NASA TECHNICAL MEMORANDUM NASA TM-75637

THEORETICAL BASES FOR CONDUCTING CERTAIN TECHNOLOGICAL PROCESSES IN SPACE

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Translation of "Teoreticheskiye osnovy provedeniya nekotorykh tekhnologicheskikh protsessov v kosmose," Academy of Sciences USSR, Institute of Space Research, Moscow, Report Pr-435, 1978, pp 1-29

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 JUNE 1979

STANDARD TITLE PAGE

1. Report No. NASA TM-75637	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle THEORETICAL BASES FOR CONDUCTING CERTAIN TECHNOLOGICAL PROCESSES IN SPACE		5. Report Date June 1979 6. Performing Organization Code
7. Author(s) A.S. Okhotin USSR Academy of Sciences Institute of Space Research		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASW-3199 13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Teoreticheskiye osnovy provedeniya nekotorykh tekhnologicheskikh protsessov v kosmose," Academy of Sciences USSR, Institute of Space Research, Moscow, Report Pr-435, 1978, pp 1-29

16. Abstract Beginning with dimensionless conservation equations, this article reviews the theoretical bases of fluid behavior aboard orbiting satellites with application to the processes of manufacturing crystals in weightlessness. The small amount of gravitational acceleration is shown to increase the separation of bands of varying concentration. Natural—convection is shown to have no practical effect on crystallization from a liquid melt. Barodiffusion is also negligibly small in realistic conditions of weightlessness. The effects of surface tension become increasingly large, and suggestions are made for further research.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified-unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 30	22. Price

THEORETICAL BASES FOR CONDUCTING CERTAIN TECHNOLOGICAL PROCESSES IN SPACE

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In recent years the field of space research has witnessed a remarkable increase in the attention devoted to the problem of space technology. Within this area the greatest interest has been stimulated by the problems of studying the behavior and manufacture of materials in a state of weightlessness. A whole series of experiments have already been performed in this regard: the study of welding on board "Soyuz-6" in 1969, the study of the process of crystallization of various materials on "Skylab" and "Apollo-Soyuz," the modeling experiments on "Salyut-5" and the short-term experiments on rocket probes in the USA. At the present time technological experiments are being conducted on the orbiting space station "Salyut-6" with the active participation of scientists from a number of socialist countries. These investigations make it possible even now to state the fundamental laws of the behavior and production of matter in weightlessness with a substantial degree of precision. And it is the analysis of these fundamental laws which makes it possible to formulate the basic technological requirements of the apparatus in space and to determine to a large extent which materials are appropriate to prepare in space. /3*

In its most general form, the system of equations describing the process of the growth of crystals can be written thusly in dimensionless form: /4

The equation of motion

$$\frac{\partial \bar{v}_i}{\partial (Fo)} + \bar{v}_i \frac{\partial \bar{v}_j}{\partial x_i} = -\frac{\partial \bar{P}}{\partial x_j} + \frac{Gr}{Re^2}\theta + \frac{Gr_D}{Re^2}\bar{C} + \frac{1}{Re}\sum \frac{\partial^2 \bar{v}_j}{\partial x_i^2}. \quad (1)$$

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*Numbers in the margin indicate pagination in the foreign text.

The equation of continuity

$$\frac{\partial(\bar{\rho}\bar{v}_i)}{\partial x_i} = 0. \qquad (2)$$

The equation of energy

$$\frac{\partial\theta}{\partial(Fo)} + \bar{v}_i\frac{\partial\theta}{\partial x_i} = \frac{1}{Pe}\sum\frac{\partial^2\theta}{\partial x_i^2}. \qquad (3)$$

The equation of convective diffusion

$$\frac{\partial\bar{c}}{\partial(Fo)} + \bar{v}_i\frac{\partial\bar{c}}{\partial x_i} = \frac{1}{Pe_D}\sum\frac{\partial^2\bar{c}}{\partial\bar{x}_i^2}. \qquad (4)$$

In this system v_0, ΔT_0, and ℓ_0 are taken as arbitrary scales of velocity, temperature change, and length, respectively. Then

$$\bar{v}_i = v_i/v_0, \qquad (5)$$

$$\theta = \Delta T/\Delta T_0, \qquad (6)$$

$$\bar{x}_i = x_i/\ell_0, \qquad (7)$$

$$\bar{P} = P/\rho v_0^2, \qquad (8)$$

where P is pressure; ΔT_0 is $[T_{wall} - T_{mass\text{-}average}]$; ΔT is the characteristic temperature gradient; ρ is density.

The dimensionless criteria in equations (1)-(4) can be represented in the following form:

The Grashof criterion /5

$$Gr = \frac{g\ell_0^3 p\Delta T}{\nu^2}, \qquad (9)$$

The Peclet criterion

$$Pe = \frac{v_0\ell_0}{a}, \qquad (10)$$

The Reynolds criterion

$$Re = \frac{v_0\ell_0}{\nu}, \qquad (11)$$

The Fourier criterion

$$Fo = \frac{v_0\tau}{\ell_0} \qquad (12)$$

The criterion of Grashof diffusion

$$Gr_{\mathcal{D}} = \frac{g l_0^3 \beta_{\mathcal{D}} \Delta c}{\nu^2}, \qquad (13)$$

The criterion of Peclet diffusion

$$Pe_{\mathcal{D}} = \frac{v_0 l_0}{\mathcal{D}}, \qquad (14)$$

where β is the volume expansion coefficient; β_D is the coefficient of volume expansion due to change in composition; v is the kinematic viscosity; a is the coefficient of thermal conductivity; g is the acceleration of tensile force; τ is time; c is concentration; Δc is the characteristic concentration gradient; and D is the diffusion coefficient.

Before proceeding to a general analysis of the system of equations (1)-(4), let us first consider for a moment each one separately.

