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NUCLEATION CATALYSIS

BY

DAVID TURNBULL AND BERNARD VONNEGUT

SCHENECTADY, NEW YORK

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DAVID TURNBULL AND BERNARD VONNEGUT

GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.

It is known that the structures of crystals and the substances that catalyze their formation closely resemble each other in atomic arrangement and lattice spacing on certain low index planes. A crystallographic theory of crystal nucleation catalysis predicts that the order of catalytic potency should be identical with the order of the reciprocal of the disregistry ($1/\delta$) between the catalyst and forming crystal on low index planes of similar atomic arrangement; that for small δ nuclei should form coherently with the catalyst—i.e., with a strain $\epsilon = \delta$; and that for δ very large $\delta \gg \epsilon$ and the interface between nucleus and catalyst can be thought of as consisting of regions of good fit separated by a dislocation gridwork. The energy of this interface should be proportional to the dislocation density, hence to $\delta - \epsilon$. There is evidence that ice nuclei may form coherently on silver iodide surfaces ($\delta = 0.0145$). Experience indicates that in general nuclei form coherently with catalysts only for $\delta \lesssim 0.005$ to 0.015 .

ACCORDING to Volmer (28), it has been known for over a hundred years that certain solid bodies (called heterogeneities, motes, inclusions, etc.) extraneous to the system promote phase transformations, particularly condensation and crystallization. Generally, this fact has been explained on the basis that some heterogeneities catalyze the formation of nuclei of the new phase.

Volmer (29) has given a formal treatment of the energetics of forming liquid nuclei on solid bodies from supersaturated vapor. The free energy difference, ΔF^* , between a liquid nucleus of critical size and the supersaturated vapor is:

$$\Delta F^* = 16\pi\sigma^3/3(\Delta F_V)^2 \quad (1)$$

where σ is the interfacial energy per area between liquid and vapor and ΔF_V is the free energy difference per volume between vapor and liquid phases of infinite extent. θ , the contact angle between the liquid and the surface of the solid catalytic body is given by the equation:

$$\theta = \arccos [(\sigma_{CV} - \sigma_{CL})/\sigma] \quad (2)$$

where σ_{CV} is the interfacial energy per area between the catalyst and vapor and σ_{CL} is the interfacial energy per area between the catalyst and liquid.

The free energy of formation ΔF_C , of a liquid nucleus of critical size on the catalyst surface is:

$$\Delta F_C^* = \Delta F^* f(\theta) \quad (3)$$

where $f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^{2/3}$ (4)

For $\theta < 180^\circ$ $f(\theta) < 1$ and $\Delta F_C^* > \Delta F^*$.

Becker and Döring (1) derived an expression for the frequency of formation per volume, I , of liquid nuclei in pure supersaturated vapors having the form:

$$I = A \exp.[-\Delta F^*/kT] \quad (5)$$

The frequency of formation per area, I_C , of liquid nuclei on the surface of the catalyst is given approximately by:

$$I_C = A(10^{-8}) \exp.[-\Delta F^* f(\theta)/kT] \quad (6)$$

Actually the exponential factor dominates Equations 5 and 6 so completely that $I_C \gg I$ for all $\theta \gtrsim 90^\circ$.

The reverse process of forming bubbles in superheated liquids also is generally catalyzed by heterogeneities. Fisher (6) has published a formal treatment of this problem.

Recently considerable information has accumulated on the catalysis of crystal nucleation by heterogeneities in supercooled liquids and in supersaturated solutions. These facts have come mainly from experiments on formation of snow crystals, solidi-

fication of pure metals, crystallization of salt hydrates, and oriented overgrowth. The purpose of the present paper is to correlate the facts pertaining to the catalysis of crystal nucleation and to develop a theory that accounts for them.

FORMAL THEORY

Turnbull has developed a theory for the kinetics of crystal nucleation on the surface of heterogeneities (9, 21-24) that is analogous to Volmer's theory for the heterogeneous nucleation of liquid nuclei. The starting point of the theory is an equation derived by Turnbull and Fisher (25) for the nucleation frequency per volume of crystals in a supercooled liquid. The equation is identical in form with equation 5, but the kinetic coefficient, A' , has a different value. For σ we must substitute σ_{LS} , the interfacial energy per area between the crystal and supercooled liquid, while ΔF_V becomes the free energy difference per volume between crystal and liquid phases of infinite extent. The numerical value of $\log A'$ is compatible with values calculated from experiments on the rate of solidification of mercury (23).

It is assumed (1) that the structure of the crystal nucleus formed on the surface of the heterogeneity derives from that of the most stable macroscopic crystal phase by distortions due to the operating interfacial tensions, and (2) that solid interfacial tensions come to equilibrium in supercooled liquids with a contact angle described by an equation analogous to equation 2:

$$\theta = \arccos [(\sigma_{CL} - \sigma_{CS})/\sigma_{LS}] \quad (7)$$

where C denotes catalyst, L liquid, and S the forming crystal. Equation 7 also implies that σ_{LS} is independent of crystal orientation. The validity of assumption (2) is supported mainly by evidence of the kind presented by Smith (18).

