RES. LAB. REPRINT
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GENERAL ELECTRIC
Research Laboratory

PRINCIPLES OF SOLIDIFICATION

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Reprinted from "Thermodynamics in Physical Metallurgy," Pages 282–306

SCHENECTADY, NEW YORK

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By David Turnbull

BROADLY, "solidification" implies the separation of a crystalline phase from gaseous or liquid solution. However, the present discussion is limited to the kinetics of formation of crystals from uniary systems of gases or liquids, and the latter process is to be discussed in more detail.

Rates of solidification may be interpreted in terms of the nucleation of crystals and their growth to macroscopic dimensions. The general theory of nucleation has been developed in a preceding paper (1)[1] of this seminar. We shall examine critically how it applies to the nucleation of crystals, particularly in liquids. Experimental results on the rate of crystal nucleation in liquids appear to be confusing and contradictory. However, many of the apparent contradictions can be resolved if the role of extraneous influences (such as heterogeneities and container walls), often overlooked or not clearly understood, is properly considered. The experimental conditions most favorable for homogeneous nucleation (i.e., nucleation in the absence of extraneous influences) can be defined and in large part fulfilled. The evidence now at hand indicates that if these conditions are established, consistent and highly reproducible results are obtained. These results are particularly interesting because of the valuable clues that they furnish to the solution of the problem of interfacial energies involving solid phases. Such data also should be valuable in evaluating theories dealing with the relation between the structure of liquids and solids.

The kinetics of growth of crystals to macroscopic size is probably better understood than their nucleation. It is generally agreed that kinetic factors determine the form of large crystals, and some important generalizations relating these kinetic factors to crystal structure have been made. Nevertheless there are many phenomena involved in crystal growth that have not yet been explained satisfactorily in terms of our present models of rate theory and of structure. The mechanism for the marked changes in growth rates brought about by adsorbed impurities is imperfectly understood. Although

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[1] The figures appearing in parentheses pertain to the references appended to this paper.

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there appears to be good evidence for the periodic discontinuities in growth rate of crystals predicted by structural and kinetic theory, the growth rates observed experimentally are larger by several orders of magnitude than predicted by the theory. These problems and others would be clarified considerably if there were a more satisfactory picture of the structure of the surface layer of a pure solid in equilibrium with its vapor or its melt. Great progress in setting up such models for solid surfaces should become possible as reliable values for interfacial energies involving solid phases become available.

NUCLEATION OF CRYSTALS

Vapor → Crystal

According to the theory reviewed in a preceding paper (1), an approximate expression for the rate of homogeneous nucleation of crystals in vapor can be written as follows:

$$I = n(p/kT)(A^*/2)(-\Delta F_v V_s/3m)^{1/2} \exp.\,[-K\sigma^3/(\Delta F_v)^2 kT] \qquad \text{Equation I}$$

where V_s is the volume per atom in the solid phase, K is a shape factor, σ is the interfacial energy between crystal and vapor, and the other symbols have been defined in the preceding paper. ΔF_v in this equation can be approximated from either of the following expressions:

$$\Delta F_v = q\,\Delta T/T_o \qquad \text{Equation IIa}$$

at constant pressure, or:

$$\Delta F_v = (kT/V_s)\ln(p_o/p) \qquad \text{Equation IIb}$$

at constant temperature; where:

q = heat of transition per unit volume of solid
ΔT = amount of subcooling below the equilibrium temperature, T_o
p_o = equilibrium vapor pressure

Equation IIb is subject only to the assumption that the vapor is ideal and is more accurate than Equation IIa which assumes the entropy of transition to be independent of temperature.

The general assumptions made in deriving Equation I have already been discussed. However, additional assumptions have to be made because the forming phase is crystalline. The most important additional assumption is that the average surface configuration presented by the crystal to the vapor is independent of the number of atoms, i, that the crystal contains. Actually, as was pointed out long ago (2), this configuration cannot be independent of i but must change more or less periodically with it—the period corresponding to the attachment of one crystal plane. However, for reasons that will be discussed in the section on kinetics of crystal growth, the change in surface configuration with i will be neglected in the treatment of the nucleation problem. Equation I also depends for its validity on the assumption that the crystal planes are equivalent crystallographically or that σ is isotropic. In general, this is probably a good approximation.

Experiments comparable to those of Volmer and Flood (3) on the rate of homogeneous nucleation of liquid in supersaturated vapors do not appear to have been performed for vapor – solid transitions. This is unfortunate, since experiments carried out on solids with relatively high vapor pressures, such as iodine or carbon dioxide, seem to be within the realm of practical realization. In view of the excellent agreement with nucleation theory obtained in the Volmer-Flood work, similar experiments on volatile solids might afford a means of evaluating solid – vapor interfacial energies and in any event would provide a test for the homogeneous nucleation theory.

Nucleation in the vapor – solid type of transition as well as in most other types generally takes place heterogeneously. However, the expression for the rate of heterogeneous nucleation in the vapor – solid transition is a simple extension of that for homogeneous nucleation (Equation I). Using the symbols of the preceding paper (1), the rate for a given substrate may then be written as follows:

$$I_s = n_s (p/kT)(A^*/2)(-\Delta F_v V_s/3m)^{1/2} \exp.\,[-K\sigma^3\{f(\theta)\}/(\Delta F_v)^2 kT] \qquad \text{Equation III}$$

$f(\theta)$ is a function of the contact angle that has been formulated by Volmer (4). It may have any value from 0 to 1, depending upon the character of the substrate. In an actual system a number of substrates, each with a characteristic θ value, may be effective as nucleation catalysts. In vapor – solid (or vapor – liquid transition) substrates having the lowest θ values would catalyze the entire transformation.

Liquid → Crystal

Theory: The following expression (1, 5) is applicable to the rate of homogeneous nucleation in the liquid → crystal reaction:

$$I = n(kT/h) \exp.\,[-K\sigma^3/(\Delta F_v)^2 kT - \Delta F_A/kT] \qquad \text{Equation IV}$$

σ is the interfacial energy between liquid and crystal and the other symbols have been previously defined. This equation is subject to the same assumptions as Equation I. If it can be completely substantiated by experiment it will provide an effective method of calculating accurate liquid – crystal interfacial energies from experimental data on homogeneous nucleation rates.

