Ervin, M. A., and D. Luss, "Temperature Fluctuations (Flickering) of Catalytic Wires and Gauzes—I Theoretical Investigation," *ibid.*, **27**, 339 (1972).

Freymuth, P., and M. S. Uberoi, "Structure of Temperature Fluctuations in the Turbulent Wake Behind a Heated Cylinder," *Phys. Fluds*, **14**, 2574 (1971).

Gillespie, G. R., and R. E. Kenson, "Catalyst System for Oxidation of Ammonia to Nitric Acid," *Chem. Tech.*, **1**, 627 (1971).

Heywood, A. E., "Platinum Recovery in Ammonia Oxidation Plants," *Plat. Met. Rev.*, **17**, 118 (1973).

Hinze, J. O., *Turbulence*, McGraw Hill, New York (1959).

Keller, R. N., E. E. Petersen, and J. M. Prausnitz, "Mixing and Chemical Reaction in Turbulent Flow Reactors," *AIChE J.*, **11**, 221 (1965).

Lee, J., and R. S. Brodkey, "Turbulent Motion and Mixing in a Pipe," *ibid.*, **10**, 187 (1964).

Newman, D. J., and B. J. Hulbert, "Nitric Acid Development Aims at Cutting Pollution and Catalyst Costs," *Europ. Chem. News*, Large Plants Supp., (Sept. 24, 26, 1971).

Nowak, E. J., "Prediction of Platinum Losses during Ammonia Oxidation," *Chem. Eng. Sci.*, **24**, 421 (1969).

Toor, H. L., "Turbulent Mixing of Two Species with and without Chemical Reactions," *Ind. Eng. Chem. Fundamentals*, **8**, 655 (1969).

Treybal, R. E., *Mass Transfer Operation*, 2nd edit., McGraw Hill, New York (1968).

Wandrey, C. and A. Renken, "Zur Beeinflussung der Produktverteilung durch periodische konzentrationsschwankungen bei der Oxidation von Kohlenwasserstoffen," *Chim. Ing. Teckn.*, **12**, 854 (1973).

Zuniga-Chaves, J. E., "The Causes for Temperature Fluctuations on Catalytic Wires," M.Sc. thesis, Univ. Houston, Texas (1974).

Manuscript received December 20, 1973; revision received January 29 and accepted January 30, 1974.

Growth Rate of an Ice Crystal in Flowing Water and Salt Solutions

The growth rate of an ice crystal in the basal plane has been measured in subcooled water flowing at velocities of 0.04 to 1 cm/s to test a theory of Fernandez and Barduhn (1967). The theory fits the data in pure water at all velocities and subcoolings studied here and at velocities up to 46 cm/s studied previously. The interfacial tension between ice and water calculated from these data is 33 ± 6 ergs/cm^2, a value in good agreement with those determined by others.

Measured growth rates of ice from solution do not follow the theory and in fact are as much as 150% higher in 0.5 to 1% NaCl solution than in pure water. High subcoolings and low flow velocities accentuate this anomaly.

JOHN G. VLAHAKIS
and
ALLEN J. BARDUHN

Department of Chemical Engineering
and Materials Science, Syracuse University
Syracuse, New York 13210

SCOPE

To test further a theory of unconfined crystal growth of Fernandez and Barduhn (1967), the growth rate of ice crystals in the basal plane (*a*-axis direction) has been measured in flowing subcooled water, aqueous NaCl, and glucose solutions over a wide range of subcoolings, flow velocities, and solute concentrations. The theory presumes that transfer of the latent heat of crystallization, by convection to the flowing stream, controls the ice growth rate and yields an expression with no empirical constants which is

$$v = \left(\frac{a}{1+b}\right) V^{1/2} \Delta T^{3/2}$$

where a is a function of the known properties of pure water and ice and b of the solution. The equation predicts zero ice growth rate (v) in quiescent water ($V = 0$) which is known to be untrue, and an attempt is made to discover the lowest flow velocity for which the theory holds. Previous work showed the relation to hold well at flow velocities up to 46 cm/s, and kinetic contributions to ice growth have been shown to be negligible even at this high flow rate.

The term b in the equation is nearly proportional to the solute concentration and it is thus predicted that ice growth rates decrease regularly as the solute concentration is increased. Previous work shows this to be untrue, and a thorough experimental investigation of this is made.

CONCLUSIONS AND SIGNIFICANCE

The measurements of ice growth rates in pure water now include flow velocities as low as 0.042 cm/s, and the equation of Fernandez and Barduhn holds well here. Previous work included, it has now been shown that the theory holds over a range of flow velocities covering three orders of magnitude. A lower limit to its applicability has not yet been detected although such a limit must exist. Limitations of the apparatus did not permit use of lower flow rates.

The equation resulting from the theory has been verified experimentally for growth in pure water over a velocity range of 1100 to 1, a subcooling range of 40 to 1, and a growth rate range of 180 to 1. The theory, along with the experimental data, yield 33 ± 6 ergs/cm^2 for the interfacial tension between water and ice, a value in good agreement with that determined by others using entirely different means. The theory predicts the radius of curvature of the ice crystal tip to be inversely proportional to the subcooling, and this has been verified by photographic methods but the proportionality constant agrees poorly

---

Correspondence concerning this paper should be addressed to A. J. Barduhn. J. G. Vlahakis is with Sanitary Science Division, U.S. Army MERDC, Fort Belvoir, Virginia 22060.

with prediction. It seems most likely that it is the radius measurements which are in error.

Ice growth measurements in solution do not agree with the model. In 0.5 to 1% NaCl solutions ice crystals were observed to grow as much as 2.5 times as fast as in pure water instead of 0.8 to 0.9 times as predicted. This anomalous effect has been observed previously, but the much more extensive data presented here show that the effect is enhanced at low flow rates and high subcoolings and tends to disappear at low subcoolings and high flow rates. The anomaly occurs in glucose solutions as well as in those of electrolytes. No useful model for this phenomenon has been forthcoming although some are examined.

The growth rate of ice crystals is of interest in fields as diverse as cryobiology, cloud physics, and desalination of sea water by freezing. The main purpose of this work was to obtain data on the growth rate of a single ice crystal in flowing subcooled water and aqueous NaCl solutions under well-defined hydrodynamic conditions since an explanation of such growth will help to understand ice growth in freezers used for desalting sea and brackish waters and also may assist in settling disagreements in the literature on the nature of ice growth.

In earlier studies, Fernandez (1967) and Fernandez and Barduhn (1967) developed a theoretical model for ice crystal growth in flowing subcooled water. The resulting equation fit the data well for water velocities between 8 and 46 cm/s, with subcoolings ranging from 0.02 to 0.70°C, but it predicted zero growth at zero water velocity, and thus must become invalid at some low flow velocity. The model assumed that the growth rate in the basal plane is determined solely by the rate at which the latent heat of solidification is transferred by convection from the crystal to the flowing water, and transport rates were predicted from boundary layer theory. No kinetic resistance to growth was observed even at the highest velocity studied.

This work is an extension of the earlier studies and is an attempt (1) to locate the onset of other mechanisms of growth at low water velocities, and (2) to investigate growth in solutions of sodium chloride. In this work, pure water velocities from 1 cm/s down to the lowest velocities possible with the apparatus, 0.04 cm/s, were studied.

The earlier studies by Fernandez and Barduhn failed to explain the ice crystal growth rate data in flowing NaCl solutions.

In addition, experimental evidence of other workers indicates enhanced growth rates over those in pure water under special conditions in dilute aqueous solutions. The proposed mechanisms given in the literature for this anomaly are contradictory and altogether unsubstantiated.

In order to investigate this effect more rigorously, growth rates were measured at five NaCl concentrations, and at each concentration at least three solution velocities were employed to determine the effect of forced convection.

The experimental system consisted of a fixed single crystal in free growth with subcooled water or salt solutions flowing past it. There were thus three independent variables, solution velocity = V, subcooling = ΔT, and solute concentration = W, affecting the dependent variable, ice crystal linear growth rate = v. Like the previous work done in this laboratory, the growth rates measured were along the a-axis or parallel to the basal plane of the ice crystal. This is the faster growth direction. Growth of the c-axis (perpendicular to the basal plane) was not investigated in this work.

PREVIOUS WORK

An extensive literature survey of what is known about ice growth in water and salt solution for crystals either confined in capillary tubes or allowed to grow freely in a larger volume of solution (unconfined growth) has been made by Vlahakis (1972). The review includes growth in quiescent water and under forced convection conditions. The work in capillary tubes is not easily interpreted because the conditions at the growing interface are difficult to establish by either experiment or calculation and because the presence of the capillary wall has unpredictable effects. This is the main reason we have chosen to work with unconfined crystals under well-defined hydrodynamic conditions where the solution velocity is an independent variable and the conditions at the growing interface can be calculated from well-established theory.

