$\bar{t}$ = mean residence time
$\bar{t}_c$ = mean residence time for an extruder with constant channel depth of screw and time elapsed from end of irradiation
$t_i$ = time of irradiation
$\bar{t}_t$ = mean residence time for tapered channel depth of screw
$u$ = velocity of flow
$V$ = holdup of extruder
$V_b$ = tangential velocity of barrel
$V_z$ = down-channel velocity component of barrel
$x$ = height in the nuclear reactor
$W$ = channel width, weight of irradiated sample

**Greek Letters**

$\theta$ = helix angle, normalized time
$\phi$ = pressure to drag flow ratio, neutron flux
$\eta$ = efficiency of flux, coefficient of exponent
$\epsilon$ = system phase shift
$\sigma$ = cross section of isotope to nuclear reaction, $cm^{-2}$
$\gamma$ = coefficient for decay, $0.693/t_{1/2}$

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*Manuscript received December 3, 1974; revision received October 15, and accepted October 17, 1975.*

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# Secondary Nucleation of Ice in Sugar Solutions and Fruit Juices

**From thermal response measurements, ice nucleation rates in distilled water, sugar solutions, and fruit juices were determined for a stirred, batch-seeded crystallizer. High resolution thermometry permitted use of initial subcoolings between 0.01° and 0.2°K. Nucleation increased with approximately the second power of subcooling. Applications to freeze concentration are considered.**

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## SCOPE

**The development of freeze concentration processes for food liquids has been hampered by the tendency for very fine ice crystals to form and for the separation of residual concentrate from the ice crystals to be difficult as a result. Incomplete separation of entrained concentrate from the ice results in substantial washing requirements and/or loss of valuable food product.**

**The size distribution of ice crystals formed during freeze concentration should depend upon the nature and interactions of the nucleation and crystal growth phenomena taking place in the crystallizer. Fundamental, quantitative understanding of these phenomena is then required for rational analysis, design, and improvement of freeze concentration processes.**

**In this work, the kinetics of ice nucleation were inferred from high resolution measurement of the initial thermal response of a batch crystallizer, following seeding. Quartz thermometry was used so that a range of initial subcooling from 10 to 200 mK could be covered. Studies were performed with distilled water, solutions of sucrose and fructose, apple juice, and orange juice. Interpretation was accomplished through an equation describing the initial thermal response. By comparison with experimental measurement of the initial response, the applicability of this equation could be evaluated, and the nucleation parameters could be inferred from the experimental response.**

## CONCLUSIONS AND SIGNIFICANCE

**Analysis of the properties of the experimental initial response confirmed a 2.5 power dependency of temperature rise upon time, as predicted by a model of size-inverse growth rate. This size dependency is taken as an indication that bulk heat and mass transfer limit the rate of growth.**

**The nucleation rate increased with approximately the second power of subcooling in the range 10 to 200 mK and appeared to be proportional to the number of seeds of identical shape. The seed area was found to correlate observed nucleation rates better than did other integral seed moments. Indications were found in the response that crystals must attain a certain minimum size in order to be effective in nucleation. Nucleation rates were of the same order of magnitude and of the same dependency upon subcooling for the various different media studied. In sucrose solution, the rate of nucleation appeared substantially independent of concentration. Formation of ice crystals in orange juice was examined photographically, as well as by the thermal response. The removal of some of the suspended matter in the juice increases the crystallization rate.**

**These results indicate that there are benefits in larger average ice crystal size which can be achieved by operating freeze concentration processes at very low subcoolings, in the range considered. It can be further inferred that staged water removal of column crystallizers should have merit because of the relative effects of solute concentration on nucleation and growth rates for ice crystals. Ice crystal recycle may also be beneficial.**

The removal of water from aqueous solutions is commercially important. Evaporation is commonly used for this purpose, but frequently desirable substances are also removed by evaporation. A more specific means of water removal is needed. One is conversion of the water into ice and the subsequent separation of the ice from the remaining liquid. If water is separated in this way from a brine, the process is titled freeze desalination, but as applied to food liquids it is named freeze concentration.

As a separation process, freeze concentration would appear well suited for the concentration of fruit juices and other food liquids, where the removal of volatile flavor components and loss of quality by thermal degradation are concerns during evaporation. Despite successful application with certain food liquids such as coffee, the process has not had commercial success with juices. The reasons for this are largely economic, centering on the higher operating and capital costs of this process compared to evaporation (Muller, 1967; Thijssen, 1970).

One cost-increasing difficulty in freeze concentration is the tendency to produce ice crystals of such small size as to hinder the separation of the crystals from the concentrate. Growth of larger crystals increases the ease with which the ice may be removed from the concentrate. Increasing the size also reduces the surface area per unit mass of ice, which in turn can help lower the total amount of entrained concentrate. Thus, greater applicability of freeze concentration centers in large measure on the production of larger ice crystals.

A rational approach to the design of improved freeze concentrators requires focusing on the ways to accelerate the growth rate of ice relative to the rate of new ice crystal formation. Freeze concentration is normally conducted in agitated solutions, where rates of mass and heat transfer are increased by the agitation. Current research indicates that primary homogeneous and heterogeneous nucleation mechanisms are of little importance in this case. Instead, the formation of ice in sugar solutions and other crystallizations under these circumstances is dominated by secondary nucleation, the process of creating ice nuclei from existing crystals (Lal et al., 1969; Clontz and McCabe, 1971; Cise and Randolph, 1972).

The mechanism of secondary nucleation is not firmly established. The best indication is, however, that the dominant process involves the collision of crystals with solid surfaces, including other crystals and the crystallizer (Strickland-Constable, 1972). Stirrer blades are thought to be particularly important in this process (Evans et al., 1974). As envisioned by Lal et al. (1969), the collisions result in the formation of particles in a range of sizes of the order of the critical nucleus size. Those larger than the critical size grow to become macroscopic, while those smaller dissolve. The change of the critical size approximately inversely to the subcooling is thereby believed to account for the variation of nucleation rate with subcooling.

Harriott (1967) indicated that the growth of ice crystals suitable for freeze desalination was best conducted at an initial subcooling of the order of 50 mK (1 mK = 0.001°K). In this region of subcooling and lower, Huige et al. (1973) were able to correlate the nucleation rate of ice, inferred from studies of a continuous crystallizer, with the 2.1 power of subcooling, while growth was reported to be first order in subcooling. From this it may be concluded that lower subcooling operation should yield larger average crystal size. However, Margolis et al. (1971) found for the crystallization of ice from brine that the apparent subcooling order was sensitive to the form of correlation employed.

