cedure is repeated until the temperatures for two successive iterations agree to within a specified tolerance at all points in the space of the die. The procedure is started by assuming the entire die is at the inlet temperature T_0.

Fully developed non-Newtonian isothermal flow was assumed to exist at the die inlet. That is, $v'_{z0}(y')$ is the solution to Equations (A6) and (A8) at $T = T_0$. $v'_{z0}(y')$ was not calculated separately, but was determined along with the overall solution of $T'(r', z')$, $v'_z(r', z')$, etc. by the procedure explained above.

Three point implicit central difference approximations were used in the y direction while two point backward differences were used in the z direction. Large temperature gradients are encountered near the tube walls and near the inlet. Thus, a finer grid was used in those regions to facilitate convergence of the numerical solution. Some details of the numerical solution and a listing of the program used here are given by Cox (1973).

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Kinetics of Ice Crystallization in Sugar Solutions and Fruit Juices

Ice-crystal secondary nucleation kinetics are derived from thermal response experiments carried out with concentrated sugar solutions and fruit juices. Variables studied include the level of supersaturation, power input, sugar concentration, sugar type, and the presence of high-molecular-weight additives. The nucleation rate is indicated to have a low-order dependence upon subcooling (about 1.25 power) for subcoolings in the range 0.25 to 1.00°C. Fruit juices are well modeled by the corresponding synthetic sugar solution. The selection and improvement of processing approaches for freeze concentration of food liquids are discussed in light of the experimental results.

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SCOPE

Freeze concentration is attractive as a means of removing water from food liquids because of the high selectivity of water incorporation into ice, because of the relatively mild processing conditions involved, and because there need not be an opportunity for the loss of volatile flavor and aroma components. Freeze concentration has been limited in application because of the economic penalty associated with loss of concentrate entrained with the ice crystals. This loss can be reduced if a larger average ice crystal size can be obtained. Ice-crystal size, in turn, is determined by relative nucleation and growth kinetics. Nucleation under typical conditions for freeze concentration is dominated by secondary nucleation.

Rates of secondary nucleation as affected by variables other than parent crystal size and density were measured from the duration of the induction period of the thermal response following seeding, under the assumption of diffusion-limited growth. Both sugar solutions and real fruit juices were examined. The results so obtained were then utilized for considerations of preferred and improved design approaches for freeze concentrators.

CONCLUSIONS AND SIGNIFICANCE

Ice secondary nucleation rates, as derived from the induction period of the thermal response, were found to vary as the 1.25 power of subcooling for temperature subcoolings in the range 0.25 to 1.00°C. The nucleation rate increases with increasing power input to the system and increases markedly with increasing sugar concentration, but is relatively independent of sugar type. The nucleation rate was also found to be suppressed by the addition of pectin or gelatin. Orange and apple juice are modeled reasonably well by the corresponding synthetic sugar solution. The transient portion of the response can be used to infer that ice-crystal growth rates are governed by established correlations for turbulent mass transfer to suspended particles, provided that the transient response is assumed to be dominated by a fixed number of crystals of largest size. Further research is required to establish the extent to which new nuclei themselves become sources of secondary nucleation.

For the nucleation kinetics found in this subcooling range the crystal-size distribution will not change much with changing subcooling for a given ice production. The decrease of ice crystal size with sugar content discourages the use of recycle as a means of building up the volume fraction of liquid in a freeze concentration process. Benefits achievable by appropriate staging of the freezing process are explored.

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Crystallization of water from aqueous solutions has a potentially wide application for water purification and for solute concentration. Because of the high purity of ice crystals formed at moderate growth rates, ice crystallization may be considered to be one of the most selective dewatering processes. The most widely publicized application of water crystallization as a separation process is for desalination of sea water (Brian, 1971). Another important application is for freeze concentration of thermally sensitive solutions, such as liquid foods, pharmaceutical solutions, blood plasma, and other products (Muller, 1967, Thijssen, 1970). In addition to selectivity, a major advantage of freeze concentration is the low temperature involved. Quality losses by thermal or biochemical degradation reactions are thus minimized. The lack of vaporization also guards against loss of volatiles.

Freeze concentration is presently used for preconcentration of coffee extract before freeze drying and for concentration of vinegar. The process also has considerable potential attraction for the concentration of fruit juices where the loss of volatile flavor and aroma substances and thermal degradation are problems with the current evaporation processes. However, following early abortive efforts (Muller, 1967), freeze concentration has not been employed commercially for fruit juices. The main drawback has been loss of viscous juice concentrate entrained with the ice crystals, with the high product value making even seemingly small losses significant economically. A promising approach towards reduced loss of entrained juice concentrate is the formation of larger and more uniform ice crystals in the crystallizer. Achieving this goal on a rational basis requires both qualitative and quantitative understanding of the underlying ice crystal nucleation and growth processes.

There is little or no information available in the literature on nucleation and growth rates of ice in juices or other liquid foods, or even in synthetic sugar solutions of corresponding composition. Thus the main objective of the present research was to determine the effect of pertinent variables on the nucleation and growth kinetics of ice in both synthetic sugar solutions and fruit juices.

SECONDARY NUCLEATION AND GROWTH OF ICE IN AQUEOUS SOLUTIONS

A number of recent studies have demonstrated that secondary nucleation (nucleation of a type which occurs only in the presence of parent crystals of the substance being crystallized) is the dominant source of new crystals under the best of current industrial crystallization conditions. Qualitative behavior has been reported by Huige and Thijssen (1969b) and others for pure water. Secondary nucleation of ice in dilute NaCl solutions has received special attention because of the interest in freeze desalination. Both batch (Sadek, 1966; Estrin, 1970; Kane, 1971; Kane et al., 1974; Cocks et al., 1971) and continuous (Margolis et al., 1971) systems have been used. A study concurrent with the present one has investigated the effects of crystallizer operating variables on secondary nucleation in glucose solutions (Huige, 1972). Despite the number of recent studies, interpretation is still empirical, and the physical mechanism of secondary nucleation itself remains a subject of considerable controversy.

