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Contact nucleation of magnesium sulfate heptahydrate in a continuous MSMPR crystallizer

by

Larry Gene Bauer

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

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Approved:

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In Charge of Major Work

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<td>area</td>
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<tr>
<td>a</td>
<td>acceleration</td>
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<td>B</td>
<td>birth function</td>
</tr>
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<td>$B^0$</td>
<td>nucleation rate</td>
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<tr>
<td>C</td>
<td>concentration</td>
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<tr>
<td>$C_0$</td>
<td>initial concentration</td>
</tr>
<tr>
<td>$C_{sat}$ or $C^*$</td>
<td>equilibrium concentration at temperature $T$</td>
</tr>
<tr>
<td>D</td>
<td>death function or diffusion coefficient</td>
</tr>
<tr>
<td>d</td>
<td>drop distance</td>
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<td>E</td>
<td>contact energy</td>
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<tr>
<td>F</td>
<td>resultant force</td>
</tr>
<tr>
<td>$F_f$</td>
<td>combined frictional force due to air, solution, and solenoid</td>
</tr>
<tr>
<td>$F_g$</td>
<td>force due to gravity</td>
</tr>
<tr>
<td>$F_r$</td>
<td>force of combined resistances</td>
</tr>
<tr>
<td>$F_s$</td>
<td>force due to spring</td>
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<td>f</td>
<td>frequency of contact</td>
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<tr>
<td>G</td>
<td>crystal growth rate</td>
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<tr>
<td>$G$</td>
<td>growth rate of very large particles</td>
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<td>acceleration due to gravity</td>
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<tr>
<td>J</td>
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</table>
\( k, k_1, k_2, k_3 \) proportionality constants
\( k_4, k_m, k_n \) crystal size
\( L, L_c, L_1 \) a particular crystal size
\( M \) molecular weight
\( M_T \) total mass of the crystals in suspension
\( m \) mass
\( m_j \) jth moment of the population distribution
\( m_o \) the mass added to the rod that just causes contact between the rod and the crystal
\( m^* \) weight of rod plus added weights
\( N \) number of nuclei produced per collision
\( n \) moles or population density
\( n_o \) nuclei population density
\( n_i \) population density of the inlet stream
\( n_o \) population density of the outlet stream
\( P \) pressure
\( P_o \) vapor pressure
\( Q \) volumetric flow rate
\( Q_i \) volumetric flow rate of inlet stream
\( Q_o \) volumetric flow rate of outlet stream
\( R \) gas constant
\( r \) radius of nuclei
\( r_c \) critical radius of nuclei

\( \text{Re}_s \) Reynolds' number for stirring

\( S \) supersaturation

\( T \) absolute temperature

\( t \) time

\( V \) volume

\( v \) molar volume

\( v_i \) initial velocity

\( v_f \) final velocity

\( w \) work

\( x \) film thickness

\( Y_A \) concentration of solution

\( Y_B \) saturation concentration

\( \alpha \) supersaturation ratio, \( \frac{C}{C_{\text{Sat}}} \)

\( \Delta G \) free energy change associated with homogeneous nucleation

\( \Delta G' \) free energy change associated with heterogeneous nucleation

\( \Delta T \) supersaturation

\( \theta \) angle measure

\( \rho \) density

\( \nu \) surface tension

\( \tau \) average residence time
INTRODUCTION

The question "why is anyone concerned about crystallization?" is frequently asked. Without crystallization one might discover that products he has come to know and depend on (such as: common table salt, sugar, penicillin, polyester fibers, and many others) would no longer be as pure or as available or available only at a higher price.

Crystallization as a process operation is important for two reasons: (1) it is a tool that can be used to separate one component from a multicomponent mixture, and (2) it is a method for providing a finished product in a crystalline form.

A problem associated with crystallization is the control of the crystal size distribution (CSD) leaving the crystallizer. Generally speaking, it is desirable to produce a CSD so that virtually all the crystals in the distribution are larger than a certain minimum size; this facilitates in liquid/solid separation thus effectively increasing the separation efficiency and hence reducing the operating cost. Usually, it is also desirable to further constrain the CSD by requiring that all the crystals in the distribution fall into a predetermined size range. Control of the CSD is paramount.
In recent years it has been shown that the most effective means of controlling the crystal size distribution leaving a crystallizer is to control the rate of nucleation within the crystallizer.

It is believed that nucleation can be initiated by homogeneous or by heterogeneous nucleation. Homogeneous nucleation is by definition a spontaneous generation of nuclei which occurs at some high supersaturation level in a solution that is void of all foreign particulate matter such as dust, seed crystals, etc. Heterogeneous nucleation, however, occurs as a result of the presence of submicroscopic particles of dust, crystallites, etc.

Experience has indicated that once nucleation has been initiated birth of additional nuclei seems to take place spontaneously. This phenomena has been called secondary nucleation (or collision breeding or contact nucleation) because it occurs as the result of interaction between crystals or between crystals and other solid objects such as the crystallizer wall, agitator, etc.

It is noted that secondary nucleation is not homogeneous nucleation nor does it occur because of the presence of foreign, submicroscopic particles in the vessel. Secondary nucleation
is the nucleating action resulting from the collision of a solute crystal with another solid object. It is the dominant, if not the only type of nucleation, occurring in an operating crystallizer.

Numerous investigators (31,37,39) using aqueous solutions of potassium chloride, potassium bromide, magnesium sulfate, ammonium chloride, potassium sulfate, ammonium sulfate, and other salts have demonstrated the phenomena of contact nucleation. They have shown that the nucleation rate increases with (1) increasing supersaturation, (2) increasing energy of contact, (3) increased rate of agitation, and (4) increasing area of contact.

Microattrition is believed to be the mechanism of contact nucleation, i.e.; microscopic dendrites growing on the crystal surface are physically loosened by the impact of the crystal/solid collision. These dendrites then separate from the crystal and form new nuclei.

In order to be able to control the CSD issuing from a crystallizer, it is necessary to quantitatively describe what is occurring within the crystallizer. This can be done by expressing the nucleation rate in terms of the operating parameters. Several investigators have proposed models
describing the system they studied. Two researchers (11,26) investigated the effect of various operational parameters on the nucleation of MgSO$_4$·7H$_2$O in a semicontinuous plug flow crystallizer. Two others (9,58) probed the effect of supersaturation and the rate of agitation on the rate of nucleation of K$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ in the transient operation of a mixed suspension, mixed product removal (MSMPR) crystallizer.

All of the investigations mentioned above give insight into the idiosyncrasies of contact nucleation and also quantitatively define the nucleation resulting at various experimental conditions. Those using the plug flow crystallizer developed an expression relating the number of nuclei resulting from a single contact to the contact energy and the supersaturation. Whereas, those using the MSMPR crystallizer developed expressions for the nucleation rate as a function of the supersaturation and the agitation rate.

The current investigation weaves together the information obtained from the aforementioned investigations. By using a MSMPR crystallizer and a point nucleation source a model is developed for the nucleation rate in a MSMPR crystallizer as a function of the energy of contact, supersaturation and average residence time in the crystallizer.
In addition to obtaining the nucleation rate model, the current work determines the number of nuclei resulting per contact. Information is also obtained on the growth rate of \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \) particles in the subsieve size range. Finally, this work checks the nucleation models presented by the previously mentioned investigators for their applicability to the \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \) system.

If the nucleation rate in a MSMPR crystallizer can be modeled as a function of the supersaturation, contact energy, and crystal surface area in the crystallizer a considerable advance can be made toward control of the CSD issuing from a crystallizer.
LITERATURE REVIEW

Solubility, Supersolubility, Saturation, Supersaturation and Undersaturation

A study of crystallization phenomena necessitates that one first of all understand its terminology. Terms such as solubility, saturation, undersaturation, and supersaturation are typical.

If one were interested in how much table salt would dissolve in water at room temperature, he could add some salt to a given quantity of water, shake vigorously, and allow the mixture to stand for a while. If all the salt added dissolves, more salt is added. This process is then continued until the liquid can no longer dissolve any more salt. This point is called the saturation point of salt in water at room temperature; it is frequently expressed as the weight percent of salt in the solution.

It so happens that the saturation point of salt and most other chemical species is a function of the temperature. A plot of concentration of the species versus the temperature of the solution is called the solubility or saturation curve. Figure 1 is such a plot.
Figure 1. Typical solubility curve. Also indicates the regions of under and supersaturation.
UNDERSATURATED REGION

SOLUBILITY OR SATURATION CURVE

SUPERSATURATED REGION

SUPERSOLUBILITY CURVE
For a given concentration, a solution can become undersaturated by simply heating it to a temperature greater than the temperature corresponding to the saturation temperature for this fixed concentration.

In a similar manner, a solution of fixed composition can become supersaturated by cooling to a temperature less than the saturation temperature corresponding to the fixed concentration.

A solution can also become undersaturated or supersaturated at a constant temperature. In these cases the concentration of the solution would have to be decreased or increased respectively in relation to the saturation concentration corresponding to the fixed temperature.

Buckley (6, p. 9-10) points out that if a crystal is placed in a saturated solution nothing happens to either the crystal or the solution. However, if the crystal is placed in an undersaturated solution it will begin to dissolve. Dissolution of the crystal will continue until the solution either becomes saturated or until the crystal is completely dissolved depending on which occurs first. On the other hand, a crystal placed in a supersaturated solution will grow. Growth will continue until the solution becomes saturated.
Miers as cited by Buckley (6, p. 9) reported the existence of a supersolubility curve. This is a curve that is approximately parallel to the solubility curve but at lower temperatures; it is also shown qualitatively on Figure 1. The supersolubility curve indicates the approximate conditions that must be achieved before incipient crystallization from a crystal free solution occurs. This curve is not always well defined.

Solubility as a Function of Particle Size

Buckley (6, p. 23) reported that Hulett (23, 24) was among the first to investigate the effect of particle size on solubility. By using fine powders of barium sulfate, mercuric oxide, and gypsum, he was able to produce temporary concentrations well in excess of the normal solubility.

Numerous attempts (15, 17, 21, 27, 28, 29, 42) as cited by Mullin (40, p. 33-35) have been made to explain this phenomenon. A classic relationship was developed by Ostwald (42) about 1900. He derived the following expression, which was patterned after the Kelvin or Thomson equation (2, p. 58) used in predicting the vapor pressure of small liquid droplets:

\[
\frac{RT \ln \frac{C_2}{C_1}}{1} = 5 \nu \left[ \frac{1}{\frac{1}{2}} - \frac{1}{\frac{1}{1}} \right]
\] (1)
where: \( R \) = the gas constant
\( T \) = the absolute temperature
\( C_2, C_1 \) = the solubility of particles of radius \( r_2 \) and \( r_1 \) respectively
\( \nu \) = the surface tension of the liquid-solid interface
\( \nu \) = the molecular volume of the particle

Freundlich (17, p. 144) later modified Ostwald's expression to give the well known Ostwald-Freundlich equation which follows:

\[
RT \ln \frac{C_2}{C_1} = \frac{2 \nu M}{\rho} \left( \frac{1}{r_2} - \frac{1}{r_1} \right)
\]

which becomes:

\[
RT \ln \frac{C_r}{C_{\text{normal}}} = \frac{2 \nu M}{\rho r}
\]

as \( r_1 \) becomes large. \( C_r \) and \( C_{\text{normal}} \) are the solubilities of particles of radius \( r \) and the normal solubility respectively; while \( M \) is the molecular weight of the solid, and \( \rho \) is the density of the solid.

The other papers, cited by Mullin, pertaining to the expressions relating solubility to particle size are, for the most part, adaptations of the Ostwald-Freundlich equation. These modifications take into consideration such things as the nonspherical shape of the particles (28), the cases where the density of the solid and/or the surface-tension of the solid-
liquid interface is not independent of particle size (21,27), and also allows for molecular dissociation of the dissolved solid (15,28). Another variation of the Ostwald-Freundlich equation is that proposed by Knapp (29) and altered still further by Dundon and Mack (15). They suggest that the total surface energy of the solid is a function not simply of the surface tension but also of the surface electric charge of the particle. The reader is referred to the original papers for a more detailed coverage of a particular subject.

Adamson (2, p. 347) states "while the experimental approach may be reaching firmer ground, the actual applicability of the Kelvin equation to the excess solubility of ionic crystals is only assumed and has not been confirmed as in the case of liquid droplets."