For the rate of heterogeneous nucleation an expression analogous to Equations III and IV applies:

$$I_s = n_s(kT/h)\ \text{exp.}\ [-K\sigma^3\{f(\theta)\}/(\Delta F_v)^2 kT - \Delta F_A/kT]$$

Equation V

where I_s, n_s and $f(\theta)$ are defined in the same way as before.

Experimental: Nucleation rates in liquid – crystal reactions have generally been measured on comparatively large continuous samples of supercooled liquid. The experimental technique used by Tammann (6) is fairly typical of that generally used to measure nucleation rates in transparent organic liquids. In his experiments the sample is held for a specified period at a temperature $\Delta T_+°$ in excess of T_0. It is then quenched to a temperature $\Delta T_-°$ below T_0. After holding at ΔT_- for a given time it is warmed to a temperature just below T_0, $T_0 - dT$, and held there until nuclei presumed to have formed at ΔT_- grow large enough to be seen and counted microscopically. It is assumed that no nuclei developed at ΔT_- become subcritical and disappear in warming to $T_0 - dT$.

This technique is not adaptable to measurement of nucleation rates in metal liquid → crystal reactions. However, in liquid metals that have been significantly subcooled the growth rate of crystals is very rapid, one might say cataclysmic, so that most of the time elapsed in the transformation is that required for forming the first crystal nucleus. Measurement of the over-all rate of transformation dilatometrically, by heat evolution, etc., thus gives the desired information on the rate of nucleation.

Experiments of this general character in which a relatively small number of nuclei are developed in the course of the transformation are particularly susceptible to the influence of nucleation catalysts as already explained (1). Since as little as one part in 10^{16} of the right kind of heterogeneity can catalyze the formation of one nucleus, the magnitude of the problem of eliminating such extraneous influences in these experiments can be appreciated. Clearly, the normal standards of chemical purity are insignificant in nucleation experiments.

In fact there is good experimental evidence (1, 7) that nucleation in practically all such experiments occurs heterogeneously. The hypothesis that the well-known effect of thermal history upon nucleation kinetics is but another manifestation of catalytic influences has been justified by many experiments (7, 8).

Mechanical vibrations are another important disturbing influence on nucleation in liquid → crystal reactions. It is well known that comparatively mild mechanical vibrations can induce nucleation of crystals in a subcooled liquid at a temperature several degrees higher than that at which it would normally occur. For example, the author has observed that gallium samples which would remain liquid indefinitely at $\Delta T_- = 45$ °C under static conditions could be made to crystallize immediately at $\Delta T_- = 30$ °C by vibrations brought about manually. It has been maintained (9) that liquids can be prevented from subcooling perceptibly by employing mechanical vibrations of sufficient intensity. Vonnegut (10) has suggested that the effect is due to cavitation at the container wall, or elsewhere, induced by the vibrations. At the instant the cavity is closed, the liquid rushing back into position has acquired an extremely high velocity so that a wave of rather high alternating positive and negative pressures will be set up. In a liquid which contracts upon solidification, the free energy of the liquid → crystal transformation is decreased in regions of positive pressure so that the effect of this positive pressure upon the rate of crystal nucleation will be roughly equivalent to lowering the temperature by an amount Δ calculable by the Clausius equation. The magnitude of local pressures that can be built up in this manner can easily account for the shift in ΔT_- due to mechanical vibration. Because the magnitudes of these pressures are unpredictable, it is evidently necessary that mechanical vibrations be minimized in experiments purporting to measure the rate of homogeneous nucleation in liquid → crystal transformations.

How then can the influence of heterogeneities and vibrations be eliminated and the actual rate of homogeneous nucleation in liquid → crystal reactions be measured? The answer to this question is suggested by the work of Volmer and Flood (3). That is to select experimental conditions such that a very large number of nuclei (i.e., large in comparison with the number of possible heterogeneities present) form in the interior of the sample. When working with large continuous specimens this solution of the problem is practicable only for substances whose crystals grow relatively slowly at temperatures where homogeneous nucleation becomes measurable. Under these circumstances, a very large number of crystals can form before the liquid is entirely transformed. These conditions are often realized in subcooled organic liquids having high viscosity, but they can never be realized in large liquid metal samples that have been significantly subcooled because of the tremendous rate of crystal growth.

In order to assure the formation of a very large number of nuclei in liquid metal specimens, it is necessary to break the liquid up into very small parts that are prevented somehow from intercommunicating. Thus, as the author has pointed out (11), the nucleation catalysts are isolated in individual parts of the specimen and are capable of promoting transformation only in that particular part in which they are localized. If the parts are small enough the vast majority of them will contain no catalyst whatever and the nucleation must be homogeneous.

As an example, suppose that a liquid metal contains 10^6 catalytic centers/cm^3 for the formation of crystals. The probability of finding 1 cm^3 of this liquid free of centers is practically nil and it would be observed that such a sample would crystallize at a very small amount of subcooling, ΔT_{-}. If 1 cm^3 of the liquid is entirely broken up into isolated droplets 10 microns in diameter, the probability of finding a catalytic center in a given droplet is only 1 in 2000. The entire sample could then be subcooled to a very much greater extent, in fact to the characteristic temperature of homogeneous nucleation. The heterogeneous component of the reaction would not be detected at all excepting with very sensitive experimental procedures. If, instead of looking at the behavior of the whole assembly of droplets, individual droplets were studied, the probability would be very large (1999/2000) that a given individual would subcool to the maximum extent.

