Secondary Nucleation of Magnesium Sulfate by Fluid Shear

The secondary nucleation of magnesium sulfate due to the action of fluid forces on a seed crystal was studied by introducing the hypothesized nuclei so generated into a region of high supersaturation. The number of nuclei observed is strongly dependent on the supersaturation at the seed and the severity of shear forces. Classical nucleation theory is used to interpret the results. These results are consistent with other experimental observations described in the recent literature on contact nucleation. The growth and nucleation process inferred is similar to that illustrated by Clontz and McCabe (1972) and suggested by Knight (1971).

C. Y. SUNG
J. ESTRIN
and
G. R. YOUNGQUIST
Department of Chemical Engineering
Clarkson College of Technology
Potsdam, New York 13676

SCOPE

The objective of this work was the experimental demonstration that fluid mechanical forces could effect the generation of secondary nuclei. This objective was achieved only insofar as nuclei were generated but a region of relatively large supersaturation had to exist within the nucleating chamber. The magnesium sulfate system was studied and the experimental results were analyzed using classical nucleation models.

CONCLUSIONS AND SIGNIFICANCE

The interpretation of the experimental results obtained called upon the existence of subcritical clusters of monomers or embryos in the vicinity of the crystal surface submerged in supersaturated solution. Through fluid shearing action these clusters were transferred to a region of greater supersaturation within the chamber and permitted to develop. By comparing the number of nuclei generated at measured supersaturations with the number suggested from a classical nucleation theory model, some agreement between the two is demonstrated. This presentation introduces a mechanism for secondary nucleation and may provide insight into the mechanisms of growth of inorganic crystals from solution.

Secondary nucleation refers to any process by which new nuclei are caused to form in a supersaturated liquid solution because of the presence of a solute crystal. This process has become increasingly important in recent years because the mechanism by which new crystals are formed in industrial crystallizers involves nucleation from seeded solution.

It has been suggested that secondary nucleation can be caused by fluid shear, that is, by flow of the supersaturated solution relative to the crystal. For instance, Powers (1963) has reported experiments in which nucleation occurred when a sucrose crystal was held on a rotating glass rod in a supersaturated solution. However, both Lal et al. (1969) and Clontz and McCabe (1972) have suggested that fluid shear alone could not produce breeding with $MgSO_4 \cdot 7H_2O$ at a $\Delta T < 4°C$, in the region of supersaturations where needle breeding did not occur and where the crystals grow in a nondendritic form. It may have been that the degree of supersaturation was, in fact, too low so that nuclei or embryos which were formed dissolved; also the magnitude of the shear was not considered.

In this work we hypothesize that secondary embryonic species can be produced by fluid shear at a growing crystal surface. We suggest that these potentially may have been present in previous work (Lal et al., 1969; Clontz and McCabe, 1972) but may have dissolved because of insufficient level of supersaturation and thus not observed.

According to the Gibbs-Thomson equation the critical size varies inversely as the supersaturation: at a given supersaturation, all particles smaller than the critical size will dissolve, and only those larger will survive. The higher the supersaturation, the smaller the critical size, and hence, the greater the number of particles finally surviving. This has been called the survival theory (Garabedian and Strickland-Constable, 1972; Strickland-Constable, 1972). According to the hypothesis in this work, fluid forces at a growing crystal surface can cause the formation of potential secondary nuclei. If the supersaturation in which these develop is great enough, then the critical size required is very small. In the work to be described here, these potential nuclei are visualized as formed due to fluid forces at a growing crystal surface, they are introduced quickly into a region of great supersaturation and there they exist as particles for which the sizes are greater than the critical size associated with this region. These particles can develop and grow to stable crystalline form.

A crystallizer was developed to test this hypothesis. A seed crystal was placed in a supersaturated solution in a region of fluid shear. Some solution from this region was made to flow to a region of high supersaturation where, presumably, the generation of stable nuclei could occur.

APPARATUS

The apparatus consisted of two constant-temperature water supply tanks and the crystallizer. The water tanks were used to provide controlled-temperature water which circulated through the bottom, middle, and upper jackets of the crystallizer.

The crystallizer in which the nucleation experiments were carried out consisted of two parts, the inner crystallizing region and the outer jackets. Auxiliary apparatus required for crystallizer operation were a variable speed agitator, a flood light, a Misco optical reader, and a temperature recorder. A schematic diagram is shown in Figure 1.

