results if the time TIME1 at the end of the time step equals or exceeds TPR. The program does not attempt to set DELTS so that TPR = TIME1. This is only a slight inconvenience when the print interval is large as compared to DELTM. Generally, we would like DELTM to be set close to the most frequent
DELTS provided that failure to converge does not ensue on a regular basis. TF is the final time of program. This means that if TIMEl equals or exceeds TF, no additional time steps are taken.

The decimal quantity $S$ between 0 and 0.5 is used to determine closeness to a mesh point. If the boundary point (either evaporation or solidification) is such that it exceeds the point that divided the mesh interval surrounding the boundary point in the ratio $(1-S)/S$, then the mesh reference point for computation is moved to the next mesh point. The introduction of $S$ is to make the transition due to passing a mesh point less abruptly discontinuous. The best values of $S$ are between 0.05 and 0.15. For computations on the solid side of the solidification boundary, we continue to use the old mesh points until the boundary point passes the point that divides the new mesh interval about the solidification point in the ratio $S/(1-S)$. This strategy causes a gradual transition from one mesh point to another. The integers $I_{11}, I_{12}$ are used as reference point indicators for the solid and liquid sides, respectively. For the evaporation boundary, $I_{13}$ is used to indicate which points are used. $I_{14}$ is used only to indicate the first mesh point to the left of the evaporation boundary.

Typical Computer Input

The definitions of the various inputs fed into the computer are given in the Glossary of Program Parameters. Typical input values are as follows:

- $I_{X} = 28$ = maximum number of mesh points
- $I_{AM} = 1$, unequal, doubled grid spacing
- $I_{NIT} = 20$, maximum number of iterations
- $I_{M} = 16$, actual number of points in mesh
- $NONCN = 0$, allowing the program to continue when non-convergence occurs with no special printout of these results.
The alloy phase diagrams are determined from the five constants $ET$, $EA$, $EB$, $EC$, and $ED$, which define the liquidus $C_L$ and solidus lines $C_S$ as two functions of the temperature, $T$:

$$C_L(T) = ED \times (ET - T)^2 + EC \times (ET - T)$$

$$C_S(T) = EB \times (ET - T)^2 + EA \times (ET - T)$$

In our example of 10 mole percent ($C_o = 0.10$) of antimony in germanium initially uniform at $970^\circ C$ ($T_o = 970$)

$$ET = \text{melting point of pure germanium } = 956^\circ C$$

$$EA = 0.128812 \times 10^{-3}$$

$$EB = -0.82218 \times 10^{-7}$$

$$EC = 0.466678 \times 10^{-2}$$

$$ED = -0.60466 \times 10^{-5}$$

The evaporation constants for the solvent and solute as defined previously under "The Equation at the Evaporative Boundary" are:

$$AU = A_u = 0.1115 \times 10^2$$

$$BU = B_u = 0.863 \times 10^4$$

$$EMU = M_u = 0.2435 \times 10^3$$

$$AV = A_v = 0.1171 \times 10^2$$

$$BV = B_v = 0.1803 \times 10^5$$

$$EMV = M_v = 0.726 \times 10^2$$

$$EK = K_e = 5.833 \times 10^{-4}$$

The diffusion coefficient of the solute in solvent in the solid and liquid states are, respectively

$$DS = D_s = 0.10 \times 10^{-6}$$

$$DL = D_l = 0.10 \times 10^{-3}$$
The density $\rho$, and latent heat of evaporation, $\gamma$, of the pure solvent are, respectively,

\begin{align*}
\text{RHO} &= \rho_v = 5.32 \\
\text{GAMMA} &= \gamma_v = 160
\end{align*}

Corresponding values for pure solute are:

\begin{align*}
\text{RHOU} &= \rho_u = 6.68 \\
\text{GAMMAU} &= \gamma_u = 39
\end{align*}

The above give two derived quantities:

\begin{align*}
\text{ALS} &= a^2 = k / \rho_v c \\
\text{ASS} &= a_s^2 = k_s / \rho_v c
\end{align*}

where

\begin{align*}
\text{CEE} &= c = 0.740 \times 10^{-1} = \text{specific heat}
\end{align*}

The two input parameters in the surface radiation terms are:

\begin{align*}
\text{EE} &= \epsilon = 0.55 = \text{emissivity coefficient}, \text{ and} \\
\text{SIG} &= \sigma = 0.136 \times 10^{-7} = \text{Stefan-Boltzmann constant.}
\end{align*}

