[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, AND METALS RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of Crystalline Nucleus Formation in Supercooled Liquid Tin[1,2]

BY GUY M. POUND AND VICTOR K. LA MER

Oxide coated droplets of molten tin of a narrow size range were supercooled to 120° below their melting point of 232°. The droplets were of the order of magnitude of 5 microns in diameter, and the specimens, which were studied by means of a dilatometric technique, each consisted of several grams or about 10^{10} of these droplets. This supercooling is 10° lower than any result previously obtained, and indicates greater purity of the droplets with respect to second-phase impurities. Rate of nucleation of crystals in the supercooled liquid droplets was measured dilatometrically as a function of temperature and droplet size. The solidification rate increases rapidly with decrease in temperature and increase in droplet size. The nucleation process appears to be inhomogeneous, *i.e.*, assisted by small particles of foreign solids randomly distributed among the droplets, because of the marked decrease in reaction rate from the beginning to the end of a rate measurement. Application of Poisson's distribution function to the data shows that the nucleating impurities are present in the droplets in amounts proportional to droplet area rather than volume. Two different theoretical equations for heterogeneous nucleation rate fit the data. The following have been computed from the data: (a) minimum solid–liquid interfacial free energy for tin is 58.5 ± 1 erg/cm.^{2} at 115°; (b) kinetic coefficient for heterogeneous nucleation is $3 \cdot 10^{34}$ cm.$^{-3}$ sec.$^{-1}$ to within a power of 10. Assuming a frequency factor RT/Nh, the theoretical kinetic coefficient for homogeneous nucleation is $3 \cdot 10^{35}$ cm.$^{-3}$ sec.$^{-1}$. This agreement is thought to be fortuitous, and indicates that the kinetic coefficient is not a reliable criterion of homogeneous nucleation.

The purpose of this investigation was to study the kinetics of formation of nuclei of the stable crystalline phase in a supercooled liquid. According to the theory of nucleation, as developed by Frenkel,[3] Volmer[4,5] and Becker[6,7] a nucleus or stable aggregate of molecules of the stable phase arises through stepwise addition of single molecules to the embryo. These additions occur as statistical fluctuations accompanied by an increase in free energy of the unstable aggregate or embryo.

The thermodynamic aspects of this theory for the simple case of homogeneous nucleation may be concisely demonstrated and summarized by calculating the free energy increase, ΔF^*, accompanying the formation of a critical nucleus of stable phase from the supersaturated medium, *i.e.*, the free energy of activation of the phase transformation process. In order to form an embryo of any given size, assuming a spherical shape

$$\Delta F = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \frac{\rho}{M} \Delta F_{\mathrm{B}} \qquad (1)$$

where

r = embryo radius
γ = interfacial free energy. This is taken as independent of embryo size for the present discussion
ρ = density of stable phase
M = molecular weight
ΔF_{B} = the Gibbs free energy change per mole accompanying the transformation from the unstable to the stable bulk phase. This is taken as independent of embryo size for the present discussion

Differentiation with respect to r and solution for the critical radius after equating to zero gives

$$r^* = -\frac{2M\gamma}{\rho \Delta F_{\mathrm{B}}} \qquad (2)$$

Substitution of (2) into (1) yields

$$\Delta F^* = \frac{16\pi M^2 \gamma^3}{3\rho^2 (\Delta F_{\mathrm{B}})^2} \qquad (3)$$

the desired free energy of activation of the process.

Volmer and Flood[8] measured the critical supersaturation pressure necessary for the spontaneous production of fog at a given temperature for a series of vapors by an adiabatic expansion method. This measurement is closely related to the actual nucleation rate. Their data are well described in terms of directly measured properties of the substance by means of the kinetic treatment of Becker and Doering.[6]

Very little significant quantitative work exists relating to the nucleation kinetics of the transformation supercooled liquid to crystalline solid. Becker[7] has postulated the form of the rate equation to be

$$k = C \exp\left(-\frac{\Delta F^*_{\mathrm{D}}}{k'T} - \frac{\Delta F^*}{k'T}\right) \qquad (4)$$

where

k = the specific rate constant
ΔF^*_{D} = the free energy of activation of diffusion in the liquid
ΔF^* = defined as in Eq. (3)
C = the frequency factor, which remains unevaluated
k' = the Boltzmann constant

In an effort to obtain some quantitative data regarding the kinetics of nucleation of crystals in supersaturated liquids, a monodisperse aerosol of supercooled liquid sulfur droplets 2 microns in diameter was chilled in a glass coil immersed in a cold bath.[9,10] The high purity of the liquid sulfur droplets in this aerosol, their isolation from each other, and the ease of counting the percentage of droplets frozen by microscopic examination, should make this preparation an ideal system for a kinetic study. Also, due to the small size of the droplets, the process of solidification should be rapid once a stable nucleus had appeared within the supercooled liquid phase. This means that the rate process measured should be essentially nucleation, rather than growth. It can be demonstrated that

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(1) Read at the A.C.S. Meeting, Chicago, Ill., September, 1950.

(2) Constructed from a Dissertation submitted May, 1950, by Guy M. Pound to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Microfilm copies of the dissertation contain further experimental details and all of the numerical data and illustrative calculations which have been omitted from this publication to conserve space.

(3) J. Frenkel, "Kinetic Theory of Liquids," Oxford Press, New York, N. Y., 1946.

(4) M. Volmer, *Z. Elektrochem.*, **35**, 555 (1929).

(5) M. Volmer, "Kinetik der Phasenbildung," Edwards Bros., Inc., Ann Arbor, Michigan, 1945.

(6) R. Becker and W. Doering, *Ann. Physik*, **24**, 719 (1935).

(7) R. Becker, *ibid.*, **32**, 128 (1938).

(8) M. Volmer and H. Flood, *Z. physik. Chem.*, **A170**, 273 (1934).

(9) This work was carried out at the writers' suggestion in collaboration with Drs. George Ford and Robert Dinegar of this Laboratory.

(10) G. Ford and V. K. La Mer, THIS JOURNAL, **72**, 1959 (1950).

this is the case by nucleating supercooled droplets with powdered rhombic sulfur and observing the rapid solidification.

However, even at temperatures as low as −45° (melting point +120°), only a very small fraction of the liquid sulfur droplets froze in an hour. At temperatures lower than −45°, the diffusivity factor in the rate equation should completely retard nucleation rate. Accordingly, the experiments were abandoned. Nevertheless, two aspects of this experiment are worthy of note: (1) It is in disagreement with the work of Gorskii[11] and coworkers in Russia who report a measurable nucleation rate in large supercooled liquid sulfur drops at a temperature of +50°. Presumably their sulfur contained second-phase impurities which served to nucleate the crystallization process. (2) The ratio of degree of supercooling attained without rapid freezing to melting temperature is seen to be greater than that listed for many other substances.[12]

Vonnegut[13] has described a promising dilatometric technique for measuring nucleation rate in a system of supercooled liquid metal droplets. The droplets are isolated from each other by a thin oxide coating at their surfaces, and a pump oil is used as the supporting fluid. The course of the freezing process is followed by observing the lowering of the dilatometer meniscus due to the shrinkage of the metal on solidification. An advantage of this technique is the ease with which the temperature of the dilatometer can be controlled by means of a thermostat bath. Vonnegut found that polydisperse tin droplets could be supercooled to about 125° (melting point 232°) before they froze rapidly, that the rate of freezing increased very rapidly with decrease in temperature, and that the rate measurements for a given specimen were reproducible. Further, he found that the rate of the reaction decreased sharply as the reaction proceeded.