At subcoolings above 250 mK, Omran and King (1974) reported that the nucleation rate of ice was only slightly above first order in subcooling in a seeded, batch, stirred crystallizer. In this case, nucleation and growth are decreased by nearly the same factor with lowered subcooling, and hence the average crystal size would be increased only slightly with decreased subcooling. This marginal improvement would not outweight the overall reduction in the rate of ice production which accompanies lowered subcooling. In summary, the evidence suggests possible benefit from a very low subcooling operation, but the uncertainty in the order of dependence of nucleation rate upon subcooling precludes a definite statement to this effect. To resolve this uncertainty, it was decided to investigate the question further, with particular reference to very low subcoolings and the application to freeze concentration of fruit juices.

## MEASUREMENT OF ICE NUCLEATION RATE

The nucleation rate of ice at low subcoolings was inferred from the initial thermal response of a batch crystallizer, following the method used by Omran and King (1974). Kane (1971) and Kane et al. (1974) have also used a thermal method to measure rates of ice nucleation, emphasizing a later portion of the response curve. Thermal techniques are in contrast with the much more tedious procedure of counting nuclei, also undertaken by Kane et al. (1974) and others (for example, Cocks et al., 1971; Wey and Estrin, 1973; Garabedian and Strickland-Constable, 1974). Schneider (1973) made use of the thermal trace and the size distribution of a sample of the crystals at the end of a batch crystallization to infer nucleation rates.

Of these methods, the use of the initial thermal response is most free of the difficulty in modeling the growth and nucleating ability of a large spectrum of crystals. This is particularly so when the assumption of a seed dominated response, as used by Omran and King (1974), can be made. Because of the slow initial change in subcooling, this method requires no major correction for subcooling change, as is necessary with the method used by Kane et al. (1974). The major obstacles to the use of the initial thermal response are the requirements of high temperature resolution and stability in the crystallizer temperature and the possibility of spurious effects from initial breeding (Strickland-Constable, 1972). Solutions to these problems were found, however.

## DESCRIPTION OF EXPERIMENTS

### Apparatus

The apparatus employed in this study is a highly refined version of that described by Omran and King (1974). A diagram of this equipment is given in Figure 1. The basic parts of the apparatus are the crystallizer cell, in which the experiments were actually conducted, the constant temperature bath, the circulating refrigerant system, and the quartz thermometer.

The cell was constructed as shown in Figure 2. The main element was a Nalgene 250 ml polypropylene beaker, approximately 7 cm in diameter and 9 cm deep. Four thin vertical polyethylene baffles (7 mm wide and 3 mm thick) were inserted in the cell extending from the bottom of the beaker almost to the top. The baffles were held in place by O shaped rings of polyethylene at the top and bottom.

The cell was covered with a 1 cm in. thick Plexiglas cover. The seed was inserted through a 5 mm diameter hole in the cover, 2.5 cm from the center line. At other times this opening was sealed with a Teflon plug. Another hole, 2 cm from the center line and opposite the first, allowed the temperature probe to pass into the cell. This hole was 9 mm in diameter and was sealed with a split Teflon retainer. A third hole in the center of the cover contained a nylon bushing through which the stirrer shaft was then inserted through the bushing. After most of the experiments had been performed, a fourth hole 10 cm in diameter, located approximately 3 cm from the center line, was added to accommodate a Beckmann thermometer.

The cover, fastened with an O clamp around its diameter, and the stirrer motor were attached as a unit to a rigid external framework. This assured reasonably reproducible positioning of the stirrer and probe in the crystallizer cell and held them in a fixed position during experiments. The stirrer used was a three bladed marine type made of polyethylene. The blades were 2 cm long and 1.8 cm wide and were pitched at a 45 deg. angle. A universal type of electric motor was used to drive the stirrer. The motor speed was measured by a stroboscope and adjusted to a constant value (640 ± 10 rev./min.) by using a variable transformer.

The temperature of the cell during the thermal response experiments was measured with a Hewlett Packard Model 2801A quartz thermometer with Model 2850B probes. This instrument was calibrated at frequent intervals with a carefully prepared bath of finely shaved ice and distilled water. The instrument can resolve temperatures within 10, 1, or 0.1 mK (± 1 unit in the last digit). The instrument produced a digital reading of the temperature at fixed time intervals, dependent on the resolution mode (every 10 s at the 0.1 mK resolution and every 1 s at the 1 mK resolution). The thermal response time of the probes was about 2 s.

The digital signal from the quartz thermometer was passed through a Hewlett Packard Model 580A D/A converter and recorded. The trace of temperature vs. time provided the basic experimental data used in this work.

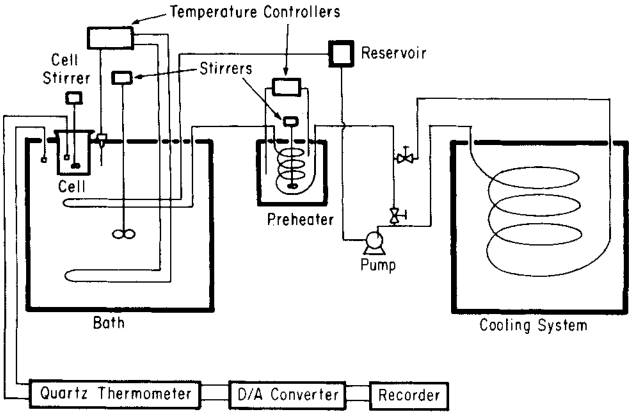

Fig. 1. Experimental apparatus.

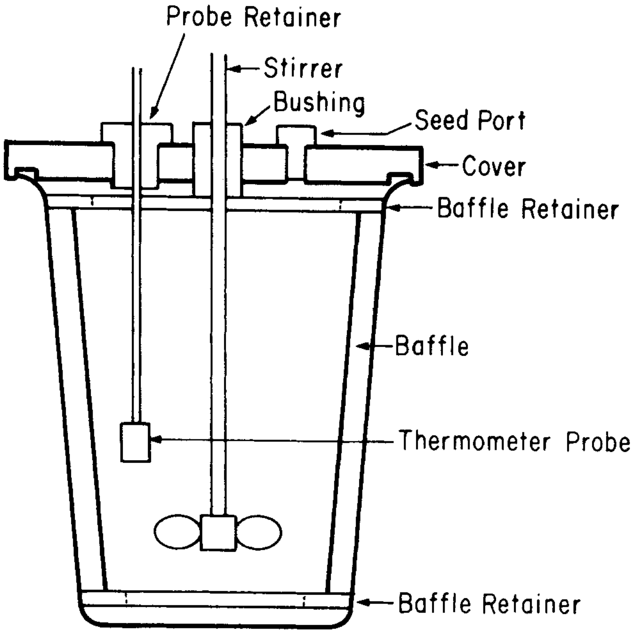

Fig. 2. Crystallizer cell.