Ice crystals have been observed to grow in aqueous solutions in the form of disks (Harriott, 1967; Sherwood et al., 1969). The intrinsic kinetics of the growth of ice particles suspended in aqueous solutions are not well established, but the growth rate for all but the smallest particles is evidently limited by heat and/or mass transfer (Fernandez and Barduhn, 1967; Harriott, 1967; Margolis et al., 1971).

There is little information on growth rates of ice in agitated sugar solutions at high concentrations. The dendritic growth velocity of ice in unstirred sugar solutions has been measured by Macklin and Ryan (1968), by Lusena (1955), and by Huige and Thijssen (1969a). Growth of ice crystals in agitated glucose solutions was studied by Huige (1972) as a function of crystallizer operating variables.

MEASUREMENT OF NUCLEATION AND GROWTH RATES OF ICE

The low temperatures associated with ice complicate the measurement of crystallization kinetics. Several workers have used optical and photographic counting techniques for ice (Schneider et al., 1969; Cocks et al., 1971; Margolis et al., 1971; Kane et al., 1974). This procedure is slow and tedious, considering the uncertainties involved.

Thermal response is a convenient method for following a crystallization process since the rise in temperature following the onset of crystal nucleation is a direct measure of the mass of the crystals formed. Heubel and Devrainne (1961) employed the thermal technique to follow the crystallization of inorganic salts in aqueous solutions. Sadek (1966) observed the onset of ice nucleation in dilute NaCl solutions by measuring the temperature of the system. Brian and Hales (1969) determined heat transfer coefficients for ice spheres melting in dilute salt solutions by measuring temperature changes. Recently, the thermal technique has been used by Kane et al. (1974) for observing ice nucleation in NaCl solutions and by Schneider (1972) for inferring growth rates of ice crystals in NaCl solutions.

A thermal response technique was used in this study to follow ice crystallization in a well-mixed, batch crystallization cell where subcooling could be closely controlled. Nucleation could be induced in the solution either by raising the level of supersaturation (heterogeneous primary nucleation) or by introducing one or more crystal seeds (secondary nucleation). Experiments were carried out under conditions where the temperature in the absence of crystallization was either constant or linearly decreasing with time.

Energy and mass balances, along with nucleation and growth rate equations, were used to describe this batch crystallization system. Combination of these balances gives the cell equation (Omran, 1972)

$$S_0 - S_t = K_c \int_0^t J(S_\theta) \left\{ \int_\theta^t G(S_\tau) d\tau \right\}^3 d\theta \qquad (1)$$

which relates the change of supersaturation in the cell to the nucleation and growth rate kinetics. J and G are the nucleation and growth rate expressions, respectively, and are considered to be functions of S, both directly and through the effect of other variables, such as mean crystal size, which also respond to S. This equation ignores any effect from growth of the seed crystal(s). Calculations showed that seed-crystal-growth thermal effects were not important (Omran, 1972). The observed relationship between S and t must be corrected for any heat transfer to the surroundings; the method used for doing this is described elsewhere (Omran, 1972).

EXPERIMENTAL APPARATUS AND PROCEDURE

Apparatus

A schematic of the experimental set-up is shown in Figure 1. The crystallization cell was a 200-ml Pyrex beaker (diameter = 5.0 cm, height = 13.0 cm), covered with a Perspex lid, which fits over the lip of the breaker. A glass stirrer in the cell was driven by a variable-speed motor, and had three sets of paddles, which were 2.25 cm in diameter with a 45° pitch. The distance between the paddle centers was 2.75 cm. A 30-gauge iron-Constantan thermocouple was used for monitoring the bath temperature; the leads passed through an opening drilled in the cell cover and connected to a $100 \mu v$ Leeds & Northrup 10-in., full-scale recorder. When crystallization was initiated by seeding, the seeds were introduced through another opening in the cover.

The crystallization cell was immersed in the cooling bath, which was filled with a 50 vol. % solution of glycol in water. The bath itself was a glass vessel, 30 cm in diameter and 20 cm in height, completely insulated except for two sections 5 cm wide which extended to half the depth of the vessel from the top. A source of light was placed at one of those sections, and the cell contents were observed through the other, which was at 90° from it. The bath contained a copper cooling coil, a 250-watt heating element, and a stirrer which kept the bath liquid well mixed. Two possible modes of bath temperature control were available. A constant bath temperature could be held to within 0.05°F using a proportional temperature controller (Cole-Parmer, Versa-Therm, Model 2156). The bath temperature could also be changed linearly with time by means of a NesLab Mode TP-2 temperature programmer, which increased or decreased the temperature of the bath by changing the set point of a mercury contact thermometer. A cooling system supplied methanol at constant temperature to the coil in the bath. In both modes the control action was achieved by control of the heat input to the bath, compensating for the continuous cooling.

Sugar solution concentrations were measured using an Abbé refractometer, and stirring rates were measured using a stroboscope.

Scope of Experiments

Sugars were chosen as solutes in the synthetic solutions because they constitute the major portion of total solutes in natural fruit juices (Tressler and Joslyn, 1970). The experiments reported here were carried out under constant initial subcooling conditions. Crystallization was induced in these experiments by introduction of ice seeds. The effects of the following variables were studied:

Initial subcooling:	0.25-1.00°C
Initial sugar concentration:	0-45 wt. %
Stirring rate:	250-800 rev./min.
Sugar type:	Sucrose, fructose and glucose
Additives:	Pectin and gelatin
Fruit Juices:	Orange and apple

Experiments carried out with an initial uniform rate of temperature decrease are described elsewhere (Omran, 1972).

