at all axial locations. The thermal entry region is observed to extend from the tube entrance to a value of the parameter x^+ approximately equal to 0.2. Non-Newtonian effects apparently do not alter the extent of the thermal entry region.

NOTATION

a_n, b_n = Fourier coefficients
a_{nO}, a_{np}, b_{np} = expansion coefficients
$\hat{a}_{nO}, \hat{a}_{np}$ = defined as $\hat{a}_{nO} = 4a_{nO}$, $\hat{a}_{np} = 4p/b\ a_{np}$
b = heat flux parameter for the special example
h = heat transfer coefficient
n = exponent in the power law model
$Nu(x^+, \phi)$ = local Nusselt number
p = integer parameter in Equation (14)
Pr = Prandtl number
$q(\phi)$ = arbitrary variation of circumferential wall heat flux
$\bar{q}$ = defined by Equation (6d)
r = radial coordinate from the center of pipe
r^+ = dimensionless radial coordinate, r/r_O
r_O = pipe radius
Re = Reynolds number
$R_{np}(r^+)$ = eigenfunctions of the characteristic Equation (14)
s = exponents in the power law model
$t(x, r, \phi)$ = local fluid temperature
$u(r)$ = local fluid velocity
v = average fluid velocity
x = axial coordinate from the inlet point
x^+ = dimensionless axial position,

$$\frac{2s}{s+2}\ \frac{x/r_O}{RePr} \quad \text{or} \quad \frac{2v}{u_{\max}}\ \frac{x/r_O}{RePr}$$

Greek Letters

α = thermal diffusivity
θ = local dimensionless fluid temperature
θ^+ = dimensionless entrance region temperature
$\hat{\theta}_{fd}$ = defined by Equation (16)
λ_{np} = eigenvalues of characteristic Equation (14)
ϕ = angular coordinate, deg.
ω = weighting function

Subscripts

av = average value
fd = far away from the entrance
m = evaluated at the mixed mean state
max = maximum value
w = evaluated at wall condition
ϵ = evaluated at the tube entrance

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Growth Rate of an Ice Crystal in Subcooled Pure Water

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New and extensive experimental data on the rate of growth of ice crystals in the *a* axis direction in quiescent and slow flowing subcooled pure water show conclusively that thermal natural convection is an important heat transfer mechanism controlling the growth rate. At zero and low forced velocities, steady growth is observed only when the crystals grow horizontally or upward. Steady downward growth does not occur in quiescent water. This is consistent with the physical properties of water and the phenomenon of thermal natural convection.

Growth rates at high water flow rates vary as the square root of the forced velocity and the 3/2 power of the subcooling and follow the theory of Fernandez and Barduhn (1967) with the ice-water interfacial energy set at 52 mJ/m² (52 erg/cm²).

SCOPE

A new experimental apparatus has been built to measure the growth rate of ice crystals in quiescent and flowing subcooled water. Forced velocities range from 7×10^{-5} to 70 cm/s (six orders of magnitude), and growth in quiescent water is also measured. The crystallographic growth direction is in that of the *a* axis. No growth in

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the c axis direction nor any growth in salt solution were measured.

To test the premise that natural convection affects growth rates, forced velocities were reduced to very small values, and the direction of growth was varied from horizontal to vertically upward and downward. Six fixed subcoolings were used, ranging from 0.1° to 1.0°K. The extensive data were taken to find the lower limits to the applicability of boundary-layer theory in forced convection; to note the effects of growth direction with respect to gravity, especially at low forced velocities; to observe the growth rates in quiescent water; and to investigate any possible kinetic effects at high flow rates.

These data were taken to improve the models used to describe ice crystal growth. Present models for growth in quiescent water presume heat transfer only by conduction, and this is inadequate.

In forced convection experiments, Vlahakis and Barduhn (1974) attempted to find the lower limit of applicability of the theory of Fernandez and Barduhn (1967) but were unable to do so because of limitations of the apparatus. The new experimental apparatus had no such deficiencies.

CONCLUSIONS AND SIGNIFICANCE

We show experimentally that when measuring ice crystal growth rates in pure water at low flow velocities, the growth direction with respect to gravity strongly affects the results. Growth vertically upward and horizontally shows about the same rates, but upward growth is a little faster. Downward growth does not occur at steady state in quiescent water, and this is explained nicely by presuming natural convection to control the heat transfer from the growing crystal tip. It is recommended that for consistency, future measurements at low or zero forced velocities be made in the upward direction, since not only is there no time dependency on the results, but also since the effects of the size of the confining space are probably least in this direction. Measurements made in quiescent water give the same rates as those obtained by extrapolating growth rates in forced convection to zero flow.

The measurements show that at high forced velocities, boundary-layer heat transfer controls the growth, and no kinetic effects exist up to forced velocities as high as 68 cm/s. To be consistent with the data, a first-order kinetic growth constant must have a value of at least 17 cm/(s °K). The theory of Fernandez and Barduhn fits the data well at the high flow rates if the interfacial tension between ice and water is set at the reasonable value of 52 mJ/m^2, but the same theory predicts tip radii of curvature which are about four times lower than those measured. However, the prediction that tip radii are inversely proportional to the subcooling is again verified as is the prediction that growth rates vary as the 3/2 power of the subcooling. Meausrements of tip radii of curvature show that not only are these radii inversely proportional to the subcooling, but they are also independent of the forced velocity and the growth direction. This gives support to the maximum growth rate principle used in the Fernandez theory.

Models of ice crystals growing from the pure melt must take natural convection into account, but most authors of the extensive literature on this subject seem unaware of this. The problem of describing such growth mathematically is being pursued, but it is difficult even with no forced flow because of the combination of the parabolic cylindrical geometry, gravity effects, and the moving boundary.

A recent paper by Vlahakis and Barduhn (1974) reported growth rates of single ice crystals with the subcooled water flowing horizontally toward the nose of the crystal at forced velocities ranging from 0.04 to 1 cm/s and on growth in sodium chloride solutions at slightly higher forced velocities with the salt concentration varying 0.15 to 6.0 wt%. It was one of the purposes of that study to find the lower limit to the forced velocity V below which the equation of Fernandez and Barduhn (1967) was no longer valid. This equation for growth in pure water is

$$v = a\, V^{1/2} \Delta T^{3/2} \tag{1}$$

where

$$a = \frac{2kA}{(27\gamma T_M \rho_i L \nu)^{1/2}} \tag{2}$$

and $A(Pr) = 1.485$ for water at 0°C.

The derivation is given in detail by Fernandez (1967).

The equation describes experimental growth rates very well at a wide range of forced velocities, but there must be a lower limit to this velocity for Equation (1) to be valid, since growth rates (v) in quiescent water ($V = 0$) are not zero. Such a limit was not found by Vlahakis. This research was undertaken to find that limit and to contribute to the solution of several other problems raised by Vlahakis and Barduhn. They speculated on the role of heat conduction in the ice, on the applicability of boundary-layer theory to these very low Reynolds number flows (10^{-4} to 10^{-2}), and on the role of natural convection in the transfer of heat.