**Computer Output**

The first line of computer outputs gives the program input parameters IX, IAM, NIT, IM, and NONCN, which are defined previously and also in the "Glossary." The next two lines of computer output give the phase diagram constants (ET, EA, EB, EC, and ED) and evaporation constants (AU, BU, EMU, AV, BV, EMV, and EK), respectively. The next printouts are for CEE, DS, DL, T0, CO, XKL, RHO, GAMMA, RHOU, GAMMAU, EE, SIG, T2, and COO, where T2 is the temperature when solidification begins for the melt of initial solute concentration CO.
The computed numbers are then outputed as follows:

IT  = actual iteration count
IM  = number of points in mesh
II1 = grid point reference for solid side of mesh
II2 = grid point reference for liquid side of mesh
II3 = grid point reference for evaporation boundary
II4 = grid point reference for point after evaporation boundary

These printouts are then followed by the computed values associated with the evaporation boundary: time, location y, concentration C, temperature T, extent of points X(IM), current time interval DELTS, dy/dt DYDT1, dC/dt DCDT1, dT/dt DTDT1. If solidification has not begun, then there is no information about the solidification boundary. Otherwise, we have position of the solidification boundary z computer language (ZII), solid solute concentration C_s (CS1), liquid solute concentration C_l (CLl), temperature T (TII), and rate of movement dz/dt (DZDTl). All decimal outputs are five per line with excess going to the next lines.

Representative Computed Results

The study of the effect of varying the grid spacing DELX on the computed results is summarized in Tables 1 through 4. The five cases considered are:

Case I: DELX = 0.01 cm  with equal spacing
Case II: DELX = 0.01 cm  with unequal spacing
Case III: DELX = 0.001 cm with equal spacing
Case IV: DELX = 0.001 cm with unequal spacing
Case V: DELX = 0.0001 cm with unequal spacing
Tables 1 and 2 indicate the insensitivity of the evaporation boundary and its temperature to grid spacing, provided that the spacing is always larger than the evaporation boundary point. Tables 3 and 4 involve solidification boundary and show that the temperature is insensitive to DELX but that the solidification boundary is quite sensitive to the choice of DELX. Thus, it is important to use DELX sufficiently small so that the solidification boundary movement is fully exhibited and not stunted by a large grid spacing relative to which the boundary size is small. The spacing affects the evaluation of the first and second temperature partial derivatives with time which are larger in absolute values for smaller spacings, due to more rapid temperature changes near the boundaries.

The figures (Figs. 2-4), prepared from the computed results in Tables 1-4, indicate the superiority of unequal over equal grid spacing. For DELX = 0.01 cm, where the spacing is coarse, little difference is found in the temperature distribution. For DELX = 0.001 cm, there is greater difference between the two because the equal spacing has limited the semi-infinite body to 27 (0.001 cm) and fixes the temperature at the end point to 970°C, thus not allowing the temperature to decline as rapidly as it should. For DELX = 0.0001 cm, the equal spacing method could not work at all because 27 (0.0001 cm) is too small a range to define a semi-infinite body even for the small time constants under consideration.

The second set of graphs, Fig. 3 (grid spacing DELX = 0.001), shows wide disparity between equal and unequal spacing whereas the first set of graphs (Fig. 2) (DELX = 0.01) shows good agreement. The smaller DELX needs more points to simulate the semi-infinite, one dimensional case and when restricted to IX = 28, fails to
Initial Melt Temp, $T_0 = 970^\circ C$

Fig. 2 Computed Temperature Distribution in Semi-infinite Body at Different Times, $t$ (initial grid spacing = 0.01 cm)
Fig. 3 Computed Temperature Distribution in the Semi-infinite Body at Different Times, $t$ (initial grid spacing = 0.001 cm)
Initial Melt Temp, $T_0 = 970^\circ$C

Fig. 4 Computed Temperature Distribution in Semi-infinite Body at Different Times, $t$ (initial grid spacing = 0.0001 cm)
allow temperature away from the evaporating surface to decline rapidly because it is artificially pegged at \( x = 28 \) (0.001) to 970°. The unequal spacing needs but six points to give equivalent extension and, when given 10 or 11 points, can adequately span a sufficient distance to simulate semi-infinity. At smaller DELX (0.0001) one cannot even attempt to use equal spacing without modifying the behavior at the last mesh point. For unequal spacing, 16 points will adequately represent the semi-infinite body for the times under consideration.