The crystallization vessel was constructed by sealing two glass plates on a Pyrex glass cylinder 6.3 cm high and 16.8 cm in diameter using silicone cement. On the top plate were positioned three glass chimneys: the largest (I.D. = 4.7 cm) permitted introduction and positioning of the seed crystal; the smallest (I.D. = 1.3 cm) was a thermometer port; while the remaining one (I.D. = 3.5 cm) accommodated the stirrer shaft. The seed crystal was grown on a small L-shaped stainless steel holder made from stainless welding rod. This holder was held in another larger stainless steel rod by a set screw. The larger rod was held securely on the cover of the largest chimney. O-rings on the cover and on the rod holding the seed sealed the interior of the crystallizer. A stainless steel disk was used to cover the hole on the top glass plate to reduce the turbulence in the chimney when the agitator was rotating. A rubber stopper was used to seal the smallest chimney.

Inside the cylindrical crystallizer were located a brass cylindrical rotor, a horizontal glass baffle, and two thermocouples. The rotor (2.5 cm high, 6.2 cm in diam. and 2.9 cm above bottom) produced the fluid shear. A bottom Teflon bearing supported the stirrer or rotor shaft. The baffle (about 0.6 cm above bottom and 12.7 cm in diam.) separated from the bulk solution a layer of greater supersaturation just above the bottom glass plate for growing the crystal nuclei. When the stirrer was rotating, a circulation existed in the crystallizer which caused solution to flow from the seed outward to the region below the baffle. This circulation was observed directly when particles of polystyrene were inserted into the solution. The thermocouples were No. 30 copper-constantan and were cemented to the bottom glass plate.

A Misco (Microchemical Specialties Co.) No. 182 optical reader measured the distance between the stirrer and the seed crystal. The accuracy of the reader with a movable cross hair and scales inside a calibrated eye piece is ± 0.002 mm. The reader was fixed so that the movable cross hair of the eye piece coincided with the face to be measured. The flood light was used to warm the free surfaces in the three chimneys and thereby to prevent nucleation on the solution surfaces.

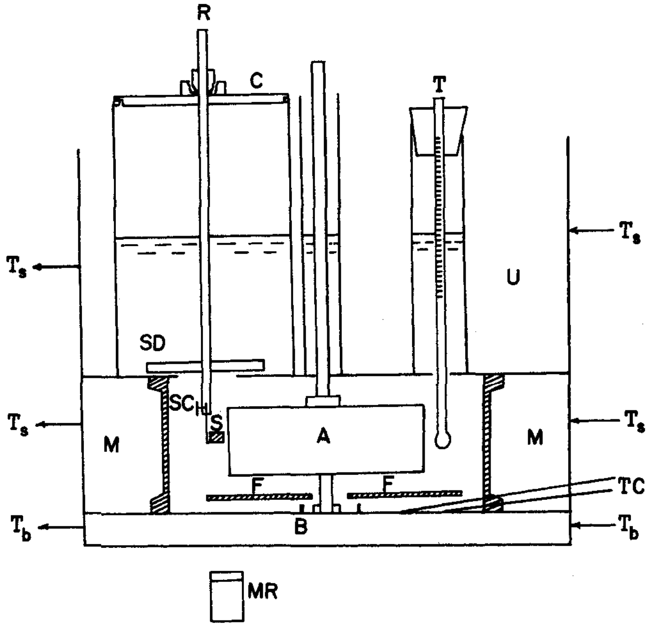

Fig. 1. Schematic diagram of crystallizer: C—stainless steel cover to prevent evaporation (O-ring sealed); R—stainless steel rod to hold the seed (O-ring sealed); A—agitator; S—seed crystal; T—thermometer; U—upper jacket; M—middle jacket; B—bottom jacket; MR—microscope; F—glass baffle; T_s—temperature of the side jackets; T_b—temperature of the bottom jacket; S_c—screw; and SD—stainless steel disk.

PROCEDURE

The magnesium sulfate solution was prepared by dissolving an excess amount of recrystallized $MgSO_4 \cdot 7H_2O$ in distilled water in a 2000-ml flask. The flask was kept in a constant temperature bath for a minimum of 48 hours. A magnetic stirrer kept the mixture well stirred and assured a uniform temperature throughout. After 48 hours, the saturated solution was transferred into the crystallizer by pressurizing the flask with air to cause solids free solution to flow to the crystallizer.

To start an experiment, the solution in the crystallizer was heated to about 7°C above the saturation temperature for a minimum of 3 hours to ensure that any solid $MgSO_4 \cdot 7H_2O$ crystals were dissolved. Then the seed crystal was introduced and pretreated for ½ hour in undersaturated solution as described below. The distance between the seed crystal and the surface of the agitator was measured. The temperature in the first tank (providing water for the bottom compartment) was lowered to 25°C and the temperature in the second tank (for upper and middle compartments) was lowered so that the required degree of supersaturation was obtained. The agitator was operated at a known rev./min. for 30 sec., the temperatures were recorded and the number of nuclei and their quality were observed every 5 minutes over a period of 2 hours.

