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THEORY OF CATALYSIS OF NUCLEATION BY SURFACE PATCHES

BY

DAVID TURNBULL

SCHENECTADY, NEW YORK

THEORY OF CATALYSIS OF NUCLEATION BY SURFACE PATCHES*

DAVID TURNBULL†

By hypothesizing a plausible distribution of units for crystal nucleation with respect to size, and that the size of the units may be of the order of the critical size for growth of a nucleus into a supercooled liquid, the multiplicity in crystal nucleation frequency sometimes observed for the isothermal solidification of small droplets is accounted for with the use of no more than two fundamental frequencies. The theory satisfactorily explains the athermal nucleation of crystals for the solidification of small mercury droplets that have "HgX" patches on their surface.

THEORIE DE L'ACTION CATALYTIQUE DES CONCENTRATIONS A LA SURFACE SUR LA GERMINATION

La multiplicité dans les fréquences de germination parfois observée lors de la solidification isotherme de petites gouttelettes est expliquée en employant une fréquence fondamentale seulement; ceci en supposant une distribution plausible des unités pour la germination des cristaux en rapport avec les dimensions, et que les dimensions des unités sont de l'ordre des dimensions critiques nécessaires pour la croissance d'un germe dans un liquide surfondu. Cette théorie explique d'une façon satisfaisante la germination athermique des cristaux pour la solidification de petites gouttelettes de mercure, dont la surface est couverte de concentrations de "HgX".

DIE THEORIE DER KEIMBILDUNGSKATALYSE DURCH OBERFLÄCHENFLECKEN

Es wird als Hypothese eine plausible Größenverteilung von Bereichen der Keimbildung vorgeschlagen. Es wird weiterhin angenommen, dass die Dimensionen dieser Bereiche von der gleichen Größenordnung wie die kritische Grösse für das Wachstum eines Keimes in eine unterkühlte Flüssigkeit sind. Dann lässt sich die Multiplizität der Keimbildungsfrequenz, die manchmal bei der isothermen Erstarrung kleiner Tröpfchen beobachtet wird, unter Benutzung von nur zwei elementaren Frequenzen erklären. Die Theorie erklärt zufriedenstellend die nicht-thermische Kristallkeimbildung bei der Erstarrung kleiner Quecksilbertröpfchen, die "HgX" Flecken auf ihrer Oberfläche haben.

Introduction

Recently the kinetics of solidification of small droplets of mercury [1] and tin [2] coated with various surface films were investigated. Isothermal data for certain mercury droplet dispersions coated with a given film were well described by a single nucleation frequency (I)/area or volume. However, the isothermal data on oxide-coated tin droplets and on mercury droplets having "HgX" patches (HgX, a strong catalyst for the formation of mercury crystal nuclei, is a decomposition product of certain mercury carboxylates) seemed to require a multiplicity of I values for their description. Although various explanations for this multiplicity, all presupposing heterogeneous nucleation, were considered [1; 2], none were fully developed.

In an earlier note [3] a new theory for the multiplicity in I was proposed. In this paper we shall give a more complete development of the theory and compare its predictions with experience.

Theory

The potency, P , of the surface of a substance in catalyzing the formation of crystal nuclei has been characterized by the contact angle θ made by the nucleus on the flat catalyst surface in contact with supercooled liquid. The less is θ , the greater is P , and we may set $P \propto 1/\theta$. The angle θ is determined

by the structure and chemistry of the catalyzing surface. Suppose that the crystal embryos have the form of spherical caps on the relatively flat catalyst surface. In order to survive as a crystal nucleus on the surface, these embryos must have attained a critical radius, r_s^* , given by [4]:

$$(1) \quad r_s^* = -2\sigma \sin \theta / \Delta F_v$$

where ΔF_v = free energy per volume for the liquid $\rightarrow$ crystal transition when both phases have an infinite volume-to-surface ratio, and σ is the interfacial energy between liquid and crystal phases. The radius, r^* , of the crystallization nucleus that forms in the body of the supercooled liquid without the aid of any catalytic surface is equal to or larger than r_s^* , and given by:

$$(2) \quad r^* = -2\sigma / \Delta F_v$$

When the linear dimension R of the catalyzing surface exceeds r^* any nucleus on this surface with a radius exceeding r_s^* becomes a *transformation nucleus*, that is, it grows on the surface to a dimension exceeding r^* and thence into the body of the supercooled liquid. However when $R < r^*$, crystal nuclei with $r > r_s^*$ formed on the catalyst surface do not become transformation nuclei except by fluctuations‡ that increase the radius of the aggregate of catalyst particle plus crystal to r^* .