In this research, we establish the lower limits of applicability of Equation (1), and we establish rather conclusively that natural convection plays an important role in the growth rates at low and zero forced fluid velocities. To do this, we have completely rebuilt the previously used ice growth cell and temperature control system so that reliable measurements can now be made in quiescent water ($V = 0$) and with very low forced velocities. The direction of the growth is always opposite to that of the forced flow except, of course, in quiescent water. The new apparatus also allows the growth directions to be vertically up or down, or horizontal to gauge natural convection effects. The directions refer to gravity and not to the crystal axes; all growth measurements are made in the a axis direction.

No work is reported on ice growth in salt water nor for growth in the c axis crystallographic direction.

PREVIOUS WORK

An extensive literature survey of what is known about ice growth in water either confined in capillary tubes or allowed to grow freely has been made by Kallungal (1975). Interpreting growth rates in capillaries is a difficult and unrewarding task, since the rates are as much dependent on the properties and physical dimensions of the capillary tube as on the characteristics of ice and water. It is much better to make such measurements with unconfined crystals under well-defined conditions, where the water velocity is an independent variable, or where natural convection can freely exert itself.

Free growth of ice crystals in quiescent water has been studied by Bolling and Tiller (1961), Hallet (1964), Farrar and Hamilton (1965), Lindenmeyer and Chalmers (1966), Pruppacher (1967), Macklin and Ryan (1968), Ryan (1969), Huige and Thijssen (1969), and Simpson et al. (1974). A review of these works shows that no two investigations agree on the growth rates, and they differ by as much as one order of magnitude for the same degree of subcooling in the range 0.1° to 1.0°K.

On the other hand, ice crystal growth in forced convection experiments studied by Bibikov (1954), Farrar and Hamilton (1965), Fernandez and Barduhn (1967), Poisot (1968), Huige and Thijssen (1969), Vlahakis (1972), and Simpson et al. (1974), are in somewhat better agreement. Growth rate data reported by Poisot and by Simpson et al. for flow velocities greater than 1.0 cm/s are in excellent agreement. The growth rate data of Fernandez and of Farrar and Hamilton are roughly 20% higher than the corresponding data of Poisot or Simpson et al., and it is now believed that in both the former studies, improper values for the flow velocities were used to interpret the results. Farrar and Hamilton and Huige and Thijssen concluded from their experimental results that for flow velocities greater than 10 cm/s, kinetic effects became important and started to affect the growth rate. Fernandez, Poisot, Vlahakis, and Simpson et al. all agree that in the entire range of forced velocities and subcoolings they investigated, the ice crystal growth rate varies as the 1/2 power of the flow velocity and the 3/2 power of the subcooling. However, Fernandez, Poisot, and Vlahakis investigated flow velocities from 0.042 to 46 cm/s in three different ranges with only a little overlapping, and it now appears that this method of study obscured some important conclusions about ice growth. In the present study, we measure growth rates at several fixed values of subcooling and with forced velocities ranging higher and much lower than all other previous studies, all with one apparatus and one observer.

ICE GROWTH MODELS IN FLOWING PURE WATER

Fernandez and Barduhn (1967) were the first investigators to propose a reasonable mathematical model that described the growth rate of single ice crystals parallel to the basal plane as a function of subcooling and flow velocity. They derived the growth model assuming that an ice crystal grown from pure water may be approximated by a parabolic cylinder (visual and photographic observations show this to be reasonable), forced flow is impressed perpendicular to the stagnation line and parallel to the axis of the parabola, the crystal is isothermal with temperature prescribed by the tip temperature; hence no heat conduction occurs in the ice, and the latent heat released by the growth is transferred to the flowing water by convection. The heat transfer rate to the stagnation line of the parabolic platelet is calculated using boundary-layer theory. It is to be noted that at the stagnation line, the boundary-layer solution is also the exact solution of the full Navier-Stokes equations (Meksyn, 1961). Any kinetic resistance measured by a temperature difference δT is assumed to be negligible, and this was confirmed previously by Fernandez and later in this work. Since the growth velocity v is found experimentally to be a function of only two independent variables, flow velocity V and subcooling ΔT, the third variable, tip radius R, was presumed to be a function of the first two, and the maximum growth rate principle was invoked to eliminate R and yield the final Equations (1) and (2).

Simpson et al. (1975) have developed two new theories for the growth of ice crystals parallel to the a axis in flowing subcooled water. The first one, an ice conduction model, assumes that the heat generated at the growth front is conducted through the ice away from the tip, since the thermal conductivity of ice is four times that of water. This heat is then presumed to be removed by forced convection from the relatively large flat faces of the crystal. None of the heat is assumed to leave the crystal tip into the flowing water. This model yields

$$v = \frac{2kA'}{(27\gamma T_M \rho_i L \nu)^{1/2}} V^{1/2} \Delta T^{3/2} \tag{3}$$

where $A' = 0.467\, Pr^{1/3} = 1.109$ for water at 0°C.

Note that this ice conduction model requires the tip of the ice crystal to be the warmest point and everywhere else in the solid to be colder. But from thermodynamics we know that the interface equilibrium temperature is a function of the radius of curvature and is given by the Gibbs relation:

$$T_M - T_i = \frac{\gamma T_M}{\rho_i L R(x)} \tag{4}$$

Hence, the tip must be the coldest spot on the crystal, since the tip radius $R(x)$ is smallest there (on the order of 1 μ). It cannot be said that Simpson et al. (1975) were unaware of the Gibb's relation because they have used it to determine the tip temperature; however, they have ignored the other necessary conclusions which follow from it in order to arrive at their final expression. Another factor they have not taken into account is the fact that growth is also taking place on the flat surface which releases heat of crystallization, and this heat must also be convected away at the same time. Also, some of the heat must be released into the flowing water at the stagnation line. Although this model predicts correctly the exponents on flow velocity and subcooling, it cannot be recognized as a valid model for ice crystal growth because it violates thermodynamic principles, and it is incomplete to the extent that heat liberated on the flat surface is neglected. If heat conduction in the ice be of importance, it must be accounted for by having the heat flow toward the tip and not away from it.

The other model Simpson et al. (1975) proposed is based on creeping flow around a parabolic cylinder. The Stokes type of solution near the nose of a parabola with a constant determined numerically by Davis (1972) was used to evaluate the velocity components in the two-dimensional heat balance equation, and the heat equation was then solved with the reasonable assumption that conduction along the stream lines is much less than conduction across them. This last assumption reduces the analysis to essentially the same equations as the boundary-layer equations. After the maximum growth rate principle was invoked, the growth velocity was found to be

$$v = \frac{2kA''}{(27\gamma T_M \rho_i L \nu)^{1/2}} V^{1/2} \Delta T^{3/2} \tag{5}$$

where $A'' = 1.188$ for water at 0°C.