Ice growth in solutions has been studied in capillaries by Tamman and Buchner (1935), Michaels et al. (1966), and Pruppacher (1967); in the unconfined quiescent state by Huige and Thijssen (1969), Lindenmeyer (1959), Lindenmeyer and Chalmers (1966), Pruppacher (1967), Ryan (1966), and Ryan and Macklin (1968); and under forced flow conditions by Fernandez (1967), Huige and Thijssen (1969), and Farrar and Hamilton (1965).

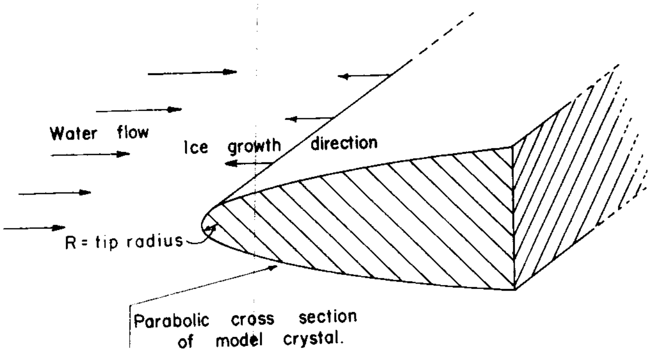
The papers on ice growth in flowing NaCl solutions, as well as those on free and capillary growth in various dilute quiescent solutions, point to anomalous growth rates with several things in common. The growth rate vs. solute concentration has a maximum; the anomaly is located in the dilute concentration range; the effect is not solute specific and occurs with both electrolytes and nonelectrolytes; and the maximum growth rate is more pronounced with increased subcooling. No suitable qualitative explanation has yet been advanced and no quantitative explanation has even been proposed.

ICE GROWTH THEORY IN PURE WATER

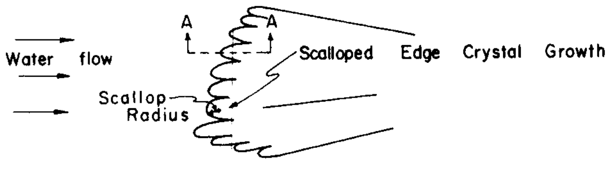
The theory of Fernandez and Barduhn applies directly to the work reported here and is well confirmed for growth in pure water. Briefly, the development starts with the assumption that the leading edge of the ice crystal has the form of a parabolic cylinder, the axis of which is much longer than the radius of curvature at the nose (see Figure 1). Visual and photographic observation shows this to be reasonable. For example, the plan view of a dendrite is shown in Figures 5 and 1b, and the width of the smallest scallop is about 40 microns while the tip radii shown in Figures 6 and 1a are about 1 micron. The length-to-radius ratio of 40 or more seems quite adequate to consider the growing ice edge to be cylindrical. Forced flow occurs perpendicular to the stagnation line of the cylinder and parallel to the axis of the parabola. All the energy liberated by growth is assumed to be transferred to the flowing liquid by convection. Thus

$$v\rho_i L = -k\left(\frac{\partial T}{\partial y}\right)_{y=0} \tag{1}$$

If growth at regions removed from the stagnation line creates temperature gradients in the ice then an additional amount of heat must be rejected to the flowing subcooled water at the crystal tip and



(a) Enlarged Cross Section A-A



(b) Plan View of Actual Growing Crystal

Fig. 1. Crystal form and model.

$$v\rho_i L - k_i\left(\frac{\partial T}{\partial y_i}\right)_{y_i=0} = -k\left(\frac{\partial T}{\partial y}\right)_{y=0} \tag{2}$$

Note that $(\partial T/\partial y_i)$ is the temperature gradient in the ice at the growing interface and $(\partial T/\partial y)$ is the gradient in the water on the liquid side of the interface. The contribution due to conduction in the ice to the growing tip is assumed to be negligible in this derivation, but a more thorough analysis of this phenomenon is being made and will be reported later.

Proceeding then from Equation (1), the gradient in the water is calculated from boundary layer theory for heat transfer by convection to the stagnation line of a parabolic cylinder (Fernandez, 1967) which yields

$$-\left(\frac{\partial T}{\partial y}\right)_{y=0} = A\left(\frac{V}{\nu R}\right)^{1/2}(T_i - T_\infty) = \frac{h(T_i - T_\infty)}{k} \tag{3}$$

The interface temperature T_i is not 0°C for ice for two reasons. First, the curvature of the cylindrical tip is strong (the tip radii are on the order of microns), and this reduces the equilibrium temperature according to

$$T_M - T_i = \frac{\gamma T_M}{\rho_i L R} = \beta/R \tag{4}$$

Second, any resistance to growth due to crystallization kinetics (particle integration) will further reduce the interface temperature by an amount δT. Fernandez showed with his data that this was negligible even at the highest flow velocities used (46 cm/s) although Huige and Thijssen (1969) disagree. The data of the latter extended only to 21 cm/s flow velocity, but the nature of the effect of flow rate on growth is quite different from ours. Both Huige and Thijssen (1969) and Farrar and Hamilton (1965) show the growth rate to level off as the flow velocity is increased above about 10 cm/s.

A possible explanation for their finding that a considerable fraction of the overall ΔT was consumed by interface kinetics is that they used $\gamma = 20$ ergs/cm^2. The value $\gamma = 33$ ergs/cm^2 appears more likely and this will reduce their calculated contribution of kinetics.

Accepting Fernandez' data, letting δT be $= 0$, and combining Equations (1), (3), and (4) yields

$$v = \frac{kA}{\rho_i L}\left(\frac{V}{\nu R}\right)^{1/2}(\Delta T - \beta/R) \tag{5}$$

Since v is found experimentally to be a function of only two independent variables (V and ΔT), the third, R, was presumed to be a function of the first two, and Fernandez invoked the principle of the maximum growth rate by maximizing v with respect to R in Equation (5) which eliminates R and yields

$$R_{\text{crit}} = 3\beta/\Delta T \tag{6}$$

and thus

$$v = \left(\frac{2kA}{(27\rho_i L\nu\gamma T_M)^{1/2}}\right)V^{1/2}\,\Delta T^{3/2} = aV^{1/2}\,\Delta T^{3/2} \tag{7}$$

It is important to observe that Equation (7) predicts ice dendrite growth rates with no empirical constants. It cannot be valid in quiescent water since ice grows at finite rates in quiescent water, but the equation predicts $v = 0$ at $V = 0$. It should be applicable, however, over a range of velocities the lower limit of which is yet to be found, and the upper limit of which will be a velocity high enough to reduce heat transfer resistance to the point where kinetics begins to affect the growth. The equation should also be applicable to the growth of crystals from any pure melt under conditions similar to those described above.

By combining Equations (4) and (6) one notes that this theory predicts that

$$(T_M - T_i)/\Delta T = 1/3 \tag{8}$$

which means that 1/3 of the impressed ΔT is always used up by curvature, leaving 2/3 for heat transfer. Note that this does not imply that higher heat transfer (and thus growth) rates would be observed with larger tip radii. A larger radius would make more than 2/3 of ΔT available for heat transfer, but it simultaneously will decrease the heat transfer coefficient and the net result will be a lower growth rate. Equation (8) is the result of maximizing the growth rate with respect to R and any R greater or smaller than $3\beta/\Delta T$ will give lower growth rates. This is obvious in a mathematical sense but perhaps not from physical intuition. It is very tempting to explain some anomalous high growth rates in salt water (discussed later) by presuming variations in tip radius.

ICE GROWTH THEORY IN SOLUTION

When ice grows from aqueous solutions the solute is rejected at the interface and builds up a concentration boundary layer which makes the equilibrium temperature at the interface different from that at the bulk solute concentration. The extent of this phenomenon depends on the relative rate of ice growth (which brings salt to the interface) and the rate of diffusion of salt away from the interface. By solving the diffusion equation simultaneously with those of energy and motion and invoking the same geometry and restrictions as in pure water, Fernandez showed that the ice growth velocity is predicted to be

$$v = a\left(\frac{1}{1+b}\right)V^{1/2}\,\Delta T^{3/2} \tag{9}$$

where

$$b = \frac{Ak(\lambda C_\infty)}{BLDC_w}\ \text{(dimensionless)}$$

and a = same as in Equation (7).

The term b is nearly proportional to the solute concentration; thus the growth rate is predicted to fall monotonically with increasing solute concentration. The term ΔT in Equation (9) is the difference between the thermodynamic freezing point and the actual temperature of the bulk solution. Fernandez thus predicts the growth rate ratio in salt water and fresh water (at fixed flow velocity and subcooling) to be

$$\frac{v(\text{salt water})}{v(\text{pure water})} = \frac{1}{1+b}$$

Values of this ratio are

Wt. % NaCl in solution	$v_s/v_p = 1/(1+b)$
0	1.000
2	0.661
4	0.489
6	0.380

Note also that the salt effect is predicted to be independent of either V or ΔT.

