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The Effective Solute Distribution Coefficient During the Freezing of NaCl Solutions

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Abstract

The variation in the effective solute distribution coefficient k [k=salinity (ice)/salinity (solution)] is studied as a function of the growth velocity ($v=3\times10^{-3}$ to 10^{-5} cm/sec) and the solute concentration of the freezing NaCl solution (1 to 100‰). The data is from ice prepared by unidirectional freezing using controlled ice-surface temperatures of -20 and -70°C. The data is in good agreement with a relation suggested by Burton, Prim and Slichter (BPS, 1953)

$$k=\frac{k^*}{k^*+(1-k^*)\exp\left[-\frac{\delta v}{D}\right]},$$

if k^* is considered to be the effective value of k at $v=0$ provided a cellular solid-liquid interface were to remain stable. Here D is the diffusion coefficient of salt in water and δ is the thickness of the diffusion limited boundary layer. When growth conditions are such that the solid-liquid interface becomes planar ("lake" ice forms), this relation still appears applicable. However, k^* must, in this case, be replaced by k_0, the equilibrium solute distribution coefficient. Substitution of the BPS relation in an ice growth equation allows the calculation of both the initial salinity and brine volume profiles for young salt ice assuming no brine drainage. The resulting profiles are in good agreement with observed young sea ice profiles and show appreciable salinity changes as a result of changes in the meteorological conditions during growth.

I. Introduction

It is well known that the physical properties of sea ice are commonly a strong function of the vertical location of the sample in the ice sheet. The major portion of this variation is attributable to pronounced vertical changes in the volume of brine in the ice which is precisely specified by the temperature and salinity profiles, provided that the ratios of the ions in the brine do not change (Assur, 1958). It is possible to make reasonably accurate predictions of ice temperature profiles at any time if the weather conditions, snow cover, and date of freeze-over are known (Bilello, 1961, 1965; Untersteiner, 1964). If the salinity profile could also be estimated, this would permit the calculation of the brine volume profile and the estimation of the profiles of elastic, viscoelastic, thermal and electrical parameters. Considering the importance of the salinity profile in sea ice physics, surprisingly little work has been devoted to it.

There appear to be two requirements for predicting the salinity profile at any given time. The first of these is to understand the laws that govern the migration and drainage of brine and solid salt trapped in the ice. This has received the most attention in that the general sequence of salinity profiles with time for annual ice has been reasonably well documented from a number of locations and found to be quite similar (Malmgren, 1927; Fukutomi, Kusunoki and Tabata, 1951; Weeks and Lee, 1958, 1962). In addition, the salinity profile in old perennial pack ice (Malmgren, 1927; Schwarzacher, 1959; Savel'ev, 1961) appears to have a characteristic shape. The process that produces these profile changes is, however, only very incompletely understood. Most of the work has been concentrated on the migration of individual brine pockets through the ice under the influence of a temperature gradient (Kingery and Goodnow, 1963; Hoekstra, Osterkamp and Weeks, 1965; Harrison, 1965) and has shown that, contrary to the suggestion of Whitman (1926), this cannot be the major process producing brine drainage. Gross brine drainage with the additional influence of gravity appears to be the most effective process (Kingery and Goodnow, 1963), but it has not been extensively studied.

The second requirment is to be able to specify the initial salinity of any increment of ice in terms of such growth parameters as the solid-liquid interface velocity and geometry, and liquid composition and mixing conditions. This, also, has not been systematically studied and is the subject of the present paper.

II. Previous Work

The statements regarding the relation between growth conditions and ice salinity found in textbooks (Defant, 1961; Zubov, 1963) are mainly based on the observations of Weyprecht (1879) and Malmgren (1927). These authors, based upon their examination of the average salinity of ~ 20 cm thick ice floes that formed under different ambient temperatures, concluded that the salinity of the ice, S_i, is some function of the growth velocity of the ice, v. Unfortunately, because the length of time necessary for these ice thicknesses to grow also depends on the ambient temperature, the effects of brine drainage are unknown. It is, therefore, difficult to know what percentage of the observed change in S_i should be assigned to changes in v and what to changes in the amount of brine drainage. In addition both Weyprecht and Malmgren pointed out that the observed decrease in S_i with depth in the ice sheet, z, could be correlated with the general decrease in v with an increase in z. As evidence Malmgren presented a salinity profile from a 6 months old ice sheet in which the profile at the time of sampling was undoubtedly dominated by brine drainage. Weyprecht presented a profile from a 19 cm thick sheet of young sea ice in which the only dominant feature was the high salinity of the surface layer. Unfortunately, this high surface salinity is undoubtedly, as pointed out by Weyprecht, the result of a solid "salt" or brine layer forming on the surface of the ice. Therefore, although the contention of Weyprecht and Malmgren that $S_i = f(v)$ may well be correct, their data would hardly seem to be conclusive.

Since this early work there have apparently been only two studies that have direct bearing on the problem of the initial entrapment of salt by sea ice. Johnson (1943) during his study of ice growth in Gullmar Fiord, obtained the final ice thickness and salinity from 19 samples that froze from water with different initial salinities. These results when plotted (Fig. 1 a) indicate no appreciable effect of growth velocity on the effective solute distribution coefficient k ($k = S_i/S_w$ where S_w is the salinity of the solution)

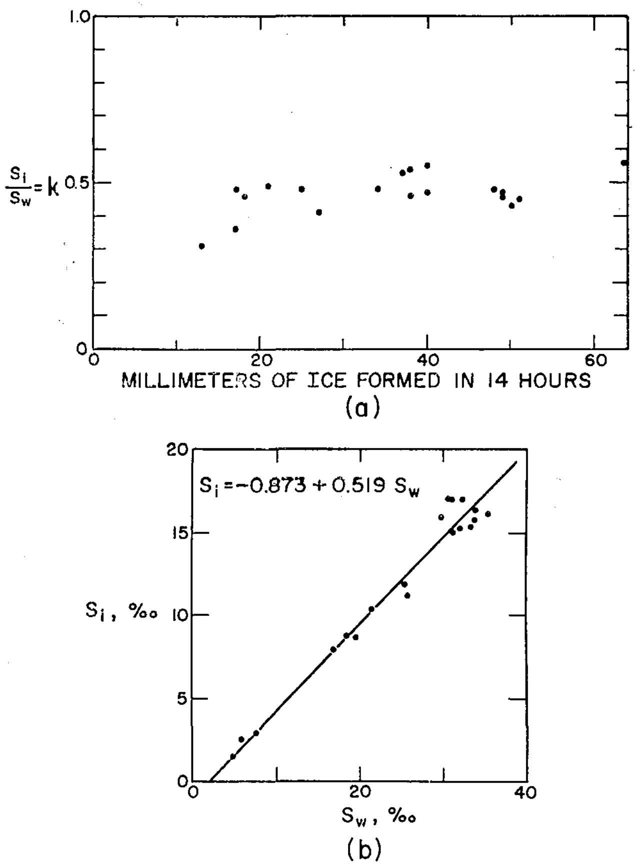

Fig. 1. a) k vs. mm of ice formed in 14 hours (Johnson, 1943)
b) S_i vs. S_w (Johnson, 1943)