It is quite remarkable that these latter two models yielding Equations (3) and (5) are of exactly the same form as that outlined by Fernandez and Barduhn using the boundary layer model Equation (1), except for a constant. Any one of the three models may be used to fit experimental data very well, provided that the value of the ice-water interfacial energy γ is adjusted to fit them. The ice conduction model yields the smallest value for $\gamma \cong 29$ mJ/m^2; creeping flow yields $\gamma \cong 33$, and boundary-layer theory yields the largest value, $\gamma \cong 52$ mJ/m^2 (see below). One must reject the ice conduction model on rational grounds, but the other two are both reasonable and yield credible values for γ. Both models predict the growth rate in quiescent water to be zero, which is untrue, obviously. Both models predict the tip radius of curvature to be $R = 3\beta/\Delta T$, and this has been shown to be questionable by Vlahakis (1974), whose radius measurement data are substantiated below. One must be very careful about accepting models simply because they fit experimental data well. The zero flow discrepancy leads us to believe that some mechanisms other than forced convection play an important part in controlling the ice growth in slow flowing subcooled water, and the tip radius problem makes one wonder about the adequacy of the models even at high forced velocities.

FREE DENDRITIC CRYSTAL GROWTH IN QUIESCENT MELT

All of the analyses for free dendritic growth found in the literature assume stationary fluid with heat transport by pure conduction. The differences among them arise from different geometries or different boundary conditions. Some account for heat conduction in the ice, and some assume an isothermal solid. Some account for curvature effects and some for kinetic effects (particle integration into the ice lattice).

Ivantsov (1947, 1959, 1962) and Horvay and Cahn (1961) solved the equations representing the freezing boundary condition for an isothermal crystal subjected to the heat conduction equation and concluded that when a crystal has the geometry of a paraboloid of revolution, a parabolic cylinder, or an elliptical paraboloid, the growth rate is time independent, and that v is proportional to $(T_M - T_i)^n/R$, with $n = 1.2$ to 2.0 as the geometry changes from a paraboloid of revolution to a parabolic cylinder. Temkin (1960), Kotler and Tarshis (1968, 1969), Trivedi (1969, 1970), and Holzmann (1970*a*, *b*) noticed that the growth rate for an isothermal crystal was not unique at a specific subcooling and introduced Gibb's relations, which included the curvature and kinetic effect, to analyze a nonisothermal crystal with the geometry of either a paraboloid of revolution or parabolic cylinder. Holzmann (1970), Hillig (1968), and Kotler and Tiller (1968) noticed that the steady growth of a nonisothermal, shape preserving crystal with the geometry of a parabolic platelet or paraboloid of revolution may not be possible owing to the violation of heat balance and considered this as the fundamental origin of dendritic branching. Bolling and Tiller (1961) modified the original isothermal analysis by assuming the entire crystal to be at the tip temperature which has been depressed from T_M by both capillary and kinetic effects, and made the determination of a unique growth rate at a fixed subcooling possible by introducing the maximum growth rate principle. This approach was adopted by Glicksman and Schaefer (1968) in analyzing their data.

Among these researchers, Kotler and Tarshis (1968, 1969) and Holzmann (1970) have compared their experimental data for *a* axis growth of ice crystals, with the analysis using a paraboloid of revolution with $\gamma = 20$ mJ/m^2, and claimed good agreement between theory and experiment. However, from experimental observation for subcoolings of 0.1° to 1.0°K, an ice crystal actually looks like an elliptic paraboloid with a very large aspect ratio or, only slightly less accurately, like a parabolic cylinder. Hence, claiming that there is good agreement between theory and experiment, when the ice crystal is approximated by a paraboloid of revolution, is unjustified, since the geometry of a crystal has a substantial influence on the heat transfer rate to it. See the very interesting analysis of this by Turian in Barduhn, Turian, et al. (1973, pages 16 to 20). Also, it should be pointed out that we have never observed in this laboratory an ice crystal growing in needle form (paraboloid of revolution) from water.

Numerical values of the growth rate of single ice crystals in quiescent water can be predicted using the various models discussed above. This has been done by Kallungal (1975), and his results can be summarized briefly by stating that both isothermal and nonisothermal models predict that the growth rate decreases as the geometry changes from a paraboloid of revolution to parabolic cylinder. The exponents on subcooling vary from 2 to 4, and the growth rates predicted at a given ΔT vary by about five orders of magnitude. It is almost a ridiculous state of affairs and makes one think that some very fundamental ideas on ice growth are completely escaping our attention and have never really been considered properly.

EXPERIMENTAL APPARATUS

The experimental apparatus for studying single ice crystal growth designed by Poisot and further modified by Vlahakis could not be used for investigating flow velocities less than 0.04 cm/s.

In order to study ice crystal growth in water velocities ranging from zero to 70 cm/s, it was necessary to design and construct a completely new experimental apparatus.

The new apparatus consists of two distilled water reservoirs, a glass tube heat exchanger, crystal growth cells, a nucleating device, a traveling microscope, a temperature measuring and recording device, and flow meters. A schematic diagram of the apparatus is shown in Figure 1.

One of the distilled water reservoirs is a well-insulated 0.056m^3 (15 gal) polyethylene tank inside of which distilled water is subcooled to less than 1°K of the desired temperature by circulating glycol solution through two coils of 13 mm (1/2 in.) tygon tube, each 7.6 m (25 ft) long. The other reservoir contains distilled water at room temperature and supplies flush solution to melt ice crystals after completion of a set of growth rate measurements.

The fifteen-tube, two-pass heat exchanger (0.3 m^2 or 3 ft^2) and the growth cell are immersed in a glycol bath and can bring the temperature of the pure water feed to within 0.01°K of the bath temperature. With this setup, it is now possible to set ΔT and V independently of each other. The horizontal crystal growth cell is either a 25.4 or 9.5 mm precision bore 76 cm long Pyrex glass tube. The larger tube is used when studying water velocities lower than 1.0 cm/s. The overlap in flow velocities studied in the two tubes allowed us to determine that the effects of tube diameter on the growth rate was nonexistent in forced flow experiments.

A 100X traveling microscope is used to observe the growth of ice crystals. A distance of 1μ can be read directly. Time elapsed is measured to 0.1 s with stopwatches. Temperature measurement of the subcooled water in the observation cell is

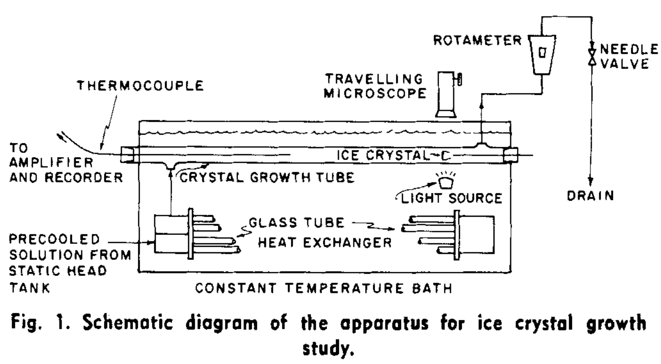

Fig. 1. Schematic diagram of the apparatus for ice crystal growth study.