EXPERIMENTAL APPARATUS

The method of measuring ice crystal growth rates is described in detail by Fernandez (1967). Briefly the apparatus is a straight horizontal glass tube, ½ in. in inside diameter, through which subcooled water flows by gravity from an overhead tank. An ice crystal is nucleated at the tip of a 0.5 mm O.D. capillary centered axially in the stream and located near the downstream end of the ½-in. tube. Its growth is monitored with a traveling 100x microscope and a stop watch. The microscope location can be measured to the nearest micron.

The flowing water temperature is measured with a single thermocouple located axially in the upstream section and covered with a 1/12-in. O.D. sheath. The voltage signal is amplified and recorded continuously so that steady conditions can be observed and the amplification is such that the entire width of a 12 in. strip chart can represent about 0.1°C when needed. An ice bath is the reference junction and the thermocouple response is near 40 microvolts per °C. Temperatures are measured to 0.002°C and presumed accurate to 0.01°C except in 6% NaCl solution where the accuracy is about 0.02°.

An aluminum cylinder surrounds the ½-in. glass tube and is insulated from it. Coolant flow through the cylinder maintains the ice growth cell nearly adiabatic. Measured axial temperature gradients in the ½ in. tube were less than 0.0017°C/cm at flow velocities of 0.5 cm/s, and less than 0.003°C/cm at 0.1 cm/s. At the lower flow rates the thermocouple was moved within 2 to 3 cm of the ice crystal since the velocity profile development length is very short and the disturbing effect of the thermocouple is quickly dissipated. At the higher flow rates the thermocouple was moved farther upstream.

In Fernandez' growth cell the water flowed at higher Reynolds numbers, and the flow path was neither straight nor of uniform size. The water passed through a 20% area reduction just before impinging on the crystal and the reported flow velocities were the bulk velocity (8 to 46 cm/s). In the present apparatus a fully developed parabolic profile existed and since the crystal was always well within 1 mm of the centerline (the field of view of the micrscope was less than 2 mm), the local velocity at the growing crystal was within 2% of the centerline velocity, and it is this centerline velocity which is reported below. The range is 0.04 to 4 cm/s and the Reynolds numbers range from 3 to 300 based on the tube diameter. Based on the calculated tip radii the Reynolds' numbers range from 10^{-4} to 10^{-2}.

In NaCl solutions the thermodynamio freezing point was taken from Scatchard and Prentiss (1933), Rodebush (1918), and Harkins and Roberts (1916). Converting to wt. % NaCl, the following equations were used:

$$W < 1.5,\ T_F = 0.5952\,W \qquad (10)$$

$$1.5 \leq W < 10,\ T_F = 0.0366 + 0.5551W + 0.00917W^2 \qquad (11)$$

Equation (10) agrees with the original source data to 0.002°C for $W < 1.0$ wt. % and to 0.004°C up to 1.5%. Equation (11) fits the data to 0.006°C from 1 to 5.5% NaCl and to 0.020° up to 10% NaCl.

Experimental checks on these values were frequently made by raising the water temperature gradually while a growing crystal was being observed under the microscope. When the crystal stops growing the temperature is raised further to blunt the tip by melting. Lowering the temperature to the point where melting stops allows the freezing point of the bulk salt solution (for ice with a large radius of curvature) to be determined within 0.005°. Such values always agreed with Equations (10) and (11) to within 0.01°C.

EXPERIMENTAL RESULTS IN PURE WATER

Data were taken on growth rates at a fixed flow velocity and a range of ΔT's. A plot on log-log scales of v vs. ΔT for velocities $V = 0.042$, 0.11, and 0.50 cm/s is shown on Figure 2. Data at $V = 0.22$ and 1.0 cm/s are of the same quality (Vlahakis, 1972), but are not shown. A least square fit of log v vs. log $(\Delta T^{3/2})$ was made in each case and the coefficient a' in

$$v = a'\,\Delta T^{3/2}$$

was plotted on log-log scales vs. the flow velocity V in Figure 3.

The agreement with Equation (7) is excellent. Also shown in Figure 3 are the data of Fernandez (1967) and of Poisot (1968) all of which were taken with similar but different pieces of apparatus in this laboratory. Figure 4 shows all 88 data points reported in this work plotted as $v/V^{1/2}$ vs. ΔT on logarithmic scales. The least square value

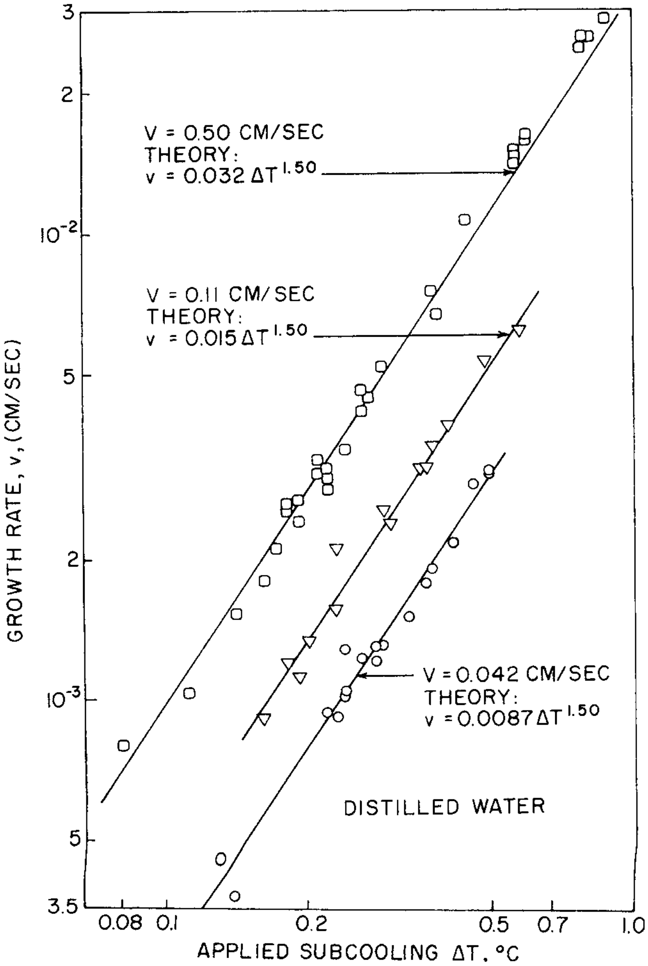


Fig. 2. Ice crystal growth rate vs. subcooling.

of a is 0.0456 $(\text{cm/s})^{1/2}$ $(°\text{K})^{-3/2}$ with a standard deviation of ± 0.0042.

The ½ exponent on V is characteristic of boundary layer theory and is shown to hold over a range of velocities covering more than 3 orders of magnitude. The data of Fernandez give a value to the coefficient a in Equation (7) which is 2½% higher than this work and the data of Poisot are 19% lower although all three sets of data firmly agree with the $V^{1/2}$ and $\Delta T^{3/2}$ dependence of the growth rate. The data of the present report are taken to be the most accurate since the cell of Poisot was not made adequately adiabatic and temperature measurement was less certain. The measurements of Fernandez at the high flow velocities were not plagued with temperature measurement problems and they essentially agree with the present work. The range of variables over which Equation (7) has been verified is given below:

Variable	Range	Ratio of extremes
v (cm/s)	4×10^{-4} to 0.07	180
V (cm/s)	0.042 to 46	1100
ΔT (°C)	0.02 to 0.87	40

Shown also on Figure 3 are the data of others mentioned previously and which show a very different trend and led Huige and Thijssen to conclude that a substantial kinetic resistance is present. The velocities range only from 1 to 21 cm/s, however. Data of Farrar and Hamilton show a similar trend but with higher growth rates.

Another strong piece of evidence supporting Equation (7) is the value of the coefficient a. Most of the factors making up this coefficient are well-known properties of water or ice except the interfacial energy γ. The term A is a dimensionless temperature gradient which comes from heat transfer theory and is a function only of the Prandtl number of the fluid which for water at 0°C is 13.4. Tables of A may be found for example in Schlichting (1955), where A is found to be 1.48. Rearranging Equation (7) and putting the property values at 0°C taken from Fernandez (p. 100); one gets

$$\gamma a^2 = 6.874 \times 10^{-2} \text{ ergs/(sec cm °K}^3)$$

Taking $a = 0.0456 \pm 0.0042$,

$$\gamma = 33 \text{ ergs/cm}^2$$

with an uncertainty of 6 ergs/cm² based on 88 data points.

