The Growth of Ice Crystals in a Stirred Tank

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Ice crystals were grown in water or sodium chloride solutions by direct contact with evaporating butane. In water subcooled 0.01° to 0.05°C., the particles grew about one-quarter to one-half as fast as predicted from heat transfer correlations. The growth rates in 2% salt solution were about sevenfold lower than those obtained in water at the same subcooling, because the concentration difference for salt diffusion lowered the interface temperature. Calculations indicate the diffusion effect to be much greater for disk-shaped particles than for spheres.

In the Cornell process for producing pure water by freezing (*14*), ice crystals are formed by evaporating butane in direct contact with the solution. Similar processes use different refrigerants or cool by evaporation of water. In laboratory and pilot-plant tests, the particle size has been varied by changing the holdup time or the rate of heat removal, but there are no published data relating the growth rate of ice particles in a slurry to the degree of subcooling and the salt concentration. The overall driving force in the freezer is typically 1 to 3°C., but most of this driving force is used for vaporization, since the total area of vapor bubbles is much less than the area of the ice crystals. The actual subcooling of the solution is probably 0.1°C. or less, based on data in this study and on reported particle sizes and holdup times (*6*).

Although a driving force of 0.1°C. is negligible from the standpoint of the energy consumption, knowledge of the growth and nucleation rates is needed for sound design of large freezing plants. Large crystals are desired for ease in handling and for rapid washing, but they take longer to grow and longer to melt than small ones. With basic rate data and equipment costs for each step of the process, the optimum particle size could be calculated for different freezing processes. Basic studies might also lead to a freezer design which would permit separate control of the nucleation and growth rates. At present the scale-up of existing freezers is uncertain because slight changes in flow pattern and temperature distribution in the solution can change the number and size of the particles produced.

Several studies have shown that ice crystals in slightly subcooled water tend to grow as hexagonal plates (*1, 5, 6*). The growth rate along the *a* axis (within the hexagonal basal plane) is usually limited by the rate at which heat can be transferred from the interface. Farrar and Hamilton measured the growth of ice crystals on a rod in a moving stream of water (*1*). The rates increased with water velocity but leveled out at velocities of 10 to 20 cm./sec. Recently Fernandez and Barduhn (*3*) found slightly higher growth rates and a steady increase in growth with velocity over the range 1 to 20 cm./sec. Thus the maximum or inherent growth rates are still in doubt. However the velocity past an ice particle suspended in a slurry will generally be less than 2 cm./sec. (1.6 cm./sec. terminal velocity for a 1-mm. sphere) and the growth along the *a* axis should be limited by heat transfer. For very small particles, the heat transfer coefficient varies inversely with size, and the inherent growth rate may become limiting. The theory for small particles is made more complex because the small radius of curvature raises the melting point and lowers the available driving force for inherent growth and heat transfer.

The growth along the *c* axis (normal to the basal plane) has been studied in capillaries by tilting a seed crystal to make the hexagonal face perpendicular to the tube axis or by using a bend in the capillary to get the same effect. Hillig (*5*) used driving forces of 0.03° to 1°C. and corrected for the temperature drop in the glass wall. Sperry (*12*) made a similar study with a further correction for the boundary layer outside the tube. The ΔT corrections were not large, and the data reported by Sperry and plotted in Figure 3 are presumably good values for the inherent growth rates for perfect crystals. As shown in Figure 3, the *c* axis rate at 0.1°C. is about 1/20 the highest measured rate for the *a* axis. On going to lower driving forces, the *c* axis rate decreases very rapidly and becomes practically zero at 0.04°C.

When an ice crystal is grown from a salt solution, the rejection of salt at the ice surface leads to a higher salt concentration and a lower freezing point. The actual overall temperature driving force, $\Delta T = T_i - T_b$, is less than the nominal value ΔT^* because of the difference in freezing points at the interface and in the bulk solution. A few tests by Farrar and Hamilton (*1*) with 5% sodium chloride showed *a* axis growth rates one-third those for pure water. This is about the effect expected based on diffusion of salt from the interface. Salt would reduce the *c* axis growth rate because of the change in freezing point near the surface and perhaps because of a change in inherent growth rate. Capillary studies with salt solutions have been inconclusive, since salt cannot escape from the system, and the accumulation leads to extremely low growth rates (*1*).