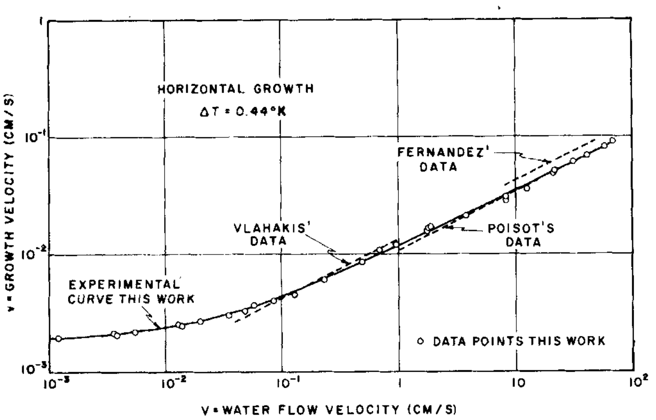

Fig. 2. Ice crystal growth rate vs. water flow velocity at a subcooling of 0.44°K.

made using a copper-constantan thermocouple in a 1.6 mm O.D. sheath and placed axially in the precision bore glass tube. The reference junction is placed in an ice bath. The voltage is amplified in a Leeds & Northrup 2920 linear amplifier and recorded on a Speedomax recorder XL-600 series. The amplifier has a maximum sensitivity corresponding to 0.0025°K and an accuracy of 0.004°K in the range of interest to us.

The measuring thermocouple tip is placed at a predetermined distance upstream from the tip of the ice crystal. The distance for an entering uniform velocity profile to develop to the point where the center line velocity is 98% of that with a fully developed parabolic profile (Langhaar 1942) was taken as the minimum distance between crystal and thermocouple tip. We report the value of flow velocity as twice the bulk velocity. A small correction for velocity development was made only at forced velocities in excess of 60 cm/s, where a 98% development could not quite be obtained.

At low flow velocities, the rate is continuously checked by weighing the discharged water over a time interval during the growth study. High flow rates are monitored with rotameters of suitable ranges. All flows are caused by gravitational head alone.

The changing of flow and growth directions from horizontal to vertical with water flowing in the direction opposite to growth was accomplished easily. It was also possible to obtain reliable horizontal growth rate data for flow velocities ranging from 0 to 68 cm/s and subcooling from 0.1° to 1.0°K. The lowest forced velocity other than 0 was 7×10^{-5} cm/s.

Growing ice crystals in the vertical direction was done for the purpose of determining the effect of natural convection on

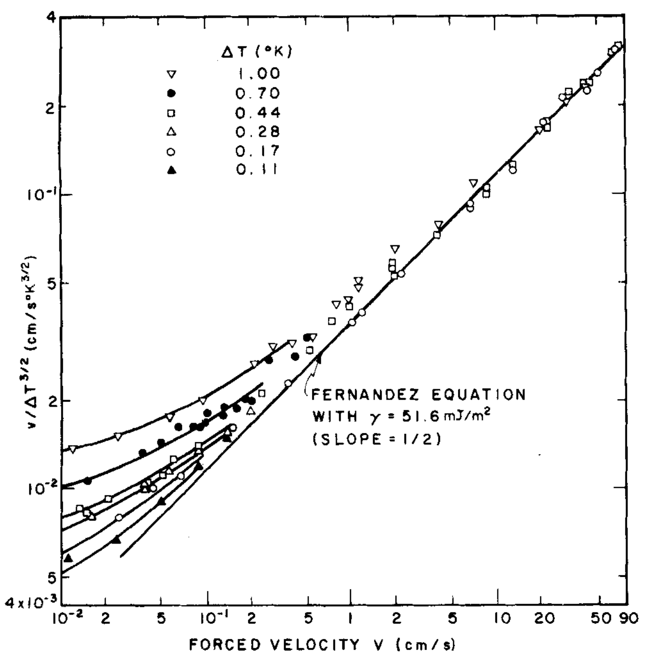

Fig. 3. Horizontal growth rates of ice crystals in distilled water (v) vs. forced flow (V).

the growth rates in slow flowing water. With the assumption that the influence of natural convection would be negligible for forced flow velocities greater than 1.0 cm/s, observation cells with proper length to use the existing horizontal experimental setup with a few minor modifications can be constructed. A cell 30 cm long is enough for 97% development of the final parabolic velocity profile at a center line velocity of 2.5 cm/s. The measuring techniques and experimental procedures for vertical flow are the same as those for the horizontal growth experiments. Detailed descriptions of equipment and experimental procedures may be found in Kallungal (1975).

EXPERIMENTAL RESULTS

When we investigate the growth rate of ice crystals in subcooled flowing water, three experimental variables, namely, temperature, water velocity, and growth orientation, need be controlled. Growth rate data were obtained by varying the forced flow velocity and by keeping the subcooling at a predetermined constant value rather than by varying the temperature at a fixed flow rate. In the study of horizontal growth, six subcoolings were employed: 0.11°, 0.17°, 0.28°, 0.44°, 0.70°, and 1.00°K. For each of these subcoolings, the flow velocity was varied from 0 to 1.0 cm/s and covered at least four orders of magnitude below 1 cm/s. For two of these subcoolings, namely, 0.17° and 0.44°K, flow velocity was varied from 0 up to 68 cm/s. For a subcooling of 1.0°K, flow velocity ranged from 0 to 40 cm/s. The fluid flow over the crystal was always in the laminar region. In the studies of crystals growing vertically up or down, a subcooling of 0.44°K was used.

Figures which are representative of all the experimental results are presented here. Complete tabulated and plotted data can be found in Kallungal's thesis.

HORIZONTAL GROWTH

An example of growth rate data over a wide range of forced velocities and with a fixed $\Delta T = 0.44$°K is shown on logarithmic scales in Figure 2. Fernandez' theory predicts the dashed lines with slope = ½, and the location depends on the value of the ice-water interfacial tension (γ) assumed. Fernandez' and Vlahakis' data are represented with $\gamma = 32$ mJ/m^2 and Poisot's data with $\gamma \approx 50$ mJ/m^2. Note that the growth rates are predicted to vary only as $\gamma^{-1/2}$.

Figure 3 presents $v/\Delta T^{3/2}$ vs. V for six different ΔT's and for forced velocities greater than 10^{-2} cm/s. The single straight line represents the theory with $\gamma = 52$ mJ/m^2, and it is clear that all the data converge to this line at the higher forced velocities.

It is also clear from Figure 3 that the lower velocity limits of applicability of the theory have been found. The lowest flow velocity at which the experimental curve deviates from Fernandez' theory ($\gamma = 52$ mJ/m^2) is a function of subcooling. We arbitrarily define the point of deviation from Fernandez' theory as that point on the experimental curve which has a 3% higher growth rate than the corresponding value predicted from the theory. We further note that the higher the subcooling, the higher is the value of the velocity at which deviation occurs, and it happens, as shown in Table 1, that at this point of deviation, $V/\Delta T$ is practically a constant.