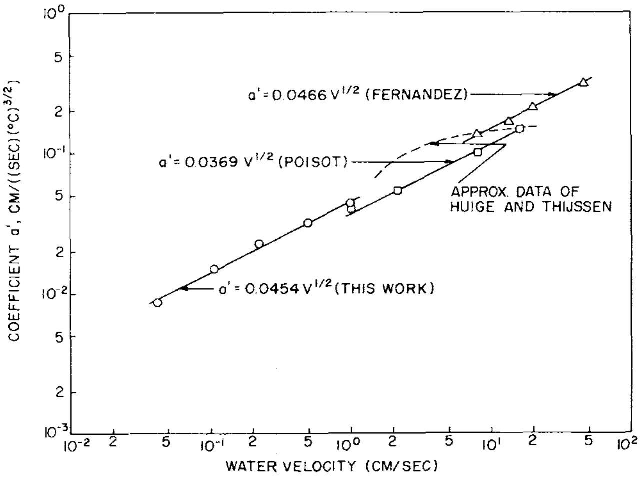


Fig. 3. Coefficient a' vs. water velocity in $v = a'\Delta T^{3/2}$.

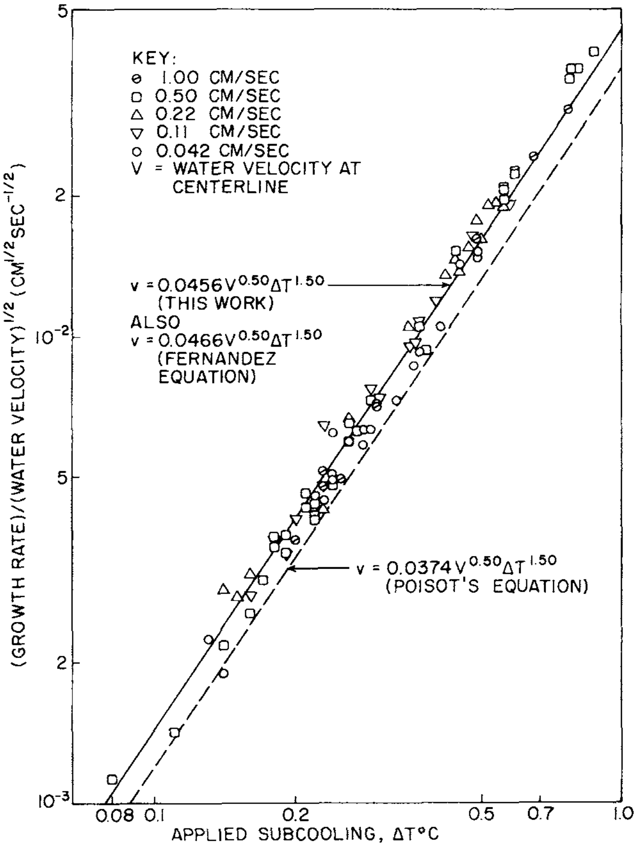


Fig. 4. Ice crystal growth rate data in subcooled distilled water.

The interfacial energy between ice and water has been determined by others using completely different methods, and the reported results are these:

Method	Reference	Reported value of γ
Ice nucleation	Turnbull (1950)	32 ergs/cm²
Contact angle	Ketcham & Hobbs (1967)	33 ± 3
Grain boundary geometry	Jones & Chadwick (1970)	41 ± 9
Calculated from a theory	Various, see Dufour and Defay (1963)	10 to 49

These interfacial energies are for the ice planes perpendicular to the basal plane. For the basal plane itself such energies have been reported to be much lower.

In spite of the very good quantitative agreement of the data with Equation (7), at least three lines of reasoning lead to questions about the model on which it is based. First, it neglects any conduction in the ice which may be important. Ice has a thermal conductivity about 4 times that of water and since the conduction path thru the ice is comparable in length to that thru the boundary layer, there may be an additional heat flux to be dissipated beyond that created by the growth, that is, Equation (2) may have to be used in place of Equation (1) in the model. Such an analysis has been made for a stationary parabolic ice cylinder and this shows the ice conduction to be very important. The analysis overemphasizes the role of conduction, however, since the crystal tip is growing in the same direction as the conducted heat flux and the rate of heat arrival at the tip will be reduced below that calculated above. The analysis with a growing crystal has not yet been made. Another problem with estimating the conduction contribution to growth is that we have not found a value for the thermal conductivity of ice in the a-axis direction and this may be greater or smaller than the all-directional conductivity of ice as reported in handbooks.

Second, it has been pointed out by Harriott (1971) that the predicted boundary layer thickness is at least as large as the tip radius of the crystal and under this condition, boundary layer theory is not supposed to be valid. If, for example, we approximate the boundary layer thickness (Δ) by k/h, then the ratio $hR/k = Nu$ gives the ratio R/Δ. Values of Nu can be calculated from Equations (3), (4), and (6), and the range of values of this give

$$\frac{1}{Nu} = \frac{\Delta}{R} \simeq 1 \text{ to } 100$$

while Δ/R should be $<< 1$ to make boundary layer theory applicable. It has been noted that while this criterion is necessary for calculation of local heat transfer rates generally over the surface of the parabola, we are using this theory only at the stagnation line and that at this location the local heat transfer rate is insensitive to the boundary layer thickness (Cole 1968). Cole states that in the case of stagnation-point flow, the solution to the boundary-layer equations is also a solution to the full Navier-Stokes equations. If this is true then there should be no lower limit on Equation (3) due to boundary layer thickening at low velocities although other mechanisms may affect heat transfer at these low flow rates. We are now working on Stokes-type flow around a cylindrical parabola to see if the heat transfer rates are appreciably different from those predicted by boundary layer theory.

Fig. 5. Photograph of growing ice crystal: top view.

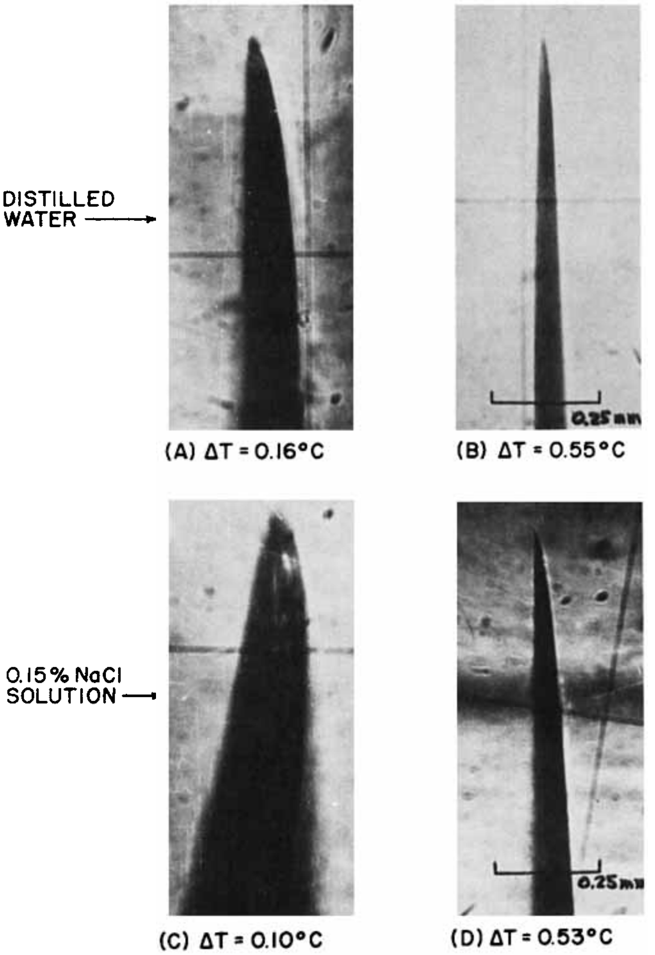


Fig. 6. Photographs of growing ice crystals at various degrees of subcooling: edge view.

Third, Equation (6) predicts a radius of curvature for the nose of the crystal tip (see Figure 1a) which has not been directly verified. To test this, some photographs of crystals growing at various ΔT's were taken. Figure 5 shows a growing dendrite in plan view and Figure 6 shows 2 dendrites growing in pure water with the crystals on edge and the stagnation line appearing as a point at the tip of a parabola. The scale is the same for both crystals, and it is obvious that the radius is larger for the smaller ΔT. Measurements of the tip radius of several of these were made indirectly by measuring the parabola width w at several distances back from the tip l. The tip radius is then given by

$$R = \frac{w^2}{8l}$$

Results of this analysis are shown in Figure 7 in which the observed radius is plotted vs. ΔT. On log-log coordinates the data fit a slope of -1 showing that ΔT and R are inversely proportional as predicted. The proportionality factor found from Figure 7 is about 6.3 times the value predicted by Equation (6), however. If one adjusts the interfacial energy to fit the observed radii of curvature, γ would have to be over 200 ergs/cm^2, a value which is incredibly high. Ryan (1966) measured ice crystal scallop radii (Figure 1b) and found them to vary inversely with ΔT also, but these radii are of course much larger than the tip radii reported here. A comparison is shown on the next page.