Based on the existing data for fixed crystals, the growth of a suspended crystal at $\Delta T = 0.1$°C. would be controlled by heat transfer for *a* axis growth, and both heat transfer and the inherent rate would determine the *c* axis growth. A crystal with a thickness of one-fourth to one-half the diameter might be expected. For higher ΔT, heat transfer would become more important, since the inherent *c* axis rate varies with about ΔT^2. If growth along both axes were limited by conduction, a nearly equidimensional particle might be expected. For driving forces of 0.05°C. or less, extremely thin plates would be produced if the published *c* axis rates apply.

Actually, pilot-plant tests show that nearly spherical crystals are produced at very low growth rates and thin crystals at high growth rates (*7*). In this study, crystals with a thickness of 0.1 to 0.5 the diameter were grown at 0.01° to 0.05°C. subcooling, which is much thicker than expected from the *c* axis growth rates. Kawasaki and Umano grew crystals with a thickness half the diameter at rates of about 10^{-5} cm./sec. (*6*), which corresponds to a driving force of about 0.02°C. Some other mechanism makes the *c* axis growth for suspended crystals much more rapid than growth in a capillary. One explanation is crystal defects, which occasionally led to more rapid growth in Sperry's tests. Random defects on the basal plane of almost all the crystals in a slurry seem unlikely, but perhaps growth at the edge gives rise to defects which propagate over the basal plane. The suspended crystals may grow by deposition of ice at the edge of the particle followed by migration of some molecules along the basal plane. At low growth rates, there would be more time for surface diffusion to create a thick particle. Surface migration may have occurred in the capillary tests, where an optically flat interface was formed up to 0.2°C. subcooling even though the edge of the capillary was cooler than the center (*12*).

THEORETICAL GROWTH CURVES

Growth curves were predicted for spheres and disks growing as suspended particles in water or in salt solutions. The interface temperature was assumed to be the true freezing point of the solution at the surface. This neglects the driving force required for the crystallization step and the increase in freezing point with surface curvature. Both effects are small for particles greater than 30 μ in diameter, and it takes only a few seconds for particles to reach this size.

The heat and mass transfer coefficients for spheres were based on the Ranz and Marshall (*8*) correlation for Reynolds numbers greater than 1 and on the correlation of Tsubouchi and Masuda (*13*) for low Reynolds numbers. The predicted terminal velocity was used to calculate particle Reynolds numbers, which gives a conservative estimate of the transfer coefficient. With moderate agitation (1 h.p./1,000 gal.), the mass transfer coefficients for suspended spheres are 1.5 to 2.5 times those predicted for particles falling at their terminal velocity (*4*); the factor increases with Schmidt or Prandtl number and would probably be 1 to 1.5 for heat transfer in water. Physical properties were obtained from the International Critical Tables with extrapolation to −1.5° and −3°C. for 3 and 6% sodium chloride. The diffusivity for salt was 0.62×10^{-5} sq.cm./sec. at −3°C. and the Schmidt number 3,270.

$$N_{Re} < 1;\; N_{Nu} \text{ or } N_{Sh} = 2 + 0.52\, N_{Re}^{1/3}\, (N_{Pr} \text{ or } N_{Sc})^{1/3} \quad (1)$$

$$N_{Re} > 1;\; N_{Nu} \text{ or } N_{Sh} = 2 + 0.6\, N_{Re}^{1/2}\, (N_{Pr} \text{ or } N_{Sc})^{1/3} \quad (2)$$

The time for spheres to grow to a given size in water was obtained by integrating Equation (3).

