Contact Nucleation of Various Crystal Types

The purpose of this study was to investigate contact nucleation for various types of crystalline materials. Selected were aqueous solutions of two hydrated inorganic salts ($MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$), one nonhydrated inorganic salt (K_2SO_4) and one organic substance (citric acid). Nucleation data were determined as number of nuclei generated per contact as a function of supersaturation and impact energy. Both of these variables strongly influenced the number of nuclei generated per contact. These data show that crystal growth and contact nucleation are related, with more rapidly growing substances giving higher yields of nuclei.

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SCOPE

In early investigations on secondary nucleation, Mason and Strickland-Constable (1965) and Lal, Mason, and Strickland-Constable (1969) made the following qualitative observations:

1. Unless a seed crystal was cured before it was immersed in supersaturated solution, new crystals would form from microscopic particles (crystal dust) washed from the crystal surface.
2. No nucleation occurred on immersion of cured seed crystals into a slightly supersaturated solution unless there was contact between the crystal and another solid material. Nucleation under these conditions is called *contact nucleation* or *collision breeding*.
3. When supersaturations were high enough to induce dendritic growth on the seed crystals, new crystals were formed by fluid movement shearing these dendrites from the parent crystal.

Clearly the conditions described in these observations indicate that when secondary nucleation occurs in crystallization processes it must occur according to Observations 1 or 2. Moreover, in systems where external seeding is not used, contact nucleation, as described in Observation 2, must be the predominant nucleation mechanism.

Clontz and McCabe (1971) and Johnson, Rousseau, and McCabe (1972) presented data quantifying the factors influencing contact nucleation for $MgSO_4 \cdot 7H_2O$. The research reported in this paper includes refinements to the previously reported work on $MgSO_4 \cdot 7H_2O$ and additional studies on $KAl(SO_4)_2 \cdot 12H_2O$, K_2SO_4, and citric acid. This study will lead to a better understanding of secondary nucleation and provide a base for modeling and controlling nucleation in crystallization processes.

CONCLUSIONS AND SIGNIFICANCE

The necessity of an impact between seed crystals and another object for nucleation to occur in slightly supersaturated aqueous solutions of the solutes investigated has been confirmed. In no case did nucleation occur without such an impact. Both impact energy and solution supersaturation were extremely important variables in determining the number of nuclei generated by a single contact with a seed crystal. Within the range of supersaturations considered, a linear relationship was found to exist between the number of nuclei and supersaturation for the three inorganic salts; this was not true for citric acid. For all four systems, however, the form of the function relating supersaturation to the number of nuclei generated by an impact was the same as that relating the linear growth rate of the crystal to supersaturation. These data imply the existence of a fundamental relationship between contact nucleation and crystal growth.

The impact energies considered in this study were within the range of those expected in a stirred tank crystallizer. No data were obtained when there was visible damage to the seed crystal. In all cases the number of nuclei generated was an exponential function of impact energy. Potassium sulfate was the only substance exhibiting a well-defined threshold energy; that is, impact energies below this level produced no nucleation. The relationship between a threshold energy and crystallizer stability should be studied further. It is shown that the number of nuclei generated by an impact can be correlated by the expression

$$N = af(\alpha) \exp (E - E_t)$$

For all four systems $f(\alpha)$ could be replaced by the linear growth rate of the system under consideration

$$N = a_1 G \exp (E - E_t)$$

Seed crystal properties were shown to influence the contact nucleation characteristics of the systems investigated: unusually smooth or hard crystal faces meant a low number of nuclei generated by an impact.

The mechanism of nucleation in crystallization operations was uncertain until the early work on contact nucleation. Strickland-Constable (1972) discussed the mechanisms of nucleation and presented evidence that contact nucleation was dominant at low supersaturations, which is the operating environment encountered in most industrial crystallizers. Clontz and McCabe (1971) and Johnson, Rousseau, and McCabe (1972) reported on several factors affecting contact nucleation and postulated possible mechanisms of contact nucleation. Their experimental work was limited to the aqueous $MgSO_4 \cdot 7H_2O$ system, and to use the magnesium sulfate heptahydrate results to describe other systems, even qualitatively, is perhaps unwarranted. Therefore, the purpose of this research was to investigate the contact nucleation characteristics of other crystalline materials and compare their characteristics with those of $MgSO_4 \cdot 7H_2O$.

EXPERIMENTAL PROCEDURE

The flow system used to study crystal formation resulting from contact with a seed crystal was essentially the same as that used by Clontz (1969) and Johnson (1970). Several modifications were made, however, in order to increase the accuracy of measuring crystal temperature and contact energy and to control the solution temperature in the crystal receiver where the newly formed crystals grew to a countable size. A flow sheet showing this equipment is presented in Figure 1.

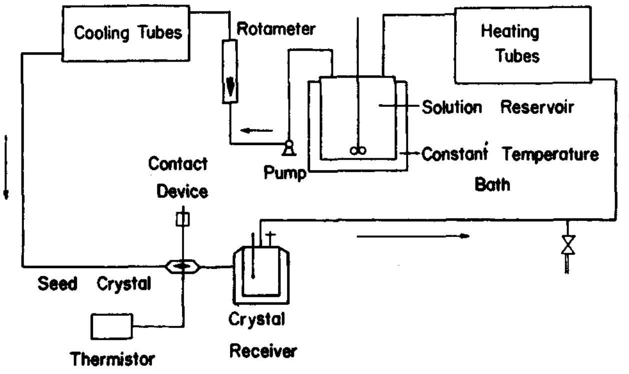

Fig. 1. Diagram of flow system.