$R\Delta T$ (micron °K)	Source
$3\beta = 0.089$	Fernandez theory, R = tip radius (1967)
0.56	Observed, this work, R = tip radius (1972)
30 to 45	Observed by Ryan, R = scallop radius (1966)

It is difficult to understand the difference between the first two figures. The theory fits the growth rate data very well over a wide range of variables, and the interfacial tension calculated from growth data is very reasonable. Both of these facts depend on the crystal tip radius conforming to Equation (6), but direct observation of this quantity agrees only that R varies inversely with ΔT. The most reasonable conclusion at this moment seems to be that the method used to measure tip radii is quite inaccurate. The submicron radius of the tip may not be consistent with the larger measurable parts of the parabola, that is, the crystal cross section may not be truly parabolic over its entire length.

Ryan's measurement of scallop radii (Figure 1b), verifies our contention that the ratio of the scallop width (twice the radius) to the tip radius is large and at least equal to 40.

TABLE 1. VALUES OF n IN $v = {}'\Delta T^n$ AS A FUNCTION OF NaCl CONCENTRATION AND SOLUTION VELOCITY

Solution velocity, V cm/s	Weight % NaCl in solution 0	0.152	0.502	0.905	1.97	6.00
0.20	(1.50)	1.71	1.91	1.89	1.90	2.03
0.85	(1.50)	1.67	1.77	1.75	1.83	1.98
3.88	(1.50)	1.48	1.59	1.52	1.56	1.49
8.85	(1.50)				1.47	
11.9	(1.50)				1.59	

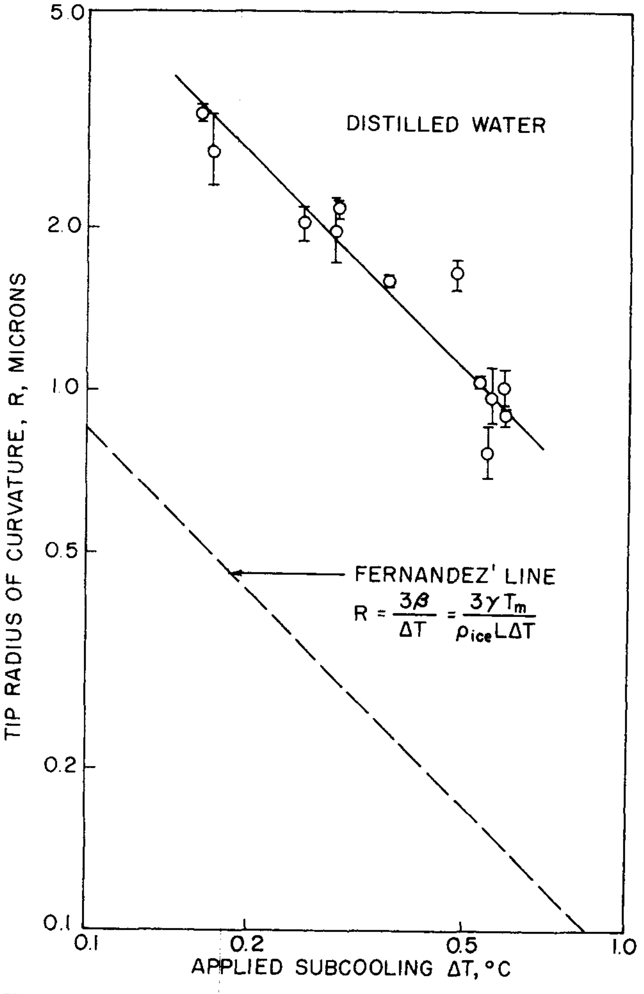


Fig. 7. Tip radius of curvature vs. applied subcooling in distilled water.

EXPERIMENTAL RESULTS IN NaCl SOLUTION

Growth rates of ice crystals in sodium chloride solutions were measured at five different salt concentrations ranging from 0.15 to 6.0 wt. % NaCl and at a minimum of three velocities (for each concentration) ranging 0.2 to 4 cm/s. At 1.97% salt, five velocities were studied ranging 0.2 to 12 cm/s. Samples of data are shown in Figures 8 and 9 which are logarithmic plots of the observed growth rate v vs. the subcooling ΔT, at a fixed flow velocity V. The first thing to note is that the lines are steeper than predicted by Equation (9), that is, the growth varies with ΔT to a power greater than 3/2. The exponent on ΔT tended toward 2 at low flow velocities, and this is not an uncommon dependence on subcooling observed by many others in quiescent water. With higher flow velocities the exponent tended toward 1.5 at all salt concentrations. At higher salt concentrations the exponent tended to be higher also and the entire effect is summarized in Table 1, which shows values of the exponent on ΔT for all NaCl concentrations and flow velocities studied. The trends are unmistakable but slightly irregular.

When the exponent on ΔT is greater than 3/2 there will be a ΔT above which the growth rate in solution will be greater than that in pure water. This is exactly what occurs in dilute solutions, especially at the lower flow velocities. The ratio of the rates in solution vs. pure water will of course increase as the ΔT becomes higher.

The data in Figure 8 for 0.5% NaCl and $V = 0.2$ cm/s show the increased growth rate over that observed in pure water for $\Delta T \overset{\sim}{>} 0.1$°C. Equation (9) calls for an 11% reduction for 0.5% NaCl.

Figure 9 data are for 6% NaCl and $V = 0.85$ cm/s. The growth rates are substantially lower than in pure water, but all points except the one at the lowest ΔT are higher than called for by Equation (9) which predicts a 62% reduction in growth rate in 6% NaCl.

Altogether 285 growth rate data points were made in salt water, and all but a very few gave values higher than predicted by Equation (9) and these were at the lowest ΔT's and highest salt concentrations. In 0.5% NaCl at $V = 0.2$ cm/s and $\Delta T = 0.9$°C. (Figure 8), the observed growth rate is 150% above that observed in pure water.

The enhanced growth in dilute solution is demonstrated for a 1.53% solution of glucose in Figure 10, a phenomenon observed by others also, for example, Huige and Thijssen. This shows that the anomalous rates are not confined to solutions of electrolytes. The enhancement in Figure 10 is 20 to 40% above pure water rates.

The most vivid display of enhanced growth is obtained by plotting the rates against the % salt in solution as is done on Figures 11 and 12 where the parameters are ΔT. Figure 11 is for $V = 0.2$ cm/s and Figure 12 is for $V = 3.88$ cm/s. The maximum growth rates occur at 0.5 to 1% NaCl. The maxima tend to disappear at low ΔT and are less pronounced at higher flow rates. The dashed lines in Figures 11 and 12 are those predicted by Equation (9)

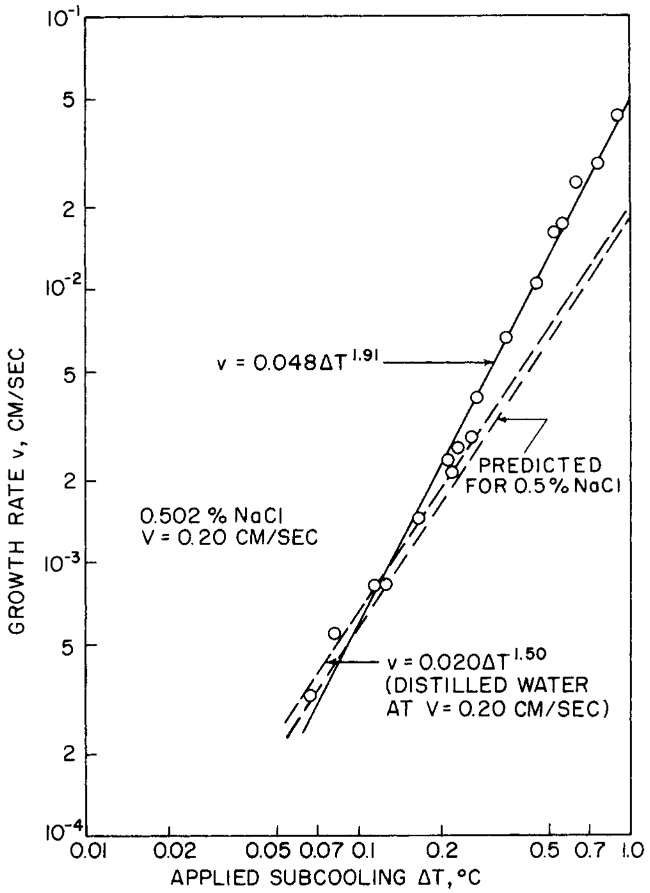


Fig. 8. Ice crystal growth rate vs. subcooling in 0.502% NaCl solution: $V = 0.20$ cm/s.