There is a quick way to determine approximate saturation temperature. A density current will either rise or descend from a crystal suspended in a solution if the solution is stagnant, depending upon whether the crystal is growing or dissolving. This current is observable because of the index of refraction difference that exists between the fluid in the current and that in the stagnant bulk.

After determining the approximate saturation temperature, the temperature was raised from the lower temperature by 0.1°C (the lower temperature is the highest temperature at which the current ascends) and kept at this constant temperature for two hours. The microscope was used to determine whether the crystal was growing. If it was, the temperature was raised again by 0.1°C. The above process was continued until the crystal did not grow or dissolve within a 2-hr. period.

Before the stirrer was started, the supersaturation in the crystallizer was $(\Delta T_c)_I$. After the stirrer had been turned on, ΔT_c increased to $(\Delta T_c)_F$ within 15 sec. and remained unchanged at that temperature. The total time of stirring was 30 sec.; hence $(\Delta T_c)_F$ can be considered to be the effective degree of supersaturation during the period in which nuclei were generated. $(\Delta T_r)_I$ is the supersaturation level at the bottom of the crystallizer when no stirring occurred (about 13°C), and $(\Delta T_r)_F$ (8.4°C) is the final degree of supersaturation attained on stirring. After the stirrer was turned off, ΔT_r increased to the steady state value $(\Delta T_r)_I$ within 8 min. ΔT_r was kept the same through all the experiments, while $(\Delta T_c)_F$ was varied from 0.85° to 3.25°C.

PRETREATMENT OF SEED CRYSTALS

Both Clontz and McCabe (1972) and Lal et al. (1969) have remarked on the surprisingly long period of pretreatment necessary to eliminate initial breeding. The techniques used by Lal et al. (1969) were employed in the present work. In particular, the method of their B-G experiments was employed.

First, the solution was heated for more than 3 hours at 47°C (saturated temperature was about 40°C) to ensure solution of any solid $MgSO_4 \cdot 7H_2O$ which might be present. It was then cooled to 43.5°C. The seed crystal was washed with distilled water and introduced into the solution. The solution was then cooled slowly, unstirred, to 41.5°C (1.5°C undersaturated) where it was kept for ½ hour. It was then cooled down to the experimental temperature, unstirred, over a period of one hour.

TABLE 1. EXPERIMENTAL RESULTS (CURED CRYSTAL)

Run No.	Seed	ΔT_c (°C)		ΔT_r (°C)		Distance, mm	No. of nuclei		Crystallization time, min.	Notes
		$(\Delta T_c)_I$	$(\Delta T_c)_F$	$(\Delta T_r)_I$	$(\Delta T_r)_F$		bottom	baffle		
1	—	3.0	4.5	12.6	8.4	—	0	0	—	Without seed crystal
2	*A*	0.25	0.85	4.5	6.1	1.735	0	0	—	
3	*A*	0.5	1.05	4.5	6.1	1.77	0	0	—	
4	*A*	1.0	2.8	12.3	7.9	1.76	16	12	10	
5	*B*	1.0	2.7	13.0	9.1	1.80	19	10	12	
6	*B*	0.5	2.3	12.3	7.9	1.80	1	0	10	
7	*B*	1.5	3.25	12.5	8.4	1.80	47	26	5	
8	*B*	0.0	1.8	12.0	7.9	1.80	0	0	—	
9	*B*	1.5	3.15	12.8	8.4	1.80	49	33	5	
10	*B*	2.9	3.0	3.0	2.9	1.80	0	0	—	Low ΔT_r
11	*C*	1.0	2.8	12.23	7.9	1.80	16	6	10	
12	*D*	1.5	3.25	12.6	8.4	4.55	0	1	12	Greater distance
13	*D*	1.5	3.20	12.55	8.1	2.36	64	34	5	
14	*D*	1.5	3.20	12.55	8.4	2.36	44	30	5	
15	*D*	1.0	2.8	12.33	8.2	1.80	19	4	12	
16	*D*	1.0	2.8	12.33	8.1	1.80	1,000	1,500	2	Untreated crystal
17	*E*	0.7	2.50	12.3	8.0	1.80	2	1	17	
18	*E*	1.2	2.85	12.3	8.4	1.80	43	4	25	
19	*F*	1.25	2.9	12.3	8.4	1.80	34	1	15	
20	*G*	0.5	2.55	12.3	8.8	1.80	0	0	—	Rev./min.: 1450
21	*G*	0.8	2.55	12.3	8.8	1.80	0	0	—	Rev./min.: 1450
22	*H*	0.8	2.6	12.3	8.55	1.80	0	0	—	Rev./min.: 1880
23	*H*	0.7	2.55	12.3	9.0	1.80	14	3	10	Rev./min.: 2440 Time of stirring 1 min.
24	*H*	0.7	2.75	12.3	8.8	1.80	12	7	10	Rev./min.: 2240 Time of stirring 1 min.
25	*I*	0.55	2.75	12.8	8.6	1.80	1	0	15	Rev./min.: 1850 Time of stirring 1.5 min.
26	*J*	3.0	3.0	3.0	3.0	1.80	0	0	—	Rev./min.: 2050 Low ΔT_r
27	*J*	0.55	2.8	12.8	8.6	1.80	25	2	15	Rev./min.: 2220 Time of stirring 1.5 min.
28	*J*	0.75	2.65	12.8	8.4	1.00	5	2	11	Rev./min.: 2400 Smaller distance