It has been known for at least sixty years that comparatively small particles of liquid gold subcool farther than do large samples in crucibles which solidify nearly at the melting temperature. However, no quantitative information regarding the amount of subcooling or the effect of time upon it seems to be available. The first more or less systematic experiments on the subcooling of small metal particles seem to have been made by Mendenhall and Ingersoll (12). They watched the solidification of some high melting metal particles 50 to 100 microns in size that were melted by heating on a Nernst glower. The maximum subcooling obtained was quite large and seemed to be proportional to the melting point of the particular element. However, the only results given were the maximum subcooling for platinum and rhodium, 370 °C in both cases. The full significance of these results and of the earlier qualitative observations was not realized and greater significance was attached to the results from subcooling experiments on comparatively large melts contained in crucibles.

Vonnegut (13) seems to have been the first to study the solidification behavior of large aggregates of small liquid particles in his investigation of the kinetics of the liquid → crystal transformation in tin. The particles of liquid tin were kept apart by an oxide film surrounding each particle, and the rate of transformation was followed dilatometrically. About the same time Cwilong (14) and Schaefer (15) established independently the maximum subcooling required for the formation of snow crystals in aggregates of small water droplets suspended in air.

In these experiments, as in the earlier small-particle experiments, the maximum subcooling was very much larger than ever attained on large samples. The author (11) suggested that this could be attributed to the isolation of nucleation catalysts effected by breaking up the sample, and with his co-workers (16, 17) extended the small-particle technique to the kinetics of liquid – crystal reactions in a large number of pure metals. The experimental details and complete results of these experiments are to be published elsewhere (16, 17) and only a summary will be presented.

Table I summarizes the results of the subcooling experiments of the author and co-workers as well as those of other investigators whose results are known to have been obtained by the small-particle technique. In nearly all cases the maximum subcooling, ΔT_-, observed for small particles is very much larger than that for large continuous samples.

The maximum subcooling recorded in the table was chosen arbitrarily in each case to correspond to a nucleation rate of the order of 1 nucleus/particle in 10 seconds. The average particle size in most of the experiments was of the order of 50 microns. Since ΔT_- is time-dependent and because nucleation rates are not closely specified, one may question whether a comparison of ΔT_- values is significant. Actually, the nucleation rate changes so sharply with temperature that ΔT_- is practically a characteristic property of the substance. The marked dependence of nucleation rate on temperature has been demonstrated by many experiments. For example, the author (11) found that mercury samples could be held for 1 hour at $\Delta T_- = 43$ °C without detectable reaction, but completely solidified within a minute at $\Delta T_- = 46$ °C. From this, it may be inferred that the rate changes by a factor of at least 10^4 in 3 degrees. Similar phenomena were found in microscopic observations of solidification (16, 17). Thus, a ΔT_- value can be bracketed within ±2% for most subcooled liquid metals such that at $\Delta T_-/1.02$ the nucleation rate, I, is too slow to measure in a reasonable period and at $\Delta T_-/0.98$ is too rapid to measure.

An analogous problem was met with and solved similarly by Volmer and Flood (4) in their experiments on the nucleation of liquids in vapors. They had no way of measuring the nucleation rate quantitatively, but it changed so markedly with small changes of the supersaturation ratio p/p_0 that it sufficed to ascribe some arbitrary finite value to the nucleation rate at the minimum value of p/p_0 at which nuclei were observed to form. Even so, the agreement that they found between interfacial tensions calculated from the results of nucleation experiments and values of these tensions measured by other methods was excellent.

For most of the metals the largest fraction of the particles crystallized at or very close to the maximum subcooling reported. This fraction was 9/10 in the case of mercury, for example. In some instances, however, a large proportion of the particles crystallized before the maximum ΔT_- was reached and only a small but significant fraction crystallized at this temperature. Some interesting observations indicating the possibility of finding a "θ spectrum" were made on metals exhibiting this behavior. For example, with lead particles it was observed that the temperature of crystallization for individual particles was sharply defined and reproducible throughout several successive liquefaction/solidification cycles. Particle "A" might be observed to crystallize consistently at a temperature very close to T_0, particle "B" at about ½ the maximum subcooling and particle "C" at the maximum. Thus, each particle might be said to have a characteristic ΔT_- and one could construct a spectrum of such values from the observations on a large number of particles. It is evident, however, that this behavior is symptomatic of the influence of heterogeneities in the particle. The characteristic ΔT_- value observed for a given particle can be related to the contact angle θ made by the crystal with the effective heterogeneity contained in the particle. Thus, a θ spectrum might be constructed from the characteristic ΔT_{-} values. Such a spectrum could be continuous or it might be more or less discrete if a large number of particles contain some specific heterogeneity. An arbitrary representation of this possibility is shown by Fig. 1.

According to the theory of homogeneous nucleation, the rate of nucleus formation in small particles I_v is related to their volume, V, by the following relation

$$I_v = IV \qquad \text{Equation VI}$$

where I is the nucleation rate per unit volume. In interpreting the small particle results it is necessary to know the relative importance of volume changes and temperature changes upon the nucleation rate. One alternative explanation of the small-particle results that has been advanced is that realizable volume changes are very important in their effect upon nucleation rate relative to the total amount of subcooling obtained. This explanation is untenable for several reasons. It is tantamount to the requirement that the temperature coefficient of nucleation rate be very much smaller than it actually is. For example, in the author's experiments on mercury, a mass, approximately 1 centimeter in linear dimension, that did not significantly subcool was broken up to particles approximately 50 microns in linear dimensions that subcooled 46 °C. The volume change was of the order of 10^7, but the rate changed by a factor of at least 10^4 in 3 degrees so that the total effect of the volume change per se is equivalent to changing the temperature 6 degrees or less. Further

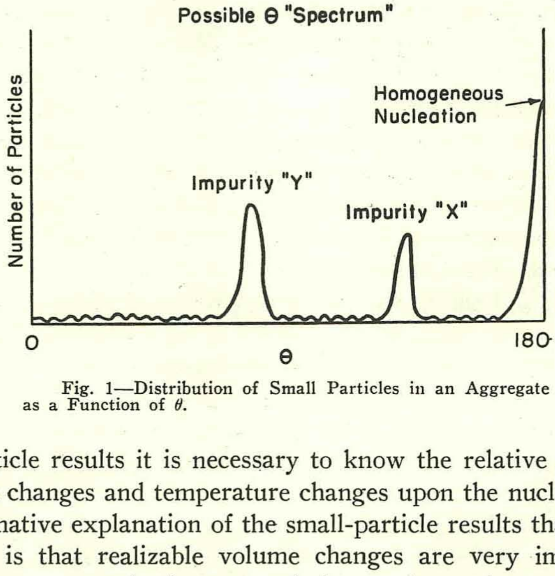

Fig. 1—Distribution of Small Particles in an Aggregate as a Function of θ.