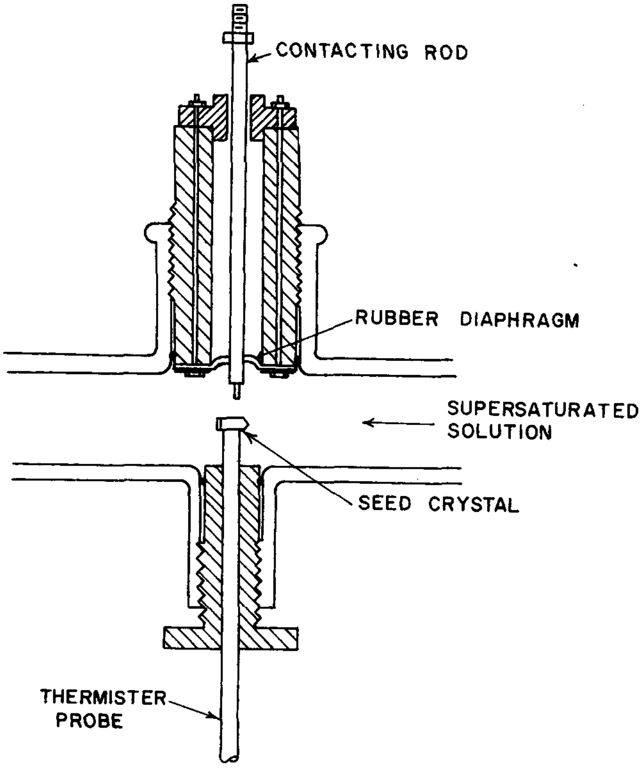

Fig. 2. Crystal contacting device.

The temperature indicating equipment used by Johnson (1970) enabled the measurement of the crystal temperature to within ± 0.1°C. A more precise measurement, required for work at low supersaturations, was accomplished by using a millivolt potentiometer connected to a thermister probe and calibrated against a standard thermometer, readable to 0.01°C.

The crystal contacting device is shown in Figure 2. By dropping a known weight from a known height, the impact energy could be calculated from the equation used by Clontz (1969)

$$E = mg(h - h_0) \tag{1}$$

where the height h_0 is that from which the weight must be dropped just to overcome the frictional resistance and bring the rod into contact with the seed crystal; it was determined precisely using a method devised by Clontz (1969). To improve Clontz' accuracy in measuring the drop height, an iron bar was directed vertically by a glass tube which was passed through a solenoid; the drop weight (17.57 g) was suspended in the glass tube when the solenoid was activated and was released on deactivation. The iron bar could be adjusted to any position desired and the drop height measured by a cathetometer which could be read to 0.01 mm. A microscope was positioned on the contacting device to observe the crystal contact and to measure crystal growth rates.

The glass crystal receiver was constructed with a water jacket allowing for control of the temperature in the growth zone. In all the results to be reported, the supersaturation in the growth apparatus was held at the same level as that of the solution in the contacting device, that is, contact and growth occurred under identical conditions.

To ensure proper alignment of the seed crystal and the impacting surface, a technique was developed which involved gluing the seed crystal to the tip of the thermister probe, placing the thermister probe with the attached crystal in the contacting apparatus, and pressing the contacting rod so as to touch the crystal surface before the glue became dry. The intent was to glue the seed crystal in situ. Proper alignment was checked through the microscope. If the seed crystal was improperly aligned, data interpretation was impossible.

The systems investigated included two inorganic hydrates—$MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ (potassium alum), one inorganic anhydrate—K_2SO_4, and one organic hydrate—$C_6H_8O_7 \cdot H_2O$ (citric acid). Several operating variables were studied with particular emphasis on supersaturation, impact energy, and growth rate. All impact runs were restricted to rod-crystal contacts; crystal-crystal contacts were not performed in these experiments due to the difficulties in determining the contact area of growing seed crystals even though recent data of Evans et al. (1974) has shown that crystal-crystal contacts contributed as much as 20% to the nucleation rate in a stirred-tank ice crystallizer. All experiments used cured seed crystals to eliminate initial breeding. Clontz and McCabe (1971) and Johnson et al. (1972) used contacting rods of different sizes and reported that the yield of nuclei was a function of contact area. Yet Bauer et al. (1974) found that the actual contact area resulting from a single contact is only a small portion of the full face of the contacting rod. Therefore, a single stainless steel contacting rod, 0.318 cm in diameter, was used in all experiments.

Johnson et al. (1972) presented data which showed that different faces of the same seed crystal yielded significantly different numbers of nuclei per contact even though all other system variables were constant. The largest face within each crystalline system was chosen as being the most important and all runs were made on that face. Crystal habits for each system are shown in Figure 3 with the face chosen for study so designated.

EXPERIMENTAL RESULTS

Metastable Regions

The metastable regions are supersaturation zones where crystals will grow but spontaneous nucleation will not occur. To eliminate the possible confusion of other types of nucleation with contact nucleation, it was necessary to conduct all experiments with supersaturations within the metastable region of the system being investigated. An equally important consideration, however, is that the system supersaturation should be controlled so as to produce a good crystalline material. As Clontz and McCabe point out in Figure 5 of their paper (1971), this latter requirement is actually more restrictive than the former. Accordingly, the experimental limits on supersaturation were set within a good growth region, defined as existing when the growing crystal surfaces are smooth clear planes, the crystal edges are sharp, and the crystal possesses its normal habit.