ΔT_r = degree of supersaturation at the bottom of the crystallizer; ΔT_c = degree of supersaturation in the crystallizer; T_b = water temperature in bottom jacket; and T_s = water temperature in upper and middle compartments.

Subscript *I* refers to time when stirrer is turned on.

Subscript *F* refers to time when stirrer is turned off.

Standard operating conditions: (1) Saturation temperature: 40°C (±0.1°); (2) $(\Delta T_r)_I$: 12.55°C (±0.3°C); (3) Time of agitation: 30 sec.; (4) Rotor velocity: 2000 rev./min.

RESULTS AND DISCUSSION

The experiments carried out in this work were intended to show whether secondary nucleation can occur in supersaturated solution because of fluid mechanical forces acting on a rigidly suspended magnesium sulfate crystal. The previous work of Lal et al. (1969) implied that fluid shear alone could not produce breeding unless assisted by dendritic growth which only occurs for $\Delta T > 4°C$. In their experiments, a crystal of magnesium sulfate was attached with cement to a glass rod, which was then immersed for half an hour in a solution of $MgSO_4 \cdot 7H_2O$ supersaturated at a ΔT of 1°C to complete the curing. The crystal on the rod was then transferred to a second vessel containing a supersaturated solution at a known ΔT. The crystal was rotated on its glass rod at a given speed and then held at the same ΔT to detect the production of further crystals. The results showed no breeding for $\Delta T < 4°C$, even at high rates of rotation. On the other hand, nucleation which did take place at $\Delta T > 4°C$ was almost always associated with observable dendritic or needle growth.

In the present experiments, the seed was rigidly supported near the stirrer (about 1.8 mm) which was different from the configuration of Lal et al. (1969), and the local temperature at the bottom of the crystallizer was low about 13°C supersaturation) which in principle permits very small crystals to grow. From the results obtained in this work, nucleation always occurred at $\Delta T > 2.3°C$ so long as a local region of high supersaturation was present. Other conditions were

Time of agitation = 30 sec.
Number of revolutions of stirrer/min. > 2000 rev./min.
$\Delta T_r = 13°C$ (initially)
Distance between seed crystal and the surface of the stirrer < 1.8 mm

Table 1 shows experimental conditions and results. Figure 2 shows the number of nuclei produced versus $(\Delta T_c)_F$, the degree of supersaturation of solution in the crystallizer in the region of the crystal. The very strong dependence of the number produced upon supersaturation is clearly indicated.

A major requirement[*] for obtaining accurate results is

---

[*] An enlarged version of the remainder of this section and additional tables showing times and numbers of crystals have been deposited as Document No. 02196 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N. Y., N. Y. 10017 and may be obtained for $1.50 for microfiche or $2.00 for photocopies.