Homogeneous Nucleation

As was previously mentioned, homogeneous nucleation is the spontaneous generation of nuclei in a solution that is void of all foreign matter. A nucleus can be defined as an accretion of molecules.

The theoretical development of the energy requirements necessary for the nucleation of a liquid droplet from a super-
saturated vapor were presented by Gibbs (20, p. 322). Consideration of the free energy change of $n$ moles of a substance undergoing condensation will yield the following

$$
\Delta G = -nRT \ln \frac{P}{P_o} + 4\pi r^2
$$

(4)

The first term is the free energy released due to condensation and the second term is the additional free energy necessary due to formation of the surface. $P$ is the pressure of the bulk vapor phase and $P_o$ is the pressure of the liquid. Since we are considering $n$ moles, we can write this as $n$ moles = $\frac{4}{3}\pi r^3 \frac{\rho}{M}$. This, of course, assumes a spherical shaped droplet.

Putting this into equation (4) we have

$$
\Delta G = -\frac{4}{3M} \pi r^3 \frac{\rho}{M} RT \ln \frac{P}{P_o} + 4\pi r^2
$$

(5)

Then by varying $n$, and thus $r$, we can obtain a plot of $\Delta G$ versus $r$. Figure 2 is such a plot. This plot assumes the usual case that $P/P_o > 1$, hence $\ln P/P_o$ is positive.

Observation of Figure 2 points out that the free energy attains a maximum value at some value of $r$. This value of $r$ is referred to as the critical radius, $r_c$. By differentiating equation (5) with respect to $r$ and setting this differential equal to zero it is seen that
Figure 2. Typical curve of free energy versus radius of a liquid droplet condensing from a super-saturated vapor. $r_c$ is the critical radius occurring at the maximum value of $\Delta G$. 
FREE ENERGY, $\Delta G$ 

$r_c$

RADIUS OF LIQUID DROPLET, $r$
\[-\frac{4 \pi r^2 \rho}{M} \frac{RT \ln \frac{P}{P_0}}{\rho} + 8 \pi r \nu = 0\]  \hspace{1cm} (6)

and \[r_c = r = \frac{2 \nu M}{\rho RT \ln \frac{P}{P_0}}\]  \hspace{1cm} (7)

Note that equation (7) is almost identical to equation (3). The only difference is the way in which the activity is expressed. The well known thermodynamic principle that a system will always strive to attain its most stable state; i.e.; its lowest energy state and equation (7) allows one to predict what will occur to a nucleus of size \(r\) in a particular situation. If \(r < r_c\) it will dissolve; if \(r > r_c\) it will continue to grow. In both cases the nucleus will act in such a fashion as to lower its free energy. It is of interest to note that for water the critical drop size is about eight angstroms and contains about ninety molecules of water (2, p. 377).

Although the preceding thermodynamic expressions were developed for the case of a vapor to liquid phase change, it is believed that they also apply for the liquid to solid phase change.

As was just mentioned, a nucleus will either grow or dissolve depending on its size. Still to be answered, however,
is the question of how does a nuclei begin. The development of nuclei is not at all understood. One theory as mentioned by Mullin (40, p. 102) is that two molecules collide and are physically held together by molecular forces. This pair of molecules then collide with a third molecule, capture it and so on.

Mullin (40, p. 102) also mentions that it is unlikely that the formation of a nucleus occurs as a result of the simultaneous collision of the required number of molecules, as this would constitute an extremely unlikely event.

Heterogeneous Nucleation

Heterogeneous nucleation, unlike homogeneous nucleation, occurs because of the presence of submicroscopic particles of dust, crystallites, etc. All other conditions being equal, nucleation will more readily occur in the presence of foreign matter than in the absence of it.

The foreign substance can be thought of as a catalyst for nucleation. It effectively reduces the energy requirement necessary for nucleation. In the previous section it was mentioned that $\Delta G_{\text{max}}$ was the energy necessary to produce a nucleus of critical size under conditions of homogeneous
nucleation. In the presence of a foreign substance the energy requirement for heterogeneous nucleation, i.e., $\Delta G'_{\text{max}}$, can be expected to be $\Delta G'_{\text{max}} < \Delta G_{\text{max}}$.

Strickland-Constable (52, p. 104) citing Turnbull (55) and Hollomon and Turnbull (22) states:

"... $V$ will have a lower value at the solid-liquid interface, and must also allow for the difference in shape of the nucleus, which will be presumably disk-like rather than spherical."

Volmer (57) developed the following expression for the free energy reduction due to a catalytic surface

$$\Delta G' = \frac{\Delta G (2 + \cos \theta) (1 - \cos \theta)^2}{4}$$  \hspace{1cm} (8)

Here $\theta$ = the wetting angle

$\Delta G$ = the free energy change associated with the homogeneous formation of a nucleus

$\Delta G'$ = the free energy change associated with the heterogeneous formation of a nucleus

Crystal Breeding

One of the enigmas of crystallization has been the ability of crystals in suspension to produce new nuclei. This phenomenon has come to be known as "crystal breeding", "secondary nucleation" or "contact nucleation".
In 1963, Mason and Strickland-Constable (37) reported their observations of "breeding of nuclei" while experimenting with aqueous solutions of magnesium sulfate, potassium chloride, potassium bromide and other inorganic salts.

"Initial breeding" was the first type of crystal breeding observed by them. Whenever a seed crystal is placed into a quiescent, supersaturated solution, a number of new crystals are observed within a few seconds time. If the seed crystal is "cured" prior to being placed in the quiescent, supersaturated solution, no new crystals are produced.

The "curing" process involves the dissolution of the seed crystal in a solution undersaturated by about one degree, for approximately thirty minutes. The dissolution step is subsequently followed by a growth step—about one-half hour in a slightly supersaturated solution. The effect of the curing process on the seed crystal is not completely understood (31). In part, what is believed to occur is that small particles of crystal dust are present on the surface of the uncured seed crystal. This dust is the source of the observed new crystals in the supersaturated solution. The curing process effectively dissolves the crystal dust that is on the surface of the seed crystal and hence no new crystals form when the cured seed
crystal is placed in a quiescent supersaturated solution. The crystal breeding caused by the presence of crystal dust on the surface of the seed crystal is referred to as "initial breeding."

In a more recent paper Strickland-Constable (53) reports an attempt to eliminate initial breeding by slow drying. He tried to dry a crystal of MgSO$_4$·7H$_2$O sufficiently slow to avoid the formation of separate crystallites on the surface. All attempts were unsuccessful. He concluded that drying the crystal affects its surface other than by just deposition of crystallites from surface adhered mother liquor. Strickland-Constable also mentions "he has yet to encounter a system where initial breeding has not been present when using an uncured crystal."

Using cured seed crystals, Mason and Strickland-Constable observed two other types of crystal breeding that they chose to call "collision breeding" and "needle breeding." These investigators noted that when a cured seed crystal was glued to the end of a stirring rod and the crystal then placed in a supersaturated solution in such a way that the crystal made no contact with the vessel walls, agitator or any other solid object, no new or secondary crystals were observed. However, if the cured seed crystal was touched lightly with a second
stirring rod a number of secondary crystals were observed shortly after the contact. Likewise, when a cured crystal was simply placed in a saturated solution and allowed to drift along with the mixing patterns of the solution, the cured crystal made many contacts with the vessel walls and agitator and consequently many new secondary crystals were observed.

Johnson, Rousseau and McCabe (26) have recently reported that collision breeding does not occur as a result of contact between a MgSO$_4$·7H$_2$O crystal and a rubber surface nor between the crystal and a polypropylene surface. However, collision breeding did occur when the crystal was tapped with a steel rod. They concluded that in order for contact nucleation to occur between a crystal and another solid, the solid must be harder than the crystal.

Johnson (25, p. 92-95) reported in related work that K$_2$SO$_4$ failed to nucleate as a result of a crystal contact with either a polypropylene tipped rod or a steel rod. Polypropylene, MgSO$_4$·7H$_2$O, and K$_2$SO$_4$ have a Knopp hardness of 10, 25 to 30, and 135 respectively. Microscopic examination of both the MgSO$_4$·7H$_2$O and the K$_2$SO$_4$ crystal indicated that the MgSO$_4$·7H$_2$O crystal surface was much rougher compared to the K$_2$SO$_4$ crystal. Johnson concluded:
"The lack of surface irregularities formed during growth is related directly to the lack of nuclei formed from contacts such as were used in studying nucleation of MgSO$_4$$\cdot$7H$_2$O."

Barring macroscopic fracture of the crystal, it can be said that collision breeding is the result of contact of a cured crystal with another solid provided (1) the solid object is harder than the crystal, and (2) the crystal surface grows under such conditions that its surface has sufficient relative roughness capable of being attrited upon contact with the solid. If there are no contacts between the cured crystal and a solid object, no secondary crystals are produced.

Needle breeding was the third type of crystal breeding observed by the Englishmen. They observed this type of breeding only at high levels of supersaturation where the cured crystal is protected from all contacts with any solid object. Dendritic growth of the crystal occurs at these large levels of supersaturation, and Mason and Strickland-Constable concluded that the long spires of the crystal which are mechanically weak are subsequently broken off by the turbulence of the solution. Needle breeding is characteristic of the type of crystal breeding that occurs at high levels of supersaturation although needle breeding may occur in parallel with collision breeding.
Melia and Moffitt (39) investigated the phenomena of secondary nucleation using aqueous, inorganic solutions and obtained results corroborating those of Mason and Strickland-Constable.

In 1967 Cayey and Estrin (8) reported that for the case of magnesium sulfate heptahydrate, the number of nuclei observed at a given supersaturation level increased as the number of seed crystals increased. They also obtained data indicating that once nuclei are produced, these nuclei must attain a definite size before they can in turn become nuclei generators. Cayey and Estrin also noted that the nucleation rate increases with increasing supersaturation.

Lai, Mason and Strickland-Constable (31), using a different approach than Cayey and Estrin, also observed that secondary nuclei are of a very small size when produced. They also noted that the nucleation rate is a very strong function of supersaturation.

Lai, Mason and Strickland-Constable proposed two mechanisms for collision breeding (1) nucleation in the liquid phase, and (2) nucleation by attrition.
Nucleation in the liquid phase

As crystals collide with one another or the walls of the container, etc., nuclei might form in the thin layer of liquid between the crystal and the solid. However, these authors offered no detailed molecular model to explain this.

Nucleation by attrition

Collision breeding may be due to the actual breakage of the crystal at the point of collision. It is known that collision breeding is strongly dependent on supersaturation, but it is difficult to conceive of a mechanism where the tendency for breakage to occur depends on the supersaturation. So, if nucleation by attrition is to be the accepted mechanism, it is necessary to make the additional qualification that the particles, resulting from collisions of crystals with other solids, be of the same order of size as the critical size for the applicable supersaturation level. The critical size, $r_c$, is given by equation (3) which is believed to describe the solubility of small particles. Then at a given supersaturation level, all particles smaller than the critical size will re-dissolve. It is evident from equation (3) that at low levels of supersaturation $r_c$ will be larger than the $r_c$ corresponding
to higher levels of supersaturation. Consequently, a larger percentage of the secondary nuclei resulting from a crystal collision can be expected to survive at the higher levels of supersaturation than at the lower levels of supersaturation.

Recently Garabedian and Strickland-Constable (18) reported that the number of nuclei observed, after a controlled contact between a seed crystal and another solid object, depended on the supersaturation during the development (growth) period and not on the supersaturation during the contact period. These observations were made during a study of collision breeding of sodium chlorate. The results of his investigation gives credence to the survival theory—nuclei smaller than the critical size redissolve.

The results of an experiment, performed by Denk and Botsaris (14), designed to take advantage of the enantiomorphic properties of sodium chlorate strongly suggest that attrition is the mechanism of contact nucleation. Sodium chlorate crystallizes in two enantiomorphic forms. Because of this fact, it was possible for Denk and Botsaris to determine whether the nuclei produced by contact of a seed crystal with a steel striker bar came from the seed crystal itself or from
the solution. Their results indicated that essentially all of the nuclei came from the seed crystal.

Other mechanisms have been proposed for secondary nucleation. Powers' suggestions, (44), resulting from his work with sucrose, emphasize the role of the surface of the seed crystal to act as a rallying place for submicroscopic size solute particles awaiting their turn to be incorporated into the crystal lattice. The shear stresses of the fluid manage to sweep away some of the crystallites which become the source of new crystals.