and a pronounced linear relation between S_i and S_w (Fig. 1 b). The other data that are amenable to a detailed examination are those of Adams, French and Kingery (1963), who formed ice by freezing sea water (33‰) to a cold Al plate. They determined the salinity of the resulting ice as a function of the growth velocity of the ice and the flow velocity of the water (v_f) over the plate. The flow velocities used in their experiments (1.9×10^2 to 4.4×10^2 cm/sec) were not sufficient to prevent dendritic growth and the usual entrapment of brine resulted. When we analyzed their results using multiple regression methods we obtained

$$S_i = 3.458 + 4.566 \times 10^3\,v + 5.414 \times 10^{-3}\,v_f, \qquad (1)$$

showing that the higher the growth velocity and flow velocity, the higher the salinity of the resulting ice. If the S_i values are corrected to $v_f = 0$ using eq. (1), we obtain a linear relation between S_i, which here is simply related to k because of the constant water salinity, and v (Fig. 2). Because the coefficient of the flow velocity is not significantly different from zero at the 0.95 confidence level and is opposite in sign from what would be expected from examining the metallurgical literature (Tiller, 1963), we will consider S_i to be a function of v only.

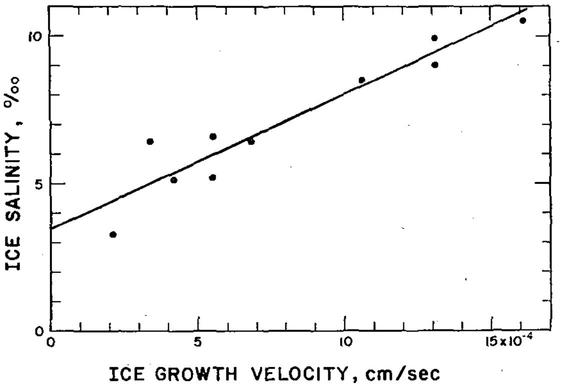

Fig. 2. S_i vs. v (Adams, French and Kingery, 1963)

The results of Johnson, and of Adams, French and Kingery are in disagreement in that they indicate that $k \neq f(v)$ and $k=f(v)$ respectively. The present study was initiated to clarify these results and to provide a firm experimental basis for predicting initial brine entrapment. Since this paper was prepared, we have received a copy of an extremely interesting paper by Tsurikov (1965) on a similar subject. Although his method of analysis is different, his experimental results are comparable, although less detailed, than those presented in the current paper.

III. Experimental Procedures

The data used in the present paper were obtained in conjunction with two separate studies of other aspects of NaCl ice. In the first study, an investigation of substructure spacing in NaCl ice crystals (Lofgren and Weeks, 1967), the freezing apparatus consisted of a 14 cm diameter Lucite tube roughly 62 cm long cemented to a 4 cm Lucite base. A copper cold-plate was placed on top of and protruded 1 cm "into" the Lucite tube. A coolant from a constant temperature bath was then circulated through the cold-plate. This arrangement was effective for cold-plate temperatures in the range −2 to −25°C. Several runs were also completed with cold-plate temperatures of −70°C. Here the experimental set-up was similar except that the cold-plate was open at the top allowing the use of a mixture of crushed dry ice and acetone as a coolant. These freezing runs lasted between 48 and 110 hours during which time 10 to 25 cm of ice formed. Salinity samples were prepared immediately upon the completion of a run by removing the complete ice block and cutting a 4 to 5 cm continuous slab from its side. This slab was then cut into 1 cm slices, each slice representing 1 cm of vertical growth. When these slices had melted and reached room temperature, the resulting water salinities were measured with a conductivity bridge. A cell constant of 10 was used for salinities >10‰.

The second set of data was obtained during an investigation of the tensile strength of NaCl ice (Weeks, 1962). Here the ice was grown in an open-top cylindrical steel tank with a height and diameter of approximately 90 cm. The sides of the tank were insulated and heated to produce one-dimensional cooling. The ambient temperature of the cold room was maintained at −20°C and a large table fan was utilized to continuously circulate air across the ice surface. The ice was allowed to reach a thickness of roughly 35 cm, which usually took 1 1/2 to 2 weeks. Upon completion of a run a 7.6 cm diameter core was taken using a modified USA CRREL corer (Bader, 1957). This core was immediately cut into a series of 2 cm horizontal layers which were used to determine the salinity profile. The chloride content of the samples was measured by allowing the specimen to melt and reach thermal equilibrium at +20°C. A standard Mohr titration (Vogel, 1952) was then performed.

In all the freezing runs utilized in this paper, the water salinity corresponding to the time of growth of each ice specimen was calculated from the results of the ice salinity profiles by assuming that the brine drainage during the time of specimen growth was negligible. This is probably a reasonably good assumption in the runs of Lofgren and Weeks (1967) because of the short time periods involved. It is undoubtedly less adequate in the runs of Weeks (1962). Because of the possible effect of brine drainage in the slower runs, the different runs are always labeled as either Weeks (1962) or Lofgren and Weeks (1967) which, in general, indicates the length of time of the freezing run. Unfortunately, it is not possible to presently correct the data for the effect of brine drainage.

To calculate the change in S_w with ice growth, assume that the salt rejected by the ice is completely mixed in the underlying solution and that H is the initial water depth, h is the ice thickness, and ρ_i, ρ_w, S_i and S_w are the densities and salinities of the ice and solution respectively. Also assume that the ice surface is fixed, that the solution displaced by volume changes during freezing can drain off through a pressure release system, and that the increment of ice growth, Δh, is sufficiently small so that S_w can be taken as essentially constant. After additional ice growth, Δh, the amount of salt (gms) in the solution is given by the amount initially there plus the amount rejected by the ice thickness, Δh, minus the amount of salt lost by drainage

$$10^{-3}\left[(H-h-\Delta h)\rho_w S_w+\Delta h(\rho_w S_w-\rho_i S_i)-\Delta h(\rho_w-\rho_i)S_w\right].$$

The new salinity of the solution is equal to this divided by $[\rho_w(H-h-\Delta h)]$ which after algebraic manipulation and neglecting terms containing Δh^2 becomes

$$S_w(\text{new}) = S_w + \frac{\Delta h}{H-h}\left[\frac{\rho_i}{\rho_w}(S_w-S_i)\right]. \tag{2}$$

In calculating the S_w values, the ratio ρ_i/ρ_w was assumed to be constant for a given freezing run.

