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# Effects of supersaturation and temperature on nucleation and crystal growth in a MSMPR crystallizer

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A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemical Engineering and Nuclear Engineering Major: Chemical Engineering

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#### INTRODUCTION

Crystallization can be defined as the formation of solid particles within a homogeneous phase. The solid particles can be formed from the vapor phase, as in the case of snow. They can be formed from a liquid melt, as in freezing of water or the manufacture of large single crystals. The solid can also be formed from liquid solutions.

This last case of crystallization from solution is very important industrially because of the wide variety of materials that is marketed in a crystalline form. The main benefit of the operation is that a crystal formed from an impure solution can itself be pure. It also affords a practical method of obtaining pure chemical substances in a satisfactory condition for packaging and storing. As a result, crystallization is used in a wide range of industries from the production of bulk fertilizers to the preparation of fine chemicals and drugs.

In industrial operations the yield, purity, size, and shape of the crystals produced are important factors. Many times, for example in sugar production, it is especially necessary that the crystals be of uniform size. Uniform size is desirable for appearance, for ease in filtering and washing, and for consistent behavior in use. Uniformity of size also minimizes caking in the package.

Attainment of the desired size distribution is one of the main objectives in the design and operation of industrial crystallizers. It is the relationship between the competing kinetic rates of nucleation and crystal growth that determines the size distribution of the product. For many years achieving the correct relationship concerning the kinetics

was very much an art rather than a science. In the last ten to twenty years, however, there has been a great deal of research effort in an attempt to better understand the kinetics of crystallization. To understand the kinetics it is necessary to understand the two mechanisms of crystallization; namely, crystal nucleation and crystal growth. These two mechanisms compete for solute in terms of their respective dependence on supersaturation. The classical theories of nucleation do not predict the observed nucleation rates in continuous crystallization from solution.

A considerable amount of theoretical work has been done in the area of continuous, mixed-suspension, mixed-product-removal crystallizers. This type of crystallizer is like many used in industrial processes. The analysis technique of using a crystal population balance provides a convenient way to study the kinetics of nucleation and growth in a mixed-suspension crystallizer.

Since both nucleation and growth are direct functions of the level of supersaturation in the crystallizer, to fully understand the kinetics of crystallization it is important to know what level of supersaturation exists. Normally the magnitude of supersaturation is quite small in a MSMPR cooling crystallizer and this makes the measurement of small changes in concentration very difficult. In most research to date, the magnitude of supersaturation has been inferred from the resulting crystal size distribution rather than the more desirable situation of predicting the crystal size distribution from knowledge of the level of supersaturation. Also, relationships between the level of supersaturation and the birth and growth rates have not been available.

The objectives of this work are therefore twofold. First of all to show that refractive index methods offer a way of continually monitoring the level of supersaturation in a MSMFR crystallizer. Secondly, to develop the needed relationships relating the birth and growth rates of crystals to the level of supersaturation and to the crystallizer temperature.

#### LITERATURE REVIEW

#### Solutions and Solubility

A solution may be defined as a homogeneous mixture of two or more substances. The substances may be in any of the three states of matter-gas, liquid, or solid. The solution is usually divided into two parts, the solutes and the solvents. It is conventional to call the component in excess the solvent. For a solution composed of an inorganic salt dissolved in water the water is the solvent and the salt the solute.

The solubility of a solute in a given solvent is usually stated as the parts by weight per part by weight of solvent. If a hydrated selt is dissolved in water, the solute concentration should always refer to the anhydrous salt. This will avoid difficulty when more than one hydrated form exists over the temperature range being considered. Solubility of salts in water is very temperature dependent, the solubility increasing as the temperature increases for most but not all common salts.

Saturation is an equilibrium condition. If a solution is saturated with respect to a solid, it is in equilibrium with the solid phase. A solution containing more dissolved solid than that represented by saturation condition is said to be supersaturated. Likewise if less dissolved solid than the equilibrium amount is present the solution is undersaturated.

If a saturated solution is cooled slowly without disturbance it can be made to show appreciable degrees of supersaturation. The state of supersaturation is an essential feature of all crystallization operations.

The terms "labile" (unstable) and "metastable" supersaturation were first introduced by Wilhelm Ostwald (46). These terms refer to supersaturated solutions in which spontaneous deposition of solid, in the absence of nuclei, will and will not occur, respectively.

Mullin (38) describes research carried out by Miers into the relationship between supersaturation and spontaneous crystallization. Mullin expresses the results of Miers in a solubility-supersolubility diagram like that in Figure 1. The solid line represents the solubility curve and the dotted line the supersolubility curve. This supersolubility curve represents temperatures and concentrations at which spontaneous crystallization occurs. These two curves divide the diagram into three zones:

(1) The stable zone where crystallization is impossible.

(2) The metastable zone where spontaneous crystallization is improbable. Growth of seed crystals will occur in this zone.
(3) The labile zone where spontaneous crystallization is probable, but not certain.

Supersaturation may in general be induced by: (a) evaporating some solvent, (b) cooling a saturated solution, and (c) reducing the solubility by addition of a third component. The first two are most widely used in industrial type crystallizers--referred to as evaporative, vacuum, or cooling crystallizers.

Ting and McCabe (59) observed that the supersolubility curve is influenced by (a) cooling rate, (b) stirring rate, (c) amount of seed crystals, and (d) size of the seed crystals.



Figure 1. Solubility-supersolubility diagram

## Nucleation

Nucleation represents the first step in crystallization. Nucleation may be defined as the formation of solid particles of solute capable of further growth. Mullin (38) and Nielson (43) both give detailed discussions of the subject. Also, for theoretical discussions of the surface chemistry involved there is the text of Zettlemoyer (63).

Nucleation may occur spontaneously or it may be artificially induced. These two cases are often referred to as homogeneous and heterogeneous nucleation, respectively. Deciding on whether a system is undergoing homogeneous or heterogeneous nucleation may be quite difficult. Mullin (38) divides all nucleation into two types he calls "primary" and "secondary". Primary nucleation refers to all cases of nucleation, homogeneous or heterogeneous, in systems that do not contain crystals. Secondary nucleation refers to cases where nucleation is induced by crystals present in the supersaturated system. He therefore gives the following breakdown:



Secondary nucleation can occur by initial breeding, needle breeding, polycrystalline breeding, or collision breeding.

#### Primary nucleation

<u>Homogeneous nucleation</u> The classical theory of nucleation is based on thermodynamics and developed in particular on the formation of a water droplet from the vapor phase. This work, first presented by Gibbs (24) and Volmer (62), has been modified and extended by many workers.

The free energy changes associated with the process of homogeneous nucleation are presented by Mullin (38) as follows. The over-all excess free energy,  $\Delta G$ , between a small solid particle of solute and the solute in solution is equal to the sum of the surface excess free energy,  $\Delta G_g$ , and the volume excess free energy,  $\Delta G_T$ .  $\Delta G_g$  represents the excess free energy between the surface of the particle and the bulk of the particle and is a positive quantity, the magnitude of which is proportional to  $r^2$ .  $\Delta G_T$  is the excess free energy between a very large particle  $(r=\infty)$ and the solute in solution; and in a supersaturated solution it is a negative quantity proportional to  $r^3$ . Thus

$$\Delta G = \Delta G_{s} + \Delta G_{T}$$
  
= 4 \pi r^2 \for + 4/3 \pi r^3 \Delta G\_{v} (1)

where  $\nabla$  is the surface energy and  $\Delta G_v$  is the free energy change of the transformation per unit volume. If  $\Delta G$  from Equation 1 is plotted as a function of r, the nucleus radius, it is seen that  $\Delta G$  passes through a maximum (see Figure 2). This maximum value,  $\Delta G_{crit}$ , corresponds to the critical nucleus,  $r_c$ , and for a spherical cluster is obtained by maximizing Equation 1:

$$\frac{d\Delta G}{dr} = 8\pi r \nabla + 4\pi r^2 \Delta G_V = 0 \tag{2}$$



SIZE OF NUCLEUS, r

Figure 2. Free energy diagram for nucleation explaining the existence of a "critical nucleus" (from Mullin (38))

$$\mathbf{r}_{c} = \frac{-2\nabla}{\Delta G_{v}} \tag{3}$$

where  $\Delta G_v$  is a negative quantity. Combining Equations 1 and 3 the critical over-all excess free energy is given by:

$$\Delta G_{\text{crit}} = \frac{16 \pi r^3}{3(\Delta G_r)^2} = \frac{4 \pi r r^2}{3}$$
(4)

This shows that the behavior of a newly created crystal nucleus in a supersaturated solution depends on its size; it can either grow or redissolve. The process which it undergoes should result in the decrease in the free energy of the system. The critical radius,  $r_c$ , therefore, represents the minimum size of a stable nucleus. If the particle is smaller than  $r_c$  it will dissolve because only in this way can it achieve a reduction in its free energy. Likewise, if a particle is larger than  $r_c$  it will continue to grow. The growth being due to an effort to minimize the free energy.

Nielsen (43) discusses a more empirical approach to the nucleation process. He proposes a relationship between the induction period, I (the time interval between mixing two reacting solutions and the appearance of the crystals), and the initial concentration, c, of the supersaturated solution:

$$I = Ke^{1-p}$$
(5)

where K is a constant and p is the number of molecules needed to form a critical nucleus. It is suggested that the induction period, which depends on the supersaturation, represents the time needed for a nucleus of critical size to be assembled. The means of observation is controlling

or

when measuring I. Therefore this approach presents a problem.

<u>Heterogeneous nucleation</u> For true homogeneous nucleation to occur the solution must be void of all foreign particles such as dust, seed crystals, etc. The production of an impurity-free system is virtually impossible. Therefore it is generally accepted that true examples of spontaneous nucleation are rarely encountered. Most nucleation of the primary type takes place as heterogeneous nucleation.

The presence of a foreign body can induce nucleation at degrees of supercooling lower than those required for spontaneous nucleation. Therefore the over-all energy change associated with the formation of a critical nucleus under heterogeneous conditions must be less than the corresponding free energy change associated with homogeneous nucleation.

Fletcher (19) applied classical nucleation theory to the growth of crystals on small foreign particles of different shapes. He developed general relationships for predicting the behavior of heteronuclei in metastable systems.

## Secondary muleation

Secondary nucleation occurs when there are solute crystals present in a supersaturated solution. Secondary nucleation is caused by interaction between crystals or between crystals and other solid objects such as the vessel walls. Strickland-Constable (55) divides secondary nucleation into four general types. "Initial" breeding occurs if untreated crystals are put in a supersaturated solution. It is caused by crystalline dust being swept off the newly introduced crystals. "Needle" breeding occurs at high levels of supersaturation when needles

or spikes called dendrites grow on the ends of crystals. The dendrites are then broken off by fluid shear. "Polycrystalline" breeding is the fragmentation of a weak polycrystalline mass. It occurs when crystals are made up of small randomly oriented crystals that are broken by agitation in the crystallizer. Ting and McCabe (59) found that if crystals are free to collide with the walls of the vessel or with other crystals that fresh nuclei are readily produced at very low supersaturations. This fourth type of secondary nucleation, called "collision" breeding is thought to be the predominant nucleation mechanism in industrial crystallizers.

In the past few years secondary nucleation has become a very active area of research. Melia and Moffitt (34) found that the number of secondary nuclei produced in the presence of a parent crystal of solute is dependent on the degree of agitation of the solution, the rate of cooling, and the degree of supercooling of the solution, but is independent of the number, size, surface characteristics, and chemical nature (provided overgrowth of solute can occur) of parent crystal. Working with  $K_2SO_4$ , Cise and Randolph (16) found secondary nucleation increases with supersaturation, seed crystal mass and size, and stirring rate. They also say nucleation depends on crystal habit. At the same size and mass concentration, crystals of polycrystalline habit generated more secondary nuclei than crystals of elongated, mono-crystalline habit. Comparison of data on both habits indicated secondary nucleation occurs on the favored face.

Larson, Timm, and Wolff (31), working with ammonium alum and ammonium

sulphate in a continuously operated mixed-suspension crystallizer, found that secondary nucleation related to the magma density.

In studying the effects of additives in a continuous crystallizer, Shor and Larson (54) found that the nucleation rate could be changed by changing the surface characteristics of the parent crystal.

Cayey and Estrin (15) confirmed the importance of cooling rate and supersaturation, but they also observed an induction period with seeded solutions of MgSO<sub>h</sub> in a pilot-scale agitated batch crystallizer.