A second mechanism proposed by Powers involves the growth of submicroscopic dendrites at the corner and edges of the seed crystal. The dendrites being mechanically weak are dislodged by the turbulence of the solution and/or by the crystal/solid contacts.

One must be aware of the inherent differences between sucrose and the inorganic salt solutions. It is conceivable that different mechanisms may govern their nucleation.

Clontz and McCabe (11) investigated the effect of (1) supersaturation, (2) energy of contact, (3) solution velocity, (4) area of contact, (5) orientation of crystal in stream of solution, and (6) angle of contact of the contacting rod (or
crystal) with respect to the seed crystal on the contact
nucleation of magnesium sulfate heptahydrate. Their experi­
mental system was composed of a stationary, cured seed crystal
and a solution of fixed supersaturation flowing continuously
around this crystal.

The device used to measure the energy striking the surface
of the seed crystal consisted of (1) a stationary crystal, and
(2) a steel rod capable of moving in the vertical direction.
The rod was supported by a spring. A known mass dropped on the
rod forces contact between the rod and the crystal. Different
contact energies were obtained by dropping the weight from
different elevations. In order to determine the number of
nuclei generated by a rod/crystal contact, the flow of solution
was discontinued shortly after contact was made. This allowed
the nuclei time to grow to a size large enough to facilitate
visual crystal counts.

McCabe and Clontz noted that lack of contact between the
rod and the crystal yielded no nucleation. They also noted
that for the range of fluid velocities examined, 0.5 to 2.5
cm/sec, the number of nuclei resulting from a single contact,
at a fixed contact energy and supersaturation, was independent
of the velocity of flow past the seed crystal. The surface of
the crystal was examined with a 40 power microscope immediately after each contact and no obvious damage to the crystal was noticed.

McCabe and Clontz like all the previously mentioned investigators, observed an increasing nucleation rate with increasing supersaturation. They also reported that for contacts resulting from nonparallel crystal and rod surfaces, larger numbers of nuclei were produced than for experiments where the colliding faces remained parallel. Edge contacts between crystal and rod generated more nuclei than did flat contacts.

These authors presented two equations relating the number of nuclei (N), energy of contact (E), supersaturation (α), and area of contact (A) which were well substantiated by the data they obtained:

\[ \frac{N}{A} = k_1 (\alpha - 1) E A^{-\frac{1}{2}} \]  \hspace{1cm} (9)

for crystal/rod contacts, and

\[ \frac{N}{A} = k_2 (\alpha - 1) E \]  \hspace{1cm} (10)

for crystal/crystal contacts.

Johnson (25) using a modified McCabe and Clontz system (11) corroborated and refined the observations of Clontz pertaining
to the effect of supersaturation, energy of contact, etc. on
the contact nucleation of MgSO$_4\cdot7$H$_2$O.

Crystal Growth

Once a nucleus exceeds the critical size for the prevailing
supersaturated solution, it will begin to grow. Growth will
continue until the supersaturation is depleted or until the
crystal is removed from the solution.

If a crystal grows in such a way as to maintain its
original shape; i.e.; to maintain its geometric similarity,
the crystal is said to be invariant under growth. Unless an
invariant crystal is a regular polyhedron, the growth rates of
the various crystal faces will be different.

Normally the growth rate of the various faces of a crystal
differ. Buckley (6, p. 122) points out:

"Because of the differences in the velocity of growth
of the various faces, a crystal continually strives
to have the slowest extending faces as its boundaries.
... No matter what the initial shape of the crystal,
it will, on growing, approximate more and more to a
final form, constant for that crystal under the given
conditions of supersaturation and temperature."

One of the first theories of crystal growth to gain
stature was that proposed by Curie (12) in 1885. In brief,
this theory suggested that a crystal will adopt a final form
such that the sum of the surface energy associated with each face will be a minimum. Curie's theory was prominent until Berthoud (4) in 1912 showed that one of the implications of Curie's minimum surface energy theory was that the greater the supersaturation of a solution the more rapid is the growth and, in consequence, the crystal habit ought to become more complex approaching a sphere as a limit. The fact is the reverse is true, the crystal becomes either needle like or tabular.

Noyes and Whitney (41) proposed a theory which in part still finds acceptance today--the diffusion theory. Their theory can be expressed in the following mathematical form:

\[ \frac{dm}{dt} = k_m A (C - C^*) \]  

as given by Mullin (40, p. 116). \( m \) being the mass of solid deposited in time \( t \), \( A \) the surface area of the crystal, \( c \) the solute concentration in the bulk of the liquid, \( C^* \) the saturation concentration of the solute, and \( k_m \) the coefficient of mass transfer. They considered that crystal growth and dissolution would occur at the same rate and would be governed by the driving force of concentration gradient. The diffusion theory as it pertains to crystal growth in effect assumes an instantaneous reaction at the crystal surface; no time is
allowed for incorporation of a solute molecule into the crystal lattice. Experimental evidence by Leblanc and Schmandt (33) and Marc (35 and 36) indicated that the rate of growth and the rate of dissolution of the same crystal at the same conditions were not equal. A crystal will generally dissolve at a faster rate than which it will grow.

Berthoud (4) was again on the scene. He assumed that the surface incorporation step was not instantaneous, that time was required to arrange and disarrange the particles at the growing surface. Modifying the Nernst equation (see Buckley 6, p. 149), Berthoud presented the following expression for the rate of crystal growth

$$\frac{dm}{dt} = \frac{AD(C - C^*)}{x + \frac{D}{k}}$$

(12)

D being the diffusion coefficient, x the film thickness through which the solute molecules must diffuse, and k the surface reaction rate constant.

A third theory of crystal growth is the adsorption layer theory initially stated by Volmer (56). Observation of the growth of mercury crystals from the vapor state, and of crystals growing layer by layer with an accompanying color change suggest
the mechanism of surface adsorption followed by complete growth of the crystal layer. The essence of the adsorption layer theory is that atoms or molecules in the near vicinity of the growing crystal surface are adsorbed on the surface at a position where the attractive forces are the greatest; i.e., where the greatest concentration of similar molecules are located. Once this entire layer of the crystal face is complete, a new layer must begin. For more detailed information on this theory and modifications of it, the reader is directed to the following papers: Brandes (5), Kossel (30), and Stranski (51).

Frank (16) proposed a crystal imperfection, or dislocation, as the mechanism for crystal growth. In this case growth is self perpetuating. His theory is known as the screw dislocation.

A number of investigators (9,19,58) have found that crystal growth appears to be a function of the crystal size. The growth rate of crystals smaller than some particular size, say \( L_c \), are dependent on the crystal size. While crystals larger than \( L_c \) have a growth rate which is believed to be independent of size, so long as the crystal is larger than \( L_c \).
Types of Crystallizers

Crystallizers exist in a countably large number of shapes and sizes, but basically there are three types—stirred tank, fluidized bed, and plug flow. Most industrial crystallizers are of the stirred tank type. These are operated either batch-wise or continuously. The continuous, mixed suspension, mixed product removal (MSMPR) crystallizer has been subjected to the most detailed analysis. In this type of crystallizer an unsaturated feed is continuously delivered to a stirred tank. Supersaturation is achieved most likely by cooling the contents of the vessel. Once nucleation has begun, a continuous slurry of crystals of varying size leaves the vessel.

Simulation of the Continuous MSMPR Crystallizer

As was mentioned previously, control of the crystal size distribution (CSD) leaving the crystallizer is desired. A number of papers (9,32,45,47,50,58) have been published which mathematically model the operation of the MSMPR crystallizer and hence predict the CSD produced for various operating conditions. One common problem with these models, as they relate to industrial scale crystallizers, is that although the models adequately fit the data for the laboratory
scale crystallizer, they may not for the industrial scale crystallizer. Usually the larger crystallizers are not ideally mixed, an assumption made and a condition usually met in the smaller scale operation from which the model was developed.

The population balance equation (47, p. 49)

\[
\frac{dn}{dt} + \frac{\lambda(Gn)}{\lambda L} + D - B + n \frac{d(log V)}{dt} = - \sum_k \frac{n_k Q_k}{V} \tag{13}
\]

is the basis of most continuous MSMPR crystallizer models. Where the terms are \( n \) the population density, \( t \) the time, \( G \) the crystal growth rate, \( L \) the crystal size, \( B \) the birth rate of new crystals, \( D \) the death rate of crystals, \( V \) the volume of the crystallizer, and \( Q \) the volumetric flow rate. The subscripts of \( n \) and \( Q \) refer to the various number of inflow and outflow streams to or from the crystallizer, and \( Q \) is taken as positive for flow out of and negative for flow into the volume, \( V \).

At steady state \( \frac{dn}{dt} = \frac{d (log V)}{dt} = 0 \). If McCabe’s \( \Delta L \) law (38, p. 772) is applicable then \( G \neq G(L) \), and if there is but a single inlet and discharge stream and the inlet stream contains no crystals, then
and equation (13) becomes

\[ G \frac{\partial n}{\partial L} + D - B = -\frac{n_o Q_o}{V} \]  

(14)

If in addition, there is no breakage \( B = D = 0 \) and if the vessel is assumed well mixed, \( n = n_o \), there results

\[ G \frac{\partial n}{\partial L} = -\frac{n}{\tau} \]  

(15)

where \( \frac{V}{Q_o} = \tau \), is the average residence time of a crystal in the vessel. The solution to equation (15) is

\[ \int_{n_o}^{n} \frac{d \ln n}{n} = -\frac{1}{G\tau} \int_{0}^{L} dL \]

\[ \ln \frac{n}{n_o} = -\frac{L}{G\tau} \quad \text{or} \quad n = n_o \exp \left(-\frac{L}{G\tau}\right) \]  

(16)

Here \( n_o \) is the population density of the nuclei.

One notes from equation (16) that if a plot of \( \ln n \) versus \( L \) results in a straight line, the nuclei population density \( n_o \) is obtained from the intercept at \( L=0 \), and the growth rate, \( G \), is obtained from the slope of the line. The nucleation rate, \( B^o \), is then the product of \( n_o \) and \( G \).
If steady state is achieved, but a plot of \( \ln n \) versus \( L \) does not yield a straight line, the growth rate is size dependent. The differential equation describing this situation is

\[
\tau \frac{d(Gn)}{dL} = -n
\]  

(17)

obtained from the general population balance equation. Abegg, Stevens and Larson (1) discuss a method of obtaining the growth and nucleation rates when \( G = G(L) \) and steady state conditions prevail.

In the event that steady state is not attained and the crystal growth rate is size dependent, data reduction to obtain growth and nucleation rates is more difficult. The transient, size dependent growth rate form of the general population balance must be used. This equation per Cise and Randolph (9) is

\[
\frac{\partial n}{\partial t} + \frac{\partial (nG)}{\partial L} + \frac{n}{\tau} = 0
\]  

(18)

In their paper they present a procedure for solving this equation making use of experimental data.

It was previously mentioned that the nucleation rate, \( B^0 \), and the crystal growth rate, \( G \), can be obtained from the
experimental determination of the crystal size distribution. The growth and nucleation rates obtained in this manner are apt to be more realistic than those results obtained when either nucleation or growth is determined separately. Most nucleation rates are not determined when nucleation and growth are occurring simultaneously and hence do not represent the condition prevailing in a crystallizer. However, analysis using the population balance technique allows this to be done.

Experimental verification of the population balance equation, particularly equation (16), was initially at least done via screen analysis of the crystals leaving the crystallizer. Excellent agreement between the experimental results and the theoretical was obtained.

In the past few years, with the aid of a more sophisticated means of particle size determination, analysis of the crystals leaving a crystallizer, particularly those in the subsieve size range (i.e., < 40 \( \mu \text{m} \)), have resulted in nucleation rates which differ from those obtained via the conventional continuous MSMPR crystallizer technique of extrapolation (9, 46, 58). Randolph and Cise (46, p. 2, 27, 28) state that the nucleation rates obtained in the conventional fashion are about a factor of 100 less than those nucleation
rates obtained from the data obtained using the modern particle counters. These investigators explain the discrepancy by the fact that the birth, growth, and washout of the very small particles are not accounted for via the sieve analysis. They then state that the extrapolation actually gives the net apparent nucleation rate and not the actual nucleation rate. However, the continuous MSMPR crystallizer kinetic correlations remain the most useful technique for CSD simulation in systems not far removed from the continuous MSMPR crystallizer operation.