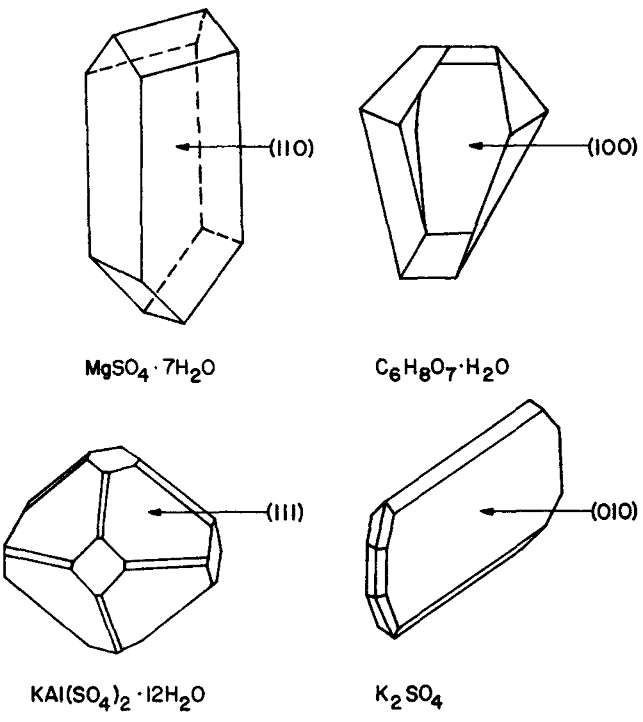

Fig. 3. Crystal structures.

The good growth regions were determined at a given solute concentration by lowering the solution temperature until veiled or spikewise growth on the seed crystal was observed. The results of these experiments are presented in Table 1.

Effect of Impact Energy

Figures 4 through 7 show the effect of impact energy on the number of nuclei produced by a single contact for the four systems. The data shown on each figure were obtained by changing the impact energy while holding constant all other variables including supersaturation, contact area, crystal temperature, and solution velocity. As shown in these figures, the number of nuclei increased exponentially with an increase in impact energy. The observed exponential relationship differs from the linear behavior reported previously for $MgSO_4 \cdot 7H_2O$ (*2*, *3*) because those studies were limited to low impact energies. The linear correlation of previous results was, therefore, simply a small portion of what is in fact, an exponential

TABLE 1. GOOD GROWTH REGIONS

Crystal	$T_s - T$ (°C)
Magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$	4
Potassium alum, $KAl(SO_4)_2 \cdot 12H_2O$	5.5
Potassium sulfate, K_2SO_4	5
Citric acid monohydrate, $C_6H_8O_7 \cdot H_2O$	>7

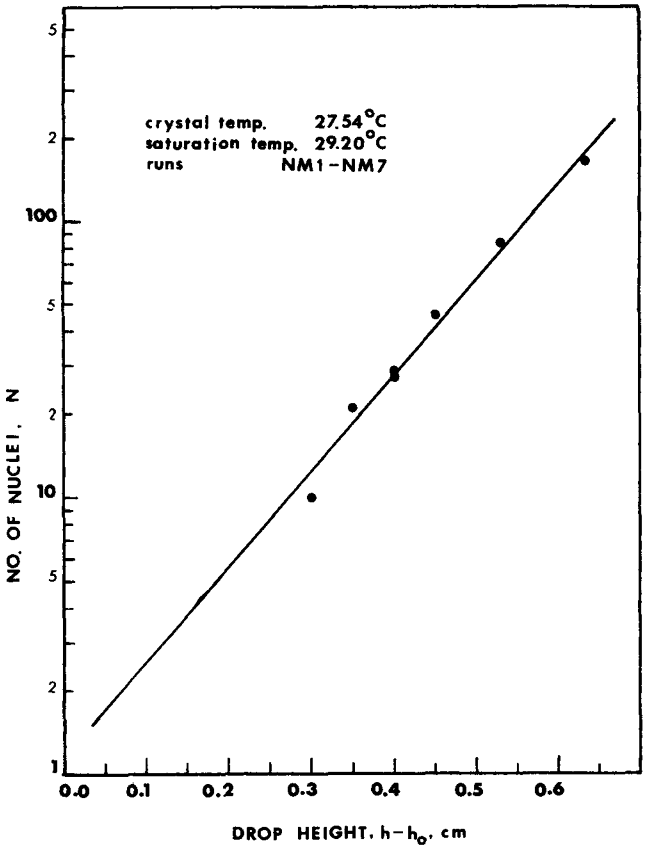

Fig. 4. *N* vs. *E* for $MgSO_4 \cdot 7H_2O$.