In earlier publications [4; 1] we have developed the theory of catalysis of nucleation by catalytic

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†General Electric Research Laboratory, The Knolls, Schenectady, New York.

‡Reiss [5] and Pound and La Mer [2] have discussed the theory for this process.

units having radii greatly in excess of r^* . We now consider the catalysis of nucleation by bodies whose radii are of the same order of magnitude as r^* . It will be supposed, for simplicity, that these bodies (we shall hereafter call them patches) are all characterized by a single value of θ and that their number is proportional to the surface area of the liquid.†

Let n_A be the number of patches per unit area with radius $\geq R$. We assume a continuous distribution of n_A with respect to R , as follows:

$$(3) \quad n_A = f(R)$$

If θ_p is the contact angle made by a crystal nucleus on a patch the critical radius r_p^* for nucleation on the surface of the patch is given by:

$$(4) \quad r_p^* = -2\sigma \sin \theta_p / \Delta F_v.$$

A crystal nucleated on the patch surface grows to the patch boundary but it will not, in general, become a transformation nucleus unless $R \geq r_s^*$ or r^* .

To a good approximation:

$$(5) \quad \Delta F_v = \Delta S_v \Delta T$$

where ΔS_v is the entropy of transition/volume and ΔT is the supercooling. The number of patches (n_A^*)/area capable of serving as transformation nuclei is found by substituting r^* or r_s^* in equation (3). From equations (1), (2), (3) and (5), it follows that the dependence of n_A^* on ΔT is

$$(6) \quad n_A^* = f(-2\sigma / \Delta S_v \Delta T)$$

or

$$(7) \quad n_A^* = f(-2\sigma \sin \theta / \Delta S_v \Delta T).$$

Let I_p be the frequency of nucleation/area of patch. Then the nucleation frequency (c)/patch is

$$(8) \quad c = I_p / a_p$$

where a_p is the area of the patch.

Now consider a collection of supercooled liquid droplets of diameter D . The average number of patches (m)/droplet capable of serving as transformation nuclei is given by:

$$(9) \quad m = n_A^* (\pi D^2).$$

c will be very strongly dependent upon temperature so that there is a very narrow temperature range in which it changes from an imperceptible to a perceptible value. For some systems m will be very much larger than unity when c becomes perceptible and the nucleation frequency/droplet for droplets of uniform size will be constant. However, there is a

†The theory to be developed is easily extended to the case where the number of patches is proportional to the liquid volume.

large probability that, for some systems, c becomes perceptible when m is of the order of unity or less. Under these circumstances, the number of patches/droplet that can serve as transformation nuclei is far from uniform and a substantial fraction of droplets will contain no supercritical patches.

Let x be the fraction of a liquid sample, consisting of uniform droplets, solidified in time t . To obtain $x = f(t)$ for m of the order unity or less, a derivation due to Kimball is directly applicable. Kimball [6] assumed that all catalytic units (average m /droplet) are equally effective and that they are distributed among the droplets according to Poisson's distribution law. With these assumptions he obtained for constant ΔT :

$$(10) \quad x = 1 - \exp\{-m[1 - \exp(-ct)]\}.$$

All supercritical patches are not equally effective as nucleation catalysts since their areas are different. Actually, however, the temperature range for which the rate of nucleation is measured is very small and the variation in r^* or r_s^* is correspondingly small (e.g., 5 to 10 per cent). Hence it may be assumed, with fair accuracy, that all supercritical patches have the same area so that equation (10) satisfactorily describes the isothermal dependence of x on t for the solidification of a collection of uniform droplets containing on the average m supercritical patches/droplet. As $t \rightarrow \infty$, x approaches a limiting value, $x_a < 1$ given by:

$$(11) \quad x_a = 1 - \exp(-m).$$

The fraction of droplets containing no supercritical patches is therefore $1 - x_a$. To obtain a more convenient relation for analysis we derive from (10):

$$(12) \quad dx/(1-x) dt = f = cm \exp(-ct)$$

and

$$(13) \quad \ln f = \ln(cm) - ct.$$

Suppose that instead of a uniform droplet diameter we have a distribution of diameters such that at time t the fraction of droplets of diameter D that have not solidified is x_D . When $t = 0$, $x_D = x_D^0$ and D' is defined by:

$$(14) \quad \frac{1}{2} = \int_0^{D'} x_D^0 dD.$$

Equation (12) becomes:

$$(15) \quad f = \{cm'[F(t, D)]/(1-x)D'^2\} \exp(-ct)$$

where

$$(16) \quad F(t, D) = \int_0^\infty x_D D^2 dD,$$

$$(17) \quad m' = \left[\int_0^\infty x_D^0 D^2 dD \right] / D'^2$$

and

$$(18) \quad \int_0^\infty x_D dD = 1 - x.$$

x_a is now given by:

$$(19) \quad x_a = 1 - \int_0^\infty x_D^0 \exp[-m'(D/D')^2] dD.$$

Although our theory and the earlier one due to Kimball give formally identical expressions for the isothermal dependence of x on t , there are important differences in the predictions of the two theories. As described by Pound and La Mer, Kimball's theory seems to require that m be independent of ΔT , while our theory requires that m increase with ΔT , according to equations (6) and (9). According to Kimball's theory, x will be perceived to approach an asymptote x_a substantially less than unity and perceptibly greater than zero only for systems in which (approximately) $0.01 < m < 3$ where m is the number of catalyst units/droplet characterized by the smallest θ value. Our theory predicts that $0 < x_a < 1$ if $0 \leq m < 3$ (approximately) when c becomes perceptible. Therefore, Kimball's theory seems to predict that the perception of $0 < x_a < 1$ should be a very improbable occurrence while our theory predicts that such perception should be possible in a fair number of instances.

Comparison of Theory and Experience

Mercury Droplets Infected with HgX Patches

Mercury droplets coated with mercury laurate or mercury stearate become infected in time with patches of a decomposition product, HgX (believed to be mercury oxide formed by hydrolysis of the carboxylates), that is a very powerful catalyst for the formation of mercury crystal nuclei. Transformation nuclei formed rapidly from these patches at only 2–4° supercooling. The fraction x of droplets solidified quickly approached an asymptote $x_a < 1$ almost as soon as the droplets reached bath temperature so that the essential features of the transformation were described by $x_a = f(\Delta T)$, where x_a increases with increasing ΔT . This type of transformation in which time does not enter into the description is called "athermal" and has been recognized in crystalline media [7] and designated the "athermal martensite transformation."

The interpretation of these results is that c is perceptible and in fact very large, at a value of ΔT which corresponds to a value of m that is essentially zero. When supercooling is increased sufficiently to make x_a perceptible ($m > 0.02$ approximately) all the patches are already covered with crystalline mercury. Thus the potential transformation nuclei are fully formed before any transformation is perceptible. These potential nuclei become active transformation nuclei immediately when ΔT is increased sufficiently to make r^* (or r_s^*) = R .

Because of the athermal nature of the transformation, c cannot be determined but n_A can be evaluated quite accurately from x_a . The value of n_A^* calculated from the earlier data [1] (sample A) is approximately given by:

$$(20) \quad n_A^* = a \exp(\beta \Delta T)$$

where a and β are constants. Combining equations (2), (5) and (6) we have

$$(21) \quad n_A = a \exp[b/R]$$

where $b = -2\sigma\beta/\Delta S_v$.