Continuous MSMPR Crystallizers and Contact Nucleation

Cise and Randolph (9), Youngquist and Randolph (58), Ottens and deJong (43) investigated contact nucleation of $K_2SO_4$, $(NH_4)_2 SO_4$, and $KAl(SO_4)_2 \cdot 12H_2O$ respectively in the continuous MSMPR crystallizer.

Using similar, if not identical equipment, Cise and Youngquist were able to study the transient population balance in the 1 to 40 $\mu$m size range. These investigations strongly suggest that (1) growth rates of particles in the subsieve size range are very much size dependent, and (2) contact nucleation is an attrition phenomenon.
By measuring the population density response to a step change in the agitation rate, they were able to observe an almost instantaneous birth of particles in the 1 to 6 \( \mu \)m size range. Based on this they concluded that the particles are born into this size range and do not grow into it which is tantamount to suggesting that attrition is the mechanism for contact nucleation. Photographs also indicated that macro-attrition of the larger seed crystals had occurred. Youngquist presented a model for the birth function, \( B \), (in the population balance equation, equation (11)) which fit his data,

\[
B = m L^b
\]  \hspace{1cm} (19)

\( B \) being the birth function, \( L \) the particle size, and \( m \) and \( b \) are empirical constants.

Analysis of the population density data and equation (11) enabled Cise to develop the following expression for the growth rate of \( K_2SO_4 \).

\[
G = G_\infty \exp \left( \frac{-k}{\sqrt{L}} \right)
\]  \hspace{1cm} (20)

Where \( G, G_\infty, k, \) and \( L \) represent the crystal growth rate at size \( L \), the crystal growth rate of "large" crystals, an empirical constant, and the crystal size respectively. Note that
the growth rate decreases with size and approaches the same
growth rate of large particles as L increases. It should be
pointed out that equation (18) is the maximum growth rate
expected as the assumption that the birth function, B, was
equal to zero was made in the development of equation (18).

Ottens and deJong (43) reported a theoretical development
for contact nucleation. The essence of their work was that
contact nucleation, J, should be

\[ J \propto \text{crystal suspension density for crystal/agitator contacts} \]

\[ J \propto (\text{crystal suspension density})^2 \text{ for crystal/crystal contacts} \]

Their experimental results using potassium alum indicated
that the nucleation rate was proportional only to the first
power of the crystal suspension density suggesting that crystal/
crystal contacts either do not occur or contribute negligibly
to the net nucleation rate.

Youngquist and Cise reported that the nucleation rate for
their respective systems was also proportional to approximately
the first power of the suspension density, again suggesting
that crystal/crystal contacts contribute negligibly to the net
contact nucleation rate.
Although the following expression for nucleation rate has no theoretical foundation many people (43, 46, 47, 58) express the nucleation rate in this fashion. It is referred to as a power law model.

\[ B^0 = f [ T, \text{RPM}, S^a, M_T^b ] \]  \hspace{1cm} (21)

Characterization of MgSO\textsubscript{4}·7H\textsubscript{2}O

The magnesium sulfate heptahydrate (or epsom salt) crystal is classified by crystallographers as orthorombic; i.e.; it has three mutually perpendicular axes of unequal length. Figure 3 from Clontz and McCabe (11) illustrates the MgSO\textsubscript{4}·7H\textsubscript{2}O crystal.

The habit or shape of the crystal is determined by the relative magnitude of the growth rates of the 110 and 111 faces. Generally speaking the crystal habit of MgSO\textsubscript{4}·7H\textsubscript{2}O is acicular at low saturation temperatures and more prismatic at higher saturation temperatures. This was pointed out by Gavrilova as cited by Johnson (25, p. 84).

Saturation data for the MgSO\textsubscript{4}·7H\textsubscript{2}O·H\textsubscript{2}O system is abundant. The best sources are Ting and McCabe (54) and Cayey and Estrin (8). Cayey and Estrin developed a linear relationship between concentration of MgSO\textsubscript{4} and temperature in the 20°C range.
Figure 3. The magnesium sulfate heptahydrate crystal. The numbers refer to the various crystal faces. From Clontz and McCabe (11).
Their relationship is the basis for all supersaturation measurements reported in this current work.

Crystal breeding and contact nucleation was defined in a previous section of this paper. A better perspective of the contact nucleation of MgSO$_4\cdot7$H$_2$O is presented by the following figures (Figures 4 and 5) from Johnson's thesis (25). Figure 4 illustrates both the effect of contact energy and the contact energy density (contact energy per area of contact) on the nucleation rate. Figure 5 demonstrates the effect of supersaturation on the nucleation rate. In this figure it is noted that the contact energy is applied in the form of a pressure contact, as opposed to an impact contact. Johnson describes a pressure contact:

"The rod was loaded by placing a weight on the end. This weight deflected the supporting diaphragm and caused the rod to touch the crystal at a fairly slow approach velocity."

Carey and Bosanquet (7) as cited by Johnson reported in a study of coal crushing that the energy required and the fracture pattern which resulted were the same regardless of whether the energy was applied by impact, pressure or a combination of sliding contact and pressure. Johnson (25, p. 102) reports: "There is no reason to believe that the same obser-
Figure 4. Effect of contact energy on the number of nuclei produced by rod-crystal impacts for various rod diameters. From Johnson (25).
ROD-CRYSTAL IMPACTS
\[ \alpha = 1.043 \]
Figure 5. Effect of supersaturation on the number of nuclei produced for pressure contacts with various size rods. From Johnson (25).
vation would not hold true for the crushing of small surface irregularities."

The growth rate of "large crystals" of MgSO₄·7H₂O was reported in a recent paper by Clontz et al. (10). Applying their data to the growth rate model presented by Berthoud (equation 12) allowed determination of the mass transfer and the surface reaction coefficients. Reproduced is their results relating supersaturation and growth rate. This is shown as Figure 6.
Figure 6. Effect of supersaturation on the growth rates of the 111 and 110 faces of magnesium sulfate heptahydrate. Redrawn from Clontz et al. (10).
111 face at $T_{\text{sat}} = 33.5^\circ C$

$\triangle$ 111 face at $T_{\text{sat}} = 38.0^\circ C$

$\nabla$ 110 face at $T_{\text{sat}} = 33.5^\circ C$

$\circ$ 110 face at $T_{\text{sat}} = 38.0^\circ C$

SOLUTION VELOCITY = 0.04 ft/sec

LINEAR GROWTH RATE, mm/min, $\times 10^3$

SUPERSATURATION, $(y_A - y_B) \times 10^3$
EXPERIMENTAL

Clontz and McCabe (11) and Johnson et al. (26) have investigated the effect of contact energy, area of contact, and supersaturation on the nucleation rate of MgSO\(_4\)·7H\(_2\)O in a semiflow system. Their findings that the nucleation rate increased with (1) the energy of impact, (2) the supersaturation, and (3) the area of contact contributes to the understanding of the mechanism of contact nucleation. Just as important and possibly more so were Johnson's discoveries (26) that, at the supersaturation level he investigated, (1) nucleation occurred only if a crystal was contacted by a solid that was equally as hard or harder than the crystal itself, and (2) that the nucleation rate was a function of the roughness of the crystal surface.

As revealing as these facts are, they contribute only in a qualitative sense in the determination of the nucleation rate in a MSMPR crystallizer. There still exists a need to quantitatively determine the net nucleation rate in terms of the contact energy for a MSMPR crystallizer.

Combination of a modification of the crystal contacting device developed by Clontz and McCabe (11) and the mathematically well defined MSMPR crystallizer should produce a technique
by which the net nucleation rate, \( (B^0) \), can be determined as a function of the supersaturation \( (S) \), the residence time \( (\tau) \), the contact energy \( (E) \), the contact area \( (A) \), and the rate of contact \( (f) \); i.e.,

\[
B^0 = g (S, \tau, E, A, f) \quad (22)
\]

In the application of this technique, it is presumed that most, if not all, of the nucleation is achieved at the crystal contactor. Determination of the CSD in the continuous crystallizer can be obtained by using a Coulter counter. The probe of the Coulter counter is placed in the crystallizer itself. This is an improvement on the technique first used by Randolph and Rajagopal (48) where the probe was placed in a side stream leaving the crystallizer. By placing the probe in the crystallizer, it sees a more representative sample than it would if it were in a side stream from the crystallizer. Application of the population balance equation to the CSD allows the determination of the nucleation rate. Hence, an expression such as equation \((22)\) can be obtained.

Cise and Randolph (9) and Youngquist and Randolph (58) determined the nucleation and growth kinetics for \( K_2SO_4 \) and \( (NH_4)_2SO_4 \) respectively in the transient operation of a
MSMPR crystallizer. By measuring the population density response to a step change in the agitation rate, they concluded (as did Johnson et al. (26)) that microattrition of the crystals in the crystallizer was the mechanism of contact nucleation.

Randolph and Cise (46) and Youngquist and Randolph (58) expressed the nucleation rate for their MSMPR crystallizer systems in the form of power law models. Typical was the one from Randolph and Cise (46)

\[ B^0 = k_N \exp \left( \frac{k_1}{T} \right) s^{2} m_j^{3} (Re_s)^{4} \]  

Note that this equation has as parameters, the temperature of the system (T), its supersaturation (s), the jth moment of the population distribution (m_j), and the agitation rate in the form of the Reynolds number for stirring (Re_s). This equation has no fundamental theoretical basis; it is purely empirical. Consequently, the nucleation as a result of a crystal/solid contact was simply inferred in the term (Re_s)^4 of equation (23). There was no way of determining the number of nuclei produced per contact for a given energy of contact because not only were the number of crystal/solid impacts unknown, but so was the energy associated with each contact.

In this work, using a MSMPR crystallizer, actual measurement of the nucleation rate resulting from a single crystal/
solid contact is intended for various conditions of contact energy, supersaturation and residence time.

Knowing the net number of nuclei produced per contact for fixed conditions of \( T \), \( s \) and \( E \), and also knowing the number of crystal/solid impacts occurring in a crystallizer and the energy associated with each impact, it would be possible to predict the nucleation rate in a MSMPR crystallizer. This information would be most important in helping to control the CSD issuing from a crystallizer.

Equipment Description and Specifications

The process flowsheet for this investigation is schematically represented in Figure 7, while the actual apparatus is shown in Figure 8 and described in the following paragraphs.

**Saturator and surge tank**

This is a 1 ft. by 1 ft. cylindrical glass container having a full volume of 22,200 ml. and a working volume of about 18,000 ml. This vessel is equipped internally with a glass coil, of about 1.4 sq. ft. of surface for the purpose of heating the process fluid in the tank. The vessel was used to provide a feed stream of constant temperature and composition to the crystallizer.
Figure 7. Process flowsheet for the investigation of contact nucleation effects of magnesium sulfate heptahydrate in a continuous MSMPR crystallizer.
Figure 8. Photograph of the apparatus used in the investigation of contact nucleation effects of magnesium sulfate heptahydrate in a continuous MSMPR crystallizer.
Saturator agitator

It is a Lightnin Model V-7 mixer, type 70537, of about 1/10 hp. It was used to maintain fluid homogeneity in the saturator tank.

Feed pump

This pump consists of a pair of Gorman-Rupp diaphragm pumps, of 100-400 ml./min. capacity. It was used to transport the process stream through the system.

Rotameter

This is a Brooks Rotameter, type 6A-1110-10. It indicated the rate of flow of the process stream through the system.

Nuclei eliminator

This is a 3 in. diameter by 16 in. plexiglass cylinder containing a glass coil with about 1 sq. ft. of heat transfer surface. The purpose of this device was to dissolve any solute particles that may not have been dissolved in the saturator tank prior to their entering the crystallizer. Warm water was inside the coil.

Filter

A Pall Disposable Filter Assembly, Number MBY2001URA, 0.35 microns was used. This filter removed solid matter in the
process stream prior to its entry into the crystallizer.

**Crystallizer**

The crystallizer is a 6.75 in. diameter by 7.5 in. high plexiglass vessel. It also has a plexiglass jacket. The full volume is 4400 ml. while the working volume is about 3500 ml. The cooling fluid flows through the jacket. The solute crystallization takes place in this vessel.

**Crystallizer agitator**

It is a Cole Parmer constant speed control unit and drive. The model no. is 600-013 and has a range of 0-3000 RPM. It was used to maintain a constant agitation rate in the crystallizer.