evidence for the relative unimportance of volume change is obtained in microscopic observations of solidification. Generally, small particles are less likely to contain heterogeneities than large particles and thus subcool the maximum amount much more frequently. Occasionally, however, a 10-micron particle is observed to solidify consistently at a temperature only a little less than T_0, while an adjacent 50-micron particle consistently exhibits the maximum subcooling. Also, it should be noted that the maximum subcooling obtained in large continuous samples sometimes approaches that observed for small particles. For example, Johannsen (18) subcooled 1-cc water samples 36 degrees, while the small-particle result is 39. Turnbull (11) subcooled 1-gram gallium samples 55 degrees compared with 76 degrees for small particles. Bardenheuer and Bleckman (21) report that they were able to subcool a 150-gram sample of iron, entirely coated with a layer of liquid slag, 258 degrees before solidification. This number is of the same order of magnitude as one would anticipate from the small-particle technique.

Some interesting correlations and consequences emerge from the data on maximum subcooling. One is that the ratio $\Delta T_{-}/T_0$ is about the same (see Table I) for many of the substances and falls within the range 0.13 to 0.25 for all. For metals crystallizing in a close-packed structure, $\Delta T_{-}/T_0$ is of the order of 0.18 excepting for lead. Such a correlation might be expected on the basis of homogeneous nucleation theory, provided the liquid – solid interfacial energy σ were proportional to the heats of fusion ΔH_f and, in addition, the entropies of fusion were constant for various substances. Since entropies of fusion are not constant, a better correlation should be obtained by comparing σ directly with ΔH_f.

Having the approximate value of the nucleation rate at one temperature, the equation of Turnbull and Fisher (5) can be used to calculate numerical values of σ. Fisher, Hollomon and Turnbull (22) first made this calculation for water. The author (16) has extended this calculation to all of the substances listed in Table I, with the results shown. In addition to the assumption made in deriving the equation, the following were used in making the calculations:

1. σ is isotropic so that $K = 16\pi/3$ corresponding to a spherically-shaped nucleus.
2. $\Delta F_A = 0$.

A value of (1/10) sec^{-1} per particle was assigned to I, and Equation IIa used to calculate ΔF_v.

Although there is no clear theoretical basis for assuming that the interfacial energy between a metal crystal and its melt is isotropic, there are certain lines of experimental evidence which indicate that this may be a fair approximation for metals having cubical crystal structures. Thus, the experiments of C. S. Smith (23) indicate that the interfacial energy between a metal crystal and the liquid phase of a different metallic element (e.g., solid copper – liquid lead) is nearly isotropic. This does not prove that the interfacial energy between a metal crystal and its own melt is isotropic, but it is strong evidence in favor of such a hypothesis. Also, C. G. Dunn and F. Lionetti (24) have shown that the interfacial energy between differently oriented crystals of silicon ferrite is practically independent of the orientation difference, Δ, when this exceeds a relatively small value. These measurements offer further indirect support for the assumption under discussion.

At present there is no direct measurement of the magnitude of ΔF_A, but the evidence indicates that it must be quite small in comparison with ΔF^* in metal liquid $\rightarrow$ crystal reactions. In all of the metals that the author and his co-workers have studied, the growth rate of crystals into their melts, when significantly subcooled, was too rapid for accurate estimation. This was also true of metals such as gallium, germanium, and bismuth, having relatively complex crystal structures. Further, it is well known that the energies of activation for viscous flow, Q, are abnormally small for liquid metals, and it is probable that ΔF_A is of the same order of magnitude as Q. For example, if Q is equated to ΔF_A in the case of mercury $\Delta F_A \approx 1.6\,kT$ while $\Delta F^* \approx 75\,kT$ at $-85\,°C$, the temperature of rapid crystallization. If ΔF_A is of this order of magnitude, equating it to zero introduces an error of less than 1% in the calculated value of the interfacial energy.

Calculation of ΔF_v by assuming a constant entropy of fusion is only a fair approximation in many cases and could be improved considerably. Improved calculations of ΔF_v are currently being carried out in this laboratory.

The validity of the assumptions made in deriving Equation IV have already been discussed. However, it is worthwhile to note that if the quantity Ih/nkT in Equation IV were in error by a factor of 10^{10} due to experimental errors in measuring I and the approximations made in deriving nkT/h, the calculated value of σ would be only 10% in error.

It is reasonable to correlate (25, 16) the gram-atomic interfacial energy, σ_g, rather than σ in ergs/cm² with the gram-atomic heat of fusion ΔH_f. σ_g is defined as

$$\sigma_g = A\,\sigma \qquad \text{Equation VII}$$

where A is the area occupied by Avogadro's number (N) atoms in the liquid – crystal interface. Neglecting a shape factor of the order of unity,[2] A is given by

$$A = N^{1/3}\,V^{2/3} \qquad \text{Equation VIII}$$

where V is the gram-atomic volume. Thus,

$$\sigma_g = N^{1/3}\,V^{2/3}\,\sigma \qquad \text{Equation IX}$$

Values of σ_g and the ratios $\sigma_g/\Delta H_f$, calculated by Turnbull (16), are given for the various metals in Table I. The constancy of $\sigma_g/\Delta H_f$ for the strictly metallic elements is striking, and deviations from the mean value are well within experimental error for these elements. The excellence of the correlation is shown graphically in Fig. 2 in which σ_g is plotted against ΔH_f. It is evident that this correlation is much superior to the correlation of ΔT_- with T_o.