Checking Program

To check the program, GaAs single crystals will be grown with controlled dopant type, dopant concentration, growth rate, and temperature gradient, as shown in Table 5. The dopant concentration, carrier mobilities, defect contents, ... will be measured along several sections on each crystal. The results will be statistically analyzed and presented in future reports.
<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>Dopant</th>
<th>Concentration</th>
<th>Growth Rate ( \text{in./hr} )</th>
<th>Temperature ( \text{°C/in.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Te</td>
<td>( 1 \times 10^{17} )</td>
<td>0.16</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Si</td>
<td>( 5 \times 10^{18} )</td>
<td>0.22</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Cr</td>
<td>( 5 \times 10^{18} )</td>
<td>0.28</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Si</td>
<td>( 5 \times 10^{17} )</td>
<td>0.16</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Zn</td>
<td>( 5 \times 10^{18} )</td>
<td>0.16</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>Cr</td>
<td>( 1 \times 10^{18} )</td>
<td>0.16</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>Te</td>
<td>( 1 \times 10^{18} )</td>
<td>0.22</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>Zn</td>
<td>( 1 \times 10^{18} )</td>
<td>0.28</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>Cr</td>
<td>( 5 \times 10^{17} )</td>
<td>0.10</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>Si</td>
<td>( 1 \times 10^{18} )</td>
<td>0.10</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>Si</td>
<td>( 1 \times 10^{17} )</td>
<td>0.28</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>Zn</td>
<td>( 1 \times 10^{17} )</td>
<td>0.10</td>
<td>6</td>
</tr>
<tr>
<td>13</td>
<td>Te</td>
<td>( 5 \times 10^{17} )</td>
<td>0.28</td>
<td>4</td>
</tr>
<tr>
<td>14</td>
<td>Zn</td>
<td>( 5 \times 10^{17} )</td>
<td>0.22</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>Cr</td>
<td>( 1 \times 10^{17} )</td>
<td>0.22</td>
<td>4</td>
</tr>
<tr>
<td>16</td>
<td>Te</td>
<td>( 5 \times 10^{18} )</td>
<td>0.10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To be grown after the results of above crystals are analyzed.
CONCLUSIONS

We have developed a computer simulation program to study the phenomena of directional combined evaporation and solidification in binary alloys. A realistic phase diagram involving curved liquidus lines is used, and the program can be used for cases where the solid and liquid material parameters (e.g., specific heat, conductivity, diffusivity, ...) are functions of both temperature and solute concentration. The program works well if one follows the guidelines outlined in the report. The computed output results include the locations and velocities of movement of both the evaporation and solidification boundaries, and the temperature and concentration profiles in the semi-infinite alloy body at selected instants of time.
APPENDIX I

IMPROVED COMPUTER PROGRAM
FILE: BINCR6 FORTRAN P1

GRUMAN DATA SYSTEM

DIMENSION X(28),T(28),TT(28),C(28),CC(28)