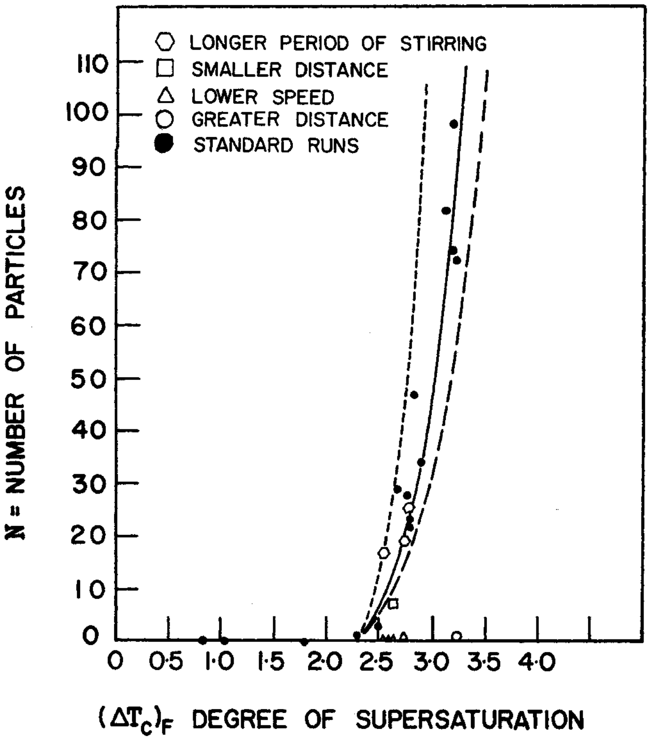

Fig. 2. Dependence of number of nuclei on supersaturation ——— $\phi(\Theta) = 0.12, \gamma = 5$ or $\phi(\Theta) = 1.0, \gamma = 2.5$; — — — $\phi(\Theta) = 0.1$; - - - - - - $\phi(\Theta) = 0.2$.

the assured elimination of initial breeding. The elimination was checked and it was concluded that the pretreatment procedure in this work is adequate to eliminate initial breeding. Experiments were carried out in the absence of seed crystals and no nucleation occurred even after the crystallizer was permitted to stand overnight. These runs showed that new particles obtained did come from the seed crystal.

Several runs were carried out under other than standard conditions. The number of nuclei produced decreased rapidly with increasing distance between the seed crystal and the stirrer. However, a smaller distance did not seem to sensitively affect the number of nuclei produced. The reason may be that all the nuclei or embryos are sheared from the surface by fluid mechanical forces so long as these fluid forces attain a certain level; below this level, only part of the nuclei are removed. Also, a longer period of stirring showed no significant effect on the number of nuclei formed.

THEORY

We call upon existing classical nucleation theory to interpret the data obtained and displayed in Figure 2. The theory has been implied by Knight (1971) who used classical heterogeneous nucleation theory to explain secondary nucleation or nuclei breeding phenomena. The following describes how this theory may be used to predict the dependence of nucleation rates on the supersaturation as observed in the present experiments.

We visualize the surface of a soluble crystal submerged in a solution which is slightly supersaturated relative to the crystalline substance. Clusters of embryonic species composed of i molecules and monomers of the solute ($i = 1$) have deposited on the crystal surface and are in the process of being incorporated into the crystalline structure. Following Knight (1971) the clusters may be visualized as taking on a spherical cap geometry and, therefore, we call upon the wetting angle Θ as a parameter. Knight (1971) also equates values of the solution-cluster and the solution-crystal interfacial energies to simplify the application of the Young equation for the contact angle Θ.

Alternatively the clusters may be visualized as not being attached to the crystal surface but rather concentrated in the stagnant region of the crystal surface and under the influence of the structured force field of the surface. This concept is implied in the suggestions of Clontz and McCabe (their Figure 18) (1972). These clusters may be compared directly with those described in homogeneous nucleation theory.

In either case the steady state concentration of embryos or clusters of size i is

$$n(i) = N \exp\left\{ - \left[\Delta G^0(i) - ikT \ln \frac{n(1)}{N} \right] \frac{1}{kT} \right\} \tag{1}$$

where

$n(i)$ = the number of embryos of size i per unit area of the substrate surface
$n(1)$ = number of monomers per unit area of substrate surface
$N = \sum_{i=1} n(i)$; total number of embryos per unit area of substrate surface
i = number of monomers making up embryos of size i

For the homogeneous mechanism, more properly, N and $n(i)$ are the number of embryos in the volume of solution contiguous with the unit surface of the crystal.

The bracketed term in the exponential of Equation (1) may be designated $\Delta G(i)$ and is the net reversible work required to form an isolated embryo of size i. By referring to the spherical cap model of the embryo, the Gibbs function for embryo formation may be written as (Zettlemoyer, 1969)

$$\Delta G(i) = - iv\Delta G_v + [36\pi\phi(\Theta)]^{1/3}(iv)^{2/3}\gamma \tag{2}$$

where

ΔG_v = Gibbs function change per unit volume due to the phase transformation (Knight, 1971)

$$\Delta G_v \approx \Delta H \left(1 - \frac{T}{T_m}\right) = \Delta H \frac{\Delta T}{T_m}$$

In our experiments $\Delta T = \Delta T_c$ as was used earlier

ΔH = the partial molecular enthalpy change due to the phase transformation—ordinarily ΔH is referred to fusion (Strickland-Constable, 1967; Knight, 1971)
$\phi(\Theta) \equiv \dfrac{2 - 3\cos\Theta + \cos^3\Theta}{4}$, where Θ is the contact angle of the embryo with the substrate. It is seen that $0 \leqq \phi(\Theta) \leqq 1$
γ = interfacial energy of the solution-crystal interface. The full significance of γ is described by Knight (1971).