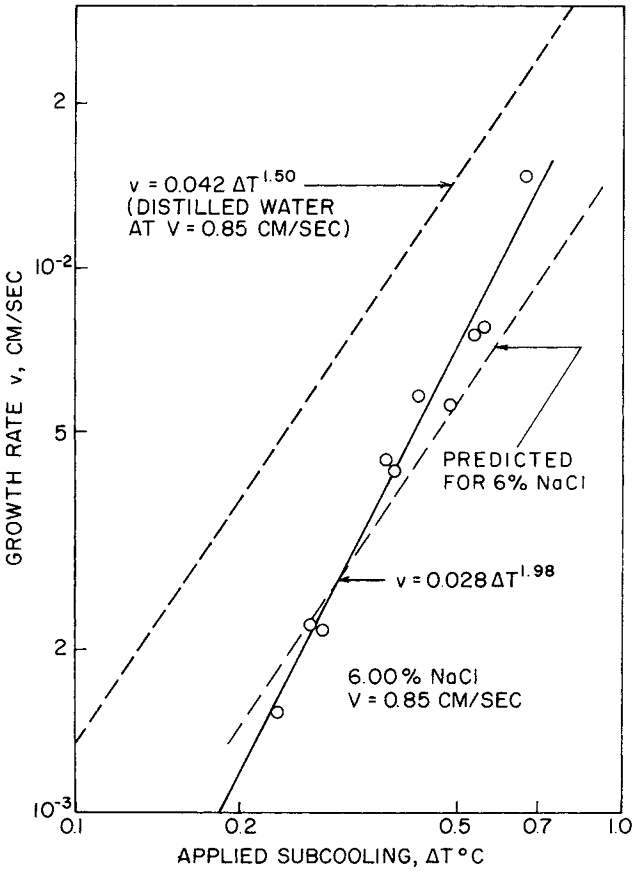


Fig. 9. Ice crystal growth rate vs. subcooling in 6.00% NaCl solution $V = 0.85$ cm/s.

which accounts simultaneously for both the transport of latent heat and of salt from the growing interface to the flowing fluid.

The effect of flow rate is shown on Figure 13 where v is plotted vs. V with ΔT as a parameter and the salt con-

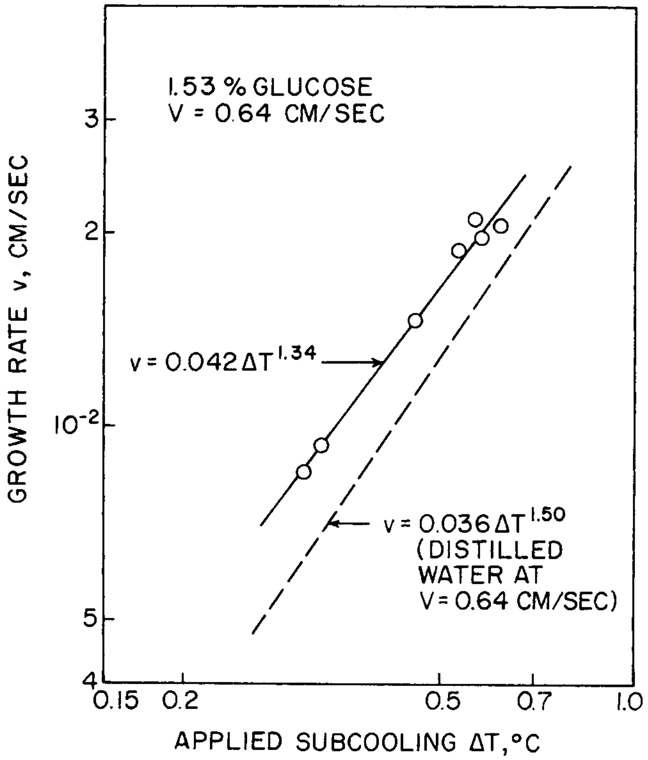


Fig. 10. Ice crystal growth rate vs. subcooling in 1.53% glucose solution: $V = 0.64$ cm/s.

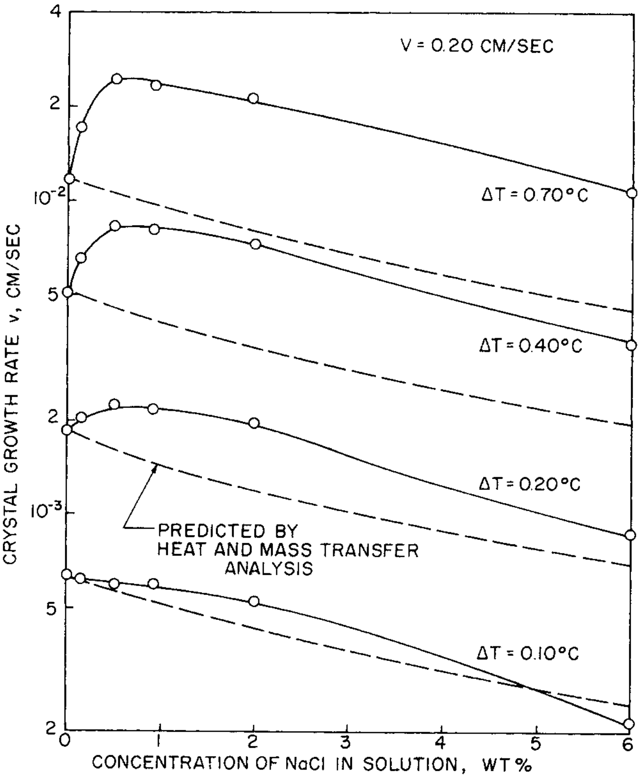


Fig. 11. Ice crystal growth rate vs. solution concentration as a function of subcooling: $V = 0.20$ cm/s.

centration is fixed at 0.9% NaCl. In this figure and for all salt concentrations up to and including 2%, all growth rates tend toward that predicted and observed for pure water [Equation (7)] as the flow increases. At 6% salt (not shown) this is not observed, however, and the data tend a little irregularly toward that predicted by Equation (9) for salt solutions with increasing velocity.

Measurements of tip radii were made for crystals growing in a 0.15% NaCl solution (results not shown, but see Vlahakis 1972) and they gave a steeper line when plotted logarithmically as R vs. ΔT than in pure water (Figure 7). Approximately, the data are represented by

$$R = 0.27\ \Delta T^{-1.5}\ (R = \text{microns})$$

The inverse relationship between R and ΔT still holds, but they are not inversely proportional as in pure water. The measured radii in either medium are about equal at $\Delta T = 0.23°$ and are near 2.4 microns. Observed growth rates in the 0.15% NaCl show little enhancement over pure water until the ΔT is considerably larger than 0.2°C. All the tip radius measurements were made at random velocities and no relation between velocity and radius could be detected.

On occasion, in about half the runs at $V = 3.88$ cm/s only, and at salt concentrations of 0.15 and 2%, two crystals were observed to grow simultaneously, one straight upstream and one off at an angle of about 45° from the centerline of the tube. In these cases the straight crystal grew at the rates presented in the figures, but the other grew at rates up to 30% less than this. Both crystals experienced the same flow velocity within 1½% and the growth rates recorded were those in the direction of growth whether straight upstream or not. It thus appears that all crystals do not necessarily grow at the maximum growth rate as presumed in the derivations of Equations (7) and (9). Whether the tip radius of the slow crystal was greater or smaller than that of the normal one is not known, although either eventuality would account for the slower growth.

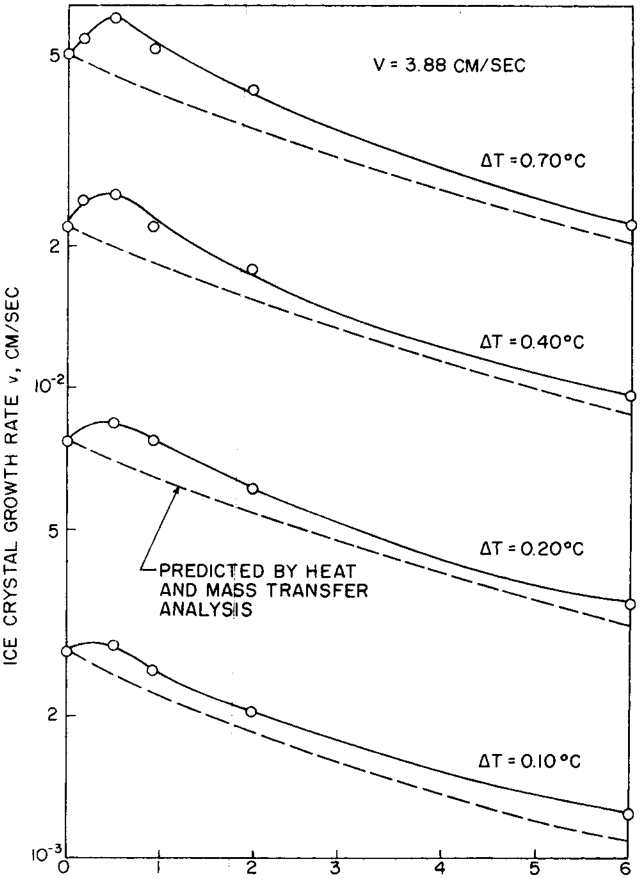


Fig. 12. Ice crystal growth rate vs. solution concentration as a function of subcooling: $V = 3.88$ cm/s.