The droplets of sample A were 100 per cent infected with HgX patches. In certain other samples a substantial fraction of the droplets were not infected at all. Therefore, it is concluded that the

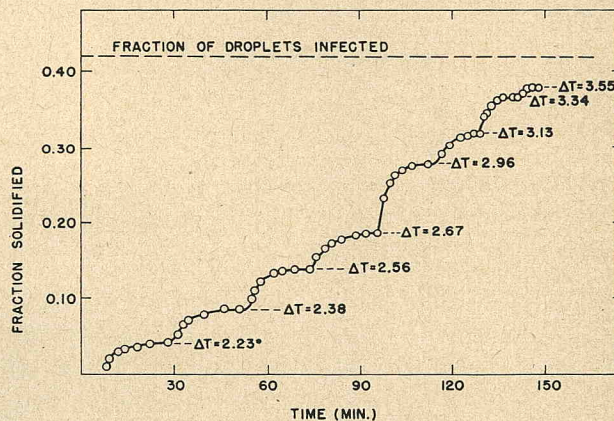


FIGURE 1. Fraction of mercury droplets solidified with successively increasing supercooling. 42 per cent of the droplets are infected with HgX patches. (Sample B).

patch sizes must be distributed about some most probable value $R = R_m$ and that equation (21) does not give a complete description of the distribution. In order to obtain such a description $x_a = f(\Delta T)$ was measured on a sample (B) in which 42 per cent of the droplets were infected with HgX. In this experiment† the sample was maintained at a cons-

†This experiment was performed by Mr. W. A. Rocco of this laboratory.

tant temperature until $x \rightarrow x_a$ then cooled to a slightly lower temperature and again held until $x \rightarrow x_a$. This procedure was repeated until nearly all of the infected droplets had solidified. The results are shown in Figure 1.

The values of x_a obtained from these data were substituted into equation (11) to obtain m . n_A^* was calculated[†] from equation (9) with $D = D' = 4.0 \times 10^{-4}$ cm. $R = r^*$ corresponding to these n_A^* values was calculated from equations (2) and (5) using the value of σ calculated from earlier results [1]. n_A is plotted against R and ΔT in Figure 2.

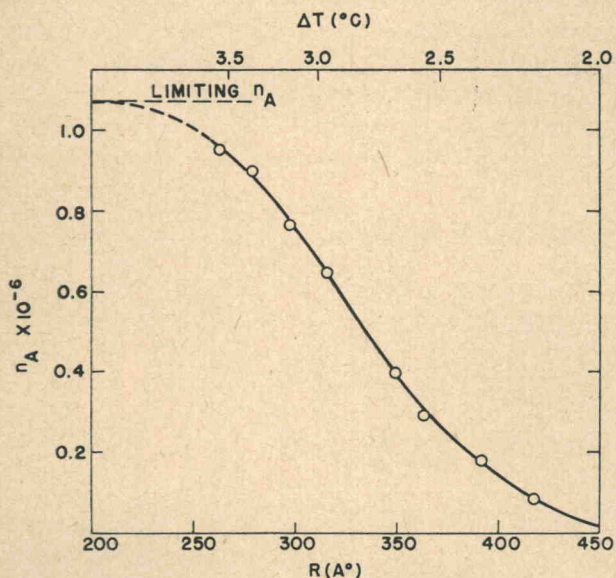


FIGURE 2. Calculated size distribution curve for HgX patches on mercury droplets of sample B.

$n_A = f(R)$ is a sigmoidal relation that is fairly symmetrical around $R = R_m$. The slope of $n_A = f(R)$ is satisfactorily described by:

$$(22) \quad \frac{dn_A}{dR} = (7.7 \times 10^{11}) \exp [-1.8 \times 10^{12} (R - R_m)^2] \text{ cm}^{-3}$$

where $R_m = 3.3 \times 10^{-6}$ cm. and $n_A = 5.3 \times 10^5 \text{ cm}^{-2}$ at $R = R_m$. The range of patch radii, 250 to 450 Å, seems plausible.