The corresponding equation for $\Delta G(i)$ describing homogeneous nucleation is

$$\Delta G(i) = iv\Delta G_v + [36\pi]^{1/3}(iv)^{2/3}\gamma \tag{2a}$$

On substituting Equation (2) or (2a) into Equation (1), we obtain

$$n(i) = N \exp\{- Ai^{2/3} + Bi\} \tag{3}$$

where, for the heterogeneous case,

$$A = \frac{[36\pi\phi(\Theta)]^{1/3} v^{2/3} \gamma}{kT} \tag{4}$$

$$B = B(\Delta T_c) = \left(\frac{v\,\Delta H}{kT\,T_m}\right) \Delta T_c \tag{5}$$

and $\phi(\Theta) = 1$ when considering the homogeneous process. Now we visualize that the $n(i)$ clusters are somehow removed from the surface or region of the surface of the substrate and a fraction of them are quickly introduced into a region of supersaturation greater than existed at the crystal. Those which are introduced into this region and are greater than the critical size, say i_1, relative to this higher level of supersaturation, will grow to become an observable crystal. If the fraction introduced to higher levels of supersaturation is η, then the total number of observed crystals N_{Tot} is

$$N_{\text{Tot}} = \eta NS \sum_{i=i_1}^{i=i_2} \exp\{-Ai^{2/3} + Bi\} \tag{6}$$

where

i_1 = critical size relative to supersaturation, ΔT_r

i_2 = largest embryo size; this is estimated by $n(i_2) = 1$

Now we wish to use Equation (6) to interpret the data obtained and displayed in Figure 2. Ordinarily the critical size of an embryo is determined by differentiating the Gibbs function, $\Delta G(i)$, with respect to i and setting equal to zero. Here

$$\frac{d(\Delta G(i))}{di} = 0;$$

$$i = i_1$$
$$\Delta T = \Delta T_r$$

That is,

$$i_1 = \left(\frac{2}{3}\frac{A}{B}\right)^3 \tag{7}$$

$$i_1 = \frac{32\pi\gamma^3\phi(\Theta)T_m^3}{3v\Delta H^3 \Delta T_r^3} \quad \text{(heterogeneous model)}$$

$$i_1 = \frac{32\pi\gamma^3 T_m^3}{3v\Delta H^3 \Delta T_r^3} \quad \text{(homogeneous model)}$$

so that i_1 is related to ΔT_r in the experiments conducted here. In particular i_1 represents the size of the smallest embryonic species which may grow when introduced into the environment whose supersaturation is given by ΔT_r.

The value of i_2 required in Equation (6) is determined from

$$n(i_2) = 1 = \eta NS \exp\{-Ai_2^{2/3} + Bi_2\} \tag{8}$$

which is an implicit equation for i_2 determined by the experimental parameter ΔT_c in B. This equation is first used to obtain the value for ηNS.

We make use of the relationships (7) and (8) and the data value at which $N_{\text{Tot}} = 1 (\Delta T_c = 2.3°\text{C})$ to obtain ηNS.

$$\eta NS = \frac{1}{\exp\{-Ai_1^{2/3} + Bi_1\}} \tag{9}$$

That is, when the supersaturation in the crystallizer is 2.3°C, the largest cluster which exists is just capable of growing when introduced into the environment whose supersaturation is ΔT_r. Thus when $\Delta T_c = 2.3°\text{C}$, $i_2 = i_1$. At any lower ΔT_c value, no nuclei are observed. Thus the coefficient, ηNS, is forced to satisfy the data at $N_{\text{Tot}} = 1$.

It is readily seen from Figure 2 that extrapolation of the curve through the data to $N_{\text{Tot}} = 1$ is generally difficult since there is significant curvature in this region. We may use an empirical approach. A plot of ln N versus $(1/\Delta T_c)^2$ is linear and extrapolation to $N_{\text{Tot}} = 1$ is accomplished readily. A better approach would have been to have many more data in the vicinity of, say, $N_{\text{Tot}} = 1$ to 3.