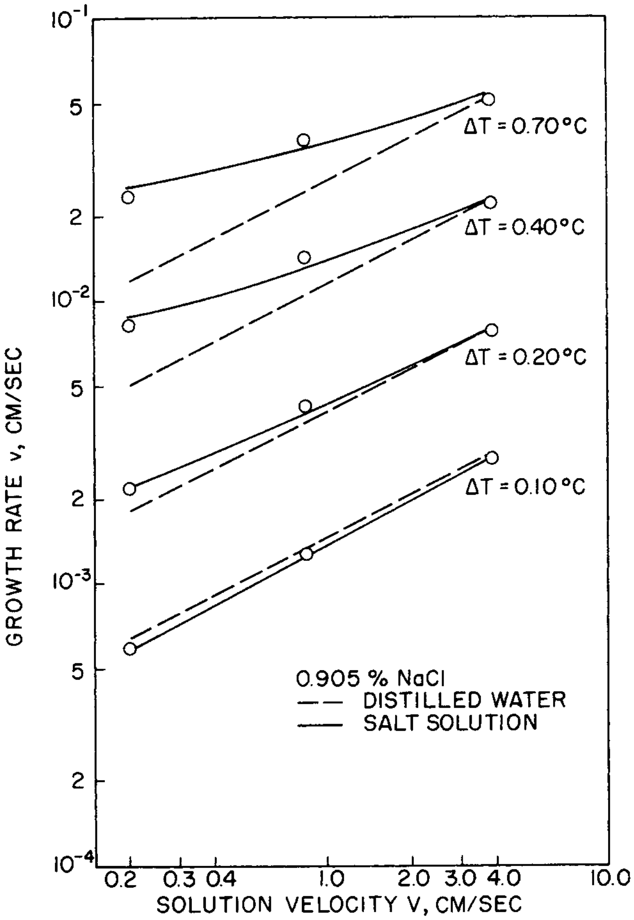


Fig. 13. Ice crystal growth rate vs. solution velocity in 0.905 wt. % NaCl solution with subcooling as a parameter.

DISCUSSION OF ANOMALOUS GROWTH RATES

In solution we observe the growth of ice dendrites to be faster than that in pure water for $0 < W \overset{\sim}{<} 2\%$ NaCl, and the effect is more marked as the flow velocity falls and as the subcooling rises. Straight heat and mass transfer theory predict growth in solution to decrease regularly as concentration increases. The same theory applied to the case of growth in pure water is verified by experiment over a wide range of variables even though some of the initial assumptions are questionable.

One important piece of evidence to consider is the result of the work of Terwilliger and Dizio (1970) who studied one-dimensional growth of planar ice where the released heat of crystallization was withdrawn through the ice. Their observations agree with their mathematical description of the process in both pure water and salt solutions. Their model predicts a continuously decreasing growth rate as the salt concentration increases. Any increase in growth rate beyond that observed by us in pure water must thus be connected with the fact that we are growing ice on a sharply curved surface since such anomalies are not observed on flat surfaces.

This leads us to look at those assumptions which have to do with curvature. The first is the parabolic shape of the growing ice tip. For all other blunt cylindrical shapes looked at (circular, hyperbolic, and ellipsoidal), the results of the complete analysis differ from that of Equations (7) or (9) only by a constant factor and in no way change the form of the equations.

The second assumption is that the radius of curvature of the tip is not an independent variable but is a function of ΔT and that it so adjusts itself that it gives the maximum growth rate possible. But we are then immediately faced with the fact that we can increase the rate easily by a factor of 2 simply by adding 0.5% salt to pure water. The properties of ice and water such as thermal conductivity, viscosity, density, freezing point depression, and heat of fusion all change regularly with salt concentration, and the changes are roughly proportional to it. Even the ice-water interfacial tension has been measured in salt solution recently by Jones and Chadwick (1971) and was found to increase slowly with concentration. Hardy and Coriell (1970) have found that many salts at concentration of 0.001 M ($\simeq$0.5 wt. %) have no effect on the tension between ice and water. In any case, if surface tension changes in solution are to account for 100% growth rate increases, then 0.5% salt would have to decrease the surface tension by a factor of 4, and each different ΔT and V used would require a different value of γ.

It does not seem probable that the solute can in some way affect the radius of curvature. If it does, in what direction shall it change R to give higher growth rates? Either an increase or decrease should reduce the growth rate.

A natural convection effect is possibly the cause of enhanced growth in salt solution. It is unlikely to be important in pure water because of its very low thermal coefficient of expansion at $0°C(-7 \times 10^{-5}\ °C^{-1})$. But density differences due to the concentration gradient near the crystal surface may be appreciable. For example, $d\rho/\rho dC$ for a 1% NaCl solution (at room temperature) is $+7 \times 10^{-3}$wt. $\%^{-1}$. Comparing a 1°C temperature change with a 1% concentration change, it is seen that density differences in the salt solution could be 100 times that in the pure water. Using criteria for the relative importance of forced and natural convection such as those of Acrivos (1966) or Collis and Williams (1959) is very uncertain since they are for very different geometries and have not been tested at the low Reynolds and Grashof numbers used in our experiments (respectively, 10^{-4} and 10^{-14}). Using them in spite of these uncertainties indicates thermal natural convection of no importance, and concentration natural convection is not important (Acrivos) or may be important (Collis and Williams).

The enhancement of anomalous growth rates at lower velocities and higher ΔT's is in agreement with what would be expected from natural convection. Lower forced velocities would make the relative contribution of natural convection more important and higher forced velocities will eventually mask the effect. Higher ΔT's will not make much change in the density directly, but they do cause higher growth rates, and this can set off the chain of events: higher salt rejection rates—higher concentration gradients—higher density gradients—higher natural convection velocities—higher heat transfer—and thus increased ice growth rates. These natural convection effects will be most noticeable in low concentration solutions where they could be large enough to overcome the normal growth-retarding effect of the salt. In higher concentration solutions the mass transfer resistance could dominate, thus giving a maximum growth rate at some particular intermediate salt concentration. None of this discussion shows definitely that free convection is or is not important, however.

Experiments are planned in which the flow is vertical, and if natural convection is important the growth rates will be different from those presented here for horizontal flow. If the difference is real, then an analysis of the phenomenon will be warranted.

Perhaps too much reliance is being put on the model of Fernandez. Tiller (1971) for example, believes that conduction in the ice may be important. He reasons that in both pure water and solutions the growing ice tip is not isothermal since the curvature changes rapidly near the tip and thus also the equilibrium temperature. Warmer temperatures back from the tip create a heat flux in the ice which adds to the heat liberated by solidification. Both these sources must be rejected to the flowing stream as shown by Equation (2). Thus isothermal ice would grow faster than nonisothermal ice. Tiller then reasons that anything done to reduce the gradients in the ice will increase the growth rate. He postulates that the addition of small amounts of solute does just this. This salt buildup at the interface is nonuniform and is highest where the growth is most rapid, that is, at the tip. In salt solutions then, the ratio of growth rates at the tip to some point removed from it will be nearer unity than it would in pure water, and this would reduce the gradients in the ice. If this effect more than compensated for the increased resistance due to salt, an increase in growth rate over that in pure water could be observed.

Kotler (1968) has put Tiller's idea into quantitative form and predicted a growth rate increase in a quiescent 0.1M KCl solution of 1% over that in pure water; however, the observed increase under these conditions was 30%. We are looking for a model which can explain increases as high as 150% in dilute salt solutions.

There are some appealing aspects to Tiller's idea when applied to the data in flowing solutions presented here, however. First it is not solute-specific and applies to electrolytes and nonelectrolytes equally. Second, the growth anomaly should be reduced in extent at higher flow velocities by removing the rejected salt from the interface more rapidly and thus making the growth conditions more like that in pure water. This is just what was observed in this work. Third, it would predict an increase in the anomalous growth with higher ΔT since high ΔT's give greater solute rejection rates and a greater nonuniformity of interface concentrations. These in turn lead to lower ice temperature gradients again. This effect of ΔT on the anomalous growth is also what we have observed. Qualitatively then these ideas are satisfying, but quantitatively they do not yet explain any observed results. Others have studied nonisothermal dendrite growth, for example, Kotler and Tarshis (1968, 1969).