The constant temperature bath was contained in a heavy glass vessel, 30 cm in diameter and 20 cm high. A 1.27 cm thick Plexiglas lid with openings for the bath elements covered the top of the bath. The external surfaces of the bath were covered with foil backed fiber glass insulation. The bath was filled with an approximately 60% solution of isopropanol in water. The bath was cooled by refrigerant circulated through a loop of copper tubing in the bath.

The temperature of the bath was regulated by a Hallikainen Model 1053A controller with a Model 1221A resistance thermometer as its sensor. This instrument regulated the power to a 250 W, submersible heating element, to maintain the desired temperature. The bath was agitated with a three bladed marine stirrer. In a few later experiments, the bath temperature was measured with an ordinary mercury thermometer with 0.1°K graduations.

Another bath of dry ice and isopropanol contained in an insulated vessel provided the primary source of refrigeration. Heat was transferred from the crystallizer to this refrigeration source by closed loop circulation of methanol. To mitigate fluctuations in the refrigerant temperature, the methanol refrigerant was passed through a coil immersed in another constant temperature bath, referred to as the preheater. This consisted of a large covered dewar filled with ethylene glycol solution, whose temperature was regulated by a Hallikainen Model 1253A controller and Model 1080D resistance thermometer.

As a result of these precautions, the temperature in the bath as measured by the quartz thermometer was found to be stable to ±2 mK at the 1 mK resolution. Inside the cell itself, the temperature variation was lessened by the averaging effect of

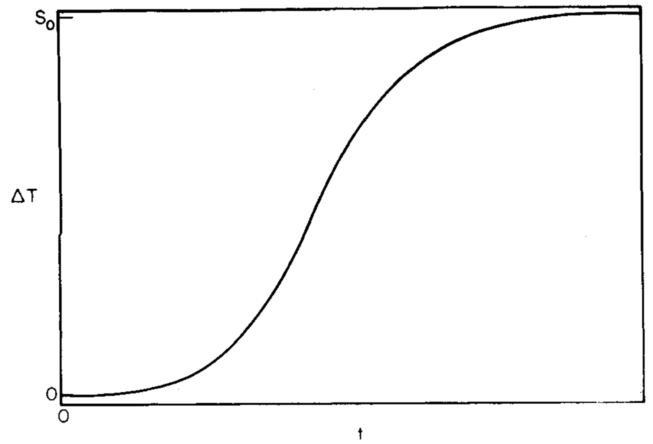

Fig. 3. Idealized thermal response curve.

the slow heat transfer through the polypropylene wall. At steady state a temperature stable to within 1 mK was obtainable over a 15 min. period, and with care the temperature could be held within ±0.1 mK for a period of several minutes. Moving the quartz thermometer probe around the cell did not affect the temperature reading within the normal uncertainty of the measurement.

### Experimental Materials

Batch crystallizer studies were conducted with the following materials:

| | |
|---|---|
| Distilled water | |
| Sucrose solution: 20, 30, and 40 wt. % | (commercial grade) |
| Fructose solution: 20 wt. % | (reagent grade) |
| Unconcentrated, pasteurized orange juice | (commerical product, Florida) |
| Filtered, unpasteurized apple juice | (commercial grade, California) |

The apple juice was obtained directly from a cannery in Sebastopol and brought to Berkeley refrigerated in ice. The juice was a nearly equal blend of Delicious and Rome Beauty varieties. All solutions and juices were used for one experiment and discarded. The orange juice was shaken to redistribute the cloud and was used within 2 days of opening; the apple juice was used within 18 hr. of acquisition. The sugar solutions were prepared just prior to use.

### Experimental Procedure

The basic type of experiment was conducted in the following manner:

1. The crystallizer cell was charged with approximately 200 g of liquid at least several degrees warmer than freezing.
2. The cell was inserted into the bath and the stirrer and cover assembly lowered into position.
3. The bath was cooled to the operating temperature and the cell allowed to come to steady state.
4. The stirrer was adjusted to 640 rev./min.
5. A seed of ice was prepared by exposing a 2.5 μl drop of distilled water, supported on a syringe needle, to a stream of cool air flowing out of a tilted dewar of liquid nitrogen. The seed froze in 30 to 60 s.
6. The seed was allowed to warm for a period of about 10 s in air, inserted into the cell opening, and dislodged into the solution by tapping.
7. An electric timer was actuated at the instant of seeding. This timer was used to locate the start of the experiment on the temperature recording, and the recording was then used to infer the nucleation kinetics in the manner to be described.

To test the effect of the number of seeds used, three 25-gauge syringe needles were fastened into a tripod. Drops were placed at the ends of these needles with the standard syringe, then frozen and tempered in a manner similar to the normal seeds. In some other experiments seeds were tempered in water in a petri dish immersed in an ice bath to test the effect of the method of tempering.

## METHOD OF ANALYSIS

An idealized thermal response curve is given in Figure 3. This curve is representative of the experimental print-out after smoothing of the digital steps. Omran and King (1974) discussed a method of inferring the rate of secondary nucleation of ice from the early temperature vs time data. This method, with some modification, was used in the present work. The following is an outline of the method; fuller detail is given elsewhere (Stocking, 1974).

The production of secondary nuclei is assumed to be dominated by the seed. The rate of secondary nucleation $J$ vs. cell subcooling $S$ is modeled with a power law as follows:

$$J = b\,S^i \tag{1}$$

The rate constant $b$ includes the effect on nucleation rate from the seed characteristics, flow conditions, etc.

To model the growth of the nuclei, the growth is assumed to be limited by heat or mass transfer rates, which are themselves estimated from the low Peclet number asymptote of conduction or diffusion into an infinite medium. The growing nuclei are assumed on the average to have a constant shape, and the overall growth rate is expressed by the increase in the maximum crystal radius $R$. With these assumptions, the growth rate $\dot{R}$ can be set proportional to the subcooling and inversely proportional to the radius $R$. Thus

$$\dot{R} = \frac{g\,S}{R} \tag{2}$$

The growth factor $g$ includes the dependency on the diffusivity, thermal conductivity, specific crystal shape, etc. To evaluate the initial temperature increase, the subcooling is assumed to be constant at the initial value $S_o$ insofar as it affects rates of nucleation and growth. By supposing also that the initial crystal size is negligible, Equation (2) may be integrated to give the size of the crystal in terms of the difference between the total time from seeding $t$ and the time elapsed since the formation of the nucleus $\theta$ by

$$R = \sqrt{2\,g\,S_o\,(t-\theta)} \tag{3}$$

With the assumption that the crystals have a geometrically similar shape, the volume of a crystal $v$ can be related to the radius by a shape factor $k_v$

$$v = k_v\,R^3 \tag{4}$$

With these models and a cell enthalpy balance, the initial temperature increase of the cell $\Delta T$ may be determined as a function of $t$. This is done by equating the cell enthalpy increase to the heat released by the growth of nuclei, the heat released by growth of the seed, and the increased heat transfer from the cell to the bath caused by the temperature increase. By neglecting for the moment the two latter terms, the following equation results:

$$M\,C_p\,\Delta T = \lambda\,\rho_I \int_0^t J(\theta)\,v(t-\theta)\,d\theta \tag{5}$$

With application of Equations (1) to (4), Equation (5) becomes with rearrangement

$$\Delta T = \frac{\lambda\,\rho_I\,k_v\,b\,4\sqrt{2}\,g^{1.5}\,S_o^{i+1.5}\,t^{2.5}}{5M\,C_p} \tag{6}$$

This is a slightly altered version of the cell equation presented by Omran and King (1974).