Table I
Summary of Subcooling Data Obtained by Small-Particle Technique

Substance	Crystal Structure	Entropy of Fusion	Max. Subcooling °C = ΔT_- Large Samples	Small Particles	$\Delta T_-/T_o$	σ ergs/cm²	σ_g cals/gm Atom	$\sigma_g/\Delta H_f$	M
Mercury (11)	hexagonal	2.38	14	46	0.197	21.6	262	0.47	0.236
Water (14, 15, 18)	hexagonal	5.28	36.8	39	0.143	32.8	471	0.33	0.149
Gallium (11)	orthorhombic	4.42	55	76	0.250	57	592	0.455	0.218
Tin (13, 19)	tetragonal	3.41	31	110	0.218	61.3	806	0.453	0.222
Bismuth (20, 17)	rhombohedral	4.60	30	90	0.165	55.5	841	0.336	0.154
Lead (16)	face-centered cubic	2.04	*	80	0.133	34.0	488	0.394	0.196
Silver (17)	face-centered cubic	2.19	*	227	0.184	128	1260	0.466	0.232
Germanium (17)	diamond	4.14	*	219	0.178	153	1790	0.352	0.185
Gold (17)	face-centered cubic	2.27	*	221	0.166	133	1320	0.436	0.216
Copper (17)	face-centered cubic	2.29	*	236	0.174	189	1410	0.453	0.222
Nickel (17)	face-centered cubic	2.43	*	319	0.185	261	1895	0.452	0.224
Palladium (17)	face-centered cubic	2.25	*	330	0.181	213	1890	0.459	0.223
Platinum (12)	face-centered cubic	2.30	*	370	0.182	245	2185	0.465	0.226

*Not definitely known but, excepting germanium, probably not more than 5 to 10 °C.

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[2] For simple cubic crystals bounded by perfect cube planes, this factor is precisely unity. However, for close-packed crystals bounded by perfect close-packed planes it is 1.08.

Another important result is that σ is of the order of ½ of ΔH_f. That is, the energy necessary to put an atom into a liquid – crystal interface is approximately ½ the energy necessary to melt one crystal lattice point occupied by the atom. Since the neglected shape factor is probably a little larger than unity (see footnote), it is likely that the approach of σ_g to $0.5\,\Delta H_f$ would be closer if the shape factor could be adequately taken into account. Of course, these conclusions depend upon the adequacy of the theory used and have to be substantiated by accurate measurements of the temperature coefficient of the rate of nucleation.

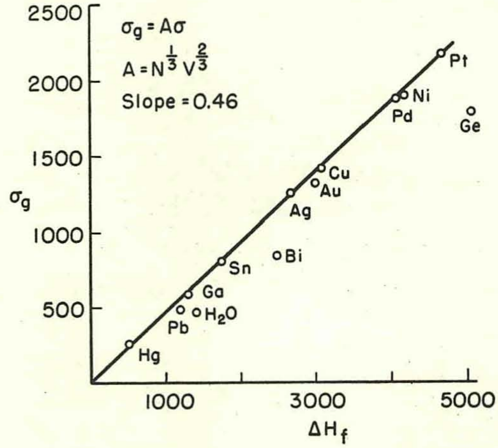

Fig. 2—Gram-Atomic Interfacial Energy as a Function of Gram-Atomic Heat of Fusion.

Water definitely departs from the correlation valid for the metallic elements, but might very well follow a similar one for related compounds. Bismuth and germanium, the only semiconductors for which results are available, also depart from the metallic relationship and appear to approach the relation that holds for water. However, the results for bismuth are preliminary and it may be that subsequent experiments will bring it in line with the other metals.

These results also show that any effect of crystal structure upon subcooling of a metal is strictly a reflection of its effect upon the heat or entropy of fusion. For example, copper and mercury, having similar entropies of fusion, can be subcooled similar amounts relative to their melting temperatures, despite the fact that their crystal structures are quite different. Of course, elements having relatively high entropies of fusion (for example, gallium and tin) can be subcooled to a much greater extent relative to their melting points than can elements having normal entropies of fusion. Undoubtedly the large entropies of fusion exhibited by gallium and tin can be attributed in part to the complexity of their crystal structures.

There is a purely empirical correlation that is entirely equivalent to the theoretical one; it is that

$$(\Delta T_{-}/T_{o})^{2/3}\,[(T_{o} - \Delta T_{-})/\Delta H_{f}]^{1/3} = \text{constant} = M \qquad \text{Equation X}$$

for all metallic elements. Values of M are given in Table I. As should be expected, the deviations of M from constancy are no larger than the deviations in $\sigma/\Delta H_f$. This correlation is nearly as good if $1/\Delta S_f$, where ΔS_f = gram-atomic entropy of fusion, is substituted for $[(T_o - \Delta T_{-})/\Delta H_f]$.

In support of the thesis that the rate of homogeneous nucleation is measured in the small-particle experiments, the following evidence is cited:

1. The reproducibility of the experiments.
2. The consistency and excellence of the correlation between σ_g and ΔH_f that would hardly be expected if σ_g were calculated from heterogeneous nucleation rates.

The final test of the thesis will be supplied by comparison of the temperature coefficient of the nucleation rate, now being measured accurately in our laboratory, with the predictions of the homogeneous nucleation theory. At present, however, it appears that the results obtained with the small-particle technique promise to introduce some degree of order in a field that heretofore had seemed chaotic and confused.

The proportionality obtained between σ_g and ΔH_f in this work is analogous to similar relations (25) between liquid – vapor interfacial energies and heats of vaporization. The success of this correlation for metals suggests that similar correlations might exist for other groups of compounds (e.g., salts, alcohols, etc.). There seems to be no reason why the small-particle technique cannot be extended[3] to an investigation of the liquid → crystal transformation in many of these compounds.