**Coulter counter**

This instrument, a portion of which is immersed in the process fluid inside the crystallizer, enabled the determination of the number and size of the crystals in the crystallizer. It is a model A.

**Crystal contactor and controller**

This is of custom construction. It is composed of a stationary platform on which a seed crystal is mounted. A solenoid holds the plunger in a vertical position. When elec-
trical power to the solenoid is interrupted, the plunger falls and strikes the crystal. As power is restored, the plunger is returned to its original position. The plunger weighs about 40 gm and is constructed so additional weight, washers of varying mass, can be added to the plunger to increase the mass striking the crystal. The drop distance can be varied up to about 1/2 an inch. The purpose of this device was to allow a known mass to drop by gravity from its normal position, strike a stationary seed crystal, and then to return to its normal position. The maximum number of contacts is approximately 120/min. The crystal contactor was believed to be the sole source of nucleation in the crystallizer. The contactor is composed of plexiglass. See Figure 9 for a schematic representation of the crystal contactor.

**Heating bath and controller**

It is a Precision Scientific Company bath catalog no. 66580. The controller catalog no. is 62690. It was used to maintain a constant temperature in the saturator tank via forced circulation of the bath fluid through the coils in the saturator tank.
Figure 9. Crystal contactor.
Pump

This pump was purchased from Eastern Industries of Hamden, Connecticut. It is a model E-1, type 100 and about 1/15 hp. It was used to circulate the heating fluid mentioned in the preceding description.

Heating bath

The heating bath is a Cole Parmer, Lab-Line Instrument, cat. no. 3052. It supplies warm water to the nuclei destroyer. It contains its own pump.

Refrigeration unit

This unit is from Blue M Electric Company of Blue Island, Illinois. It has model no. PCC-24SSA and a range of -23 to ambient deg. C. It was used to cool the ethylene glycol - water mixture. The cooling fluid was delivered to the jacket of the crystallizer.

Insulated tank

It is a 30 gal. ss. drum. It was used as an ethylene glycol - water reservoir.

Pump

This pump was also obtained from Eastern Industries.
It is a model E-1, type 100 and about 1/15 hp. It was used to transport the cooling fluid from the insulated tank to the crystallizer jacket.

**Rotameter**

This is a Brooks Rotameter, type 1110. It was used to indicate the flow rate of the cooling stream to the jacket of the crystallizer.

**Thermometer**

Four of these were used. They were obtained from Scientific Glass Apparatus Company. They are of the total immersion type and have a range of 0(0.1)50 deg. C. They were used to indicate the temperature of the process fluid in the crystallizer and in the saturator tank, and the temperature of the cooling fluid before and after the crystallizer.

**Description of Experimental Operation**

The experimental apparatus was designed to crystallize $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in a continuous manner. The equipment is schematically represented in Figure 7. The primary features of the apparatus are a saturator-surge tank, a nuclei eliminator, an in line filter, the crystallizer, a Coulter counter, and a crystal contactor. See Figure 9 for a depiction of the crystal
contactor. Some associated equipment such as pumps, a constant temperature bath, and a refrigeration unit was also used. A complete listing of the apparatus was given in the preceding section entitled Equipment Description and Specifications.

MgSO₄ solution was pumped from the saturator-surge tank through the rotameter to the nuclei eliminator, where any fines that did not dissolve in the saturator-surge tank were dissolved. The solution then entered the filter where all particles larger than 0.35 microns were removed, thus minimizing heterogeneous nucleation. Following filtration, the feed stream entered the crystallizer. The level in the crystallizer was maintained by an external leg.

Immersed in the crystallizer was the probe of the Coulter counter and also the crystal contactor. The Coulter counter was used to obtain the CSD in the crystallizer while the crystal contactor served as a crystal/solid contacting device which gave rise to nucleation. The slurry leaving the crystallizer was recycled to the saturator-surge tank. There it was heated to a temperature greater than the saturation temperature where all the crystals were dissolved. The process was then repeated.
As was previously mentioned, all references to saturation and supersaturation are based on the model developed by Cayey and Estrin (8). This model describes saturation of the MgSO$_4$·H$_2$O system in the vicinity of 20°C.

A typical experimental run began by circulation of the feed stream, which was saturated at approximately 22°C, through the rotameter, the nuclei eliminator, the filter and the crystallizer and back into the saturator-surge tank. The feed stream was circulated at a temperature of 26°C for at least four hours and usually overnight. This was done to insure dissolution of all crystals in the crystallizer and the remainder of the system. Following circulation of the feed stream, the feed pump was adjusted to the proper flow rate thus fixing the average residence time ($\tau$). The coolant stream was then allowed to flow through the jacket of the crystallizer at a predetermined rate.

At this point a reading was taken on the Coulter counter primarily to observe the "electronic noise" level. If the noise was too intense, the run was postponed. Normally however, the noise was sporadic and caused little or no problem.

The rate of the ethylene glycol coolant stream was continually monitored, adjusting as necessary, until the temperature in the crystallizer attained the desired level.
Then the uncured seed crystal, which was mounted on the platform of the crystal contactor, was put into the crystallizer. Initial breeding was observed almost immediately. The decay of the initial breeding required three to four residence times. Contacting of the crystal was begun shortly after placing it in the crystallizer. A contacting rate of eight, thirteen, or twenty contacts per minute was used.

The energy the falling plunger had, at the moment of impact with the crystal surface, was predetermined and was maintained essentially constant throughout the course of the run. A latter section will describe how this contact energy was determined.

The temperature of the suspension in the crystallizer was frequently monitored. At approximately five and one-half residence times from the time crystal contacting began, a sample of the mother liquor was withdrawn from the crystallizer. The sample was drawn through a porous cotton plug which was attached to the tip of a pipette. This was done to insure that no crystals were in the sample of mother liquor. The sample was analyzed gravimetrically for MgSO₄ content. From the result of this analysis, the supersaturation level in the crystallizer was determined.
At precisely six residence times, with time zero being the
time at which crystal contacting commenced, the CSD in the
vessel was observed using the Coulter counter. This process
required approximately fifteen minutes.

After completion of the size distribution analysis, the run
was terminated. The entire run required approximately three
hours excluding the circulation time for crystal dissolution.

Coulter counter

Use of the Model A Coulter counter with a $140 \mu m$ aperture
tube allowed the observation of particles of 13 to 67 microns
equivalent spherical diameter. A screen with openings of
approximately 82 microns was placed around the aperture to
prevent its plugging. Calibration of the aperture tube with
and without the screen, using pecan spores, gave virtually
identical calibration constants and particle counts. It was,
therefore, concluded that the screen prevented plugging of the
aperture tube but otherwise created no problems giving results
identical to those for the case of no screen for particles
smaller than the screen openings.

Growing seed crystal

Because of the supersaturated condition in the crystal-
lizer, the seed crystal grew during the course of the experi-
mental run. Consequently, the vertical "drop distance" between the plunger and the crystal surface slowly decreased. To compensate for this condition, the drop distance was periodically increased as measured by a cathetometer. The distance of increase was based on the growth rate of the seed crystal which was previously measured, for the particular operating conditions, to one ten-thousandth of an inch.

**Area of contact**

An attempt was made to keep the contact area between the plunger and the crystal constant by insuring that the cross sectional area of the plunger was the smaller of the two areas. The diameter of the tip of the plunger was one-eighth of an inch.

However, it was soon discovered that it was difficult to initially attain total contact between the total area of the plunger and the crystal. Furthermore, it was virtually impossible to maintain the same area of contact throughout the course of the one to two hour experiment. This is not difficult to understand when one realizes that the crystal surface is growing at a rate of one to three microns per minute during the entire run. An additional complication was that the crystal surface did not always grow isometrically. Frequently
the initially flat surface was slightly terraced by the end of the run.

In order to approximate the area of contact a piece of carbon paper was laid on the crystal surface and the plunger was allowed to drop and strike the carbon paper. The plunger made an impression on the surface of the carbon coating. This impression was assumed to be the area of contact between the plunger and the crystal surface. The contact area was always less than $5 \text{ mm}^2$. This area was measured by having a photomicrograph made of the impression, measuring the area of the impression as it appeared on the photograph with a planimeter, and then scaling it back down to actual size.

The area of contact was measured in the previously described manner at the start and at the end of an experimental run. These areas change somewhat during the course of a run.

**Determination of energy of contact**

The plunger, which was used to contact the crystal surface, was composed of a three-eighths inch outside diameter plexiglass tube capped with a plexiglass rod tapered to a one-eighth inch diameter tip. It should be mentioned that this technique is similar to that of Clontz and McCabe (11). For
the purpose of determining the impact energy of the plunger at the crystal surface, the plexiglass tip was temporarily replaced with a copper tip of the same diameter. A copper wire was fed internally the length of the plunger and soldered to the copper tip.

A copper plate was then mounted under the falling plunger where the crystal would normally be. A copper wire was also soldered to this plate. The contactor, with the plunger in place, was then put in the crystallizer. Recall that MgSO₄ solution is electrolytic. The two copper leads were then connected to an oscilloscope where the voltage difference between the two plates could be observed. If there was no physical contact between the plates, some small finite voltage difference was discernable. The instant the copper plates came in contact, a zero voltage difference was observed.

The contactor was allowed to operate at a rate of about thirty taps per minute. It was noted that the mass of the plunger itself was not sufficient to cause contact. Additional mass was added to the plunger in order to just cause contact between the two plates on twenty successive strokes of the plunger. It was observed that this technique was sufficiently accurate in that a difference in mass of one-tenth
of a gram either produced or did not produce contact on twenty successive strokes.

The drop distance was then altered and again the mass necessary to just cause contact between the two plates on twenty successive strokes was determined. Figure 10 is a plot of the mass required to just cause contact for a given drop distance.

It was concluded that the mass, for a given drop distance, necessary to just cause contact was the mass required to just overcome the combined resistances to the falling plunger. Any mass exceeding this "zero mass" was concluded to strike the crystal surface with some positive energy. See Appendix A for a mathematical discussion supporting this conclusion.

It should be pointed out that the energy striking the crystal surface is not necessarily transferred to the crystal. All that is being measured is the energy contacting the crystal surface.

**Ideally mixed vessel**

One of the assumptions usually made in simplification of the population balance equation is that the crystallizer is well mixed; i.e.; the concentration within the vessel is independent of location.
Figure 10. Total mass required to just cause contact between the plunger and the crystal (includes the mass of the plunger).
TOTAL MASS OF PLUNGER PLUS ADDITIONAL WEIGHTS, g

DROP DISTANCE, 1/32 in.
In order to determine whether or not the crystallizer was well mixed, an exit age distribution analysis was performed. See Levenspiel (34, p. 250) for the mathematical development. In essence, for a well mixed vessel the following relationship holds

\[ C = C_0 e^{-t/\tau} \]  

(24)

Where \( C \) is the concentration at any time, \( C_0 \) the initial concentration, \( t \) the time, and \( \tau \) the average residence time. Then if \( \ln \left( \frac{C}{C_0} \right) \) is plotted versus time, \( t \), a straight line should result and the slope of this line would be equal to \(-1/\tau\). A comparison is then made between the \( \tau \) given by theory and the \( \tau = V/v_f \) actually measured, the volume of the vessel being \( V \) and the volumetric flow rate being \( v_f \).

Ragweed pollen with a diameter of about 18 microns was used to conduct the analysis described above. It was placed in the crystallizer, at an agitation rate of 500 RPM and the feed stream off, and was allowed to mix for a few minutes. Following this a particle count was made with the Coulter counter counting the total number of particles greater than 13 microns in a 2 ml. sample. This value was used as the initial concentration, \( C_0 \), in the above relationship. At time
zero the feed pump was turned on and the pollen began leaving the vessel. The particle concentration was measured as a function of time. Figure 11 is a plot of this data.

Calculation of the slope of this line inferred a value for $\tau = 11.8$ minutes. The measured value of $\tau = \frac{V}{v_f} = 11.1$ minutes. Based on this it was concluded that the vessel was relatively well mixed.

Minimization of nucleation by sources other than the crystal contactor

It would be desirable to unequivocally give assurance that the crystal contactor was the sole source of nucleation within the crystallizer. Clearly this was impossible to guarantee. On the other hand, numerous steps were taken to minimize, if not eliminate, nucleation by sources other than the crystal contactor.