*NAMELIST /INVAR/CEE,DS,DL,T0,C0,XKL,RHO,GAMMA,RHOU,GAMMAU,EE,SIG
* ,ET,EA,EB,EC,ED,AU,BU,EMU,AV,EV,EMV,EK,IX
ABS1(X)=-ABS(X)
UP(V)=EX*X(AU-BU/(273.12+V)))/SQRT(EMU*(273.12+V))
VE(V)=EK*(1.**((AV-BV)/(273.12+V)))/SQRT(EMV*(273.12+V))
FS(V)=(EB*(ET-V)+EA)*(ET-V)
FL(V)=(ED*(ET-V)+EC)*(ET-V)
XCL(V)=ET-2.*V/(EC+SQRT((EC)**2+4.ED*(V))
XCSL(V)=ET+2.*V/((EC-EA)+SQRT((EA-EG)**2+4.ED*V))
DFL(V)=-(2.*ED*(ET-V)+EC)
IF=1
10=8
READ(II,10) IX,IAM,NIT,IM,NONCN
110 FORMAT (1615)
NITH=NIT/2
NITQ=NITH/2
NIT=NITH*NITQ
64 READ(II,101) ET,EA,EB,EC,ED
AQUAN=-((EA-EC)**2/4.*((EB-ED))
101 FORMAT (7E10.0)
READ(II,101) ET,EA,EB,EC,ED
AQUAN=-((EA-EC)**2/4.(*((EB-ED))
READ(II,101) A1,BU,EMU,AV,EV,EMV,ET
ALS=XKL/RHO*CEE
IKS=1.*XKL
ASS=1.*ALS/1.03
AS=SQRT(ASS)
AL=SQRT(ALS)
100 READ(II,102) DELX,DELT1,DELT2,DELH,IF,S
DELH=AMAX1(DELH1,DELH1/124.)
T2=XCL(CC)
COFL=FL(T2)
277 DO 1 I=1,IX
IF(I-2) 2,3,4
2 X(1)=0.
GO TO 1
3 X(2)=DELX
GO TO 1
4 IF(IAM) 5,6,7
5 X(I)=X(I-1)+DELX
GO TO 1
6 X(I)=X(I-1)+X(I-1)
1 CONTINUE
999 WRITE(10,101) IX,IAM,NIT,IM,NONCN
WRITE(10,10) ET,EA,EB,EC,ED
WRITE(10,10) A1,BU,EMU,AV,EV,EMV,ET
WRITE(10,10) CEE,DS,DL,T0,C0,XKL,RHO,GAMMA,RHOU,GAMMAU,EE,SIG,T2
*CO
TPR=DELP
RAT=1.
TI=1
TII=0
CSTL=C0

52
FILE: BINCR6 FORTRAN P1

G R U M M A N D A T A S Y S T E M

VI1=0.
VI2=0.
II1=2
II2=2
II3=2
D2T2=0.
D2T3=0.
D2T4=0.
D2C3=0.
D2C4=0.
D2C2=0.
D2T1=0.
D2C1=0.
D2T2=0.
D2T3=0.
D2T4=0.
D2T5=0.
D2C6=0.
D2T6=0.
TIME=0.
DCF0=0.
DTD0=0.
DELTS=DELTS/8.
TIME=TIME+DELTS
DO 10 I= 1, IM
C(I)=CO
CC(I)=C0
TT(I)=TO
TT(I)=TO
IFL=0
IPS=0
III=II2
10 T(I)=TO
IFL=0
IPS=0
III=II2
11 IT=0
IF(IFL.EQ.1)GO TO 199
IF(IFL.EQ.1)GO TO 11, 11, 20
11 U0=UF(T0)
V0=VF(T0)
IFI=1
199 IF(IFL.EQ.0) CSL1=CS1
IF(IFL.EQ.0)IFS=2
DYDT0=U0*EMU*SL1/RHO+V0*EMV*(1.-CSL1)/RHO
HBN=-EM*SIG*(273.12+TSI1)**4-U*GAMMAU*CSL1-V0*GAMMA*(1.-CSL1)
DCDT0=DCF0*DYDT0-(U0-V0)*CSL1
DZDT0=DTD0*DYDT0+HBN
20 YI2=YI1+DELTS*DYDT0
IF(IFL.EQ.0) ZI2=I2
IF(IFL.EQ.0) ZI2=ZI1+DELTS*DZDT0
IF(ZI2.GT.X(I2+1))ZI2=(X(I2)+YI2)/2.
TSI2=TSI1+DELTS*DZDT0
II2=TSI2
CSL2=CSL1+DELTS*DCDT0
IF(IFL.EQ.0)CL2=CSL2
77 IF(IFL.EQ.0)GO TO 777
IF(IFL.GT.1)GO TO 877
IIIT=0

ORI G I N A L   PA GE   IS
OF POOR QUALITY

53
877  CS2=FS(TI2)
CL2=FL(TI2)

777  D2C2= D2(ZI2,CL2,X(I2),CC(I2),X(I2+1),CC(I2+1))
CC(I2)= (CC(I2) + C(I2) + 5*DELT*(D2C1+D2C2)*DL )/2.
CALL MOTON(X(I2),CC(I2),ZI2,CL2,X(I2+1),CC(I2+1))
IF( (ZI2.LT. X(I2-1)) CC(I2-1) = CC(I2) + (X(I2-1) - X(I2)) * 
  (CL2-CC(I2))/ (ZI2-X(I2)) )
IF( (I1-I13-1) )