With these assumptions the following expression is derived for the frequency of heterogeneous formation of crystal nuclei.

$$I_C \sim 10^{-8} A' \exp.[-\Delta F^* f(\theta)/kT] \quad (8)$$

Equation 8 makes the important prediction that the kinetics of heterogeneous nucleation of crystals can be described as a function of temperature in terms of the parameters that describe homogeneous nucleation and a single additional parameter, θ . This prediction is fulfilled by recent results (23) on the frequency of crystal nucleation in supercooled mercury droplets coated with mercury acetate. The nucleation frequency per droplet is proportional to droplet area and the measured kinetic coefficient, $10^{-8} A'_{\text{exp.}}$, is in excellent agreement with the value $10^{-8} A'$ predicted by Equation 8. Kinetic coefficients calculated from isothermal experiments on mercury stearate-coated droplets (23) and on oxide-coated tin droplets (14, 31) are in fair agreement with

the values calculated from the theory. In these experiments a given isotherm could not be described by a single value of I_0 , so the results are not so conclusive as those on acetate-coated mercury droplets. This agreement between theory and experiment indicates that assumption (1) is approximately valid in some heterogeneous nucleation processes.

The formal theory implies little about the molecular mechanism of nucleation catalysis. In order to obtain a better understanding of this mechanism, we shall examine how the catalytic potency of a heterogeneity is affected by its structural relationship with the forming crystal.

STRUCTURAL RELATIONS IN NUCLEATION CATALYSIS

Ice Formation. In most heterogeneous nucleation processes, the temperature dependence of the nucleation rate is so great that there seems to be a narrow temperature range in which the nucleation catalyst becomes active. The crystal nucleation rate becomes perceptible at the threshold temperature, T_i , of catalytic activity. Often T_i is shifted 1° or less by changing the cooling rate (from the equilibrium temperature into the supercooled range) a factor of 10.

Vonnegut (30) and Schaefer (16) have measured T_i for the formation of ice crystals in a supercooled fog containing suspended particles of various substances. Some of the results are summarized in Table I. a_0 and c_0 are the dimensions of a hexagonal unit cell. Δa and $\Delta(c_0/a_0)$ are the amounts that the dimensions of the catalyst unit cell exceed the ice unit cell. T_m is the melting temperature of the forming crystal, and $\Delta T_i = T_m - T_i$ is the supercooling at which the catalyst becomes active. δ is the discrepancy on a low index plane; for the (001) plane of ice $\delta = |\Delta a/a_0|$. The most potent catalyst known for the formation of ice crystals is silver iodide. Vonnegut (30) has proposed that the effectiveness of silver iodide derives from the remarkably close fit between its lattice structure and that of ice.

Table I. Supercooling ($T_m - T_i = \Delta T_i$) Corresponding to Maximum Temperature at Which Various Substances Catalyze Formation of Ice Nuclei

Substance	$\Delta T^\circ \text{C.}$	$\delta = \Delta a/a_0 $	$\Delta(c_0/a_0)/(c_0/a_0)$
Silver iodide (30)	2.5 ± 0.1	0.0145	+0.0043
Lake Albany clay (16)	11 ± 1		
Volcanic ash (Crater Lake) (16)	16 ± 1		
Cryolite (16)	20 ± 1		
Topaz (16)	23 ± 1		

Schaefer (16) measured the catalytic activity of several naturally occurring inorganic substances, and part of his data are given in Table I. Most of these substances are chemically complex and it is not certain what structure caused the formation of ice in a given instance.

Crystallization of Mercury. ΔT_i has been measured for various surface films on small mercury droplets (23). The results for droplets about 10 microns in diameter are given in Table II. A cooling rate $\sim 1^\circ$ per minute was used in these measurements.

Table II. ΔT_i for Nucleation of Mercury Crystals Coated by Various Films (23)

Film	ΔT_i	
HgX	3.7 ± 0.5	
Mercury sulfide (black), HgS	12 ± 1	0.19
Mercury acetate, HgAc	45 ± 1	
Mercury iodide, Hg ₂ I ₂	48 ± 1	
Mercury stearate, Hg(St)	58 ± 1	
Mercury laurate, Hg(Lau)	77 ± 1	

Table II gives the major component of the film; it is possible that catalysis was effected, in some instances, by minor components of unknown character. Therefore, ΔT_i for the major component must be equal to or greater than the value given in

the table. Kinetic evidence indicates that mercury nuclei form in the body of mercury laurate-coated droplets without the aid of the film (homogeneous nucleation).

These results demonstrate again that the potency of different nucleation catalysts varies widely. We may think of the existence of a spectrum of catalysts with bands corresponding to different catalytic structures ranging all the way from the equilibrium temperature to the temperature of homogeneous nucleation.

Data adequate for comparing the structure of the major film component with that of solid mercury exist only for mercurous iodide and mercuric sulfide. The arrangements of mercury atoms in solid mercury and mercurous iodide on low index planes are not similar. Mercury-mercury separations in the two crystals differ by 10 to 30%. The arrangements of mercury atoms on a (111) plane in solid mercury and on the closest packed plane in mercuric sulfide are similar with atomic separations differing by 19%. Therefore, it seems that the structure of solid mercury resembles more closely that of mercuric sulfide than of mercurous iodide, and the experiments are compatible with the concept that the order of catalytic potency is the same as the order of structural similarity.

HgX, the most effective catalyst for the nucleation of mercury crystals, formed from the mercury laurate or mercury stearate films. The chemical evidence suggests that HgX may be a mercury oxide resulting from hydrolysis of the carboxylates. Mercuric oxide has no low index plane, populated by mercury atoms, structurally similar to the low index planes of pure mercury; the mercury-mercury separations in the two crystals differ by 5 to 10%. It is possible that HgX is mercurous oxide, but the authors found no information on the structure of mercurous oxide.