It would be very desirable to reinvestigate the kinetics of many solid → solid transformations by the small-particle technique. Some evidence that there is an effect is furnished by the results of several

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[3] This suggestion was made by Dr. R. A. Oriani of this laboratory.

investigators (26, 27) who observed that the $\gamma \rightarrow \alpha$ transformation in small iron particles precipitated from copper was very much slower than in large iron samples. It is possible that the interfacial energies between solid phases involved in transformations may bear a relation to the heat of transformation that is analogous to that discovered in liquid → crystal reactions.

KINETICS OF CRYSTAL GROWTH

General Principles

It might be expected that small crystal nuclei and embryos that appear most frequently should have a form that minimizes their surface energies. It has been supposed at times that the form of large crystals also is of necessity determined by the condition of minimum surface energy. However, there is abundant evidence which indicates that the form of large crystals is almost always determined by the effects of orientation upon growth rate rather than by purely thermodynamic factors. The insignificant contribution of surface energy to the free energy of large crystals can easily be shown. Consider a metal crystal having linear dimensions of the order of 1 centimeter and having two possible sets of crystal faces that differ in surface energy by 1000 erg/cm^2. The vapor pressure of a crystal having the higher surface energy faces exposed is larger by a factor of about $1 + 10^{-7}$ than that for a crystal having the other set of faces exposed. A temperature fluctuation of the order of 10^{-6} °C is sufficient to change the vapor pressure by this factor. Although many processes in nature take place when the driving force is this small, the influences of minute temperature fluctuations during crystal growth are sufficient to obliterate the importance of pure thermodynamic factors in determining crystal form.

It is readily demonstrated (28) that crystal planes perpendicular to the direction of most rapid growth grow out of existence while the planes that finally appear are those perpendicular to the direction of slowest growth.

A generalization due to Bravais (29) is that the most closely packed planes develop during crystal growth. Thus, the most closely packed planes are normal to the direction of slowest growth and contain the directions of most rapid growth. This generalization can be explained as follows: an atom added to a close-packed plane bonds with nearest neighbors with which its interaction is greatest, while an atom added in a direction normal to a most closely packed plane must bond with nonnearest neighbors with which its interaction is weaker. The former event is more probable than the latter so that, after a closely packed plane is formed, growth will tend to progress in directions contained within it rather than in directions normal to it.

There are many exceptions to the Bravais generalization. Some of them are attributed to external disturbing influences such as the effect of other components in the system. Many examples are known in which the crystal form is completely altered when developed in the presence of compounds strongly adsorbed on the crystal faces. Other exceptions cannot be explained in this way, but Donnay and Harker (30) have shown that many of these can be rationalized in terms of an extended law which they formulate, that includes the law of Bravais as a special case. Their law reduces to that of Bravais if the lattice is of the hexahedral mode and the space group is devoid of screw axes and glide planes.

Growth of Crystals in Supersaturated Vapor

According to kinetic theory, the number of atoms from the vapor added to 1 cm^2 of crystal surface per second is:

$$dn/dt = \alpha\,(p - p_o)/(2\pi mkT)^{1/2} \qquad \text{Equation XI}$$

where α = fraction of impinging molecules retained
p = pressure of supersaturated vapor
p_o = pressure of vapor in equilibrium with the crystal

This relationship has been verified for large crystals, although values of α obtained in different investigations have not been consistent. There is good evidence, however, that α is greatly diminished by adsorbed surface films of foreign substances. Volmer and Estermann (31) have measured α values of the order of 0.9 for surfaces of mercury crystals free of adsorbed films. It is possible, therefore, that α is close to unity for most clean, solid surfaces. This might be considered surprising, since in general an atom must impinge on the surface of a growing crystal at a point where its binding energy is considerably less than average. The fact that atoms do stick most of the time seems to imply that atoms immediately adsorbed on their crystal surface are very mobile and in addition have a mean lifetime on the surface that is large relative to the surface jump period.

In fact, there is a good experimental basis for the existence of a mobile layer of atoms on solid surfaces. Volmer and Estermann (32) performed the classic experiment in demonstration of this.

After permitting mercury vapor to impinge upon the surface of a growing crystal for a definite period, they found that the crystal was 1000 times greater in its largest dimension, and only 1/10 as large in thickness, than could be accounted for on the basis of the collision frequency, adopting the concept that each atom struck at the point of impingement. They rejected the implausible hypothesis that the crystal plastically deformed during the course of its growth and proposed instead that atoms attached themselves to the growing lattice only after having migrated great distances within an adsorbed layer of mobile mercury atoms.

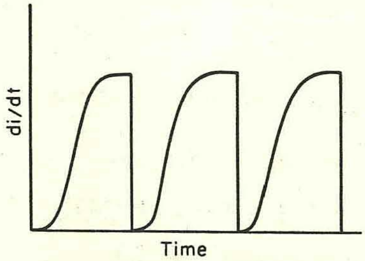

Fig. 3—Schematic Representation of Periodic Discontinuities in Crystal Growth Rates with Addition of Lattice Planes.

A large number of subsequent investigations have provided evidence for the existence of a mobile layer on the surface of many types of solids. One of the most striking of these was that of Kowarski (33) in which Brownian movement of a 1-micron liquid droplet on a solid surface of P-toluidine was observed. There is reason to believe that a mobile "self-adsorbed" layer exists on clean surfaces of all solids, at least at temperatures not too far removed from their melting points.

The Problem of Two-Dimensional Nucleation

Consider the attachment of atoms in the initiation of a new layer on a perfect crystal plane. It is evident that the energy decrease in the attachment of the first few atoms is much smaller than that of the atoms which finally perfect the new layer. Thus, there should be a period of slow attachment of atoms while a two-dimensional nucleus is formed followed by a period of rapid growth of this nucleus to a complete crystal plane. The resulting fluctuations in growth rate, di/dt, with the addition of successive crystal layers is shown schematically in Fig. 3. Kossel (34) and Stranski (35) have developed the theory of two-dimensional nucleation and growth.