87  XP=YI2
CP=CSL2
GO TO 184

84  XP=X(I1-I2)
CP=CC(I1-I2)

184  D2C4=D2(XP,CP,X(I1-I2),CC(I1-I2),ZI2,CS2)
CC(I1-I2) = C(I1-I2) + 5*DELT*(D2C3+D2C4) * DS
CALL MOTON(X(I1-I2),CC(I1-I2),XP,CP,ZI2,CS2)

83  IF( (ZI2.EQ.I13) ) GO TO 85

787  IF(I1-EQ.I11) CALL NOTON(X(I1),CC(I1),ZI2,CL2,X(I1+1),CC(I1+1))
IF( (ZI2.LT. X(I1-1)) CC(I1-1) = CC(I1) + (X(I1-1) - X(I1)) * 
  (CL1-CC(I1))/ (ZI2-X(I1)) )
IF( (I1-I13-1) )

185  IF( (IFS.EQ.3) ) GO TO 485

485  IF( (ZI2.LT. X(I1-I2)) TT(I1-I2) = TT(I1) + (X(I1-I2) - X(I1)) * 
  (TI2-TT(I1))/ (ZI2-X(I1)) )
IF( (I1-I13-1) )

269  IF( (IFS.EQ.0) ) GO TO 299

DCLDX=(CL2-CC(I1-I2))/ (ZI2-X(I1-I2))
IF ( (D2C2.GT.0.) ) DCLDX=DCLX-D2C2* (X(I1)-ZI2)/2.
IF ( (D2C2.LT.0.) ) D2C2=0.
DTLDX= (TI2-TT(I1-I2))/ (ZI2-X(I1-I2))

54
IF (D2T2.LT.0.) DTLDX=DTLDX-.5*D2T2*(X(II2)-ZI2)
IF (II3.EQ.II1) GO TO 386
XP=X(II1-1)
TP=TT(II1-1)
CP=CC(II1-1)
GO TO 486
386 XP=YI2
TP=TSI2
CP=CSL2
DCSDX=(CS2-CP)/(ZI2-XP)
DTSDX= (TP-TP)/(ZI2-XP)
GO TO 686
486 DCSDX=(CP-CS2)/(XP-ZI2) -D2C4*(XP-ZI2)/2.
DTSDX= (TP-TI2)/(XP-ZI2) -D2T4*(XP-ZI2)/2.
586 DTDX=(D*L*DCDX+DS*DCSDX)/(CS2-CL2)
DTDX=(XKS*TSI2-XT(II2)-X(II2))/YI2
DCDX=(TSI2-TP)/(XP-ZI2)
DCSDX=(CP-CS2)/(XP-ZI2)
GO TO 772
772 TII=ET
771 COE1=XKS/(ZI2-XP)
COE2=XKL/(X(II2) -ZI2)
587 IF (ABS(DTDX-DTDX1)-1.E-3*ABS1(DTDX+DTDX1)) 298,298,770
770 TII=(TII+TII2)/2.
IF (DZDT.LT.).)DZDT=DZDT1
DZDT1=(DZDT+DZDT1) /2.
ZI2=ZI1+.5*DELTS*(DZDT1+DZDT0)
IF(ZI2.GT.X(II2+1))ZI2=(X(II2)+YI2)/2.
IIT=IIT+1
GO TO 877
298 IF(TI.GT.TT(II2))TI=TT(II2)
IF(TI.LT. TSI2) TI=TSI2
IF(II1-II3-1)398,498,598
598 D2T6=D2(YI2,TSI2,X(II3)) ,TT(II3),X(II3+1),TT(II3+1)
D2C6=D2(YI2,CSL2,X(II3) ,CC(II3) ,X(II3+1),CC(II3+1))
DTDX=(TSI2-XT(II3))/ (YI2-X(II3)) -D2T6*(X(II3)-YI2)/2.
DCDX=(CSL2-CC(II3))/ (YI2-X(II3)) -D2C6*(X(II3)-YI2)/2.
GO TO 599
498 DTDX=DTSDX+D2T4*(XP-ZI2)
DCDX=DCSDX+D2C4*(XP-ZI2)
D2T6=D2T4
D2C6=D2C4
GO TO 599
398 DCDSX=DCSDX
DTDX1=DTDX
GO TO 599
299 DTDX=(TT(II2)-TII2)/ (X(II2)-YI2) -.5*D2T2*(X(II2)-YI2)