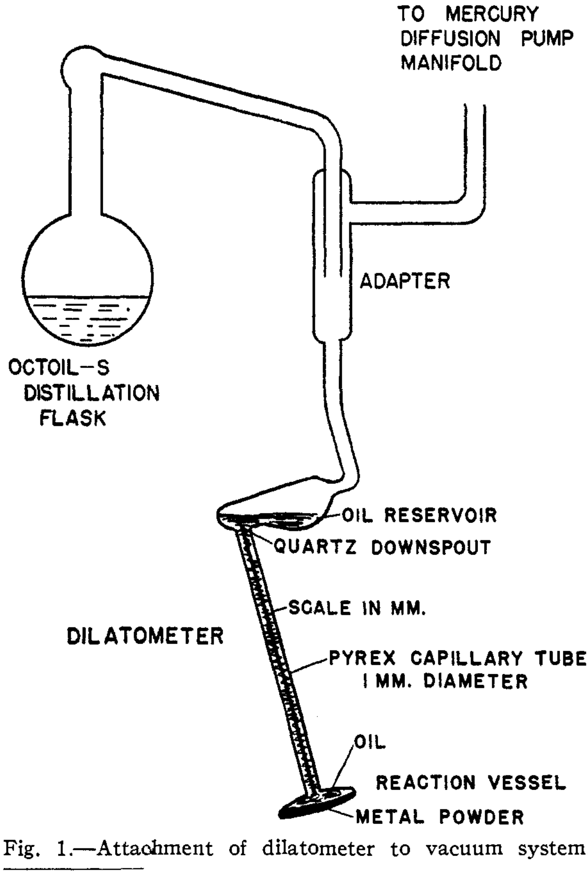

Fig. 1.—Attachment of dilatometer to vacuum system.

Vonnegut recognized that the polydispersity of his specimens rendered interpretation of the results difficult. Polydispersity is of prime importance because the probability of occurrence of a nucleus in a droplet of supercooled liquid should be proportional to the third power of the droplet radius according to nucleation theory. Accordingly, his technique was applied by us to nucleation rate measurements on supercooled liquid tin droplets of carefully controlled size. Such measurements may be used to test various theoretical equations for nucleation rate as applied to the transformation supercooled liquid → solid, and to obtain information regarding interfacial free energy[12,14–17] between solid and liquid. This is a most important factor in all proposed nucleation rate equations (*e.g.*, Equations (3) and (4)). Solid–liquid interfacial free energy is a quantity that is difficult to measure and few experimental values are available.

II. Description of Experimental Work

A. General.—The isothermal rate at which a specimen containing about 10^{10} droplets (equivalent to about 7 g. or 1 cc.) of supercooled liquid tin froze was measured dilatometrically. These droplets were so small that crystallization of a droplet was completed very rapidly once the crystalline nucleus had formed. The droplets were separated from each other by a thin protective coating of tin oxide to prevent interaction. The rates of nucleation were studied at various constant degrees of supercooling, using droplets whose radii were restricted to definite ranges of size. A Roller air classifier was used in selecting the specimens from relatively large amounts of polydisperse C.P. grade tin powder.

Figure 1 shows a diagram of the apparatus employed. The dilatometer was designed to permit efficient degasification of the specimen and to provide good heat transmission

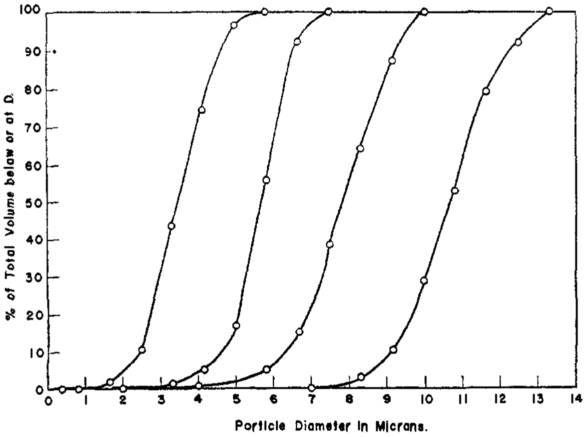

Fig. 2.—Particle size analysis of the powdered tin specimens.

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[11] F. K. Gorskii, *J. Expl. Theor. Phys.* (*U.S.S.R.*), **18**, 45 (1948).

[12] J. H. Hollomon and D. Turnbull, Am. Inst. of Met. Eng. Symposium on Solidification, New York, Feb. 12, 1950 (to be published).

[13] B. Vonnegut, *J. Colloid Sci.*, **3**, 563 (1948).

[14] V. K. La Mer and G. M. Pound, *J. Chem. Phys.*, **17**, 1337 (1949).

[15] F. P. Buff and J. G. Kirkwood, *ibid.*, **18**, 991 (1950).

[16] G. M. Pound and V. K. La Mer, *ibid.*, **19**, 506 (1951).

[17] G. C. Benson and R. Shuttleworth, *ibid.*, **19**, 130 (1951).

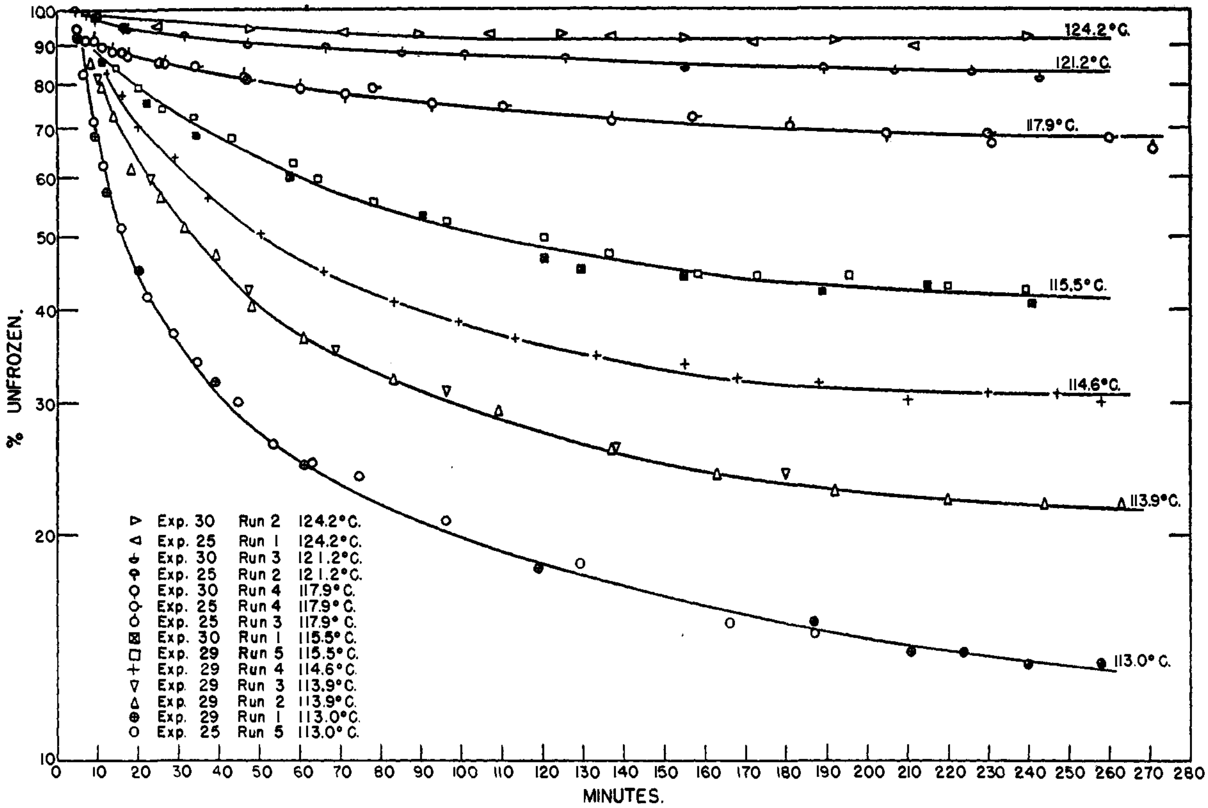

Fig. 3.—% unfrozen *vs.* time for 2.5-5μ tin droplets.