It might also be supposed that the kinetics of incorporation into the crystal structure could determine the rate of growth. In the limit of total kinetic control, the growth

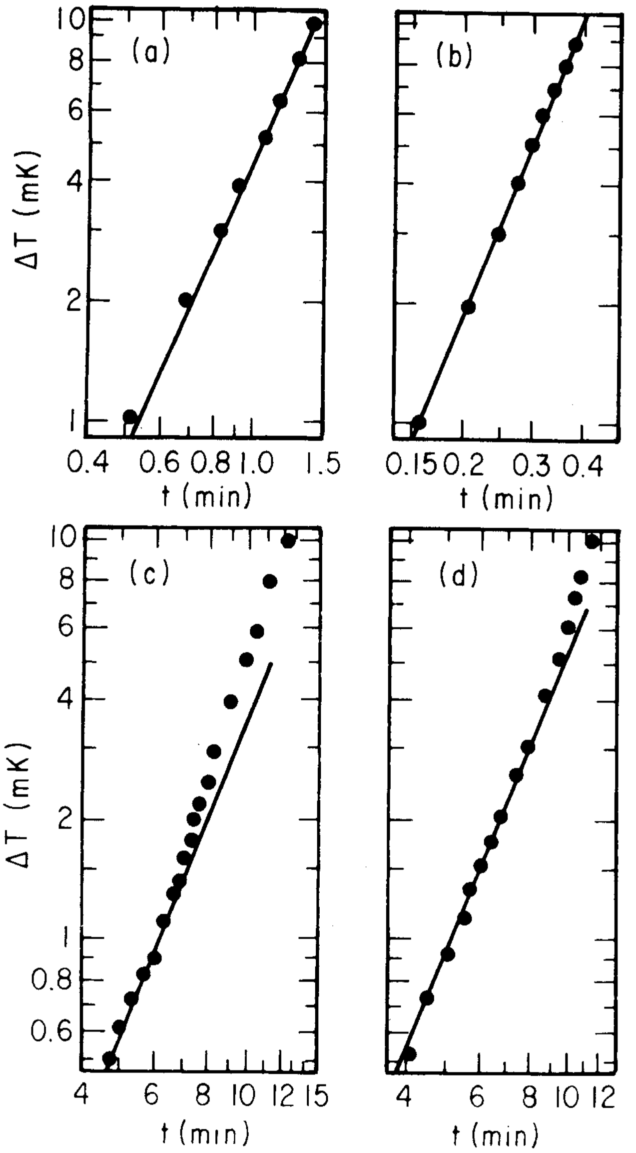

**Fig. 4. Increase in cell temperature with time for various runs. a. Distilled water, $S_0 = 64$ mK, 1 mK resolution; b. distilled water, $S_0 = 110$ mK, 1 mK resolution; c. 20 wt. % fructose solution, $S_0 = 32$ mK, 0.1 mK resolution; d. 40 wt. % sucrose solution, $S_0 = 92$ mK, 0.1 mK resolution.**

rate would seemingly be independent of crystal size. In this case, the growth rate model would take the form

$$\dot{R} = g' S^m \tag{7}$$

where $g'$ is a growth factor and $m$ the growth subcooling order. In such a case, an equation similar to Equation (6) can be obtained:

$$\Delta T = \frac{\lambda\, \rho_I\, k_v b (g')^3\, S_o{}^{i+3m}\, t^4}{4M\, C_p} \tag{8}$$

It may be seen that the time order of the thermal increase is itself dependent on the size order of the growth rate. For size independent growth, Equation (8) predicts an increase in cell temperature with the fourth power of time, while for size inverse growth, Equation (6) predicts a 2.5 power increase. This difference can be used to determine from experimental data which model of the growth and thermal response is better.

### Growth Order of Secondary Nuclei

From Equations (6) and (8), it may be inferred that if the logarithm of the cell temperature increase $\Delta T$ is plotted vs. the logarithm of time, the slope of the resulting line is related to the size dependence of the growth rate of nuclei. Figure 4 shows such a plot of data recorded after seeding in distilled water at two different initial subcoolings and in two different sugar solutions. The straight lines have slopes of 2.5. Good agreement between the actual response and that predicted by the size inverse model is evidenced at early times. The data in Figures 4*c* and 4*d* were obtained by using the highest resolution setting of the quartz thermometer. Other data taken in this mode were consistent with the 2.5 model as well. Thus it was assumed that the size inverse model holds for the growth of the small nuclei. Data taken at the 1 mK resolution did not always show such close agreement, but this failure is attributable to loss of measurement precision, since round-off errors become so much larger (Stocking, 1974).

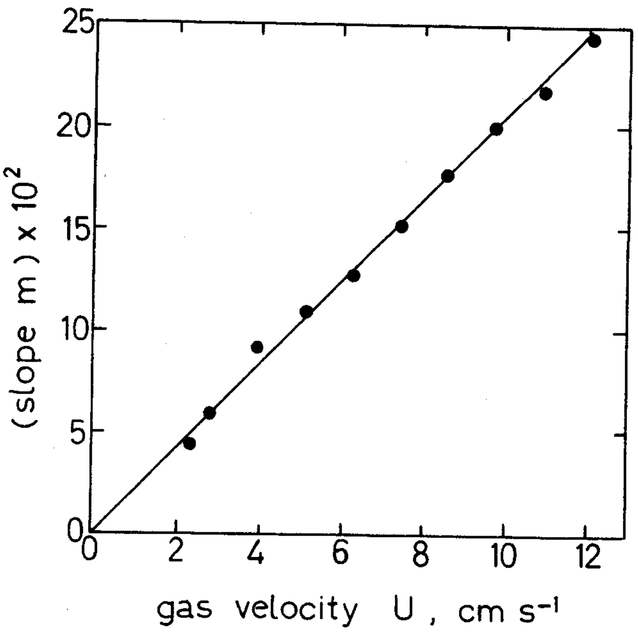

**Fig. 5. More precise analysis of the early thermal response.**

### Interpretation of Thermal Response Curves

It may be seen from Figure 4*c* that the temperature can depart from the 2.5 power increase after cell temperature increases of only a few mK. The point of departure was found to shift to higher values of the temperature increase at larger values of the initial subcooling. To apply the analytical model first developed by Omran and King (1974) to the present case, therefore, only the very first part of the thermal response trace should be used.