The equation of motion - the Navier-Stokes equation - (1), characterizes the generation of motion in a liquid from changes in its density due to temperature or concentration variation (such as in unstable stratification). According to this, the expression for density has the form

$$\rho = \rho_0(1+\beta\Delta T) + \rho_0(1+\beta_{\mathcal{D}}\Delta C). \qquad (15)$$

If the dependence of ρ on concentration can be neglected, such as, for example, in the case of greatly diluted solutions, then the $\frac{Gr_{\mathcal{D}}}{Re^2}\bar{c}$ term in equation (1) may be omitted. In a stationary regime the term in equation (1) containing a Fourier criterion may also be omitted. In the majority of cases (of processes /6 of material manufacturing) the term containing the Peclet criterion is also neglected, due to the small value of the second derivative of velocity.

Therefore, when performing a qualitative analysis of the growth of crystals in a melt, we can write equation (1) in the form

$$\bar{U}_i \frac{\partial \bar{U}_i}{\partial x_i} = -\frac{\partial \bar{P}}{\partial x_j} + \frac{Gr}{Re^2}\theta + \frac{Gr_{\mathcal{D}}}{Re^2}\bar{c} \qquad (16)$$

From this it is possible to estimate by order of magnitudes that at small velocities of generated motion ($Re \ll 1$), the value of $Gr/Re^2 \sim 1/Re$, whence $Gr \sim Re$. Then at large velocities ($Re \gg 1$), the value of $Gr/Re^2 \sim 1$, which means $Re \sim \sqrt{Gr}$. Naturally the quantity which determines the velocity is still the Grashof criterion. At appropriate boundary conditions the equation of motion describes such processes important to space technology as thermocapillary convection. This type of flow is treated in more detail below.

The equation of continuity, (2), for the case of binary mixing (henceforth, in order to simplify the mathematical exposition, we shall always consider crystal growth only in binary mixtures, since the essence of the procedure does not change in multiple-component mixtures; only the mathematical apparatus is more complicated), can be written in the form

$$\frac{\partial \bar{x}_i}{\partial \tau} = \frac{1}{Pe_{\mathcal{D}}}\Delta \bar{x}_A, \qquad (17)$$

where $\Delta\bar{x}_A$ is the relative change in the content of the component A of the binary mixture, and the criterion $Pe_{\mathcal{D}}$ can be represented in the form

$$Pe_{\mathcal{D}} = Re \cdot Pr_{\mathcal{D}}, \qquad (18)$$

where $Pr_{\mathcal{D}}$ is the Prandtl diffusion criterion or the Schmidt criterion:

$$Pr_{\mathcal{D}} = Sc = \frac{\nu}{\mathcal{D}}. \qquad (19)$$ /7

If only free convection takes place during the process of crystalline growth, then expression (17) transforms to

$$\frac{\partial \bar{x}_A}{\partial \tau} = \frac{1}{Sc} \Delta \bar{x}_A . \qquad (20)$$

The equation of continuity is usually introduced in this form into the system of equations in order to describe the process of transport in the growth of crystals.

The equation of energy, (3), for the process of heat transport during crystalline growth, is nothing other than the equation of thermal conductivity, which can be written in general form as:

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{Pe} \theta + \frac{Br}{Pe} \Phi^* , \qquad (21)$$

where the Peclet criterion

$$Pe = Re \cdot Pr , \qquad (22)$$

while the Prandtl criterion

$$Pr = \frac{\nu}{a} \qquad (23)$$

The quantity B_r is the Brinkmann criterion

$$Br = \frac{V y^2}{\rho \lambda \Delta T} . \qquad (24)$$

where V is the volume; λ is the thermal conductivity; and Φ^* is the dissipative function in dimensionless coordinates, taking into account the velocity gradients.

If the process of heat transport only describes natural convection, then the equation of motion can be written in a simpler form:

$$\frac{\partial \theta}{\partial \tau} = \frac{\theta}{Pr} . \qquad (24)$$

We should note that the Peclet criterion is different for liquids /8 and for gases, since for gases the values of "a" and "D" have the same order of magnitude, while for liquids, $D \ll a$, and so

$P_e \ll P_{eD}$. Consequently, for two liquids with the same Peclet numbers, their temperature distributions are determined by their thermal conductivities, while the concentration distribution is determined by the convection processes.

The equation of convective diffusion, (4), describes a nongravitational process taking place in crystalline growth. Therefore, the analysis of this equation is extremely important in the preparation of materials in a condition of weightlessness. In stationary conditions in a binary combination the equation takes the form

$$\bar{v}_i \frac{\partial \bar{c}}{\partial x_i} = \frac{1}{Pe_D} \frac{\partial^2 \bar{c}}{\partial x_i^2} \qquad (25)$$

which makes it possible to perform qualitative analysis by inspection. Since the value of the Peclet criterion determines the mechanism of redistribution of components in the melt, it is clear that when $P_e \gg 1$ the contribution of the right-hand side of equation (25) is small and that the mechanism of distribution is essentially determined by the convective current with the velocity $\overleftarrow{\nu_i}$. If we have $P_e \ll 1$, then the process of formation of a concentration profile accounts for the main diffusion. Since the value of the Prandtl diffusion criterion does not depend on the hydrodynamic processes in the melt, while the value of the Reynolds number is determined in our example by convective currents, we can choose that value of the Peclet criterion from equation (18) at which the effect of convection on the concentration profile disappears. Let us designate this value as $P_{eD}^* = 1$. Then $R_e P_{eD} = 1$ and taking the analysis of equation (16) into account, we can write down $(Gr \cdot Pr_D^*) = 1$ for small velocities of motion, while for large velocities, $(\sqrt{Gr} \cdot Pr_D^*) = 1$. Since the movement of the critical value of the Peclet number ($Pe_D^* = 1$) is only possible at small values /9 of the Reynolds criterion, that is, at small flow velocities, and considering that $Pr_D \gg 1$ in liquids, the relationship $(Gr Pr_D)^* = 1$ will be correct for a melt.