The growth velocity for each depth below the upper ice surface, z, corresponding to the center of each salinity sample was obtained by a least-squares fit of an equation of the form

$$t = \alpha_1 h + \alpha_2 h^2 + \alpha_3 h^3 + \alpha_4 h^4, \tag{3}$$

to the time (t) vs. ice thickness (h) data. These relations were then differentiated to obtain an estimate of the growth velocity, $v = \mathrm{d}h/\mathrm{d}t$, at any position in the ice sheet for each freezing run. A detailed discussion of this method can be found in Lofgren and Weeks (1967). A complete listing of all the water and ice salinity and growth velocity values used in this paper as well as considerable additional data from the ternary system $NaCl$-Na_2SO_4-H_2O is presented in Weeks and Lofgren (1967).

IV. Theoretical Considerations

If a melt is allowed to solidify so slowly that the temperature and concentration gradients in both the liquid and the solid are negligibly small, the ratio of the amount of impurity incorporated into the solid, C_s, to that present in the liquid, C_l, is referred to as the equilibrium distribution coefficient, $k_0=C_s/C_l$. For a given system the value of k_0 is commonly calculated from the position of the liquidus and solidus curves on the phase diagram. If, however, solidification proceeds at an appreciable rate, the solute impurities rejected by the solid phase accumulate in the melt next to the interface at a higher rate than they can diffuse away into the bulk melt. This causes the concentration of the melt at the interface, C_i, to be appreciably higher than the concentration of the bulk melt some distance from the interface, C_l. If local equilibrium holds at the interface then $C_s=k_0 C_i$. Unfortunately, it is difficult to precisely measure C_i and, therefore, it is necessary to substitute the known values of C_l. This allows one to define the effective distribution coefficient $k=C_s/C_l$; if $k_0<1$ as in salt-water systems, then $k_0<k<1$.

In analyzing the data in the present paper, we will utilize the theory of Burton, Prim and Slichter (BPS) which was developed to compute k in terms of k_0 and the growth conditions (Burton, Prim and Slichter, 1953; Burton and Slichter, 1958). This theory has been quite effective in treating experimental results in the field of metallurgy. An outline of the BPS development is as follows: It is known that during crystal growth, the magnitude of the concentration gradient ahead of the advancing solid-liquid interface depends upon the solidification rate, v; the effective distribution coefficient, k; the diffusion coefficient of solute in the melt, D; and the nature of the fluid flow produced by stirring or convection. The concentration of solute in the liquid at the interface, C_i, will increase until a steady state value is reached where the flow of solute away from the interface (by fluid transport, diffusion, and entrapment in the ice) equals the flow of solute to the growing interface. It is convenient in the BPS analysis to fix the coordinate system so that $x=0$ at the solid-liquid interface and extends in a positive direction into the melt. This considers crystal growth as a flow of liquid toward the interface in the negative x direction. In any type of fluid flow next to a growing crystal, the fluid velocity will approach zero at the solid-liquid interface with the exception of the flow normal to the interface produced by crystal growth. There will, therefore, be a region at the interface where the flow is laminar and the fluid velocity is sufficiently small so that molecular diffusion becomes the primary means of transporting the excess solute away from the growing crystal. Beyond this region of thickness $x=\delta$, transport of solute by fluid motion becomes the dominant process.

It will be assumed that, because of mixing, C approaches a constant value C_l at a distance δ from the growing interface while for distances less then δ the fluid velocity component normal to the interface approaches that due to crystal growth, v. If the problem is considered to be 1-dimensional, for a steady state at $x<\delta$, the continuity equation is

$$D\frac{d^2C}{dx^2}+v\frac{dC}{dx}=0\ , \tag{4}$$

with the boundary conditions

$$(C_i-C_s)v+D\frac{dC}{dx}=0 \text{ at } x=0\ , \tag{5}$$

and

$$C=C_l \text{ at } x\geq\delta\ .$$

The solutions of eq. (4) with these boundary conditions are

$$\frac{C-C_s}{C_l-C_s}=\exp\left[\frac{v}{D}(\delta-x)\right]\ , \tag{6}$$

and the concentration C_i in the liquid at the interface ($x=0$), is

$$\frac{C_i-C_s}{C_l-C_s}=\exp\left[\frac{v\delta}{D}\right]\ . \tag{7}$$

By choosing δ properly, eq. (7) can be forced to give the correct value of C_i (Fig. 3). Because $C_s/C_l=k_0$, eq. (7) can be rewritten as

$$k=\frac{k_0}{k_0+(1-k_0)\exp\left[-\frac{v\delta}{D}\right]}\ . \tag{8}$$

Here $\frac{v\delta}{D}$ should be considered as a normalized growth velocity which contains the three main parameters that control k. Because it has been shown (Burton and Slichter, 1958; Oliver, 1964) that δ/D varies only slightly with v, δ/D can be determined by measuring k in crystals grown at different values of v but with similar mixing conditions.

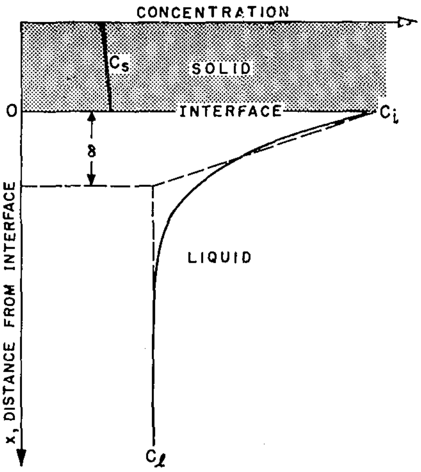

Fig. 3. Schematic representation of the solute distribution near a solid-liquid interface assuming a diffusion layer of thickness δ. The solid line represents the actual and the dashed line the approximate concentration profile

For salt-water systems this whole problem is considerably complicated by the fact that the amount of salt actually incorporated in solid-solution in the ice is extremely small; *i. e.*, within the limits of the usual analytical techniques. Therefore, for most purposes ice can be considered to be a pure phase showing no solid-solution. Current estimates of k_0 for ice-salt systems suggest that $k_0<10^{-4}$ (Harrison and Tiller, 1963). The solute buildup ahead of the advancing solid-liquid interface produces constitutional supercooling causing a planar interface to become unstable, changing to a highly sutured cellular or dendritic interface (Harrison and Tiller, 1963; Lofgren and Weeks, 1967). This results in gross solute entrapment in the deep intercellular grooves characteristically found in salt and sea ice. The resulting salinity of the salt ice, S_i, is the product of this bulk entrapment. Similar effects have recently been discussed in metal systems (Kramer, Bolling and

Tiller, 1963; Biloni and Bolling, 1963), however, no systematic study of the degree of overall entrapment as a function of growth conditions appears to have been made.