Omran and King defined a value of the temperature increase of 5 mK as a standard and then measured the time required after seeding of the cell for this increase to occur. Obviously, in the present case, a lower value of $\Delta T$ would have to be used for such a calculation. At such low values, uncertainty in the value of the temperature increase at a given time exists because of the limited resolution of the quartz thermometer. A way to improve this situation is to use data from several points which allow averaging of random errors in the data. Since all values of the temperature increase depend upon the precision of reading the initial subcooling, it is also possible that the data points can all contain a constant error in $\Delta T$, resulting from $S_o$ being located within a precision interval of the quartz themometer.

Given the 2.5 power in time increase of the temperature, it may be noted that a plot of apparent temperature increase vs. time to the 2.5 power has a slope which is not affected by a constant absolute error in the temperature increase measurements. This fact was used for a more precise determination of the time required for a 1 mK temperature increase. Data were plotted in the form shown in Figure 5. The intercept of such a plot corresponds to the inferred error in the initial subcooling, in this case about −0.15 mK. From the slope of the line drawn through the data, the time elapsed between seeding and a temperature increase of 1 mK was determined. Time values found in this manner were defined as the induction time and used along with Equation (6) to determine the rate of nucleation.

### Thermal Corrections

In order to use these induction times to obtain nucleation rates, correction must be made for the increased heat transfer from the cell as its temperature increases from the heat of ice formation. The heat released by the growth of the seed must also be considered. These corrections were made by first finding the time derivative of the temperature increase from Equation (6) by using the uncorrected induction time. Then these other two heat effects were superimposed, and the resulting differential equation was solved for the actual cell temperature increase with time. In this way, the measured induction times could be related to the induction times which would have been observed in the absence of these secondary effects. The correlation of Brian et al. (1969) was used to estimate the seed growth rate. The cell heat transfer characteristics were inferred from a trace of the cooling curve of the cell without ice present.

### Crystal Growth Rate Model

The nuclei were assumed to grow as oblate spheroids. From photographs of the disk shaped crystals taken at the ends of several runs, an estimate of the crystal aspect ratio $\omega$ was made. This ratio is that of the semiminor axis to the semimajor axis. Transport rates were predicted from the potential gradient at the surface of a stationary, isopotential oblate spheroid of fixed size (Moon and Spencer, 1961). For heat transfer limited growth, the following equation for the growth factor results:

$$g = \frac{k\sqrt{1-\omega^2}}{\lambda\, \omega\, \rho_l \operatorname{arc\,cot}\left(\dfrac{\omega}{\sqrt{1-\omega^2}}\right)} \tag{9}$$

Here, $k$ is the thermal conductivity of the liquid. For mass transfer limited growth, another equation applies:

$$g = \frac{D_{sw}\sqrt{1-\omega^2}\,\dfrac{d\rho_s}{dT}}{\rho_s''\, \rho_l\, \hat{V}_w\, \omega \operatorname{arc\,cot}\left(\dfrac{\omega}{\sqrt{1-\omega^2}}\right)} \tag{10}$$

The distilled water case was taken to be heat transfer limited, and the other cases mass transfer limited. The effects of heat transfer on the mass transfer process and vice versa were neglected.

This treatment predicts that the ratio of the gradient at the semimajor axis to that on the semiminor axis is the same as the aspect ratio itself. If the growth at the axes is indeed proportional to the gradient, then the aspect ratio should be unchanged by the growth process.

The oblate spheroid growth model was refined by use of correction factors to account for the boundary layer motion during growth and the transpiration motion resulting from the phase density difference between ice and the liquid (Stocking, 1974). This was done in an approximate manner with the equations presented by Brian and Hales (1969) for correction factors applicable to a sphere. The semimajor radius was substituted for the spherical radius. The rate of growth of the semimajor axis predicted by the growth rate factors was then modified by the correction factors so predicted.

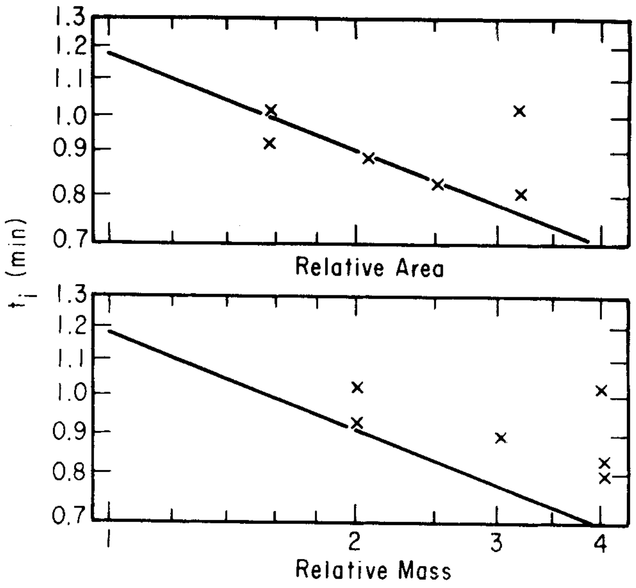

Fig. 6. Effects of seed moments on induction times.

TABLE 1. MAXIMUM CRYSTAL SIZE AT DEVIATION FROM 2.5 POWER

| Material | $S_o$ (mK) | Time of deviation (min.) | $R$ ($\mu$m) |
|---|---|---|---|
| Distilled water | 80 | 0.55 | 150 |
|  | 33 | 1.25 | 144 |
| 20 wt. % sucrose | 124 | 1.25 | 81 |
|  | 43 | 4.50 | 85 |

## SIGNIFICANCE OF THE DEVIATION FROM THE 2.5 POWER

The eventual deviation of the thermal response from the 2.5 power implies the loss of validity of one or more of the assumptions used in deriving Equation (6). With increasing particle size, it is expected, for one, that the nuclei themselves should become active in nucleation. In magnesium sulfate crystallization, Cayey and Estrin (1967) found that the nucleation by the growing second generation crystals began to occur when the nuclei exceeded threshold size. Bauer et al. (1974) and Ramshaw (1974) have suggested from hydrodynamic considerations that such a threshold should exist.

A check was made whether the departure from the 2.5 power was consistent with a crystal size based nucleation threshold. From the elapsed time after seeding at which the departure occurred in several experiments, the size of the largest crystals at the point of departure was estimated from Equation (3) and the oblate spheroid growth model. Results for distilled water and 20 wt.% sucrose solution are given in Table 1. The agreement in the particle size estimated at high and low subcooling suggests that the threshold size argument accords with the deviation from the 2.5 power. The change in subcooling from the initial value should not be the principal cause of departure from the 2.5 power, since the change is still percentwise small at that point. On the other hand, departure from the size inverse growth law is another possible cause of departure from the 2.5 slope which cannot as readily be ruled out.