Naturally, this description of the features of each equation which are applicable to a condition of weightlessness is of only the most general character, since a more detailed analysis forms the subject of specialized investigation.

For our purposes it is certainly more important to establish the fact of the impossibility of a general solution to this system of equations (1-4). We can only qualitatively state that the generation of motion in liquids and gases in the process of obtaining crystalline materials can take place because of a variety of processes: the development of natural convection, the accidental pulsation of velocities in an unequally heated liquid under conditions of stable stratification, the presence of a temperature or concentration gradient at a free surface (thermocapillary convection), changes in the density of the material or a phase transition, or peculiar boundary conditions which lead to the development of Stefanov convection, and other phenomena.

Since preserving an absence of motion of internal current from any of the phenomena enumerated above is the fundamental requirement for obtaining materials from a melt or a gas through the process of crystallization, it is therefore obvious that the choice of methods and materials must be performed in such a way as to remove or keep at a minimum the causes of any such motion. Since a large number of the causes are nongravitational in nature, it is therefore necessary even in space to conduct a selection of materials, starting with the values of the criteria stated in equations (1-4), and methods of obtaining and maintaining the boundary conditions and flow conditions of the crystallization process, so that the possibility of generating motion with the liquid or gas is minimized. /10

Since it is not possible in carrying out the process of obtaining crystalline materials in orbiting space stations to speak of a condition of ideal weightlessness (it is well known that the value of "g" in such vehicles varies from 10^{-3} to 10^{-8}, depending on the structure of the satellite and the conditions of its orbit), it is more accurate to consider the flow of these processes under conditions of microgravitation. In this condition it is possible to create working conditions within the technological apparatus at which the values of the Grashof criterion, which is directly proportional to the value of the acceleration of free fall, will be such that the possibility of creating free convection may be large. We will henceforth consider, however, that the methods and apparatus have been chosen to condition the values of the Grashof criterion at such a level that the presence of natural convection in obtaining crystalline materials can be ignored. Incidentally, we should note that it is possible to create these conditions even in terrestrial technological establishments, but because of the presence of the value g = 1 on earth, their realization is only possible in very small volumes or thin sheets. But this is far from always corresponding to the dimensional requirements of producing crystalline materials.

Thus, starting from the fact that the general solution to the system of equations (1-4) is lacking and ignoring the presence of free convection in conditions of weightlessness, the description of separate steps in the process of obtaining crystalline materials in space is only possible by means of a solution to the partial problem. By way of example let us introduce some - in our opinion highly characteristic - processes which occur during the production of materials in the conditions of interplanetary space.

First of all, let us estimate the value of acceleration at which the effect of natural convection may be ignored in the transport process in melts and gases. Let us designate this value $g = ng_0$, where n is the value of load lightening and /11 g_0 is the acceleration from the gravitational field at the surface of the earth. We must find "n."

Since it is well known that the effect of natural convection in thermal transport disappears at $R_a = G_r P_r < 10^3$, then, using relationships among criteria given above, we can obtain

$$n = \frac{\nu D}{g_0 \beta l^3 \Delta T} \tag{26}$$

A more exact value of the quantity n can be obtained by solving the problem for more specific conditions of the process. For example, one of the possible situations in preparing crystals from a melt is the equality of the velocity of motion created by natural convection to the velocity of motion of the liquid at the front of crystallization. Since the motion at the front is conditioned by the different densities of the liquid and solid phases, its velocity is thus:

$$v = v_f \left(1 - \frac{\rho_T}{\rho_{zh}}\right) \tag{27}$$

where v_f is the velocity of the moving front of crystallization; ρ_T and ρ_{zh} are the densities of the solid and liquid phases, respectively. Taking into account what was said above about the equality of the Grashof and Reynolds criteria, we obtain

$$n = \frac{v_f \left(1 - \frac{\rho_T}{\rho_{zh}}\right) \nu}{g_0 l^2 \Delta T \beta} \tag{28}$$

or for the case $Re = \sqrt{Gr}$

$$n = \frac{v_f^2 \left(1 - \frac{\rho_T}{\rho_{zh}}\right)^2}{g_0 l^2 \Delta T \beta} \tag{29}$$

We could use as another example the growth of crystals in the gaseous phase, where the characteristic velocity is the velocity of Stefanov flow:

$$\upsilon = \frac{\mathcal{D}}{1-c_x}\left(\frac{\partial c}{\partial n}\right)_{n_0=0} \tag{30}$$

where c is the mass concentration of the gas, x is the cold surface, and n_0 is the normal to the surface. /12

The total transfer of matter across the surface of the growing crystal is equal to

$$j = -\mathcal{D}\left(\frac{\partial c}{\partial n_0}\right)_{n_0=0} + \upsilon c_x \tag{31}$$

In turn, the expression for the total transfer of matter in the one-dimensional stationary case can be found from the equation for convective diffusion, (4), and is equal to

$$j = \upsilon = \frac{\mathcal{D}}{c}\ln\frac{1-c_\Gamma}{1-c_x} \tag{32}$$

where Γ is the heated surface.