Specimen (experiment) No.	Rate Measurement No.	Temp. °C.	Oxidation treatment	Mass of tin specimen, g.	Melting treatment
25	1	124.2	Sub-normal	5.427	Normal
25	2	121.2	Sub-normal	5.427	Normal
25	3	117.9	Sub-normal	5.427	Normal
25	4	117.9	Sub-normal	5.427	Normal
25	5	113.0	Sub-normal	5.427	Normal
29	1	113.0	Sub-normal	5.230	Normal
29	2	113.9	Sub-normal	5.230	Normal
29	3	113.9	Sub-normal	5.230	Severe
29	4	114.6	Sub-normal	5.230	Normal
29	5	115.5	Sub-normal	5.230	Severe
30	1	115.5	Severe, also graphite added	7.491	Normal
30	2	124.2	Severe, also graphite added	7.491	Normal
30	3	121.2	Severe, also graphite added	7.491	Normal
30	4	117.9	Severe, also graphite added	7.491	Normal

for dissipation of the heat of solidification. About 7 g. of oxide-coated solid tin spheres of the size ranges given in Fig. 2 was placed in the dilatometer, and the system was degassed at 170° for several hours. When the pressure remained at approximately 10^{-6} mm., Octoil-S was distilled into the dilatometer. Nitrogen was admitted at atmospheric pressure to discourage bubble formation, and the temperature of the silicone oil-bath surrounding the dilatometer was then raised to above the melting point of tin (usually to 265°). The dilatometer was sealed off and immersed in a constant temperature bath set at 100 to 120° below the melting point of tin. The dilatometer was still tilted in such a way that the oil covered the downspout to the capillary so that no gas could enter the capillary during the 2.5 minutes that was normally required for nearly complete thermal equilibrium with the thermostat bath and accompanying contraction of the oil in the reactor. After this length of time, the dilatometer was righted to its normal vertical position, the oil in the reservoir flowed away from the top of the downspout, and the meniscus quickly descended a short distance to the calibrated portion of the capillary tube due to slight further thermal contraction. The fall of the meniscus due to solidification shrinkage of the metal was then recorded as a function of time. A set of experimental results is shown in Fig. 3.

Since some of the specimen would freeze before the first reading was taken, it was necessary to base the percentage unfrozen at any time on the percentage remaining unfrozen at the final reading in the rate measurement. To determine this quantity, the dilatometer was removed from the thermostat and chilled in cool air to solidify all of the tin. The dilatometer was then returned to the thermostat bath. The difference between the final reading in the rate measurement and the reading at complete solidification permits calculation of the percentage remaining unfrozen at the final meniscus reading. The value of percentage unfrozen corresponding to any previous meniscus reading can then be computed.

To compute the percentage remaining unfrozen, it was necessary to know the change in specific volume accompanying solidification of the tin. This quantity was measured by immersing a dilatometer of molten tin droplets in the thermostat bath which was set at a temperature below the freezing point but sufficiently high that the rate of freezing was negligible (above 140°). The meniscus reading was taken, and the dilatometer was removed from the

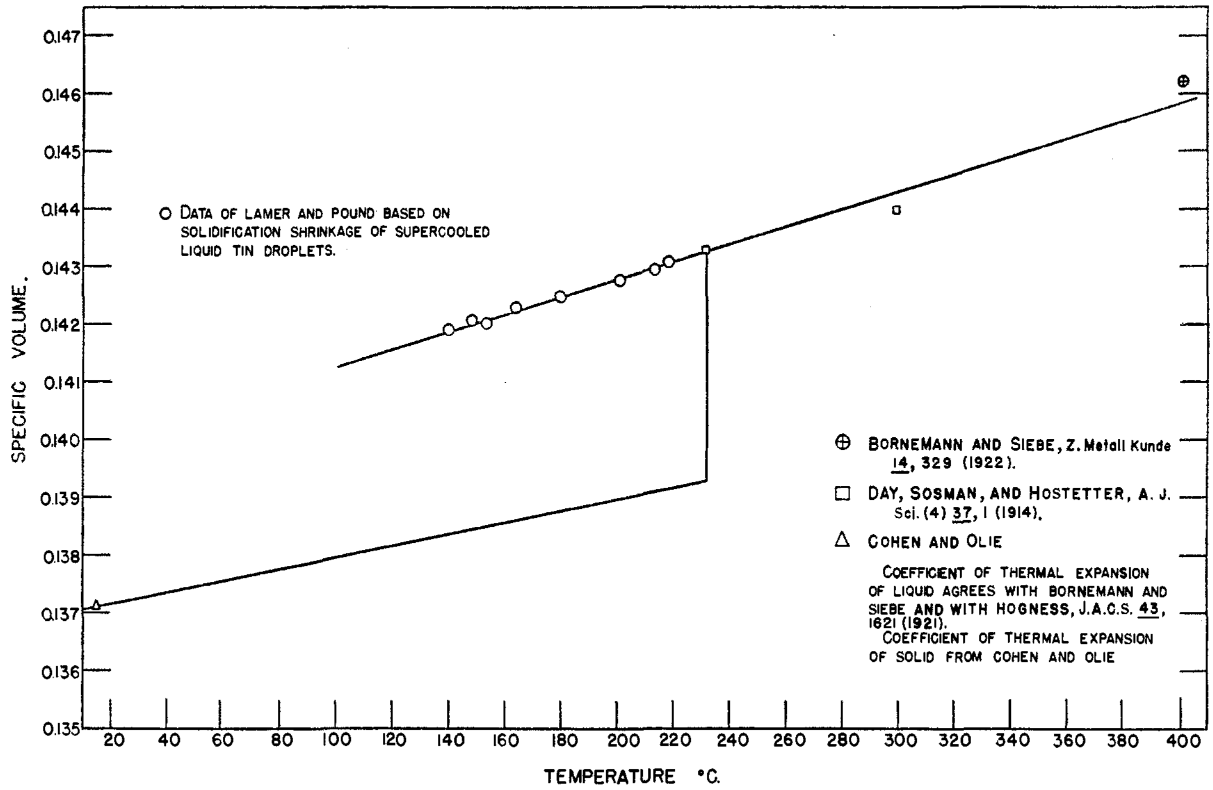

Fig. 4.—Specific volume of tin as a function of temperature (Cohen and Olie, ref. 18.).

thermostat. After the specimen had been completely frozen, the dilatometer was re-immersed in the thermostat and the meniscus read. The difference between initial and final readings in the thermostat, when referred to 1 g. of tin, represents the specific volume decrease on solidification. Cohen and Olie[18] have measured the specific volume of solid tin as a function of temperature as represented in the lower curve of Fig. 4. When our values for specific volume change are added to this curve, one can plot the specific volume of supercooled liquid tin as a function of temperature. Since the experimental data plot linearly, a short extrapolation into the region of rapid solidification is entirely justified.

B. **Preparation of Tin Powders.**—The tin powders used were supplied by various companies, including the Metals Disintegrating Company of Elizabeth, New Jersey, and Eimer and Amend of New York. They are prepared by forcing a mixture of air and molten tin of a C.P. grade through a nozzle against a wheel with rotating blades. The particles are spherical and range in diameter from 1 to 30 microns. The analysis of the Eimer and Amend powder, as given by Dr. W. A. Taebel of that company, is: arsenic 0.0005%; copper 0.005; iron 0.005; lead 0.05. The writers measured the stannic oxide content of this powder by weight loss during hydrogenation and found it to be less than 0.1%, even after oxidizing the surface in preparation for a rate measurement.

Many tin powders were tried, but the Eimer and Amend powder seemed to be the purest with respect to second-phase impurities (*e.g.*, Fe_2O_3) in that it was the most difficult to freeze. Accordingly, quantities of this material were fractionated in a Roller air classifier to give the size fraction indicated in Fig. 2. The particle size distribution was obtained by measuring hundreds of particles under a microscope.

The specimens were placed in a casserole, and heated in an oven at 170° for half an hour in order to put a thin oxide coating on the metal spheres.

C. **Controls Employed to Check Results.**—From control experiments made on dilatometers filled only with oil, the effect of drainage was found to be negligible. No further change in the volume of the Octoil-S occurred with time once thermal equilibrium had been reached (some 2.5 minutes after immersion in the thermostat). Also, no further change of molten tin specimen plus oil occurred with time once thermal equilibrium had been reached at temperatures too high for appreciable nucleation rate (above 140°). A similar statement is true for solid tin specimen plus oil at temperatures below the melting point of tin. From these facts, it is concluded that the volume changes observed were due solely to solidification shrinkage of the tin specimens.

The small temperature variation of the thermostat bath (control was to ±0.02°) and accompanying thermal expansion and contraction of the Octoil-S gave an uncertainty of ±0.2 mm. in the reading of the meniscus. The total drop of the meniscus during freezing of a 7-g. sample was about 30 mm. using 1-mm. diameter capillaries. Accordingly, the percentage of the sample that remained unfrozen at any time was known to about ±1.5% on an absolute basis. Most of the rate measurements were repeated at least once, and, in general, the results were reproducible within the precision measure of this experiment (±1.5%). It should be emphasized that in order to obtain the reproducibility of results at a given temperature that is indicated in the data of Fig. 3, it was necessary to make the rate measurements at almost exactly the same temperature (within 0.03°).