Mullin and Leci (39) studied the seeding of citric acid solutions in an agitated vessel. Secondary nucleation was observed to occur in a series of pulses, mainly during the latent period. The nucleation rate decreased with an increase in seed size or in the number of seeds of a given size.

Because collision breeding appears to be the primary type of nucleation in most industrial crystallizers, determination of the mechanism associated with it has been the topic of much recent work (3,6,16,17).

#### Crystal Growth

There are three main steps in a crystallization process: (1) formation of a supersaturated solution; (2) nucleation of particles; and (3) growth of the particles. Growth and nucleation normally occur simultaneously in industrial crystallizers. However, it has been observed that in some systems there are certain levels of supersaturation where growth will occur and not nucleation. It also has been seen that in certain cases even at levels of supersaturation which will normally

support nucleation, there will be no nucleation unless seed crystals are introduced.

There are several texts which deal with the growth of crystals. Among the books which include large sections on the subject are those by Mullin (38), Nielsen (43), Van Hook (61), and Ohara and Reid (45). For a more comprehensive account of the historical development the reader is referred to Buckley (10) or Strickland-Constable (55).

As Mullin (38) points out in his book, many attempts have been made to explain the mechanism and rate of crystal growth. He uses the three general headings of "surface energy", "adsorption layer", and "diffusion" to classify the many theories.

The surface energy theories are based on the work of Gibbs (24). He noted that an isolated droplet of fluid is most stable when its surface free energy, and thus its area, is a minimum. He then suggested that crystal growth might be considered as a special case of this principle: the total free energy of a crystal in equilibrium with its surroundings at constant temperature and pressure would be a minimum for a given volume. Therefore, if a crystal is allowed to grow in a supersaturated solution, the development of the various faces should be in such a manner as to ensure that the whole crystal has a minimum total surface free energy for a given volume. Mullin (38) points out that, although there have been modifications to this original idea of Gibbs, so far there is no general acceptance of the surface energy theories because there is little quantitative evidence to support them.

The adsorption layer theory of crystal growth was first stated by

Volmer (62). Volmer's theory is based on thermodynamic reasoning. When units of the crystallizing substance arrive at the crystal face they aren't immediately integrated into the lattice, but merely lose one degree of freedom. They are still free to move across the face by surface diffusion. Atoms, ions or molecules will link into the lattice in positions where the attractive forces are greatest; i.e. where the greatest concentration of similar molecules are located. Under ideal conditions this step-wise build-up will continue until a layer is complete. Then before a new layer can be started a new monolayer island must be created. Both Buckley (10) and Mullin (38) give accounts of how this theory has been modified by people like Brandes, Stranskii, and Kossel. But all of the modifications had the same problem. That was the initiation of a new layer on the surface. Frank (20) and later Burton, Cabrera, and Frank (12) solved this problem by introducing the idea of screw dislocations. Most crystals contain dislocations, which cause steps on the crystal surface. As pointed out be Frank (20) the screw dislocation eliminates the necessity for surface nucleation in the adsorption layer theories.

The third class of crystallization theories, the diffusion theories, have their origin in the work of Noyes and Whitney (44). They viewed the deposition of solid on the crystal surface as essentially a diffusional process. They also assumed that crystallization and dissolution were reverse processes, and the rates of both were governed by the concentration difference between the surface and bulk of the solution.

The crystallization equation proposed was

$$\frac{dm}{dt} = K_{m}A(c-c^{*})$$
(6)

where m  $\equiv$  mass of solid deposited in time t; A = surface area of crystal; c = solute concentration in supersaturated solution; c<sup>\*</sup> = equilibrium saturation concentration; and  $K_m$  = coefficient of mass transfer.

Based on the assumption that there would be a thin stagnant film of the liquid adjacent to the crystal face, through which the solute would have to diffuse, Nernst (42) modified Equation 6 to

$$\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}\mathbf{t}} = \frac{\mathbf{D}}{\mathbf{s}} \mathbf{A}(\mathbf{c} - \mathbf{c}^*) \tag{7}$$

where D = diffusion coefficient of solute, and S = length of diffusion path or film thickness.

Equation 7 implies an almost infinite growth rate as \$, the film thickness, gets very small, i.e. when crystals are very small. This is not observed. Also observations show that crystallization and dissolution are not necessarily reverse processes. Based on these facts Berthoud (8) proposed a modification to the diffusion theory. He suggested that crystal growth was a two-step process. The first step is a diffusion process with solute moving from the bulk of the fluid to the solid surface. The second step is a first-order "reaction" step where the molecules arrange themselves into the crystal lattice. These two steps can then be represented by the equations:

$$\frac{dm}{dt} = K_{d}A(c-c_{i}) \qquad (diffusion) \qquad (8)$$

and

$$\frac{dm}{dt} = K_r A(c_i - c^*) \quad (reaction) \tag{9}$$

where  $K_d$  = coefficient of mass transfer by diffusion;  $K_r$  = rate constant for the surface reaction; and  $c_i$  = solute concentration in the solution at the crystal-solution interface.

Equations 8 and 9 can be combined by eliminating  $c_i$ . Then an over-all driving force,  $c-c^*$ , can be used to give a general equation for crystal growth

$$\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}\mathbf{t}} = K_{\mathrm{G}} \mathbf{A} (\mathbf{c} - \mathbf{c}^{*})^{\mathrm{q}}$$
(10)

where  $K_{G}$  is an over-all crystal growth coefficient. The exponent q is usually referred to as the order of the over-all crystal growth process.

The diffusion theories cannot be reconciled with the adsorption layer and dislocation theories. Although it is acknowledged that the diffusion theories have grave deficiencies (e.g. they cannot explain layer growth or the faceting of crystals), it is convenient to measure and report growth rates in diffusional terms. The utilization of the mathematics of mass transfer processes make this the preferred approach, from the chemical engineers' point of view, despite its many limitations.

If  $K_{\rm G}$  in Equation 10 above is independent of size, the crystal remains geometrically similar as it grows. McCabe's  $\Delta$ L Law, McCabe (33), states that all geometrically similar crystals of the same material suspended in the same supersaturated solution grow at the same rate regardless of their size.

As pointed out by Misra (37), when the diffusion process is the rate controlling step the growth rate becomes dependent upon the rate at

which solute arrives at the surface. The transfer rate is then related to fluid dynamics around the crystal and crystal size plays a role in determining the growth rate. Violation of the  $\triangle L$  Law can then be expected in these cases. Then Equation 10 must be replaced with one of the form

$$\frac{dm}{dt} = K_{G}A(e-e^{*})^{q} f(L)$$
(11)

where f(L) is a function of the crystal size. Various forms of the function f(L) have been proposed:

Bransom (9):  $f(L) = L^b$ Canning and Randolph (14):  $f(L) = (1+a_1L)$ Abegg, Stevens, and Larson (1):  $f(L) = (1+aL)^b$ 

## Types of Crystallizers

Most crystallizers can be divided into three general types: evaporative, cooling, and precipitation. Evaporative crystallizers usually operate under a vacuum and depend on the removal of solvent by evaporation, causing the deposition of the solute. Systems that have flat solubility curves are best handled with this type of crystallizer. A cooling crystallizer takes a hot concentrated feed solution and cools it by refrigeration (also sometimes by evaporation). The solute is deposited due to the reduced solubility at the lower crystallizer temperature. Systems exhibiting steep solubility curves can be handled in cooling crystallizers. In precipitation crystallizers supersaturation is produced by addition of a third component in which the solute is insoluble or by producing an insoluble reaction product with a chemical reaction. Industrial crystallizers may be of any of the above types. For additional information on industrial crystallization equipment the reader is referred to Bamforth (2), Bennett (7), Saeman (51), or Mullin (38).

Laboratory crystallizers are usually of the cooling or precipitation type. Much of the work has been done in batch equipment because of easier operation and control. However in the last decade much more emphasis has been placed on continuous crystallizers. Continuous crystallization is widely used in industrial applications and its use in the laboratory is an attempt to obtain kinetic data applicable to industrial systems. Batch and continuous systems are both important in laboratory work and the type of system selected depends on the investigation being performed.

# Crystal Population Balance

Crystallizers of the continuous mixed-suspension, mixed-productremoval type are widely used in both industry and the laboratory. Such crystallizers behave as though they are perfectly mixed. Therefore, for any arbitrarily small element of volume in the crystallizer, a full and uniform particle-size continuum can be assumed to exist. Also the distribution of the product crystals is the same as the distribution in the volume of the crystallizer. For laboratory crystallizers the constraints and conditions permitting this type of operation are relatively easy to attain. Although perfect mixing is rarely achieved in industrial crystallizers, many industrial units do approximate these constraints.

The following is an application of the population balance theory to the steady-state operation of a MSMPR (mixed-suspension, mixed-productremoval) crystallizer following the presentation of Randolph and Larson (50). The constraints and assumptions used in the analysis are as follows:

- (a) perfect mixing
- (b) no classification at withdrawal
- (c) breakage assumed negligible
- (d) uniform shape factor.

Steady-state operation requires that the feed rate, composition, and temperature remain constant, and that the crystallizer volume and temperature remain constant.

The population density, n, is defined by

$$\lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} = \frac{dN}{dL} = n$$
(12)

where N is the number of crystals in the size range  $\triangle L$  per unit volume of suspension. The number of crystals in the size range  $L_1$  to  $L_2$  is then given by

$$\mathbf{N} = \int_{L_1}^{L_2} d\mathbf{L}.$$
 (13)

The number of crystals in a given size range must be conserved with no accumulation if the system is operating at steady-state. For a number balance on an arbitrary size range  $L_1$  to  $L_2$  in the volume V of the crystallizer we have:

Input to size range  $\Delta L =$ Output from size range  $\Delta L$  or,

$$Q_{1}\bar{n}_{1}\Delta L\Delta t + VG_{1}n_{1}\Delta t = Q\bar{n}\Delta L\Delta t + VG_{2}n_{2}\Delta t \qquad (14)$$

where

Q<sub>i</sub> = volumetric flow rate in (volume/time) n
i = average population density in the range L<sub>1</sub> to L<sub>2</sub> in the feed (numbers/length-volume) ΔL = L<sub>2</sub>-L<sub>1</sub> (length) Δt = increment of time (time) V = volume of crystallizer (volume) G<sub>1</sub> = growth rate of crystals of size L<sub>1</sub> (length/time) n<sub>1</sub> = population density of crystals of size L<sub>1</sub> (numbers/length-volume) n<sub>2</sub> = population density of crystals of size L<sub>2</sub> (numbers/length-volume) G<sub>2</sub> = growth rate of crystals of size L<sub>2</sub> (length/time) Q = volumetric flow rate out (volume/time) Dividing thru by Δt and rearranging,

$$V(G_{2}n_{2}-G_{1}n_{1}) = (Q_{1}\vec{n}_{1}-Q\vec{n})\Delta L$$
(15)

Letting  $\Delta L$  approach zero so that the average values of n become point values; Equation 15 becomes

$$\frac{\mathrm{Vd}(\mathrm{Gn})}{\mathrm{dL}} = Q_{1}n_{1}-Qn \qquad (16)$$

In there are no crystals in the feed solution, n. =0, and

$$(V/Q) d(Gn)/dL + n = 0$$
 (17)

Equation 17 represents the population balance for a MSMPR crystallizer. It may be simplified further if, for the system being studied, McCabe's  $\triangle$  L Law holds. Then G is not a function of L.

$$G \mathcal{Z}(dn/dL) + n = 0 \tag{18}$$

where  $\mathcal{Z}$ , the drawdown time, equals V/Q. Equation 18 can be integrated,

letting n<sup>o</sup> denote the population density of zero-size particles or nuclei,

$$S_{n^{0}}^{n} \quad \frac{dn}{n} = - \int_{0}^{L} \quad \frac{dL}{Gz} \tag{19}$$

which gives

 $n = n^{\circ} \exp(-L/G \gamma)$ (20)

Equation 20 is the fundamental relationship giving the number distribution of the crystal product obtained from a MSMFR crystallizer operated under the given conditions. A plot of log n versus L gives a straight line with an intercept at L = 0 of n<sup>o</sup> and a slope of  $-1/G \mathcal{T}$ . Therefore, under the constraints and assumptions made earlier, if an experiment is carried out at a residence time,  $\mathcal{T}$ , the crystal growth rate, G, and the nuclei density, n<sup>o</sup>, can be determined from measurement of the population density, n, as a function of size, L.