Here, then, for the case Re = Gr, it can be shown that

$$n = \frac{\mathcal{D}\nu}{l^3 g_0 \beta \Delta T}\ln\frac{1-c_\Gamma}{1-c_x} \tag{33}$$

and for the case Re = $\sqrt{\mathrm{Gr}}$

$$n = \frac{\mathcal{D}^2}{l^3 g_0 \beta \Delta T}\left(\ln\frac{1-c_\Gamma}{1-c_x}\right)^2 \tag{34}$$

Note that (33) and (34) coincide exactly with expression (26) except for the logarithmic factor. Let us introduce some numerical quantities. For semiconductors of the type $A^{sh}B^{u}$, taking $\ell = 10^{-2}$m with a temperature gradient ~ 200°/cm, the value of Gr = 2n10^6. The value then of Pr D. ~ 30-300. Whence, according to (26), n ~ 10^{-7} or 10^{-8}, while according to (28),

$n \sim 10^{-10}$ if the growth of the $A^{sh}B^{u}$ crystals proceeds at a rate of 3 x 10-8 cm/sec. For crystalline growth from a gaseous state, if we take Cr = 0.5 and $C_x = 0.25$, the value of n is $\sim 10^{-6}$ according to equations (33) and (34).

These examples testify to the relation between the completion of crystals and the value for the strength of "g." However, the required level of n for crystalline growth is different for /13 liquids from that of gases. This is related to the different intensity of natural convection as well as to what is more important for processes conducted in weightlessness, the different Prandtl diffusion numbers, which for gases are on the order of unity while for liquids they are of the order of 10 to 1000 and above. Thus, even very slow motion with Re << 1 leads to a significant redistribution of the components of a mixed regime.

The estimates from the formulas (28, 29, 33, 34) provide the possibility of determining conditions at which natural convection, even if its intensity is relatively great, will have no practical effect on the purity of the manufactured crystal. Its effect is significantly greater on the growth of crystals from the gaseous phase than on those grown in melts; the stated functional dependences make this obvious. This signifies as well that we approach complete weightlessness more completely with the same value of n in the process of obtaining materials from the gaseous phase than we do in production processes in melts.

One of the characteristic types of structural imperfections in a monocrystal is the presence of a mixed band parallel to the front of crystallization. One of the most frequent solutions to the system of equations (1-4) is a distribution of concentration along the length of a crystal which depends on the frequency of pulses in the rate of growth and on their amplitudes. From this we can obtain a function relating the value of the strength of acceleration to the distances between mixed bands.

Let us assume that the concentration of the mixture is low, that the depth of the melt is infinite, and introduce a movable system of coordinates whose origin ($z = 0$) is fixed at the center of the front of crystallization, while the z-axis extends into the solid. Under these assumptions the equation of convective diffusion can be written in the form: /14

$$\frac{\partial^2 \varphi}{\partial \bar{z}^2} + \bar{v}\frac{\partial \varphi}{\partial \bar{z}} = \frac{\partial \varphi}{\partial (F_0)} \qquad (35)$$

where $\bar{z} = \frac{z h v_0}{D}$, $\phi = \frac{C}{C_\infty}$, $\bar{v} = \frac{v}{v_0}$, and C_∞ is the concentration of an infinite distance from the coordinate origin. The local conditions of the problem can be written in this system in the form

$$\varphi(F_0, \infty) = 1, \quad \varphi(0, \bar{z}) = \varphi_0(\bar{z})$$
$$\frac{\partial \varphi(F_0, 0)}{\partial \bar{z}} + \bar{v}(1-K)\varphi(F_0, 0) = 0 \qquad (36)$$

where K is the coefficient of distribution of the mixture, $\phi_0(\bar{z})$ is the distribution of the mixture in the melt at the moment $F_0 = 0$.

Let us further assume that the process of crystallization, which proceeds with the constant velocity $\bar{v}$ at the moment $F_0 = 0$, includes periodic oscillations of small - compared to $\bar{v}$ - amplitude. We note that

$$\bar{v} = 1 + \varepsilon \sin(\omega \cdot F_0) \qquad (37)$$

where ε is the amplitude of the oscillation ($\varepsilon \ll 1$) and ω is the frequency of the oscillation. If the solution to equation (35) is of the form

$$\varphi = \varphi_0(\bar{z}) + \varepsilon \varphi_1(F_0, \bar{z}) + \cdots \qquad (38)$$

then, skipping the calculation, it can be rewritten in the form

$$\varphi = K\left[\frac{1}{K} + \varepsilon\varphi_1(Fo,0)\right] \tag{39}$$

where

$$\varphi(Fo,0) = \frac{1}{\omega}\,\frac{1-K}{K}(1-\cos\omega Fo) - \frac{1-K}{\omega}\int_0^{Fo}\Phi\,d\theta - \frac{1}{\omega\cdot K}\left\{\frac{\operatorname{erf}x}{\sqrt{\pi}} + \left(K-\frac{1}{2}\right)\left[1-\exp(K^2-K)Fo + \operatorname{erfc}\left(K-\frac{1}{2}\right)\sqrt{Fo}\right]\right\}, \tag{40}$$

$$\Phi = \left[\frac{\omega}{K}\sin\omega(Fo-\theta) - \cos\omega(Fo-\theta)\right]\exp\left(-\frac{\theta}{4}\right)\times \left[\frac{1}{\sqrt{\pi\theta}} - \left(K-\frac{1}{2}\right)^2\exp\left(K-\frac{1}{2}\right)^2\theta\cdot\operatorname{erfc}\left(K-\frac{1}{2}\right)\theta\right] \tag{41}$$

and $\operatorname{erf}x = \frac{2}{\pi}\int_0^x e^{-x^2}dx$ is the error function while $\operatorname{erfc}x = 1-\operatorname{erf}x$ /15
is the complementary integral of probability.