By estimating values of A and B, N_{Tot} in Equation (6) may be determined and compared with the experimental N_{Tot} as a function of ΔT_c. Estimated values of the properties implied in Equation (6) are

γ = 5 erg/cm^2 (Preckshot, 1952)
T = 311°K
v = 2.4×10^{-22} cm^3/molecule
T_m = 313°K
ΔH = 48.2×10^7 erg/cm^3 (Perry, 1963)
k = 1.38×10^{-16} erg/°K-molecule
$0 \leq \phi(\Theta) < 1$ (heterogeneous model)
$\phi(\Theta)$ = 1 (homogeneous model)

Using the above values for the physical properties, we make $\phi(\Theta)$ the data fitting parameter. The solid curve in Figure 2 is computed with $\phi(\Theta) = 0.12$. The sensitivity of the fit to the choice of $\phi(\Theta)$ is indicated in the other curves displayed when $\phi(\Theta) = 0.1$ and $\phi(\Theta) = 0.2$. These values are acceptable on physical grounds.

Since $\phi(\Theta) = 1$ for the homogeneous model we make γ the data fitting parameter. The value $\gamma = 2.5$ gives the solid curve in Figure 2 when $\phi(\Theta) = \phi(180°) = 1$.

It is seen that the model, with the parameter values chosen, fits the data extremely well.

For this interpretation of the experimental data to be convincing, values of ηNS and i_1 are of interest. In the above computations

$$\eta NS = 6.63 \times 10^{16}$$

$$i_1 = 257$$

The value of i_2 corresponding to 3.25°C is 283. These i values are reasonable. The number obtained for ηNS is rather large for a monomolecular layer upon a 1-cm^2 surface. The number is more appropriate to a volume contained adjacent to the surface of about 0.05mμ in depth. Because of this value it would seem that the homogeneous model is more appropriate.

Another calculation based upon the values of A and ηNS obtained is justified. We consider the operation of the crystallizer at a value of $\Delta T_c = \Delta T_c^*$ such that i_2, the size corresponding to the largest single embryo, is a critical value, $i_2 = i_2^*$. That is, i_2^* and ΔT_c^* satisfy Equations (10) and (11) simultaneously

$$i_2^* = \left(\frac{2}{3}\frac{A}{B^*}\right)^3 \tag{10}$$

$$n(i_2^*) = 1 = \eta NS \exp\{-Ai_2^{*2/3} + B^* i_2^*\} \tag{11}$$

The solution of Equations (10) and (11) simultaneously yield B^* and i_2^*. From B^* the corresponding $\Delta T_c = \Delta T_c^*$ may be determined. This ΔT_c^* value corresponds to the supersaturation at which nucleation would be spontaneous in the region of the crystal surface. The equation for B^* from the above procedure is

$$B^* = \left\{\frac{A^3\left[\left(\frac{2}{3}\right)^2 - \left(\frac{2}{3}\right)^3\right]}{\ln \eta NS}\right\}^{1/2} \tag{12}$$

The value of ΔT_c^* obtained from Equation (12) is

8°C. This is in fact the value which is given in Figure 5 of the paper by Clontz and McCabe (1972). This figure shows 8°C to be the supersaturation level at which nucleation phenomena of some form occur under virtually all conditions of growth for the magnesium sulfate system.

The results obtained and the interpretations suggested are consistent with those of Denk and Botsaris (1972). These workers found that at low supersaturations, a parent seed of sodium chlorate submerged in a supersaturated solution gave rise to nuclei which originated from the seed or from the solution in the vicinity of the seed depending upon the rate of stirring. At low rates of stirring or in stagnant solution the nuclei were apparently influenced by both sources. This is certainly the interpretation implied in the above discussion. Denk and Botsaris (1972) had determined these results by using the two enantiomorphic forms of the sodium chlorate crystal.

The mechanism implied here is not necessarily the primary one occurring in industrial crystallizers. Certainly direct collision with other solid surface by crystals must give rise to additional nuclei.

Further support for the process visualized here lies in the work of Lal et al. (1969) and Youngquist and Randolph (1972). Lal et al. (1969) interpret their data, giving contact nucleation rates as a function of ΔT, as being surface energy determined—as implied in the Gibbs-Thomson equation. Youngquist and Randolph (1972) display the distribution of micron size ammonium sulfate crystals generated by contact nucleation: that distribution is not unlike that given by Equation (3). Their supersaturation levels were not known but were small, and as a consequence nuclei and embryos were possibly being observed and counted by their elegant counting device.