Besides the text by Randolph and Larson (50) other references (5, 30,48,52) also deal with a mathematical approach to the particle size distribution. Canning and Randolph (14) derive an empirical model to describe crystallization systems where growth rate increases with increasing crystal size in violation of McCabe's  $\Delta L$  Law. Canning (13) points out that test work with industrial crystallization systems indicates that results often deviate from the basic design theory. But he goes on to point out that an awareness of these deviations can make it possible to use data that otherwise might be discarded.

Relation between Crystal Size Distribution and Kinetics

Kinetic information is important to both the designer and operator of a crystallizer. Knowing the kinetics of a system is the key to understanding the factors influencing crystal size distribution (CSD). By using the population balance it is possible to obtain insight on how crystallization kinetics affects CSD.

To date, the attempts to find a satisfactory theoretical relation for nucleation rate,  $B^{\circ}$ , have not been too successful. Nielsen (43) notes that a power-law function of supersaturation does a good job of approximating the theoretical expressions. Randolph and Larson (50) have had considerable success with the empirical expression

$$B^{o} = K_{1}(c-c_{s})^{m} = K_{1}s^{m}$$
 (21)

where s is the supersaturation, c-c<sub>s</sub>.

The growth rate, G, can also be expressed as a power-law function of supersaturation.

$$G = K_{\rho} B^{n}$$
 (22)

By definition,

$$B^{\circ} = \frac{dN}{dt} = \frac{dN}{dt} \Big|_{L=0} = \left(\frac{dN}{dL}\right) \Big|_{L=0} \left(\frac{dL}{dt}\right)$$
(23)

Therefore, the nucleation may be expressed in terms of the growth rate and the population density of nuclei by

$$B^{O} = n^{O}G$$
 (24)

If growth is a linear function of supersaturation then n = 1. Equations 21 and 22 may then be combined by elimination of s to give

$$B^{o} = K_{\overline{N}} G^{\overline{m}}$$
 (25)

Or by combining Equations 24 and 25

$$n^{\circ} = K_{N}^{\circ}$$
(26)

Equation 26 relates the population density of nuclei to the crystallization kinetics.

It was shown earlier that by steady state operation of a MSMFR crystallizer, the population balance enables the experimenter to determine  $n^0$  and G at a given residence time. By operating a MSMFR crystallizer at different supersaturation levels the kinetic order can be obtained from Equation 26.

A great many parameters of crystallizer operation have been found to influence the crystallization kinetics and the CSD. Some of the more important parameters are temperature, level of supersaturation, impurities, suspension density, and stirrer speed. Several investigators (22,29,32,45,49,54) have reported the effects of one or more of these parameters.

# Importance of Supersaturation in Understanding the Operation of a MSMPR Crystallizer

Supersaturation is the driving force for the crystallization process. It was shown earlier that both nucleation and crystal growth can be stated as power-law functions of supersaturation.

$$B^{o} = K_{l} s^{m}$$
 (21)

$$G = K_{2}s^{n}$$
 (22)

Because nucleation and growth are occurring simultaneously and in the same environment, they are dependent on the same level of supersaturation.

Therefore Equations 21 and 22 can be combined to give

$$B^{o} = K_{N}G^{(m/r)} = K_{N}G^{i}$$
 (27)

This represents a more general form of Equation 25 where n = 1. i then represents the order of nucleation with respect to growth. While n is the order of growth with respect to supersaturation and m is the order of nucleation with respect to supersaturation.

The level of supersaturation in a MSMPR crystallizer often markedly affects the CSD of the product. An analysis of the effect can be made by following the work of Randolph and Larson (50). In their analysis they assume that the suspension density (mass of solids per volume of slurry) can be fixed at a given level regardless of the holding time.

As was shown previously for the MSMPR crystallizer, where crystal growth is not size-dependent, the population balance yields

$$n = n^{o} \exp(-L/G \mathcal{E})$$
(20)

Randolph and Larson (50) also show that a mass balance with one mixed withdrawal point gives

$$G = M_{\rm T}/6K_{\rm r} \mathcal{T}An^{\rm O} (G\mathcal{T})^{\rm S}$$
<sup>(28)</sup>

where

G = growth rate  $M_T$  = suspension density  $K_v$  = volumetric shape factor  $\mathcal{T}$  = residence or drawdown time  $n^{\circ}$  = population density of nuclei  $\beta$  = density

The effects of supersaturation on CSD can be observed by considering two crystallizations carried out at the same temperature but at different supersaturations. A convenient way to assure different supersaturations is to operate at different residence times while maintaining the same suspension density.

For crystallizations 1 and 2 operating to produce the same suspension density, Mr, Equation 28 gives

$$M_{T} = 6K_{v} \rho n_{1}^{o} (G_{1} \tau_{1})^{4} = 6K_{v} \rho n_{2}^{o} (G_{2} \tau_{2})^{4}$$
(29)

or

$$\frac{\mathbf{n}_{2}^{O}}{\mathbf{n}_{1}^{O}} = \left(\frac{\mathbf{G}_{1} \cdot \mathbf{\tau}_{1}}{\mathbf{G}_{2} \cdot \mathbf{\tau}_{2}}\right)^{4}$$
(30)

Using Equations 26 and 27 to eliminate  $G_1$  and  $G_2$  gives

$$\frac{n_{0}^{2}}{n_{1}^{0}} = \left(\frac{\gamma_{1}}{\gamma_{2}}\right)^{\frac{4(1-1)}{(1+3)}}$$
(31)

and combining Equations 30 and 26 to eliminate n° gives

$$\frac{G_2}{G_1} = \left(\frac{\gamma}{\tau_2}\right)^{\frac{4}{(1+3)}}$$
(32)

As pointed out by Randolph and Larson (50), examination of Equations 20, 31, and 32 for  $\gamma_1 > \gamma_2$  gives rise to the following observations:

(a) When the kinetic order i is equal to one, the CSD is unaffected by the supersaturation level, i.e.,  $n_1^{\alpha} = n_2^{\alpha}$ ,  $G_1 \geq G_2 \geq Z_2$ , although growth rates increase in proportion with  $(\geq_1/2)^{\alpha}$ .

(b) When the kinetic order i is greater than one, say three, n° increases with a decrease in holding time (increase in supersaturation) by a factor  $(\gamma_1/\gamma_2)$  to the 4/3 power and G again increases but to a lesser degree than when i = 1, namely by the factor  $(\gamma_1/\gamma_2)$  to the 2/3 power. The net result is smaller crystal size at shorter holding times (higher supersaturation).

(c) When kinetic order is less than one, the crystal size increases with increase in supersaturation.

In summary, it appears that the higher the supersaturation, the smaller the crystal size for systems which exhibit kinetic orders greater than one. Also, the higher the order of nucleation, the more difficult it will be to produce crystals of large size.

## Effects of Secondary Nucleation

Many crystallization systems exhibit secondary nucleation effects. When secondary nucleation is present it is necessary to use a kinetic model which accounts for the nuclei formation directly related to the solids in suspension.  $K_1$  used in Equation 21 must then be defined as:

$$\mathbf{K}_{1} = \mathbf{K}_{1}^{\prime} \mathbf{M}_{T}^{j} \tag{33}$$

In this case  $K_1^{i}$  accounts for the temperature effects in the system and  $M_T^{j}$  accounts for the secondary nucleation effects. Equation 21 then becomes:

$$B^{o} = K_{1}^{\prime} M_{T}^{j} s^{m}$$
(34)

Likewise when there are secondary nucleation effects  $K_{N}$  should be defined as:

$$K_{N} = K_{N}^{'} M_{T}^{j}$$
(35)

Then Equation 27 becomes:

$$B^{o} = K_{N}' M_{T}^{j} G^{(m/n)} = K_{N}' M_{T}^{j} G^{i}$$
 (36)

## Measurement of Supersaturation

If the concentration of a solution can be measured, and the equilibrium saturation concentration at the same temperature is known, it is a simple calculation to determine the supersaturation of the solution. There are many ways of measuring supersaturation, but not all of these are readily applicable to practical use.

Solution concentration may be determined directly by analysis, or indirectly by measuring some property of the system that is a sensitive function of concentration. The direct methods are either gravimetric determination or chemical analysis of the solution. Properties frequently chosen for indirect methods include density, viscosity, refractive index and electrical conductivity. As discussed by Mullin (38), these properties can often be measured with high precision, especially if the measurement is made under carefully controlled conditions in the laboratory. However, for the operation of a continuous crystallizer the demand is usually for an <u>in situ</u> method, preferably one capable of continuous operation. Under these conditions problems may arise from the temperature dependence of the property being measured. In general, density and refractive index are the least temperature-sensitive properties.

#### Refractive index

Critical angle refractometry is based on the physical fact that light travels at different speeds in different mediums. Refractive index is defined as the ratio of the velocity of light in a sample medium to the velocity in a reference medium. The most common reference medium is air. Gibb (23) gives the following relationship for the refractive index of a transparent isotropic medium:

$$N_{v} = \sin i_{a} / \sin r$$
(37)

where is and r are the angles of incidence and refraction, respectively.

Both angles are measured from a plane normal to the surface of the medium in question.



Figure 3. Angles of Incidence and Refraction

Although  $N_v$  is a relative measurement (based on the reference medium) it is the value most often found in the literature. In general, the refractive index of a substance decreases with increasing temperature and with increasing wave length of the illuminating ray. Unless otherwise stated, standard temperature is assumed to be 20°C and the standard wave length 589 mp (sodium D line). Because refractive index is a function of temperature, it is important to control this variable. The variation of refractive index with temperature is very nearly linear over a limited range.

## Use of refractive index in crystallization measurements

The first reported use of measuring supersaturation of a solution by measuring changes in refractive index appears to be the studies by Miers (35) in 1904 and by Miers and Issac (36). In this study a solution of sodium nitrate and water was cooled. Measurements of refractive index changed linearly until the solution reached its saturation temperature. At the saturation temperature the refractive index levelled off until a shower of nuclei appeared. Upon appearance of the nuclei the refractive index began to decrease and continued to do so until the system reached equilibrium. The change in refractive index was proportional to the change in the solution concentration.

Since that time refractive index measurements have been used to measure the supersaturation at different points along the surface of a growing crystal (11) and to measure concentration changes in a batch system (39,41).

Jenkins (25) used a Zeiss dipping refractometer in his work. He used the refractive index to follow concentration changes of a solution. He noted that the method had distinct advantages over some other methods, the main advantage being it is quite rapid. He observed that with his method the process liberated heat, slightly increasing the temperature of the solution as shown by thermometric measurements. This had two effects; (1) slowing down crystallization by reducing the supersaturation, and (2) decreasing the refractive index of the solution, thus <u>apparently</u> increasing the rate of the process. These effects partially neutralized each other but the second was greater, so the rate is apparently increased in the earlier, and retarded in the later part of the run. To obtain accurate determinations in very rapid runs corrections had to be made for this effect.

Klekar (28) used a differential refractometer in his measurements on a MSMPR crystallizer. The supersaturation was directly measured from a continuous sampling of the contents of the crystallizer.
#### THEORETICAL DEVELOPMENT

Objectives of Present Work

The objectives of the present work are twofold. The first is to demonstrate that the measurement of refractive index is a feasible in situ method of continuously monitoring the supersaturation in a MSMFR crystallizer. As was mentioned earlier the level of supersaturation in a crystallizer represents the magnitude of the driving force for the two mechanisms of crystallization, nucleation and growth. To fully understand the kinetics of crystallization and the resultant CSD a method of measuring the crystallizer supersaturation is needed. From the work done in the past it appears that refractive index measurement is a very promising method of indirectly monitoring the supersaturation.

The second objective rests on the success of the first. For, if the continuous measurement of supersaturation in a MSMFR crystallizer is possible, then there is much additional information about the crystallization process which may be investigated. Not the least of which is the kinetic relationships between the nucleation and growth rate and the level of supersaturation. If the supersaturation can be measured directly this provides a chance to check out the power-law relationships for growth and nucleation. If the power-law relations are correct, then temperature effects can also be studied. The complete kinetic relations as functions of both supersaturation and temperature would then be obtainable.