Crystallization of Aluminum. It has long been known that certain addition elements, such as titanium and zirconium, markedly refine the as-cast grain size of aluminum. For example, 0.1% titanium additions to a pure aluminum melt result in a fine-grained equiaxed grain structure as compared with the very coarse columnar structure that often forms in castings to which no additions have been made (5). It is important in practice to promote the formation of metals of fine-grained structure, as their mechanical properties are often markedly superior to those of metals having a coarse grain structure.

The mechanism of grain size refinement by additions to the melt has long been disputed. However, recent results of Eborall (5) and Cibula (3, 4) on the casting of aluminum and its alloys strongly support the idea that grain refinement is largely effected by nucleation catalysts. Aluminum melts with or without elements that did not cause grain-size refinement supercooled about 1° before solidifying, but when grain-size refining elements were present solidification began without perceptible supercooling. Cibula found the average grain diameter of aluminum with titanium additions, when centrifuged immediately before solidification, is about ten times larger than in a casting that had not been subjected to a centrifugal field when in the molten state. Therefore, he concluded that the grain-size refinement is largely effected by insoluble impurities and that the mechanism is nucleation catalysis.

From indirect evidence (3) it was inferred that the nucleation catalysts were carbides of the effective addition elements, with the exception that the potent grain-size refinement effect of titanium and boron in combination is ascribed to titanium boride (4). Titanium carbide was identified in a casting to which titanium was added and the arrangement of metal atoms in the closest packed planes of the carbides of the effective addition elements (and of titanium boride) is similar to that in the closest packed plane of aluminum (111). Table III compares the nucleating effect of various metal additions (ascribed to carbides and borides) in the crystallization of aluminum. The carbides of elements not effective in refining grain size contain no low index

Table III. Nucleation Catalysis by Metal Carbides and Borides in Casting of Aluminum Face-Centered Cubic Structure
(After Cibula, 3)

Metal Compound	Formula of Compound	Crystal Structure	δ For Close Packed Planes	Nucleating Effect
Vanadium carbide	VC	Cubic	0.014	Strong
Titanium carbide	TiC	Cubic	0.060	Strong
Titanium boride	TiB ₂	Hexagonal	0.048	Strong
Aluminum boride	AlB ₂	Hexagonal	0.038	Strong
Zirconium carbide	ZrC	Cubic	0.145	Strong
Niobium carbide	NbC	Cubic	0.086	Strong
Tungsten carbide	WC	Hexagonal	0.035	Strong
Chromium carbide	Cr ₃ C ₂ , Cr ₇ C ₃	Complex	...	Weak or nil
Manganese carbide	Mn ₃ C, Mn ₇ C ₃	Complex	...	Weak or nil
Iron carbide	Fe ₃ C	Complex	...	Weak or nil

plane having an atomic arrangement similar to the atomic arrangement in a low index aluminum plane. For the effective catalysts $\delta \gtrsim 0.15$ for close packed planes.

Crystallization of Other Metals. Reynolds and Tottle (15) have obtained some interesting qualitative results on nucleation catalysis in the crystallization of zinc, aluminum, magnesium, lead, and copper. They coated the walls of the mold into which the metals were cast with a dispersion of small particles of various metals. The extent of grain-size refinement in the part of the casting in contact with the mold wall was assumed to be a measure of the catalytic potency of the metal particles that formed the coating. Significant grain-size refinement was observed when the disregistry between similar low index planes of the catalyst and forming metal was less than 10%.

Oriented Overgrowth. Often crystals form on the surface of a foreign crystal with a definite orientation relation. This phenomenon is called oriented overgrowth or epitaxy. Generally, the orientation relation is: The planes and directions in the two crystals in which the atomic arrangement is most similar are parallel. It is generally believed that oriented overgrowth is caused by oriented nucleation on the catalyst surface (10). Therefore, we shall see how experience on oriented overgrowth relates to other nucleation catalysis phenomena.

Recently Thomson (20), Van der Merwe (26), and Johnson (10) have reviewed the results on oriented overgrowth. It had been generally believed that the necessary condition for oriented overgrowth is $\delta \lesssim 0.10$ to 0.20. However, Johnson (10) and Schulz (17) have found instances of oriented overgrowth for δ as large as 0.50. This is in agreement with the fact that certain substances, such as mercurous iodide, apparently weakly catalyze the nucleation of mercury crystals, though their structures are very different from that of mercury.

To test quantitative theories for oriented overgrowth, it is necessary to know how δ varies with the critical supersaturation ratio, C/C_0 , necessary for the growth. Unfortunately, we now have very little knowledge of this variation. It seems possible that the maximum disregistry $\delta \sim 0.10$ to 0.20 supposedly compatible with oriented overgrowth may correspond to C/C_0 values at which accidental heterogeneities on the catalyst surface or elsewhere become active nucleation catalysts.

Crystallization of Salt Hydrates. Telkes (19) found that Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) may not crystallize from an aqueous solution until the solution is undercooled on the order of 17° C. below the equilibrium temperature of 32.34°. She established that the addition of 2 to 3% borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) reduces the undercooling necessary for recrystallization to 1° or 2°. Telkes points out that the effectiveness of borax in nucleating Glauber's salt is plausible from a crystallographic point of view, because the two crystal structures belong to the same space group (C_{2h}^6) and $\delta = 0.015$ for the basal planes.