The degree of deviation of the concentration from uniformity (that is, where the rate of crystallization is constant) is determined from (38) by the derivative of $\varepsilon\phi_1(Fo, 0)$. Taking equation (40) into account, this is proportional to ε/ω. The distance between bands $L \sim 1/\omega$. If the direction of heat flow in the melt coincides with the direction of g, there can occur a dampening with time of the pulses in velocity and temperature, which last two are proportional to each other. Then, as was shown above, when Re << 1, Re ~ Gr; consequently $\nu \sim \varepsilon \sim ng_0$, while the frequency of these oscillations $\omega \sim \sqrt{ng_0}$. Hence, for Re << 1 the ratio $\varepsilon/\omega = \sqrt{ng_0}$; consequently the band intensity as well declines $\sim\sqrt{ng_0}$. In the case of Re >> 1, we established Re ~ $\sqrt{Gr}$, so $\varepsilon \sim \sqrt{ng_0}$ and the ratio ε/ω, that is, the band intensity, is independent of ng_0. The distance between bands, however, L, is always proportional to $1/\sqrt{n}$. So if under terrestrial conditions $L = 10^{-4}$ m, for $n = 10^{-6}$ it is increased to 10 cm.

It could happen that the pulses in the melt are related to turbulent natural convection. It is more convenient in this case to find the amplitude of the pulses from the equation for the balance of turbulent energy, where it is only multiplied by the terms for dissipation and generation. For this example let us assume that the generation of turbulence is only dependent on pulsations in density, so that

$$(\bar{v}')^2 \sim \ell_0 \overline{\rho' v'} n g_0 \tag{42}$$

where ρ', ν' are the pulses in density and velocity, ℓ_0 is the path length of a period. When we see that $\rho' \sim \nu' \sim T'$ and that $\varepsilon \sim \bar{\nu}'$, we find from (42) that /16

$$\varepsilon \sim \sqrt{n g_0 \ell_0} \tag{43}$$

Using the Taylor hypothesis about the relation between the spatial and time scales of the turbulence,

$$\tau = \frac{\ell_0}{v_0} \tag{44}$$

where τ is the time scale of the pulsation, we find for the frequency

$$\omega = \frac{1}{\tau} \tag{45}$$

Since for naturally turbulent convection $Re \sim \sqrt{Gr}$ or $\nu_0 \sim \sqrt{n g_0}$, the ratio ε/ω is

$$\frac{\varepsilon}{\omega} \sim \ell_0^{3/2} \tag{46}$$

The scale ℓ_0 of the turbulence depends only on the geometry of the system, so when the current flow is turbulent, the band intensity does not depend on n. We have from (44) and (45) that

$$\omega \sim \frac{1}{\sqrt{n g_0}} \tag{47}$$

and the distance between bands varies as $n^{-\frac{1}{2}}$.

It can be shown that in monocrystalline blocs the dimensions and orientation of the blocs also become functions of the pulsations; that is, they depend in the final analysis on the value of the strength of acceleration. And since the dimensions of the blocs or the distances between bands determine the values of many structurally sensitive physical properties of semiconducting and metallic materials, it is possible to get a dependence of these properties on the quantity ng_0. Starting from this fact, we can draw conclusions about the desirability of the study of a graph of properties versus strength of acceleration in the range from $\sim 10^{-10}\ g_0$ to $\sim 10^{2}\ g_0$. This makes it possible to establish the parameters of changes in /17 the physical properties of materials from the value of ng_0, and on this basis to determine by means of calculations what properties materials prepared in weightlessness will possess. Such functional relationships may provide the basis for establishing the benefit of producing one material or another in space. Research we have performed on the dependence of the electrical conductivity of a number of melts of the Te-Se system on the value of ng_0 allow us to state the character of the dependence and to confirm the hypothesis stated above.

In growing monocrystals in melts, a number of situations can arise which create a redistribution of the mixture across the solid body. One of these situations might be the distortion of the front of crystallization in the case where the density of the melt differs from the density of the solid body. In this case there is a motion of the melt along the normal to the front of crystallization with the velocity

$$\upsilon_{n0} = V_{n0}\left(1 - \frac{\rho_T}{\rho_{zh}}\right) \tag{48}$$

where V_{n0} is the projection of the velocity of crystallization ν along the normal to the front. When the front of crystallization is distorted, in transverse directions, components of the velocity ν_{n0} arise which also lead to the appearance of a profile of concentration in the solid phase. We shall solve the problem for the lines of flow in the form of a right-angled parallelopiped, although in principle it is possible to obtain the solution for any geometry of lines. Let us assume, then, that the z-axis coincides with the axis of the line of flow, while the y-axis lies on the plane of the front of crystallization. Using the equations of motion (1) and continuity (2), and limiting our examination to binary melts, we obtain for the distribution of c, the mass concentration of the light component, along the front of crystallization:

$$c(y, z=0) = \bar{c}\,\frac{\gamma}{e^{\gamma}-1}\,\exp(\gamma, y) \qquad (49)$$ /18

where $\bar{c}$ is the average concentration of the light component on the front of crystallization, and

$$\gamma = \frac{Pe_{cp}(1-k)\left(\frac{\rho_T}{\rho_{zh}}\sin^2\psi - \frac{1}{2}\sin 2\psi \cdot v_y\right)}{\frac{\rho_T}{\rho_{zh}}(\operatorname{tg}\psi - 1) + v_y\cos^2\psi - \frac{\alpha_T}{\alpha_{zh}}\left[\frac{1}{2}\sin 2\psi\left(2-\frac{\rho_{zh}}{\rho_T}\right)+\sin\psi\right]} \qquad (50)$$

In expression (50), Ψ is the angle between the front of crystallization at the given point and plane normal to the axis of the line; $\alpha_{zh} = \frac{\partial \rho_{zh}}{\partial c}$; $\alpha_T = \frac{\partial \rho_T}{\partial c}$. In the solution of formula (49), which we will not perform here, it is assumed that the value γ = const, that diffusion disappears in the solid phase, the diffusion velocity of each component is small compared to the velocity of crystallization, and that the depth of the melt is infinite. It is obvious from inspection of (49) that the concentration of the light component at $k > 1$ and $0 < t < 90$ increases with increasing values of "y" and does not depend on gravitational mechanisms for the generation of motion.