## Supersaturation Relationships

The functional relationships given earlier are:

$$B^{o} = K_{1}s^{m}$$
 (21)

for nucleation and,

$$G = K_2 s^n$$
 (22)

for growth. If a MSMPR crystallizer is operated at the same conditions except for varying residence times (which will change the supersaturation level), then log-log plots of nucleation rate versus supersaturation and growth rate versus supersaturation can be made. If these plots are linear then Equations 21 and 22 are verified. From the slopes the parameters m and n may be calculated. The constants  $K_1$  and  $K_2$  may be computed from the intercepts of the log-log plots.

As a further check a log-log plot of nucleation versus growth may be prepared. If Equation 27 is correct,

$$B^{o} = K_{R}G^{(m/n)} = K_{N}G^{1}$$
 (27)

then this plot should also be linear. And the slope and intercept may be used to calculate i and  $K_{\rm N}$ , respectively. Since i = m/n and  $K_{\rm N} = K_{\rm l}/(K_2)^{(m/n)}$  these values should check out with the earlier calculated values.

If linear log-log plots aren't obtained then relationships different from the power-law functions of supersaturation would be needed to describe the crystallization kinetics. Development of such relationships should be greatly aided by having an actual measurement of the supersaturation level.

If the measurement of supersaturation in an operating crystallizer

is possible then effects of other parameters of the crystallization system may also be studied. By varying such parameters as temperature, stirring rate, and impurity levels it would be possible to see how this affected the overall kinetics and the order of growth and nucleation (m and n)

### Effects of Temperature

To obtain the complete kinetic relationships for crystal growth and nucleation it is advantageous to study the temperature effects. A study of Equations 21 and 22 reveals that in each case there are three parameters that may vary with temperature. They are: the rate coefficient,  $K_1$  or  $K_2$ , the power parameter, m or n, and, indirectly, the supersaturation, s. Supersaturation is not directly temperaturedependent, but may be supported at different levels for different temperatures due to the combined kinetics of growth and nucleation at the temperatures involved. Analogous to the kinetic relations for chemical reactions, it would not be expected that the power values, m and n, would change with the temperature of growth or nucleation. This leaves only the rate coefficients,  $K_1$  for nucleation and  $K_2$  for growth, as temperature dependent parameters in the power-law functions.

As noted by Genck (21), both of these coefficients might reasonably be expected to follow an Arrhenius-type temperature dependency. Assuming this type of dependency the following equations are applicable:

$$K_{1} = k_{\gamma} \exp(-E_{N}/RT)$$
(38)

and

$$K_{\rho} = k_{\rho} \exp(-E_{\rho}/RT)$$
(39)

where  $k_1$  and  $k_2$  are frequency factors; and  $E_N$  and  $E_G$  are activation energies for nucleation and growth, respectively. The activation energies may be calculated by operating the crystallizer at different temperature levels. A different  $K_1'$  and  $K_2$  value can be calculated for each temperature using the methods described above. Then semi-log plots of  $K_1'$  and  $K_2$  versus 1/T can be made. If Arrhenius-type dependency is indeed followed the semi-log plots will yield straight lines. The slopes of such plots can then be used to calculate the values  $E_N$  and  $E_G$ . While the intercepts yield values for  $k_1$  and  $k_2$ . Complete kinetic relationships for nucleation and growth will then be available:

$$B^{O}/M_{T}^{j} = k_{l} \exp(-E_{N}/RT) s^{m}$$
(40)

and

$$G = k_{\rho} \exp(-E_{\rho}/RT) s^{n}$$
(41)

#### EXPERIMENTAL

### Equipment

A simplified flow diagram of the equipment used is shown in Figure 4. The equipment can be divided into five primary subsystems: (1) the crystallizer, (2) the feed supply system, (3) the withdrawal system, (4) the coolant system, and (5) the sampling and instrumentation equipment.

#### Crystallizer

The crystallizer used in the present work was a mixed-suspension mixed-product-removal cooling crystallizer. It was a plexiglass cylindrical vessel equipped with three baffles and a propeller type agitator. The overall volume of the vessel was approximately 14 liters, however the active volume used was 10 liters. A partial draft tube was achieved by the helical stainless steel cooling coil which was immersed in the crystallizer. The agitator which was vertically mounted in the center of the vessel was powered by a Model V-7 Lightnin Mixer. The direction of flow was down the center and up the outside annular space between the cooling coil and vessel wall. The agitator speed was adjustable to provide good mixing of the mother liquor and crystal suspension.

Previous studies (4,18) have shown that it is important to insure isokinetic withdrawal in a MSMPR crystallizer. Therefore the product withdrawal tube was placed parallel to the circulation flow and the withdrawal was made in the direction of flow.



Figure 4. Flow diagram for the crystallization system

A sketch of the crystallizer is shown in Figure 5.

#### Feed supply system

The feed solution was prepared and stored in a 55 gallon stainless steel drum. The outside of the tank was insulated. An electrical immersion type tank heater was used to heat the solution. The heater was thermostat controlled to maintain the desired temperature in the feed tank throughout the experimental runs. The feed solution was mixed by a three-bladed impeller powered by a 3/4 horsepower Lightnin mixing motor.

The feed solution was pumped to the crystallizer by an Eastern 1/15 horsepower centrifugal pump that was controlled by a Variac variable powerstat. Also included in the feed line were a rotameter to monitor the flow rate, a needle valve for flow control, and a 0.35 micron Pall Disposable Filter Assembly. The feed inlet to the crystallizer was from above with discharge into the center of the vessel.

A heat exchanger was also incorporated into the feed line to help maintain temperature control. The thermostat control on the immersion heater in the feed drum produced some fluctuations in the temperature of the feed solution. A small glass heat exchanger was used to decrease the amplitude of these fluctuations and therefore maintain better temperature control in the crystallizer. The feed solution was fed through a single spiral tube. Water from a constant temperature bath was passed through the shell side of the heat exchanger.



Figure 5. Crystallizer vessel

### Withdrawal system

The average outflow from the crystallizer was too small to withdraw continuously without size classification. Therefore intermittent product withdrawal was used so that high withdrawal velocities could be achieved. To accomplish the intermittent withdrawal, a Sargent Laboratory Relay was used in conjunction with an adjustable time delay unit. A copper electrode was used to sense the liquid level. The probe was set at the maximum desired liquid level for the vessel. When the liquid level reached the height of the probe it would complete a circuit and activate the relay-time delay system. This system would then start the withdrawal pump which ran for a preset length of time until the time delay shut off. Withdrawal times of 2, 10, or 15 seconds could be used. The withdrawal pump was a Jabsco self-priming, centrifugal pump. The slurry withdrawal tubing between the crystallizer and the pump was 3/8 inch i.d. stainless steel. This tubing was wrapped with an electricalheat tape to provide some initial heating of the slurry before it was returned to the feed tank.

## Coolant system

The coolant used was a mixture of water and ethylene glycol. The mixture was stored in another insulated 55 gallon stainless steel drum. The coolant supply was kept at a constant temperature by a Blue M Refrigeration Unit which had a maximum capacity of 350 watts. The coolant was pumped through the stainless steel coil in the crystallizer by an Eastern 1/15 horsepower centrifugal pump. The coolant flow rate was controlled by a Variac connected to the pump.

# Sampling and instrumentation

The differential refractometer used in the experiments was a Waters Associates Model R-404. The unit has two cells, one for the reference material and one for the sample. The refractometer measures the deflection of a light beam resulting from the difference in refractive indices between the sample and the reference liquid. The instrument is capable of measuring changes of  $1 \times 10^{-7}$  RI units. The output signal from the refractometer is in millivolts. With the use of calibration curves the output may be converted to refractive index units, or in the case of the present work to concentration units. The output was recorded by using a Beckman Instruments Offner Type strip chart recorder. To insure thermal accuracy of the refractometer a Haake FJ circulating water bath was used to keep the temperature of the refractometer constant.

The sample withdrawal port was in the side of the crystallizer as shown in Figure 5. The opening was covered with a fine mesh screen with an aperture of 75 microns to prevent crystals from leaving the vessel. Small 1/8 inch plastic tubing was used for the flow to the refractometer. A Masterflex variable speed drive pump with solid state controller unit was used in the sampling line between the crystallizer and the refractometer to provide a constant flow rate. Masterflex pump head number 7014 with a range of 7.5 to 150 ml/min was used.

To provide a reference solution a "saturator" was installed inside the crystallizer. This was a Pyrex tube 1 and 1/8 inch in diameter and 7 inches long. The bottom of the tube was sealed using a Millipore

Swinnex-25 filter unit with a 1/10 inch outlet. Plastic tubing was connected to the outlet to allow liquid withdrawal. The filter unit contained 25 mm filter paper with a maximum opening of 0.85 micron. The top of the "saturator" cylinder was left open but mounting was such that the top was above the liquid level in the crystallizer.

The "saturator" was filled approximately half full with  $KNO_3$  crystals and then filled with distilled water. The arrangement provided a supply of saturated  $KNO_3$  solution at the same temperature as the crystallizer and thus represented a reference for supersaturation measurements. Withdrawal from the "saturator" to the reference cell was periodic and was accomplished using a second Masterflex pump. If the liquid in the "saturator" became depleted during an experimental run it could be momentarily lowered below the liquid level of the crystallizer and refilled with the crystal slurry. The bed of undissolved  $KNO_3$  crystals was more than ample to ensure a saturated solution at all times during the run.

For those experimental runs where the crystallizer temperature was greater than the room temperature an electrical heating tape was used on all sampling lines to prevent in-line crystallization and flow blockage.

### Calibration of Refractometer

Before the refractometer can be used in the experiments it must be calibrated. The refractometer measures the difference between the refractive indices of a sample solution and a reference solution.

Calibration allows the refractive index difference to be converted to a concentration difference, a value of supersaturation.

Solutions of known concentration were prepared by adding known weights of KNO<sub>2</sub> to known weights of water. Each of these known solutions was then used in the reference cell of the refractometer to produce a calibration curve. Each reference solution was handled in the same manner and each resulted in a calibration curve. Successive known weights of water were added to each reference solution. After each water addition a small amount was placed in the sample side of the refractometer and a reading made. At all steps of the procedure the solution concentration was calculated by gravimetric methods. The results were plotted as calibration curves. The slopes of the calibration curves were calculated to give the change in refractive index per change in concentration,  $\Delta R.I./\Delta Conc.$  This therefore gives the relationship between refractometer reading and supersaturation. A total of eight different calibration curves were obtained, each with a different reference concentration. The curves all had linear slopes for a small change in concentration, and the curves were all nearly parallel. The calibration curves are shown in Figure 6. The resulting slopes are given in Table 1. Averaging the values given in Table 1 yields a calibration value of -175 µRI/mssu.

Figure 6. Refractive index calibration curves for KN03

- $\Delta$  Run 4c  $\Delta = \operatorname{Run} 4e$   $\circ - \operatorname{Run} 5e$   $\diamond - \operatorname{Run} 6e$   $\diamond - \operatorname{Run} 7e$   $\Box - \operatorname{Run} 8e$   $\circ - \operatorname{Run} 9e$   $\diamond - \operatorname{Run} 10e$   $\times - \operatorname{Run} 11e$



Run number	Slope, µRI/mssu <sup>8</sup>
4c	-177
5e	-203
бе	-162
7c	-180
8c	-210
9 <b>c</b>	-143
10c	-169
llc	-154

Table 1. Slopes of the refractometer calibration curves

```
^{8} µRI = 10<sup>-6</sup> refractive index units
```

mssu = millisupersaturation unit or  $10^{-3}$  grams KNO<sub>3</sub>/gram H<sub>2</sub>O.

#### Procedure

# Feed preparation

In preparing the feed solution reagent grade potassium nitrate was used. Feed of the desired concentration was prepared by dissolving the required weight of salt in distilled water. For each series of experimental runs the feed concentration was selected to be that of a saturated solution at a temperature one to two degrees centigrade above the crystallizer temperature being used. During the crystallizer operation the feed solution was maintained at a temperature at least three degrees above the saturation temperature to ensure that all crystals were dissolved.