The existence of a nucleation threshold size is supported by reference to ice nucleation rates measured from direct crystal counts by Garabedian and Strickland-Constable (1974). In this work, a single, plate shaped crystal of ice was introduced into subcooled water which was stirred for a fixed period of time. The authors noted a sudden increase in nucleation at higher subcooling, dependent on the time of stirring. By extrapolation of the results in Table 1, it can be predicted that the deviation from a seed dominated response would occur after 5 s for a subcooling of 0.51°K and after 10 s for a subcooling of 0.26°K. In the 10 s series, the increase was noted by Garabedian and Strickland-Constable at a subcooling of 0.25°K and in a parallel 5 s series at 0.45°K. In another 5 s series, no strong increase was seen at subcoolings up to and including 0.45°K. Given some inaccuracy of the thermometric measurements of subcooling, the agreement between their observed deviations and extrapolations from the present data is rather good and further supports the threshold size concept.

## RESULTS

From Equation (6), it may be observed that the induction time is directly related to the nucleation rate. Under the same growth conditions, variation in the induction time can be ascribed to changes in the nucleation rate. This allowed effects on the nucleation rate to be investigated by study of the resultant changes in the induction times. Absolute rates of nucleation were also inferred from induction time measurements which permit comparison under varying growth conditions.

The initial introduction of a dry seed can produce a onetime crop of nuclei in excess of the steady state yield. This phenomenon can be prevented by curing the seed, that is, letting the crystal melt or dissolve slightly before use as a seed (Strickland-Constable, 1972). In the present case, the seeds were cured by letting them melt slightly in room air before seeding. Since experiments conducted tempering ice seeds in water slightly above freezing temperature yielded induction times equivalent to the air tempered ones, it was presumed that the air curing was sufficient to check initial breeding.

A number of experiments were conducted with varying numbers of seeds from one to three. These experiments were performed with distilled water and were measured at the 0.1 mK resolution. The results were in good agreement with the hypothesis that nucleation was proportional to seed number. Despite altered induction times, departure from the 2.5 power slope came at approximately the same elapsed time from seeding. Since nuclei growth is little changed with seed number, this is consistent with the threshold theory. Experiments with larger seeds were performed in conjunction with one series of multiple seed studies at the same initial subcooling. As shown in Figure 6 there was fair agreement with the hypothesis that nucleation was proportional to seed area, but not with proportionality to seed mass.

The main part of this experimental effort was devoted to measuring the induction time for various initial subcoolings and in different media. A span of initial subcooling from 6 to over 200 mK was covered. Data for water and sugar solutions are shown in Figure 7. The same information is displayed for apple and orange juice in Figure 8.

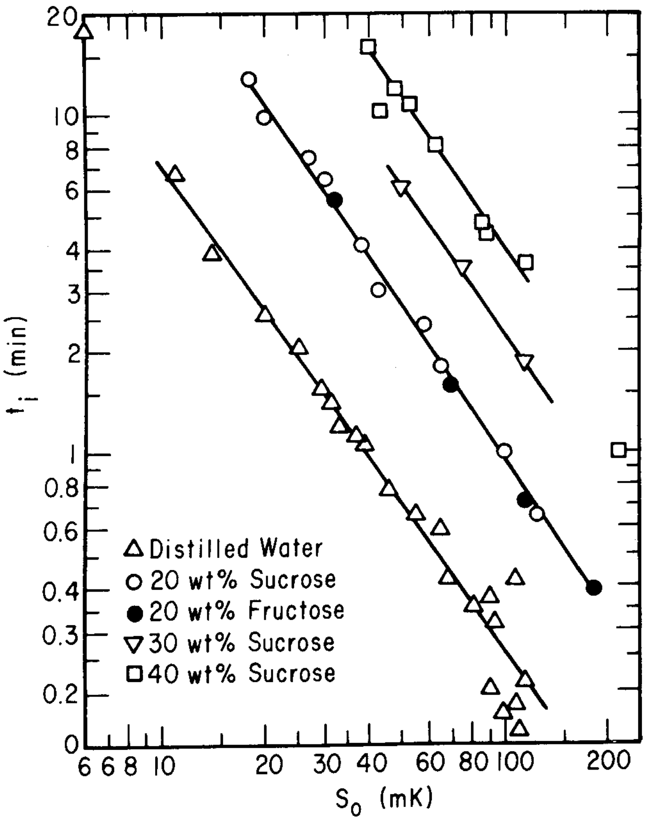

Fig. 7. Induction times vs. initial subcoolings for water and solutions.

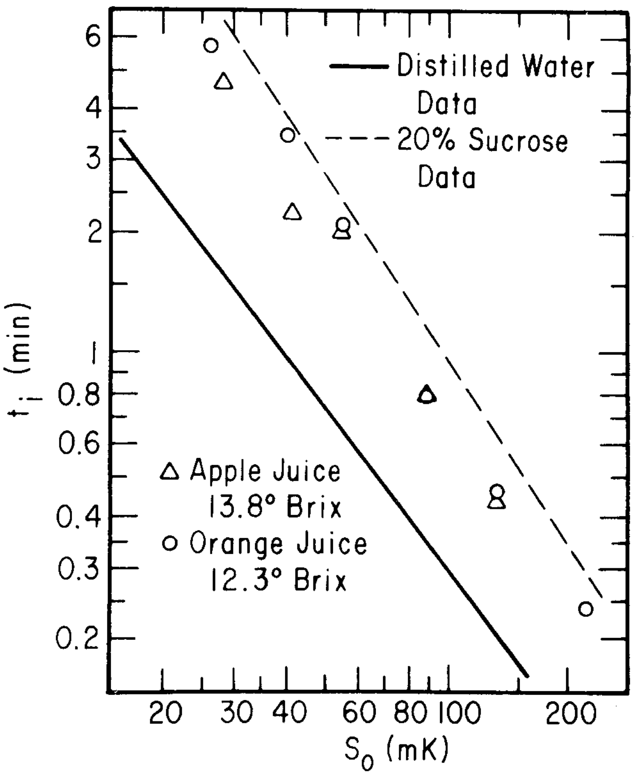

Fig. 8. Induction times vs. initial subcooling for fruit juices.