The same specimen could be used for several rate measurements, *i.e.*, until the experiment was no longer reproducible and the freezing rate tended to increase with each succeeding rate measurement. This "wearing out" of a specimen is thought to be due to a progressive flaking off of the oxide coating from the small spheres of tin.

By reference to Fig. 3 and the accompanying key to the data, the following experimental facts may be illustrated: Specimens of different mass gave identical results when the percentage unfrozen was plotted *versus* time, indicating that dissipation of the heat of solidification was not a factor. Varying the degree of superheating upon melting had no effect on the results, indicating that no thermal history effect was involved in the measurements. Varying the severity of the oxidation treatment had no effect on the results. Neither did mixing the powdered tin with twice its volume of finely divided graphite. This finding indicates that the droplets were really independent of each other during freezing.

III. Discussion of Results

A. Heterogeneous *versus* Homogeneous Nucleation.—The isothermal rate measurement data

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(18) E. Cohen and J. Olie, *Z. physik. Chem.*, **71**, 385 (1910).

for the 2.5–5 micron diameter tin droplets are given in Fig. 3, where $\log_{10}$ of per cent. remaining unfrozen is plotted *versus* time. Lowering the temperature from 124 to 113° produces a very pronounced increase in the rate of freezing. Elementary theory would predict that the rate of solidification should be first order. However, inspection of the data shows that the logarithm of per cent. unfrozen is not linear with time, but exhibits marked curvature with decreasing slope.

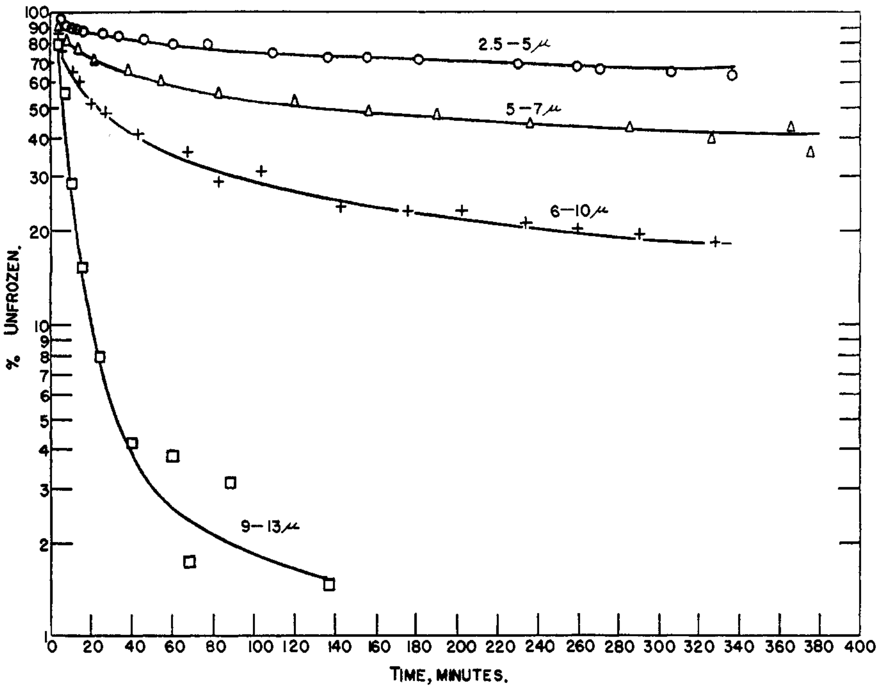

Fig. 5.—% unfrozen *vs.* time, for tin droplets of various sizes, temp., 117.9°.

It does not seem possible that the polydispersity in these carefully fractionated specimens is sufficient to account for failure of the first order rate law to hold. In this connection, it would be very useful to know the dependence of solidification rate on droplet radius. The experimental isotherms of Fig. 5 show that rate of solidification increases with increase in droplet size, but the exact dependence on radius is difficult to determine due to the non-linearity of the plot. Nucleation theory predicts that the rate should vary as the cube of the radius, and noting from Fig. 2 that the maximum difference in droplet size is about twofold, the largest droplets should freeze at a maximum of 8 times the rate of the smallest droplets. The change in slope of the isotherms in Fig. 3 and 5 is much greater than this.

A more plausible interpretation resides in the assumption that the nucleation process is heterogeneous, *i.e.*, due to the presence of small particles of solid foreign nuclei randomly distributed among the tin droplets. There is much qualitative evidence to support this view. It is well recognized that to obtain maximum supercooling of liquids they must be specially purified, and that the addition of foreign particles of almost any type catalyzes the nucleation rate. For example, when finely divided U.S.P. grade ferric oxide was mixed with the solid tin spheres and the rate technique repeated, it was found that less than 50° of supercooling could be attained.

As discussed in the section on Description of Experimental Work, a thin film of oxide was produced on the tin spheres to prevent their coalescence on melting. In a search for such substances, the writers found that powdered graphite was an almost unique material in that it did not catalyze the nucleation rate. Hence, it has been used as an alternative protective film to augment the action of the stannic oxide film. This had no effect on the rate of solidification. Neither did varying the severity of the oxidation treatment. Accordingly, it is believed that there was no appreciable internucleation of the droplets. Further important evidence for the non-interaction of the droplets are the facts that the rate measurements on a given specimen were reproducible and that the particle size analysis was unchanged by the rate technique.

The hypothesis of heterogeneous nucleation by solid foreign impurities is consistent with the data in Fig. 3. For example, those droplets containing the larger number of more effective foreign nuclei will solidify first and thus yield a rapid initial rate. As these droplets are depleted, leaving the droplets that are relatively free of foreign nuclei or contain only less active foreign nuclei, the rate will fall off.

As discussed in Appendix A and illustrated by Fig. 10 and 11, the data are fitted reasonably well by a formula derived by Professor G. E. Kimball, who applied the Poisson distribution function to the problem of random distribution of small particles of foreign impurities among the large number of tin droplets. This result further substantiates the hypothesis of heterogeneous nucleation. Also, application of this formula to the data of Fig. 5 indicates that the number of foreign nuclei per droplet is more nearly proportional to the droplet surface area than to the volume.[19]

B. **Fitting an Equation to the Data.**—As developed in Appendix B and summarized in Fig. 6, three equations, each based on a different mechanism, are proposed to describe the activational free energy of a heterogeneous nucleation process as a function of temperature. It would be desirable to see which of these equations fits the data, and from this deduce the mechanism of the process. Unfortunately, both Frenkel's and Volmer's equations can be made to fit the data. Further, it is seen that if the term δ in the equation proposed by the writers were sufficiently small, their equation would reduce to the equation for homogeneous nucleation, which is sufficiently similar to Volmer's equation that it describes the data. Accordingly, on the basis of the present data, one can neither decide which proposed mechanism for heterogeneous nucleation is actually operating nor eliminate any one of them as a possibility. One probable reason for

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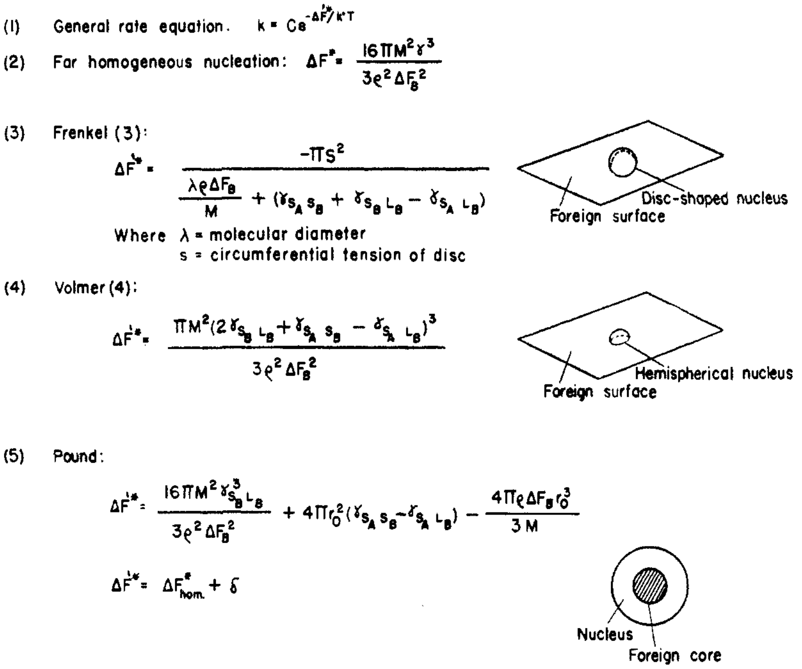
[19] The authors are indebted to Drs. F. C. Frank and David Turnbull for pointing out the importance of this result.