In the next section, the BPS theory will be applied to a set of data where a cellular interface was always stable during growth ("salt ice"). The agreement between the theory and the data is quite satisfactory permitting a number of useful calculations to be made. It should, however, be noted that the utilization of the BPS theory necessitates that one only consider the entrapment averaged over a large number of intercellular grooves and completely ignore the detailed mechanism of the entrapment process. It is highly desirable that a more detailed theory for gross solute entrapment be developed based on the detailed morphology of the solid-liquid interface during freezing. A preliminary approach to such a theory developed by Dr. W. A. Tiller (personal communication) is included in Weeks and Lofgren (1967).

When a planar interface became stable the salinity values were specifically designated as "fresh" ice. The two different interface types were readily separated on the basis of visual examination: a planar interface produces clear glass-like ice with regular polygonal boundaries (Fig. 4 a) while a cellular interface produces cloudy-milky ice with irregular highly-sutured grain boundaries (Fig. 4 b). The transition between these two ice types was quite sharp usually occurring within a vertical distance of 1 cm. The general range of conditions for this transition are shown in Fig. 8.

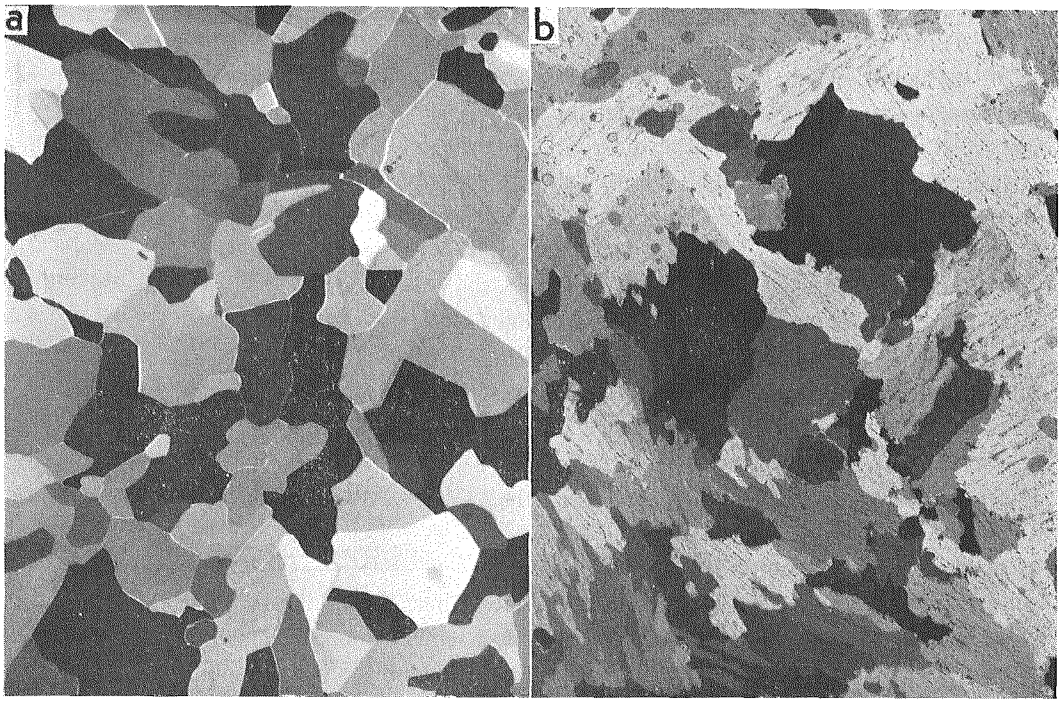

Fig. 4. a) Fresh ice with polygonal grain boundaries
b) Salt ice with internal substructure and highly sutured grain boundaries

V. *Data Analysis*

When $k_0<1$, as in salt-water systems, eq. (8) can be rearranged as

$$\ln\left(\frac{1}{k}-1\right)=\ln\left(\frac{1}{k_0}-1\right)-\frac{\delta v}{D}. \tag{9}$$

This is a straight line on a $\ln\left(\frac{1}{k}-1\right)$ vs. v plot with a slope of $-\delta/D$ and a zero intercept of $\ln\left(\frac{1}{k_0}-1\right)$. Because v and k are known from experiment, the quantity δ/D can be estimated by least-squares (Fig. 5). The data of Lofgren and Weeks (1967) are plotted as dots and they are approximated quite well by a straight line throughout most of the v range (correlation coefficient $=0.94$). The slope determined by this method gives $\delta/D=5\,090$ sec/cm. The diffusion coefficient of NaCl in aqueous solutions is considered to be roughly 10^{-5} cm^2/sec (Harned and Owen, 1958). This gives an approximate value for δ of 0.05. This is in the range of δ values that have been determined for metal systems showing natural convection (Chalmers, 1964). This estimate of δ should be considered as a minimum because D (effective) $>D$ as a result of microturbulence.