A computer program described by Stocking (1974) was written to infer nucleation rates from these induction time data after the method already presented. The logarithm of the calculated nucleation rate was fitted by linear, least-squares regression as a function of the logarithm of the initial subcooling for each type of liquid. The results of this work are summarized in Table 2. It may be seen that the nucleation order is about 2.1, on the average. Reference to the confidence intervals shows that there is no statistically significant difference in the nucleation order from material to material or with respect to sucrose concentration. For this reason, a constant subcooling order of 2.1 was assumed, and the data were then used to compute a nucleation rate constant $b_c$ based on this order. These values are given in Table 3. It may be seen that values of $b_c$ range from a low of $1.8 \times 10^4$ nuclei/s $K^{2.1}$ in orange

TABLE 2. NUCLEATION RATE EXPRESSIONS FROM INDUCTION TIME DATA

$J = b\, S_o^{i}$

| Material | $i$ | 90% confidence interval of $i$ | $b$ based on $i$ ($10^{-4}$ nuclei/ $s$ °K$^{i}$) |
|---|---|---|---|
| Distilled water | | | |
| All data | 2.152 | ±0.053 | 2.4 |
| Sucrose | | | |
| 20 wt. % | 2.058 | ±0.066 | 2.5 |
| 30 wt. % | 1.93 | ±0.72* | 1.4 |
| 40 wt. % | 2.10 | ±0.15 | 3.1 |
| Fructose | | | |
| 20 wt. % | 1.99 | ±0.24 | 4.0 |
| Apple juice | | | |
| 13.8° Brix | 2.09 | ±0.31 | 3.5 |
| Orange juice | | | |
| 12.3° Brix | 2.17 | ±0.15 | 1.8 |

* Large uncertainty arises from small sample size.

TABLE 3. NUCLEATION RATE EXPRESSIONS FROM INDUCTION TIME DATA

$J = b_C\, S_o^{2.1}$

| Material | $b_C$ ($10^{-4}$ nuclei/s °K$^{2.1}$) | 90% conf. interval on $b_C$ ($10^{-4}$ nuclei/s °K$^{2.1}$) |
|---|---|---|
| Distilled water | | |
| All data | 2.1 | 0.8-5.0 |
| Sucrose | | |
| 20 wt. % | 2.9 | 1.9-4.2 |
| 30 wt. % | 2.2 | 1.6-2.9 |
| 40 wt. % | 3.1 | 1.6-6.0 |
| Fructose | | |
| 20 wt. % | 5.5 | 2.9-10 |
| Apple juice | | |
| 13.8° Brix | 3.7 | 1.9-7.0 |
| Orange juice | | |
| 12.3° Brix | 1.8 | 1.1-3.0 |

juice to a high of $5.5 \times 10^4$ nuclei/s K$^{2.1}$ in fructose solution. A value of $2.5 \times 10^4$ nuclei/s K$^{2.1}$ may be taken as representative of these data. By assuming the nominal area of the seed to be that of a sphere of the same volume, an average nucleation rate per unit seed surface is then $3 \times 10^{10}$ nuclei/s m$^2$ K$^{2.1}$.

Because of the commercial importance of orange juice and the fact that it alone of the materials investigated contained appreciable suspended matter (cloud), some further experiments were conducted with it (Stocking, 1974). Samples of filtered juice and centrifuged juice were used, as well as natural juice. At the conclusion of a fixed time, photographs of a portion of the juice were taken. Crossed Polaroid filters rendered the ice crystals visible in these photographs because of the birefringence of the ice. While lacking high contrast, the photographs gave sufficient detail to show that the filtered or centrifuged juice contained more larger crystals than did the untreated juice. Interpretation of these photographs (Stocking, 1974) suggests that the removal of suspended particles from the juice acts to increase the growth rate, and possibly the overall nucleation rate as well. In any case, no loss of ice quality accompanied the removal of the suspended particles. Furthermore, the removal of the smallest cloud particles, of the order of 10 $\mu$m and below, seemed to have at most a small effect.

The shapes of the thermal-response curves for fruit juices and sugar solutions were compared to check for any apparent dissimilarity. The curves were very similar in shape, suggesting that no major disparities in the nucleation and growth processes are evidenced in the fruit juices.

The thermal response data for distilled water were also analyzed from another point of view suggested by Kane et al. (1974). These authors considered the thermal response which would be predicted for size independent growth and a nucleation rate proportional to an integral order moment of the crystal size distribution. This analysis leads to a parameter $\beta$ which is a function of the growth and nucleation rates. The parameter $\beta$ is identified with the nucleation rate per crystal in a continuous stirred tank crystallizer at the same conditions. By using an approximate analysis based on the equations presented by Kane et al. (1974), values of $\beta$ were estimated from the portion of the thermal response curve immediately following that used in the previously discussed approach. The values of $\beta$ found in this manner can be correlated in the subcooling interval between 10 and 100 mK by

$$\beta = 4.7\, S_o^{1.6} \tag{11}$$

where $\beta$ is in reciprocal seconds and the initial subcooling $S_o$ is expressed in mK. Further details are given by Stocking (1974).

## DISCUSSION

The size inverse growth model for ice suggested by the thermal response time order is in qualitative agreement with the finding of Wey and Estrin (1973). They inferred from population distribution measurements that the growth rate of crystals decreases with increasing size up to a crystal radius of approximately 300 $\mu$m. This size dependence lends credence to the assumption that heat and mass transport control growth, which has been suggested by Margolis et al. (1971) and by Schneider (1973).

The success of the growth model suggests that crystallization kinetics are so fast as to play only a minor role. This contradicts Huige et al. (1973) who asserted that the crystallization kinetics should have a major influence. What they report as the influence of crystallization kinetics appears to be the difference between their prediction of the growth rate of ice based on heat and mass transfer limits, on the one hand, and the measured value on the other hand. Since this difference increased with the rate of stirring, it seems likely that it mirrors the difficulties in accurately predicting and measuring ice-crystal growth rates.

This same problem of predicting ice-crystal growth rates appears to be the cause of the disparity between this work and that of Omran and King (1974) regarding the effect of sucrose content on nucleation. In the former case, the rate of ice nucleation in 30 wt. % sucrose solution was found to be of the order of ten times higher than that in distilled water. When data from Omran (1972) are recalculated by using the methods of the present study (Stocking, 1974), the nucleation rate in 30 wt. % sucrose solution is found to be only a factor of 2 higher. This change is explained mainly by the inclusion of the correction factor for the moving boundary layer, which increases in importance the higher the sucrose content. Since the recalculated values are in good agreement with the relative rates of nucleation found in the present study, it is concluded that no conflict between the experimental results of the two studies exists in this regard.

Because of the simplification of the actual crystal growth made with the assumption of the oblate-spheroid model for the growth rate prediction, it is rather likely that errors in the absolute rate of growth exist in the present instance as well. Since these errors are in turn reflected in the nucleation rates, the absolute values of the nucleation rate should be considered only approximate. The growth model, however, does appear to have the correct qualitative behavior with respect to both size and subcooling. Thus, the subcooling order should be considered to be fairly well founded. This value is in complete agreement with the subcooling order of 2.1 found by Huige et al. (1973) in a continuous crystallizer in the same subcooling range. The value of approximately unity for the subcooling order determined by Omran and King (1974) is distinctly different, but this value applies to a higher range of subcooling. In a few of the experiments made at higher subcoolings in the present work, a change from the disklike crystal morphology encountered in most of this study to the needle or dendrite form was observed. This change in the growth form could account for the difference in the nucleation order.