(1) General rate equation. $k = Ce^{-\Delta F'^{*}/k'T}$

(2) For homogeneous nucleation: $\Delta F^{*} = \dfrac{16\pi M^2\gamma^3}{3\rho^2\Delta F_B^2}$

(3) Frenkel (3):

$$\Delta F'^{*} = \frac{-\pi s^2}{\dfrac{\lambda\rho\Delta F_B}{M} + (\gamma_{S_A S_B} + \gamma_{S_B L_B} - \gamma_{S_A L_B})}$$

Where λ = molecular diameter
s = circumferential tension of disc

(4) Volmer (4):

$$\Delta F'^{*} = \frac{\pi M^2(2\gamma_{S_B L_B} + \gamma_{S_A S_B} - \gamma_{S_A L_B})^3}{3\rho^2\Delta F_B^2}$$

(5) Pound:

$$\Delta F'^{*} = \frac{16\pi M^2\gamma^3_{S_B L_B}}{3\rho^2\Delta F_B^2} + 4\pi r_0^2(\gamma_{S_A S_B} - \gamma_{S_A L_B}) - \frac{4\pi\rho\Delta F_B r_0^3}{3M}$$

$$\Delta F'^{*} = \Delta F^{*}_{\text{hom.}} + \delta$$

Fig. 6.—Theoretical equations proposed for description of heterogeneous nucleation (see Appendix B).

this state of affairs is that the data had to be taken over a very short temperature range (about 10°) because the nucleation rate increased from a value that was too low to measure to one that was immeasurably high upon decreasing the temperature 10°. Accordingly, the data do not provide a rigorous test of the equations. However, it should be pointed out that the Frenkel equation involves one more empirical constant than the Volmer equation, and therefore the data probably provide a more severe test for the Volmer equation.

The constants of the Frenkel equation which can be evaluated from the data, *i.e.*, s and $(\gamma_{S_A S_B} + \gamma_{S_B L_B} - \gamma_{S_A L_B})$, are relatively uninteresting from a theoretical point of view. A similar statement is true for $(2\gamma_{S_B L_B} + \gamma_{S_A S_B} - \gamma_{S_A L_B})$ as obtained from an application of Volmer's equation to the data. A much more interesting quantity to evaluate would be $\gamma_{S_B L_B}$, the interfacial free energy between solid and liquid tin.

This quantity occurs in the expression for ΔF^*, the activational free energy for homogeneous nucleation. Now the nucleation process at hand is not homogeneous, but it is seen that the expression for ΔF^* is similar in form to that for $\Delta F'^*$ in Volmer's equation for heterogeneous nucleation. In fact, it is evident that the equation for homogeneous nucleation could also be used to correlate the data. If this were done, a value for $\gamma_{S_B L_B}$ would be obtained which would not be the true value. But it would still be significant in that it would be a minimum value, *i.e.*, the actual value of $\gamma_{S_B L_B}$ could be no lower than this figure obtained from an analysis of the heterogeneous nucleation data.

To illustrate this information, the following outline of a method[20-22] for applying the expression for homogeneous nucleation (Eq. 3) to the data is presented.

The rate equation may be taken as

$$k = Ce^{-\Delta F^*/k'T} \qquad (5)$$

where

k = specific rate constant
C = frequency factor
ΔF^* = activational free energy
k' = Boltzmann's constant = R/N
T = absolute temperature

Substituting (3) into (5), and taking logarithms

$$\ln k = \ln C - (16\pi M^2\gamma^3 S_B L_B/3k'T\rho^2\Delta F_B^2) \qquad (6)$$

All of the quantities on the right side of (6) are relatively independent of temperature except ΔF_B, which is known as a function of temperature (Fig. 7). Accordingly, if an equation of this form describes the data, a plot of ln k *versus* $1/\Delta F_B^2 T$ should give a straight line.

Such a plot is given in Fig. 8. Reasonably good straight lines are obtained. The values of "first order" reaction rate constant k for a given line in Fig. 8 were obtained by taking slopes of the experimental isotherms in Fig. 3 at a constant fraction remaining unfrozen. As discussed in Part A of this section, the data of Fig. 3 do not represent a first order reaction. However, if one assumes that the same droplets with whatever nucleating impurities they may contain are in the process of isothermal solidification at a given fraction of tin remaining unfrozen regardless of the temperature of the process, then one may approximate the rate constants of this small portion of the specimen as a function of temperature by taking the slopes of the isotherms in Fig. 3 at the specified fraction remaining unfrozen. The extent of this small portion is somewhat indefinite, for solidification of droplets immediately above and below the specified fraction remaining unfrozen will contribute to the shape of the curve where the slope is being measured. Therefore, the reaction rate constant as determined by taking the slope at a specified fraction remaining unfrozen represents some sort of an average value for a range of sizes of droplets which contain various impurities.

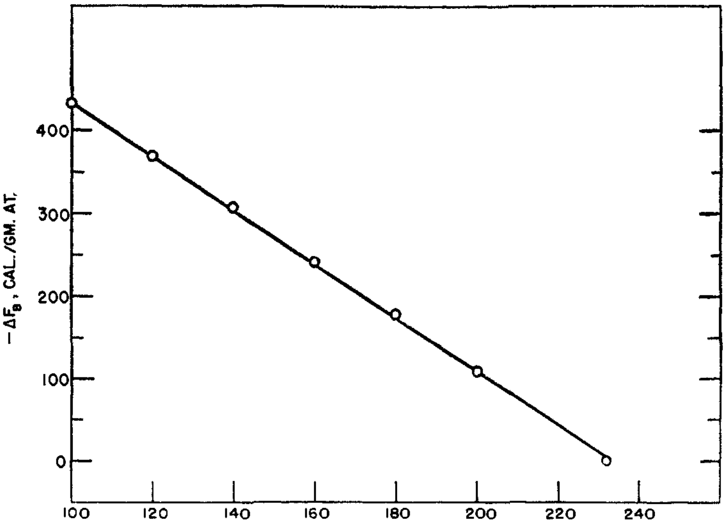


Fig. 7.—Calculated bulk free energy change for the transformation supercooled liquid → white tin. Based on data of: Brönsted, *Z. physik. Chem.*, **88**, 479, (1914); Kelley, *Bur. of Mines Bull.*, 383 (1936).

There are some specific sources of error in this method of determining k. In the first place, a certain amount of error arises in measuring the slope of the isotherm. Also, the shape of the isotherm itself is sensitive to small changes in temperature. This uncertainty would manifest itself as

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(20) This calculation was performed independently by the writers in 1948 in an analysis of Vonnegut's data.[10]

(21) D. Turnbull, *J. Chem. Phys.*, **18**, 768 (1950).

(22) D. Turnbull, "Isothermal Rate of Solidification of Aggregates of Mercury Droplets" (to be published).

error in the value for the slope. The magnitude of these errors is difficult to evaluate, but it is believed that the correlation given in Fig. 8 is probably as good as could be expected.

The slope of a line in Fig. 8 is $(-16\pi M^2\gamma^3_{S_BL_B}/3k'\rho^2)$. Hence, $\gamma_{S_BL_B}$ can be computed directly from the slope as measured from this plot by multiplying by $-3k'\rho^2/16\pi M^2$ and taking the cube root. As explained above, this value for $\gamma_{S_BL_B}$ will be a minimum value. Using the value of the slope and the value of ln k at a given temperature, ln C can be computed from (6).[23] The units of the frequency factor C are min.$^{-1}$. It would be interesting to express the nucleation rate in terms of number of crystalline nuclei formed per second per cc. of supercooled liquid tin, i.e., in units of the kinetic coefficient C'. This may be done by dividing C by 60 and multiplying by the number of tin droplets per cc. of supercooled liquid tin. The latter number can be estimated using a value for average droplet diameter taken from Fig. 2. The result of this computation is somewhat artificial in that the nucleation occurs at the surface of a catalytic body rather than in the volume of the liquid by a homogeneous mechanism. However, the computation must be done in this way to provide a numerical comparison with the predictions of homogeneous nucleation theory.