Procedure

Sugar solutions were prepared using distilled water and Mallinckrodt analytical grade sucrose, fructose, and glucose. The water was filtered before make-up using a No. 50 Whatman filter paper, the solutions were refiltered using the same type of filter paper, and then the concentration was determined. When additives to the solutions were used, a concentrated aqueous solution of the additive was first prepared, and then a small volume of this solution was added to the contents of the cell.

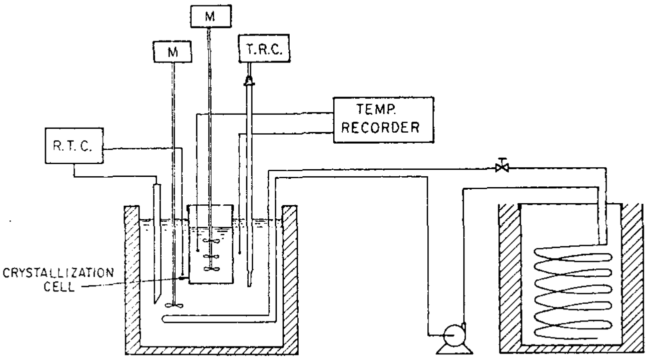

Fig. 1. Experimental apparatus.

Real juices were prepared by diluting commercial frozen concentrate with fitered distilled water. The diluted juice concentrates were not filtered again.

A run was begun by lowering the bath temperature to 5°C, adding the sugar solution to the cell and letting it cool to 5°C. The bath temperature was then lowered at 0.5°C/min. When the cell temperature approached the desired initial subcooling, the bath temperature control was changed to the proportional temperature controller. The solution was held at the desired subcooling for about 10 min, with no evidence of primary nucleation, and then a single ice-crystal seed was introduced by means of a cold spatula. The temperature of the solution was recorded continuously with zero time being taken as the point of introduction of the seed.

The ice seeds were spherical ice particles with a diameter of 2 to 3 mm, formed by freezing water drops from a syringe in liquid nitrogen. Immediately before use as seeds these particles were immersed in a beaker containing water at 0 to 1°C for 30 s, during which time partial melting of the surface was observed.

QUALITATIVE OBSERVATIONS

Several observations were made which are important for interpretation of the nucleation mechanism occurring in the experiments:

1. In the experiments where no seeds were used and the temperature was lowered at a constant rate, the subcoolings required to initiate heterogeneous primary nucleation were much larger than the subcoolings used in the seeded, secondary nucleation experiments. For 0.5°C/min. cooling rate and a stirring rate of 600 rev./min., critical subcoolings ranged from 4 to 7°C for sugar contents up to 45 wt. %.
2. When stirred (600 to 1200 rev./min.) solutions of 0 to 45 wt. % sugar were held at 1°C subcooling for as long as two hours without seeding, there was no evidence of nucleation.
3. At the onset of nucleation in the unseeded, constant-rate-of-subcooling experiments there was a sudden burst of nuclei, and the temperature rose rapidly toward the equilibrium temperature of the solution. On the other hand, nucleation after the addition of seeds in the secondary nucleation experiments occurred at a more uniform and much slower rate.
4. At stirring speeds under 250 rev./min. the seed(s) floated freely on the surface, moving with the solution. Nucleation was much slower.
5. When an untreated ice seed was held stationary at the tip of a syringe in an unstirred solution, no nucleation occurred for subcoolings up to 1°C, but thin platelets grew on the surface of the seed. Touching this stationary seed with the glass stirrer caused some nuclei to appear in solution.

INTERPRETATION OF TEMPERATURE-TIME RESPONSE

Figure 2 shows a typical temperature-time curve for an experimental run in which the subcooling of the solution is held constant before crystallization is started by seeding the solution at $t = 0$. After the introduction of the seed, the temperature of the solution remained constant for a period of time. During this period some nuclei became visible and others kept forming in the solution. This was followed by a rise in the temperature of the solution (end of Stage I). After the early rise (Stage II) the temperature rises in a monotonic fashion (Stage III) until the equilibrium temperature of the solution is reached.

The nucleation rate can be determined from the time required for a specified, small temperature change at the end of Stage I, subject to certain assumptions. The secondary nucleation rate is expressed as

$$J = k_n\, S^i \qquad (2)$$

where the nucleation order i characterizes the dependence of J upon subcooling. The nucleation rate constant k_n is a function of all other variables (solute concentration, seed-crystal size and number, temperature, power input) affecting the nucleation rate. Secondary-nucleation rate expressions often contain a factor for the effect of the crystal-suspension characteristics, for example, a moment of the crystal-size distribution; however, since the seeds were of a uniform size and past history the effect of that factor was not determined, and the effect is included in k_n.

In Stage I diffusion-limited growth of small, spherical crystals is postulated. For the relatively low subcoolings used in this work the high-flux correction to the mass transfer coefficient is not important, and the growth-rate expression for diffusion from a sphere into an infinite medium becomes

$$G = \frac{D}{r}\,\phi\, S \qquad (3)$$

(Brian and Hales, 1969). For pure water growth was taken to be heat transfer controlled ($G = kS/r\Delta H_c$).