At the beginning of each temperature series approximately 25 to

35 gallons of feed solution was prepared. This amount of solution was sufficient to keep the heating coil submerged and to redissolve the crystals that were recycled in the product slurry. The feed concentration was checked by hydrometer and/or gravimetric methods at the beginning of each experimental run. Periodically over a series of runs small additions of make-up water were required to replace water lost from the feed tank by evaporation. In all cases it was attempted to keep the feed concentration approximately the same for a series of runs. Coolant system

Refrigeration was provided by a Blue M portable cooling unit equipped with a 1/3 h.p. motor and having a maximum capacity of 350 watts. The coil of the cooling unit was placed in a mixture of ethylene glycol and water (approximately 25 gallons). The refrigeration unit was turned on prior to the beginning of a run so that the coolant solution could be cooled to a temperature  $10^{\circ}$ C below the operating level of the crystallizer. The time required for this initial cooling down depended upon the coolant temperature desired and varied from a couple of hours to overnight.

During an experimental run the coolant was circulated through the stainless steel coil inside the crystallizer and returned to the storage drum by means of a centrifugal pump connected to a Variac powerstat. Steady state temperature in the crystallizer was maintained by varying the coolant flow with changes in the powerstat setting. At the beginning of a run the temperature of the coolant mixture would rise until steady state operation was achieved. At steady state there was usually only a

one or two degree centigrade temperature difference between the coolant and the crystallizer.

Due to the limited heat removal capacity of the Blue M unit the coolant sometimes continued to rise in temperature at short residence times. It was then necessary to increase the flow rate of the coolant by adjustment of the powerstat. This procedure changed the amount of coolant available to carry away heat and was continued throughout the run as needed. In these runs it was necessary to start with a lower initial temperature of coolant.

### Operation of crystallization system

The feed solution was stirred and heated to the required temperature. The coolant mixture was cooled to the desired temperature. The feed flow and coolant flow were started at the same time. The feed flow rate was adjusted to give the proper flow rate. The feed solution was pumped from the drum through a final filter, a control valve, a rotameter, and into the crystallizer. When the crystallizer was filled the vessel stirrer was started and adjusted to a speed of 2000 RFM. Also the operation of the level controller and the product removal pump was initiated. The coolant flow rate was adjusted to bring the crystallizer to the desired temperature level. During the run adjustments were made in the feed and coolant flow rates to maintain a constant residence time and crystallizer temperature.

The crystallizer was operated for a minimum of eight residence times to achieve steady state. Then supersaturation measurements were started. The supersaturation data was collected for two to six residence times.

Sampling of the crystal suspension was then initiated. Two samples of the crystal suspension were obtained approximately one half hour apart.

After all of the data for a run had been collected the feed and coolant pumps were shut off, the crystallizer was emptied, and then filled with distilled water.

## Sampling and filtration of crystals

A graduated vacuum flask was employed to withdraw samples of the crystal suspension from the operating crystallizer. This method resulted in quick removal of the sample which prevented size classification and led to consistency in the method of sempling. The size of the samples varied depending upon the suspension density but were generally in the range of 400 to 800 milliliters in size. Samples withdrawn from various locations in the crystallizer for the same run revealed similar size distributions. This offers supporting evidence for the assumption of perfect mixing in the operating crystallizer.

After obtaining the sample it was important that the mother liquor be filtered off as quickly as possible to prevent new crystallization or the dissolving of existing crystals. Therefore the samples were immediately filtered by suction after being withdrawn from the crystallizer. Either Whatman No. 5 or Whatman No. 41 filter paper was used in a 9 cm. Coors filter. After being filtered the crystals were washed at least three times with mother liquor and once with a final wash of acetone. Suction was continued until the crystals were dry enough for easy removal. Then they were placed on a paper and allowed to air dry for at least

a day before being sized. When the crystals were dry their total weight was recorded for use in calculating the suspension density.

The crystals were separated and sized using a set of 3-inch, U. S. Standard sieves. Initial agitation was provided by a Ro-Tap testing sieve shaker. Each sample was shaken for an hour. It was found that better separation occurred when additional shaking was provided by hand. Sieves of the following mesh and aperture sizes were used (the apertures expressed in millimeters are in parentheses): 16(1.19), 18(1.00), 20(0.841), 25(0.710), 30(0.600), 35(0.500), 40(0.420), 45 (0.355), 50(0.300), 60(0.250), 70(0.212), 80(0.180), 100(0.150), 120 (0.125), 140(0.106), 170(0.090), 200(0.075), and the pan. The crystals were then removed from each screen and placed on weighing papers. The weight of each size fraction was then found using a Mettler Balance. From the various weights the population density could be calculated. Supersaturation measurement

While the crystallizer was coming to steady state the refractometer was turned on to warm up and the constant temperature bath was brought up to the desired temperature. Also the saturator was filled with solution from the crystallizer. Before collecting data the recorder was turned on and the refractometer was zeroed using distilled water in both cells. When the crystallizer had reached steady state the sampling pumps for both the saturator and the mother liquor were started. The recorder was started and supersaturation readings were taken for a minimum of two residence times. Flow from the crystallizer was intermittent

however. Initially the reference side of the refractometer was flushed and filled using solution from the saturator. Then this flow was shut off with the reference cell of the refractometer then containing stagnant liquid. If and when the temperature in the crystallizer changed by more than  $0.1^{\circ}$ C the saturator pump was again started and the reference cell filled with new solution from the saturator. If the saturator was emptied during a run then it was refilled from the top with crystallizer solution. As solution was passed through the saturator the crystal bed grew. Therefore after a few runs it was necessary to clean excess crystals out of the saturator.

Supersaturation data was collected for at least two residence times during each run. At the end of the run all lines, the refractometer, and the pumps were flushed with distilled water.

#### RESULTS

## Treatment of Data

As was mentioned earlier a sieve analysis was used to obtain the weight fractions for the various size ranges. To obtain population densities this weight distribution had to be converted to number of particles. The procedure used to find the population densities was as follows:

a) The arithmetic average diameter, L, of each fraction was determined. This is just the arithmetic average of the aperture for the sieve the fraction was collected on and the aperture of the sievedirectly above in the nest.

b) The weight of each fraction was converted to number of crystals by dividing by the cube of the average diameter,  $\overline{L^3}$ , the volumetric shape factor,  $K_v$ , and the density of the solid crystals. The volumetric shape factor relates the particle volume to the size cubed. For this analysis a shape factor of 1.0 was assumed for potassium nitrate. (See Appendix A.)

c) The number of crystals in the size fraction was then divided by  $\triangle L$  to obtain the population density, n.  $\triangle L$  represents the width of the fraction and it is obtained by taking the difference in aperture diameter between successive sieves.

d) The population density of crystals was then put on a basis of 100 ml. by multiplying by the ratio of 100ml. volume to the suspension sample volume,  $V_s$ .

The above calculations can be combined into one equation which gives the population density as a function of the weight fraction obtained:

$$n = \left(\frac{W}{K_{v}L^{3}\rho\Delta L}\right)\left(\frac{100}{V_{g}}\right)$$
(42)

See Appendix B for the breakdown of the different size fractions.

The readings from the differential refrectometer were in millivolts. However once the refractometer had been calibrated it was a simple multiplication to change the millivolt readings to concentration differences and thus supersaturation. It must be emphasized here that the calibration as well as all data collection had to be done at a specific constant temperature. This is the reason for the Haake constant temperature bath. The water flow from this bath was circulated through the refractometer unit at all times to maintain a constant temperature. This constant temperature was 35°C which was selected so as to be well above the crystallizer temperature for all runs.

As was mentioned earlier the supersaturation reading was recorded over a period of two to six residence times. During this recording time, which was all at steady state operation of the crystallizer, there were fluctuations in the supersaturation reading. These fluctuations were due to slight variations in flows and the normal cycling which occurs with an operating system. Refractive index and also supersaturation are extremely temperature sensitive. The operating crystallizer did go through thermal cycling. In all cases this cycling was held to  $\pm 0.5^{\circ}$ C.

However this thermal cycling was responsible for much of the fluctuations in supersaturation. In most cases the fluctuations in supersaturation were on the order of  $\pm 20\%$ , however in a few runs the fluctuations became as great as  $\pm 50\%$ . Because of these fluctuations a time-averaged value of supersaturation was obtained for each run during steady state operation. It is the time-averaged values which were used for plotting and further kinetic analysis.

The physical arrangement of equipment used in the measurement of supersaturation resulted in a slight variance in the supersaturation reading which could be accounted for. This was because of the screen over the sample port. As was mentioned earlier the sample port was covered with a fine screen with 75 µm apertures. The purpose of the screen was to filter out the crystals from the suspension and have only mother liquor for supersaturation measurement. However, since the screen had an aperture of 75 µm, crystals smaller than this size could pass on through with the mother liquor. Since the refractometer was always operated at a temperature well above that of the crystallizer these crystals would be redissolved in the refractometer and thus increase the mother liquor concentration. A correction can be made for this increase in concentration by using the population density plot. By integrating under the curve from size zero to size 75 µm the total mass of crystals going through the screen can be calculated. It is then a simple calculation to find the increase in concentration of the mother liquor due to redissolving. This calculation was performed and it was found that the concentration change represented an adjustment in super-

saturation amounting to only 1-2% of the measured value for almost all cases. There were one or two cases where this correction was as high as 5% for a maximum.

The sampling screen and the sampling technique employed also offered a potential problem in the supersaturation measurement which could not be corrected for. This problem concerned the build-up of a crystal film or thin cake on the surface of the screen. If such a cake were to form on the screen then mother liquor being drawn through the screen could have some of its supersaturation relieved by growth of the crystals in the film. This would result in too low of a concentration of the mother liquor and therefore too small of a supersaturation measurement. In testing earlier designs for sampling this problem had arisen. However, with the design presently being used, no such problem was experienced. The screen was placed flush with the wall and the flow in the crystallizer tended to wash the screen surface clean. Only a small film was ever observed and it did not appear to affect the supersaturation readings. There was no visible drop off of supersaturation as sampling time was increased.

There were times when the suspension density was so high that the screen became plugged with enough crystals to stop the sampling flow. In these cases the line was back flushed with small amounts of distilled water or air in a hypodermic needle. This usually worked to clean the screen and allow the continued measurement of supersaturation after the system had recovered and returned to steady state.

# Determination of Growth and Nucleation Rates

It was shown earlier that Equation 20 is the fundamental relationship giving the number distribution of the crystal product obtained from a continuous MSMPR crystallizer operating at steady state.

$$n = n^{O} \exp(-L/G \zeta)$$
(20)

A plot of log n versus L gives a straight line with an intercept at L = 0 of  $n^{\circ}$  and a slope of  $-1/G \gamma$ . This relationship therefore gives a method of determining the growth and nucleation rates from the population density data obtained for each run. A semilog plot of population density versus size was made for each set of data. An example of one such plot is shown in Figure 7. An exponential least squares analysis was completed for each plot. (See Appendix C.) This gave the best fit intercept and slope for the data which were in turn used to calculate the nucleation rate,  $B^{\circ}$ , and the growth rate, G, using Equation 20.

In each experimental run two samples were taken yielding two population density plots. A least squares analysis was done for both plots and the data set giving the best correlation of fit was used to calculate the growth and nucleation rates for that run.

Nucleation rate is a function of the suspension density in the crystallizer. For  $KNO_3$  the relationship is a direct one with the suspension density,  $M_{\rm p}$ , being to the first power (53,58):

$$B^{O} = f(M_{\rm P}) \tag{43}$$

In the experimental runs the suspension density varied from one run to another. Therefore for the calculated nucleation rates to be comparable

Figure 7. Typical plot of crystal size distribution for KN03



from run to run it was necessary to put them on a common basis. This was done by using a suspension density basis of 1.0 g./100ml. To achieve this all nucleation rates were divided by the suspension density for that run.

The suspension density for a given crystallizer run was calculated from the crystal suspension samples obtained. The total weight of crystals obtained in each sample after filtration and drying was divided by the total volume of sample taken from the crystallizer. If the crystallizer is well mixed and the sampling procedure is valid then this value of sample suspension density should be representative of the suspension density present in the crystallizer. The extent to which this is true may be questionable, however. Often the two suspension samples taken for any one given run resulted in different suspension densities. Although in most cases the differences were not great.

The experimental results for all of the runs are tabulated in Appendix D.

#### Growth and Nucleation Kinetics

#### Supersaturation dependency

The growth and nucleation kinetics were studied as a function of supersaturation. To do this the supersaturation level was varied by varying the residence time. By holding all other parameters constant and varying the residence time from run to run a change in supersaturation level with corresponding change in growth and nucleation rates was achieved. This experimental procedure was followed at four different

temperature levels from 10°C to 25°C.