The experimental work described here is quite similar to that carried out by Garabedian and Strickland-Constable (1972) in that a supersaturation change is brought about after generation of nuclei or embryos. Their runs in which the supersaturation was increased showed no significant increase in new crystals, contrary to what would have been expected from this work. An explanation may be that the increase in supersaturation was brought about over one hour after the generation of nuclei; after this period of time any species of subcritical size may have dissolved.

CONCLUSIONS

We believe that this experimental work provides strong evidence that fluid forces are able to produce a secondary embryonic species because of a seed crystal placed in a supersaturated magnesium sulfate-water solution. The reasoning behind this conclusion is entirely inferential. The number of nuclei produced is very strongly dependent on the supersaturation. However, these nuclei attain the status of growing crystals only by having a local region of higher supersaturation into which they are introduced. No nuclei were obtained when the supersaturation at the crystal was less than 2.3°C, no supersaturations greater than 3.25°C were attempted. This range is entirely below the 4°C level mentioned in the previous studies (Lal et al., 1969; Clontz and McCabe, 1972).

The experimental data can be interpreted by using classical homogeneous or heterogeneous nucleation theory.

ACKNOWLEDGMENT

This work was made possible through a research grant from the National Science Foundation, Grant No. GK-13215.

NOTATION

$\Delta G^0(i)$ = standard state Gibbs function of formation of an embryo
ΔG_v = Gibbs function change per unit volume due to the phase transformation
ΔH = the partial molecular enthalpy change due to the phase transformation
i = number of monomers making up embryos of size i
i_1 = critical size relative to supersaturation, ΔT_r
i_2 = largest embryo size; this is estimated by $n(i_2) = 1$
N_{Tot} = total number of observed crystals
$N = \sum_{i=1}^{i=i_2} n(i)$, total number of embryos per unit area of substrate surface
$n(i)$ = the number of embryos of size i per unit area of the substrate surface
S = effective surface area of the seed crystal
T_m = the ordinary equilibrium temperature corresponding to a flat interface
ΔT_r = Degree of supersaturation at the bottom of the crystallizer (in the region of high supersaturation)
ΔT_c = Degree of supersaturation in the crystallizer (at the existing crystal surface)
v = volume per monomer
$\phi(\Theta) = \dfrac{2 - 3\cos\Theta + \cos^3\Theta}{4}$
Θ = contact angle between embryo or cluster and substrate
γ = interfacial energy of the solution-crystal interface
η = fraction of embryos transferred to solution whose supersaturation is ΔT_r

LITERATURE CITED

Clontz, N. A., and W. L. McCabe, "Contact Nucleation of Magnesium Sulfate Heptahydrate," *Chem. Eng. Progr. Symp. Ser. No. 110*, 67, 6 (1971).

Denk, E. G., Jr., and G. D. Botsaris, "Fundamental Studies in Secondary Nucleation from Solution," *J. Crystal Growth*, **13/14**, 493 (1972).

Garabedian, H., and R. F. Strickland-Constable, "Collision Breeding of Crystal Nuclei: Sodium Chlorate. Part I," *ibid.*, 506.

Knight, C. A., "Breeding of Crystal Nuclei by Classical Nucleation: Theory and Some Observations and Experiments," *ibid.*, **11**, 201 (1971).

Lal, D. P., R. E. A. Mason, and R. F. Strickland-Constable, "Collision Breeding of Crystal Nuclei," *ibid.*, **5**, 1 (1969).

Mason, R. E. A., and R. F. Strickland-Constable, "Breeding of Crystal Nuclei," *Trans. Farad. Soc.*, **62**, 455 (1966).

Perry, J. H., "Chemical Engineering Handbook," 4th Edit., p. 3-222, McGraw-Hill, New York (1963).

Powers, H. E. C., "Nucleation and Early Crystal Growth," *Ind. Chem.*, **39**, 351 (1963).

Preckshot, G. W., and G. G. Brown, "Nucleation of Quiet Supersaturation KCl Solutions. Effect of Some Ionic Crystals," *Ind. Eng. Chem.*, **44**, 1314 (1952).

Strickland-Constable, R. F., *Kinetics and Mechanism of Crystallization*, Academic Press, p. 104 (1967).

———., "The Breeding of Crystal Nuclei—A Review of the Subject," *AIChE Symp. Ser. No. 121*, **68**, 1 (1972).

Youngquist, G. R., and A. D. Randolph, "Secondary Nucleation in a Class II System: Ammonium Sulfate—Water," *AIChE J.*, **18**, 421 (1972).

Zettlemoyer, A. C., *Nucleation*, Marcel Dekker, 161 (1969).

Manuscript received March 6, 1973; revision received and accepted June 4, 1973.