MECHANISM OF NUCLEATION CATALYSIS

To summarize the experimental findings: There is good qualitative evidence that potent nucleation catalysts have low index

planes in which the atomic arrangement is similar to that in certain low index planes of the forming crystal; there are tenuous indications that the order of potency of catalysts corresponds to the order of the reciprocal of the disregistries ($1/\delta$) on these low index planes.

In view of these findings it is desirable to formulate a crystallographic theory of nucleation catalysis. A theory may be derived based in part on concepts advanced by Frank and Van der Merwe (7) in their treatment of the energetics of formation of oriented monolayers on crystalline substrates.

It may be assumed that the lattice structure in the surface of the catalyst is identical with that of similar elements in its body and that surface elements are not strained by the formation of nuclei upon them. If a nucleus is strained by the amount δ in two dimensions, so that it precisely fits a surface element of the catalyst, it is said to be coherent with that element. The lattice parameter of the nucleus in a direction normal to the surface element will assume the value necessary to minimize the free energy of the system. (A nucleus formed in a notch or at a step in the catalytic surface might be coherent in three dimensions. However, for θ very small it turns out that the free energy of nuclei is less for two- than for three-dimensional coherency.) The basic postulate of the theory is that the interfacial energy between the nucleus and catalytic surface element is a minimum when the nucleus forms coherently.

In general, the condition of minimum free energy will be that the nucleus is not coherent but strained an amount $\epsilon < \delta$, where

$$\epsilon = |(x - a_0)/a_0| \quad (9)$$

and a_0 and x are the lattice parameters of the nucleus in the strain-free and strained condition, respectively. Therefore, the actual disregistry between a nucleus and the catalytic element is $\delta - \epsilon$. When $\delta > \epsilon \gtrsim 0$ the nucleus is said to be incoherent with the catalytic element.

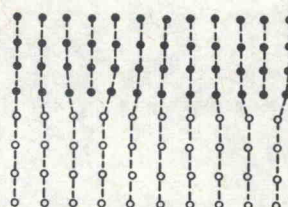


Figure 1. Cross Section $\perp$ to (100) Plane of Two Misfitting Simple Cubical Lattices

Showing that interface between them can be described by small regions of relatively good fit bounded by dislocation network

When the disregistry < 0.20 , the boundary region between the nucleus and catalyst surface can be pictured as made up of local regions of good fit bounded by line dislocations, as indicated schematically in Figure 1. [The concept that interphase boundaries may be described in terms of a dislocation model has been developed by Van der Merwe (27) and Brooks (2).] The dislocation density per area, ρ , will be proportional to $\delta - \epsilon$. Frank and Van der Merwe (7) have shown that

the energy due to dislocations in a misfitting monolayer is proportional to ρ . We shall assume that the interfacial energy between the nucleus and catalyst due to the dislocation gridwork is proportional to ρ . Therefore, we may express σ_{SC} as the sum of two terms:

$$\sigma_{SC} = \gamma + \alpha(\delta - \epsilon) \quad (10)$$

where γ is an interaction term due to bond type, chemistry, etc., and $\alpha(\delta - \epsilon) \propto \rho$ is a structural term.

It follows from Equation 10 that:

$$m = \cos \theta = [\sigma_{CL} - \gamma - \alpha(\delta - \epsilon)]/\sigma_{LS} \quad (11)$$

and

$$1 - m = \beta + \alpha(\delta - \epsilon)/\sigma_{LS} \quad (12)$$

where

$$\beta = 1 - (\sigma_{CL} - \gamma)/\sigma_{LS} \quad (13)$$

Now suppose that a nucleus having the shape of a sector of a sphere of radius, r , forms on a catalyst surface (see Figure 2, 22);

then the free energy increase due to formation of the nucleus is (δ):

$$\Delta F = V(\Delta F_V + c\epsilon^2) + 2\pi r^2(1-m)\sigma_{LS} + \pi r^2(1-m^2)(\sigma_{SC} - \sigma_{LC}) \quad (14)$$

where V = the volume of the sector; $c\epsilon^2$ = the strain energy per volume of the nucleus; c will be expressed in terms of the appropriate elastic coefficients as the need arises.

$2\pi r^2(1-m)$ = area of the nucleus in contact with extended phase
 $\pi r^2(1-m^2)$ = area of nucleus in contact with the catalyst

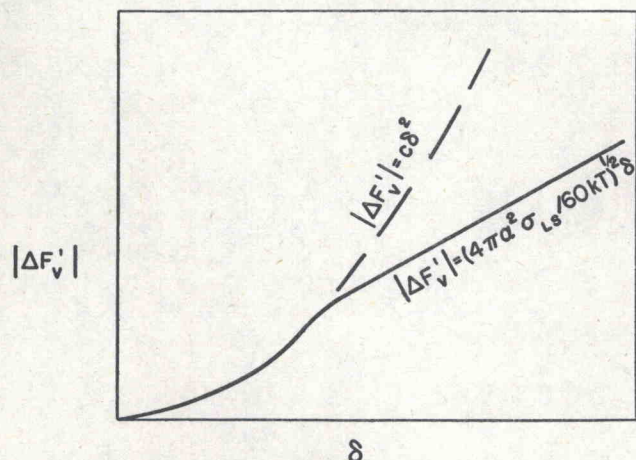


Figure 2. $|\Delta F_V'|$ as a Function of Disregistry, δ

Parabolic part of curve indicates coherent nucleation. Straight line portion indicates incoherent nucleation with $\delta > \epsilon$.