Substituting Equations (2) and (3), Equation (1) becomes

$$S_0 - S_t = K_c \int_0^t k_n S_0{}^i \left\{ \int_\theta^t \left[\frac{1}{2} D\phi S_0 \right]^{1/2} \frac{1}{(\tau - \theta)^{1/2}}\, d\tau \right\}^3 d\theta \qquad (4)$$

After time t_0 when a small change δ in temperature has occurred, integration of Equation (4) yields

$$\delta = \frac{4\sqrt{2}}{5} K_c(\phi D)^{3/2}\, k_n (S_0)^{\frac{2i+3}{2}} (t_0)^{5/2} \qquad (5)$$

Since all other variables are known from the experimental conditions, i and k_n can be determined by suitable plotting of the observed values of t_0 vs. S_0. Values of D were taken from existing data for sugar-water solutions (Henrion, 1964; Gladdan and Dole, 1953; Gosting and Morris, 1949; Longsworth, 1952; Chandrasekaran and King, 1972) corrected for temperature (Omran, 1972).

An inherent assumption in Equations (4) and (5) is that the nucleation rate expression applies uniformly throughout Stage I. This in turn requires that the nucleation rate be dominated by the seed crystal and not be significantly affected by the newly formed crystals. The concept of a critical minimum size for the parent crystal to be a source of secondary nuclei was discussed by Heubel and Devrainne (1962) in the context of KNO_3 nucleation. Cayey and Estrin (1967) report that during the course of batch crystallization of $MgSO_4$ from aqueous solution the generated nuclei showed no activity for further nucleation until they had reached a size of about 200 μm. Recently, Cocks et al. (1971) reported results for batch secondary nucleation of ice which show a linear increase in the number of particles with time during the equivalent of Stage I; this corresponds to nucleation dominated by the seed without a significant contribution from new nuclei. On the other hand, Kane et al. (1974) report observing an exponential growth of the number of particles with time during thermal response experiments on ice nucleation. The exponential increase corresponds to the predictions of their long-time solution for the transient response, assuming a size-independent growth rate and proportionality of the secondary nucleation rate to a moment of the crystal-size distribution. The faster-than-linear increase in the number of particles would correspond to new crystals being active centers of nucleation.

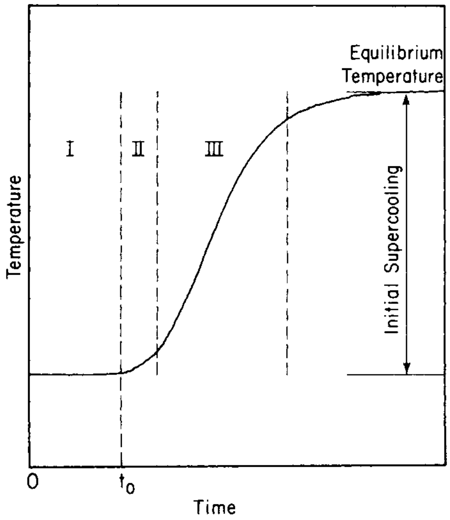

Fig. 2. Temperature-time response curve.

The assumption of secondary nucleation being dominated by the seed during Stage I has been examined further by Stocking (1974) in experiments carried out with more precise thermometry. His experiments verify the proportionality of temperature rise to the 5/2 power of elapsed time, as is predicted by Equation (5). This result corresponds to a linear rather than exponential increase in the number of particles during Stage I and confirms the assumption that nucleation from the seed dominates that portion of the response. It is suggested that Kane et al. may have observed their more-rapid-than-linear increase in particle number at a time later than the induction period (Stage I) of their response.

The assumption of diffusion-limited growth during Stage I may be subject to more question, however. There are indications (Strickland-Constable, 1972; Mullin and Leci, 1972; Cise and Randolph, 1972) that much slower rates prevail for extremely small crystals than are predicted by the diffusion analysis used in Equations (4) and (5), even allowing for surface curvature effects. These slow rates may be the results of kinetic-limited growth, following from a relatively defect-free state. There are no reports of slow growth for ice, however, and Hillig (1958) has shown that the inherent kinetic growth rate for ice is quite large. Even if it occurred, a slow-growth phenomenon would not be important if diffusional growth limitations predominate for nearly all of t_0. If a slow-growth mechanism is an important limit but is solely a function of crystal size rather than degree of supersaturation, then one would expect values of i derived from Equation (5) still to be correct, while the actual values of k_n would be higher than those derived from Equation (5). Similarly, ice crystals are known to grow in the shape of flat disks rather than perfect spheres. This will serve to change the multiplicative constant in Equation (3), thereby affecting k_n to some uniform extent, but it should not affect either the values determined for i or the dependence found for k_n on other variables.

The exponent on S_0 obtained in Equation (5) is critically dependent upon the postulate that the growth rate is linear in subcooling. A variation of growth rate with subcooling to a power (3/2) higher than unity has been reported by Fernandez and Barduhn (1967) for a condition where the rate is still dominated by heat and mass transfer. This presumably results from adaptation of the radius of a growing tip to changes in subcooling in a convective-flow field. That effect would not be expected for growth dominated by molecular diffusion or heat conduction in the surrounding medium [as would occur for small particles and is postulated in Equation (3)] or for growth where turbulent effects outweigh convective flow effects.

KINETICS OF SECONDARY NUCLEATION OF ICE

Figures 3 and 4 show logarithmic plots of t_0 vs. S_0 for sucrose solutions of different concentrations and with different stirring speeds. For these figures and for all other secondary nucleation data t_0 was taken to correspond to $\delta = 0.005$°C temperature rise above the initially constant subcooling. It should be noted that the experimental data tend to form straight lines with slopes near -1. From Equation (5) a slope of -1 for t_0 vs. S_0 would correspond to a nucleation order i of unity. Similar straight lines with slopes near -1 for t_0 vs. S_0 were obtained for solutions of other sugars, for sugar solutions with additives and for fruit juices (Orman, 1972). The intercepts and consequent values of k_n varied considerably, however. The changes in k_n reflect the influence of power input, sugar concentration, and the type of sugar.