If linear extrapolation is used to obtain a zero intercept, a value for $k_0 \sim 0.26$ is obtained from Fig. 5. This should be considered as the k_0 value if a cellular substructure were to remain stable at extremely low growth velocities. This value will be designated as k^* to distinguish it from the true equilibrium k_0 value. As can be seen from Fig. 5, at growth velocities $<5\times10^{-5}$ cm/sec, the data asymptotically approach a much larger $\left(\frac{1}{k}-1\right)$ value. This tendency is also clearly demonstrated by the data of

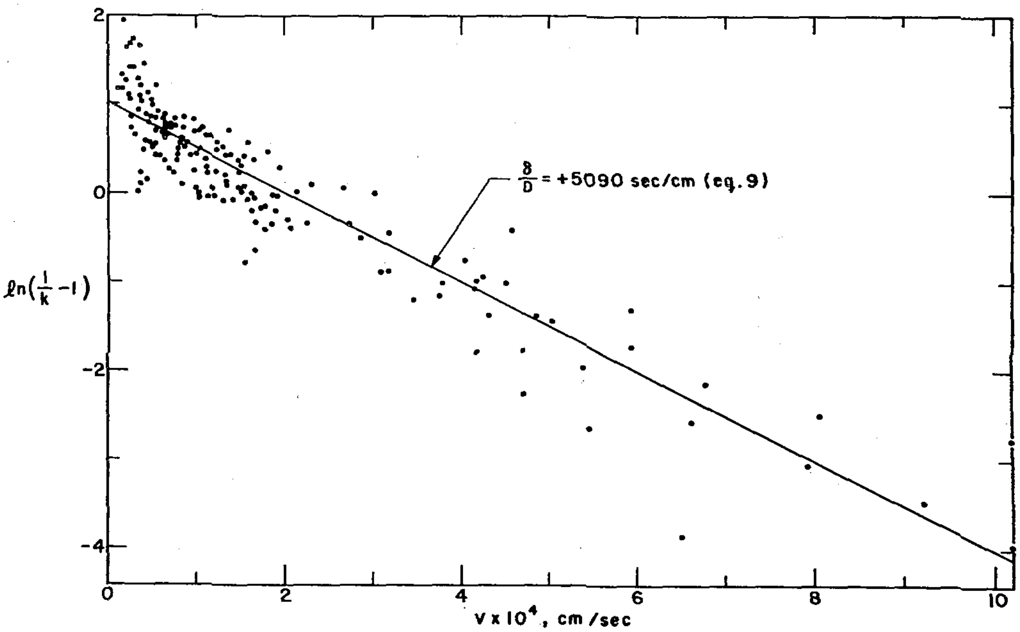

Fig. 5. Plot of $\ln\left(\frac{1}{k}-1\right)$ vs. v for salt ice runs. The value of δ/D is estimated by least squares. Only the data of Lofgren and Weeks (1967) are used

Weeks (1962) which, although not shown, overlap the plotted data. The drift toward higher $\left(\frac{1}{k}-1\right)$ values at low v is probably related to changes in the morphology of the solid-liquid interface as conditions are approachedwhere a planar interface becomes stable.

Four runs in which the transition to fresh ice occurred are shown in Fig. 6. These runs indicate quite clearly that the true zero intercept is considerably larger than the linear intercept. It appears to occur at a $\left(\frac{1}{k}-1\right)$ value of roughly 6 which corresponds to a $k_0 \sim 10^{-3}$. Further experimentation at low growth velocities and with stirred solutions would be needed to refine this value. If the runs in Fig. 6 are compared with eq. (9) as calculated from Fig. 5, it is readily apparent that systematic deviations from eq. (9) occur well before the apparent salt→fresh ice transition occurs. These deviations are also presumably related to changes in interface morphology.

In plotting the data presented in Fig. 5, a very few anomalous S_i values from both the upper and lower portions of the ice sample were excluded. The general tendency for the upper portion of directionally solidified metal ingots prepared from a completely

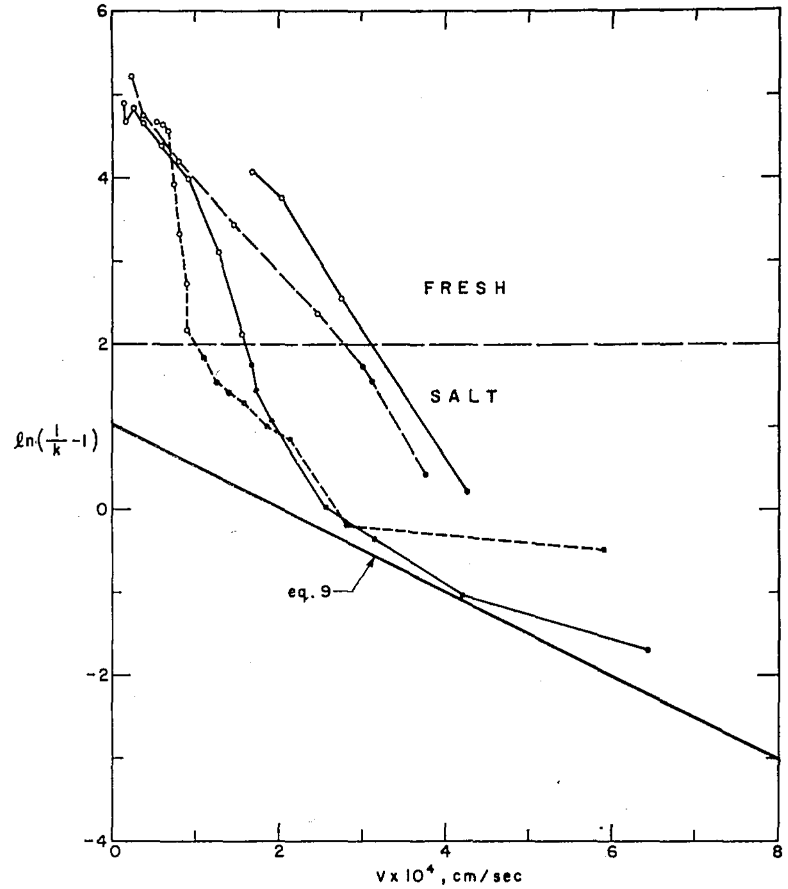

Fig. 6. Plot of ln $\left(\frac{1}{k}-1\right)$ vs. v for runs showing the salt ice→fresh ice transition (solid black symbols indicate salt ice, open symbols indicate fresh ice)

molten sample to show anomalous solute concentrations has also been noted by Yue and Clark (1960). In both salt ice and metals, this effect can undoubtedly be explained by the observation that it may take several centimeters to develop the strong preferred orientation so characteristic of the columnar zone (Walton and Chalmers, 1959; Perey and Pounder, 1958; Weeks and Assur, 1963). The rapid increase in S_i values in the lower few centimeters of the ice sheet is a phenomena that is not encountered in metals. If these S_i values were not excluded the general results would be the same, only the apparent scatter would increase.

Figure 7 shows the relationship between k and the normalized growth velocity $\delta v/D$. The relationship is to a good approximation linear except at both very high and very low values of v where k asymptotically approaches 1 and k_0 respectively. Equation (8) fits the data quite well for all values of v except the very low velocities mentioned in the discussion of Fig. 5.