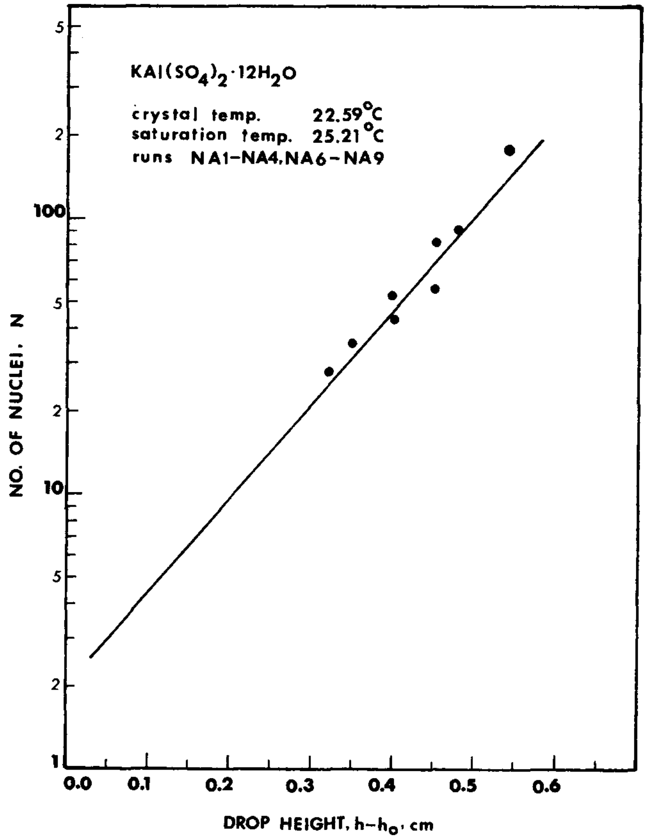

Fig. 5. *N* vs. *E* for $KAl(SO_4)_2 \cdot 12H_2O$.

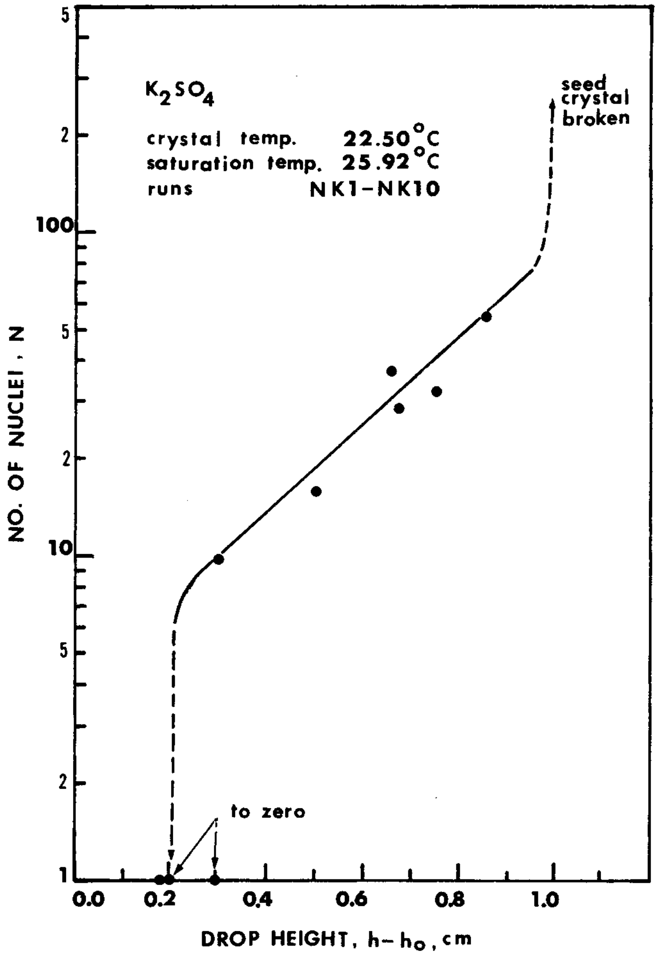

Fig. 6. *N* vs. *E* for K_2SO_4.

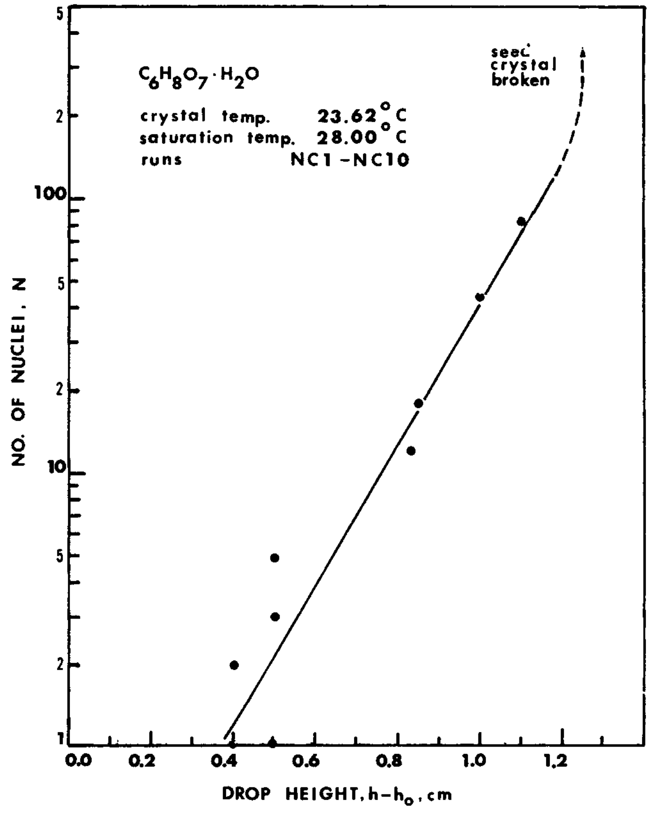

Fig. 7. *N* vs. *E* for citric acid.