The slopes of log t_0 vs. log S_0 were determined by linear regression analysis, and the relationship

$$i = \frac{5(-\text{slope}) - 3}{2} \qquad (6)$$

derived from Equation (5) was used to obtain i. Equation (5) was then employed to obtain the indicated value of k_n. The results are summarized in Table 1.

Effect of Subcooling

Within the standard deviation of the data the order of nucleation is independent of the sugar concentration, the type of sugar, and the stirring rate. The values of i range from 1.14 to 1.40, and a value of 1.25 will be taken as representative of the order of ice nucleation for subsequent analysis of the data. A recent study (Brian et al., 1974) gives a value of i equal to 1.75 for secondary nucleation of ice in dilute sodium chloride solutions. Estrin (1970) reports a first-order dependence of ice nucleation on the supersaturation for secondary nucleation in sodium chloride solutions. Huige (1972) concluded that secondary nucleation of ice from glucose solutions was second order.

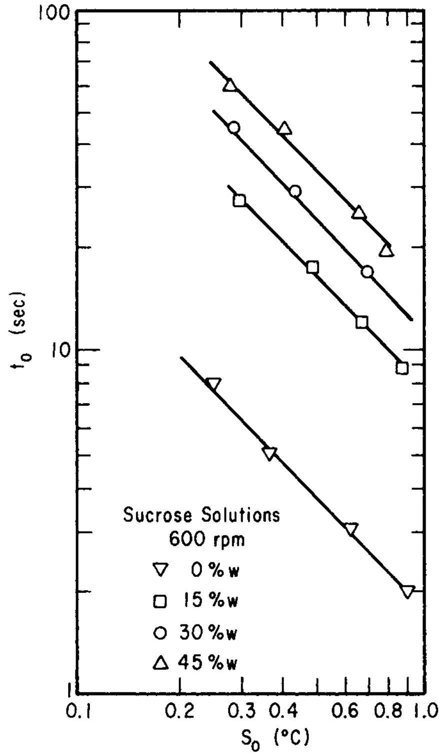

Fig. 3. Effect of sugar concentration on t_0 vs. S_0.

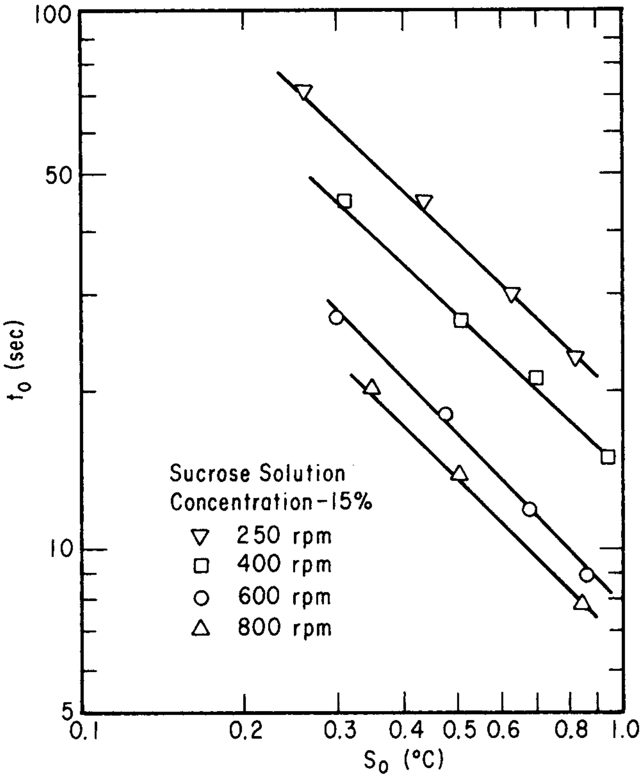

Fig. 4. Effect of stirring rate on t_0 vs. S_0.

TABLE 1. EFFECT OF EXPERIMENTAL VARIABLES ON NUCLEATION RATE PARAMETERS

Range of subcoolings: 0.25-1.00°C

Experimental variable			Nucleation Parameters	
Type of sugar	Conc., $\%_w$	Stirring rate, rev./min.	i	$k_n \times 10^{-2}$ Nuclei/cm^3 s(°C)^i
	pure water	600	1.20	0.41
A. Sucrose	15	600	1.25	8.47
Sucrose	30	600	1.28	49.59
Sucrose	45	600	1.25	200.00
B. Glucose	15	600	1.28	6.75
Fructose	15	600	1.30	7.00
C. Sucrose	15	250	1.40	1.15
Sucrose	15	400	1.14	2.03
Sucrose	15	600	1.25	8.47
Sucrose	15	800	1.33	12.35
D. Orange Juice	30	600	1.20	27.77
Apple Juice	30	600	1.37	20.50

It appears that the order of the nucleation is a characteristic property of the substance crystallizing out, in this case ice. The low-order dependence on subcooling is similar to the behavior reported in the literature for secondary nucleation of other substances (Clontz and McCabe, 1971).

Effect of Power Input

The power input per unit mass ϵ in a stirred system is a logical way of expressing the overall energy dissipation level in that system and thereby interpreting the effect of stirring rates on nucleation rates. Also, transport coefficients to spherical particles supsended in agitated liquids have been successfully correlated using power inputs (Brian et al., 1969), and it is helpful if nucleation and growth can be related to the same variable.