Our considerations will apply whether the extended phase (denoted by symbol L) is a supercooled pure liquid or supersaturated solution of liquid or gas. When $\Delta F_V + c\epsilon^2 < 0$, ΔF goes through a maximum having coordinates ΔF_C^* and r^* . In order to survive as a nucleus for further growth, a strained embryo on a catalyst surface must attain the size r^* . The critical free energy, ΔF_C^* , is given by:

$$\Delta F_C^* = 4\pi\sigma_{LS}^3(2+m)(1-m)^2/3(\Delta F_V + c\epsilon^2)^2 \quad (15)$$

We wish to know the relation between ΔF_V and δ that holds when the nucleation rate is perceptible. Taking a perceptible rate to be $1 \text{ cm.}^{-2} \text{ sec.}^{-1}$ it follows from Equation 8 that corresponding to this rate $\Delta F_C^* \sim 60kT$. For $c\delta^2 > |\Delta F_V'|$ and making the approximation $2 + m \sim 3$ a linear relation between $|\Delta F_V'|$ and δ obtains:

$$|\Delta F_V'| = (4\pi\sigma_{LS}/60kT)^{1/2}(\beta\sigma_{LS} + \alpha\delta) \quad (16)$$

where $|\Delta F_V'|$ is the value of $|\Delta F_V|$ corresponding to $I_C = 1 \text{ cm.}^{-2} \text{ sec.}^{-1}$.

The potency, P , of a nucleation catalyst for a given transformation is:

$$\propto 1/(\beta\sigma_{LS} + \alpha\delta)$$

In general, P depends upon the disregistry, δ , and an interaction term, β , that may not be related to δ . From this relation, it is predicted that the order of catalytic potency will not always be identical with the order of $1/\delta$.

The condition that P be a function of $1/\delta$ only is that $\beta = 0$. From Equation 13, $\beta = 0$ when

$$\sigma_{CL} - \gamma = \sigma_{LS} \quad (17)$$

Actually Equation 17 may be approximately valid for many nucleation processes and it is interesting to find what the theory predicts when the equation holds. (Equation 17 follows approximately for the nucleation of crystals in supercooled liquids if the interaction energy due to bond type, chemistry, etc., between the catalyst and the crystal is the same as between the catalyst and liquid. Such a relation is plausible.) For $\beta = 0$, Equation 16 becomes:

$$|\Delta F_V'| = (4\pi\sigma_{LS}/60kT)^{1/2}\alpha\delta \quad (18)$$

When $|\Delta F_V'|$ given by Equation 18 becomes larger than $c\delta^2$, the nucleus forms coherently and we shall have instead of Equation 18 a parabolic relation between $|\Delta F_V'|$ and δ :

$$|\Delta F_V'| = c\delta^2 \quad (19)$$

The approximate condition for coherent nucleation is:

$$\delta \gtrsim (4\pi\sigma_{LS}/60kT)^{1/2}(\alpha/c) \quad (20)$$

Figure 2 shows schematically the variation of $|\Delta F_V'|$ with δ predicted by our theory.

In the solidification of pure liquids $|\Delta F_V'|$ can be closely approximated by:

$$|\Delta F_V'| = |\Delta S_V| \Delta T \quad (21)$$

where ΔS_V is the entropy of fusion per volume. Since ΔS_V is assumed independent of temperature, ΔT will vary with δ in the same way as $|\Delta F_V'|$.

In precipitation of crystals from a supersaturated solution:

$$|\Delta F_V'| = (RT/V) \ln(a/a_s) \quad (22)$$

where V is the molar volume of the precipitate, a_s is the activity of the solute in equilibrium with the precipitate, and a is the solute activity in the supersaturated solution. Therefore, $\ln(a/a_s)$ varies with δ in the same way as $|\Delta F_V'|$.

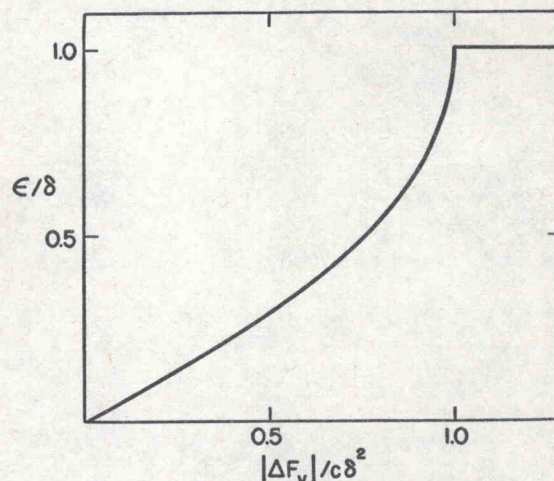


Figure 3. ϵ/δ as Function of $|\Delta F_V|/c\delta^2$

Nucleation is coherent for $|\Delta F_V|/c\delta^2 > 1$ and incoherent for $|\Delta F_V|/c\delta^2 < 1$.