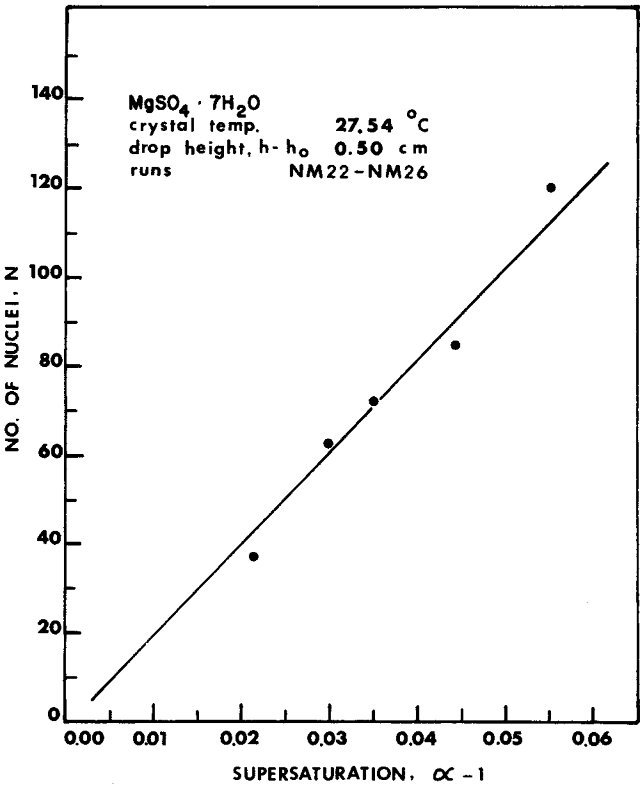

Fig. 8. *N* as a function of supersaturation, $MgSO_4 \cdot 7H_2O$.

relationship. The independent variable in each figure is expressed as $h - h_0$, which can be converted to impact energy by using Equation (1).

Data at low impact energies are limited due to an uncertainty of crystal-rod contact which resulted in scattered data. This problem was most pronounced with citric acid, an extremely viscous system; the data scatter may have been the result of the high viscosity or slight changes in the crystals used in the experiments.

As shown there was no measurable threshold energy before nucleation began for the two inorganic hydrates, but there was for K_2SO_4. The results for citric acid are inconclusive because of experimental difficulties in evaluating h_0 accurately for a highly viscous system.

Visual observation of the seed crystals through a low powered microscope confirmed that no major damage was caused by the metal rod impacting the seed crystal surface, except at the highest impact energies investigated. Where such damage did occur, results were scattered and, in general, nucleation was much higher than would have been predicted by merely extrapolating lower energy data.

Effect of Supersaturation

Figures 8 through 11 demonstrate the influence of supersaturation on the number of nuclei produced by a single contact. In these figures supersaturation is expressed as a supersaturation ratio α which is the ratio of the mole fraction of solute in the system to that at equilibrium. To remain within the good growth region most of the data were taken at temperatures within 4 degrees below the saturation temperature. For the systems $MgSO_4 \cdot 7H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$, and K_2SO_4, the yield of nuclei increased linearly with an increase in supersaturation. Figure 11, however, shows that citric acid did not follow the linear dependence; instead ln N was proportional to $(\ln \alpha)^{-1}$, which, as will be shown, corresponds to the same dependence as the linear growth rate of this crystal.

Growth Rates

The linear growth rate data for potassium alum and citric acid were taken immediately before crystal-rod contacts were made. Measurements of crystal growth were accomplished as described by Clontz et al. (1972). No attempt was made to eliminate the diffusional resistance to crystal growth because to do so would have made the estimation of zero impact energy less reliable. Growth rate data for $MgSO_4 \cdot 7H_2O$ have been reported by Clontz et al. (1972). The growth rate of K_2SO_4 was extremely slow and no attempt was made to evaluate it quantitatively.

Figure 12 shows the observed linear dependence of growth rate on supersaturation for potassium alum; the behavior is also typical of $MgSO_4 \cdot 7H_2O$. Figure 13 shows that the data for citric acid growth follow the relationship between rate and supersaturation suggested

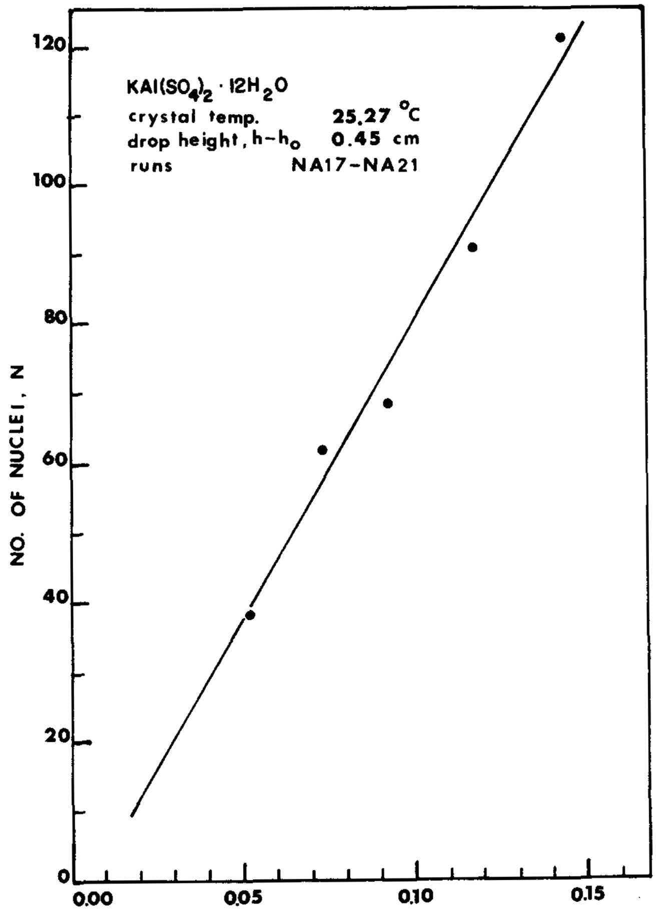

Fig. 9. *N* as a function of supersaturation, $Kal(SO_4)_2 \cdot 12H_2O$.