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DCDX1 = (CC*(II2) - CL2) / (X*(II2) - YI2) -.5*D2C2*(X*(II2) - YI2)

59 9 U1 = U(TSI2)
  V1 = V(TSI2)
  HB1 = BE + SIG*(273.12 + TSI2)**4 - U1*GAMMAU*CSL2 - V1*GAMMA*(1. - CSL2)
  DYT1 = U1*EMU*CSL2/RHOU - V1*ENV*(1. - CSL2)/RHO
  DCDT1 = DCDX1*DYDT1 - (U1 - V1) * CSL2
  DTDT1 = DDTXT1*DYDT1 + HB1
  IF (IFL.LT.2) GO TO 76
  IF (IFS.GE.1) GO TO 174
  IF (TSI2 .GT. TT(II2)) GO TO 399
  TT2 = XCL(CSL2)
  IF (TSI2 .GT. TT2) GO TO 174
  IF (TSI2 .GE. TT2 -.05) GO TO 400
  IF (D1TS.LT.DELTK) GO TO 400
  GO TO 399

76 YI = YI1 + .5*(DYDTO + DYDT1) * DELTS
  IF (IFS.EQ.0) ZI = YI
  TSI = TSI1 + .5*(DTDT + DTDT1) * DELTS
  IF (IFS.EQ.0) TSI2 = TSI2
  YI2 = (YI + YI2) / 2.
  IF (IFS.EQ.0) YI2 = YI2
  CSL = (CSL + CSL2) / 2.
  IF (IFS.EQ.0) CSL2 = CSL2
  IF (II1 - II2) .LT. 24, 96, 96
  II2 = II2 + 1
  IF (IT - NITH) 48, 174, 160
  IF (IT - NITH) 48, 47, 48
  IF (DELTS - DELTK) 48, 48, 53
  DELTS = DELTS/RAT
  IF (RAT - 1.) 153, 153, 154
  RAT = 2.*RAT
  DELTS = DELTS/2.
  GO TO 152

154 TIME1 = TIME + DELTS
  DO 45 I = II3, IM
    TT(I) = (TT(I) + (RAT - 1.)*T(I))/RAT
    CC(I) = (CC(I) + (RAT - 1.)*C(I))/RAT
  45 IF (IT .EQ. NITH + 1) GO TO 20
  IF (IT = NITH) 161, 174, 161
  161 IF (IT .EQ. NITH) 77, 77, 402
  DO 402 IF (DELTS.GT.DELTK) GO TO 399

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IFL = 2
GO TO 77

26 IF (NONCN) 99, 48, 48
7 IFL = IFL + 1
DZDT1 = DZDT
IF (IFS.NE.0) ZI2 = ZI1 + 0.5 * DELTS * (DZDIO + DZDT1)
TSI2 = TSI
YI2 = YI
IF (IFS.EQ.0) ZI2 = YI2
CSL2 = CSL
IF (IFS.NE.0) TI2 = TI
IF (TI2 .LT. TSI2) TI2 = TSI2
IF (IFS.EQ.0) CL2 = CSL2
GO TO 77

399 IF (DELTLE .LE. DELTK) GO TO 26
IT = NITH
IFL = 1
GO TO 153

117 IF (TIME.EQ. TIME1) TIME1 = TIME1 + DELTS:
TIME = TIME1
IF (RAT .NE. 2. .AND. RAT .NE. 0.) DELTS = DELTS/RAT
RAT = 1.
IF (IT .LT. ITQ) 82, 82, 81
82 IF (DELTLE .GT. DELT/2.) GO TO 81
DELT = DELTS + DELTS
RAT = 2.
GO TO 81

81 TIME1 = TIME1 + DELTS

282 D2C1 = D2C2
D2C3 = D2C4
D2C5 = D2C6
D2T3 = D2T4
D2T1 = D2T2
D2T5 = D2T6
DYDT0 = DYDT1
DCDT0 = DCDT1
U0 = U1
V0 = V1
DTSDX1 = DTSDX
DCSDX1 = DCSDX
IF (IFS.NE.0) DCDX0 = DCDX1
IF (IFS.NE.0) DTDT0 = DTDT1
IF (IFS.NE.0) DZDT0 = DZDT1
CSL1 = CSL2
TSI1 = TSI2
YI1 = YI2
ZI1 = ZI2
IF (IFS.NE.0) CS1 = CS2
HB0 = HB1
CL1 = CL2
TI1 = TI2
IF (YI2 .LT. X(II3)) GO TO 410