In the more realistic case, when the depth of the melt is finite, the effect of changes in the average concentration shows in the distribution of concentration in a cross-section. Assuming this change in the functional dependence on the weight of the liquid phase f has the form

$$\bar{C} = \bar{C}_0 f^{k-1} \tag{51}$$

we obtain finally

$$c(y,0) = \frac{\gamma}{e^{\gamma}-1}\bar{C}_0\left[1-\frac{b}{\ell}(1-y)\sin\Psi\right]^{k-1}\exp(\gamma\cdot y) \tag{52}$$

where b is the thickness of the boundary diffusion layer, and ℓ is the depth of the liquid phase. Since in the result from expression (51) we did not take into account the nonstationary terms, the condition of its applicability is that $\ell/b \gg 1/Pe_{\mathcal{D}}$. In summary, we can say that the formation of the field of /19 concentration in a cross-section of the crystal is determined fundamentally by the value of the Peclet diffusion criterion, the ratio b/ℓ and by the angle Ψ. When $Pe_{\mathcal{D}} \leqq 1$, the decisive element will be the change in the content of the melt, and a decrease in the difference in the concentration can be achieved by increasing the depth of the melt. As an illustration, let us introduce the results of calculation from formula (52) for the block $Cd_xHg_{1-x}Te$ in the line of a rectangular section of 1.5 x 0.5 cm with a velocity $\nu = 1.4 \times 10^{-5}$ cm/sec by the Bridgman method, and compare them to the experimental data. For this material, $k = 4$, $Pe_{\mathcal{D}} = 0.2$, and we obtained excellent agreement at a distance from the start of the block by 2.5 cm (ℓ = 5 cm) in the cross-section for the theoretical and experimental results for the distribution of the concentration of the mixture, using only the mechanism described above without including any gravitational causes of motion in the material.

The examples which have been performed of the common cases of solutions to the system of equations (1-4) display the possible means of analysis of the various methods and conditions of the production of crystalline materials both in terrestrial conditions and in weightlessness. We will not continue to enumerate these frequently-encountered examples, but will only note that many of the requirements of technological experiments in space can be theoretically analyzed ahead of time with sufficient precision and the appropriateness of their behavior in weightlessness determined.

We should point out that it would be incorrect, however, to consider the problem of space technology dependent only on the equations of transport which have been introduced. As a general rule, in addition to these processes there also exist in the conditions of preparing crystalline materials in space a whole series of other factors determining the performance. One of the possible processes which affect the production of crystals in weightlessness may be barodiffusion. Its effect, however, is only noticeable when a number of conditions are /20
fulfilled. In order to determine these, let us evaluate the effect of a centrifugal field on the redistribution of the components in the mixture. Limiting ourselves for the sake of simplicity to the case of an ideal binary mixture, we set down:

$$C_2 S \omega_y^2 r = \mathcal{D} \frac{dC_2}{dr} \qquad (53)$$

$$\frac{S}{\mathcal{D}} = \frac{x_1 M_1^2 M_2 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)}{RT\rho_1 \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right)} \qquad (54)$$

Here C_i is the concentration (the number of molecules in a unit volume), $i = 1, 2$. The index "1" refers to the heavy component, "2" to the light component, ω_y is the angular velocity of rotation, x_i is the molar share, μ_i is the molecular weight, ρ_i is the density of the pure matter, S is the coefficient of sedimentation, R is the universal gas constant, T is the temperature of the mixture, r is the distance from the axis of rotation.

Assuming $S/\mathcal{D}$ is a constant for the given mixture, we find that the ratio of the concentration at the points r_1 and r_2 is equal to

$$\frac{C_2(r_2)}{C_2(r_1)} = \exp\left[\frac{S}{\mathcal{D}}\omega^2(r_2-r_1)\frac{r_1+r_2}{2}\right] \qquad (55)$$

With this functional relationship one can determine, for example, the value of the distance necessary for the generation of barodiffusion. So, for example, for germanium lightened with silicon ($x_1 = 0.99$, $x_2 = 0.01$), we have $S/\mathcal{D} = 5 \times 10^{-6}$ $\sec^2/m^2$, $r_2 - r_1 = 10^{-2}$ m, $\omega_y = 8 \times 10^{-2}$ $\sec^{-2}$.

When the concentrations $C_2(r_2)$ and $C_2(r_1)$ differ by 1%, the power of the exponent in (55) is equal to ~ 0.01. This means $(r_1 + r_2)/R = r_0 \sim 2.5 \times 10^6$ m

Obviously, only other, more favorable values in equation (55) will lead to observation of the effect of barodiffusion in the preparation of crystals under the real conditions of space flight. /21

As has already been indicated above, another possible process is the generation of thermocapillary convection at the surface of the material. Its intensity is defined by the Marangoni criterion:

$$Ma = \frac{\partial \sigma_0}{\partial T}\frac{\Delta T d}{a \nu \rho} \qquad (56)$$

where σ_0 is the coefficient of surface tension, ΔT is the fall of temperature in the surface layer, and a is the thermal conductivity. The relationship between the strength of thermocapillary and natural convection is evaluated by a ratio of the criteria:

$$\frac{Ma}{Gr} = \frac{\nu \frac{\partial \sigma_0}{\partial T}}{\rho \beta g d^2 a} \qquad (57)$$

or, more correctly

$$\frac{Ma}{Ra} = \frac{\frac{\partial \sigma_0}{\partial T}}{\rho \beta g d^2} \qquad (58)$$

The velocity of the capillary motion is defined by the expression

$$v = \frac{r^2}{8\nu}\left(\frac{2\sigma_0 \cos\theta_c}{r\rho \ell} - g \sin\alpha\right) \qquad (59)$$

where r is the capillary diameter, α is the angle of inclination of the capillary to the horizontal, ℓ is the length of the column of liquid in the capillary, and θ_c is the moistening angle.