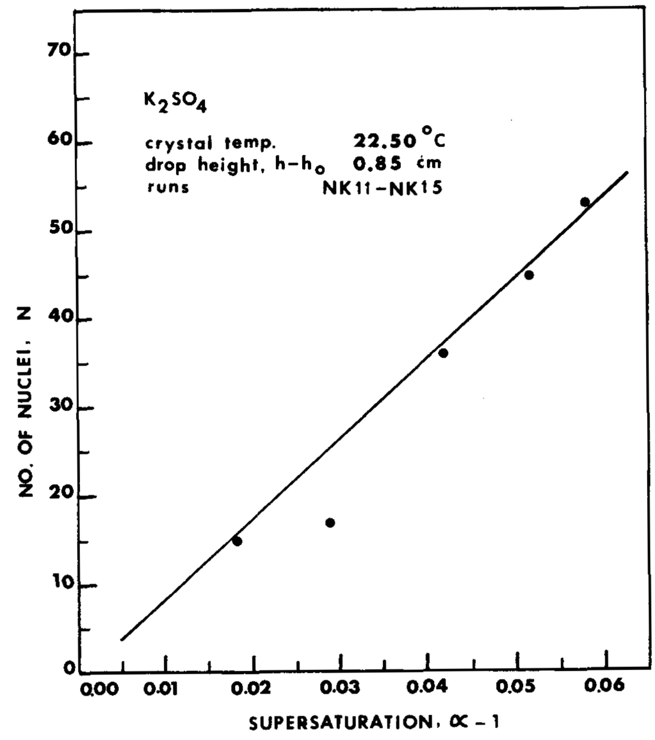

Fig. 10. *N* as a function of supersaturation, K_2SO_4.

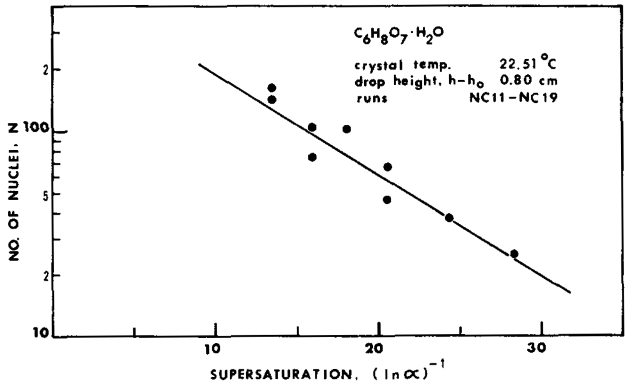

Fig. 11. *N* as a function of supersaturation, citric acid.

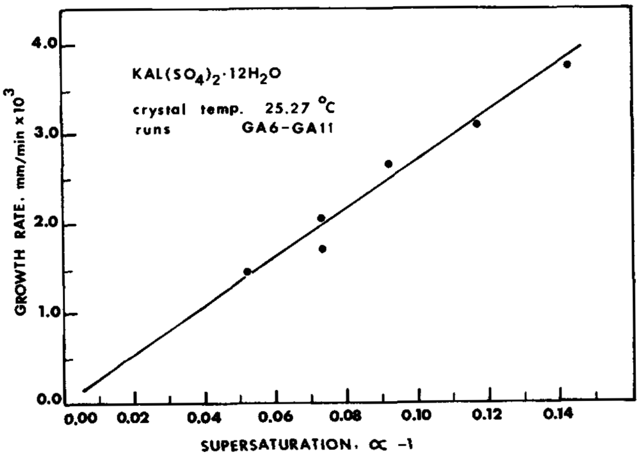

Fig. 12. Growth rates of $KAl(SO_4)_2 \cdot 12H_2O$.

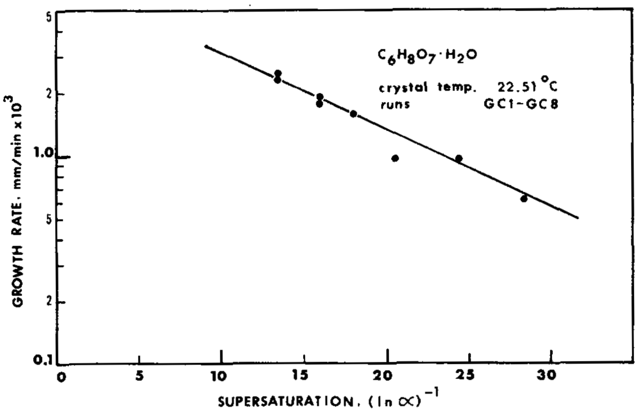

Fig. 13. Growth rates of citric acid.

by the Stranski-Kossel mononuclear two-dimensional growth model

$$G = k_G \exp\ (-\gamma/\ln_\alpha) \qquad (2)$$

so that a straight line is obtained by plotting ln G vs. 1/ln α. The data fit seems good even though the model applies, strictly speaking, only to surface reaction limited growth, and there was no confirmation of such a situation in these experiments.

Crystal Structure

Attempts were made to relate crystal properties to contact nucleation characteristics of the various seed crystals. Since this form of nucleation results from the impact of seed crystals with other objects, crystal hardness and roughness were obvious choices for study.