II3 = II3 + 1
D2T5 = D2(YI1, TSI1, X (II3), X (II3), X (II3 + 1), TT (II3 + 1))
D2C5 = D2(YI1, CSL1, X (II3), CC (II3), X (II3 + 1), CC (II3 + 1))
FILE:  BINCR6  FORTRAN  P1

54 IF(TT-NIT) 98,98,42
14 IF(DELP.EQ.C.)GO TO 42
TPR=TPR+DELP
42 WRITE(IO,100) IT,IM,II1,II2,II3
WRITE(IO,102)TIME,Y1,CSL1,TSI1,U1,V1,HB1,DYDT1,DTDT1,DELTS
143 WRITE(IO,102) (TT(I),I=II1,IM),(CC(I),I=II1,IM)
152 FORMAT(5E14.6)
98 DO 97 I=II1,IM
   TTT=TT(I)+RAT*(T(I)-T(I))
   TT(I)=TT(I)
97 CONTINUE
   DO 197 I=II1,IM
   CCC=CC(I)+RAT*(CC(I)-C(I))
   C(I)=CC(I)
197 CC(I)=CCC
   IFL=1
GO TO 27
44 CSS=FS(T12)
   CLL=FL(T12)
   DEL= (CLL-CL2)/((CLL+CC(I12)) - 2.*CSS) *(Y(I12)-Y12)
   ZI2=Z12+DELZ
   DZDT=DELZ/DELTS
   DTDT=DZDT
   CL2=CLL
   CS2=CSS
   DCDT=0.
   DTDTX=0.
   ZI2=FS(T12)
   WRITE(IO,103)TIME,Y1,CSL1,TSI1,U1,V1,HB1,DYDT1,DTDT1,DELTS
193 FORMAT(' SOLIDIFICATION HAS BEGUN '/(5E14.6))
199 FIX=1
GO TO 174
99 READ(IO,INVAR)
   IF(IX.GT.7)GO TO 999
STOP
END

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APPENDIX II

GLOSSARY OF PROGRAM PARAMETERS

IX = maximum number of points in mesh, ≤ 28
IAM = spacing option: 0 indicates equal, 1 unequal doubling
NIT = maximum iteration count
IM = number of points in mesh
NONCN = nonconvergence option: 1 indicates proceed and printout
        0 indicates proceed but do not printout
        -1 indicates program stop
IT = actual iteration count
NITH = half of NIT
NITQ = quarter of NIT
NITL = 3/4 NIT
IFL = indicator of convergence: 2 on convergence,
     < 2 before convergence
IFS = indicator of beginning of solidification: IFS = 0 before solidification,
     IFS > 0 after solidification
III = grid point reference for solid side of mesh
II2 = grid point reference for liquid side of mesh
II3 = grid point reference for evaporation boundary
II4 = grid point reference for point after evaporation boundary
III = grid point reference for point after solidification boundary
DELT = maximum time interval (step size)
DELM = minimum time interval
DELTK = larger of quantities DELT/1024 and DELTM
DELTS = current time interval
TIME = time at beginning of time interval
TIME1 = time at end of time interval
DELP = time print interval
TPR = time for printing results
TF = final time
YI, YII, YI2 = values of y (evaporation boundary)
ZII, ZI2 = values of z (solid-liquid boundary)
TI, TII, TII, TI2 = temperatures at solid-liquid boundary
TSI, TSI2, TSI2 = temperatures at evaporation boundary
CSL, CSL1, CSL2 = concentration at evaporation boundary
CS1, CS2 = concentration of solid at solid-liquid boundary
CL1, CL2 = concentration of liquid at solid-liquid boundary

DZZDT, DZDTT, DZDTO, DZDT1 = derivative of solid-liquid boundary
dy

DYDTO, DYOT1 = derivative of evaporation boundary
dt
dt
dt

DCDSTO, DCTST1 = derivative of concentration at evaporation boundary
dt

dx

DTSSTO, DTSST1 = derivative of temperature at evaporation boundary
dt

DCSDX0, DCDX1 = derivative of concentration at evaporation boundary
dx

DCSX0, DCDX1 = derivative of concentration at solid-liquid boundary
dx

DCLDX = derivative of concentration in liquid at solid-liquid boundary
dx

DCLDX = derivative of concentration in liquid at solid-liquid boundary
dx

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D2T1, D2T2 = \left( \frac{\partial^2 T}{\partial x^2} \right) \text{ at liquid side of solid-liquid boundary}