$$\frac{dd_p}{dt} = \frac{2\,h\,\Delta T}{\lambda\,\rho_s} \quad (3)$$

For spheres in salt water, the growth is arbitrarily expressed in terms of salt diffusion from the interface rather than water diffusion to the interface. The effect of interface motion was not considered.

$$\frac{dd_p}{dt} = \frac{2\,k_c}{\rho_s}\,\Delta c \left(\frac{\rho - c}{c}\right) \quad (4)$$

The concentration difference lowers the temperature driving force as shown in Equation (5), where ΔT^* is the nominal driving force

$$\Delta T = \Delta T^* - \left(\frac{dT_i}{dc_i}\right) \Delta c \quad (5)$$

Combination of Equations (3), (4), and (5) gives the actual driving force for heat transfer

$$\Delta T = \frac{\Delta T^*}{1 + \phi} \quad (6)$$

where

$$\phi = \left(\frac{dT_i}{dc_i}\right) \left(\frac{h}{\lambda\, k_c}\right) \left(\frac{c}{\rho - c}\right)$$

For 6% salt solution, the value of ϕ is 9.74 N_{Nu}/N_{Sh}, which means that mass transfer lowers the effective driving force by a factor of 10.74 for small particles. For 1-mm. particles, ϕ is 2.2, and ϕ approaches 9.74 $(N_{Pr}/N_{Sc})^{1/3}$ or 1.65 for large particles. The increased density of the 6% salt solution has a slight compensating effect: the density difference is 50% greater and h for large particles 8% greater than in water.

If ice crystals grow as thin disks, the terminal velocity is less than for spheres but the heat transfer area is greater. The average coefficient is less than for a sphere of the same diameter, but the coefficient for the edge is greater than for the faces. For an approximate analysis, the effective area was taken as the edge area plus the area of one face, and the average coefficient was assumed to be that for a sphere at the same Reynolds number. The terminal velocities for the disks were obtained with published drag coefficients, which approach $20/N_{Re}$ at low Reynolds numbers.

The *c* axis growth rate is α times the *a* axis rate, and for simplicity, α is assumed constant. When the diameter increases by Δd_p and the thickness by $\alpha(\Delta d_p)$, the volumes added to the edge and faces are $\pi d_p(\alpha d_p)\Delta d_p/2$ and $(\pi d_p^2/4)\alpha(\Delta d_p)$. Thus 2/3 of the growth is at the edges and 1/3 at the faces for any constant value of α. However heat released at the edge is conducted to the face with a very small driving force because the conductivity of ice is four times that of water and the external thermal boundary layer is relatively thick. The contribution of crystal conduction decreases with increasing particle size or increasing Nusselt number, and counting half the face area is just a rough approximation.

The disk growth curve was obtained by integrating Equation (10), which was derived by counting only one face for heat transfer; counting both faces would change the factor 0.25 to 0.5.

$$M = \rho_s \frac{\pi\, d_p^2}{4} (\alpha\, d_p) \quad (7)$$

$$\frac{dM}{dt} = \frac{3}{4}\,\pi\,\alpha\,\rho_s\, d_p^2\, \frac{dd_p}{dt} = \frac{hA\,\Delta T}{\lambda} \quad (8)$$

$$A = \pi d_p\, \alpha\, d_p + \frac{\pi d_p^2}{4} = \pi d_p^2\; (\alpha + 0.25) \quad (9)$$

$$\frac{dd_p}{dt} = \frac{4}{3} \left(\frac{\alpha + 0.25}{\alpha}\right) \frac{h\,\Delta T}{\lambda\,\rho_s} \quad (10)$$

The growth of disks in salt solution introduces another complication. Heat can be conducted through the disk and away from the faces, but salt diffusion occurs only from the growing surfaces. Growth curves were calculated for the case where all the ice is deposited at the edges and one-third of the ice migrates to the faces. The effective area for heat transfer was taken as the edge area plus half the face area. If only two-thirds of the ice is deposited at the edge, the growth rates would be about 1.5 times those shown. The mass transfer coefficient was taken as the value for a sphere at the same Reynolds number, which is conservative, since the concentration boundary layer would start at the edge of the disk if there were no mass transfer from the faces. The growth curves were ob-