Hardness tests were conducted on a Kentron microhardness tester. The phrase *microhardness testing* is generally accepted to imply the measurement of hardness at low loads. Because hardness represents a conglomeration of properties such as resistance to abrasion, scratching, cutting, plastic deformation, and others, it is difficult to place confidence in the absolute value of such measurements. An evaluation of the hardness of the four crystalline materials considered in this research is presented in Table 2, which gives an idea of the relative hardness of different crystals.

TABLE 2. HARDNESS OF CRYSTALS

Crystal	Hardness (Knoop scale)
Citric acid monohydrate	18
Magnesium sulfate heptahydrate	38
Potassium alum	45
Potassium sulfate	84

Examination of the crystal surfaces and photomicrographs of those surfaces failed to produce a precise comparison of surface roughnesses because of the difficulty in maintaining the integrity of a crystal surface once it had been removed from the mother liquor. Nevertheless, it appeared that citric acid had the smoothest surface of those investigated. Combining this fact with the microhardness tests seems to show that if crystals have about the same degrees of roughness, as did the inorganic materials, then ease of contact nucleation is a function of crystal hardness.

DISCUSSION

Impact Energy

Three key factors in analyzing results are (1) all crystal-rod impacts weere made so that the impacting surfaces were parallel, (2) the area of impact was held constant, and (3) impacts were limited to a single preselected face of the seed crystal. It is clearly impossible to control these factors in stirred-tank crystallizers; such systems may be even further complicated by the existence of multiple sources of nucleation. Evans et al. (1974) have observed, for example, that crystal-crystal contacts contributed as much as 20% to the overall nucleation rate in a stirred ice crystallizer. They showed that the contribution of crystal-crystal contacts to the nucleation rate is a function of solids concentration in the magma and observed the 20% contribution at a solids concentration of 10% by volume. These authors also speculate that fluid shear may contribute to their observed nucleation rates; the data of Sung et al. (1973) show, however, that very high supersaturations (about 13°C) are required for nucleation by fluid shear in the $MgSO_4 \cdot 7H_2O$ system. In spite of these difficulties, models such as those suggested by Bennett et al. (1973) and Ottens and deJong (1972) have successfully incorporated many of the qualitative and quantitative aspects of contact nucleation presented in the earlier papers of Clontz and McCabe (1971) and Johnson et al. (1972). The data presented in this paper should be useful in updating these models.

One of the particularly vexing problems in extrapolating these fundamental studies to stirred-tank systems is determining precisely the energy of impact between a crystal and the impeller. An estimate may be obtained from the expression

$$E = \frac{1}{2} m_c v_t^2 \qquad (3)$$

An examination of the experimental studies of Ottens and deJong (1972), Youngquist and Randolph (1972), Cise and Randolph (1972), Shah et al. (1973), and Ness and White (1974) shows that the impact energy levels in their systems, as calculated using Equation (3) and the maximum seed size reported in their studies, were significantly lower than those investigated in this study. Nevertheless, Youngquist and Randolph (1972) observed that crystal-impeller collisions often resulted in macroscopic damage to the crystal, even at the relatively low energy levels of their study. Considering the random nature of crystal contacts in their system, it is highly probable that a significant portion of the contacts were crystal-impeller edge or impeller-crystal edge. If this is the case, the impact energy, albeit small, is transferred from the impeller to the crystal across an infinitesimally small contact area, setting up high localized stress within the crystal resulting in macroscopic crystal damage. It is clear from the results presented here that the form of the function relating nucleation rate and impact energy is exponential. However, this function, which is used in models such as those proposed by Bennett et al. (1973), may be invalid when macroscopic crystal damage is significant.

While the experimental data presented here indicate a relationship between nucleation rate and impact energy given by

$$B^0 = a\, f(\alpha) \exp\ (E - E_t) \qquad (4)$$

it must be remembered that these data were obtained utilizing contacts between a stainless steel rod and a seed crystal. The material of construction of the impeller has been shown to be important in controlling the rate of nucleation from crystal-impeller contacts. Shah et al. (1972) demonstrated that the nucleation rate of $MgSO_4 \cdot 7H_2O$ in a batch-stirred crystallizer was reduced by a factor of four when the impeller was constructed of polyethylene rather than stainless steel. In their experiments crystal-crystal contacts were completely eliminated because only one seed crystal was used. Evans et al. (1974) showed that the nucleation rate in an ice crystallizer could be reduced by more than 30% when the crystallizer impeller and baffles were coated with neoprene or silicone rubber. These data obviously mean that some of the energy of impact is absorbed by the contacting element, whether it be an impeller or baffles. Consequently, the direct use of Equation (3) in a system model based upon Equation (4) is limited to a single material of construction. It seems apparent that the constant a in Equation (4) must depend upon the material of construction of the impacting object.

Supersaturation and Growth

All studies on contact nucleation have shown the nuclei produced by a single contact to be a function of supersaturation. Representing this function as $f(\alpha)$

TABLE 3. COMPARISON OF GROWTH RATE WITH NUMBER OF NUCLEI PRODUCED PER CONTACT

Crystal	$MgSO_4 \cdot 7H_2O$	$KAl(SO_4)_2 \cdot 12H_2O$	$C_6H_8O_7 \cdot H_2O$	K_2SO_4
Crystal temperature, °C	22.51	22.51	22.51	22.51
α-1	0.05	0.05	0.05	0.05
Growth rate (mm/min) $\times 10^3$	2.32[a]	1.33	1.17	slow
No. of nuclei produced per contact[b]	115	98	31	22

[a] Clontz' et al (1972).
[b] Data at a drop height 0.60 cm, drop weight 17.57 g, and contact area 8 mm².

$$N = k_1 f(\alpha) \tag{5}$$

Growth rate is also related to supersaturation, for example, by the function $g(\alpha)$

$$G = k_2 g(\alpha) \tag{6}$$

The data for the systems considered in this study indicate that $f(\alpha)$ is proportional to $g(\alpha)$, so that

$$N = k_3 G \tag{7}$$

where k_1, k_2, and k_3 are functions of temperature.