It is also of interest to compute the size of a stable nucleus in homogeneous nucleation from Eq. (2) using the value for $\gamma_{S_BL_B}$ computed from the data. Actually, this will be a minimum size, because the value of $\gamma_{S_BL_B}$ is a minimum value.

C. Calculated Results.—The more important assumptions in this calculation may be summarized as follows: (1) The reaction rate constant k may be evaluated by taking slopes of the isotherms of Fig. 3.

(2) As mentioned in the Introduction and Appendix B, it is assumed that the molar bulk free energy change accompanying the formation of a nucleus and the solid–liquid interfacial free energy are independent of nucleus size. This assumption is probably not exactly true,[24] but nucleation data from condensation in supersaturated vapors indicates that the decrease in these values with decrease in nucleus size is probably small.[14,25]

(3) The nuclei in homogeneous nucleation are spherical in shape. This assumption is undoubtedly wrong, but the difference in area between the surface of a sphere and the more probable many-sided polyhedron is small.[26]

The calculated results are summarized in Table I. Referring to Fig. 8 which was explained in the preceding section, it is seen that the slope increases as one goes to lines representing smaller percentages remaining unfrozen. This is reasonable because the portion that is more difficult to freeze should have the higher activational free energy. This tendency is reflected in the increasing value of $\gamma_{S_BL_B}$ minimum with decrease in percentage remaining unfrozen as indicated in Table I. There is, as yet, no other method, experimental or theoretical, for determining $\gamma_{S_BL_B}$.

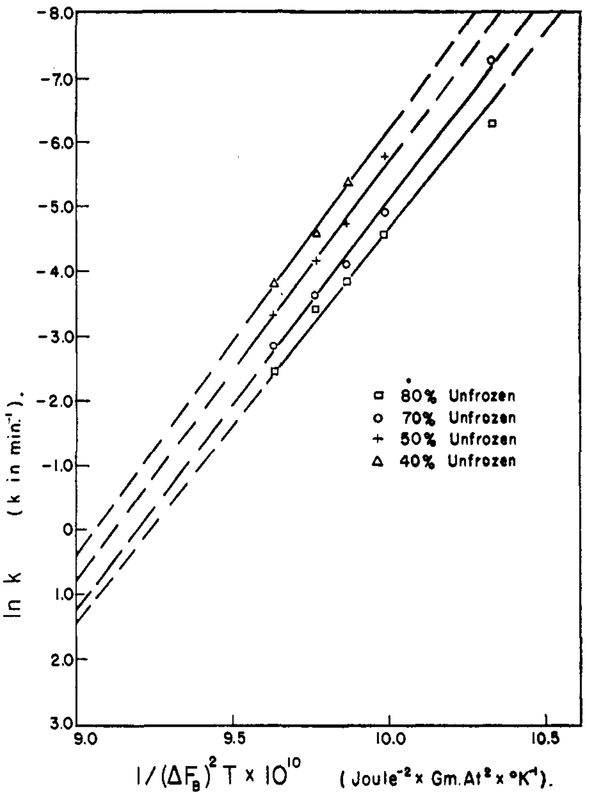

Fig. 8.—Logarithm of reaction rate constant *versus* $1/(\Delta F_B)^2T$. (k evaluated by taking slopes from Fig. 3 at a specific fraction remaining unfrozen.)

TABLE I

RESULTS CALCULATED FROM DATA FOR 2.5–5-MICRON TIN DROPLETS

Unfrozen, %	Minimum solid–liquid interfacial free energy, ergs/cm.^{2}	Kinetic coefficient cc.$^{-1}$ sec.$^{-1}$ for heterogeneous nucleation[a] $\times 10^{-33}$	Minimum nucleus size for homogeneous nucleation at 113.0° Radius, Å.	No. tin atoms
80	57.2	1	11.4	232
70	58.1	1	11.6	243
50	58.3	30	11.7	245
40	58.9	100	11.8	253

[a] These apply to either Volmer's or the writers' mechanism for heterogeneous nucleation.

The increase in kinetic coefficient with decrease in percentage remaining unfrozen is anomalous. The variation is believed to be beyond the precision of the method. It is of interest to compare the value for the kinetic coefficient of this heterogeneous nucleation process with that predicted by Turnbull and Fisher[27] for homogeneous nucleation in supercooled liquids. Their expression is

$$C' = n\frac{k'T}{h}e^{-\Delta F^*_D/k'T} \tag{7}$$

where

C' = kinetic coefficient in sec.$^{-1}$ cc.$^{-1}$
n = number of atoms/cc. supercooled liquid
k' = Boltzmann's constant
h = Planck's constant
ΔF^*_D = free energy of activation of diffusion in the liquid

It is customary to assume that $-\Delta F^*_D \cong k'T$, and hence that $e^{-\Delta F^*_D/k'T} \cong 1/3 \cong 1$. For the case of supercooled liquid tin, C' assumes by this method

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(23) Notice that the same value for C will be obtained whether one uses the expression for homogeneous nucleation (the writers' expression for heterogeneous nucleation may reduce to this form) or Volmer's equation for heterogeneous nucleation. The value of C calculated here applies to the case of Volmer's or the writers' mechanism for heterogeneous nucleation.

(24) J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **17**, 338 (1949).

(25) Other free energy requirements for activation have been suggested in a private communication from Dr. W. H. Rodebush. These are not yet evaluated and are probably small.

(26) I. N. Stranski and R. Kaischew, *Z. physik. Chem.*, **B26**, 81, 114, 312 (1934); *Physik. Z.*, **36**, 393 (1933).

(27) D. Turnbull and J. C. Fisher, *J. Chem. Phys.*, **17**, 71 (1949).

a value 3×10^{35} cc.$^{-1}$ sec.$^{-1}$. The agreement with the value computed from the data is probably fortuitous. This does not necessarily mean that (7) would be inapplicable to the case of homogeneous nucleation of supercooled liquid tin. The point here is that the kinetic coefficient is not a reliable criterion of homogeneous nucleation.

If one computes the experimental kinetic coefficient on the basis that the droplets are nucleated by impurities covering the surfaces, one gets approximately 10^{30} cm.$^{-2}$ sec.$^{-1}$ at 50% unfrozen. Assuming that the theoretical kinetic coefficient for heterogeneous nucleation is given by an expression analogous to (7) in which n is taken to mean the number of atoms per cm.^{2} in contact with the catalyzing foreign impurity,[28] the theoretical C' becomes approximately 10^{28} cm.$^{-2}$ sec.$^{-1}$. Thus, it is possible that the Turnbull expression[28] for kinetic coefficient in heterogeneous nucleation may satisfactorily describe the data.

Appendix

A. Application of the Poisson Distribution Function to the Data.[29]—On the basis of qualitative experimental results, it has been shown (Discussion of Results) that nucleation of the crystalline phase in supercooled liquid tin droplets is heterogeneous. The nucleation is thought to be accomplished by small particles of solid impurities randomly distributed among the large number of tin droplets. Professor G. E. Kimball has pointed out that if this hypothesis is correct, it should be possible to describe the data of Figs. 3 and 5 by means of a relationship derived with the aid of the Poisson distribution function. His derivation of Eqs. (8) to (13) follows: Let

N_0 = number of droplets of supercooled liquid present initially
N = number of droplets unfrozen at time t
m = arithmetic average number of foreign nuclei or centers per droplet (that are active at the temperature T of interest)

In time dt, the probability that any one active center nucleates is k dt, where k is the first order rate constant in min.$^{-1}$. If the droplet has p active centers, the probability that it will be unfrozen at time t is e^{-pkt}. This assumes that all centers active at this temperature are equally effective as nucleating agents and that they act independently. Assuming that the Poisson function is applicable to the distribution of the active centers among the droplets, the number of droplets with p centers is

$$N_0(m^p e^{-m}/p!)$$

The number at time t that are unfrozen and contain active centers is

$$N_0 \sum_{p=1}^{\infty} \frac{m^p e^{-m}}{p!} e^{-pkt}$$

The probability that a droplet with no active centers freezes in time dt is k_0dt. where k_0 is the first order rate constant for homogeneous nucleation. Thus, considering the homogeneous nucleation rate, the probability of a droplet remaining unfrozen at time t is $e^{-k_0 t}$. The number of droplets without active centers is $N_0 e^{-m}$. The number at time t that are unfrozen and are without active centers is $N_0 e^{-m} \cdot e^{-k_0 t}$. This assumes that all the droplets are of the same size. Accordingly

$$N = N_0 e^{-m} e^{-k_0 t} + N_0 \sum_{p=1}^{\infty} \frac{m^p e^{-m}}{p!} e^{-pkt} \quad (8)$$