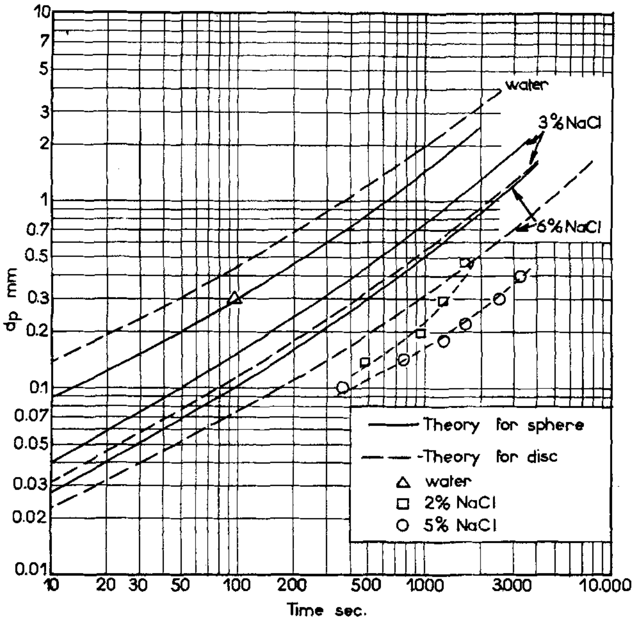

Fig. 1. Growth of ice crystals in a stirred tank at ΔT = 0.05°C.

tained from Equations (6) and (10) with a new value of ϕ.

$$\phi_{\text{disk}} = 9.74 \frac{N_{Nu}}{N_{Sh}} \left(\frac{0.25 + \alpha}{\alpha}\right) \text{ for } 6\% \text{ salt solution}$$

$$\phi_{\text{disk}} = 34.1\, N_{Nu}/N_{Sh} \text{ for } \alpha = 0.1 \qquad (11)$$

The theoretical growth curves in Figure 1 show that disks should grow about twice as fast as spheres in pure water. Because the area for mass transfer is less the area for heat transfer, disks grow more slowly than spheres in 3 or 6% sodium chloride solution. The curves have an initial slope of 1/2, since the transfer coefficients for very small particles vary inversely with particle size. For particles larger than 2 mm., the slopes are about 1, as the coefficients are almost independent of size. Over most of the range of interest, the linear growth rate decreases with increasing particle size, and comparisons of growth rates should be made at the same size.

EXPERIMENTAL STUDIES

Batch freezing tests were made in a Plexiglas tank 5½ in. in diameter and 8 in. high with four three-quarter height baffles 90° apart. The slurry was stirred by a 1½-in. downward pumping propellor adjusted to create a shallow vortex. With the top of the baffles 1 in. below the liquid level, ice and butane reaching the surface were redispersed in the vortex. Liquid *n*-butane was passed through a cooling coil in an ice-salt bath and introduced underneath the propellor. For runs with water, the butane vapor was passed through a throttling valve to a wet-test meter and then vented. The tank pressure and thus the evaporation rate were adjusted with the throttling valve. In tests with salt water, vapors were removed by a vacuum pump, and the tank pressure was adjusted by bleeding air into the pump.

The slurry temperature was measured with a Beckman thermometer, and for some runs a thermistor enclosed in a glass rod was also used.

The procedure for nucleating crystals evolved after several trials. With water at 0°C. the butane flow was momentarily increased several-fold. With high agitation the solution cooled rapidly to about —0.05° or —0.10°C., nucleation occurred, and the temperature rose to —0.01° to —0.03°C. Attempts to seed undercooled water (—0.05°C.) with a mass of tiny crystals or even a single chip of ice gave so many small crystals that the temperature rose almost to zero, and the driving force could not be measured. Slow cooling of water below 0°C. was also unsuccessful; crystals formed at —0.4°C. and the water temperature rose to 0°C. The same rapid cooling procedure was used to start runs with salt solutions. The maximum subcooling reached was somewhat greater (0.1° to 0.3°C.) than with water, and the driving force reached was also generally larger. One run was stopped when hydrate crystals formed 0.5°C. above the freezing point of the solution.