In light of the maximum growth rate principle which predicts the tip radius to be inversely proportional to ΔT ($R = 3\beta/\Delta T$), the deviations in Table 1 must occur at a fixed Reynolds number at the tip given by

$$Re = RV/\nu = 3\beta V/(\nu\,\Delta T) \qquad (6)$$

The actual value of the Reynolds number given by Equation (6) may be in question because β depends on γ,

TABLE 1. LOWEST FLOW VELOCITY FOR FERNANDEZ' THEORY TO HOLD

(with $\gamma = 52$ mJ/m²)

Subcooling ΔT (°K)	V_{min}(cm/s)	$V_{min}/\Delta T$(cm/s °K)
0.17	1.0	5.9
0.44	2.6	5.9
1.00	6.0	6.0

TABLE 2. HIGHEST FLOW VELOCITY FOR GROWTH RATE TO BE INDEPENDENT OF FLOW VELOCITY

Subcooling ΔT (°K)	$(V_{max}) \times 10^4$ (cm/s)	$(V_{max}/\Delta T) \times 10^3$ (cm/s °K)
0.11	6.0	5.5
0.17	9.0	5.3
0.28	15	5.4
0.44	25	5.7
0.70	40	5.7
1.00	55	5.5

and the tip radius measured in this work does not agree with our estimate of $\gamma = 52$ mJ/m².

Eliminating $V/\Delta T$ from Equation (6) by use of the average value in Table 1, and using the properties of ice and water with a value of $\gamma = 52$ mJ/m², one may determine a minimum value for the tip Reynolds number for Fernandez' theory to hold, which is

$$Re_{min} = 5 \times 10^{-3} \quad (7)$$

For flow velocities from 0 to 10^{-2} cm/s, the growth rate is plotted vs. forced velocity at fixed subcoolings in Figure 4. The prediction from Fernandez' theory deviates considerably from the observed experimental values, and this deviation becomes larger as the flow velocity is decreased. At these low forced velocities, Fernandez' theory predicts growth rates lower than those observed experimentally.

From Figure 4 it is also clear that the growth rate is independent of the forced velocity when this velocity is adequately low. We define the point at which the growth rate first begins to depend on the flow velocity as that point on the experimental curve which has a 3% higher growth rate than the quiescent water growth rate. It is interesting to observe once again that the higher the subcooling, the higher is the value of velocity at which the flow velocity dependence begins, and it happens, as shown in Table 2, at this point of deviation, $V/\Delta T$ is very nearly constant also.

Proceeding as before to convert the average value of $V/\Delta T$ into a tip Reynolds number with $\gamma = 52$ mJ/m², one arrives at

$$Re_{max} = 4 \times 10^{-6} \quad (8)$$

Between these two values of the Reynolds number as given by Equations (7) and (8), the ice growth rate is not independent of forced velocity, but neither does it fit Fernandez' equation.

Earlier work done by Vlahakis showed that growth rates of ice crystals could be predicted from Fernandez' theory provided a value of $\gamma = 33$ mJ/m² was used in Equations (1) and (2). At first this seems to be a contradiction to the results obtained in this work. But a careful study of Figures 2 and 3 indicates that the velocity range Vlahakis studied, namely, $V = 0.042$ to 1.0 cm/s, happens to be in a region where the experimental curve of growth rate vs. forced flow velocity crosses the theoretical line predicted from theory with $\gamma = 33$ mJ/m². Hence, in this region one could force fit (innocently) the experimental data to Fernandez' equation and obtain a value of γ in the neighborhood of 33 mJ/m². Kallungal (1975) shows that the reason for this inadvertent fitting was that Vlahakis happened to use high ΔT's with high forced velocities and low ΔT's with low forced velocities in this transitional region, and this tended to distort the true picture and make it very natural to observe an apparent agreement with Fernandez.

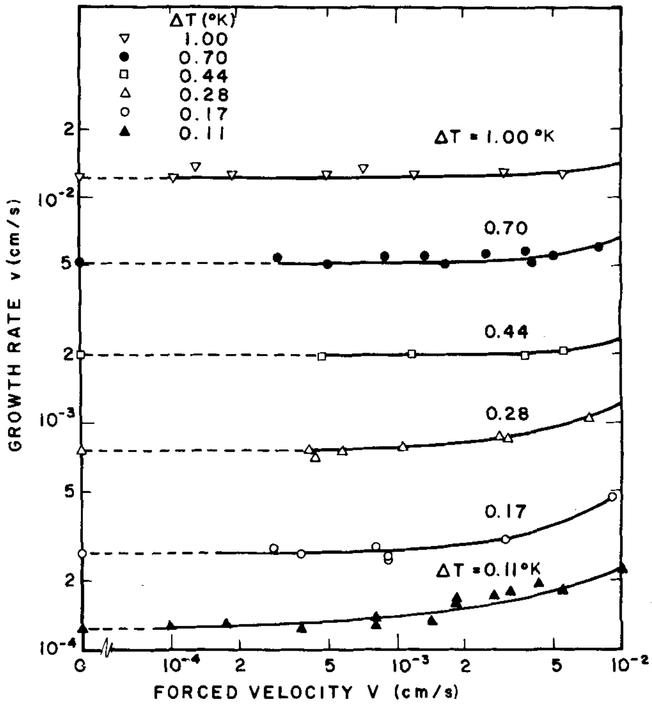

Fig. 4. Horizontal growth rates of ice crystals in quiescent and slow flowing distilled water.

Actually, the data of Vlahakis (but not his interpretation of them) agree both with those of Poisot and with this work. Only the data of Fernandez are now considered to be inaccurate, and this is due solely to his forced velocity measurement.

VERTICAL GROWTH

Ice Growing Down—Water Flowing Up

It should be noted that in all growth rate measurements, the forced flow is always opposite in direction to the growth direction, and we will thus mention henceforth only the growth direction.

When downward growth rates were measured, it was observed that these rates were a very strong function of

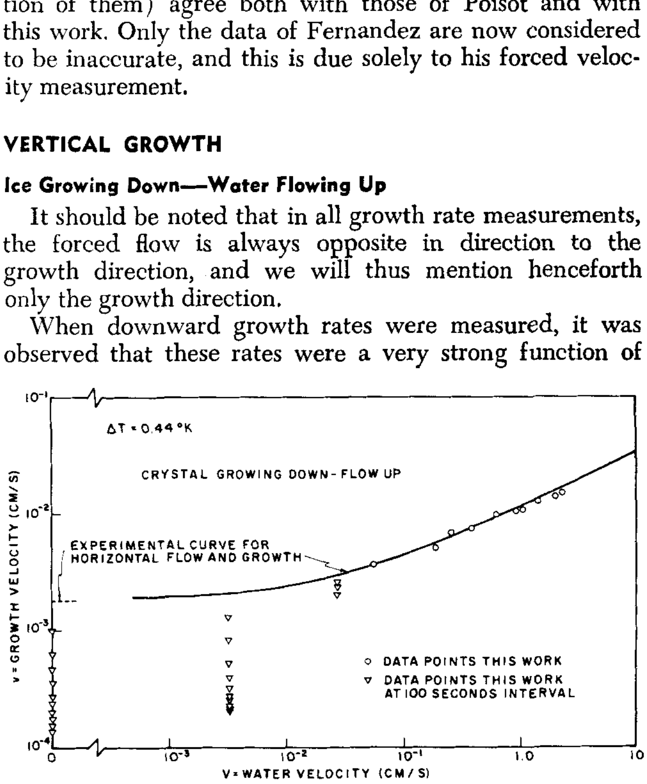

Fig. 5. Vertical downward growth rate of ice crystals vs. forced flow velocity at subcooling of 0.44°K.