Changing the summation from $p = 1$ to $p = 0$

$$N = N_0 e^{-m}(e^{-k_0 t} - 1) + N_0 \sum_{p=0}^{\infty} \frac{m^p e^{-m}}{p!} e^{-pkt} \quad (9)$$

Since

$$\sum_{p=0}^{\infty} \frac{m^p e^{-pkt}}{p!} \equiv \sum_{p=0}^{\infty} \frac{(me^{-kt})^p}{p!} = \exp(me^{-kt})$$

$$N = N_0 e^{-m}(e^{-k_0 t} - 1) + N_0 e^{-m} \exp(me^{-kt}) \quad (10)$$

If the self-nucleation rate is negligible (k_0 nearly zero), the first term vanishes. Then

$$N = N_0 \exp[-m(1 - e^{-kt})] \quad (11)$$

Considering the limiting cases, for $kt << 1$

$$N = N_0 e^{-mkt} \quad (12)$$

For $kt >> 1$

$$N = N_0 e^{-m} \quad (13)$$

These relationships are illustrated in Fig. 9.

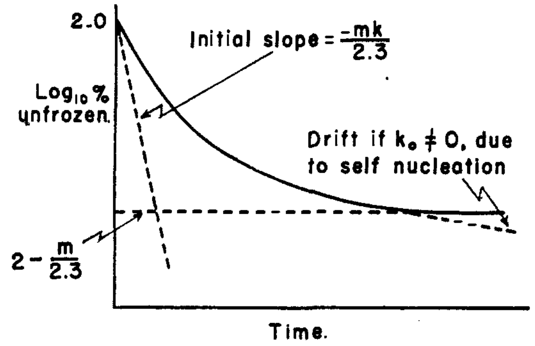

Fig. 9.—Illustrating equations 10, 11, 12 and 13, Appendix A.

In order to fit these equations to the data, it is desirable to know whether self-nucleation can be neglected or not. The most certain way of determining this would be to conduct rate measurements that extend over a long period of time, but this method is not practical due to the difficulty of maintaining a constant temperature in the thermostat bath. Professor R. S. Halford has suggested that a sequential analysis plot of the type shown in Fig. 10 should be helpful. There it is seen that the slopes of the experimental curves approach a very low value with time.

Accordingly Eq. (11) was chosen to be fitted to the data. Results for typical data are shown in Fig. 11. It is seen that a reasonably good fit is obtained. Probably a somewhat better fit of the 113.0° experimental curve would have resulted if a small self-nucleation term had been included in the equation.

The experimental conditions do not quite meet all of the requirements of this theory. In the first place, the droplets are not precisely monodisperse. Secondly, all centers active at a given temperature are probably not equally effective as nucleating agents. For example, foreign nuclei that are active at a given temperature should be even more active at a lower temperature, so that nucleation rate data taken at the lower temperature should be the result of nuclei active at higher temperatures as well as nuclei that have just become active at the lower temperature. This should be particularly true of the earlier parts of the rate measurement. Accordingly the rate constant k is probably some sort of average value for many kinds of nuclei.

Nevertheless, the fact that the data are fitted fairly well by the theoretical equation indicates that the hypothesis of heterogeneous nucleation by randomly distributed impurity particles is at least consistent with experimental results.

It would be very desirable if the rate constants obtained by application of this theory to the data could be used to compute activational free energies. However, we feel that this is not justified, because by this procedure one considers the effect of different foreign nuclei at different temperatures. Actually, one should consider the effect of the same foreign nuclei at different temperatures. For this purpose, we prefer the method outlined in the Discussion of Results.

The present analysis also gives some insight into the manner in which foreign catalytic bodies are distributed among the droplets. Applying Eq. (13) to the data of Fig. 5, one finds that m is more nearly proportional to droplet surface area than to volume. This indicates that the droplets are

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[28] D. Turnbull, *J. Applied Phys.*, **21**, 1022 (1950).

[29] Appendix A is based on private communications from Professors G. E. Kimball and R. S. Halford of Columbia University.

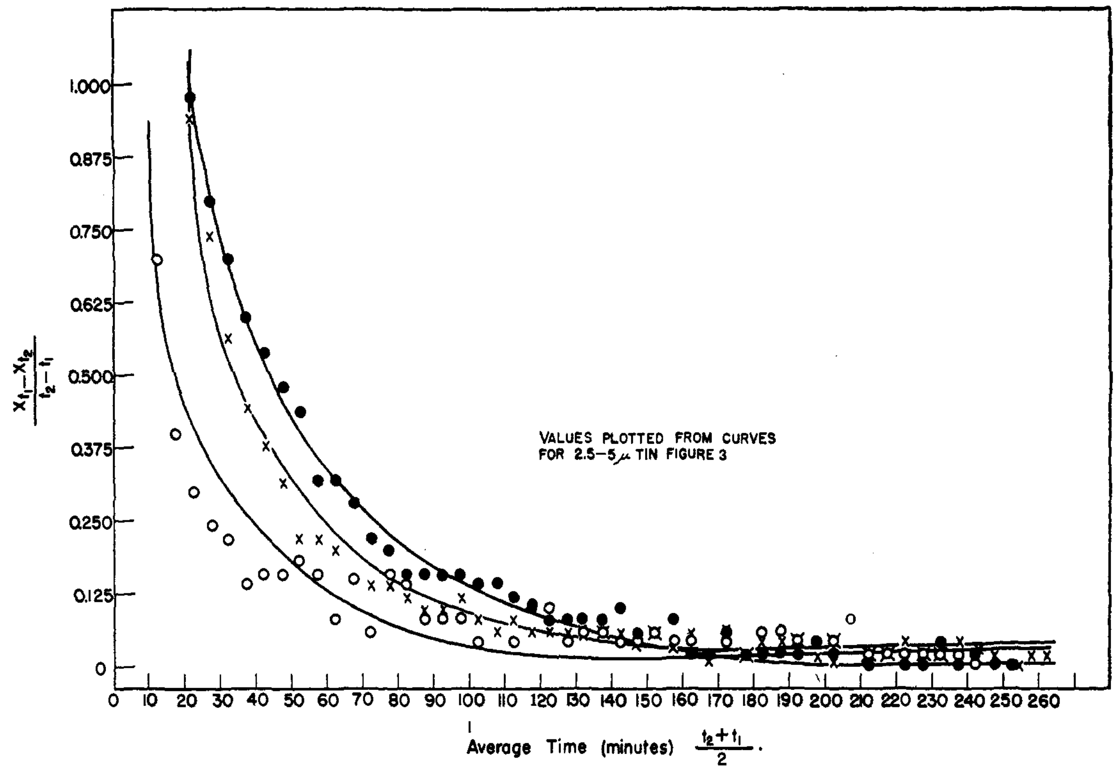

Fig. 10.—Plot of: $\frac{X_{t_1} - X_{t_2}}{t_2 - t_1}$, $\frac{X_{t_2} - X_{t_3}}{t_3 - t_2}$, etc. *vs.* $\frac{t_1 + t_2}{2}$, $\frac{t_2 + t_3}{2}$, etc.; X = % remaining unfrozen; t = time in minutes; O, slopes at 117.9°; ●, slopes at 114.6°; X, slopes at 113.0°.