As was mentioned earlier past work has indicated that power-law empirical models provide the best relationships between growth and nucleation rate and supersaturation. The approach used then was to see if the data did indeed fit a power-law relationship; and, if it did, to find the best empirical relationship. To test the power-law relationships a graphical procedure was used. Growth rate versus supersaturation was plotted on log-log paper to see if a straight line resulted as is indicated by the relation given in Equation 22 where

$$G = K_2 s^n$$
 (22)

In all of the cases the resulting fit of the data showed that growth rate is approximately a linear function of supersaturation, that is from the slope n is found to be approximately 1.0. Therefore the growth rate versus supersaturation data was plotted on linear paper and the resulting figures are 8-11. Although there is a great deal of scatter in the data, a linear relationship seems to best describe the fit.

It should be noticed here that some of the curves do not pass through the origin if extrapolated. That is, the growth rate becomes zero at a positive value of supersaturation. There are perhaps two explanations which might explain this. The first possibility is that the data cover only a linear portion of a higher order curve. The range of supersaturation measured is relatively small. No values were obtained below 0.0035 g.  $\text{KNO}_3/\text{g}$ . H<sub>2</sub>O at any of the temperatures. Therefore extrapolation below this range with a linear curve may not give the



Figure 8. Relationship between growth rate and supersaturation







Figure 10. Relationship between growth rate and supersaturation



Figure 11. Relationship between growth rate and supersaturation

correct relationship which would be found at the lower values of supersaturation. The small range of supersaturation observed in these experiments may represent linear portions of a higher order curve. A higher order relationship may be needed to describe the entire range of supersaturation.

The second possibility is that there may be a minimum driving force (level of supersaturation) required to produce a net growth rate. It is difficult to visualize any physical model of growth which would explain this type of relationship. It would seem that any supersaturation should result in some finite growth rate. Therefore the first explanation would appear to be the correct one.

Jones and Mullin (26) observed a similar relationship in their work with potassium sulphate. They found there was a positive value of supersaturation even when the overall linear growth rate was zero. Mullin (38) points out that this is the relationship one would expect if the Burton-Cabrera-Frank growth equation is used. This equation approximates to a growth rate proportional to the supersaturation squared at low values of supersaturation. But at high supersaturations the equation reduces to a linear relationship between growth rate and supersaturation. This points out a very important limitation of both growth and nucleation relationships found in the present work. That is they are only good for the range of parameters that were studied. They should not be extrapolated beyond that range.

Power-law relationships were also expected for the nucleation versus supersaturation data. As with the growth rate a graphical approach was

employed to test for the validity of Equation 34.

$$B^{o} = K_{\underline{1}} N_{\underline{T}} s^{\underline{m}}$$
(34)

Log-log plots of nucleation rate (corrected for suspension density) versus supersaturation were made for each of the temperature levels studied. These plots are shown in Figures 12-15. The data has a great deal of scatter but the figures also show the best least squares fit of the data points. The slopes are quite steep resulting in a rather large value for the power exponent m.

In looking at the nucleation rate data another form of the powerlaw relationship was suggested. It was felt that the supersaturation value should possibly be corrected by a value  $s^*$ . This  $s^*$  would represent a minimum value of supersaturation required in the crystallization system to produce any net nucleation rate. If  $s^*$  was subtracted from the measured value to give a quantity  $(s-s^*)$ , then the power-law model would take on the form:

$$B^{o} = K_{1}^{\prime} M_{T}^{j} (s-s^{\star})^{m}$$

$$(44)$$

Since both growth rate and nucleation rate are dependent upon the same level of supersaturation the proper value of  $s^*$  might be suggested by the positive intercept in the corresponding growth rate curve. Figures 16-18 give the corresponding plots to fit this new relationship given in Equation 44 for all temperatures except 25°C. (The data at 25°C was found to give a better fit using Equation 34.) From these plots it is found that a power of m = 1.7 best fits the data for all the temperatures studied.

In developing the power-law expressions it was shown that as a



Figure 12. Relationship between nucleation rate and supersaturation


Figure 13. Relationship between nucleation rate and supersaturation



SUPERSATURATION, G-KNO3/G-H2O

Figure 14. Relationship between nucleation rate and supersaturation



Figure 15. Relationship between nucleation rate and supersaturation



(SUPERSATURATION - 0.0015), G-KNO3/G-H20





(SUPERSATURATION - 0.002),  $G-KNO_3/G-H_2O$ 





Figure 18. Relationship between nucleation rate and  $(s-s^*)$ 

check a log-log plot of nucleation rate versus growth rate could be prepared. This plot should also be linear and fit the relationship:

$$B^{o} = K_{N}^{'} M_{T}^{j} G^{1}$$
(36)

To perform this check the plot of  $B^{\circ}$  (corrected for suspension density) versus G was made for each of the temperatures studied. The plots are shown in Figures 19-22. The slopes yield a value for i of 1.7. This supports the idea that the nucleation relationship should be of the form:

$$B^{o} = K_{\perp}^{\prime} M_{T}^{j} (s - s^{\dagger})^{m}$$

$$(44)$$

As was shown earlier the growth rate is an approximately linear function of supersaturation. It was also shown during the section on model development that i = (m/n). We have seen that n is approximately equal to 1.0 and that i is approximately equal to 1.7, so therefore m should be equal to 1.7 as was found in using the relationship of Equation 44.

It should also be noted that the data shows much less scatter than the plots involving supersaturation. Since this type of plot does not involve data from the supersaturation measurement this indicates the scatter in earlier plots can be attributed to errors in measurement of the supersaturation. This is as might be expected since the supersaturation value is very small and quite sensitive to small changes in temperature, pressure, impurities, etc.

A summary of the experimental parameters for the power-law relationships is given in Table 2.



GROWTH RATE, µm/min





GROWTH RATE, MM/MIN





Figure 21. Relationship between nucleation rate and growth rate



Figure 22. Relationship between nucleation rate and growth rate

Growth rate	e as function of	supersaturation
<u>10°C</u> :		G = 7008-0.167
<u>14°C</u> :		G = 730s-1.68
<u>20°C</u> :		G I 10658-3.86
<u>25°C</u> :		G I 6008-0.028

Table 2. Summary of experimental power-law relationships

Nucleation rate as function of supersaturation

<u>10°C</u> :	$B^{0}/M_{T} = 1.71 \times 10^{9} (s)^{2.48}$
	$B^{0}/M_{T} = 8.52 \times 10^{7} (s - 0.0015)^{1.79}$
<u>14°C</u> :	$B^{0}/M_{T} = 1.33 \times 10^{12} (s)^{3.50}$
	$B^{0}/M_{T} = 2.87 \times 10^{7} (s - 0.002)^{1.70}$
20°C:	$B^{0}/M_{T} = 1.07 \times 10^{11} (s)^{3.67}$
	$B^{0}/M_{T} = 6.09 \times 10^{7} (s - 0.0036)^{1.89}$
25°C:	$B^{o}/M_{T} = 4.35 \times 10^{6} (B)^{1.58}$

Nucleation	rate a	s function	l of g	rowth 1	rate
				·	

<u>10°C</u> :	$B^{o}/M_{T} = 453G^{1.72}$
<u>14°C</u> :	$B^{O}/M_{T} = 359G^{1.74}$
<u>20°C</u> :	B <sup>o</sup> /M <sub>T</sub> = 145g <sup>1.76</sup>
<u>25°</u> C:	$B^{O}/M_{T} = 240G^{1.43}$

## Temperature dependency

The temperature dependency of the growth and nucleation kinetics was also investigated in this work. A series of experimental runs was carried out at four different temperature levels:  $10^{\circ}$ C,  $14^{\circ}$ C,  $20^{\circ}$ C, and  $25^{\circ}$ C.

It was pointed out in the section on theoretical development that one would expect only the rate coefficients  $K_1^{'}$  and  $K_2$  to be temperature dependent parameters in the power-law functions. It was further noted that these coefficients might reasonably be expected to follow an Arrhenius-type temperature dependency. To check this type of dependency semilog plots of  $K_1^{'}$  and  $K_2$  versus 1/T were made and are shown in Figures 23 and 24. Straight lines were evidenced which supports an Arrheniustype dependency.

The relationships describing the dependency are therefore of the form:

$$K_{1} = k_{1} \exp(-E_{N}/RT)$$
(38)

$$K_2 = k_2 \exp(-E_G/RT)$$
(39)

The calculated value of the slopes can then be used to estimate the activation energies,  $E_N$  and  $E_G$ , required for nucleation and growth respectively. The frequency constants  $k_1$  and  $k_2$  may be calculated from the intercepts. This information was then combined with the earlier obtained information on supersaturation dependency to give the complete kinetic relationships for growth and nucleation rates. These relationships are given in Table 3.

Figure 23. Temperature dependency of proportionality constant for nucleation rate



 ${\sf K}_1', \ {\sf PROPORTIONALITY}\ {\sf CONSTANT}\ {\sf FOR}\ {\sf NUCLEATION}\ {\sf RATE}$ 

Figure 24. Temperature dependency of proportionality constant for growth rate



Table 3. Complete kinetic relationships

Activation energy for growth =  $7.3 \times 10^3$  cal/gmole  $k_2 = 2.86 \times 10^8$ G =  $2.86 \times 10^8 \exp(-7.3 \times 10^3/\text{RT})$  (s)<sup>1.0</sup> Activation energy for nucleation =  $-2.54 \times 10^4$  cal/gmole  $k_1 = 1.8 \times 10^{-12}$  $B^0/M_T = 1.8 \times 10^{-12} \exp(2.54 \times 10^4/\text{RT})$  (s-s\*)<sup>1.7</sup>

The activation energy for growth is positive and suggests the same form as that found in most chemical reaction kinetics. This says that when there is an increase of temperature the growth rate increases also. However the activation energy for nucleation is a negative value. Although this is not the normal occurrence there are a few chemical reactions which exhibit negative values also. What this means qualitatively is that as the temperature increases the nucleation rate of crystallization decreases. This inverse relationship of nucleation rate versus temperature for KNO<sub>2</sub> was also observed by Genck (21).

The temperature dependency of the growth rate may also be investigated by observing the growth rate change for a given residence time when the temperature increases. By using residence time in place of supersaturation as a constant parameter the measurement errors are limited. It is seen from Table 4 that for a constant residence time the growth rate increases as the temperature increases. It may also be seen that as residence time increases the growth rate decreases. Both of these observations are as would be expected.

esidence time, min.	10 <sup>0</sup> C	Growth 14°C	rates, µm/m 20°C	in. 25°0
< 15			6.91 7.60	6.93
15 to 20	4.42 4.67 4.68	4.61 4.76 5.05 5.13 5.32 5.35	5.52 5.68 5.94 5.99 6.40	5.41 5.49 5.76 6.44
20 to 25	3.20 3.84 4.06 4.15	3.69 3.81 4.21 4.25 4.31 4.40 4.60	4.51 4.90 5.27	4.71 5.09 5.35 5.38
25 to 30		3.29 3.35 3.50 3.56	3.80 4.13 4.15 4.17 4.21 4.61	3.27 4.07 4.17
30 to 35	2.68 2.85	2.34 3.02	3•38 3•56	3.23 3.49
35 to 40	2.40	2.66 2.85	3.02	3.42
>40	2.19	2.28 2.40 2.54	2.48 2.52 2.79	2.40 2.77

Table 4. Growth rate as a function of temperature and residence time

Discussion of Inverse Nucleation Rate with Temperature

One of the more interesting observations of the present work is that for a given supersaturation the nucleation rate is inversely related to temperature. That is at a constant level of supersaturation if the temperature level is increased the nucleation rate is decreased. This is just the opposite of what would normally be found with Arrheniustype kinetics. However it is not the first time such a relation has been observed. Kern and Abegg (27) reported such a change with a proprietary substance and Genck (21) previously observed this with KNO<sub>3</sub>. In both of these earlier cases supersaturation was not measured, however. Genck (21) therefore suggested that the decrease in nucleation rate with increasing temperature is the result of a decrease in the supersaturation level supported. With the measurement of supersaturation in the present work this does not appear to be the cause.

To explain this phenomenon one must postulate some ideas about the mechanisms that might be occurring at the crystal surface. Surface diffusion and overall activation energy could both play a major role in causing the observed relationship. In either case one must start by looking at the surface characteristics of a growing crystal. In all likelihood the idea put forth by Powers (47) is correct. He presumed that the surface of the crystal is covered by a fluidized layer. This layer is made up of molecules of solute loosely bond to the growing crystal face.