Power inputs to the system at various stirring rates were calculated from the correlations of Nagata et al. (1964) for unbaffled vessels. For 15% sucrose solutions stirring rates from 250 to 800 rev./min. correspond to a range of power input per unit mass of 200 to 3250 cm^2/s^3. For a supersaturation of 0.063 g/cm^3, which is equivalent to a subcooling of 0.5°C, Figure 5 shows the effect of ϵ on k_n derived from the data of Figure 4 and other, intermediate stirring speeds, with i fixed at 1.25. k_n initially increases with about the first power of ϵ, but at higher values of ϵ the increase appears to taper off. For KCl the nucleation rate obtained from continuous crystallizer data was found by Estrin (1970) to be proportional to the first power of ϵ, which was varied over a limited range, from 30,000 to 50,000 cm^2/s^3. A recent study (Johnson et al., 1972) on contact nucleation caused by impact indicates a trend similar to that shown in Figure 5. The number of nuclei formed after contacting a single crystal with another crystal or solid increased with impact energy and finally levelled off at high values of impact energy. At low levels of impact energy the number of nuclei formed showed a first-order dependence on the contact energy.

Effect of Sugar Concentration

From Figure 3 and Table 1 it is apparent that the nucleation rate constant is a strong function of the sugar concentration. To determine this dependence more explicitly, k_n for various concentrations was determined by interpolating to the same degree of supersaturation and power input to the system. The details of these calculations are given elsewhere (Omran, 1972). Figure 6 shows the dependence of k_n on the sucrose concentration in the solution at a supersaturation of 0.04 g/cc and a power input per unit mass of 2000 cm^2/s^3. A strong dependence is clearly indicated. The nucleation rate observed for pure water (Table 1 and Figure 6) agrees reasonably well with an extrapolation of the observations of Sherwood et al. (1969) for 3.5 wt. % NaCl solutions.

A possible explanation of the high nucleation rate constants in concentrated sugar solutions is increased ordering in the solution as the sugar content is increased. The sucrose-water system exhibits considerable hydrogen bonding (Walrafen, 1966), and probably this phenomenon affects the ordering of water molecules enough to influence the phase transformation. It should be noted, however, that the conclusion regarding the effect of sugar concentration upon k_n does rely upon the assumption of diffusion-controlled growth and the values reported for the dependence of diffusivity upon concentration.

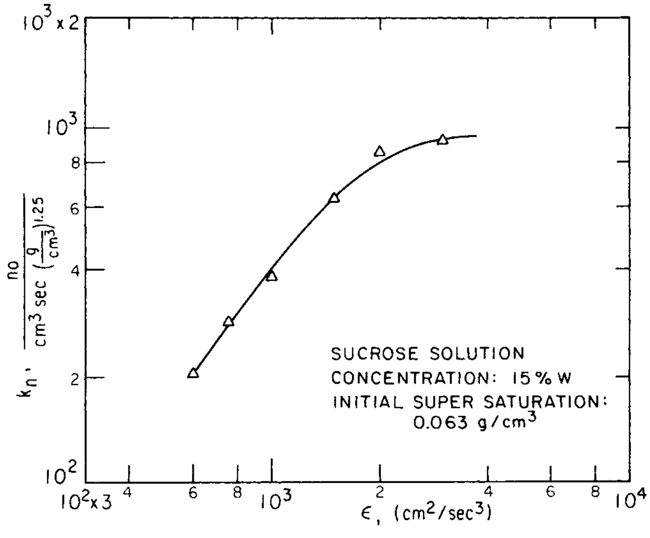

Fig. 5. Effect of specific power input on nucleation rate constant.

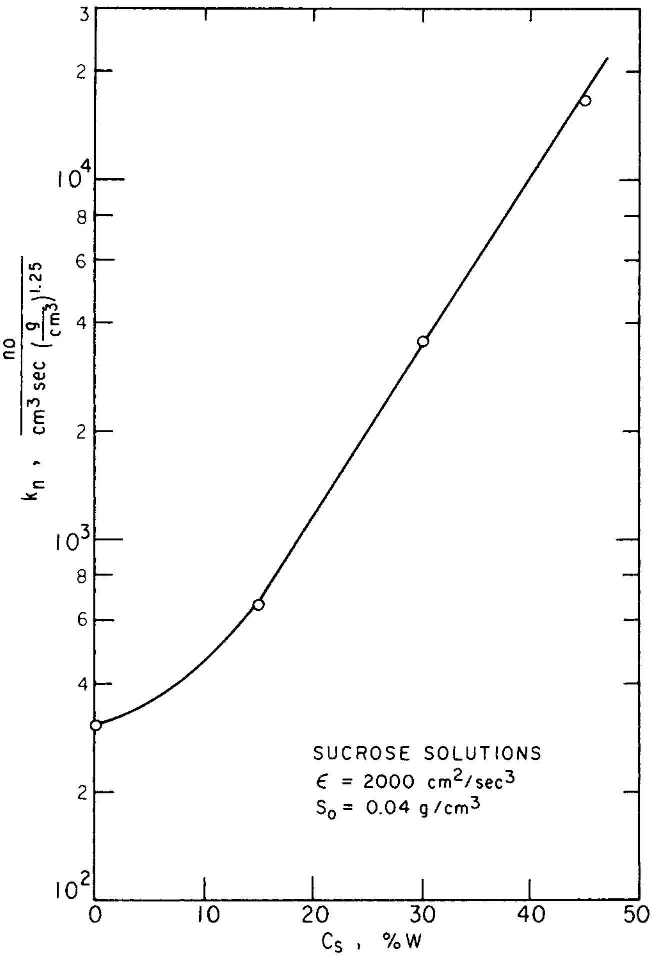

Fig. 6. Effect of concentration on nucleation rate constant.