In the case of ideal weightlessness,

$$v = \frac{r\sigma \cos\theta_c}{4\rho\nu\ell} \qquad (60)$$

and

$$\ell^2 = \frac{1}{16}\frac{\sigma_0 r^2}{\nu v^2}\cos\theta_c\left[\exp\left(-\frac{8v\tau}{r^2} - 1\right)\right] + \left(\frac{1}{2}\frac{\sigma r^2}{\rho\nu}\cos\theta_c\right)\tau + \ell_0 \qquad (61)$$

where τ is the rise time of the melt in the capillary to the height ℓ with velocity ν. A measure of the relative strength of the capillary force in the melt is the Bond criterion: /22

$$B_0 = \frac{\sigma_0}{\rho n g_0 \ell^2} \qquad (62)$$

It is not difficult to see that if n is small the capillary force prevails, and the surface is strongly distorted.

As is clear in the Marangoni and Bond criteria, the value of the surface tension σ_0 plays a decisive role. This value is important in the study of interphasic tension, which in the process of crystallization in weightlessness can sometimes play a determining role. Let us examine how this parameter varies in different materials, with the condition that we will only consider homogeneous liquids. The expressions for the determination of the coefficient of surface tension are quite numerous. They all correlate to one model or another of liquidity and have their advantages and disadvantages. We are greatly interested in the dependence of the surface tension on the curvature of the surface of the melt, which can be described with sufficient accuracy by the thermodynamic equation of Gibbs. The dependence has the form

$$\frac{d\ln\sigma_0}{d\ln r} = \frac{2\left(\frac{\delta}{r}\right)\left[1+\frac{\delta}{r}+\frac{1}{3}\frac{\delta^2}{r^2}\right]}{1+2\frac{\delta}{r}\left[1+\frac{\delta}{r}+\frac{1}{3}\frac{\delta^2}{r^2}\right]} \qquad (63)$$

where r is the radius of the spherical surface of tension, and δ is the distance between the surface of tension and the Gibbs surface of the section. The concept of surface tension represents an isobaric-isothermal potential and can be reversed in principle in application. In the first approximation, surface layers can be considered to be phases of variable content, whose composition depends on the boundaries separating the phases. From a thermodynamic viewpoint, the process of formation of a single phase has a surface tension of

$$\sigma_0 = F_s - \mu\Gamma \qquad (64)$$ /23

where F_s is the specific free surface energy (equal to $U_s - TS_s$), U_s is the total internal energy of the hypothetical surface phase, S_s is the surface change in entropy, μ is the chemical potential, and Γ is the adsorption.

The value

$$\Gamma = \frac{N^s - N_1}{A} = h_{ef}\,(C^s - C_1) \tag{65}$$

where N^s is the number of particles in the surface phase, N_1 is the number of particles in the macrophase portion, A is the increase of the area of the two phases, h_{ef} is the thickness of the surface phase, equal to the distance from the interphasic surface to a hypothetical surface where the composition of the phase does not differ from the composition of the volume within, and C^s and C_1 are the concentrations of the components.

For a multicomponent phase,

$$\sigma_0 = \mathcal{F}_s - \sum_{i=1}^{i=k} \mu_i \Gamma_i \tag{66}$$

where k is the number of components, composed of τ-particles.

It is obvious that these functional relationships are of a rapid descriptive character, yet they show in what direction the process of surface tension will flow and that in a clear way they do not depend on the strength of the tension. In order to determine the temperature variation of the coefficient of surface tension, it is necessary to take account of the fact the density in the region of a phase transition changes completely over a distance of the order of a molecular diameter with strongly varying oscillations. In this circumstance it is necessary to distinguish liquid metals from nonmetals, since the intraionic forces in metals depend on densities. It is extremely important to establish the inversion curve $\sigma_0 = f(T)$, figure 2, for various metallic liquids. These values were /24 obtained in liquids in equilibrium with a saturated gas in order to eliminate transport of material across the liquid-gas interface. Confirmation of the presence of an inversion of σ_0 is provided by the observation, on resting drops of liquid metal, of superficial grains whose form and dimensions appear to be related to the tendency of the system toward an inversion $\sigma_0 = f(T)$. Analysis has shown that all these grains are based on planes, the planes of close packing. Beginning with what has already been said, it is possible to propose a physical model of surface tension which expresses it in terms of the free energy necessary to remove an atom from the volume of the liquid to a surface at T = 0°K, minus the change in the free energy proportional to the ratio of the characteristic frequency of oscillation in the volume and at the surface. In this treatment, superficial capillary waves are regarded as elastic waves and used for the description of thermal processes in the melt. It must always be borne in mind that if there is vapor escaping from the surface of the melt, that is, if the melt is not in equilibrium, then there will be a decrease in surface tension at all temperatures.

A well-known theory suggests that if an oscillation of density exists in the liquid it will always produce the inversion $\sigma_0 = f(T)$. Unfortunately, we lack a mathematical description of these processes which is sufficiently precise for quantitative calculations. We can conclude, however, that surface tension, especially in weightlessness, can play an important role in the process of crystalline formation and changes substantially the laws of behavior obtained from the system of equations (1-4). This effect should be particularly pronounced in the growth of crystals of small dimensions (and it is with just these that a majority of the technological processes in space are now conducted) because of the comparatively extensive propagation of fluctuations in surface phenomena, especially that of an inversion of surface tension.
The functional relations which we have obtained of this process, /25
when applied to quantitative calculations and related to the

system of equations (1-4), will undoubtedly lead to a more exact evaluation not only of the form but also of the quality of materials produced in weightlessness.