If k is plotted vs v on a log-log scale for the freezing runs in which the sea ice-lake ice transition occurred, Fig. 8 results. Within the limited water salinity range studied in this figure (1 to 3.3‰), the transition between the two ice types occurred at k values of 0.1 and with ice salinities in the range 0.1 to 0.15‰. This is in the solute concentration range encountered in normal lake water (Hutchinson, 1957). For growth velocities encountered in nature the composition of lake water is apparently such that

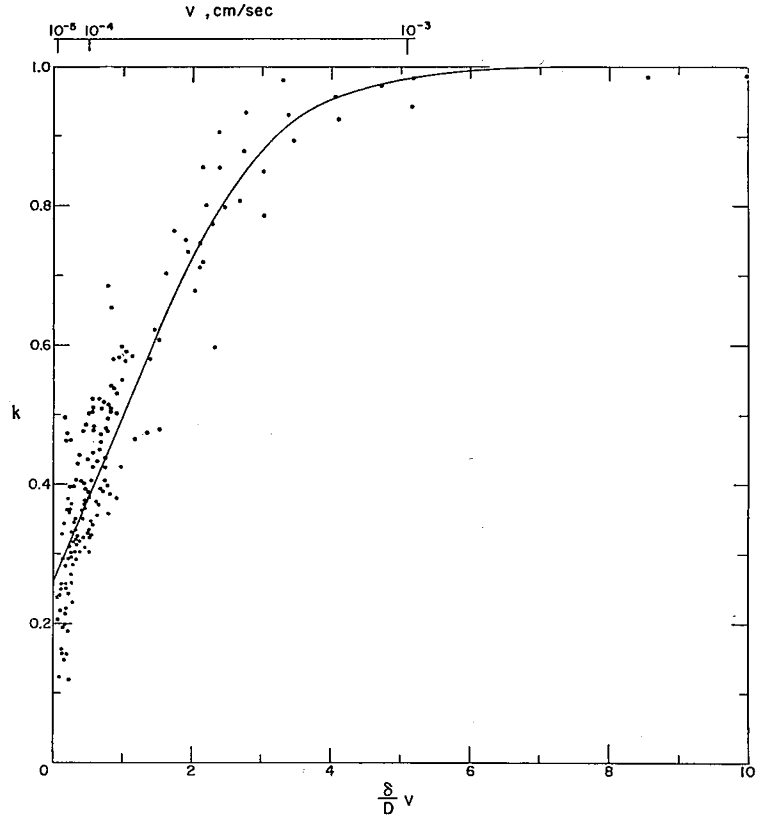

Fig. 7. Plot of k vs. $\delta v/D$. The curve is eq. (8) fit by least squares from Fig. 5

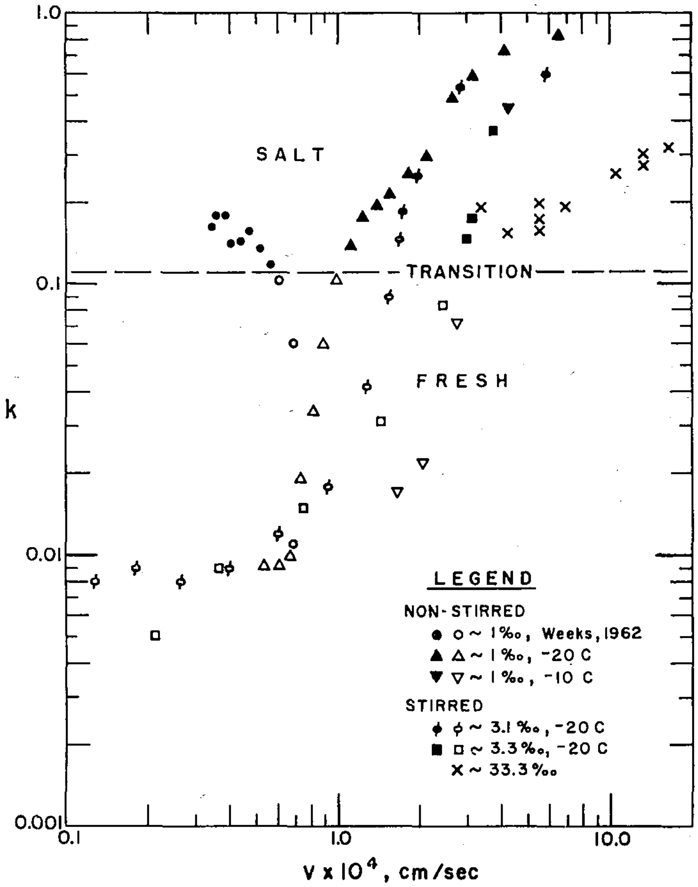

Fig. 8. Plot of k vs. v in runs showing salt ice - fresh ice transition (solid black symbols indicate salt ice, open symbols indicate fresh ice, the $\times$s indicate data from Adams, French and Kingery, 1963)

slight differences in the bulk composition and in the mixing conditions in the water can determine whether the resulting ice forms with a planar or a cellular interface. These changes in interface morphology can explain the inconsistent c-axes orientations observed in lake ice (Knight, 1962) as discussed by Weeks (1964 a, b). In the current runs a c-axis horizontal orientation was established before the transition to fresh ice occurred. After the transition the horizontal orientation remained stable, although the characteristically sutured grain boundaries and the substructure disappeared (see Fig. 4).

It should be noted that the two stirred runs changed to "fresh" ice at higher growth velocities than the unstirred runs. This is undoubtedly the result of a decrease in the value of δ with increased mixing in the liquid. The data of Adams, French and Kingery (1963) when plotted on this graph suggest that in their experiment the transition to "fresh" ice would have occurred at $v \sim 2 \times 10^{-4}$ cm/sec. Unfortunately, their lowest velocity was 4×10^{-4} cm/sec. Because their solute concentration was much higher, this suggestion should be verified experimentally.

The fact that in the run of Weeks (1962) the value of k increases with decreasing

v can be explained as follows. Apparently the initial mixing of the salt and water was incomplete leaving a stable fresh water layer on top of the salt water. This caused "fresh" ice to form first and then change over to salt ice as freezing progressed.

Figure 9 shows the relationship between the average salinity of the water and the average salinity of the ice. Three sets of freezing conditions were used: cold-plate temperatures of approximately −70 and −20°C (Lofgren and Weeks, 1967) and air temperatures of −20°C (Weeks, 1962). All three sets of data show a pronounced linear relationship between S_i and S_w which is strongly dependent on the growth velocity. The fact that all three sets of data intersect the origin adds significance to the meaning of the data. It is easily seen that the rate of salt entrapment is greatly increased as the growth velocity is increased.