Reference has already been made to the paper by Ottens and deJong (43). Recall that they showed that for the $\textbf{KAl(SO}_4\textbf{)}_2 \cdot 12\textbf{H}_2\textbf{O}$ water system crystal/crystal contacts contributed in a negligible manner, if at all, to the overall nucleation rate. The nuclei were propagated primarily by crystal/agitator collisions. In addition, they concluded that contacts of the crystals with the walls of the vessel
Figure 11. Exit age distribution of the ragweed particles in the crystallizer. Agitation rate is 500 RPM.
contributed negligibly, if at all, to the overall nucleation rate.

Johnson et al. (26) demonstrated that for MgSO$_4$·7H$_2$O crystals, contacts made by a surface that is not as hard as the crystal resulted in no nuclei. For this reason, the agitator used in the crystallizer was coated with a soft rubber latex.

Based on the results of both Ottens and deJong (43) and Johnson et al. (26) it was concluded that contact nucleation by crystal/crystal, crystal/wall and crystal/agitator was minimized.

Cayey and Estrin (8) in their study of secondary nucleation obtained results suggesting that a nuclei must attain some minimum size before it would be capable of undergoing contact nucleation. Their data inferred that this size was approximately 150 microns. By operating at relatively small residence times, an attempt was made to keep all the particles in the crystallizer at sizes smaller than 150 microns.

In order to determine the extent of homogeneous nucleation in these experiments, many preliminary experimental runs were performed. In each of these runs, the seed crystal was placed in the crystallizer and cured for about thirty minutes at about
3°C above the saturation point. The temperature of the crystallizer was then lowered to some predetermined level and held there for at least twice the time the crystal was held at these conditions in the actual experimental run. Normally, the supersaturation was equal to or greater than that used in the actual runs. In almost all of the preliminary runs no nucleation was observed. It was, therefore, concluded that for the operating conditions used in these experiments, homogeneous nucleation was not a factor.

In many of the preliminary experimental runs, the concentration of the crystals in the crystallizer was observed after the crystal contacting rate was set to zero. That is, the concentration of the crystals in the crystallizer was monitored after the crystal contacting was stopped, while the feed rate, temperature of the crystallizer, and all other parameters remained fixed.

After the crystal contacting had proceeded for six to twelve residence times—long enough to build up a crystal concentration of 200 to 500 particles greater than 13 microns per ml of solution, the contacting was stopped. The seed crystal affixed to the crystal contactor was allowed to remain in the crystallizer. Observation of the total number of
particles greater than 13 microns was measured with the Coulter counter as a function of time. In all cases, the entire crystal population decayed to a value near zero in three to four residence times. Figure 12 is typical of the decay of the crystal concentration.

This is fairly strong evidence that the nucleation resulting from the crystal contactor is the dominant if not the sole source of nucleation in the crystallizer.
Figure 12. Typical decay of the crystal concentration in the crystallizer following the cessation of crystal contact. Preliminary run 8/17.
RESULTS AND DISCUSSION

The results of this study are derived primarily from (1) observation and measurement of the parent crystal which was subjected to a controlled contact and from (2) measurement of the CSD obtained as a result of the crystal contacting.

The effects of repeated contacting on the parent crystal surface structure and growth rate were determined by direct observation and measurement of the crystal.

The effect of supersaturation, impact energy, contact frequency and area of contact was determined from measurement of the CSD of the crystalline product. The apparent affect of residence time was also determined.

Experimentally determined size distributions and other data are reported in Appendix B while an evaluation of the results is given in the ensuing paragraphs.

Character of the Parent Crystal

The crystals used for contacting in this investigation were grown in the laboratory at room temperature in a solution saturated at approximately 28% w MgSO$_4$. Normally the seed crystals were 6 to 9 mm wide, 5 to 6 mm thick, and 12 to 25 mm long.
Prior to use, the 110 face of the crystal that was to be contacted was examined by both touch and by a light reflection test in order to evaluate the smoothness of the crystal surface. Only those crystals that appeared to be flat and smooth were used. The crystal was then cemented to the crystal contactor. Generally, a crystal was used only once. Occasionally, however, one was reused if it still appeared smooth and flat. Apparently, this caused no abnormal results.

At the beginning of an experiment the alignment of the crystal and the contacting rod were adjusted so that visually it appeared that the full area of the contacting rod was parallel with and touching the crystal surface.

The contactor was designed to repeatedly strike the crystal in one place. Unfortunately, closer inspection indicated that the contactor did not fall exactly in the same place each time. It appeared that the maximum variation was about 1 mm.

Photomicrographs were taken of the crystal surface to determine if any visual damage occurred from the repeated contacting. Figures 13 to 16 inclusive show a typical crystal surface before and after contacting. Figures 13 and 14 are the ones taken prior to contacting at a magnification of 47
and 115 respectively, while Figures 15 and 16 were taken after contacting at a magnification of 47 and 115 respectively. Observation of the pictures indicate that on a microscopic scale the crystal surface is far from smooth.

Visual observation of the contacted surfaces, in most instances did not indicate any damage to the crystal surface. The diagonal distance in Figure 13 is approximately equal to the diameter of the contactor. All the photomicrographs, therefore, show only the area of the crystal covered by the contactor. No alteration of the surface features is noticeable. It should be pointed out that the resolution of the photomicrographs is such that surface features of 10 microns or less can be discerned. This is a size level smaller than is detectable on the Coulter counter used for CSD determinations. Even at the higher magnification (Figures 14 and 16) there is no noticeable difference in the features of the crystal surface in pre and post contacting photographs.

It should also be noted that, because of the observation described in the next section, complete contact of the tip of the contacting rod with the crystal surface was not achieved on each contact. Only 6-10% of the area of the contactor actually touched the crystal. The effect of this
Figure 13. Photomicrograph of the 110 face of a typical seed crystal prior to contacting. Magnification is 47 times. The vertical distance of the picture corresponds to an actual distance of 2.5 mm and the horizontal distance to 1.9 mm.
Figure 14. Photomicrograph of the 110 face of a typical seed crystal prior to contacting. This is the same region of the crystal surface as in Figure 13. Magnification is 115 times. The vertical distance of the picture corresponds to an actual distance of 1 mm and the horizontal distance to 0.78 mm.
Figure 15. Photomicrograph of the 110 face of a typical seed crystal after contacting. This is the same region of the crystal surface as in Figures 13 and 14. Magnification is 47 times. The vertical distance of the picture corresponds to an actual distance of 2.5 mm and the horizontal distance to 1.9 mm.
Figure 16. Photomicrograph of the 110 face of a typical seed crystal after contacting. This is the same region of the crystal surface as in Figures 13, 14 and 15. Magnification is 115 times. The vertical distance of the picture corresponds to an actual distance of 1 mm and the horizontal distance to 0.78 mm.
diminished contact area is not obvious on any of the photographs.

Consequently, it must be concluded that in these experiments contact nucleation did not result from what might be called macroscopic attrition or fracture. However, this does not preclude a submicroscopic attrition of the same sort. Further, the growth rate of the parent crystal was the same for the area of contact as elsewhere on the crystal. Therefore, it appears that the contacting had no effect on the crystal growth rate.

Area of Contact

It was discovered that there was no way of maintaining a full face contact between the contacting rod and the crystal surface. Hence, some estimate of the contact area was needed. This was done by allowing the contacting rod to drop from its usual position and strike a piece of carbon paper lying on the surface of the seed crystal. An impression was made on the carbon paper. A photomicrograph of this impression was made—magnified 13 times. A planimeter was then used to determine the area of the impression.

Normally a carbon paper impression of the contact area was obtained prior to the start of an experiment and then
again at the end. Figures 17 and 18 are typical photomicrographs of the carbon paper impressions of the contact area before and after an experiment, respectively. The distance between two successive marks on the scale shown in these pictures is one millimeter.

Normally, a carbon paper impression of the contact area was made for a single drop of the contacting rod and then again for five successive drops. This was done because at the time this technique was conceived, it was not known whether or not the impression made by a single drop of the contactor would be discernible. In almost all of the experiments a single drop made an impression clear enough to be detected.

The contact areas, based on a single drop of the contacting rod, were surprisingly small—all had an area of less than 1 mm$^2$. The largest measured area was 0.534 mm$^2$ while the smallest was 0.210 mm$^2$. At most, these areas were about 6% of the entire area of the face of the contacting rod.

The contact area as determined at the start and then again at the end of an experiment was not constant. It was common to have the area increase as much as 50% from start to finish. The actual area change was on the order of 0.15 mm$^2$. 
Figure 17. Typical photomicrograph of the carbon paper impression of the contact area prior to the start of an experiment.
Figure 18. Typical photomicrograph of the carbon paper impression of the contact area at the end of the experiment.
There are a number of uncertainties in these measurements and even in their significance. Surely during the course of a run the contact area would vary from contact to contact. Also, different portions of the crystal surface would be the sites of contact. It is clear, however, that the actual contact area resulting from a single contact is small—of the order of 10% of the full face of the contacting rod—and that it was of this order throughout the entire experiment.

The use of the above measurements in attempting to correlate contact area with nuclei production was unsuccessful. However, the success in relating the other variables to the number of nuclei produced per contact suggests that a relatively uniform average contact area was achieved during each of the experiments.

Nucleation Rate Measurement

The Value of the nucleation rate \( B^0 \) is obtained by comparing the measured CSD with that predicted by the population balance equation, equation (13). The experimental conditions of this research were such that (1) the volume of the crystallizer was held constant, (2) there was a single inlet and discharge stream for the crystallizer, (3) the inlet stream was free of crystals, and (4) the crystallizer
was well mixed. Furthermore, as a consequence of the results of experiments on the decay of the crystal concentration as shown by Figure 12, B and D in equation (13) can be neglected. Hence, the phenomenon of nucleation can be considered to occur only at the surface of the parent crystal. Hence, equation (13) reduces to

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} = - \frac{n}{\tau}$$

(25)

and at steady state

$$\frac{d(Gn)}{dL} = - \frac{n}{\tau}$$

(26)

If \( G \neq G(L) \), then the solution to equation (26) is equation (16)

$$n = n^0 \exp \left( - \frac{L}{G\tau} \right)$$

(16)

Dallons (13) pointed out that the number of particles per unit volume in a given size range, say \( L_1 \) to \( \infty \), can be determined by

$$N (L_1, \infty ) = \int_{L_1}^{\infty} n \, dL$$

(27)
Substituting for $n$ from equation (16) gives

$$N(L_1, \infty) = \int_{L_1}^{\infty} n^0 \exp \left(-\frac{L}{G\tau}\right) dL$$

(28)

and

$$N(L_1, \infty) = n^0 G\tau \exp \left(-\frac{L_1}{G\tau}\right)$$

(29)

This expression allows the determination of the total number of particles per unit volume greater than size $L_1$ in a crystallizer which meets the constraints imposed in the derivation of equation (16). For this investigation the only condition not known to be satisfied a priori is $G \neq G(L)$. To determine if $G \neq G(L)$, one needs only to compare

$$\ln N(L_1, \infty) = \ln n^0 G\tau - \frac{L_1}{G\tau}$$

(30)

with a plot of the experimental $\ln N$ versus $L$. If the resulting plot is linear, then $G$ is not a function of $L$.

Further, from the slope of such a plot, the value of $G$ can be determined, and the value of $n^0$ can be evaluated from the intercept at $L = 0$. Finally,

$$B^0 = n^0 GV$$

(31)
Figure 19 is a typical plot of the log N versus L obtained from the current study—experiment 9/14 A. In this particular case the slope was found to equal -0.0185 from which G was determined to be 2.24 microns per minute. The intercept obtained by the extrapolation to L = 0 was 950. The nuclei population density was 40.4 nuclei/ml micron.