Effect of the Sugar Type

In addition to sucrose, fructose and glucose are important constituents of the dissolved solids in fruit juices. As is shown in Table 1, for 15% solutions under the same conditions of supersaturation and agitation, the nucleation rate constants for these two monosaccharides are about 20% less than those for the disaccharide, sucrose.

Effect of Additives

Because of the interfacial phenomena involved in the phase transformation, additives that affect the surface properties of the crystals and other structures in the solution can influence nucleation rates.

Pectic compounds are present in most fruit juices, and therefore the effect of pectin on ice crystallization is of particular interest. The effect of added soluble pectin was tested with a 15% sucrose solution, stirred at 600 rev./min. and with an initial subcooling of 0.66°C. Figure 7 shows the effect of increasing amounts of pectin on the nucleation rate constant. The results are represented as the ratio of the nucleation rate constant in the presence of pectin to that for a sucrose solution containing no pectin. It is assumed that the pectin content does not alter D. There is a decrease in the nucleation rate constant as the amount of pectin is increased, levelling off at about 0.50 g pectin/100 ml solution. A similar inhibiting influence on

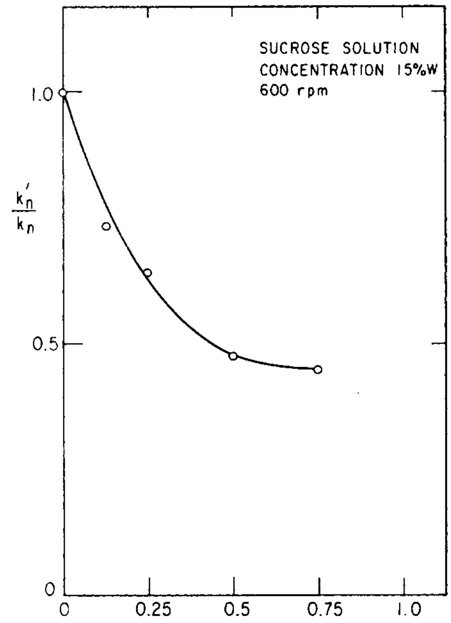

Fig. 7. Effect of pectin on nucleation rate constant.

nucleation was observed in the heterogeneous nucleation experiments and for gelatin, both in the presence and absence of ice seeds (Omran, 1972).

GROWTH OF ICE CRYSTALS

The growth of ice crystals in agitated aqueous salt solutions has been reported to be limited by mass and heat transfer in the solution adjacent to the crystal interface (Harriott, 1967; Margolis et al., 1971). Transport-limited growth can also be expected for ice crystallization from sugar solutions. Moreover, it can readily be shown that mass transfer of the sugar should dominate over heat transfer in determining ice crystal growth rates in solutions containing 15 wt. % or more sugar (Omran, 1972).

An analysis of Stage III of the response has been carried out under the assumption that the response is dominated entirely by the growth of the oldest and therefore largest crystals (Omran, 1972). It is further postulated that the number of large crystals contributing in this way to the response remains constant at some effective value during this portion of the response. The results of this analysis are in agreement with the postulate that growth rates are proportional to the first power of subcooling and also give mass transfer coefficients conforming to the general behavior expected for mass transfer by turbulent diffusion to dispersed particles. If the correlation of Brian et al. (1969) is postulated as valid, then the responses observed in Stage III give quantitative agreement if the effective number of crystals dominating the growth is 10 to 15% of the number formed during Stage I, with all these effective crystals being taken to have been formed at time zero.

The analysis of Kane et al. (1974), under their assumptions, leads to a self-preserving crystal-size distribution at long times during a transient secondary-nucleation response. In that case they indicate that the response of Stage III is more sensitive to nucleation kinetics than to growth kinetics. Since the questions of the conditions under which new crystals contribute to secondary nucleation and the quantitative way in which they do contribute are unresolved, it is not certain that the assumption of growth of an effective, constant number of crystals dominating the response in Stage III is viable.

CRYSTALLIZATION OF ICE IN FRUIT JUICES

Since sugars constitute the major portion of the dissolved material in fruit juices, it is reasonable to endeavor to relate the ice nucleation and growth properties of real juices to those of model solutions composed of three simple sugars—sucrose, glucose, and fructose.

Nucleation parameters for orange juice and apple juice concentrates are shown in Table 1. The results may be compared with the values of k_n and i for 30% sucrose solution at 600 rev./min. and with extrapolations of the results for glucose and fructose solutions. The sugars in orange juice bear a ratio sucrose:glucose:fructose of approximately 64:18:18, while those in apple juice are in the approximate ratio 14:14:72 (Tressler and Joslyn, 1970). The nucleation orders are seen to be about the same as for the model sugar solutions, and the values of k_n for the juices are about a factor of 2 lower than those for the equivalent sugar solution. This lower value of k_n may be associated with the natural pectin content.

PROCESSING IMPLICATIONS

The rate of secondary nucleation of ice is not as sensitive to the supersaturation level as is that for primary nucleation. Over the range of conditions covered in this study it has approximately the same order of dependence on supersaturation as does the growth process. As long as this behavior holds, there will be no great benefits of crystal size gained by operating freeze concentrators at extremely low subcoolings, as has often been recommended by others. It is, of course, imperative to maintain the subcooling at all points in the crystallizer below the critical limit for primary heterogeneous nucleation (4 to 7°C in this study) in order to prevent massive nucleation and a consequent marked reduction in crystal size. If there is a critical lower limit to the subcooling below which secondary nucleation ceases to be operative but which is still large enough for growth of large crystals to occur, then seeded crystallizers operating below this limiting subcooling could be attractive for producing large ice crystals. The existence of such a lower limit was not explored in this work.