A recent advertisement by Applied Science Publishers (1972) for "Discourses on Physical Science" quotes Faraday remarking about Arago who ". . . discovering the phenomenon of magnetic rotation, yet not perceiving its physical course, had that philosophic power of mind which enabled him to refrain from suggesting one." The authors have adopted this quotation as a motto. We do not perceive the physical course of anomalous ice growth. We like to think it is our "philosophic power of mind" which prevents us from suggesting one.

ACKNOWLEDGMENT

This work was supported by the Office of Saline Water, U.S. Department of Interior.

NOTATION

a = symbol for group of constants in Equations (7) and (9)
a' = constant in $v = a'\Delta T^n$
A = dimensionless temperature gradient at ice-water interface
= $f(Pr \text{ only}) = 1.48$ for water at 0°C
B = dimensionless concentration gradient at ice-water interface
= $f(Sch)$ only = 9.8 for 5% NaCl solution at its freezing point. It is the same $f(Sch)$ as A is of (Pr)
C_∞ = bulk liquid phase concentration, mol/l
C_w = water concentration in solution $\simeq$ 1 g/cc
D = solute diffusion coefficient, cm^2/s
h = heat transfer coefficient, cal/(cm^2-s-°C)
k = thermal conductivity of water or salt solutions, cal/(cm-s-°C)
k_i = thermal conductivity of ice
L = heat of solidification of water, cal/g
n = exponent on ΔT in growth rate laws
Nu = Nusselt number, hR/k
Pr = Prandtl number = $C_p\mu/k$ = 13.4 for water at 0°C
R = tip radius of curvature, cm
Re = Reynolds number, RV/ν
Sch = Schmidt number = $\mu/(\rho D)$ = 2430 to 3470 in NaCl solution at freezing point as conc. varies from 0 to 6 wt. %
T = temperature, °K
T_F = freezing point of bulk solution, °K
T_i = ice-water interface temperature, °K
T_M = ice point = 273.2°K (or normal melting point of pure solvent)
T_∞ = bulk solution temperature, °K
v = ice crystal growth rate, cm/s
V = water or solution velocity, cm/s
W = weight per cent NaCl in solution
x, y = boundary layer coordinates, y = perpendicular to interface
β = $\gamma T_M/(\rho_i L)$, cm °K
γ = ice-water interfacial energy, ergs/cm^2
Δ = boundary layer thickness
ΔT = $T_M - T_\infty$ = applied subcooling °C in pure water, or $T_F - T_\infty$ in solution
δT = kinetic temperature driving force, °C
(λC_∞) = °C depression of freezing point due to solute
ν = kinematic viscosity of water or solutions, cm^2/s
ρ_i = density of ice, g/cm^3

LITERATURE CITED

Acrivos, Andres, "On the Combined Effect of Forced and Free Convection in Laminar Boundary Layer Flows," *Chem. Eng. Sci.*, **21**, 343 (1966).

Applied Science Publishers Ltd. Ripple Road, Barking, Essex, England. Advertisement for the Royal Inst. Library of Science—Physical Sciences 10 Vol., Sir. W. L. Bragg and George Porter (eds.) 1972.

Barduhn, Allen J., Raffi M. Turian, Joshy P. Kallungal, Jenn-Ming Stephen Huang, and Thomas A. Viscusi, Final Report Submitted to Office of Saline Water, U.S. Dept. Interior on Grant No. 14-30-2763, pp. 23-26 (1973).

Cole, Julian D., Perturbation Methods in Applied Mathematics, p. 160, Blaisdell, Waltham, Mass. (1968).

Collis, D. C., and M. J. Williams, "Two Dimensional Convection From Heated Wires at Low Reynolds Numbers," *J. Fluid Mech.*, **6**, 357 (1959).

Dufour, L., and R. Defay, Thermodynamics of Clouds, pp. 5, 131-150, 225-234, Academic Press, New York (1963).

Farrar, John S., and W. S. Hamilton, "Nucleation and Growth of Ice Crystals," Office of Saline Water Res. and Dev. Prog. Rept No. 127 (1965).

Fernandez, Remigio, "The Growth of Ice in Flowing Water and NaCl Solutions," Ph.D. thesis, Syracuse University, New York (1967).

———., and Allen J. Barduhn, "The Growth Rate of Ice Crystals," *Desalination*, **3**, 330 (1967).

Hardy, S. C., and S. R. Coriell, "Morphological Stability of Ice Cylinders in Aqueous Solution," *J. Crystal Growth*, **7**, 147 (1970).

Harkins, William D., and W. A. Roberts, "The Freezing-Point Lowerings in Aqueous Solutions of Salts. . . .," *J. Am. Chem. Soc.*, **38**, 2676 (1916).

Harriott, Peter, Cornell University, Private communication to A. J. Barduhn, (Aug. 1971).

Huige, N. J. J., and J. A. C. Thijssen, "Rate Controlling Factors of Ice Crystal Growth. . . .", in *Industrial Crystallization*, pp. 71-88, Hodgson, London (1969).

Jones, D. R. J., and G. A. Chadwick, "Experimental Measurement of the Solid-Liquid Interfacial Energies of Transparent Materials," *Phil. Mag.*, **22**, 291 (1970).

———————., "Experimental Measurement of Solid-Liquid Interfacial Energies," *J. Crystal Growth*, **11**, 260(1971).

Ketcham, W. M., and P. V. Hobbs, "An Experimental Determination of the Surface Energies of Ice," *Phil. Mag.* **19**, 1161 (1969).

Kotler, G. R., and L. A. Tarshis, "On Dendritic Growth of Pure Materials," *J. Crystal Growth*, **3**, **4**, 603 (1968).

———————., "An Extension to the Analysis of Dendritic Growth in Pure Systems," *ibid.*, **5**, 90 (1969).

Kotler, G. R., "Theoretical Investigations of Dendritic Growth," Ph.D. thesis, Stanford Univ., Calif. (1968).

Lindenmeyer, C. S., "The Solidification of Supercooled Aqueous Solutions," Ph.D. thesis, Harvard Univ., Cambridge, Mass. (1959).

———., and F. Chalmers, "Growth Rate of Ice Dendrites in Aqueous Solutions, *J. Chem. Phys.*, **45**, 2807 (1966).

Michaels, Alan S., P. L. T. Brian, and Peter R. Sperry, "Impurity Effects on the Basal Plane Solidification Kinetics of Supercooled Water," *J. Appl. Phys.*, **37**, 4649 (1966).

Poisot, J. M., "The Linear Growth Rate of Ice Crystals in Flowing Subcooled Water," M.S. thesis, Syracuse Univ., New York (1968).

Pruppacher, Hans R., "Some Relations Between the Structure . . . and . . . Growth Rate of Ice Crystals . . .," *J. Colloid Interface Sci.*, **25**, 285 (1967).

———., "On the Growth of Ice in Aqueous Solutions Contained in Capillaries," *Z. Naturforschg.*, **22a**, 895 (1967).

Rodebush, Worth H., "The Freezing Points of Concentrated Solutions . . .," *J. Am. Chem. Soc.*, **40**, 1204 (1918).

Ryan, B. F., "The Growth of Ice Parallel to the Basal Plane . . . ," *J. Crystal Growth*, **5**, 284 (1966).

———., and W. C. Macklin, "The Growth of Ice in Supercooled Aqueous Solutions," *ibid.*, **2**, 337 (1968).

Scatchard, George, and S. S. Prentiss, "The Freezing Points of Aqueous Solutions," *J. Am. Chem. Soc.*, **55**, 4355 (1933).

Schlichting, H., *Boundary Layer Theory*, p. 272, Pergamon Press, N. Y. (1955).

Tammann, G., and A. Buchner, "Die Unterkuhlungsfahigkeit des Wassers und die lineare Kristallisationsgeschwindigkeit des Eises in Wassringen Losungen," *Z. Anorg. Allgem. Chem.*, **222**, 371 (1935).

Terwilliger, J. P., and S. F. Dizio, "Salt Rejection Phenomena in the Freezing of Saline Solutions," *Chem. Eng. Sci.*, **25**, 1331 (1970).

Tiller, W. A., Stanford Univ., private communication to J. Vlahakis, (Oct., 1971).

Turnbull, D., "Formation of Crystal Nuclei in Liquid Metals," *J. Appl. Phys.*, **21**, 1022-1028 (1950).

Vlahakis, John G., "The Anomalous Growth of Ice Crystals in Flowing NaCl Solutions," Ph.D. thesis, Syracuse Univ., New York (1972).

———., H. Chen, M. S. Suwandi, and A. J. Barduhn, "The Growth Rate of Ice Crystals . . ." Office of Saline Water Res. Dev. Prog. Rept. No. 830, Distributed by NTIS, No. PB-217615 (1972).

Manuscript received June 4, 1973; revision received February 12 and accepted February 13, 1974.