Solidification of Tin Droplets Coated with Tin Oxide

Pound and La Mer [2] established that the major fraction of nuclei for the solidification of oxide-coated tin droplets formed isothermally. The rate determining step is the formation of a tin nucleus on a supercritical patch (thermal nucleation). Crystalline tin may also coat subcritical patches but these

[†]It was established from the droplet size distribution that m values calculated from equations (11) and (19) did not differ to an important extent.

cannot serve as transformation nuclei. Therefore, it follows that the solidification rate at a given temperature, T_1 , and extent of transformation x will be more rapid when the sample is quenched to T_1 after having been held at a temperature a few tenths of a degree above T_1 than if the sample is quenched to T_1 from above the melting temperature.

Pound and La Mer [2] established that two of their isotherms could be described approximately by the Kimball equation (10) with m increasing with ΔT . They gave no explanation for the dependence of m on ΔT . According to equation (13), $\ln f$ should be a linear function of t . We have measured f between $x = 0.3$ and $x = 0.7$ for the four of Pound and La Mer's isotherms corresponding to the greatest supercooling and the droplet size distribution corresponding to $D' = 3.75$ microns (D between 2.5 and 5.0 microns). Figures 3, 4, 5, and 6 show $\ln f$

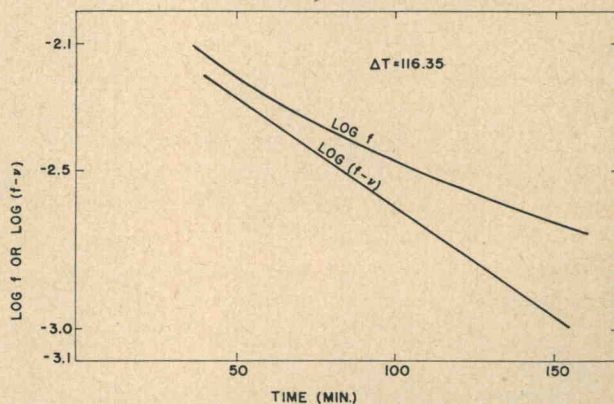


FIGURE 3. Test of equations (18) and (20) using Pound and La Mer's data on the solidification of oxide-coated tin droplets ($\Delta T = 116.35$).

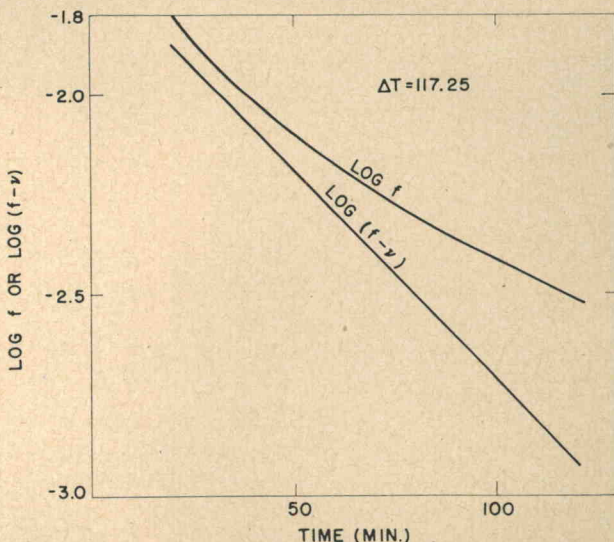


FIGURE 4. Test of equations (18) and (20) using Pound and La Mer's data on the solidification of oxide-coated tin droplets ($\Delta T = 117.25$).

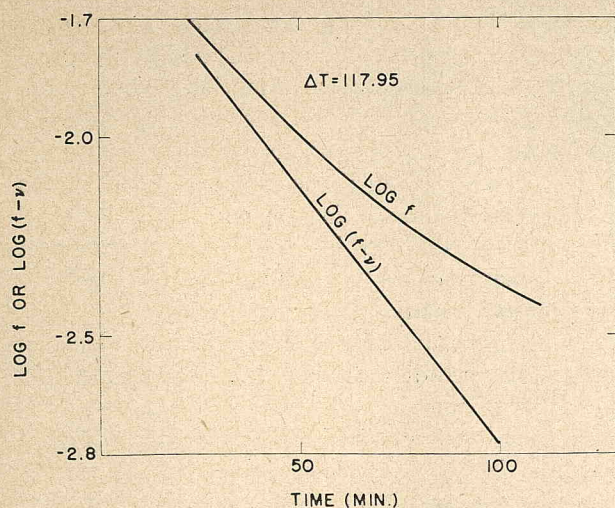


FIGURE 5. Test of equations (18) and (20) using Pound and La Mer's data on the solidification of oxide coated tin droplets ($\Delta T = 117.95$).

as a function of t for each of the four ΔT values. In all cases f and hence the transformation rate dx/dt , tends to be larger at the longer times than predicted by the Kimball equation. The existing non-uniformity of droplet size would cause f to fall off more sharply with time (see equation (15)) than predicted by the Kimball equation.