Because of the highly nonlinear nature of $f(\alpha)$ and $g(\alpha)$ exhibited by citric acid, it is somewhat surprising that Equation (7) holds for it as well as the inorganics, for which $f(\alpha)$ and $g(\alpha)$ are linear. This observation raises the strong implication that contact nucleation is related to crystal growth, at least in cases where the impacts are of the type considered in this investigation. Since both growth and contact nucleation are apparently surface phenomena, such a relationship seems quite feasible.

Equation (7) was written to relate the growth rate and number of nuclei produced by a single contact for one face in a particular crystal-solvent system. There is no reason to expect that it should hold for different systems or for different crystal faces in the same system. To compare the different systems all operating conditions must be constant. While this was not feasible experimentally for the four systems investigated, it was possible to calculate numbers of nuclei per contact and growth rate for all systems at the same temperature, supersaturation, and impact energy. The resulting comparison, shown in Table 3, indicates that both growth rate and number of nuclei produced by a single contact follow the order $MgSO_4 \cdot 7H_2O > KAl(SO_4)_2 \cdot 12H_2O > C_6H_8O_7 \cdot H_2O > K_2SO_4$. Note, however, that there is no general proportionality between N and G. The only known instance where there was an inverse relationship between N and G was reported by Johnson et al. (1972) who presented data on the (111) face of $MgSO_4 \cdot 7H_2O$. This crystal face grows more rapidly than the (110) face, but the number of nuclei produced by an impact on the (111) face was substantially lower than for an impact on the (110) face. This observation was attributed to the extreme smoothness of the (111) face.

ACKNOWLEDGMENT

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NOTATION

a, a_1 = proportionality constants
B^0 = nucleation rate
E = contact energy
E_t = threshold energy
$f(\alpha)$ = function relation number of nuclei per contact and supersaturation
g = gravitational acceleration
$g(\alpha)$ = function relation crystal growth and supersaturation
G = linear growth rate, mm/min
h = drop height
h_0 = drop height required to overcome resistance of equipment
k_1, k_2, k_3 = proportionality constants
N = number of nuclei per contact
m = mass of drop weight
m_c = mass of crystal, g
T = system temperature, °C
T_s = saturation temperature, °C
v_t = impeller tip speed
y_A = mole fraction of solute in liquid, $\dfrac{\text{mole solute}}{\text{mole solute} + \text{mole } H_2O}$
$y_{A,s}$ = saturation mole fraction in the liquid at crystal temperature
α = supersaturation ratio, $y_A/y_{A,s}$
γ = constant in Stranski Kossel growth equation

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Drag Reduction in Solid-Fluid Systems

Pressure drop measurements were made on a variety of dilute solid-liquid suspension systems in order to study the effects of particle shape and size, concentration, fluid viscosity, and tube diameter on friction factor. The central objective was to determine under what conditions drag reduction would occur.

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SCOPE

There have been many conflicting reports on measurements of drag for the turbulent flow of dilute solid-liquid suspensions through pipes. Some have shown drag increases above the drag of the liquid at the same flow rate; some have shown little effect; some have shown drag lower than the drag of the liquid at the same flow rate; and some have been mistakenly described as showing decreased drag. The measurements reported here were made over a wide range of Reynolds numbers in a 6.3-mm and a 25.5-mm I.D. tube in order to determine when and if such decreased drag (drag reduction) occurs.

Spherical, platelet, and needle-shaped rigid particles (nonfibrous) of many types and sizes from submicron to 420 μm were used in a range of concentrations up to 4% by weight to determine their drag effect. Fibrous solids of uniform varieties, such as chopped nylon and rayon fibers, and nonuniform varieties, such as dispersed newsprint and asbestos, were extensively tested over the same concentration range.

CONCLUSIONS AND SIGNIFICANCE

Drag reduction could always be obtained with fibrous additives of l/d greater than 25 to 35 if the concentration was sufficiently high. The drag reduction behavior of these suspensions is different from that of high polymer and soap solutions. Laminar flow behavior is stabilized giving lower than normal friction factors and transition to turbulent flow extends over a range of up to two decades or more of Reynolds number. Four flow regions can be recognized. High l/d promotes drag reduction for a given d. Smaller diameter, more flexible fibers, are more effective at equal l/d values. No drag reduction was obtained with spherical, platelet, or needle-shaped rigid solid additives.

Concentration studies pointed up the need for measurements over a range of flow rates as the relative drag reducing abilities of different concentrations of additives vary with the flow region. The relative dispersing abilities of fluids of different viscosity apparently affect the drag reducing character of the suspensions more than viscosity.

Examination of solid-gas suspension data in the literature shows similar flow behavior. It is believed that electrostatic charges on the particles have a major effect on solid-gas friction factor behavior.

The drag ratio DR for conduit flow of an incompressible fluid-additive system is defined as

$$DR = \frac{(\Delta P/L)_{\text{fluid-additive}}}{(\Delta P/L)_{\text{fluid}}} \quad \overline{V} = \text{constant}$$

The fluid-additive system is said to be drag reducing if the drag ratio is less than unity. Drag reduction for steady flow

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