For growth to occur the molecules are drawn from this fluidized layer to be anchored in true lattice bondings on the growing layer fronts.

This involves surface diffusion of the molecular aggregates. If, as would be expected, the surface diffusion rate increases with temperature; then the incorporation of the molecules into the lattice would occur more quickly. This means there would be fewer molecules available in the fluidized layer and it would not be as extensive as it was at lower temperatures.

Powers (47) also proposed that secondary nucleation is very dependent upon the fluidized layer. He postulated that secondary nucleation occurs when fluid shear and collisions cause some of the fluidized layer to be drawn off to form new nuclei. If at a higher temperature the increased surface diffusion depletes the fluidized layer faster than it is regenerated by fresh solute from the solution then there would be less secondary nucleation. This could therefore explain the decrease in nucleation rate as temperature is increased.

Powers (47), Melia and Moffitt (34), and Sung, Estrin, and Youngquist (56) all point out that many times secondary nucleation is associated with dendritic-type growths appearing on the surface of the parent crystal. The shearing action of the fluid and collisions within the system tear off the dendrites to form new nuclei. It is worthwhile to think about how increased surface diffusion, resulting from increased temperature, might influence the growth of dendrites. If dendritic growth is an important part of secondary nucleation, then the fewer the number of dendrites the lower the nucleation rate.

In a study of ice crystals N. H. Fletcher (19) points out that surface diffusion provides a stabilizing mechanism by tending to destroy

any perturbations on the growth surface. He states that the effect of surface diffusion is very considerable and has a large influence on the growth morphology. Van Hook (61) discusses a correlation between d, the diameter of the crystal, and  $x_t$ , the thickness of the crystalmedium interface. If  $x_t \ll d$ , polyhedra forms prevail, but if  $x_t \gg d$ , then dendrites appear. So we can see that if surface diffusion is increased due to increased temperatures it is likely that dendritic growth and nucleation rate will be decreased.

The second major influence of the temperature on the observed nucleation rate may come from the overall activation energy considerations. Decreased nucleation rates with increasing temperature have been observed in melts. If the crystal surface is indeed covered with a fluidized layer of solute as Powers (47) suggests, then the nucleation behavior might be considered to be much the same as nucleation from a melt. Some insight might then be gained by looking at the mechanism which causes inverse nucleation rate in melts.

By following the development of Mullin (38), it can be shown how the abnormal nucleation characteristic observed in melts occurs. First the nucleation rate is expressed in the form of the Arrhenius reaction velocity equation commonly used for the rate of a thermally activated process:

$$B^{o} = A_{1} \exp(-\Delta G/k_{b}T)$$
(45)

where  $A_1$  equals a constant,  $\Delta G$  equals the over-all excess free energy,  $k_{\rm b}$  equals the Boltzmann constant, and T is the temperature.

The Gibbs-Thomson relationship may be written as

$$\ln S = \frac{2\nabla V}{k_{\rm b} Tr} \tag{46}$$

where v is the molecular volume and  $S = c/c_s$ . This then gives

$$-\Delta G_{\mathbf{v}} = \frac{2 \mathbf{T}}{r} = \frac{k_{\rm b} T \ln(S)}{\mathbf{v}}$$
(47)

Using Equation 4 it can be shown that

$$\Delta G_{\text{erit}} = \frac{16\pi v^3 v^2}{3(k_b T \ln(S))^2}$$
(48)

and from Equation 45

$$B^{o} = A_{1} \exp\left[\frac{-16\pi \sqrt{3}v^{2}}{3k_{b}^{3} T^{3} (\ln (s))^{2}}\right]$$
(49)

This equation indicates that three main variables govern the rate of nucleation: temperature, T; supersaturation, S; and interfacial tension,  $\nabla$ .

Tamman (57) observed that in dealing with melts the rate of nucleation usually increases exponentially as supersaturation increases. But as higher levels of supersaturation are reached the nucleation rate reaches a maximum and subsequently decreases. Tamman suggested that this behavior was caused by the sharp increase in viscosity with supercooling which restricted molecular movement and inhibited the formation of ordered crystal structures. Turnbull and Fisher (60) quantified this observed behavior with a modified form of Equation 49:

$$B^{o} = A_{1}' \exp \left[ \frac{-16\pi r^{3} v^{2}}{3k_{0}^{3} T^{3} (\ln(s))^{2}} + \frac{\Delta G'}{k_{0}T} \right]$$
(50)

which includes a "viscosity" term. When  $\Delta G'$ , the activation energy for molecular motion across the embryo-matrix interface, is exceptionally large (as in the case of highly viscous liquids and glasses) the other exponential term is small because under these conditions s is generally large.  $\Delta G'$  then becomes the dominant factor in the rate equation and a decrease in nucleation rate is predicted.

Previously reported experimental observations of this reversal of the nucleation rate have been confined to melts, but it should also be expected in highly viscous solutions. Mullin and Leci (40) also observed such a behavior in aqueous solutions of citric acid.

Since the apparent reversal of nucleation rate was observed in the present study using  $KNO_3$ , it might be concluded that the activation energy,  $\Delta G'$ , of this system must be quite large. This would result in the second exponential term of Equation 50 being dominant. In the temperature range studied the "viscosity" term would then have the controlling influence over the observed nucleation rate.

# CONCLUSIONS

1. The data from the experiments show a large amount of scatter in the supersaturation measurement. There are three facts which must be kept in mind. The first is that the magnitude of the values being measured is quite small. The second is that the crystallizer was operating continuously and some variation in time is expected. Thirdly, the temperature range for the experiments was small. Considering the nature of the experiments it is not too surprising that the supersaturation measurement is a difficult one. The experiments were designed to study both mechanisms of nucleation and crystal growth simultaneously.

A linear function describes the relationship between growth rate and supersaturation as well as any other power-law function. However the growth relationships found in the work are only good for the range of values studied and should not be extrapolated. The functional relationships observed clearly should not be expected to exist over the entire range of supersaturation. Instead it would appear that the linear relationship represents only a small portion of a higher order curve.

2. The growth rate constant increases as the temperature increases. There is a positive activation energy associated with growth rate. This was shown somewhat inconclusively when observing the growth rate as a function of supersaturation. But the observation was supported when growth rate is viewed as a function of temperature and residence time.

3. Under the experimental conditions of this work, the best powerlaw relationship for nucleation is one of the form:  $B^{\circ} = f(s-s^{*})^{m}$ .

Using this relationship the data suggests a value of approximately 1.7 for m.

4. The nucleation rate decreases as the temperature increases at a constant value of supersaturation. This means that with an Arrhenius-type of temperature dependency the nucleation rate has a negative value for an activation energy. This is an inverse effect from that which normally would be expected. Mullin (38) points out however that the size of the critical nucleus is dependent on temperature. The size of a critical nucleus increases with temperature increases. At a higher temperature a higher free energy of formation is required to obtain a critical nucleus capable of further growth. This has some effect on how the nucleation rate changes with changes in temperature. This analysis would apply only for homogeneous nucleation, however. In the MSMPR crystallizer used in this work secondary nucleation was the main source of nuclei. As the temperature is increased the surface activity is increased resulting in a more ordered surface. Consequently fewer nuclei are produced during crystal contacts.

5. A linear relation between nucleation rate and suspension density,  $B^{0} = f(M_{m}^{1.0})$ , seems to be supported by this work.

6. There is a very good correlation of the nucleation versus growth rate data. Nucleation rate is approximately a 1.7 power function of the growth rate.

7. The population density data obtained from the sieve analysis is very good and supports the view that  $KNO_3$  shows size independent

growth.

8. The quantitative results of the supersaturation measurement obtained in this work were not good. However the refractometer still appears to be a valuable tool for qualitative analysis. It responds very rapidly to changes in supersaturation and therefore offers a good way of monitoring steady state operation.

#### RECOMMENDATIONS

1. The measurement of supersaturation was not too successful in these experiments because of the scatter in the data. However further investigation could still be useful. One such study would be to investigate other systems which show a higher level of supersaturation. This could be with an organic system such as sucrose.

2. In attempting to determine why there was so much scatter in the present studies the saturator design and method of obtaining a saturated reference solution became prime suspects. Therefore further work might entail finding a better way of producing a saturated reference. This could involve either a new saturator design or some completely different approach. In the present saturator design saturation is approached from a supersaturated solution. A better design idea might be to approach saturation from an undersaturated solution.

3. One of the more important results found in the present work was the inverse relationship of nucleation rate with temperature. That is KNO<sub>3</sub> appears to exhibit a decrease in nucleation rate as temperature is increased. Further studies should be done at different temperature levels to investigate this phenomena.

4. The range of supersaturations obtained in the present work was fairly limited. By using different operating conditions or a different crystallization system this range of supersaturation could possibly be expanded.

5. The refractometer seemed to respond quickly to upsets or changes in the crystallizer system. Some thought should be given to using the

refractive index measurement to monitor dynamic changes in a crystallizer system. This could either be in a continuous system or it could be applied to time studies in a batch crystallizer.

6. If a staged crystallizer system were being used the differential refractometer might offer an excellent method of checking relative concentration differences between vessels within the system.

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# NOMENCLATURE

- a proportionality constant
- a, proportionality constant
- A surface area of crystal
- A<sub>1</sub> proportionality constant
- A<sub>1</sub> proportionality constant
- b exponential power for size-dependent growth relationships
- B<sup>O</sup> nucleation rate
- c solute concentration in supersaturated solution
- c<sup>\*</sup> equilibrium saturation concentration
- c solute concentration in the solution at the crystal-solution interface
- c<sub>s</sub> saturation concentration of solute
- d equivalent diameter of crystal
- D diffusion coefficient of solute
- E<sub>c</sub> activation energy for growth
- $E_{_{NV}}$  activation energy for nucleation
- G growth rate of crystals
- $G_1$  growth rate of crystals of size  $L_1$
- G<sub>2</sub> growth rate of crystals of size L<sub>2</sub>
- $\Delta G$  over-all excess free energy
- $\Delta {\tt G}$  activation energy for molecular motion across the embryo-matrix interface
- $\Delta G_{crit}$  over-all excess free energy of a particle with radius  $r_c$  $\Delta G_c$  surface excess free energy
- $\Delta G_{t}$  volume excess free energy

 $\Delta G_{u}$  free energy change per unit volume

- i m/n, nucleation rate power dependency on growth rate
- i angle of incidence
- I induction period, time interval between mixing two reacting solutions and the appearance of the crystals
- j nucleation order related to  $M_m$
- k<sub>b</sub> Boltzmann constant
- k<sub>1</sub> frequency factor for nucleation rate
- k<sub>2</sub> frequency factor for growth rate
- K constant
- K<sub>d</sub> coefficient of mass transfer by diffusion
- K<sub>n</sub> over-all crystal growth coefficient
- K<sub>m</sub> coefficient of mass transfer
- $K_{\overline{N}}$  proportionality constant for nucleation rate as function of growth rate
- $K_{\overline{N}}^{'}$  proportionality constant for nucleation rate temperature effects as function of growth rate
- K\_ rate constant for the surface reaction
- Ky volumetric shape factor
- K<sub>1</sub> proportionality constant for nucleation rate as function of supersaturation
- K<sup>'</sup><sub>1</sub> proportionality constant for nucleation rate temperature effects as function of supersaturation
- K<sub>2</sub> proportionality constant for growth rate as function of supersaturation
- L crystal size, equivalent diameter
- L arithmetic average crystal diameter
- $\Delta L$  width of size fraction,  $L_2$ -L

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M

n

n

no

n<sub>i</sub>

n

n<sub>2</sub>

N

NO

N

р

q

Q

Q,

T

r,

r

R

8

s\*

t

T

- mass of solids deposited

- m

suspension density

number of crystals

volumetric flow rate out

volumetric flow rate in

particle radius

critical radius

law expressions

 $\Delta t$  increment of time

temperature

time

gas constant

angle of refraction

c-c, supersaturation

100

(as exponent) nucleation rate power dependency on supersaturation

(as exponent) growth rate power dependency on supersaturation

average population density in the range  $L_1$  to  $L_2$  in the feed

population density of zero-size particles or nuclei

population density of crystal suspension

population density of crystals of size L1

population density of crystals of size Lo

order of over-all crystal growth process

refractive index of transparent isotropic medium

number of molecules needed to form a critical nucleus

constant value of supersaturation used for correction of power-

number of crystals at zero size

- v molecular volume
- V volume of crystallizer
- $V_c$  volume of a single crystal
- V volume of sample
- W weight of crystals
- $\mathbf{x}_{t}$  thickness of crystal-medium interface
- 5 film thickness or length of diffusion path
- **P** density of crystals
- $\gamma$  V/Q, residence time
- **▼** surface energy

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#### APPENDIX A.