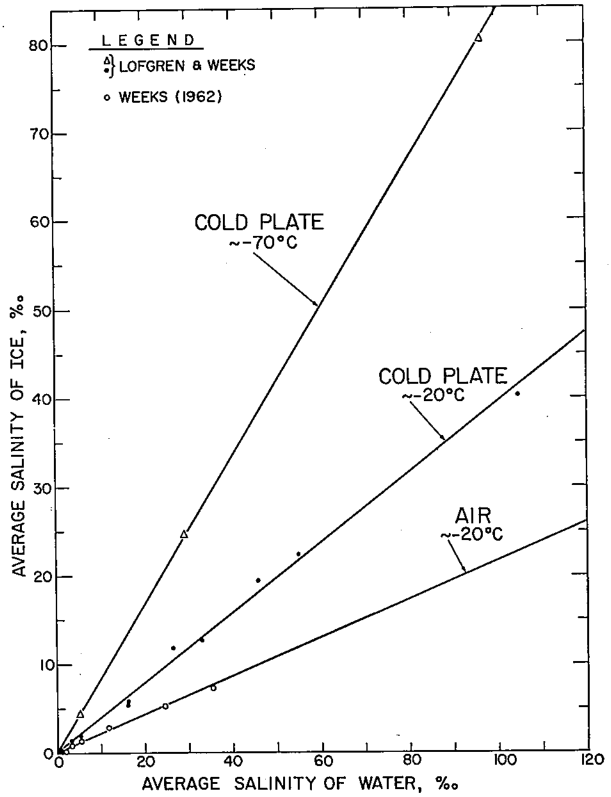

Fig. 9. Average ice salinity vs. average solution salinity for different ice surface temperatures

VI. Initial Salinity and Brine Volume Profiles

Now that the relation between k and v has been found to be quite well represented by eq. (8), we may express S_i as

$$S_i = S_w \left[\frac{k^*}{k^* + (1-k^*) \exp\left[-\frac{\delta v}{D} \right]} \right]. \tag{10}$$

The initial salinity distribution in an ice sheet may now be calculated by use of a growth equation. When account is taken of convective heat transfer at the air-ice interface, the fresh ice growth equation becomes (Neumann, 1949; Adams, French and Kingery, 1960)

$$t=\frac{\rho_i Lh}{\Delta\theta_a}\left(\frac{1}{e}+\frac{h}{2\kappa}\right), \tag{11}$$

where t=time, h=ice thickness, ρ_i=density of the ice, L=latent heat of fusion of the ice, $\Delta\theta_a$=difference between the ambient air temperature (θ_a) and the freezing temperature of the water (θ_w), e=overall coefficient of surface heat transfer, and κ=thermal conductivity of the ice. For the purposes of this paper the complications introduced in the definitions of L and κ for sea ice will be neglected (Anderson, 1960; Schwerdtfeger, 1963). In the case of variable $\Delta\theta_a$, $\frac{1}{t}\int_0^t \Delta\theta_a \mathrm{d}t$ should be substituted for $\Delta\theta_a$ throughout the paper.

From eq. (11)

$$\frac{\mathrm{d}t}{\mathrm{d}h}=\frac{\rho_i L}{\Delta\theta_a}\left(\frac{1}{e}+\frac{h}{\kappa}\right), \tag{12}$$

and because $v=\frac{\mathrm{d}h}{\mathrm{d}t}$ we may substitute for v in eq. (10). Also, at the instant a given increment of ice forms, h (the ice thickness) $=z$ (the distance of the increment below the ice-air interface). Therefore, eq. (10) becomes

$$S_i=S_w\left(\frac{k^*}{k^*+(1-k^*)\exp\left[-\left(\frac{\delta}{D}\right)\left(\frac{\Delta\theta_a}{\rho_i L\left(\frac{1}{e}+\frac{z}{\kappa}\right)}\right)\right]}\right). \tag{13}$$

This equation is plotted for several different $\Delta\theta_a$ values in Fig. 10 using L=70 cal/gm (Schwerdtfeger, 1963); ρ_i=0.925, a representative value for bubble free sea ice (Assur,

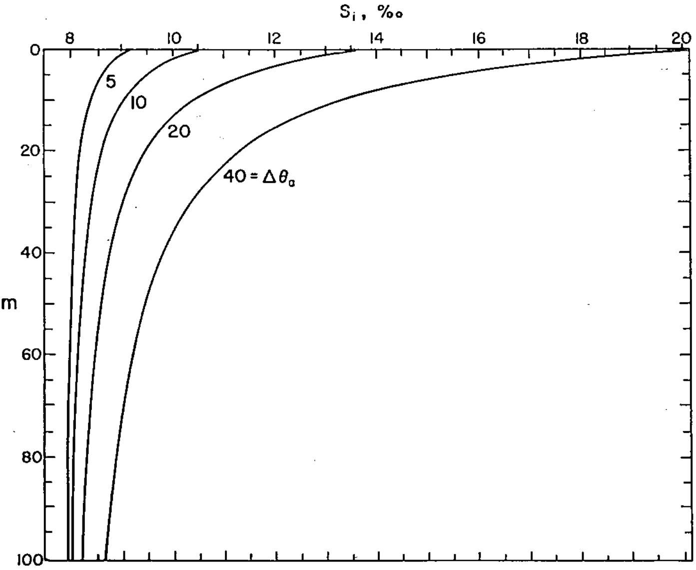

Fig. 10. S_i vs. z for different values of $\Delta\theta_a$

1958; Anderson, 1960); $e=5.56\times10^{-4}$ cal/cm^2·sec·°C (Adams, French and Kingery, 1960; based on field data of Anderson, 1961) and $\kappa=5\times10^{-3}$ cal/cm^2·sec·°C (Anderson, 1960). Both the shape of the upper part of the calculated salinity profile and the magnitude of the calculated salinity increase in the upper part of the ice sheet are similar to actual profiles observed in young sea ice (Weeks and Lee, 1958; Adams, French and Kingery, 1963).

Figure 11 shows a plot of S_i vs. z for three different values of e at a constant value of $\Delta\theta_a=20$. The case of $e=\infty$ occurs when the upper ice surface temperature, θ_0, equals the ambient air temperature while $e=2.78\times10^{-4}$ cal/cm^2·sec·°C corresponds to the e value for still air as determined by Adams, French and Kingery (1960). The pronounced effect of wind velocity on the salinity profile in the upper layer of sea ice is quite apparent.