The number of particles per unit volume, greater than L1, was obtained directly from the Coulter counter. As mentioned previously, a screen with openings of approximately 82 microns was placed over the aperture tube to prevent plugging of the aperture. Because of this screen, the sample measured by the Coulter counter was not N (L1, ∞) but N (L1, 82). Hence, the distribution the counter actually measured was given by

\[ N (L_1, 82) = \int_{L_1}^{82} n^0 \exp \left( \frac{-L}{G \tau} \right) dL \quad (32) \]

and

\[ N (L_1, 82) = n^0 G \tau \left[ \exp \left( \frac{-L_1}{G \tau} \right) - \exp \left( \frac{-82}{G \tau} \right) \right] \quad (33) \]

Taking the logarithm of each side of equation (33) gives

\[ \ln N (L_1, 82) = \ln n^0 G \tau + \ln \left[ \exp \left( \frac{-L_1}{G \tau} \right) - \exp \left( \frac{-82}{G \tau} \right) \right] \]

\[ - \exp \left( \frac{-82}{G \tau} \right) \] \quad (34)
Figure 19. A typical plot of the CSD obtained in the current study, Experimental run 9/14 A.
If the term \( \exp \left( \frac{-82}{G_T} \right) \) is zero or if the expression \( \exp \left( \frac{-82}{G_T} \right) \approx \exp \left( \frac{-L_1}{G_T} \right) \), then equation (34) is approximated by

\[
\ln N \left( L_1, 82 \right) = \ln n^0 G T - \frac{L_1}{G_T}
\]  

(35)

Note that equation (35) is identical to equation (30), and consequently the value of the slope and the intercept yield the correct value of \( G \) and \( n^0 \) respectively.

The value of the argument, \( \exp \left( \frac{-82}{G_T} \right) \), is a function of \( L_1 \), \( G \), and \( \tau \). \( \tau \) is fixed for each experiment. For any particular value of \( G \), the value of the first term of the argument of

\[
\ln \left[ \exp \left( \frac{-L_1}{G_T} \right) - \exp \left( \frac{-82}{G_T} \right) \right]
\]

is the largest when \( L = 0 \). The significance of the second term in the argument, therefore, increases as \( L_1 \) increases. Closer agreement between equation (34) and equation (35) is, therefore, expected when \( L_1 \) is small.

In order to determine the magnitude of the error introduced because of the above discrepancy, the growth and nucleation values from Figure 19 were used to determine an expected size distribution as predicted by equation (34). The plot of this calculation is shown on Figure 20 along with the assumed linear size distribution (from which \( G \) and \( n^0 \) were taken) and the data from Figure 19. It can be seen that the
Figure 20. Comparison of the curves predicted by equation (30) and equation (34), using the values of $G$ and $n^0$ obtained from Figure 19.
2000 ACTUAL EXPERIMENTAL DATA
CURVE PREDICTED BY EQUATION (34)
CURVE PREDICTED BY EQUATION (30)

CUMULATIVE NUMBER DENSITY, NUMBER OF PARTICLES > SIZE L / ml \( \mu m \)

L, PARTICLE SIZE, \( \mu m \)
curve per equation (34) is virtually linear to about 36 microns. Generally speaking, it can be said that the data can be correlated by equation (34), and had the screen not been covering the aperture tube, the data would be expected to be linear in the entire range of observation. In the derivation of equation (34) it was assumed that $G \neq G(L)$. The relatively good correlation suggests that this was a good assumption.

Further observation of Figure 20 indicates that virtually the same value of the intercept at $L = 0$ is obtained from both equation (30) and equation (34). For values of $L$ equal to or less than 36 microns, the curve from equation (34) is linear and has a slope slightly larger than that of the line given by equation (30) and the data points. Consequently, $G$ as determined from the data is about 9.8% larger than the growth rate determined from the curve given by equation (34).

A similar analysis was done for the worst possible cases of all the experimental runs of this study. In these analyses the values of $G$ and $n^0$ used were those obtained from the plot of $\log N (L_1, \infty)$ versus $L$. This is reasonable since a good fit is obtained for the smaller values of $L$. The result of these comparisons was not surprising. There was almost complete agreement of one curve with the other for values of
L less than 29 microns. For values of L greater than 29 microns, the curve of log N (L, 82) was always lower than the curve of log N (L,8).

It was, therefore, concluded that the growth rates and nucleation rates obtained from the plot, assuming equation (34), were virtually identical to those obtained from the plot assuming equation (30).

Nucleation as a Function of the Supersaturation

The determination of the nucleation rate is given by equation (31)

\[ B^o = n^o G V \]  

From graphs similar to Figure 19, the value of both \( n^o \), the nuclei population density, and G, the growth rate of the crystals in the size range observed, were obtained for the different experiments. The product of \( n^o \) and G with V, the volume of the crystallizer, yielded the nucleation rate \( B^o \); i.e.; the number of nuclei generated per minute. Since it was desirable to determine the number of nuclei generated per contact, the value of \( B^o \) was divided by f, the frequency of contact. \( B^o/f \), then, represented the number of nuclei
produced per contact. Figure 21 is a plot of $B^0/f$ versus $\Delta T$, the supersaturation.

Figure 21 depicts an increase in the number of nuclei per contact with an increase in the supersaturation. Clearly, the supersaturation level in a crystallizer is one of the key variables affecting the level of nucleation. The curve of Figure 21 also points out the relatively high dependence of nucleation rate on supersaturation in the supersaturation range of three or greater. All other parameters being equal, it would be desirable to operate the crystallizer at a much lower supersaturation for best control of the nucleation rate.

Clontz and McCabe (11) and Johnson et al. (26) found that the number of nuclei/mm$^2$ of contact area increased as the supersaturation increased.

Figure 21 depicts an increase in the number of nuclei per contact with increasing supersaturation, and if a relatively uniform average contact area between the different experiments were achieved, the results suggested by Figure 21 would parallel the finding of Clontz and McCabe (11) and of Johnson et al. (26).
Figure 21. Number of nuclei generated per contact as a function of the supersaturation.
Apparent Effect of Residence Time on Nucleation Rate

Randolph and Cise (46) reported that nucleation rates obtained using sieve analyses and those obtained using modern electronic particle counters differ by as much as a factor of 100. They explained this discrepancy by suggesting that the washout of very small particles, having very small growth rates, were not accounted for in the sieve analyses. Based on their observation one would expect to detect an apparent increase in nucleation rate with increasing residence time. Figure 22 exhibits such a phenomena.

The curve of Figure 22 suggests that the number of nuclei produced per contact increases with an increase in the average residence time. The inset table of Figure 22 shows that the data points are at slightly different supersaturations. Using Figure 21 to adjust the values of $B^0/f$ to a common supersaturation level of $4.04^\circ C$, it is seen that the same general trend of the curve of Figure 22 is maintained. Hence, more nuclei are apparently produced per contact as the residence time increases.

It is difficult to conceive of a mechanism of contact nucleation that would be a function of residence time. However, if the nuclei produced as a result of a crystal contact
Figure 22. Number of nuclei generated per contact as a function of the residence time.
\( f = 8 \) CONTACTS PER min

\( E = 28,000 \) ergs
are "born" at some size less than 13 microns, and if these nuclei had a small, size dependent growth rate, then the longer the average residence time, the longer the opportunity these nuclei would have to grow to a size to which they could be detected. Hence, the apparent increase of nucleation with increasing residence time supports the views of Randolph and Cise (46).

Nucleation as a Function of the Frequency of Contact

In a mixed suspension crystallizer, crystals are subjected to repeated contacts from other crystals, agitators and vessel walls. The effect of these repeated contacts on the nucleating properties of the crystal surface is of interest. It is necessary to know if the restoration time of the crystal surface is large compared to the frequency of contact. Consequently, a number of experiments were performed investigating the effect of frequency of contact on the number of nuclei generated per contact. Figure 23 is the result of these experiments.

One notes from the Figure that the supersaturation level varied slightly from one experiment to the next as did the residence time. The variation of residence time can be ignored, and Figure 21 can be used to adjust the values of
Figure 23. Number of nuclei generated per contact as a function of the contact rate.
$B^O/f$ to a common supersaturation level of 4.1° C. Rigorously, point seven of Figure 23 cannot be adjusted on the basis of Figure 21 as the frequency of contact differs. Nonetheless, for lack of any better information this adjustment will still be made.

The adjusted values of $B^O/f$ of the data points of Figure 23, to a supersaturation of 4.1, are shown in Figure 24. Figure 24 indicates that the number of nuclei generated per contact declines somewhat as the contact rate increases. Because of the scatter in the data additional research is needed to definitely establish the relationship of $B^O/f$ to $f$ in the range of 8 to 20 contacts per minute.

Johnson (25) investigated a similar phenomena. His results indicated that approximately fifteen seconds were necessary in order to obtain the same number of nuclei per contact on two successive contacts. The fact that his experiments were performed at supersaturations of only 0.5 to 1.0° C, explains why such a relatively long time between contacts was required before the crystal surface would regenerate itself.

Based on a comparison of the results of this section with Johnson's results on regeneration of the crystal
Figure 24. Nuclei produced per contact as a function of the rate of contact. The values of $B^0/f$ have been adjusted to account for a change in supersaturation from the actual value to a value of $4.1^\circ C$. 
\[ \Delta T, ^\circ C \quad \tau, \text{ min} \]

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</tr>
<tr>
<td>8</td>
<td>4.09</td>
<td>10.5</td>
</tr>
</tbody>
</table>

* ADJUSTED TO THIS VALUE

\(E = 28,000 \text{ ergs}\)
surface, it can be seen that supersaturation is an important factor in surface restoration. This implies that growth of the crystal surface is involved in the restoration process, which in turn implies that submicroscopic attrition of particles is very likely the mechanism of contact nucleation.

Nucleation as a Function of Contact Energy

Clontz and McCabe (11) and Johnson et al. (26), studied the nucleating properties of MgSO₄·7H₂O in a semiflow system. For a fixed supersaturation level they found that the number of nuclei produced per unit of contact area per contact was a function of the energy of contact. Figures 4 and 5 show the results of their work.

Johnson (25) also reported:

"It seems reasonable that at a given set of conditions there is the potential for forming some maximum number of nuclei per unit contact area...provided there is no major damage done to the crystal face by the impact."

The results for pressure contacts shown in Figure 5 and similar results by Johnson for crystal rod impacts have shown that there appears to be some maximum nucleation level as the contact energy increases.

Although it is not obvious from Figure 5, Johnson (25) comments:
"At higher (contact) energies, there was no further increase in numbers of nuclei formed although there was a considerable amount of scatter in the data."

This scatter sometimes was as high as 50%.

The crystals in an operating crystallizer would be subjected to a wide spectrum of different contact energies. In order to quantitatively define the nucleation rate as a function of contact energy for a MSMPR crystallizer, several experiments were performed with contact energy as the varying parameter.

These results are shown in Figure 25. The data suggests an increase in $B^0/f$ as $E$ increases from 0 to 15K ergs followed by a decline in $B^0/f$ until $E$ reaches 28K ergs. In these experiments, however, it was impossible to keep the residence time and the supersaturation the same from run to run. The variation in residence time can be ignored. When the results shown by points four through seven are adjusted to a common supersaturation base of $4.1^\circ C$, using the relationship of Figure 21, they all result in values of $B^0/f$ close to 12,000. Similar adjustments of the values of $B^0/f$ for points one, two and three cause point one to remain as is, point two to decrease slightly and point three to increase somewhat.
Figure 25. The number of nuclei produced per contact as a function of the energy of contact.
$f = 8$ CONTACTS PER min

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$E$, CONTACT ENERGY $\times 10^{-3}$ ergs
Observation of these adjusted points still shows the trend that $B^0/f$ increases until $E = 15K$ ergs and then declines until $E = 28K$. This could just be scatter in the data as observed by Johnson (25), or possibly the number of nuclei produced per contact actually decreases at the larger contact energies. If the latter is true, it can be explained on the basis that "high points" of the crystal surface are actually being fractured at the higher contact energies and this necessitates additional time for them to grow to a size to which they would again contribute to contact nucleation.

Crystal Growth Rates

In order to design a crystallizer to produce crystals of a desired size, it is necessary to know the growth rate of the crystals. In addition some observers (46) have reported that the growth rate of a crystal is a function of its size—the smaller particles growing at a slower rate than the larger crystals. Measurement of the crystal growth rate was done in these experiments to obtain design information and also to provide additional information on the size dependency of the growth rate of MgSO$_4$·7H$_2$O.
Growth rates of "small" crystals

Data for the growth rate of "small" crystals; i.e.; those of the same size observed by the Coulter counter, were obtained from the slope of plots similar to Figure 19. The results of those findings are shown in Figure 26, where the growth rate is plotted versus the supersaturation.

A least squares fit has been drawn through the data points, to establish a trend. The trend line is oriented properly, with a positive slope, but the magnitude of the slope is somewhat less than expected.

It can be seen from Figure 26 that the range of growth rates, of the equivalent spherical diameter of the crystals, was 1 to 2.5 microns per minute.