D2T3, D2T4 = \left( \frac{\partial^2 T}{\partial x^2} \right) \text{ at solid side of solid-liquid boundary}

D2T5, D2T6 = \left( \frac{\partial^2 T}{\partial x^2} \right) \text{ at evaporation boundary}

D2C1, D2C2 = \left( \frac{\partial^2 C}{\partial x^2} \right) \text{ at liquid side of solid-liquid boundary}

D2C3, D2C4 = \left( \frac{\partial^2 C}{\partial x^2} \right) \text{ at liquid side of solid-liquid boundary}

D2C5, D2C6 = \left( \frac{\partial^2 C}{\partial x^2} \right) \text{ at solid side of solid-liquid boundary}

U0, U1 = rates of evaporation of solute

V0, V1 = rates of evaporation of solvent

HBO, HB1 = heat balance sum of evaporation and radiation terms

EMU, EMV = molecular weight of solute and solvent atoms

RHOU, RHO = density of solute and solvent

GAMMAU, GAMMA = specific heats of solute and solvent

AU, BU, AV, BV, EK = evaporation constants for solute and solvent

UE, VE = arithmetic function definition for evaporation rates

ET, EA, EB, EC, ED = phase diagram constants

FS, FL = arithmetic functions for solidus and liquidus curves
AS, AL = temperature diffusion coefficients
ASS, ALS = squares of temperature diffusion coefficients
XKS, XKL = $k_s$, $k_p$ for interphase boundary equation
DS, DL = mass (concentration) diffusion coefficient
EE, SIG = radiation constants $\epsilon, \sigma$
TO, CO = initial temperature and concentration distribution
COO = equals CO
APPENDIX III

LIST OF SYMBOLS

\( A_A \) \( \frac{k_A}{\rho_A}c \)

\( A_s \) \( \frac{k_s}{\rho_s}c \)

\( A_u, B_u \) evaporating constants for solute

\( A_v, B_v \) evaporating constants for solvent

\( c \) specific heat, \( \text{cal/g/°C} \)

\( C \) solute concentration

\( C_\ell \) solute concentration in liquid

\( C_0 \) initial solute concentration in liquid

\( C_s \) solute concentration in solid

\( D_s \) density of solid, \( g/cm^3 \)

\( D_\ell \) density of liquid, \( g/cm^3 \)

\( E_T \) melting point of solvent, \( °C \)

\( E_A, E_B \) coefficients of solidus

\( E_C, E_D \) coefficients of liquidus

\( f_\ell \) liquidus equation

\( f_s \) solidus equation

\( K_e \) constant in evaporation equations = \( 5.83 \times 10^{-5} \)

\( k_\ell \) thermal conductivity of liquid, \( \text{cal/sq cm/cm/sec/°C} \)

\( k_s \) thermal conductivity of solid, \( \text{cal/sq cm/cm/sec/°C} \)

\( M_u \) molecular weight of solute

\( M_v \) molecular weight of solvent
S time constant

t time, second

T temperature, °C

T_i temperature at solid-liquid interface, °C

T_f temperature in liquid, °C

T_o initial melt temperature, °C

T_s temperature in solid, or surface temperature, °C

T_1 surface temperature, °C

T_2 final surface temperature, °C

U solute evaporating rate, mol/cm^2/sec

V solvent evaporating rate, mol/cm^2/sec

v position and temperature-dependent variable

x distance from initial melt surface, cm

y distance at phase change boundary, cm

\dot{y} rate of movement of phase change boundary, cm/sec

z distance at phase change boundary, cm

a constant

\epsilon emissivity coefficient

\rho density, g/cm^3

\rho_u density of solute, g/cm^3

\rho_v density of solvent, g/cm^3

\gamma latent heat of fusion, cal/g

\gamma_u latent heat of fusion, or specific heat, of solute, cal/g or cal/g/°C

\gamma_v latent heat of fusion, or specific heat, of solvent, cal/g or cal/g/°C

\sigma Stefan-Boltzmann constant = 1.35 \times 10^{-6}
REFERENCES