After nuclei formed, freezing was continued until 10 to 30% of the water was converted to ice. The butane flow and stirrer speed were adjusted to try to maintain a constant temperature, but the driving force fluctuated by 100% or more during some runs. The driving force could not be measured continuously for salt solutions because the freezing point decreased with time. To measure the nominal driving force, the butane flow was shut off, and the solution and crystal temperatures quickly rose to the true freezing point $T_{f,b}$. For a 0.05°C. rise in temperature the amount of ice formed and the change in salt concentration are very small, corresponding to only about 0.001°C. change in freezing point. Therefore the temperature rise was taken as the driving force for ice growth prior to interrupting the butane flow. This method assumes that the probe always gives the bulk solution temperature, although it occasionally contacts the cooler film around evaporating butane drops or the warmer film around the ice crystals. The thermistor readings were more reliable for the determination, since the Beckman thermometer responded to changes in tank pressure, and the pressure correction was about as large as the actual temperature rise. Also, the Beckman thermometer had a time constant of 15 sec., compared to about 2 sec. for the enclosed thermistor.

The particle size was followed by withdrawing samples on a sieve and measuring 10 to 30 particles with a cold-stage microscope. Most of the particles were within 50% of the number-average size, and the determination took less than 1 min. The particles were roughly ellipsoidal in shape, and the thickness was estimated to be 0.1 to 0.5 times the diameter.

GROWTH RATES

Some typical growth curves are shown in Figure 1. Only one run was made with water at a driving force as large as 0.05°C., and the temperature suddenly increased

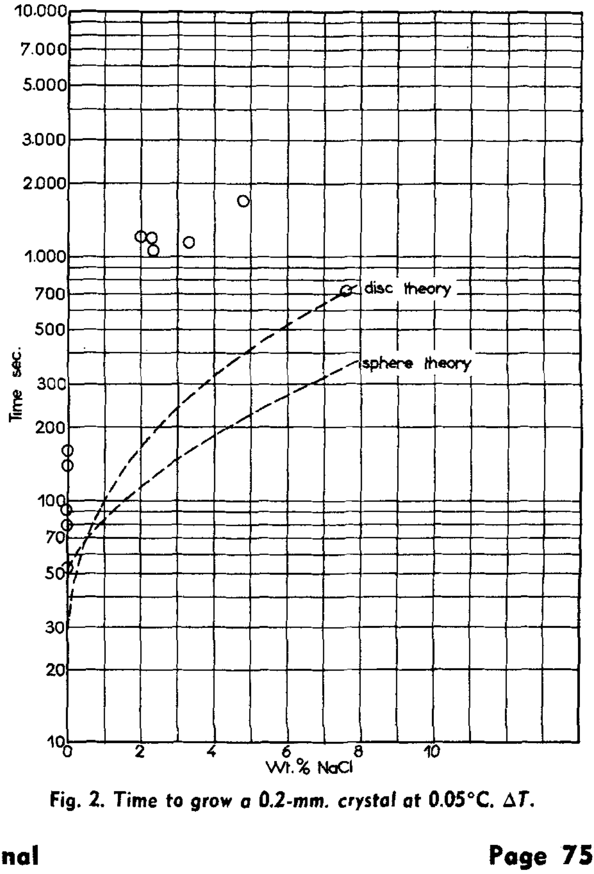

Fig. 2. Time to grow a 0.2-mm. crystal at 0.05°C. ΔT.

to 0°C. to end the run at 100 sec. Runs at −0.01 to −0.02°C. lasted longer and gave curves parallel to the predicted curves but displaced to the right. In the longest run, 1.8-mm. crystals were formed after 2 hr. at −0.01°C.