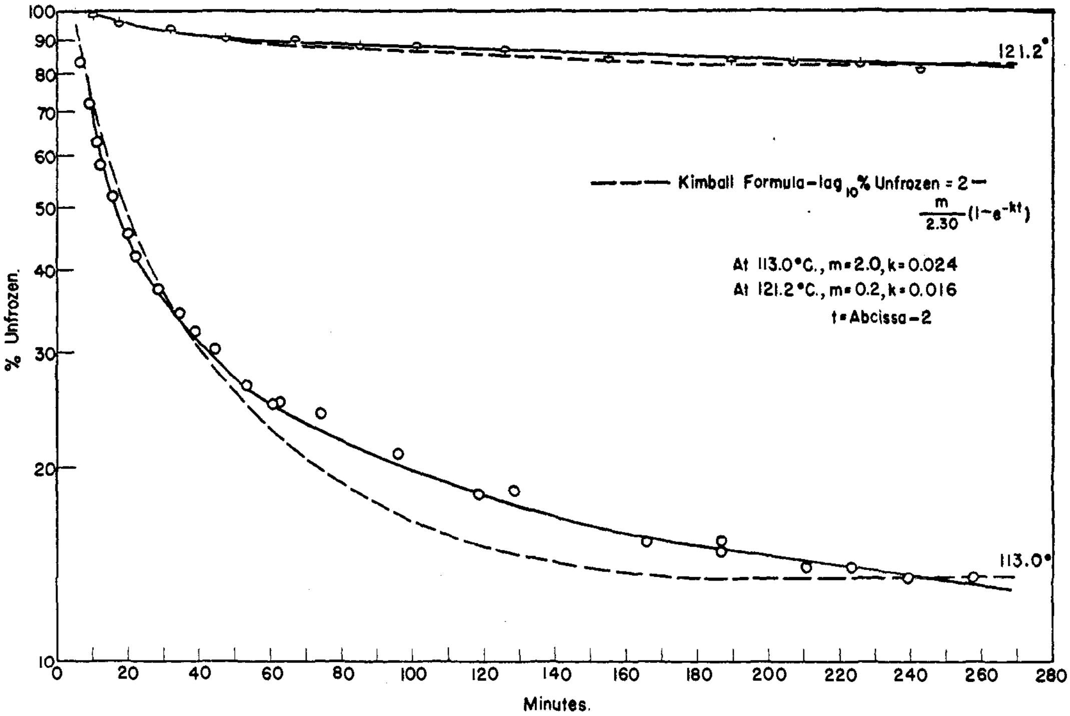

Fig. 11.—% unfrozen *vs.* time for 2.5–5μ tin droplets, comparison of the Kimball formula with experimental data.

probably nucleated by solid foreign impurities at their surfaces.

B. **Thermodynamic Theory of a Mechanism for Heterogeneous Nucleation.**—The specific rate constant of many physico-chemical processes can be expressed by an equation of the form

$$k = Ce^{-\Delta F^*/k't} \qquad (14)$$

In ordinary chemical kinetics studies, ΔF^* is not strongly dependent on temperature, and this equation can be used directly to interpret the data. However, in phase transition kinetics, ΔF^* is generally a strong function of temperature so that ΔF^* in Eq. (14) must be given more explicitly in terms of temperature if the equation is to be useful in correlating experimental information. In general, a unique formula for ΔF^* may be derived for the case of each mechanism assumed for the nucleation process. This provides a possible method for determining the mechanism.

The object of this section is to suggest a mechanism for heterogeneous nucleation and supply the appropriate expression for the activational free energy. In the following, one may consider that the process is the seeding of a supercooled liquid to form the stable crystalline phase.

Assume that the foreign solid body is smaller than that of a stable nucleus spontaneously formed without the assistance of foreign nuclei. This is the case of crystallization on extremely fine colloidal powders. Assume spherical shapes and no effect of nucleus size upon either interfacial free energies or molar bulk free energy changes accompanying the transformation.

Let

r_0 = foreign seed radius
r' = radius of aggregate containing foreign core
$\Delta F'$ = free energy of formation of the aggregate
ΔF_B = molar bulk free energy change
ρ = density of deposited phase
M = molecular weight
$\gamma_{S_AL_B}$ = interfacial free energy, foreign nucleus to crystal
$\gamma_{S_BL_B}$ = interfacial free energy, crystal to liquid
$\gamma_{S_AL_B}$ = interfacial free energy, foreign nucleus to liquid
r'^* = critical radius of aggregate containing foreign core
$\Delta F'^*$ = free energy of activation for nucleus formation

The free energy of formation of such an aggregate containing a foreign core is

$$\Delta F' = 4\pi r_0^2(\gamma_{S_AS_B} - \gamma_{S_AL_B}) + 4\pi r'^2\gamma_{S_BL_B} + \frac{4\pi}{3}(r'^3 - r_0^3)\frac{\rho\Delta F_B}{M} \quad (15)$$

Maximizing $\Delta F'$, holding r_0 constant

$$\frac{\partial \Delta F'}{\partial r'} = 0 = 8\pi r'^*\gamma_{S_BL_B} + \frac{4\pi r'^{*2}\rho\Delta F_B}{M} \quad (16)$$

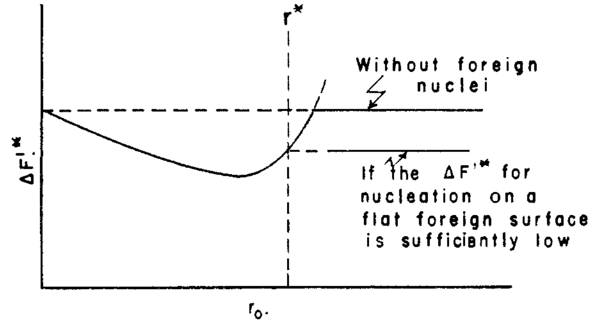

Fig. 12.—Plot of equation 18, Appendix B, for a case where $\gamma_{S_BL_B} > |(\gamma_{S_AL_B} - \gamma_{S_AL_B})| > \frac{2}{3}\gamma_{S_BL_B}$.

$$r'^* = -2\gamma_{S_BL_B}M/\rho\Delta F_B \quad (17)$$

$$\Delta F'^* = 4\pi r_0^2(\gamma_{S_AS_B} - \gamma_{S_AL_B}) + \frac{16\pi M^2\gamma^3_{S_BL_B}}{3\rho^2\Delta F_B{}^2} - \frac{4\pi\rho\Delta F_B r_0^3}{3M} \quad (18)$$

The corresponding quantity in the absence of foreign nuclei is given by Eq. (3).

Comparing (18) with (3), we see that $\Delta F'^*$ may be expressed in the form

$$\Delta F'^* = \Delta F^* + \delta \quad (19)$$

where

$$\delta = 4\pi r_0^2(\gamma_{S_AS_B} - \gamma_{S_AL_B}) - 4\pi\rho\Delta F_B r_0^3/3M \quad (20)$$

With reference to Fig. 6, the temperature dependency of $\Delta F'^*$ is found to be unique. If this formula is to have any experimental significance, δ will be negative.

The next step in this development is to consider the dependency of activational free energy upon the radius r_0 of the foreign seed. A physical picture of the effect of varying r_0 may be obtained with reference to Eq. (18), by considering that the free energy change due to creation of the seed-crystal interface is negative and proportional to r_0^2 while the negative bulk free energy change that is *not* obtained due to the existence of the foreign core is proportional to r_0^3. Obviously, there is a value for $r_0 = r_0^*$ which corresponds to a minimum value for $\Delta F'^* = \Delta F'^{**}$ and a maximum nucleation rate. This can be calculated by minimizing δ.

$$\frac{\partial\delta}{\partial r_0} = 0 = 8\pi(\gamma_{S_AS_B} - \gamma_{S_AL_B})r_0^* - \frac{4\pi\rho\Delta F_B r_0^{*2}}{M} \quad (21)$$

$$r_0^* = \frac{+\ 2(\gamma_{S_AS_B} - \gamma_{S_AL_B})M}{\rho\Delta F_B} \quad (22)$$

$$\delta^* = \frac{16\pi M^2}{3\rho^2\Delta F_B{}^2}(\gamma_{S_AS_B} - \gamma_{S_AL_B})^3 \quad (23)$$

$$\Delta F'^{**} = \Delta F^* + \delta^* = \frac{16\pi M^2}{3\rho^2\Delta F_B{}^2}[\gamma^3_{S_BL_B} + (\gamma_{S_AS_B} - \gamma_{S_AL_B})^3] \quad (24)$$

If $\delta = 0$, rate of nucleation on the foreign seeds would be comparable with normal homogeneous nucleation rate. Expressing this as

$$\delta = 0 = 4\pi r_0^2(\gamma_{S_AS_B} - \gamma_{S_AL_B}) - \frac{4\pi\rho\Delta F_B}{3M}r_0^3 \quad (25)$$

$$r_0 = \frac{3M(\gamma_{S_AS_B} - \gamma_{S_AL_B})}{\rho\Delta F_B} \quad (26)$$

Comparing (26) with (22), we see that an increase in r_0 of 50% decreases heterogeneous nucleation rate from its maximum to a negligible value. Considering equations (26), (22) and (2), we may illustrate this as in Fig. 12.

New York, N. Y. Received June 15, 1951