## IMPLICATIONS FOR FREEZE CONCENTRATION CRYSTALLIZER DESIGN

As just mentioned, the growth of crystals at higher subcoolings took the form of needles or dendrites, in contrast to the disk shaped crystals found at lower subcoolings. This changeover occurred at approximately 100 mK subcooling, consistent with the report of Harriott (1967) on the subject. This change in morphology is in itself sufficient reason to operate at lower subcoolings, since the surface-to-volume ratio of the crystals is much improved. In this lower subcooling range, the nucleation rate was found to decrease with more than the second power of subcooling. The growth rate appears to be controlled by heat and mass transfer and would therefore decrease with approximately the first power of subcooling. Thus, the lower the subcooling, the more nucleation is suppressed relative to growth, and the larger the average crystal size should be, given the same production of ice. Balancing this is the increased residence time required to obtain the same ice production, so that some economically determined optimum must exist.

The nucleation rate seems substantially independent of sucrose concentration. The growth rate is significantly reduced with increasing sucrose concentration because of the greatly lowered diffusion coefficient of water at higher concentrations of sucrose. The ratio of nucleation to growth rates is therefore highest in the most concentrated solution. From the crystal size standpoint, this means that continuous production of ice in a single stirred tank is unfavorable. Designs which utilize the less concentrated solution for much of the growth should lead to larger crystal size, as well as a higher growth rate. Staging of the crystallization with two or more stirred tanks is an obvious improvement. Seeded column or plug flow crystallizers would also have the feature of more growth occurring in dilute solution. For smaller scale freeze concentration, semibatch operation of a stirred tank would be a possibility. This would entail continuous removal of the ice and recycle of the juice until the desired concentration was reached. While preserving the simplicity of the stirred tank, it would also remove the disadvantage of always operating under the most unfavorable conditions for growth vs. nucleation.

From the preliminary study of the effect of crystal size on nucleation rate, it would appear that the nucleation rate does not increase faster with increasing crystal size than the surface area increases. Therefore, the introduction of ice crystals to a crystallizer would not increase nucleation to a greater extent than growth. This facilitates use of ice recycle, such as in the manner suggested by Omran and King (1974) where advantage is taken of the fact that the growth rate is highest relative to the nucleation rate at the lowest concentration of solute.

The effect of crystal size on nucleation rate found in this study leads to doubts around the use of nucleation models which presume nucleation rate proportional to the mass of a crystal, as has been postulated by Ottens and de Jong (1973). It also appears likely from the analysis of the present results that a nucleation threshold size exists, which would complicate correlation of nucleation rates with moments of the crystal size distribution, as suggested by Kane et al. (1974). More work in this regard should be done before such models are used too extensively. The changeover from size inverse to size independent growth expected for larger crystals (Wey and Estrin, 1973) also complicates the picture. Because the more rapid growth at smaller sizes leads to rapid growth of crystals out of this size interval, the number of very small crystals is usually less than the number of ones of larger size in most practical crystallizer situations. Therefore, influence of very small crystals on the overall nucleation and growth rates in the crystallizer may be negligible in many applications of interest. Finally, it should be recognized that nucleation rates are affected by crystallizer geometry, agitator speed, and ice-crystal density; these facts should be taken into account in any attempt to utilize the results of this study for the design crystallizers.

## ACKNOWLEDGMENT

This study was supported by Grant No. 12-14-100-9906(74) from the Agricultural Research Service, U.S. Department of Agriculture, through the Western Regional Research Center. One of the authors (J. H. Stocking) was also supported through a fellowship from the National Science Foundation and a grant from the General Electric Company. Mention of a specific product name does not imply endorsement by the U.S. Department of Agriculture to the exclusion of other products which may also be suitable.

## NOTATION

$b$ = nucleation rate constant in Equation (1) (number/min. · $°K^{-i}$)

$b_c$ = nucleation rate constant based on a nucleation order of 2.1 (number/min. · $°K^{-2.1}$)

$C_p$ = specific heat capacity of contents of crystallizer cell (cal/g °K)

$D_{sw}$ = normal binary diffusion coefficient of solute in water (cm$^2$/min.)

$g$ = growth rate factor in Equation (2) (cm$^2$/min. · °K)

$g'$ = growth rate factor in Equation (7) (cm/min. · $°K^m$)

$i$ = nucleation order in Equation (1)

$J$ = nucleation rate for crystallizer cell (number/min.)

$k$ = thermal conductivity (cal/min. cm. °K)

$k_v$ = volume shape factor in Equation (4) (dimensionless)

$M$ = total mass of the crystallizer (g)

$m$ = growth order in Equation (7)

$R$ = maximum crystal radius at time $t$ (cm)

$\dot{R}$ = time derivative of $R$ (cm/min.)

$S$ = the bulk subcooling (°K)

$S_o$ = value of the bulk subcooling at seeding (°K)

$T$ = temperature of the crystallizer cell (°K)

$\Delta T$ = increase in temperature of cell, compared to that at time of seeding, $= S_o - S$ (°K)

$t$ = elapsed time from seeding (min.)

$t_i$ = induction time, defined in text (min.)

$\hat{V}_w$ = partial specific volume of water (cm$^3$/g)

$v$ = volume of a single ice crystal (cm$^3$)

**Greek Letters**

$\beta$ = crystallization parameter defined by Kane et al. (1974) ($s^{-1}$)
$\theta$ = elapsed time after seeding at which crystal was formed (min.)
$\lambda$ = latent specific heat of ice (cal/g)
$\rho_I$ = density of ice ($g/cm^3$)
$\rho_s$ = weight concentration of the solute ($g/cm^3$)
$\rho_s''$ = equilibrium weight concentration of solute at ice surface ($g/cm^3$)
$\omega$ = crystal aspect ratio, that is, thickness to diameter ratio

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*Manuscript received June 6, 1975; revision received November 4, and accepted November 5, 1975.*

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# Optimal Feedback Control of Time-Delay Systems

**The suboptimal control policy obtained from series expansion of time-delay terms is useful when the delays are small. The second method involving direct search on the constant gain matrix is applicable even for large delays. Both of these proposed methods are computationally simple and lead to easy implementation in practice.**

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## SCOPE

**Engineering systems often contain delayed elements such as recycle streams, transportation lags, and time-delayed feedback signals. In particular, such delayed elements are commonly encountered in the chemical and petroleum industries, and, for proper control, such time lags cannot be neglected. The dynamic behavior of such time-delay systems can be modeled adequately by differential-difference equations, that is, differential equations with delayed arguments.**