There is experimental evidence for the existence of such periodic discontinuities in crystal growth rates. Marcelin (36) first observed the phenomenon in his experiments on the crystallization of P-toluidine from solution. Thickening of the crystal could be followed by the change in color of interference tints that accompanied it. These tints were observed to deepen in a stepwise manner—each step sweeping rapidly over the crystal surface. From the change in wave length accompanying a step, Marcelin calculated that some of the steps were indeed of the order of 1 molecular layer in thickness. Observations similar to Marcelin's have been made on the crystal growth of many other substances. For example, Volmer (37) has reported on similar phenomena in the electrodeposition of cadmium and tin.

Qualitatively these experiments seem to confirm the Kossel-Stranski mechanism. However, the lengths of the two-dimensional nucleation periods are very much shorter than have been calculated on the basis of the idealized Kossel-Stranski theory. In fact, calculations based on the theory (38) indicate that a crystal ought not to grow at a measurable rate for a vapor supersaturation of a few per cent, while experience proves that crystals do grow quite rapidly under such conditions.

Probably the solution of this dilemma is that the crystal is not perfect to its outermost boundary. Thomson (38) has advanced an explanation in these terms that is quite plausible. He points out that the growth of crystal layers takes place not by direct attachment of atoms from the vapor but by attachment from the mobile self-adsorbed layer which can be assumed to have a relatively constant configuration with respect to the vapor. The energy ε_l required for attaching an atom to a two-dimensional nucleus from this self-adsorbed layer must be much less than the energy ε_v of attaching it directly from the vapor. It is reasonable to suppose that the ratio $\varepsilon_l/\varepsilon_v$ is of the order of the ratio of the liquid – crystal interfacial energy to the liquid – vapor interfacial energy. The surface energy opposing the initial nucleation of the crystal is the interfacial energy between the vapor and the self-adsorbed layer, σ_v, plus the interfacial energy between the self-adsorbed layer and the crystal, σ_l. If the mobile layer is relatively dense, σ_v, which should remain nearly constant during crystal growth, predominates over σ_l so that on this basis the neglect of two-dimensional nucleation in the initial nucleation process would be justified.

In order to decide whether or not the mobile transition layer scheme proposed by Thomson is adequate by itself to explain rapid crystal growth at small supersaturations, a much more detailed model of the layer is necessary than is now available. There is little doubt that the layer is liquid-like or gas-like in its mobility. The most important problem remaining is whether or not its concentration approaches that of a liquid phase. If its concentration is quite small so that it covers only a small fraction of the surface, its existence could have little bearing on the problem of two-dimensional nucleation.

Others have ignored the existence of the mobile layer or assumed the concentration within it to be quite small and have attempted to resolve the problem in terms of specific lattice imperfection models. For example, Burton, Cabrera and Frank (39) have shown that a growing crystal can present a virtually constant configuration to the phase in which it is growing when screw dislocations terminate in the face of the crystal.

Although two-dimensional nucleation has to take place in order for a crystal to grow into its melt, we know that again there is a very large discrepancy between the prediction of the idealized theory, that growth rates cannot be significant excepting for large supercooling, and the experimental fact that growth does proceed at a substantial rate for very small undercooling when a nucleus exists. It is obvious that the theories mentioned above for getting around this problem, based upon various types of crystal imperfections, apply with equal force for the liquid – crystal case. The application of the mobile transition layer scheme to this type of reaction is not quite so clear. However, it is reasonable to suppose that a semimobile layer exists between the liquid and solid that is intermediate in structure between the two phases. It is possible to construct a transition layer such that atoms can be added to the growing crystal with only minor changes of lattice parameter and coordination number within the layer and at its boundaries. Thus, the over-all average interfacial energy between the liquid and growing crystal will fluctuate but little because the layer configuration can remain nearly constant with the addition of atoms.

Growth of Crystals Into Subcooled Melts

We have supposed that the attachment of a vapor atom to the self-adsorbed layer on crystals requires no activation energy. This supposition not only appears reasonable on theoretical grounds, but seems to be justified by experience. On the other hand, experience has shown that the growth of crystals into their own melts requires an activation energy, at least for substances whose molecules are relatively complex. The kinetic process is one in which the atom or molecule has to move across an interface whose thickness is of the order of molecular dimensions. Grain growth in pure solids is an analogous process.

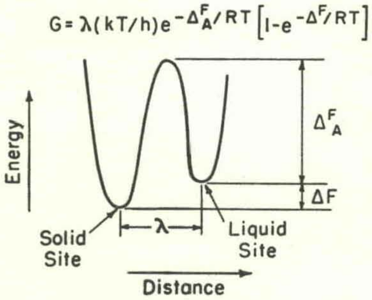

Fig. 4—Schematic Energy-Configuration Diagram at Solid-Liquid Interface.

No detailed models seem to have been proposed for the activated configuration involved in the growth of crystals into melts. Perhaps the activation consists in making holes at the interface and moving atoms or molecules from the liquid into these holes. Such ideas have been advanced for the cause of activation in grain growth. However, assuming only the existence of an activated state, we may apply the quasi-thermodynamic absolute rate theory and derive an expression for the rate of isothermal growth. The energetics involved in the transmission of liquid atoms across the interface are represented schematically in Fig. 4. ΔF_A is the free-energy difference per gram atom between activated complexes and atoms in the liquid. ΔF is the difference in free energy per gram atom between liquid and solid atoms. Here it is assumed that the crystal is sufficiently large that ΔF is independent of size and that the problem of two-dimensional nucleation can be neglected. Then the frequency of transmission r_s of atoms from liquid to solid is according to rate theory:

$$r_s = (kT/h)\ \text{exp.}\ [-\Delta F_A/kT] \qquad \text{Equation XII}$$

while the frequency of transmission γ_l from solid to liquid is:

$$r_l = (kT/h)\ \text{exp.}\ [-(\Delta F_A + \Delta F)/RT] \qquad \text{Equation XIII}$$

The net transmission frequency from liquid to solid is:

$$r_s - r_l = r = (kT/h)\ [1 - \text{exp.}\ \{-\Delta F/RT\}]\ \text{exp.}\ [-\Delta F_A/RT] \qquad \text{Equation XIV}$$

r is related to the linear rate of growth G (cm/sec) by the equation

$$r = G/\lambda \qquad \text{Equation XV}$$

where λ is the interatomic spacing in the interface. Thus,

$$G = \lambda (kT/h)\ (1 - \text{exp.}\ [-\Delta F/RT])\ \text{exp.}\ [-\Delta F_A/RT] \qquad \text{Equation XVI}$$