However, these results and the theory are easily reconciled by taking into account the auxiliary

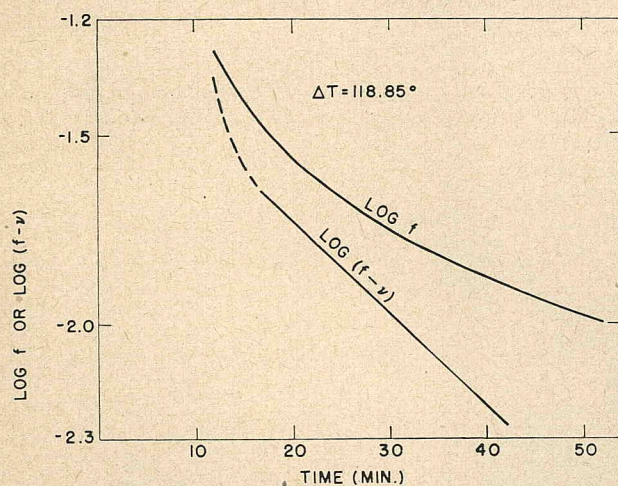


FIGURE 6. Test of equations (18) and (20) using Pound and La Mer's data on the solidification of oxide-coated tin droplets ($\Delta T = 118.85$).

steady nucleation process suggested by Pound and La Mer. Let the frequency of the auxiliary nucleation be ν per droplet; then

$$(23) \quad f = cm \exp(-ct) + \nu$$

and

$$(24) \quad \ln(f - \nu) = \ln(cm) - ct.$$

By proper selection of ν a good straight-line relation between $\ln(f - \nu)$ and t is obtained for each of the four values of ΔT . These relations are shown in Figures 3, 4, 5 and 6.

Thus each of Pound and La Mer's isotherms can be satisfactorily described by three parameters c , m , and ν , each of which is a function of ΔT and droplet size. m is the number of supercritical patches per droplet. c is given by equation (8) and is the frequency of forming a tin nucleus on a patch. ν is a steady nucleation frequency per droplet that may correspond to the frequency of homogeneous nucleation or possibly to the heterogeneous nucleation frequency per area of inactive surface.

The values of c , ν , and m that describe Pound and La Mer's data are summarized in Table I. The un-

TABLE I
NUMERICAL VALUES OF CONSTANTS THAT DESCRIBE POUND
AND LA MER'S DATA

$\Delta T(^{\circ}\text{C})$	m	$c (\text{sec}^{-1})$	$\nu (\text{sec}^{-1})$
107.65	0.090		
110.85	0.20		
113.85	0.40		
116.35	0.74	2.64×10^{-4}	1.67×10^{-5}
117.25	0.87	4.05×10^{-4}	3.00×10^{-5}
117.95	1.10	5.00×10^{-4}	4.24×10^{-5}
118.85	1.08	9.5×10^{-4}	11.6×10^{-5}

certainty in each value is of the order of ± 10 per cent. There is an additional uncertainty due to the neglect of the non-uniformity of the droplet size. It is hoped that this uncertainty is minimized by the evaluation of f in the vicinity of $x = 0.5$ ($x = 0.3$ to $x = 0.7$) for all four isotherms. Also listed in the table are m values calculated from x_a for the three isotherms corresponding to the smallest ΔT 's. This calculation is approximately valid since the contribution of ν to the rate is less the less is ΔT .