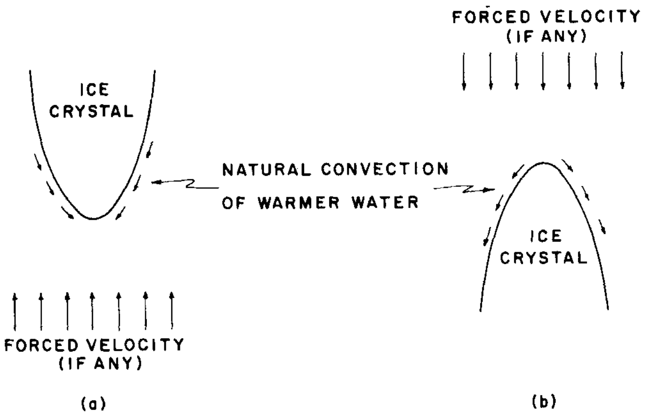

Fig. 6. Natural convection with ice crystal growing vertically. a) down b) up.

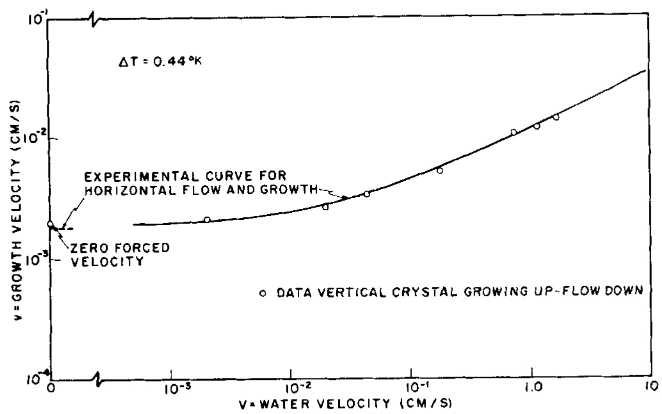

Fig. 7. Vertically upward growth rate of ice crystals vs. forced flow velocity at subcooling of 0.44°K.

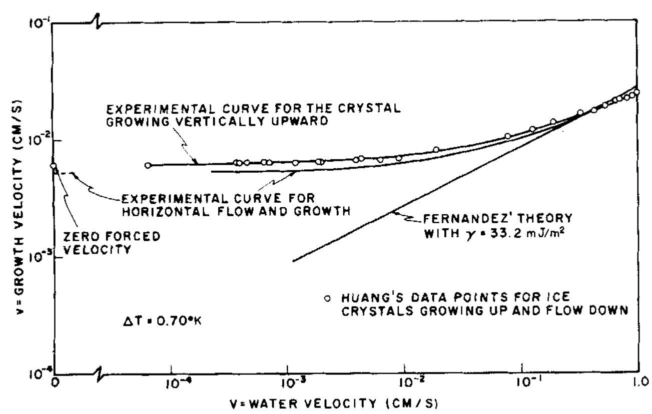

Fig. 8. Vertically upward growth rate of ice crystals vs. forced flow velocity at subcooling of 0.70°K.

time for water velocities less than 6×10^{-2} cm/s at a subcooling of 0.44°K (see Figure 5). There was no steady state. This phenomenon may be explained by considering the natural convection caused by density change with temperature. We know that for temperatures in the range of $-1.0°$ to 0°C, the density of water increases with increasing temperature. Hence, as the ice crystal grows, the liberated heat of solidification warms the water in contact with the crystal, and the warm water, being denser than the water surrounding it, will flow downward in a natural convection flow. Since the crystal itself is growing down, it will continue to see warmer and warmer water as it grows into this region. Hence, the growth rate will continuously decrease with time unless there is a forced flow which can overcome this natural convection velocity and thus provide for the liberated heat to be convected away from the growing crystal tip rather than toward it. When this phenomenon occurs, we may expect the effect to be most pronounced in quiescent water. The effect should decrease as the forced velocity is increased. Finally, a forced flow velocity will be reached when the natural convection velocity is completely obscured, and the growing crystal will begin to see water only at the bulk temperature, and hence grow at velocities independent of time. Figure 6*a* shows this effect pictorially.

From experimental results as seen in Figure 5, we note the value of this limiting forced flow velocity to be near 6×10^{-2} cm/s at a subcooling of 0.44°K. Above this velocity, the warmer water will be carried away by the flowing water, and the crystal grows at a steady state.

Ice Growing Upward

An investigation was also made with ice crystals growing upward. A few of the data are plotted in Figures 7 and 8. The data shown in Figure 8 were taken by Huang in this laboratory. Under this condition, no time dependence in the growth rate was observed at any flow velocities, including zero. Figure 6*b* shows the flow patterns for upward growth, where the natural convection flow is in the same direction as the forced flow (if any). Whether or not flow is forced, the warmer water is carried away from the growth direction to the back of the crystal, so that the tip experiences only fresh subcooled water at T_∞. In further support for this proposed mechanism, it was also observed that the growth rate at very low velocities was about 5 to 8% higher than the corresponding horizontal growth rates at a subcooling of 0.44°K and about 10 to 15% higher at subcooling of 0.7°K. When an ice crystal is growing upward, the natural convection velocity adds to the forced velocity. Hence, we can expect the growth rates to be slightly higher than the values observed in the horizontal growth experiments. Naturally, one would also expect this effect to be more pronounced at higher subcoolings owing to stronger convection currents that would be caused by the higher temperature gradients. At this stage we are able to comment on the effect of natural convection only in a qualitative manner, as a mathematical analysis of this phenomenon has not yet been made.

In the case of horizontal flow, the natural convection flows are perpendicular to the growth direction and to any forced flow. The crystal will thus grow into undisturbed bulk subcooled water at a steady state. The addition of the forced and natural velocities is vectorial, and the resultant will be smaller in this case, however, than for upward growth. Thus one would expect the heat transfer and growth rate to be slightly smaller for horizontal as opposed to upward growth. This is what we observe.

The natural convection velocities are very small in water near 0°C since the coefficient of expansion for water at this temperature is only -7×10^{-5} °K^{-1}, as compared to more normal liquids which have a value at least (-10) times this. Thus, these feeble natural convection currents are completely obscured by very small forced velocities.

Of the dozen or so theories of ice growth found in the literature, not one author even mentions this phenomenon as part of the mechanism affecting the growth rate of ice. Experimental evidence is necessary before a model is proposed or meaningful mathematical analysis is made.