# VOLUMETRIC SHAPE FACTOR

A precise calculation of the volume of a solid body of regular geometric shape can only be made when its length, breadth, and thickness are known. For the crystals grown in a continuous crystallizer these three dimensions can never be precisely measured. For calculation purposes the equivalent diameter of the particle is used. In a sieving analysis the second largest dimension of the particle is the equivalent diameter used (38).

For a single particle, the volume can then be defined as a function of this equivalent diameter.

$$\mathbf{v}_{e} = \mathbf{K}_{e} \mathbf{d}^{3} \tag{51}$$

In this equation  $V_c$  is the volume, d is the equivalent diameter, and  $K_v$  is the volumetric shape factor. It can be seen that  $K_v$  varies depending upon the shape of the crystals. For spherical (diameter = d) and cubical (length of side = d) particles,  $K_v$  is equal to 47/6 and l, respectively. In general the shape factor can be adequately determined from a screen analysis of several samples of the crystalline form.

Previous investigators (21,53) have found a volumetric shape factor of 1.0 for potassium nitrate. Therefore in this analysis a value of 1.0 was used for  $K_{\mu}$ .

# APPENDIX B.

CALCULATION OF NUMBER OF CRYSTALS FROM WEIGHT OF

# KNO IN SCREEN ANALYSIS

$$n = \frac{W}{K_{v}L^{3}\Delta L \rho}$$
(52)

For KNO3:

 $K_v = 1.0$  (See Appendix A)  $p = 2.11 \text{ g./cm}^3 = 2.11 \text{ x10}^{-12} \text{ g./µm}^3$  (Reference 38)

Sieve #	L,microns	△L,microns	$\rho K_{v} \overline{L}^{3} \Delta L, gmicron$
18	1095	190	0.5264
20	921	159	0.2621
25	776	131	0.1292
30	655	110	0.0652
35	550	100	0.0351
40	460	80	0.0164
45	388	65	8.011×10 <sup>-3</sup>
50	328	55	4.095×10 <sup>-3</sup>
60	275	50	2.194x10 <sup>-3</sup>
70	219	38	8.422x10 <sup>-4</sup>
80	196	32	5.084x10 <sup>-4</sup>
100	165	30	$2.844 \times 10^{-4}$
120	138	25	1.386x10 <sup>-4</sup>
140	116	19	6.258x10 <sup>-5</sup>
170	98	16	3.177x10 <sup>-5</sup>
200	83	15	1.810x10 <sup>-5</sup>

### APPENDIX C.

### EXPONENTIAL LEAST SQUARES ANALYSIS

The various plots of population density versus crystal diameter show the expected scatter of experimental data. Theory has shown that the semi-log plots should be linear. And indeed in this work all such plots were found to yield straight lines. The important parameters to be obtained from the plots were the slope and intercept. To obtain the best values for these two parameters a least-squares program was run on a Hewlett Packard 9100 Calculator.

The program computes the least squares fit and correlation coefficient of n pairs of data points for an exponential function of the form:

$$y = ae^{bx}$$
 (53)

The equation is linearized into

$$\ln y = \ln a + bx \tag{54}$$

cr

$$Y = A + bx \tag{55}$$

Using a linear regression method,

$$b = \frac{n \xi x Y}{n \xi x^{2}} - \frac{\xi x \xi Y}{(\xi x)^{2}}$$
(56)

$$A = \frac{\sum Y - b\sum x}{n}$$
(57)

The correlation coefficient is given by (Note:  $Y_i$  0; i = 1,\*\*\*,n)

$$r = \frac{n\Sigma xY - \Sigma x\Sigma Y}{((n\Sigma x^2 - (\Sigma x)^2)(n\Sigma Y^2 - (\Sigma Y)^2))^{0.5}}$$
(59)

#### APPENDIX D.

## RESULTS OF EXPERIMENTAL RUNS

#### Notes for the Appendix:

Run 3- Large variance in supersaturation reading for unknown reasons.

Run 8- Bad population density, bad sample.

Run 14- Too large of sample taken for sieving, giving bad population density plots.

Run 23- Large variation in supersaturation recorded.

Run 27- Variation in feed solution.

Run 30- Bad temperature control on the run, probably not at steady state.

Run 34- Build-up of cake on sampling screen, had to back flush sample lines several times.

Runs 37-39- Sampling screen loose.

Runs 46-47- Feed concentration changing.

Run 53- Large variation in feed flow rate, probably not at steady state.

Run 54- Plugging of sample lines, first attempt at running above room temperature.

Run 72- Too large a suspension density, suspect feed concentration changing. Also amount of feed solution getting very low, may be getting feedback of product stream crystals.

Run 74- Steady state not achieved.

Run,	<u>7</u> ,	8,	<u>M</u> <sub>T</sub> ,	Growth,	$\underline{B^{o}},$	<u> </u>	Temp.,
(#)	(min.)	$\left(\frac{g \cdot KN0}{g \cdot H_20}\right)$	$\left(\frac{g}{100ml}\right)$	$\left(\frac{jum}{\min}\right)$	no. nin-100ml	no. min-100m	ī) <sup>(°</sup> C)
73	25.0	0.0047	0.51	3.20	3280	6400	10.1
74	20.5	0.0035	0.67	4.15	3260	4900	10.1
75	33.8	0.0045	0.63	2.68	1240	1970	10.0
76	23.4	0.0055	0.65	3.84	2500	3850	10.0
77	18.0	0.0067	1.47	4.42	11,200	7600	9.8
78	19.0	0.0051	0.97	4.68	4700	4850	10.1
79	43.3	0.0050	1.21	2.19	1740	1450	10.1
80	30.5	0.0057	1.18	2.85	3660	3100	10.2
81	38.0	0.0048	0.80	2.40	1580	197 <b>5</b>	10.2
82	21.2	0.0052	1.11	4.06	5400	4850	10.0
83	18.1	0.0052	0.71	4.67	4200	5900	10.0
			<u> </u>				
4	33.0	0.0071	0.72	2.34	2430	3370	14.4
5	25.0	0.0077	1.45	3.69	4170	3640	14.3
6	17.5	0.0090	0.77	4.76	5800	7500	14.2
7	19.0	0.0078	1.26	4.61	7400	5900	14.1
8	44.0	0.0082	0.95	2.40	1385	1460	14.2
9	29.0	0.0054	1.15	3.29	3300	2870	14.2
10	24.0	0.0063	1.02	3.81	4550	4450	13.9

 $B^{O}$  : nucleation rate actually found from the data.

 $B^{\circ} = B^{\circ}/M_{T}$ , nucleation rate corrected for the suspension density present during the run.

Run,	<u>~,</u>	<u> </u>	<u>M</u> ,	Growth,	Bo <sup>a</sup> ,	$\underline{B}^{ob}$	Temp.,
(#)	(min.)	$\left(\frac{g.KN0}{g.H_20}\right)$	$\left(\frac{g.}{100ml.}\right)$	$\left(\frac{\mu m}{\min}\right)$	$\left(\frac{\text{no.}}{\text{min-100m}}\right)$	no. 1)(min-100	ml) (°C)
3	21.0	0.0051	1.30	4.60	4940	3800	14.2
36	31.4	0.0063	0.74	3.02	1780	2400	13.8
37	20.4	0.0053	1.17	4.21	5760	4920	14.1
38	17.9	0.0052	0.94	5.05	4700	5000	14.4
39	22.6	0.0058	1.61	4.31	4950	3080	13.9
40	26.3	0.0051	1.11	3.35	3 <b>775</b>	3400	14.2
41	36.6	0.0050	1.14	2.66	2050	1800	14.2
43	41.0	0.0078	1.12	2.54	1570	1400	14.2
44	26.2	0.0062	1.19	3.50	3650	3070	14.2
45	21.0	0.0060	0.78	4.25	3570	4580	14.2
46	16.6	0.0051	0.82	5.51	4690	5700	14.2
47	17.9	0.0061	2.09	5.13	10,500	<b>50</b> 30	13.8
49	36.5	0.0070	0.71	2.85	1100	1550	14.2
50	27.0	0.0086	0.62	3.56	1615	2650	14.2
51	20.7	0.0092	0.43	4.40	2160	5000	14.6
52	17.9	0.0104	0.61	5.32	2590	4250	14.1
<b>5</b> 3	50.5	0.0080	0.68	2.28	650	950	14.2
<del></del>							
13	29.0	0.0075	3.24	4.15	3820	1180	20.
14	21.0	0.0058	2.12	5.27	4560	2150	20.
16	45.0	0.0075	3.89	2.79	2340	600	20.
17	21.0	0.0087	4.15	4.90	11,900	2870	20.

Run,	٢,	_8,	<u>M</u> .,	Growth,	B <sup>o</sup> ,	B, <sup>b</sup>	Temp.,
(#)	(min.)	$\left(\frac{g.KN0}{g.H_20}\right)$	$\left(\frac{g.}{100ml.}\right)$	$\left(\frac{\mu m}{\min}\right)$	no. min-100ml	$\binom{no.}{min-100m}$	□) (°c)
18	35.0	0.0077	3.83	3.56	3300	860	20.
19	15.0	0.0091	0.52	6.91	2550	4900	20.
20	25.6	0.0073	2.60	4.61	4400	1700	20.
21	18.0	0.0085	1.96	5.99	6045	3080	20.
22	17.0	0.0092	1.3Û	5.52	6540	5020	20.
23	13.0	0.0068	2.68	7.60	10,860	4050	20.
24	30.0	0.0075	2.61	3.80	4030	1550	20.
25	38.5	0.0071	2.24	3.02	2460	1100	20.
26	32.7	0.0067	1.53	3.38	2140	1400	20.
27	15.8	0.0058	1.29	5.94	6230	4830	20.
28	26.2	0.0068	1.35	4.13	2520	1870	20.
29	41.7	0.0064	1.73	2.48	3480	1160	20.
30	17.2	0.0061	2.26	6.40	6610	2920	20.
31	30.0	0.0065	1.30	4.21	1370	1050	20.
32	45.3	0.0070	2.19	2.52	1735	790	20.
33	25.6	0.00-3	3.06	4.17	6520	2140	20.
34	17.0	0.0059	2.02	5.68	8180	4060	20.
35	21.6	0.0070	2.21	4.51	6990	3160	20.
<u></u>							
54	19.8	0.0105	2.64	4.82	12,000	4550	26.0
55	19.1	0.0069	2.55	5.41	8000	3140	25.0
56	32.1	0.0070	2.68	3.49	4000	1490	25.0

Run,	<u>۲,</u>	<u> </u>	M <sub>m</sub> ,	Growth,	B <sup>O</sup> ,	Bob	Temp.,	
(#)	(min.)	$\left(\frac{g.KN0}{g.H_20}3\right)$	$\left(\frac{g.}{100ml.}\right)$	$\left(\frac{\mu m}{\min \cdot}\right)$	no. nin-100ml	no. min-100m	ī) (°C)	
57	26.8	0.0066	3.13	4.07	5600	1790	25.0	
58	23.4	0.0083	2.61	4.71	6180	2370	25.0	
60	29.0	0.0076	1.44	3.27	3600	1400	25.0	
61	19.6	0.0081	2.60	6.44	5975	2300	24.9	
62	41.6	0.0072	2.69	2.77	3400	1260	25.2	
63	20.6	0.0067	2.53	5.35	6570	2600	25.1	
64	35.0	0.0072	2.24	3.23	3100	1380	25.2	
55	22.0	0.0074	2.61	5.09	<b>5</b> 850	2240	25.0	
66	18.4	0.0090	2.40	5.76	7700	3200	24.9	
67	19.8	0.0098	3.39	5.49	9450	2800	24.8	
68	13.8	0.0087	3.34	6.93	18,470	5500	24.8	
69	21.0	0.0081	3.66	5.38	7770	2120	24.8	
70	27.4	0.0073	1.65	4.17	3000	1820	25.1	
71	36.8	0.0076	3.46	3.42	3100	900	25.1	
72	49.0	0.0080	4.09	2.40	3360	820	25.2	