Pound and La Mer's isothermal results for four different droplet size distributions indicate that m is proportional to droplet area [2].† Values of $n_A^* = m/\pi D'^2$ were calculated from the m values listed in Table I, which correspond to $D' = 3.75 \times 10^{-4}$ cm. As a function of ΔT , n_A^* is satisfactorily described by equation (20) with $a = 1.41 \times 10^{-6} \text{ cm}^{-2}$ and $\beta = 0.238^{\circ}\text{K}^{-1}$. a and β were calculated from the constants of the straight line obtained by plotting $\log n_A^*$ against ΔT (see Fig. 7). From equation (21) and the value of σ estimated by Pound and La Mer

†This fact was established independently by F. C. Frank.

we obtain the following expression for n_A :

$$(25) \quad n_A = 1.41 \times 10^{-6} \exp[3.14 \times 10^{-6}/R] \text{ cm}^{-2}.$$

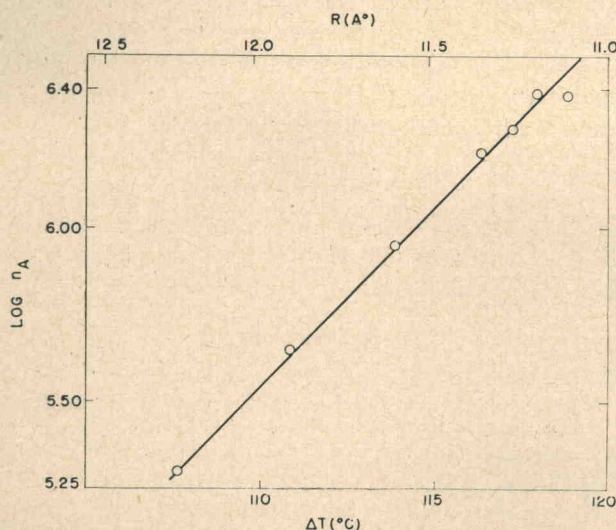


FIGURE 7. Calculated size distribution curve for the patches that catalyzed the formation of tin crystal nuclei in Pound and La Mer's sample.

$\log c$ and $\log \nu$ are plotted against $1/(\Delta F_v)^2 T$, where ΔF_v is expressed in ergs/c.c., in Figure 8. c is described by the equation:

$$(26) \quad c = 10^{11 \pm 6} \exp[-1.74 \times 10^6/(\Delta F_v)^2 kT],$$

and ν by:

$$(27) \quad \nu = 10^{17 \pm 6} \exp[-2.60 \times 10^6/(\Delta F_v)^2 kT].$$

Now the area of a patch of critical size is of the order of 10^{-13} cm^2 , hence I_p the frequency of nucleation per cm^2 of patch is (see equation (8)):

$$(28) \quad I_p = K_s \exp[-1.74 \times 10^6/(\Delta F_v)^2 kT]$$

where $K_s = 10^{24 \pm 6} \text{ cm}^{-2} \text{ sec}^{-1}$. This value of K_s is in fair agreement with the value $10^{27.5} \text{ cm}^{-2} \text{ sec}^{-1}$ predicted by the theory of heterogeneous nucleation [1].

ν might be interpreted as the frequency of homogeneous nucleation or the frequency of heterogeneous nucleation on an inactive surface. If we assume homogeneous nucleation:

$$(29) \quad \nu/\nu_{D'} = I = K_v \exp[-2.60 \times 10^6/(\Delta F_v)^2 kT]$$

where I = nucleation frequency per volume and $\nu_{D'}$ is the volume of a droplet of diameter $D' = 3.75 \times 10^{-4} \text{ cm}$. To describe the data on this basis $K_v = 10^{27 \pm 6} \text{ cm}^{-2} \text{ sec}^{-1}$, a value in poor agreement with $K_v = 10^{36}$ predicted by the theory of homogeneous nucleation [1].