Growth rate of the parent crystal

The growth rate of the 110 face of the parent crystal, which was the same face on which the contacting occurred, was determined with a micrometer. Because of the terracing effect that the parent crystal exhibited, it was extremely difficult to obtain exact growth rates.

The results of the measurement of the growth rate of the 110 face of the crystal are shown in Figure 27. It should be noted that direct comparison of the growth rates of the
Figure 26. The growth rate of "small" crystals shown as a function of the supersaturation. Small crystals are those of the same size observed via the Coulter counter---13 to 70 microns.
$G$, CRYSTAL GROWTH RATE AS DETERMINED FROM THE SLOPE, $\mu$m/min

$\Delta T$, SUPERSATURATION, $^\circ$C
Figure 27. Measured growth rate of the 110 face of the parent crystal as a function of supersaturation.
MEASURED GROWTH RATE OF SEED CRYSTALS, µm/min

ΔT, SUPERSATURATION, °C

2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6

3.1 3.3 3.5 3.7 3.9 4.1 4.3 4.5 4.7 4.9 5.1 5.3 5.5
"small" crystals as shown on Figure 26 with those of the parent crystal as shown on Figure 27 would be erroneous—the growth rates of the small crystals are expressed as that of the equivalent spherical diameter while those of the parent crystal are facial growth rates. Increasing the facial growth rate by a factor of about two converts the facial growth rate to a characteristic diameter of the parent crystal. Hence, the parent crystal grew at approximately three to twelve times the rate of the "small" crystals. This supports the observation of those who have reported size dependent growth rates. It is conceivable that the growth rate might be size dependent but that the change in it, with size, could be relatively small, and this would explain the fact that the data obtained from the Coulter counter implied that $G \neq G(L)$.

**Mechanism of Contact Nucleation**

If the mechanism of contact nucleation were known, it would be a significant step forward in the design, operation, and control of crystallizers. In the current work a number of observations were made that aid in the understanding of contact nucleation.

The first of these was the observation that the mere presence of the parent crystal in an agitated, supersaturated
solution was not sufficient for nucleation to occur. In one experiment the parent crystal was submersed in a solution supersaturated to about 4°C for about twenty-one hours. The residence time for this run was fourteen minutes, and the agitation rate was 350 RPM. There was no contact between the crystal and the contacting rod and no new crystals resulted. Based on this and other similar runs, it can be clearly stated that physical contact with the crystal is required in order for nucleation to occur.

What actually occurs to or at the crystal surface as a result of a contact is not understood. It could be that the contact breaks off particles of less than ten microns in size. No evidence of crystal fracture of particles greater than this size was noted from the observation of the photomicrographs of the crystal surface prior to and after contacting.

One can obtain an estimate for the upper bound of the size of the nuclei produced by a single crystal contact by using the area of contact as measured by the carbon paper impression. The volume produced, between two successive contacts, by the growth of this portion of the crystal surface can be calculated. Knowing this volume and the number of nuclei produced per contact, it is possible to obtain the average volume for a
single particle, assuming the nuclei have identical size and shape. Using this approach and assuming the nuclei were spherical, the diameter of the nuclei was found to be approximately three microns. This can be considered as an upper limit to the size of the particles produced since neither observation of the photomicrographs nor visual observation of the crystal surface indicated a gross depression. It is, therefore, clear that the entire volume produced between contacts, due to growth, is not displaced. In addition, it is unlikely that the full contact area as determined by the carbon paper technique was touching.

The range of residence times used in these experiments was ten to fifteen minutes. In this period of time the nuclei produced by a single contact could grow to populate the CSD in the manner observed in this experiment.

It is, therefore, concluded that the particles produced by a crystal/rod contact are at most on the order of two microns in size and very likely they are much smaller.

One thing is certain however. The number of nuclei produced per contact is a strong function of supersaturation. One explanation of this phenomena is the survival theory--nuclei greater than the critical size survive while the others
dissolve. The observations of Garabedian and Strickland-Constable (18)—the number of nuclei observed after a controlled contact between a seed crystal and another solid object depended on the supersaturation during the development (growth) period and not on the supersaturation during the contact period—certainly supports the survival theory.

The influence of the frequency of contact at a fixed supersaturation is informative as it enables one to neglect the effect of the survival theory. The fact that the crystal surface deteriorates in its nucleating properties with an increase in the frequency of contact suggests that something occurs at the crystal surface—as opposed to nuclei dissolving because they are smaller than the critical size—to inhibit the formation of nuclei. It is only reasonable to believe that the growth of the surface features are being inhibited. With suppressed growth comes incomplete rejuvenation of the crystal surface and hence a deterioration of nucleation. All the facts suggest that the mechanism of contact nucleation is microattrition.
CONCLUSIONS

1. It was established that periodic contacting of a crystal of MgSO$_4$$\cdot$7H$_2$O mounted in a continuous MSMPR crystallizer produced a concentration of nuclei that could be measured using a Coulter counter, the probe of which was placed within the crystallizer.

2. It was demonstrated that the mere presence of the parent crystal in an agitated, supersaturated, solution was not sufficient for the onset of nucleation. Actual physical contact of this crystal with the contacting rod must occur otherwise no nuclei are produced.

3. Supersaturation has a pronounced affect on the net number of nuclei produced per contact. Increasing the supersaturation also results in an increase in the net nucleation rate.

4. It was observed that an increase in the average residence time of the particles in the crystallizer resulted in an apparent increase in the number of nuclei produced per contact. Phenomenologically, the residence time has no affect on the number of nuclei produced per contact. It was,
therefore, concluded that the observed phenomenon was caused by the growth of very small particles, growing at a very low rate, into a size range at which they could be detected.

5. A deterioration of the nucleating properties of the crystal surface occurred at a frequency of about eight contacts per minute.

6. The energy of contact affects the number of nuclei produced per contact. This number initially increased to some maximum value with an increase in contact energy but then declined with a further increase in the contact energy. A possible explanation of this observation is that localized "high points" on the crystal surface are completely destroyed at the higher contact energies but are only slightly altered at the lower contact energies.

7. The growth rate of the parent crystal was approximately five to ten times larger than the growth rate of the "small" crystal—a fact that suggests that growth rate is size dependent.

8. The information obtained in this investigation and conclusions made on the basis of this information suggest that
microattrition of the features of the crystal surface is the mechanism of contact nucleation.
RECOMMENDATIONS

1. There is a definite need for a particle counter that has a particle resolution on the order of one micron, when placed in a continuous system, and a near instantaneous readout of the CSD. A model T Coulter counter is suggested. If an instrument similar to the one described above can be attained, it would be possible to operate at much lower, more realistic levels of supersaturation.

2. The experiments in this study were performed in a range of residence times that are subject to highly unstable conditions. It is suggested that any further work in this area be done at either lower or greater residence times than those of this study.

3. The phenomena of surface restoration needs additional study. It seems like this is an area that could lead to additional insight into the mechanism of contact nucleation.

4. The effect of contact energy on the nucleation rate is not clearly understood. Additional investigation is necessary.

5. The effect of contact area is elusive. To what extent is the energy density, E/A, a factor affecting the nucleation rate?
6. A series of neutral solution experiments is suggested. A neutral solution being one in which neither growth nor dissolution of nuclei will occur. A solution at the saturation point, for a fixed temperature, would be one example. In this environment the number and size of nuclei resulting from a single contact (or more in different locations) of a parent crystal could be determined—extremely valuable information.
BIBLIOGRAPHY


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APPENDIX A

The development of the equation describing the impact energy at the crystal surface is discussed in this Appendix.

The distance the contacting rod drops each time is adjustable. The weight added to the falling rod, in the form of steel washers, is also variable.

As the rod drops, it encounters several resistances. These are (1) frictional forces due to contact between the rod and the solenoid, the air, and the MgSO₄ solution, (2) back pressure of the solution, and (3) the resistance offered by the supporting spring. The spring which is atop the solenoid housing aids the solenoid in supporting the rod.

The forces acting on the rod as it falls are (1) F_g, the weight of the plunger, (2) F_s, the force of the spring, (3) F_f, the frictional forces of solution, air and the solenoid, and (4) P_s, the solution back pressure. Per Newton's second law (see Resnick and Halliday (49, p. 86))

\[ F = m \ a \]  \hspace{1cm} (36)

\[ F = F_g - F_s - F_f - P_s = m \ a \]  \hspace{1cm} (37)

where \( F \) is the resultant force acting on the rod, \( m \) is the
mass of the rod, and \( a \) is the acceleration imparted to the rod. The weight of the rod is \( F_g \), and \( F_g \) equals \( mg \).

If all the resistance forces are negligible, then

\[
F = F_g = m g = m a \quad \text{(38)}
\]

which is tantamount to saying that the rod is a free falling body.

The work done by the rod, per Resnick and Halliday (49, p. 142) is equal to the change in the kinetic energy of the rod. So

\[
W = F d = \frac{1}{2} m v_f^2 - \frac{1}{2} m v_i^2 \quad \text{(39)}
\]

where \( W \) is the work, \( d \) being the distance through which the net force acted, \( v_f \) and \( v_i \) being respectively the final and the initial velocity of the rod. Since the rod is starting from rest, \( v_i \) is zero, and

\[
W = F d = \frac{1}{2} m v_f^2 \quad \text{(40)}
\]

and

\[
W = m g d = \frac{1}{2} m v_f^2 \quad \text{(41)}
\]

or

\[
v_f = \sqrt{2 g d} \quad \text{(42)}
\]

Equation (41) indicates the work done by the rod, in free fall, as it drops a distance \( d \). The rod strikes the crystal surface with an energy equal to the work given by equation
(41). If free fall of the rod were occurring, the energy with which the crystal is struck could be calculated simply by knowing the mass of the rod and the distance through which it falls.

The assumption of free fall is not a good one. Calling the combined resistance $F_r$, $F_r = F_s + F_f + P_s$. Then equation (37) can be rewritten as

$$F = F_g - F_r = m a$$

(43)

$F$ also represents the force striking the crystal. For a fixed drop distance, $d$, it is necessary to determine the value of $F_r$ acting on the rod at the instant the rod comes in contact with the crystal. By knowing the mass, $m_o$, of the rod plus the additional mass that just causes contact

$$F_r = m_o g$$

(44)

That is, the force $m_o g$ is the force that is necessary to overcome the combined resistance, $F_r$.

The net force striking the crystal is then determined from equation (43).

$$F = F_g - F_r = m^* g - m_o g = g(m^* - m_o)$$

(45)
m* refers to the weight of the rod and all additional weight. The energy striking the crystal surface is determined from equation (40).

\[ W = F \cdot d = \frac{1}{2} m v_f^2 \]  

\[ W = g(m^* - m_o) \cdot d = \frac{1}{2} m^* v_f^2 \]  

(40)

(46)

A relationship similar to equation (46) was used by Clontz and McCabe (11) in determining the energy contacting the crystal surface.

The assumption that equation (44) describes the total resisting forces for a mass m that is greater than \( m_o \) is probably not exactly correct. This is due to the fact that the greater the mass, \( m^* \), the larger the velocity of the rod. The velocity approaches, as a limit, the free fall velocity. Since the velocity changes, the viscous drag on the rod will also change. Hence, the total resisting force for \( m > m_o \) will be different than the total resisting force at \( m = m_o \).

It is conceivable that the increase in viscous drag occurring with an increase in m is negligible. If this were true, equation (45) would still be valid. Based on preliminary estimates of the shear stress acting on the rod surface, it appears that the viscous forces are less than 5% of the force.
due to gravity. It is, therefore, assumed that the change in
magnitude of the viscous forces occurring because of an
increase in \( m^* \), is negligible. A determination of the mass \( m^0 \)
in air gave results virtually identical to that in the MgSO\(_4\)
solution. This indicates that the only forces of any magnitude
in this system are \( F_g \) and \( F_s \). So it is concluded that equation
(46) is a reasonable estimate of the energy striking the
crystal surface. Recall that equation (46) gives an estimate
only of the energy striking the crystal, not of the energy
actually transmitted to the crystal.
Table 1. Relationship of data points on figures to run numbers

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\[\textsuperscript{1}\]From a single drop of the plunger.
\[\textsuperscript{2}\]As determined from the slope of the curve on the log N versus L plot.
\[\textsuperscript{3}\]Of seed crystal as measured.
\[\textsuperscript{4}\]Due to terracing of seed crystal, the measured value is only a poor estimate of the actual G.
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5 d = slight depression noticeable during light reflection test.
   r = reused crystal.
   t = terraced.