ΔF may be approximated by

$$\Delta F = \Delta H_f\, \Delta T_- / T_o \qquad \text{Equation XVII}$$

and ΔF_A can be rewritten

$$\Delta F_A = \Delta H_A - T\, \Delta S_A \qquad \text{Equation XVIII}$$

where ΔH_A and ΔS_A are the heat and entropy of activation, respectively. Then G may be recast as follows:

$$G = \lambda (kT/h)(1 - \text{exp.}\ [-\Delta H_f \Delta T_- / RT_o T])\ \text{exp.}\ [(-\Delta H_A - T\Delta S_A)/RT] \qquad \text{Equation XIX}$$

Qualitatively, at least, experience about growth rates can be pictured in terms of Equation XVI or XIX. ΔF is nearly independent of the orientation of the growing crystal face for reasons that have already been discussed. However, the configuration of the activated state should be orientation-dependent and, therefore, ΔF_A should be a function of the orientation of the growing face. The equations predict that G should be zero at T_0 and at the absolute zero with a maximum at some intermediate temperature $T_{max.}$. If ΔF_A is quite large relative to $RT_{max.}$ a well-defined maximum is exhibited (40) in the experimental G versus ΔT_- curve (see Fig. 5a). However, if ΔF_A is not much greater than $RT_{max.}$, the largest observed value of G is apparently independent of temperature over a long range (see also Fig. 5). The explanation for this temperature independence is that in very rapid crystal growth, the heat of solidification liberated at the interface warms it to a temperature greater than the external measuring device so that the value of G actually observed is characteristic of a smaller ΔT_- than is recorded. Volmer (40) points out that the temperature of the interface does not coincide with T_0, as is sometimes supposed, but a temperature determined by a steady-state condition in which the rate of conduction of heat away from the advancing interface equals its rate of production by the transformation.

For relatively complex organic molecules ΔF_A is usually quite large relative to $RT_{max.}$ and experimental curves of the type showing a well-defined maximum are most often obtained. One important contributory factor to the large ΔF_A for these molecules undoubtedly must be the large steric factor associated with the attachment of a molecule to the crystal. In the case of metal atoms such a steric factor does not exist and even metal crystals such as gallium having a fairly complicated structure grow with great rapidity into their subcooled melts. In fact, ΔF_A is relatively so small for metals that it is not possible to quench any liquid metal through the temperature range where G is a maximum before it is entirely transformed to one or more crystals.

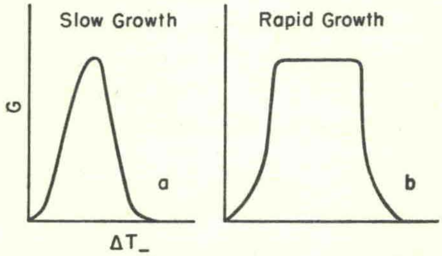

Fig. 5a—Rate of Growth of Crystal into Melt When Temperature of Liquid - Crystal Interface = "Bath" Temperature.

Fig. 5b—Rate of Growth When Interface Is Hotter Than Bath.

Because of their rapid growth rates, metal crystals can grow isothermally when they are undercooled only slightly. Under normal conditions of metal solidification, the interface between the crystal and melt is hotter than its surroundings, and the rate of growth is limited by the speed with which heat can diffuse away from the interface. This leads to the well-known pattern of dendritic growth because, as is true in other types of diffusion, heat can diffuse away from a protuberance, such as a needle point or platelet edge, much more rapidly than from a location somewhere near the middle of a flat surface. Dendritic growth is also observed in the growth of salt crystals from solution when the conditions are such that the process is limited by the diffusion of salt from the body of the solution to the crystal surface.

Metals solidified so that the temperature gradient is normal to the container wall usually exhibit a fiber texture in which the fiber axis is parallel to the temperature gradient. In this type of solidification, nucleation at the container walls may be assumed to result in small grains of random orientation. However, grains oriented with their directions of most rapid growth parallel to the temperature gradient get ahead of grains not so oriented, and the front of advancing crystals finally consists only of grains having nearly the orientation of rapid growth. Barrett (41) has summarized the preferred orientations obtained in cast metals. For example, in face-centered and body-centered cubic metals, the cube axis is normal to the cold surface of the container.

SUMMARY

The rate of separation of crystals from uniary systems of gases or liquids can be interpreted in terms of the nucleation and growth of crystals to macroscopic dimensions. Rates of nucleation of crystals in subcooled liquids obtained by measurements on large continuous samples have not been self-consistent, and there is good evidence that nucleation in these experiments is almost always catalyzed by heterogeneities. Isolation of these catalysts can be effected by breaking the sample up into a large number of small particles prevented by a suitable means from intercommunicating. Under these conditions, the majority of the particles contain no catalysts, and nucleation takes place homogeneously.

The maximum subcooling obtained in small particles is reproducible and usually much larger than ever observed on large continuous samples. Gram-atomic liquid – solid interfacial energies calculated from these data on the basis of the homogeneous nucleation theory are directly proportional to the gram-atomic heats of fusion for the strictly metallic elements.

Crystal form is determined by relative rates of growth in different crystallographic directions rather than from the condition of minimum surface energy. Growth of crystals apparently takes place by attachment of atoms from a mobile self-adsorbed layer, rather than directly from the parent phase.

There is experimental evidence for periodic retardation in crystal growth rates corresponding to the completion of single crystal planes. Although this retardation was expected on theoretical grounds, its period is shorter than predicted by several orders of magnitude. It is possible that this discrepancy can be accounted for in terms of a fairly dense, mobile, self-adsorbed layer.

In general, the growth of crystals into their own melts requires an activation energy, and the kinetics of growth can be interpreted qualitatively in terms of absolute rate theory.

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