Assuming $\beta = 0$, we now find for a given δ what value of ϵ corresponds to highest probability, p , of nucleus formation. Since $p \propto \exp.[-(\Delta F_C^*)/kT]$ we require the value of ϵ that corresponds to a minimum ΔF_C^* . Setting $d(\Delta F_C^*)/d\epsilon = 0$ (see Equation 15) and making the approximations $1 + m \approx 2$, $(2 + m) \approx 3$, we find:

$$\epsilon/\delta = 1 - (1 - |\Delta F_V|/c\delta^2)^{1/2} \quad (23)$$

For $\beta \neq 0$, $\epsilon = (\delta + \beta\sigma_{LS}/\alpha) - [(\delta + \beta\sigma_{LS}/\alpha)^2 - |\Delta F_V|/c]^{1/2}$. Figure 3 shows ϵ/δ as a function of $|\Delta F_V|/c\delta^2$.

For $|\Delta F_V| > c\delta^2$ the root of Equation 15 is imaginary, which means that $\Delta F_C^* = 0$ and the nucleus will always form coherently with $\epsilon = \delta$ as indicated in the figure. When $c\delta^2 > |\Delta F_V|$, $\delta > \epsilon$.

Elimination of ϵ from Equation 15 gives:

$$\Delta F_C^* = \pi\alpha^2\sigma_{LS}\delta^2(1 - |\Delta F_V|/c\delta^2)/[\Delta F_V + c\delta^2\{1 - (1 - |\Delta F_V|/c\delta^2)^{1/2}\}]^2 \quad (24)$$

In summary, our simple crystallographic theory of nucleation catalysis for $\beta = 0$ makes the predictions:

1. When catalysts and the forming crystals have similar low index planes, the order of the catalysts in $|\Delta F_V'|$ will be

identical with their order in δ —i.e., if $\delta_1 > \delta_2 > \delta_3$, then $|\Delta F'_1| > |\Delta F'_2| > |\Delta F'_3|$.

2. For values of δ sufficiently small so that Equation 20 is approximately fulfilled, nuclei will form coherently with the catalyst and $|\Delta F'_v| = c\delta^2$. [A related problem, the thermodynamics of formation of coherent precipitates from a solid solution, has been treated by Leschen and Fisher (12).]

3. For δ very large nuclei will form incoherently with negligible strain and $|\Delta F'_v|$ will be a linear function of δ .

COMPARISON OF THEORY AND EXPERIENCE

There are a few data on nucleation catalysis sufficiently quantitative to test some of the predictions of the simple theory.

Values of A'_{exp} (Equation 8) calculated from the kinetic data on the solidification of mercury (23) and tin (14, 31) droplets coated with various films are generally in good agreement with A'_{th} values calculated from nucleation theory on the assumption that the strain, ϵ , is zero. [However, kinetic results on mercury droplets coated with mercurous iodide could not be interpreted on the basis that the mercury nucleus had the normal structure (23).] If ϵ were not zero, the "melting point" of the nucleus would be less than T_m and A'_{exp} would be larger than the apparent A'_{th} . Pound and LaMer's value of $10^{-8} A'_{\text{exp}}$ (10^{30}) for oxide-coated tin droplets is at least a factor of 100 larger than $10^{-8} A'_{\text{th}}$ (10^{28}), but the disagreement corresponds to a coherency strain of the order of only 0.01.

Because the structures of the surface films in the mercury and tin experiments are very different from the structures of the metal crystals, the crystallographic theory predicts, in good agreement with experience, that ϵ should be negligible.

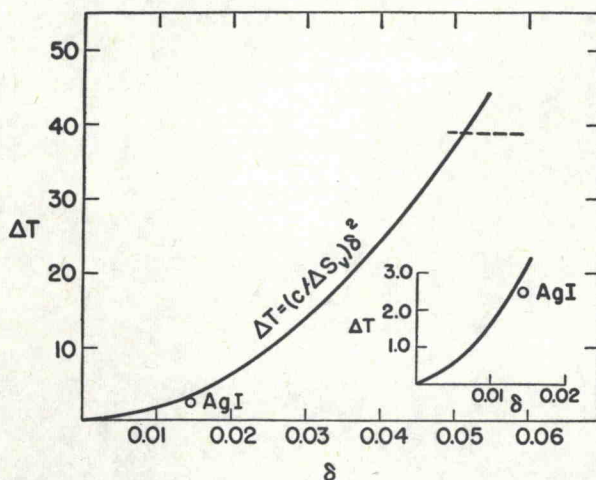


Figure 4. Supercooling Corresponding to Coherent Nucleation of Ice Crystals on Catalyst Planes

As function of disregistry δ with (001) planes of ice

The authors have not attempted to evaluate α and, therefore, have no predictions on the maximum value of δ at which nuclei will form coherently. However, it is interesting to calculate the supercooling, ΔT , or supersaturation ratio, a/a_s , as a function of δ , assuming coherent nucleation for all values of δ . $\Delta T = f(\delta)$ for coherent nucleation of crystals in pure liquids is found by combining Equations 19 and 21. This function was evaluated for the nucleation of aluminum and ice crystals on their closest packed planes (111) and (001), respectively. The appropriate values of c as a function of the elastic coefficients were calculated by methods summarized by Hearmon (8) and Zener (32) and are given in Table IV. Coefficients c' refer to a cartesian xy plane || (111) of the crystal and the c coefficients to xy || (100).