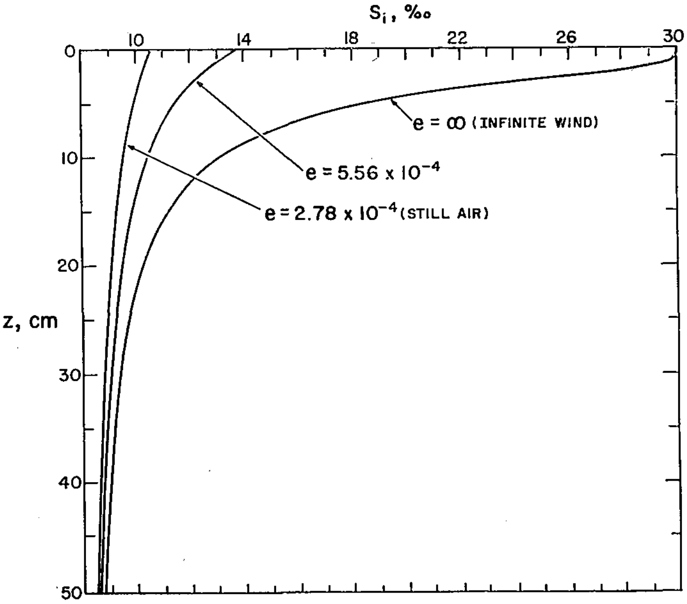

Fig. 11. S_i vs. z for 3 different values of e at $\Delta\theta_a=20$

It is, however, not the salinity profile but the brine volume profile that determines the properties of a sheet of sea ice. Because the brine volume at any given location in an ice sheet is uniquely specified by the salinity of the ice and the ice temperature, it is also possible to calculate initial brine volume profiles. It is known that at temperatures down to −8°C and slightly below, the freezing point of the brine in sea ice can to a good approximation be described by

$$\theta_i = -mS_b\,, \tag{14}$$

where S_b is the salinity of the brine, m is the slope of the liquidus curve from the phase diagram ($m\sim0.054$°C/gm salt/Kgm brine; Miyake, 1939; Defant, 1961, p. 44–45) and θ_i is the ice temperature. Also the brine volume ν can be approximated by

$$\nu=\frac{\rho_i}{\rho_b}\left(\frac{S_i}{S_b}\right), \tag{15}$$

where ρ_i/ρ_b is roughly constant (Assur, 1958). Therefore,

$$\nu = -m\frac{\rho_i}{\rho_b}\left(\frac{S_i}{\theta_i}\right). \tag{16}$$

Now θ_i at any z where $0 \leq z \leq h$ can be expressed as

$$\theta_i = \left(\frac{h-z}{h}\right)\Delta\theta_0 + \theta_w, \tag{17}$$

with $\Delta\theta_0 \equiv \theta_0 - \theta_w$ where θ_0 is the temperature of the snow-ice or air-ice interface and θ_w is the freezing temperature of the water. This, of course, assumes that the temperature profile is linear. Field observations have shown that this is a good approximation. By substituting eqs. (13) and (17) into eq. (15) a relation can be obtained for ν in terms of the important growth parameters. This relation is, however, awkward because it contains temperature in terms of both $\Delta\theta_a$ and $\Delta\theta_0$. This can be avoided for snow free ice since

$$\frac{\mathrm{d}t}{\mathrm{d}h} = \frac{\rho_i L}{\Delta\theta_a}\left(\frac{1}{e} + \frac{h}{\kappa}\right) = \frac{\rho_i L h}{\kappa\Delta\theta_0}, \tag{18}$$

and

$$\Delta\theta_0 = \frac{h\Delta\theta_a}{\kappa\left(\frac{1}{e} + \frac{h}{\kappa}\right)}. \tag{19}$$

Making suitable substitutions we obtain

$$\nu = -\frac{m\rho_i S_w\left\{\dfrac{k^*}{k^* + (1-k^*)\exp\left[-\left(\dfrac{\delta}{D}\right)\left(\dfrac{\Delta\theta_a}{\rho_i L\left(\frac{1}{e} + \frac{z}{\kappa}\right)}\right)\right]}\right\}}{\rho_b\left[\dfrac{(h-z)\Delta\theta_a}{\kappa\left(\frac{1}{e} + \frac{h}{\kappa}\right)} + \theta_w\right]}. \tag{20}$$

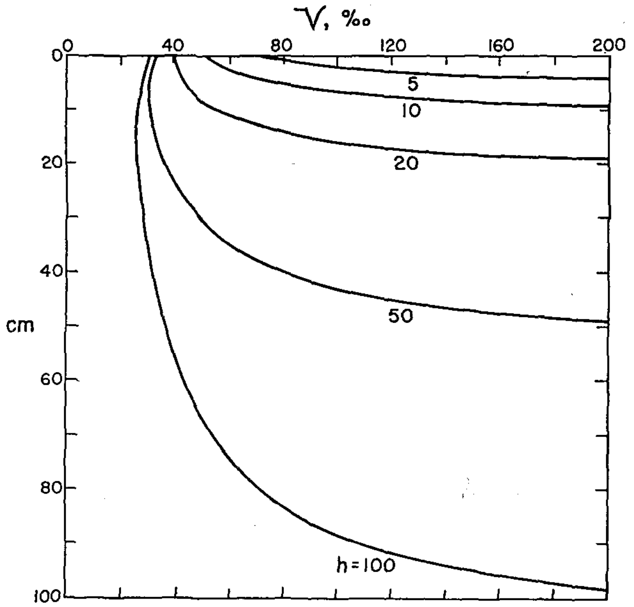

Fig. 12. Brine volume, ν, vs. z for $\Delta\theta_a=20$ and $e=5.56\times10^{-4}$

This relation gives ν at any position (z) in an ice sheet of thickness h in terms of parameters associated with the weather conditions ($\Delta\theta_a$, e) and the salinity of the underlying sea water (S_w, θ_w). Figure 12 shows several computed ν profiles using eq. (20). It is interesting to note that as the ice sheet thickens a minima develops in the ν profile. Once the brine volume profile is established for an ice sheet it is then possible to calculate physical property profiles following the general approach discussed by Assur and Weeks (1963).

As is apparent from comparing the calculated salinity profiles in Figs. 10 and 11 with natural salinity profiles, the characteristic increase in S_i near the bottom of young sea ice sheets is completely absent. The reason for this absence is presumably that brine migration after initial entrapment has been completely neglected in the present treatment. It is hoped that this study will lead to further work which will take brine drainage into account.

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