The presence of pectins or gelatin reduces the rate of secondary nucleation of ice in sugar solutions. Pectins are available cheaply from natural sources (for example, citrus peel) and may be of use as additives for some juices containing little or no pectin, so as to inhibit secondary nucleation and thereby lead to larger ice crystals. From the standpoint of producing large ice crystals, it would thereby be undesirable to depectinize fruit juices before freeze concentration.

Under fixed conditions of power input and subcooling, much smaller ice crystals are grown when the content of dissolved sugars is high. This result was apparent visually in the present experiments and relates to the fact that the growth rate decreases because of the reduction in diffusivity as the sugar content increases, while the secondary nucleation rate actually increases with increasing sugar content. This behavior points to a severe disadvantage of small ice crystal size in freeze concentration processes which use recycle of the liquid concentrate (see, for example, Dooley and Lineberry, 1966), since concentrate recycle increases the dissolved solids content of the liquid in the freezer. Recycle of concentrate, where employed, is designed to overcome the limitation on the maximum volume fraction of ice which can be formed in the freezer. Another way of overcoming that problem which should lead to larger ice crystal sizes is to use staged successive crystallizers, each forming and removing a portion of the ice.

If the ice crystal size does not change detrimentally, the loss of entrained concentrate with the product ice can be reduced in staged freeze concentration by moving the ice from stage to stage countercurrent to the liquid (Crosby, 1962; Ganiaris, 1966). In such a process it may be desirable to recycle some concentrate within each stage so as to remain below the maximum operable volume fraction ice in each stage without too many stages being required. Also, in a process of this sort the initial ice crystals are formed from the most concentrated solution; this will reduce the crystal size in that stage and will lead to a large number of crystals and a consequent smaller crystal size for the product ice from the process. This drawback can be overcome (Omran, 1972) by recycling part of the product ice crystals back to the most concentrated stage to serve as seeds. The seeds will serve to reduce the subcooling in that stage. This will reduce the number of new nuclei formed, promote melting of very small crystals through the surface curvature effect, and lead to a larger crystal size for the product ice. This modification is illustrated in Figure 8.

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NOTATION

C_i = interfacial solute concentration
C_p = specific heat of solution
D = diffusion coefficient
G = linear growth rate of a crystal; $G(S_t) = G$ as a function of S_t
ΔH_c = heat of crystallization of ice
i = nucleation order, Equation (2)
J = nucleation rate per unit volume
k_n = nucleation rate constant, Equation (2)
k_v = shape factor for crystal volume
K_c = crystallization cell constant $= \dfrac{\Delta H_c \rho_c k_v}{\rho_s C_p}$
r = crystal radius
S = subcooling (temperature difference)
S_0 = initial subcooling
t = time
t_0 = duration of constant supersaturation stage
T = solution temperature
T_0 = saturation temperature

Greek Letters

δ = temperature change at end of constant supersaturation stage
• = power input per unit mass
ϕ = constant [Equation (2)] $= \dfrac{\rho_s}{\rho_c C_i} \cdot \dfrac{dC}{dT^0}$, where $\dfrac{dC}{dT^0}$ is the slope of freezing pt. curve at T
ρ_c = density of crystal
ρ_s = density of solution
θ, τ = time variables

Subscripts

t = function of t

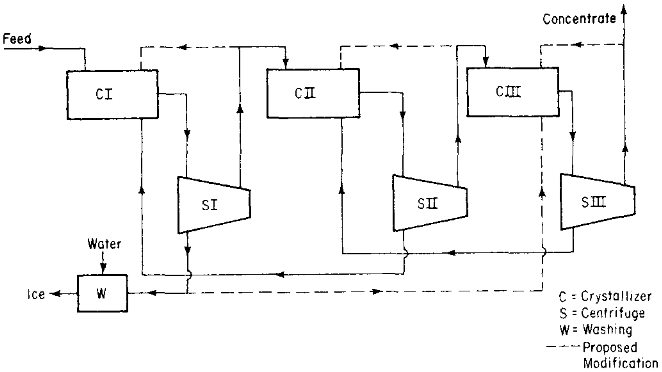

Fig. 8. Multistage countercurrent recycle freeze concentration process.

θ = function of θ
τ = function of τ

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Joule-Thomson Coefficients of Argon-Carbon Dioxide Mixtures

Adiabatic Joule-Thomson coefficients are presented for argon and two argon-carbon dioxide mixtures (46.4% CO_2 and 75.4% CO_2) in the single-phase part of the range: $-120 < T < 110°C$, $P < 190$ atm. Results are analyzed in terms of the virial equation (including terms to account for the quadrupole moment of CO_2), several forms of the Redlich-Kwong equation, and the Benedict-Webb-Rubin equation. In general, the best results were obtained by the Redlich-Kwong equation as modified by Barner et al. (1966).

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SCOPE

Methods of predicting the thermodynamic properties of mixtures, and thus phase and chemical equilibria, are essential if design work on new systems is not to remain tied to specific laboratory studies. The Joule-Thomson coefficient, which is zero for ideal gases, is a particularly rigorous test of predictive theories. This coefficient μ is defined as $(\partial T/\partial p)_H$; it is usually determined by the numerical differentiation of experimental curves of temperature vs. pressure obtained by the expansion of a gas to successively lower pressures through an adiabatic valve or porous plug. Precise measurements of ΔT and Δp make it possible to avoid the inherently inaccurate numerical or graphical differentiation by doing the experiment differentially. The pressure drop is confined to less than two atmospheres, for which ΔT is typically about one degree Celsius.

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