The growth curves for salt solution showed a steady increase in particle size with time, although the rates were lower than expected. The effect of salt concentration on ice growth is compared with theory in Figure 2. The times to grow 0.2-mm. crystals were obtained by interpolation or slight extrapolation of growth curves similar to those shown in Figure 1. The times were corrected to a common driving force by the factor $\Delta T/0.05°C$. (This factor varied from 0.2 to 1.0 for water and from 0.6 to 1.4 for salt solutions.) The time to grow a 0.2-mm. crystal in 2% salt solution is about ten times that in water. The predicted ratio is 7 for disks and 2.2 for spheres. The point at 7.6% salt is probably in error, since a maximum in the curve is unlikely. The large range of times for growth in water may be partly caused by too small a correction factor for the driving force.

The effect of driving force on growth rate is shown in Figure 3. The experimental points were obtained from the slopes of the growth curves or by drawing a line parallel to the theoretical curve when there was only one data point. The data for water indicate a slope of 1.4, although a slope of 1.0 would fit within experimental error. A slope greater than 1 would be expected if the data of Farrar and Hamilton are the inherent growth rates for the *a* axis. Extrapolation of the lowest dashed line gives rates comparable to those predicted for heat transfer at 0.01°C.

The growth rate in 2% salt solution seems proportional to the nominal subcooling, but there are not enough data for proof. Based on the theory for disks, the actual subcooling is about 1/5 ΔT^* or 0.006 to 0.014°C., and plotting the points against the calculated subcooling would give a fair fit with the data for water. Note that the diffusion effect becomes less important as the particle size increases, and a fivefold reduction in rate for 0.2-mm. particles is consistent with a tenfold increase in time to grow a 0.2-mm. particle.

The general magnitude of the growth rates shows that conduction of heat from the particles is a significant but perhaps not the only important factor. The lower than expected growth rates could mean an appreciable crystallization resistance, particularly at the very low driving forces. However the heat transfer rates could be lower than predicted because of incomplete dispersion of the ice crystals or temperature gradients in the tank. Butane drops evaporate more rapidly near the top of the tank, and slurry circulating near the bottom will become warmer because of ice growth. If there is no mixing with colder solutions, a 20% ice slurry will loose two-thirds of its subcooling in 1 sec. at the rate of growth measured for 0.2-mm. particles in 2% salt solution.

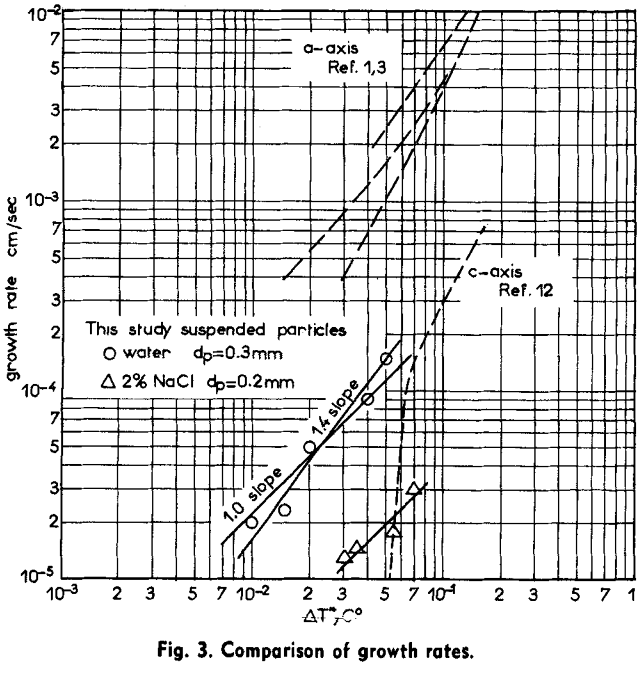

Fig. 3. Comparison of growth rates.