GROWTH IN QUIESCENT WATER

Figure 4 shows that ice growth rates at very low forced velocities are independent of this velocity and equal to those observed in quiescent water. Under these conditions, the growth rate depends solely on the subcooling and the orientation. We do not consider downward growth (no

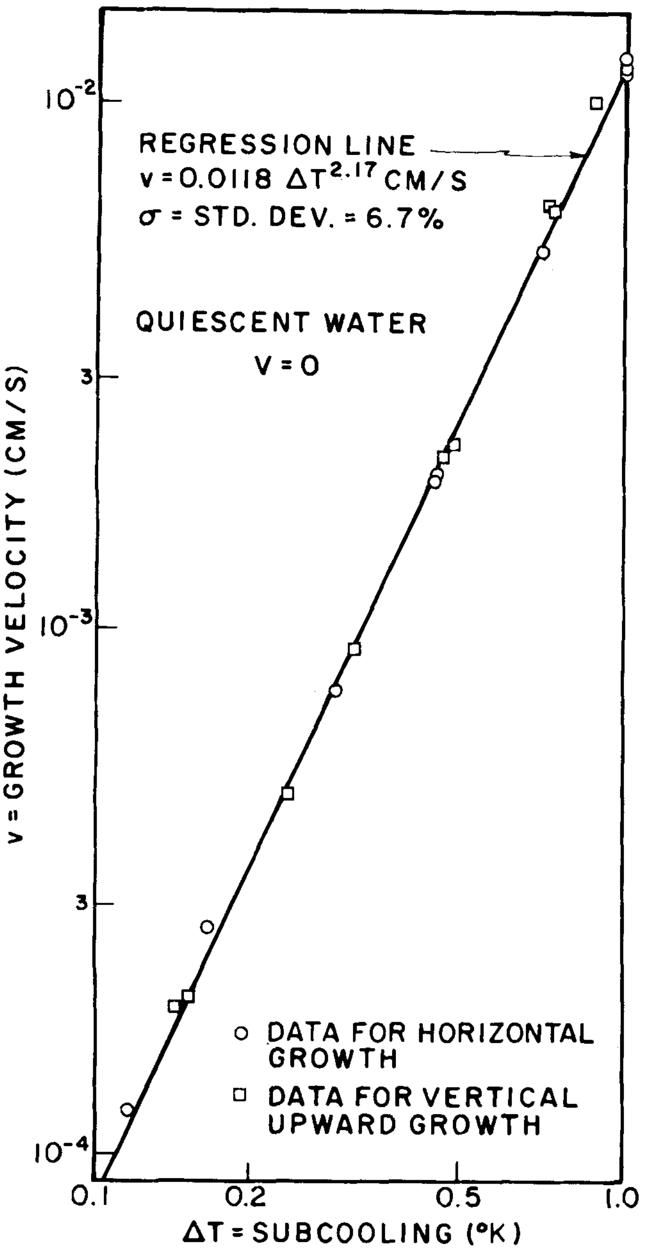

Fig. 9. Ice crystal growth rate vs. subcooling in quiescent water.

steady state) and plot the growth rates for both horizontal and upward growth vs. ΔT on log scales in Figure 9. The points fall on a straight line and fit the relation

$$v = 0.0118 \Delta T^{2.17} (\text{cm/s}) \tag{9}$$

with a standard deviation of 6.7% for eighteen points. This is an empirical equation, and we have as yet no quantitative theory to explain it. But, the observations on natural convection tell us a lot about what models to start with.

We believe these data in quiescent water to be the best available with which to test any theory for the range of ΔT's used, 0.1° to 1.0°K. Kallungal (1975) shows all the other growth rate data from the literature, and they vary by a factor of 10 for a given ΔT. Considering the fact that none of the other workers recognized the importance of the orientation of the growth direction, and further that the size of the cell in which the crystal grows will have a strong effect because of the effect on natural convection currents, it is no wonder that they disagree. We believe our data to be general because the cell was large compared to the crystal and because the growth rates were observed both by extrapolating at finite forced velocities to zero and also by observation in truly quiescent water.

Figure 10 compares growth rates in all three directions as a function of time for a ΔT of 0.44°K and in quiescent water. Only horizontal and upward growth yield steady states. The reference line with slope of $-\frac{1}{2}$ is shown because many pure conduction theories for unsteady state heat transfer show this time dependence. It is obvious that pure conduction theories are not applicable.

TIP RADIUS OF CURVATURE OF ICE CRYSTALS

Photographs of growing ice crystals were made with their basal plane on edge so that the parabolic shape could be observed and the tip radii (R) measured. These radii are on the order of 1 μ, and blown up views of the pictures were necessary. Samples are shown in Kallungal's thesis (1975). These radius measurements agree well with those of Vlahakis and show the radius to be inversely proportional to the applied ΔT as Fernandez' theory requires. It was also shown by Kallungal that the radius is independent of the forced velocity and of the growth direction.

The proportionality constant between R and ΔT^{-1} does not agree with the theory, however. Using $\gamma = 52$ mJ/m^2, Kallungal gives radii about four times those predicted. At this point we are not certain whether it is the radius measurements or the theory which are at fault.

ICE-WATER INTERFACIAL TENSION

From the best fit to Fernandez' equation using all the data where the tip Reynolds number was greater than 5×10^{-3}, one may find the best value of a in Equation (1). Forced velocities used ranged from about 1 cm/s up to the highest value of 68 cm/s, and there were twenty-nine data points conforming to the requirements. The least-square value of a is determined to be 0.0365 ± 0.0016 cm$^{1/2}$ s$^{-1/2}$ °K$^{-3/2}$, and thus

$$v = 0.0365\, V^{1/2} \Delta T^{3/2} \tag{10}$$

with a standard deviation of 4.4%.

From Equation (10), one evaluates the implied value

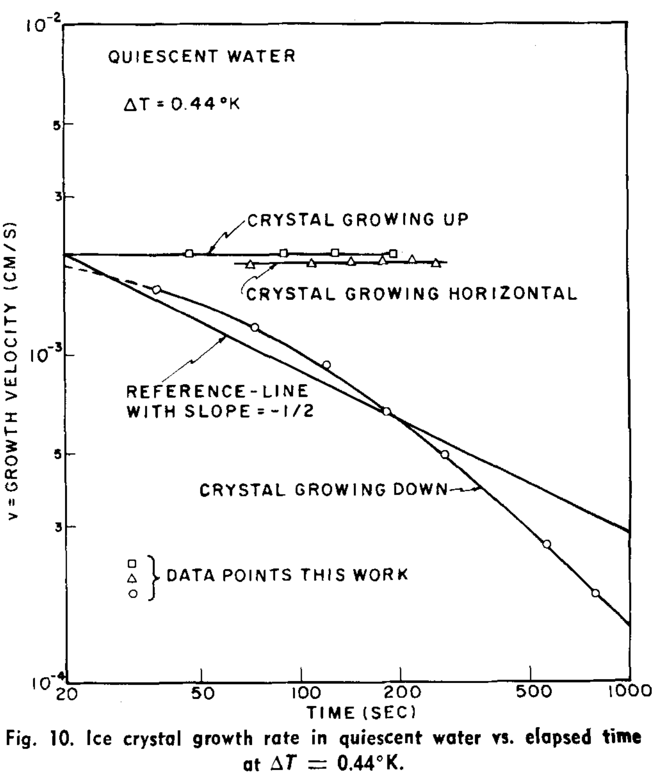

Fig. 10. Ice crystal growth rate in quiescent water vs. elapsed time at $\Delta T = 0.44$°K.