As no reports of measured elastic coefficients of ice have been found, $\Delta T = f(\delta)$ was evaluated from the theoretically calculated values of Penny (13) and plotted in Figure 4. A point corre-

Table IV. Coefficients

Forming Crystal	Temp., ° K.	Plane	In terms of elastic coefficients	Numerical, dyne cm. ⁻²
Ice	273	Hexagonal (001)	$c_{11} + c_{12} - 2c_{13}^2/c_{33}$	1.7×10^{11}
Aluminum	933	(111)	$c'_{11} + c'_{12} - 2c'_{12}/c'_{11}$	7.2×10^{11}
NaCl	300	(100)	$c_{11} + c_{12} - 2c_{12}^2/c_{11}$	5.34×10^{11}

sponding to silver iodide (the only available datum, see Table IV) is shown. In view of the large uncertainty in the elastic constants, the remarkable agreement between the silver iodide point and the calculated relation (2.5° vs. 3.1°) may be fortuitous. However, the result gives some support to the concept that ice nuclei form coherently on a silver iodide surface. The supercooling corresponding to coherent nucleation rises very sharply with disregistry, so that at $\delta \sim 0.055 \Delta T \sim 40^\circ$.

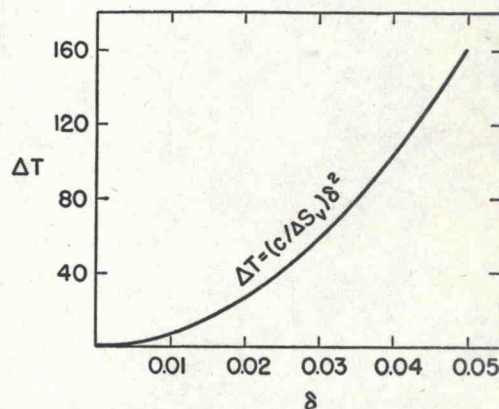


Figure 5. Supercooling Corresponding to Coherent Nucleation of Aluminum Crystals on Catalyst Planes

As function of disregistry, δ with (111) planes of aluminum

The elastic constants for aluminum are those given by Zener, but corrected for temperature variation on the assumption that c varies with T in the same way as the rigidity modulus, M . Ké's (11) measurement of $M = f(T)$ for an aluminum single crystal was used to make the calculation. The resulting relation $\Delta T = f(\delta)$ is shown in Figure 5. Cibula finds that titanium carbide, titanium boride, and aluminum boride for which $\delta \sim 0.04$ to 0.06 catalyze formation of nuclei for $\Delta T < 1^\circ$. The authors' relation indicates that coherent nucleation for a disregistry $\delta = 0.04$ cannot take place until $\Delta T > 100^\circ$. It seems either that aluminum nuclei must form incoherently for all $\delta \gtrsim 0.005$ or that some of the assumptions of the theory are not valid for the catalysts under consideration.

Combination of Equations 18 and 21 gives $a/a_s = f(\delta)$ valid for the formation of coherent nuclei from a supersaturated solution. Figure 6 shows the relation $a/a_s = f(\delta)$, calculated from elastic coefficients tabulated by Hearmon, for coherent nucleation of sodium chloride on (100) planes at room temperature. $a/a_s = 1.06$ at $\delta = 0.01$ and 2 at $\delta \sim 0.035$. It is doubtful that supersaturation ratios as large as 2 are required to initiate oriented overgrowth for $\delta \sim 0.035$. It is unlikely that sodium chloride nuclei form coherently for $\delta \gtrsim 0.015$.

In view of the foregoing calculations and experimental evidence, it seems that nuclei are likely to form coherently only for $\delta \lesssim 0.005$ to 0.015; for $\delta > 0.02$ the strain, ϵ , is probably much smaller than δ .

As α has not been calculated from theory, it is interesting to

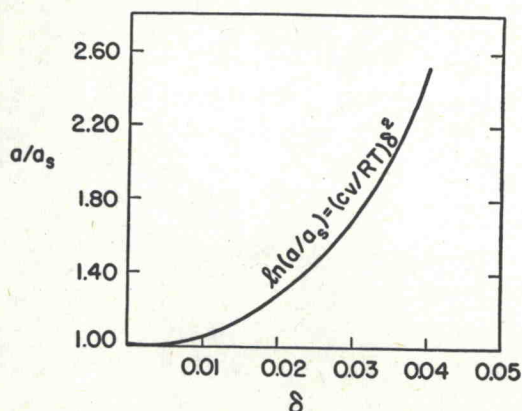


Figure 6. Supersaturation Ratio Corresponding to Coherent Nucleation of Sodium Chloride Crystals on Catalyst Planes

As function of disregistry δ with (100) planes of sodium chloride

estimate α from the data on the crystallization of ice and aluminum. For the formation of ice nuclei the critical disregistry δ_c at which nucleation becomes incoherent (see Equation 20) is estimated to be on the order of the disregistry between ice and silver iodide, $\delta_c \sim 0.015$. Taking the value of $\sigma_{LS} = 32$ ergs per sq. cm. we calculate from Equation (20) $\alpha \approx 180$ ergs per sq. cm. For $\delta - \epsilon = 0.10$ we have a structural interfacial energy $\alpha(\delta - \epsilon) = 18$ ergs per sq. cm. For aluminum $\delta_c \gtrsim 0.005$ and using $\sigma_{LS} = 93$ ergs per sq. cm. we find $\alpha \approx 310$ ergs per sq. cm. For $\delta - \epsilon = 0.10$ $\alpha(\delta - \epsilon) = 31$ ergs per sq. cm. The basis of the σ_{LS} values has been explained elsewhere (21). These values of α seem plausible.