Nucleation rates were not measured, but nucleation was less of a problem than had been expected. According to Farrar and others (*2, 11*), nucleation in water requires a subcooling of about −2°C. with the value decreasing somewhat with vigorous agitation and increasing with salt concentration. In these tests, nucleation occurred at solution temperatures 0.1° to 0.3°C. below the freezing point, and nuclei probably formed in the cold boundary layer around evaporating butane drops. The small volume of boundary-layer fluid limited the number of nuclei formed and permitted growth studies at reasonable driving forces. Secondary nucleation did not occur to an appreciable extent in most of the runs, as judged by the narrow distribution of particle sizes and the steady increase in average size. This is in contrast to the results reported for driving forces of 0.1° to 0.3°C. (*11*), where many tiny crystals were formed and the average size went through a maximum with time. The critical subcooling above which dendritic growth is likely seems to be about 0.1°C. in salt solutions and somewhat lower in water. The stability of dendritic growth has been considered (9), but the solutions do not apply for growth from a concentrated solution (high water concentration).

The practical implications of this study are that large (1 mm.) crystals can be grown with about 2 hr. holdup time at 0.05°C. subcooling. The time could be greatly decreased with little thermodynamic penalty by using higher driving forces, if means of reducing secondary nucleation or intermittently melting the nuclei could be developed.

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NOTATION

c = salt concentration, g./cc.
d_p = diameter of disk or sphere
h = heat transfer coefficient
k_c = mass transfer coefficient
M = mass of crystal
N_{Nu} = $\frac{hd_p}{k}$, Nusselt number
N_{Pr} = $\frac{c_p \mu}{k}$, Prandtl number
N_{Re} = $\frac{d_p v \rho}{\mu}$, Reynolds number
N_{Sc} = $\frac{\mu}{\rho D}$, Schmidt number
N_{Sh} = $\frac{k_c d_p}{D}$, Sherwood number
T = temperature
t = time
ΔT = overall driving force $T_{f,i} - T_b$
ΔT^* = nominal driving force, $T_{f,b} - T_b$
ΔT^* = $(T_{f,b} - T_{f,i}) + (T_{f,i} - T_i) + (T_i - T_b)$

α = thickness/diameter for disk
ρ = fluid density
ρ_s = solid density
λ = heat of fusion
ϕ = diffusion factor in Equation (6)

Subscripts

i = interface
b = bulk
f, b = freezing point of bulk solution
f, i = freezing point of solution at interface

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On a Conjecture of Aris: Proof and Remarks

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In this paper a conjecture of Aris is proved to be correct, that of all catalyst particles of fixed volume for isothermal first-order chemical reactions the spherical particle has the lowest effectiveness factor. The method of proof uses a process of symmetrization. Some conjectures are also made about other chemical reactions. The method of proof is also valid for two-dimensional domain (infinite cylinder).

The purpose of this paper is to explore the effect of particle shape on effectiveness factors and to point out some features of the problem which to the authors' knowledge have not been dealt with, and in particular to investigate certain extremal properties related to catalyst shape. In retrospect it seems that the results are obvious, but they did come as a surprise first. To review the situation briefly, effectiveness factor plots which appear in textbooks (*1*, *3*) usually are concerned with spheres, infinite cylinders, and infinite slabs. If for a first-order isothermal reaction the effectiveness factor η is plotted against ϕ_T, the Thiele parameter, where

$$\phi_T = R\sqrt{\frac{k}{D}}$$

and where R is the radius of the sphere or the cylinder or the half thickness of a slab, then for the same value of ϕ_T the effectiveness factor for the sphere is greater than that for the cylinder and that for the latter is greater than that for the slab. It has also been shown by Aris (*2*) that the curves may be brought together asymptotically by defining a modified Thiele parameter

$$\phi_A = \frac{V_p}{S}\sqrt{\frac{k}{D}}$$

and, furthermore, that η as a function of ϕ_A may be represented for the three shapes mentioned above with rea-