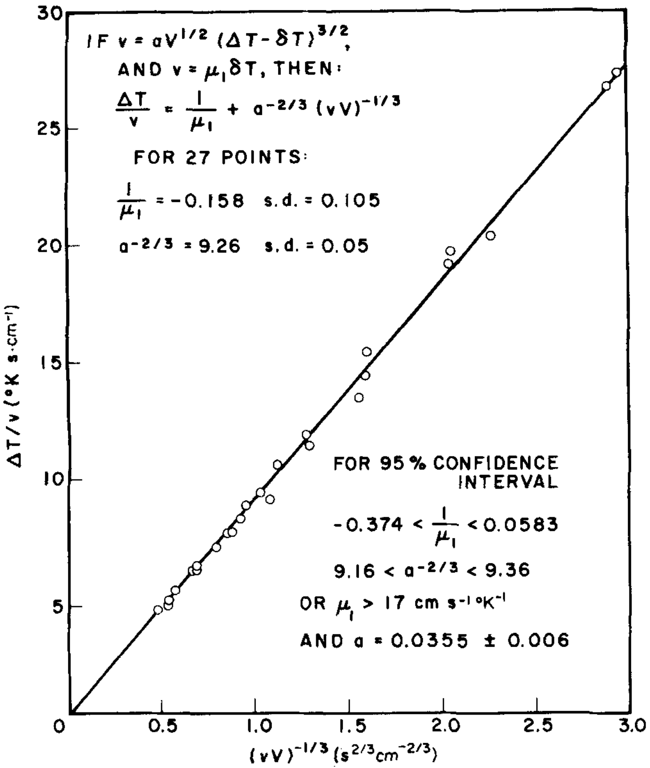

Fig. 11. Determination of kinetic effect on ice growth in *a* axis direction.

of γ, the ice-water interfacial tension, to be

$$\gamma = 52 \pm 4 \text{ mJ/m}^2 \tag{11}$$

This value of γ is the value required to fit Fernandez' equation using the data of Kallungal. The data of Poisot give the same value within experimental error, and the data of Vlahakis do not disagree with it, although he interpreted his data differently from the present analysis.

It is necessary to refer to the conclusions from tip radius measurements above, however, since these indicate that there may be some deficiency in the theory, and the calculated value of γ from growth rate measurements has some uncertainty attached to it. Since Fernandez' theory predicts that

$$R = 3\beta/\Delta T = 3\gamma T_M/(\rho_i L \Delta T)$$

a value of γ may also be predicted from the tip radius measurements, and this yields $\gamma = 170$ mJ/m^2, which is improbably high. Some experimental measurements of this quantity, made by entirely different methods, agree with our new value from Equation (11), however. Both Jones (1973) and Skapski et al. (1957) report $\gamma = 44 \pm 10$ mJ/m^2, for example. Jones measured angles at grain boundaries in ice, and Skapski used a capillary cone method.

ESTIMATION OF KINETIC CONSTANT FOR THE *a* AXIS GROWTH

Our experimental results show that all the data at high flow velocities lie on the line predicted from Fernandez' theory with $\gamma = 52$ mJ/m^2 and with the a axis kinetics negligible. This would mean that we cannot calculate a value of the kinetic constant from the experimental data. However, one can make an estimate of the minimum possible value for the kinetic constant.

If we assume that any kinetic resistance creates a temperature difference δT between the ice and the water at the interface, then this difference must be subtracted from the overall driving force ΔT. Thus

$$v = a\, V^{1/2} (\Delta T - \delta T)^{3/2} \tag{12}$$

If we let μ_1 be the first-order rate constant for the kinetic step, then

$$v = \mu_1\, \delta T \tag{13}$$

Combining Equations (12) and (13) and rearranging so as to get a form for a linear plot to find μ_1, one arrives at

$$\Delta T/v = 1/\mu_1 + a^{-2/3}\,(vV)^{-1/3} \tag{14}$$

A plot of $\Delta T/v$ vs. $(vV)^{-1/3}$ is shown in Figure 11, and the data fall on a plausible straight line going nearly through the origin. The actual intercept by a least-square analysis is

$$1/\mu_1 = -0.158 \pm 0.105°\text{K s/cm} \tag{15}$$

where the 0.105 is the standard deviation. The small negative values of μ_1 are, of course, impossible, but by extending the uncertainty to a 95% confidence interval, it is found that $1/\mu_1$ must be less than $+0.0583$. Thus

$$\mu_1 > 17 \text{ cm/(s °K)}$$

This sets only a probable lowest value on μ_1 and in no way determines its value any further.

The same analysis may be used to estimate the value of a in Equation (1), and it yields a value 3% less than the analysis (using the same data) which led to Equation (10).

ACKNOWLEDGMENT

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NOTATION

a	=	constant defined by Equation (2), (cm$^{1/2}$ s$^{-1/2}$ °K$^{-3/2}$)
A	=	function only of Prandtl number and = 1.485 for water at 0°C [see Equation (2)]
A'	=	dimensionless constant, see Equation (3)
A''	=	dimensionless constant, see Equation (5)
k	=	thermal conductivity of water (J/cm s °K)
L	=	latent heat of fusion of ice per unit mass (J/gm)
R	=	tip radius of growing crystal (cm)
Re	=	tip Reynolds number = RV/ν
T_i	=	ice-water interface temperature (°K)
T_M	=	thermodynamic melting point of ice (273.15°K)
T_∞	=	bulk water temperature far upstream from ice crystal (°K)
ΔT	=	degree of subcooling in bulk water (°K) vs. ice with large R ($= T_M - T_\infty$)
v	=	ice crystal growth rate (cm/s)
V	=	forced velocity of subcooled water (cm/s)

Greek Letters

β	=	$\gamma T_M/(\rho_i L)$ (cm °K)
γ	=	interfacial tension between water and ice (mJ/m^2 = erg/cm^2)
μ_1	=	first order kinetic constant of crystal growth (cm/s °K)
ν	=	kinematic viscosity of water (cm^2/s)
ρ_i	=	density of ice (gm/cm^3)

The units given are convenient examples only. Equations being evaluated numerically must use consistent units.

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Liquid Diffusion in Microporous Alumina Pellets

The effect of the ratio of the molecular solute diameter to the pore diameter and adsorption equilibrium on the liquid phase effective diffusivity for different hydrocarbon solutes was studied in two alumina pellets. A semiempirical correlation based on the relative dimension of the solute molecule with respect to the average pore dimension, the equilibrium partition coefficient, and the porosity is proposed for a variety of binary hydrocarbon systems. The correlation shows that the effective diffusivity is strongly influenced by both the adsorption coefficient as well as the ratio of the solute molecular size to the average pore size.

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SCOPE

The rate of microsolute diffusion in liquids within microporous material such as solid catalysts has been seen to be less than would be observed in unrestricted liquid medium. This has been variously attributed to the existence of a hydrodynamic drag. Various models, theoretical as well as empirical, have related this drag coefficient to the ratio of the relative size of the diffusing molecular to the pore size.

While the effect of the ratio of the molecule size to the pore size has been the subject of a number of studies,