CONCLUSIONS

A formal theory of nucleation catalysis, based on the assumption that the strain ϵ in the nucleus is zero, leads to the prediction that the kinetics of heterogeneous nucleation can be described by a single parameter, the contact angle θ , in addition to the parameters required to describe homogeneous nucleation.

The kinetics of heterogeneous nucleation of mercury and tin crystals in the corresponding supercooled liquids are, in most instances, satisfactorily described on the basis of the formal theory. Results on ice formation, casting of metals, crystallization of salt hydrates, and oriented overgrowth indicate that the most effective nucleation catalysts have structures with a symmetry and lattice spacing similar to that of the forming crystal.

A simple crystallographic theory of nucleation catalysis predicts that the order of potency of various catalysts will be identical with the reciprocal of their disregistry ($1/\delta$) with low index planes of the forming crystal; that at relatively small values of δ nuclei will form coherently (coherency strain $\epsilon = \delta$) with the catalyst and $|\Delta F'_v|$, the free energy of transition corresponding to a perceptible nucleation rate, will be proportional to δ^2 ; and that for δ very large $\epsilon \rightarrow 0$ and the interface between nucleus and catalyst will consist of small regions of good fit separated by a gridwork of dislocations. $|\Delta F'_v|$ will be proportional to δ .

There is evidence that ice nuclei may form coherently on silver iodide surfaces ($\delta = 0.0145$).

Qualitative evidence on the solidification of metals and oriented overgrowth indicates that, in general, the coherency strains are very small relative to δ for $\delta \lesssim 0.02$.

Quantitative data are needed on the kinetics of oriented nucleation of salt crystals as a function of supersaturation, and measurements on the kinetics of heterogeneous nucleation of crystals in supercooled liquids should be extended to test the effects of additional kinds of catalysts.

ACKNOWLEDGMENT

The authors gratefully acknowledge helpful conversations with J. G. Leschen, J. C. Fisher, and R. L. Fullman concerning some of the subjects discussed in the paper.

NOMENCLATURE

a	= activity of solute
a_0	= lattice parameter in low index comparison plane of structure from which nucleus derives
a_s	= activity of solute in saturated solution
Δa	= difference in lattice parameter in low index comparison plane of nucleation catalyst and structure from which the nucleus derives
A	= kinetic coefficient ($1/\text{time} \times \text{volume}$) for nucleation of liquid in supersaturated vapor
A'	= kinetic coefficient ($1/\text{time} \times \text{volume}$) for nucleation of crystals in supercooled liquids
A'_{exp}	= experimental kinetic coefficient
A'_{th}	= kinetic coefficient predicted by nucleation theory
c	= coefficients of elasticity
c_{11}	
c_{12}	
c_{13}	
c_{33}	
c'	
c'_{11}	= length of hexagonal axis in hexagonal unit cell
c'_{12}	
c_0	= concentration of solute
C_0	= concentration of solute in saturated solution
ΔF^*	= free energy required to form a nucleus of critical size
ΔF_c^*	= free energy required to form a nucleus of critical size on the surface of a nucleation catalyst
ΔF_v	= difference in free energy per volume between two phases, of infinite volume
$\Delta F'_v$	= value of ΔF_v corresponding to a perceptible nucleation rate
I	= nucleation frequency per volume
I_c	= nucleation frequency per area of surface of nucleation catalyst
k	= Boltzmann's constant
m	= $\cos \theta$
M	= rigidity modulus
p	= probability of nucleation
P	= potency of nucleation catalyst
r	= radius of sphere, a sector of which constitutes a nucleus on catalyst surface
r^*	= value of r corresponding to nucleus of critical size on the catalyst surface
R	= molar gas constant
ΔS_v	= entropy of phase transition per volume
T	= absolute temperature, $^{\circ}\text{K}$.
T_i	= absolute temperature at which nucleation is perceptible
T_m	= absolute temperature at which liquid and crystalline phases are in equilibrium
ΔT_i	= $T_m - T_i$
V	= phase volume per mole
x	= lattice parameter of strained nucleus
α	= structural free energy per area $\times (\delta - \epsilon)$ of crystal-catalyst interface
β	= $1 - (\sigma_{CL} - \gamma)/\sigma_{LS}$
γ	= nonstructural component of σ_{CS}
δ	= $ \Delta a/a_0 $
δ_c	= maximum value of δ compatible with formation of coherent nuclei on catalyst surface
ϵ	= $ (x - a_0)/a_0 $
ρ	= dislocation density per area of interface between crystal and catalyst
σ	= interfacial free energy per area
σ_{CL}	= value of σ for catalyst-liquid interface
σ_{CS}	= value of σ for catalyst-crystal interface
σ_{CV}	= value of σ for catalyst-vapor interface
σ_{LS}	= value of σ for liquid-crystal interface
θ	= contact angle of forming phase on catalyst surface

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RECEIVED for review December 13, 1951.

ACCEPTED March 31, 1952.

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Research Laboratory
SCHENECTADY, N. Y.