Assuming heterogeneous nucleation on the inactive surface of the droplet we obtain:

$$(30) \quad \nu/a_{D'} = I_s = K_s \exp[-2.60 \times 10^6/(\Delta F_v)^2 kT]$$

where I_s is the nucleation frequency per area of inactive surface and $a_{D'}$ is the area of the droplet of diameter D' . K_s is found to be $10^{23.4 \pm 6} \text{ cm}^{-2} \text{ sec}^{-1}$ in

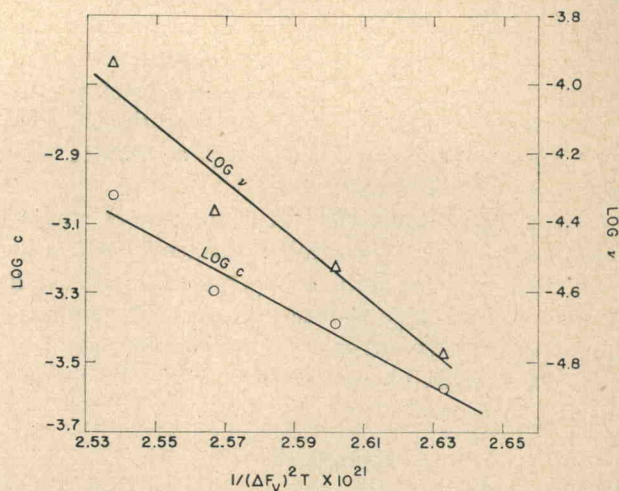


FIGURE 8. Dependence of ν and c , for the nucleation of tin crystals in Pound and La Mer's sample, upon supercooling.

fair agreement with the value $10^{27.5}$ predicted by the theory of heterogeneous nucleation.

Crystallization of Small Water Droplets

Dorsch and Hacker [8] have measured the initial freezing temperature, T_i , of water droplets as a function of their diameter D and found that T_i decreased with decreasing D . In order to explain these results Levine [9] postulated that a variety of types of units that catalyze ice nucleation ordinarily exist in water, each variety characterized by a particular ΔT corresponding to the initiation of freezing. Let n_v be the number of units/volume that initiate freezing at a supercooling of ΔT or less. Levine showed that the dependence of T_i on D is satisfactorily described by assuming n_v proportional to $\exp(\beta \Delta T)$.† He gives no theory for the increase of n_v with ΔT .

One possible interpretation for the dependence of n_v on ΔT in the freezing of water is that nucleation is effected by patches characterized by a single θ and a size distribution function of the form $n_v = a \exp(b/R)$. However, Dorsch and Hacker made no

†The formal analogy between Levine's statistical theory for the initiation of freezing and Weibull's [10] (see also Fisher and Hollomon [11]) theory for the stress specimen-size relationship in brittle fracture is noteworthy. According to Griffith [12] brittle fracture is initiated by microcracks. The larger the radius, r , of the crack the less is the fracture stress. Weibull showed that the experimental stress-size relationship can be explained on the assumption that $n_A = a \exp(b/r)$ where n_A is the number of microcracks per area having a radius $\geq r$.

quantitative measurements on the time dependence of solidification of the droplets as a function of D and ΔT . It is possible, therefore, that the catalytic units responsible for solidification in their experiments were supercritical at all values of ΔT . The dependence of n_v on ΔT , deduced from their results, can be accounted for on the assumption of a statistical distribution of catalyst units with respect to the contact angle, $\theta[n_v = f(\theta)]$ such that the number per volume, n_v , characterized by a contact $< \theta$ increases with increasing θ .

The temperature coefficient of the rate of nucleation I_s on a particular catalyst surface is very large so that I_s changes from an imperceptible value to a magnitude too large to measure over 2–3° temperature range. Hence to a gross approximation a catalyst unit characterized by a given θ may also be characterized by a particular value of ΔT .

Conclusions

The multiplicity in crystal nucleation frequency that has been observed for the solidification of small droplets is readily accounted for by the patch nucleation theory with the use of no more than two fundamental nucleation frequencies for a given dispersion at a given temperature. It is shown that the data are described by plausible distributions of patches with size. Also the theory satisfactorily explains the athermal formation of crystal nuclei in solidification processes.

Although the existing data are accounted for on the assumption that the patches are distributed over the droplet surface, the surfaces of very small particles suspended in the droplet might under certain circumstances constitute the patches. Formally the theory is analogous for suspended particles and patches in the droplet surface.

Acknowledgement

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