Besides making use of the value of the surface tension, it is also necessary to analyze thoroughly the process of wetting of the wals of the container by the liquid. This process is governed by the local moistening angle θ_c, which comes into the balance equation in the form

$$\sigma_{zh-T} + \sigma_{zh-p} \cos \theta_c - \sigma_{zh-T} = 0 \qquad (67)$$

where σ_{zh-p} is the coefficient of surface tension between the liquid and its vapor, σ_{zh-T} is that between the liquid and the wall of the vessel, and σ_{p-T} is that between the vapor and the wall of the vessel. We should note here that the local moistening angle is an autonomous physical parameter whose theory has been poorly developed. We can make the following comments at this point. First, the value of θ_c is a physical constant for a particular vapor, liquid and solid, and should be the same under terrestrial and space conditions. However, this condition can be violated in the neighborhood of a critical point where the thickness of the transition layer between the liquid and vapor increases, the compressibility increases, and the strength of the tension provides a large portion of the surface energy. Second, despite the assumption of a constant local moistening angle, the ratio of the radius of the sphere assumed by the liquid, h, to the radius of the container, R, plays an important role in the behavior of the liquid in the container. Thus it has been shown that at high initial values of the ratio ($h/R > 2$) even nonmoistening liquids can form spheres of gas within the liquid in weightlessness, while for small values ($h/R < 2$) liquid can form vapor within a gas even at $\theta_c < 90°$. We must note that the existing thermodynamic models, based on the /26 analysis of the free energy of a system, qualitatively describe the effect of the local moistening angle of a liquid in a container. The assumption of a regular functional relationship, however, which makes it possible to include this process in the system of equations (1-4), is accompanied by great difficulties. This is no less necessary in the analysis of results, even if only in order to evaluate qualitatively the effect of these forces on the process of obtaining crystalline materials and their quality in weightlessness.

Somewhat unconnected to the foregoing, there is the question of possible internal activity during the process of preparing crystalline materials in weightlessness, although, if it takes place it must be included in a general way in the overall system of equations describing the phenomenon as a whole. Among such activity there are also processes whose effect can be beneficial to the quality of the material prepared in weightlessness. Unfortunately this question has been hardly studied in the course of the general analysis of the flow of technological processes in a state of weightlessness. To be sure, much more has been done in this regard in the area of the study of periodic nonlinear control oscillations on separate sides of technological processes (intermingling of the melt, outgassing, formation of small parts from the melt, etc.). Here a series of experimental studies have been completed, and the general theory is very well known on the basis of the theory of nonlinear oscillation. The joint solution of these functions together with the equations of the transport processes has not been completed, however, due to the mathematical complexity of the analysis. The solutions of these problems do possess undoubted practical interest, however.

In conclusion we may say the present work examines and sets out ways of considering the fundamental phenomena determining the flow of processes producing crystalline materials in space. Naturally, in such a small work, we do not have the possibility /27 of considering in detail all the known phenomena affecting technological processes in space and of producing a mathematical exposition of the separate functional relationships we have given. Nonetheless, we can state that, based on the analysis performed here of the general functional relationships, we can already establish with substantial theoretical assurance the suitability of performing one process or another, or the suitability of producing one material or another in space. For this it is necessary to know the temperature dependences of the physical parameters introduced in the equations adduced above, and the criteria for materials in liquid or gaseous states and their changes at points of phase transition. Unfortunately, these properties either have not been investigated at all or have only been partially studied for many promising materials in space technology (an incomplete collection of properties, for example, or a narrow temperature interval, etc.). This in turn makes it impossible at this point to perform many quantitative calculations. In those cases where the present-day understanding makes it impossible to give a quantitative or qualitative analysis of the action of processes in space, it is necessary to perform further theoretical and experimental study. We have attempted to give some direction to these studies in the present work.

FIGURES

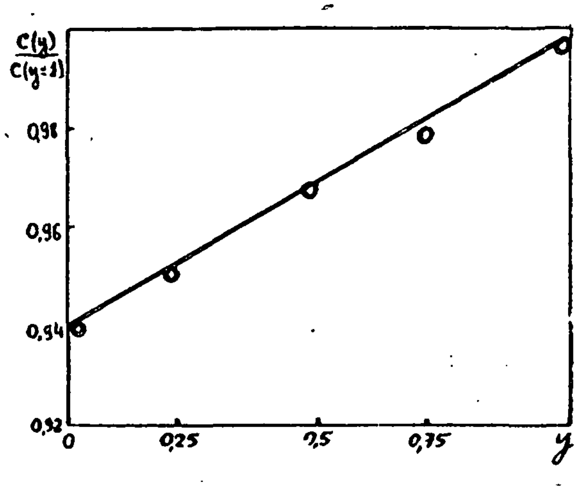

Fig. 1. Distribution of the mixture along the front of crystallization in $Cd_xHg_{1-x}Te$.

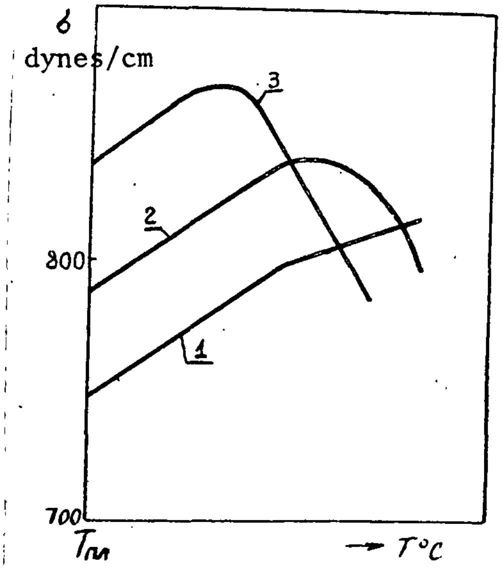

Fig. 2. Inversion or turning of surface tension, shown in dynes/cm, with temperature T of the melt (1: cadmium, 2: zinc).

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